Symposium 1

Batteries and Supercapacitors

Batteries for a Renewable Energy Economy

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The need to find energy sources to replace oil, gas and coal is increasingly urgent both because of diminishing supplies and global warming. Solar, wind and tidal generation of electricity probably all have a role to play but share a common problem – nature controls when the power is generated and the pattern of generation does not match the demands of consumers, whether industrial or domestic. Hence, energy storage is essential as a buffer between generation and use of such electricity. Moreover, the challenge is to store energy on the MW scale in each unit and such units are inevitably comparable to a chemical plant. Fuel cells and batteries seem a natural way to store electricity. Cycles based on water electrolysis and a fuel cell, however, presently suffer from a very poor energy efficiency, probably ~ 40 %, largely due to the overpotentials still associated with oxygen evolution and reduction. In comparison, batteries can deliver energy efficiencies > 80 % for a charge/discharge cycle.

Redox flow cells have a particular advantage for large scale energy storage - namely, the amount of energy stored is determined by the volume of the electrolyte(s) and the concentration of reactants and the electrolyte(s) are stored external to the cells. Moreover, their engineering and factors determining performance are quite different to other batteries and an energy storage system would be more akin to an electrolytic plant for the manufacture of a chemical than a conventional battery.

The considerations that determine the selection of cell chemistry will be discussed and illustrated using data from systems presently under investigation. Typical performance data will be presented and the factors that limit performance will be discussed. Potential problems with both the electrode reactions and separator will be highlighted.

In Southampton, we have a programme to develop ‘the soluble lead acid battery’. This is a lead acid battery with a methanesulfonic acid electrolyte in which lead(II) is highly soluble (> 3 M). Its key advantage over other redox flow batteries is that it operates without a membrane/separator. Detailed performance data for the system will be presented in a later lecture during the conference.

Application of Ionic Liquids to Li batteries and Supercapacitors

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Ionic liquids (ILs) have recently attracted many researchers as novel electrolyte materials for the electrochemical devices. The thermally-stable and non-flammable nature of ILs can improve the safety of Li batteries and supercapacitors in abuse. In addition, condensed ionic state in ILs is favorable for the increase of energy density of supercapacitors. Authors have applied several ILs to these devices [1-3] and tried to sort out what happens in the electrochemical devices using ILs.

Among a lot of the series of ILs, quaternary ammonium (QA) cation – imide combination is fairly interesting for the higher electrochemical stability especially in the reduction [3,4]. This is advantageous for the application to the Li battery system and Li/$LiCoO_2$ cell with the ILs as an electrolyte base could work reversibly (one example is shown in Figure 1), indicating that QA-imide ILs were quite stable even at the Li reduction potential [2].

In the presentation, for the Li battery system, the way we reached the cyclic QA-imide IL "PP13-TFSI (N-methyl-N-propylpiperidinium bis (trifluoro methanesulfonyl)imide)" will be introduced. Surface analysis results of the electrode after the cell operation, which is closely related to the electrochemical stability against the electrode, will be focused. A brief introduction of the current status of the supercapacitors using ILs will also be made.

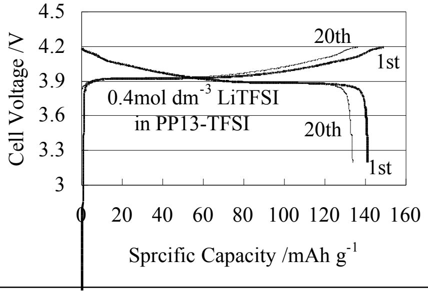

Figure 1:

First and 20th charge-discharge curves for Li/$LiCoO_2$ cell containing 0.4 mol dm^{-3} LiTFSI in PP13-TFSI,. Charge cut off:4.2 V CC mode, discharge cut off: 3.2 V CC mode, charge and discharge current rate: C/10. Modified from ref. [2].

[1] H. Sakaebe and H. Matsumoto: Electrochem. Commun. 2003; 5: 594–598.

[2] H. Sakaebe, H. Matsumoto and K.Tatsumi, Journal of Power Sources 2005; 146: 693-697.

[3] H. Matsumoto, H. Sakaebe, and K. Tatsumi, Journal of Power Sources 2005; 146: 45–50.

[4] H. Matsumoto and Y. Miyazaki; Chem. Lett. 2000; 922.

Research and Development Considerations for the Performance and Application of Supercapacitors

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Electrochemical capacitors (ultracapacitors) are being developed as an alternative to pulse power batteries. In this paper, the differences between pulse batteries and ultracapacitors are discussed and how these differences are reflected in the design and testing of the two types of devices. Research and development on high power ultracapacitors has been underway for over 15 years. Properly configured, ultracapacitors are inherently high power devices so that much of the research has been directed toward increasing their energy density (Wh/kg) without unduely sacrificing their high power and long cycle life. The characteristics of the ultracapacitors depend primarily on the specific capacitance (F/gm and F/cm3) of the electrode materials and the ionic resistivity and voltage window of the electrolyte. In addition to the energy density, the key performance characteristics of the cells are their resistance, RC time constant, and pulse power (W/kg) for high efficiency (95%). Most of the research on ultracapacitors has utilized activated carbons for at least one of the electrodes. In these carbons, charge is stored in the micropores by double-layer processes. Recently carbons are being used that store charge using intercalation and absorption processes that result in much higher specific capacitance than is achievable using double-layer processes. In this paper, the recent work using the advanced carbons is reviewed and future use in ultracapacitors projected. Another approach to increasing the energy density of ultracapacitor- like devices is to combine a carbon electrode with an electrode using pseudo-capacitance or Faradaic chemical processes for charge storage. Considerable progress has been made in the development of such devices in recent years and that research is reviewed in this paper.

NMR Studies of Lithium-Ion Battery Materials: Applications to the Li_2MnO_3-$Li(NiMn)_{0.5}O_2$ System, Layered Oxysulfides and Other Paramagnetic Materials

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^{6}Li MAS NMR spectroscopy has been used to study local electronic structures and Li local environments in a variety of potential cathode materials for lithium ion batteries including spinels and layered cathode materials such as $Li[M'_xM_{1-x}]O_2$ (M,M' = Mn, Ni, Co etc.). We first developed a fundamental understanding of the causes of the large (hyperfine) NMR shifts typically observed in these paramagnetic samples. This knowledge was then applied, in conjunction with X-ray and neutron diffraction studies, to follow structural changes after charging and discharging of a battery, to help establish why some materials function well as electrode materials and others fail.

We will discuss results for two systems. In the first example, the effect of synthesis method and electrochemical cycling on the local and long range structure of members of the Li_2MnO_3-$Li(NiMn)_{0.5}O_2$ pseudobinary will be described. Second, an investigation of new materials including layered oxysulfides will be presented. Insertion reactions and lithium-mobility in these compounds will be described.

Microprobe Studies of Local Interfacial Phenomena at Lithium-Ion Battery Composite Cathodes

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A continuous degradation of lithium-ion batteries upon aging and/or cycling often limits the performance of portable electronic devices and presents a significant barrier for vehicular applications. The impedance growth that is observed at both electrodes is associated with an ion-blocking surface film as well as an electronically insulating barrier formed within the electrode. The resistances to both ion and electron transfer constitute the overall charge transfer impedance and contribute to the overall electrode impedance. In contrast to the anode, the cathode SEI layer is so thin that its presence has not been confirmed until recently. Surface sensitive techniques were used to detect, monitor and analyze surface layers on composite cathodes [1,2,3].

Interfacial phenomena occur and manifest themselves at nano- or micro-scales and can be detected and characterized only by techniques of suitable sensitivity and resolution. *In-situ* and *ex-situ* application of non-invasive and non-destructive microscopies to characterize local physico-chemical properties of the electrode/electrolyte interface provide unique insight into the mechanism of chemical and electrochemical processes, which are responsible for the electrode degradation. *Ex situ* Raman mapping of cathodes from tested high-power Li-ion cells, showed that the state of charge (SOC) of oxide particles on the cathode surface was highly non-uniform despite deep discharge of the Li-ion cells at the end of the test. *In situ* Raman microprobe monitoring of the SOC of individual oxide particles in the composite cathode revealed that the charge/discharge rate varied with time and location [4]. CSAFM and SEM images of aged composite electrodes showed surface deposits and morphology changes. Surface analysis revealed that surface decomposition products originate from $LiPF_6$ decomposition and oxygen, water, and C-O-H, -C=O surface functional groups adsorbed at carbon additives catalyze and/or react with the electrolyte. These surface reaction products create electronic barriers within the composite electrode, which lead to inconsistent kinetic behavior of individual oxide particles and contribute to the overall impedance of the composite cathodes.

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References

1. Y.Wang, X. Guo, S. Greenbaum, J. Liu, and K. Amine. *Electrochem. Solid-State Lett.,* **2001**, 4, A68
2. M. Balasubramanian, H. S. Lee, X. Sun, X.Q. Yang, A. R. Moodenbaugh, J. McBreen, D. A. Fischer and Z. Fu, *Electrochem. Solid-State Lett*., **2002**, 5, A22.
3. D. Aurbach, K. Gamolsky, B. Markovsky, G. Salitra, Y. Gofer, U. Heider, R. Oesten, and M. Schmide, *J. Electrochem. Soc*., **2000**, 147, 1322.
4. Jinglei Lei, Frank McLarnon, Robert Kostecki, *J. Phys.l Chem. B*. **2005**, 109, 952.

Combinatorial and High Throughput Studies of Alloy Negative Electrodes for Li-ion Batteries

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Although carbon or graphite was shown to be a possible practical negative electrode for lithium-ion batteries in the 1980's it took almost a decade for all manufacturers to agree that graphitized materials were the most suitable of carbonaceous materials. Now, almost all Li-ion batteries use highly graphitic carbons as negative electrode materials.

The recent launch of a 14430-sized lithium-ion battery using a tin-based negative electrode (Sony, Japan) makes it clear that silicon and tin-based alloys will begin displacing graphite as the dominant negative electrode material in Li-ion batteries. Sony has announced that the electrode material in their cell is an "amorphous tin-cobalt-carbon" material.

Given that it took the Li-ion battery community about 10 years to settle on graphitic carbons as the best choice for Li-ion battery negative electrode materials based on the **single** element, carbon, how long will it take to find the "best" alloy negative electrode material given the myriad of possible choices available? For example in a patent by Kawakami et al. [1], the inventors claim Sn-A-X materials as excellent negative electrode materials where A indicates at least one transition metal element and X indicates at least one element selected from the group consisting of O, F, N, Mg, Ba, Sr, Ca, La, Ce, Si, Ge, C, P, B, Pb, Bi, Sb, Al, Ga, In, Tl, Zn, Be, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, As, Se, Te, Li and S, where the element X is not always necessary. Which combination of these elements is "best" from the viewpoints of capacity, capacity retention, potential, safety, toxicity, manufacturability and cost?

It is clear that combinatorial methods for synthesizing and screening the myriad of choices are needed. In this lecture, I will describe the combinatorial infrastructure in place at Dalhousie University [e.g. 2] and how it is being used to help **understand** those factors that lead to the "best" negative electrode material.

References:
[1]. Soichiro Kawakami and Masaya Asao US Patent #6,949,312 (2005).
[2]. M.D. Fleischauer, T.D. Hatchard, A. Bonakdarpour and J.R. Dahn, Measurement Science and Technology **16,** 212 (2005).

New lithium salts for liquid or solid polymer electrolyte

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In electrolyte, the salt selection obeys to several criteria, the first of all being its electrochemical stability. The other salt criteria are their conductivity, cationic transference number, cost and molar weight. Due to the low dielectric constant of polymeric solvents, the use of organic lithium salts, in particular of superacid, became widespread. Indeed they have both low lattice energy and poorly nucleophilic anions. As ether is a hard base and lithium cation a hard acid, the interaction between POE matrix and Li^+ is very strong, resulting in a low cationic transference number, t^+, generally markedly lower than 0.5. While POE/$(CF_3SO_2)_2NLi$ and POE/$(CF_3SO_2)_3CLi$ complexes are the highest conducting polymer electrolytes, both have a poor cationic transference number in poly(oxyethylene) as compared, in particular, to lithium triflate. Now, an improvement in the battery performance can be obtained by an increase of the cationic transference number [1,2].

We therefore prepared new organic salts based on fluorinated and non-fluorinated anion.

To find an alternative to the fluorinated salts, Reibel et al. [3] developed aromatic sulfonimides. Anionic charge delocalization is essential in aprotic electrolytes to increase the dissociation of this non-fluorinated salt, therefore its ionic conductivity. We selected therefore aromatic amidure salts. The evaluation of the charge delocalization effect of aromatic nitro substituents was performed.

As for non-fluorinated, aromatic anions were selected according to the possibility (i) to introduce electron-withdrawing groups and (ii) to graft the salt in polymer backbone ($t_+=1$). Moreover, aromatic anions generally presented low mobility [4], which might be due to their rigid skeleton. We selected, for example pentafluoro benzene sulfonate lithium salt. The syntheses and electrochemical characterizations: conductivity, transference number, electrochemical stability, of these salts were evaluated.

References

[1] M. Doyle, T.F. Fuller, J. Newman, Electrochim. Acta 39 (1994) 2073.
[2] K.E. Thomas, S.E. Sloop, J.B.Kerr, J. Newman, Journal of Power Sources 89 (2000) 132.
[3] L. Reibel, S. Bayoudh, P. Baudry, H. Majastre, Electrochim. Acta 43 (1998) 1171.
[4] F. Alloin, S. Bayoud, B. Azimipour, L. Reibel, J-Y Sanchez, Electrochim. Acta 45 (2000) 1193.

The conductivity of crystalline polymer electrolytes

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For some thirty years it was believed that ion transport in polymers occurred only in the amorphous state above the glass transition temperature T_g, with the polymer segmental motion playing a pivotal role in enabling ion transport. Such thinking has raised the level of conductivity to values in excess of 10^{-5} Scm^{-1}. However, the level of conductivity that may be achieved in these amorphous polymer electrolytes has proved insufficient for many applications, including the important application of rechargeable lithium batteries.

Crystalline counterparts of amorphous polymer electrolytes were considered to be insulators. This view has been recently overturned by the discovery of ionic conductivity in the crystalline polymer-salt complexes PEO_6:$LiXF_6$ where x= P, As, Sb.[1] These three complexes have been shown not only to conduct but to do so better than the amorphous phases of the same composition, Fig. 1. The key to the ionic conduction in the crystalline polymer electrolytes is their structure, Fig. 2.[2] The structure is composed of cylindrical tunnels, formed by PEO chains, within which the Li^+ ions reside. The anions do not coordinate the cations and located outside the tunnels. The tunnels provide convenient pathways along which the lithium ions may migrate. The levels of conductivity of these electrolytes are not high, however, they can be significantly improved by modifying the stoichiometric materials by isovalent and aliovalent doping.[3.4] There are other factors that influence the conductivty of these materials which include molecular weight of the polymer, its dispersity, end-capping of polymer chains. We shall discuss various strategies for modifying these materials that permit elevation of the conductivities beyond those obtained with traditional components.

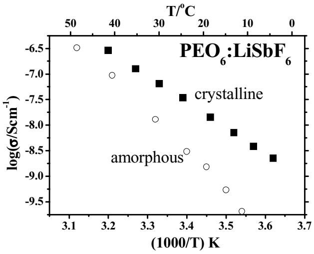

Fig.1

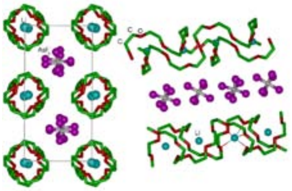

Fig.2

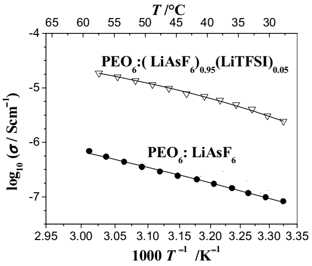

Fig.3

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[1] Z. Gadjourova, Y. G.Andreev, D. P. Tunstall and P. G. Bruce, *Nature* 2001, **412**, 520.
[2] G. S. MacGlashan, Y. G. Andreev and P. G. Bruce, *Nature* 1999, **398**, 792
[3] A. M. Christie, S. J. Lilley, E. Staunton, Y. G. Andreev and P. G. Bruce, *Nature* 2005, **433**, 50.
[4] C. Zhang, E. Staunton, Y. G. Andreev and P. G. Bruce, *J. Am. Chem. Soc.* 2005, **127**, 18305.

A New Type of Battery Using a Magnetic Field

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A new type of battery is proposed that utilizes the occurrence of an inviscid flow in a magnetic channel to maintain the oxidant stream separated from the reductant solution in diffusional contact by a magnetic wall. The main part of the system is, as shown in Fig. 1a, composed of an invisible magnetic channel formed by a magnetic field and a ferromagnetic track, which confines, e.g., a liquid stream of oxidant solution on the cathode. As shown in Figs. 1b and 1c, under a magnetic field, in the neighbourhood of ferromagnetic materials or diamagnetic materials, magnetic flux densities take a heterogeneous distribution, so that the magnetic channel shown in Fig. 1a is formed.

The concept of the magnetic-channel-flow battery is shown in Fig. 2; for a paramagnetic solution containing cathodic active species, though invisible, magnetic channels formed on platinum plated iron tracks imbedded in a plastic plate are established, which are surrounded by a diamagnetic solution with anodic active species. The tracks are also used as the cathode, whereas the anode is placed over the cathode. As the magnetic wall sustains the magnetic channel flow from all sides, the channel also acts as an elastic tube, which allows us to make an inviscid flow of the oxidant. These facts are quite useful for high battery performance since a large amount of active material can be supplied, and much larger area of liquid-liquid interface than that of conventional systems can be available.

As for the possibility and performance of this type of battery, a Daniel-cell-type battery was first examined; copper ion from copper sulphate is employed as an oxidant and zinc sulphate as a reductant. Copper ion is paramagnetic, so that an oxidant solution containing 1 mol dm^{-3} copper sulphate is injected to a magnetic channel formed by an iron track placed in a magnetic field. As an ambient reductant solution, 1 mol dm^{-3} diamagnetic zinc sulphate solution surrounds the magnetic channel, slowly circulated. The performance attained up to 22 mA cm^{-2}.

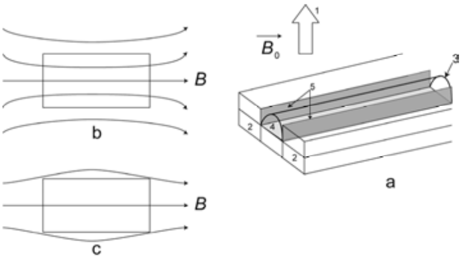

Fig. 1 Formation of magnetic channel.
a, a magnetic channel; b and c, magnetic flux densities for ferromagnetic and diamagnetic materials, respectively.

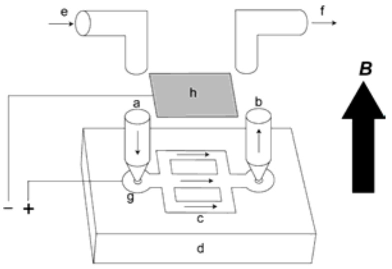

Fig. 2 A magnetic-channel-flow battery

Electrodeposited nano-sized thin films of Sb and Sb-Sb2O3 as anode materials in Li- ion batteries.

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In today's commercial batteries graphite is used as anode material, but research is made on metal-based anode materials to enhance capacity and improve rate capability. Sb can react with Li to form Li_3Sb, which leads to a theoretical capacity of 660 mAhg^{-1} compared to 372 mAhg^{-1} for graphite. However, the problem is (as is the case for a number of different lithium-alloying metals) that large volume changes during cycling leads to particle pulverization and loss of electronic contact. The use of nano alloys or intermetallics (with metals active and inactive to lithium alloying) can minimize the volume stress avoiding cracking and pulverisation of the anode. We have chosen to study electrochemically deposited nanothin films of Sb and Sb-Sb_2O_3. As no binder or electron conducting material is needed in making the films, the electrodes are also suitable model systems for SEI (Solid Electrolyte Interface) studies.

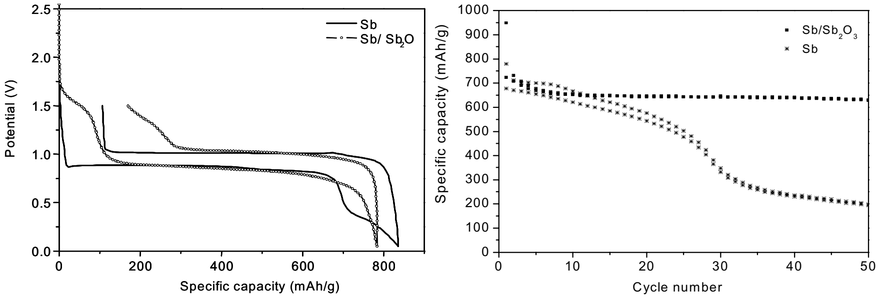

Figure 1. Electrochemical results of a pure Sb electrode and an electrode with co-deposited Sb/Sb_2O_3; the first cycle (a) and the cycling capacity (b).

By adjusting the pH in the electro deposition electrolyte, pure Sb films and Sb films with codeposition of Sb_2O_3 are achieved. In Figure 1a the first cycle of the two films are shown. The presence of the oxide is seen in the reduction potential around 1.6 V where the plateau is most likely due to formation of Li_2O. For pure Sb a plateau, not observed for the Sb_2O_3, is seen below 0.4 V. A possible explanation to this plateau is an additionally formed SEI layer. The cycling stability of the electrodes is improved dramatically, when Sb_2O_3 is codeposited in the films (Figure 1b). In this presentation it will be discussed how the presence of oxide and the SEI layer influences cycling performance. The results will be used to shed some light on the complex reactions occurring in composite electrodes containing antimony, such as Cu_2Sb and AlSb.

Electrochemical synthesis and capacitance of porous composite of carbon nanotubes and polyaniline

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Previously, the authors reported codeposition of polypyrrole (PPy) and multiwalled carbon nanotubes (MWNTs) composite films, via electrochemical oxidation from a solution/suspension of pyrrole monomer and acid-treated MWNTs[1-3]. The acid treatment introduces carboxyl and hydroxyl functional groups that are increasingly negatively charged when deprotonated by raising the pH of the aqueous suspension. The charge on the nanotubes both stabilises the dispersion and allows them to act as the counter ion or dopant for the electropolymerisation of the monomer. Subsequently, the nanotubes are, to some degree, ionically bound to the polymer. This interaction has been shown to produce a large negative potential shift in the composite redox peaks, and to result in the intercalation of both cations and anions during the redox processes; both effects contribute positively to the high electrochemical capacitance of the composite material [1-4]. The current study was motivated by the hope that incorporating negatively charged nanotubes into polyaniline (PAn) might produce similar effects; electrodes based on PAn are desired in order to extend the voltage range of supercapacitors based on polymer nanocomposites[4]. Nanoporous composite films of MWNTs and PAn were grown electrochemically from acidic aqueous solutions, such that the constituents were deposited simultaneously onto graphite electrodes. Scanning electron microscopy revealed that the composite films consisted of nanoporous networks of MWNTs coated with PAn. Cyclic voltammetry and electrochemical impedance spectroscopy demonstrated that these composite films had similar electrochemical response rates to pure PAn films, but a lower resistance and much improved mechanical integrity. The specific capacitance of the composite films, per unit area of the original electrode, reached as high as 3.5 F/cm^2, a significantly greater value than that of 2.3 F/cm^2 for pure PAn films prepared similarly.

1. G.Z. Chen, M.S.P. Shaffer, D. Coleby, G. Dixon, W.Z. Zhou, D.J. Fray, A.H. Windle, Adv. Mater., 12 (2000) 522.
2. M. Hughes, G.Z. Chen, M.S.P. Shaffer, D.J. Fray, A.H. Windle, Chem. Mater., 14 (2002)1610.
3. G.A. Snook, G.Z. Chen, D.J. Fray, M. Hughes, M. Shaffer, J. Electroanal. Chem., 568 (2004) 135
4. C. Downs, J. Nugent, P.M. Ajayan, D.J. Duquette, K.S.V. Santhanam, Adv. Mater., 11 (1999) 1028.

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Rechargeable lithium/air battery

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Rechargeable lithium batteries are now a major technology, driven by their superior energy density compared with alternative rechargeable batteries. There is much interest in increasing further the energy density. This is limited by the positive electrode, $LiCoO_2$, which can cycle only around 0.5 Li per formula unit. Intensive research world-wide on new intercalation cathodes will increase the amount of Li that may be stored, but only by a factor of 2. To achieve the desired leap forward in the performance of rechargeable lithium-ion batteries, we must investigate electrode reactions that are radically different from the conventional intercalation process. One approach is the use of an air cathode.

Abandoning the intercalation cathode in a lithium battery and allowing Li to react directly with O_2 from the air at a porous electrode increases the theoretical charge storage to 1800 $mAhg^{-1}$! The reactants no longer have to be carried on-board the cell and the supply of O_2 is, in principle, infinite. The result is a form of battery/fuel cell hybrid. Whereas the air electrode in aqueous batteries is well known, studies addressing the O_2 electrode in non-aqueous Li batteries have been very limited in number.[1-2] The electrode reactions are fundamentally different in non aqueous cell. Here we demonstrate two essential prerequisites for the successful operation of a rechargeable Li/O_2 battery; that the Li_2O_2 formed on discharging such an O_2 electrode is decomposed to Li and O_2 on charging (shown here by *in situ* mass spec, Fig1), with or without a catalyst, and that charge/discharge cycling is sustainable for many cycles.

More details on the characterisation of the O_2 cathode will be presented, including the influence of catalysts on the electrode reaction. Results of studies by X-ray diffraction and gravimetric analysis will also be presented.

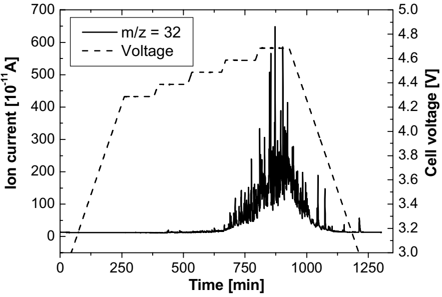

Figure 1. **Variation of ion current corresponding to O_2 evolution as a function of time during the charge of an Li_2O_2 electrode. The voltage was increased by 100 mV every 120 min.**

References
(1) K. M. Abraham & Z. Jiang, *J. Electrochem. Soc.* 143, 1-5, (1996)
(2) (a) J. Read, *J. Electrochem. Soc.* 149, A1190-A1195 (2002). (b) J. Read, K. Mutolo, M. Ervin, W. Behl, J. Wolfenstine, A. Driedger, & D. Foster, *J. Electrochem. Soc.*, 150, A1351-A1356 (2003).

Study on the $LiFePO_4/CaB_6$ Composites used as cathode for a Li-ion Battery

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As an alternative cathode material $LiFePO_4$ has two fatal disadvantages: low electric conductivity and low tap density, which makes it difficult that $LiFePO_4$ is used as the cathode for the commercial lithium ion battery.

A novel composite used CaB_6 as an additive was firstly found to use to improve the electrochemical performance of $LiFePO_4$. Pure $LiFePO_4$ was synthesized by solid sate reaction and $LiFePO_4/CaB_6$ composite with different contents of CaB_6 was prepared by two different methods. The samples were characterized by the granularity, morphology, electric conductivity, tap density, X-ray diffraction and electrochemical performance. The results showed that the tap density and electronic conductivity of $LiFePO_4$ doped with CaB_6 were significantly improved. The electronic conductivity of $LiFePO_4/CaB_6$ composite prepared was increased by five orders of magnitude and its tap density was enhanced by 65%.

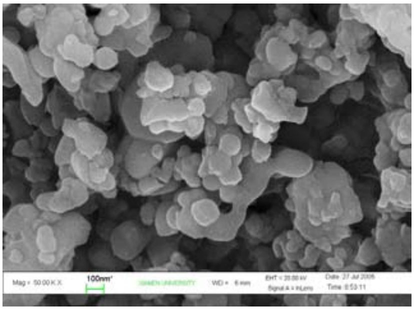

Fig.1 SEM of prepared $LiFePO_4/CaB_6$ composite

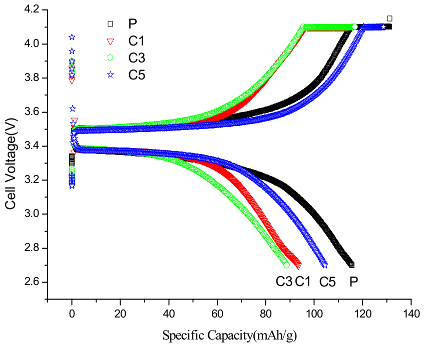

Fig.2 Charge-discharge curves of the batteries at 40mA/g employing the different $LiFePO_4/CaB_6$ composites as cathodes respectively

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Electron Microscopy contribution to the characterization of cycled Li-ion electrode materials (Conversion and CDI mechanisms)

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Batteries performances depend on many factors amongst which the most critical are the selection/synthesis of the appropriate electrode material and the control of the electrode/electrolyte interface upon cycling. In order to address these issues, electrochemists have to design new electrode materials, to finely tune the electrode texture for maximum electrochemical efficiency, to spot interfacial modifications/growing layers or, in short, to 'enter the private life' of a battery.

Electron Microscopy is a powerful tool to help scientists throughout these different steps. This point will be exemplified with descriptive examples selected from our recent works on electrode materials reacting without alloying or insertion of lithium.

Two different types of mechanism will be studied:

- Conversion Reaction for most of transition metal compounds (oxides, nitrides, borates, fluorides, sulphides), with the decomposition of a transition metal oxide into metallic nanograins embedded in a lithiated matrix during discharge, and the re-oxidation of the so-formed nanoparticles during the following charge.

TEM studies realized on phosphides will be shown[1-2].

- Combination displacement/intercalation (CDI) mechanism giving reversible capacities as high as 270 mAh·g^{-1} (more than twice that of electrode materials presently used in commercial Li ion batteries) Studies realized on CuM_2X_4/Electrolyte/Li cells (where M=Ti, Cr and X=S or Se) will be presented[3].

These promising results could enable a breakthrough in the performance improvement of future batteries.

1- F. Gillot, S. Boyanov, L. Dupont, M-L. Doublet, M. Morcrette, L. Monconduit , J-M. Tarascon, Chem. Mater.17, 6317, 2005.
2- "A Two-Step Insertion / Conversion Reaction in the FeP Anode for Li-Ion Batteries",S. Boyanov, F. Gillot, L. Dupont, M. Womes, J.M. Tarascon, L. Monconduit J. Bernardi, M-L. Doublet, Chemistry of materials (submitted)
3- "Copper extrusion/re-injection in Cu-based thiospinels by electrochemical and chemical routes", V. bodenez, L. Dupont, M. Morcrette, C.Surcin, D.W. Murphy, and J-M. Tarascon, Chemistry of Materials (submitted)

Effect of Cu_2O Coating on graphite as Anode Material of Lithium Ion Battery in PC-based electrolyte

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Graphite has been regarded as the most dominant anode material in lithium ion battery for its good cycle performance, high energy density, low cost, and low toxicity. However, its application in propylene carbonate (PC) based electrolyte has been greatly hindered due to its severe exfoliation caused by PC solvated lithium ions. A lot of efforts have been made to solve this problem since propylene carbonate system obtains better low-temperature performance compared with ethylene carbonate system. Here we introduced a method to suppress the degradation of graphite in PC electrolyte by coating Cu_2O as a protective layer.

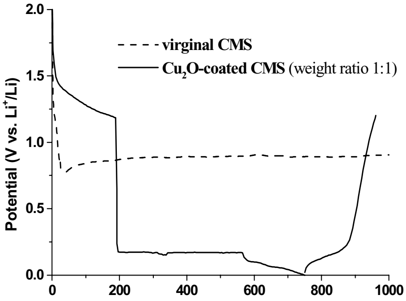

Fig. 1.The discharge and charge profiles of CMS and Cu_2O-coated CMS in PC-DMC (1:1 v/v) electrolyte.

Fig.1 shows the discharge and charge curves of CMS (an artificial graphite) and Cu_2O coating CMS in PC-DMC (1:1 v/v) electrolyte during the first charge and discharge cycle. For virginal CMS, the voltage plateau of the discharge curve indicates that there is no intercalation of lithium ion into graphite, because the graphite structure was destroyed by PC solvated lithium ion and a good SEI film could not be formed. However, after coating with Cu_2O on the surface, there is no potential plateau around 0.8V, revealing that the exfoliation has been greatly suppressed by the coating Cu_2O layer. The potential plateau around 1.3V is due to the lithium ion intercalation into Cu_2O. The reversible capacity of modified CMS is as high as 240mAh/g. By the way, CV and EIS were measured to investigate the effects of the coating.

In summary, with simple coating of Cu_2O on an artificial graphite, the exfoliation of the graphite in PC-based electrolyte has been suppressed.

Acknowledgment

Financial supports from Natural Science Foundation Committee of China (50573012), Shanghai Committee of Science & Technology (0452nm064 & 04QMX1406) and Humboldt Foundation are greatly appreciated.

Nanostructured titania with improved properties as anode materials for lithium batteries

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Nanostructured TiO_2 has been one of the widely investigated transition metal oxides for Li insertion because it is not only a low-voltage insertion host for Li, but also a fast Li insertion/extraction host, which renders it a potential anode material for high-power lithium batteries [1, 2].

The electrochemical behaviors (lithium insertion/extraction) of anatase and rutile with different particle sizes and shapes have been studied in this paper. In the case of anatase [3], mesoporous TiO_2 sub-micron spheres consisting of interconnected nanoparticles with size of *ca.* 7 nm show much higher capacity, better capacity retention and improved rate performance than those of the commercial samples having the same particle size (~ 300 nm). About 0.95 mol Li can be inserted into the mesoporous TiO_2 while only 0.44 mol Li can be inserted into commercial TiO_2 in the first discharge process. Mesoporous TiO_2 spheres are able to reversibly accommodate Li up to $Li_{0.63}TiO_2$ (210 mA h g^{-1}) at 1-3 V *vs.* Li^+/Li with a good capacity retention on cycling. Another excellent property of this mesoporous TiO_2 spheres is the high rate capability. A specific charge capacity of around 210 mA h g^{-1} was obtained at a rate of C/5 after 40 cycles; this value is lowered to 190 mA h g^{-1} at C/2, 175 mA h g^{-1} at 1C, 155 mA h g^{-1} at 2C, 116 mA h g^{-1} at 5C, and finally, 88 mA h g^{-1} at 10C.

In the case of rutile [4], up to 0.8 mol Li can be inserted into nano-sized rutile at room temperature while only 0.1 - 0.25 mol Li can be inserted into micro-sized rutile (500 nm - 20 μm). Nano-sized rutile is able to reversibly accommodate Li up to $Li_{0.5}TiO_2$ at 1 - 3 V *vs.* Li^+/Li with excellent capacity retention and high rate capability on cycling. A specific charge capacity of around 160 mA h g^{-1} was obtained at a rate of C/20 after 50 cycles; this value is lowered to 150 mA h g^{-1} at C/5, 132 mA h g^{-1} at 1C, 110 mA h g^{-1} at 5C, 100 mA h g^{-1} at 10C, 81 mA h g^{-1} at 20C, and finally, 70 mA h g^{-1} at 30C. As far as titania is concerned, it is the best rate performance ever measured especially at higher rate.

Present results provide evidence for the usefulness of nanostructured titania as novel anode materials for lithium batteries.

References

[1] G. Sudant, E. Baudrin, D. Larcher, J. M. Tarascon, *J. Mater. Chem.* **15**, 1263 (2005).
[2] R. Armstrong, G. Armstrong, J. Canales, R. Garcia, P. G. Bruce, *Adv. Mater.*, **17**, 862 (2005).
[3] Y.-G. Guo, Y.-S. Hu, J. Maier, *Adv. Mater.* submitted.
[4] Y.-S. Hu, L. Kienle, Y.-G. Guo, J. Maier, *Adv. Mater.* in press (2006).

Electrochemically deposited nanostructured ni-co oxide for supercapacitor application

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Electrochemical capacitors are the charge-storage devices having the capability to store higher power density than batteries and higher energy density than dielectric capacitors. They are of significant importance in the portable devices as well as electric vehicles. Several metal oxides were synthesized for supercapacitor electrode in the past few years. In the present study, electrochemical synthesis and capacitive characterization of nanostructured Ni-Co oxide are presented

The Co-Ni oxide was potentiodynamically deposited on a stainless-steel electrode of 1 cm x 1 cm area in the electrolyte solution of 0.1 M $NiCl_2{\cdot}6H_2O$ + 0.05 M $CoCl_2{\cdot}6H_2O$. The deposited electrodes were further heat-treated at 300°C and characterized by scanning electron microscopy (SEM), cyclic voltammetry (CV) and charge-discharge (CD) cycling. The electrochemical characterization was performed in a three-electrode cell with different concentration of KOH solution as electrolyte.

The SEM images of the deposited Ni-Co oxide indicate that the deposite is highly porous and the Ni-Co oxide is in the form of nano-rods. The EDX elemental mapping study showed that the Ni, Co and O elements are present uniformaly in the deposite. The CV measurements showed that the nature of the CV curve was close to rectangular shape. From the CD measurements, a specific capacitance (SC) of 331 F/g was obtained at 1 mA/cm^2. Fig. 1 shows the CD cycling data for 1st and 1000th cycles. A SC decrease of only ~2% was observed after the CD cycling of 10000 cycles. This indicates that the Ni-Co oxide electrode is a potential candidate for supercapacitor applications.

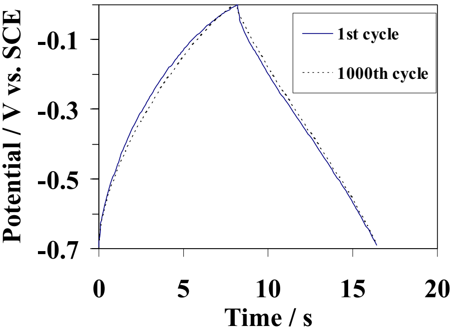

Fig. 1 CD cycling stability curves of the Co-Ni oxide electrode at various current densities.

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High Rate Capability of Platelet Structure Carbon Nanofibers as Anode Materials for Lithium Ion Batteries

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Porous anodic alumina is a useful template for the preparation of various nanofibers with controlled fiber diameter. The authors have prepared carbon nanofibers by liquid phase carbonization of poly(vinyl)chloride (PVC) in pores of the template. The carbon nanofibers thus obtained have a platelet structure with the graphitization degree increasing with heat treatment temperature. The platelet structure carbon nanofibers are of interest as anode materials for lithium ion batteries since diffusion length of the intercalated lithium ions is short, possibly improving the rate capability. Thus, in the present study we have examined the influence of fiber diameter and heat treatment temperature on anode characteristics of the carbon nanofibers for lithium ion batteries, with particular attention paid to their rate capability.

A mixture of PVC powders and porous anodic alumina template with pore diameters of 30 or 200 nm were heated in a stream of high purity argon gas to 600°C. Then, the template was dissolved and fibrous carbon precursors were obtained. The precursors were further heated to 1000, 1500 and 2800°C. The anodes were prepared by coating a mixture of carbon nanofilaments and polyvinylidene fluoride on porous nickel sheets. The anodes with acetylene black as a conducting material were also prepared. A liquid electrolyte of 1.0 mol dm^{-3} $LiClO_4$ dissolved in EC+DEC (1:1 by volume) was used.

The carbon nanofibers heat-treated at 2800°C was highly graphitized, and their charge-discharge curves revealed a plateau region close to 0.1 V vs Li/Li^+, being similar to typical graphite. However, the reversible capacity was less than 200 mA h g^{-1} at a current density of 50 mA g^{-1}, which was far lower than the theoretical capacity of graphite (372 mA h g^{-1}). The lower capacity of this material might be related to the development of loops connecting each ~5 layers at the edge of graphene layers.

Higher capacity and higher rate capability was obtained for the carbon nanofibers heat-treated at 1000°C. Further, it was confirmed that the reversible capacity became higher with reducing fiber diameter, particularly at high current density, for the carbon nanofibers heat-treated at this temperature. The addition of conducting material in electrode further improves the rate capability due to low electrical conductivity of the active materials formed at 1000°C.

Graphite/sulfur lithium ion cell using lithium compensation of a lithium foil

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Non-lithiated cathode materials were widely investigated for use with lithium metal anodes, in cells based on polyethylene oxide electrolytes. Sulfur-based materials have capacities of more than trible that of lithium cobalt oxide, though at a lower average discharge voltage. These materials are inherently safer than lithiated cathode materials because they cannot be overcharged. To be used in a lithium ion cell, an alternative source of lithium must be provided. The lower voltage is not necessarily a problem, given reduction in the operating voltage of electronic circuits.

In this study, graphite/sulfur composite lithium ion cells have been constructed with a lithium metal foil incorporated in the anode. The foil can be used to compensate for the irreversible capacity of the anode, allowing anode materials with large reversible and irreversible capacities to be used. The foil also enables high capacity, non-**lithiated** cathode materials (nano sulfur composite, which is prepared as described in [1]) to be used in lithium ion cells.

The cathode was nano sulfur composite. The anode used was graphite. In a dry glove box, the Celgard 2400 porous membrane was used as the separator, and put between the cathode and the anode to form a model cell, and a lithium metal foil was put between the anode and the separator, which was sealed in a coin type battery after addition of 1 M $LiPF_6$-EC/DEC electrolyte solution. The test was carried out at a constant current density of 0.25 mA cm^{-2} and within the voltage range of 1.0-3.0 V.

Fig. 1 shows the cycling performance of the test cell. It indicates that the test cell can be cycled. This paves the way to fabricate cell with the sulfur based cathode materials.

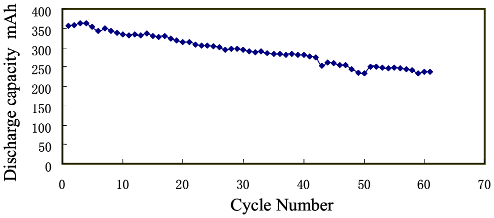

Fig 1 Cycling performance of Nano sulfur composite/graphite test cell

References

[1] J L Wang, J Yang, J Y Xie, et al. Advanced Mater, 2002, 14 (13-14): 963-965.

Ethylene carbonate — organic ester based mixed electrolytes for electrical double layer capacitors

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The electrochemical characteristics of electrical double layer capacitor (EDLC) single cells, based on the nanoporous carbon cloth electrode (thickness ~300 µm) in 1M $(C_2H_5)_3CH_3NBF_4$ solution in various non-aqueous organic carbonate and organic ester binary, ternary and quaternary solvent systems (ethylene carbonate (EC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), diethyl carbonate (DEC), methyl formate (MF), methyl acetate (MA) and ethyl acetate (EA)) mixed in the x:y, x:y:z and x:y:z:f volume ratios, respectively) have been studied using the cyclic voltammetry (CV) and the electrochemical impedance spectroscopy (EIS) methods [1]. The specific capacitance C_s, phase angle δ, series (R_s) and parallel resistance (R_p) values dependent on the conductivity of solvent system used have been calculated. The region of ideal polarisability of nanoporous carbon electrodes $\Delta E \geq 3.0$V for 1M $TEMABF_4$ in various non-aqueous solvent systems has been achieved. Specific conductivity values have been obtained from –40°C< to < 50°C and compared with electrochemical characteristics. All experiments discussed were made inside the glove box Labmaster 130 at very clean and dry conditions. The two-electrode system was set in a hermetic aluminium test cell to ensure the gas tightness of the cell. Between working electrodes the 25 µm thick Celgard separator sheet was used. Impedance spectra were recorded using Solartron FRA 1255 and potentiostat 1286 over a frequency range $5\times10^3 \ldots 1\times10^{-3}$ Hz, and 5 mV modulation was used. The ac response of the EDLC filled with the electrolyte having a good specific conductivity (EC:EA, EC:MA, EC:MF (1:1), EC:DMC:EA, EC:DMC:MA or EC:DMC:MF (1:1:1) solvent + 1M $(C_2H_5)_3CH_3NBF_4$) shows only very weak dependence of R_{pore} on the potential difference applied if $\Delta E \leq$ 2.7 V, and R_{pore} increases noticeably with ΔE only at $\Delta E >$ 2.7 V. For other systems, having lower specific conductivity the values of R_E and R_{pore} depend noticeably on ΔE in a good agreement with the dependence of the phase angle δ on ΔE, obtained at low frequencies. Thus according to the experimental data, the deviation of mixed solvent + 1M $(C_2H_5)_3CH_3NBF_4$ | NPCE interface from the purely adsorption limited system increases with ΔE. According to the experimental results, comparatively low values of phase angle δ at $f < 5\times10^{-2}$ Hz ($\delta \leq -82°$ at $f \leq$ 1mHz) have been obtained for EC:EA, EC:DMC:EA and EC:DMC:MA (1:1 and 1:1:1 volume ratio) containing single cells. Thus, the nearly ideal capacitive behaviour, like for NPCE | AN has been observed only for systems having high specific conductivities.

Reference

1. Alar Jänes, Enn Lust, Use of organic esters as co-solvents for electrical double layer capacitors with low temperature performance, J. Electroanal. Chem., (accepted).

Synthesis And Characterization Of Comb Shape Single Ion Conductors Based On Polyepoxide Ethers And Perfluorinataed Lithium Salts

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Most single ion conductors for lithium batteries are synthesized by fixing either alkyl sulfonate or carboxylate to the polymer backbones. However, due to their limited solubility and dissociation in polyether media, their ambient conductivities are usually in the range of 10^{-7}-10^{-8} S.cm^{-1} [1, 2]. There are several approaches to improve the ambient conductivities of single ion conductors. One is to modify the structure of the host polymer to lower its glass transition temperature and thus improve ionic conductivity through increased ion mobility. Another is to modify the structure of the anion by placing strong electron-withdrawing atoms, such as fluorine, adjacent to it to decrease the electron density on the anions and thus increase the ionic conductivity through increased number of free conducting lithium cations. The best approach, of course, is to combine the above two favorable changes in one structure. It was shown in our group[3] that the comb-shaped polyepoxides with trimethylene oxide (TMO) as side chains have lower glass transition temperatures with increasing lithium salt concentration than those with EO as side chains, which is more effective in providing higher chain mobility especially at lower temperatures. In this paper we synthesized two polyepoxide ether prepolymers, one with TMO units in the side chain and the other with EO units in the side chain, and different allyl groups containing lithium salts, either perfluorinated or non fluorinated. The focus of this paper is to compare the effect of the structure of polymer and lithium salts on the ionic conductivities of the resulting single ion conductors. The TMO polymers showed a much lower conductivity than the EO polymers for the alkyl and fluoroalkylsulfonate anions due to poor dissociation of the lithium cations, apparently due to the lower dielectric constant of the TMO polymers. The larger and more electron withdrawing imide anions appear to overcome this problem.

Although the polyelectrolytes reported here appear to meet the bulk conductivity requirements of practical lithium batteries, there appears to be a major problem asociated with yje interfacial impedance. Measurements of this property have shown unaccetably high impedance values for practical operation.

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References

1. Kobayashi N.; Uchiyama, M.; Tsuchida, E. *Solid State Ionics*, **1985,** *17*, 307.
2. Ito, Y.; Ohno, H. *Solid State Ionics*, **1995,** *79*, 300.
3. Kerr, J. B.; Liu, G.; Curtiss, L. A.; Redfern, P.C. *Electrochimica Acta*, **2003,** *48*, 23

Relation between electronic resistance and capacitance for highly aqueous RuO_2

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Due to promising high capacity per gram supercapacitors based on the pseudo capacitance of hydrous ruthenium oxide (RuO_2 xH_2O) have been the focus of numerous recent studies. In order to optimize the performance of this transition-metal-oxide compound a good understanding of the influence of the preparation parameters on its electrochemical behaviour is required and especially the influence of annealing treatments on the gravimetric capacitance C_g (F/g) of the material. Many authors have pointed out that two parameters are very important for an optimal behaviour of the material: first a good electronic conductivity in the bulk material and second a high ionic conductivity of protons in the hydrated pores and boundary regions in between the material's particles [1].

Samples annealed at high temperature (17 hours at 300°C in air) exhibit a small capacitance as the bound water in the pores is removed during the heat treatment. On the other hand samples annealed at low temperatures (17 hours at 25°C or 75°C in air) also exhibit low capacitance albeit they contain more water.

In order to understand why the voltammogram of these last samples show a characteristic reduction of capacitance at low potential we compared the potential dependent capacitance, during the anodic sweep of the CV between +0.8V and -0.2V toward a carbon quasi reference, with the evolution of the potential dependent bulk electronic resistance Z_e of the material measured in situ for the same potential range. The set-up for in situ measurements of the potential dependent electronic resistance has been described before [2].

The observed close similarity of the curves suggests that the electronic resistance of the bulk is the main parameter controlling the capacitance of highly hydrous RuO_2 at low potential. This result is supported by Electrochemical Impedance Spectrometry (EIS) measurements showing that the real part, Z_r at 10 mHz, of the overall impedance (ionic and electronic) exhibits the same evolution with the potential than Z_e.

[1] D. A. McKeown, P. L. Hagans, L. P. L. Carette, A. E. Russel, K. E. Swider and D. R. Rolison, Structure of Hydrous Ruthenium Oxides: Implications for Charge Storage, Journal of Physical Chemistry B, 103, 4825 (1999)

[2] M. Hahn, M. Bärtschi, O. Barbieri, J-C. Sauter, R. Kötz, R. Gallay, Interfacial Capacitance and Electronic Conductance of Activated Carbon Double-Layer Electrodes, Electrochemical and Solid-State Letters, 7(2), A33 (2004)

A dilatometric study of ion intercalation from aprotic solutions into carbonaceous materials

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Lithium-ion batteries (LiB) and electrochemical double layer capacitors (EDLC) both take advantage of electrochemical ion insertion into carbonaceous electrode materials. For the graphite based LiB anode, the intercalation of Li ions is the actual mechanism of charge storage. For the activated (hard) carbon based EDLC electrodes, the insertion of the electrolyte ions, usually R_4N^+ and BF_4^-, may well contribute to charge storage, besides double layer charging. The role of insertion processes for EDLC voltage limitation has only recently been suggested [1].

Electrochemical dilatometry was applied to highlight the influence of different material parameters – the type of carbon, solute and solvent – on the charge specific expansion of LiB and EDLC systems.

The updated setup allows measurements of single oriented crystals (HOPG), bound powder based electrodes, as well as binder-free carbon powders. The separate determination of both height and volume changes of one and the same material provides valuable information on the preferential particle orientation in powder-type electrodes.

In general, the charge specific expansion is much more pronounced for Et_4N^+ and BF_4^- than for Li^+ insertion, obviously accounting for the different size of the ions. On the other hand, the qualitative behaviour is in most cases similar: An irreversible swelling during the first cycle is followed by a rather reversible expansion / contraction during subsequent cycling. Furthermore, the progressive exfoliation of graphite in some propylene carbonate LiB electrolytes is demonstrated.

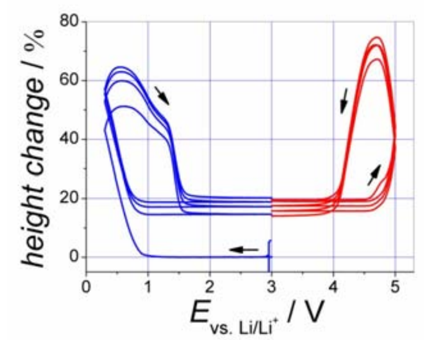

Figure 1:

Powder graphite (MCMB 25) height change recorded during voltammetric (CV) experiment. Sweep rate 2 mV/s. Electrolyte: 1 M Et_4NBF_4 in propylene carbonate.

[1] M. Hahn, O. Barbieri, F.P. Campana, R. Kötz, R. Gallay: Appl. Phys. A 2006; A82: 633-638.

Mesoporous Nickel/CNT Nanocomposite Electrodes For Electrochemical Capacitors

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Electrochemical capacitors are becoming attractive energy storage systems particularly for applications involving high power requirements. The capacitance in an electrochemical capacitor can arise from the charging or discharging of the electrical double layers (electrical double layer capacitance) or from faradaic redox reactions (pseudocapacitance). Carbon materials with very high-surface area are widely used for electrical double layer capacitors (EDLC). Subsequently, conducting polymers and transition metal oxides with relatively high-surface-area have been identified as possible electrode materials for supercapacitors (pseudocapacitors). Among the various materials investigated over the years, amorphous $RuO_2 \cdot xH_2O$ prepared by the sol-gel process has become the leading electrode material for supercapacitors as it exhibits a high specific capacitance (720 F/g). However, the high cost of ruthenium and environmental problem of electrolyte such as strong acidic media have limited its commercial use. Accordingly, there is a strong incentive to find alternative electrode materials, which are inexpensive and exhibit pseudocapacitive behavior similar to that of hydrous RuO_2. Much attention is now focused on the oxides of manganese, nickel, cobalt, and vanadium as candidates for development of supercapacitors.

It was known that the charge storage reaction of transition metal oxides confined mainly to their surface layer. Therefore, in order to obtain high performance with both high power and high energy densities, it is important to design and fabricate nanostructured electrode materials that provide interconnected nanopaths for electrolyte-ion transport and electronic conduction. Since conventional nanoparticulate systems have a disordered porosity with voids of varying cross section interconnected by narrower intervoid spaces, materials moving within the pore structure encounter a considerably tortuous path, impeding reaction rates. By contrast, materials with high surface areas and a uniform, ordered pore network would be expected to exhibit superior performance in electrochemical systems which rely on liquid diffusion within the electrode material.

In this study, ordered mesoporous nickel electrodes including CNTs as conducting agents were fabricated by the liquid-crystal template assited electrodeposition in the presence of surfactants. More details about the synthesis and electrochemical properties of mesoporous nickel/CNT nanocomposite electrodes will be presented at the meeting.

Additives for performance improvement of Li ion battery

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Three kinds of additives, electrolyte stabilizer, solid electrolyte interphase (SEI) forming additive, and over-charging inhibitor, were considered for the performance improvement of lithium ion battery.

Ethanolamine was used as an electrolyte stabilizer. The cyclic voltammograms of graphite and $LiCoO_2$ electrodes in $LiPF_6$/EC+DMC+EMC with and without ethanolamine, and the cyclic stability of C/$LiCoO_2$ battery were measured. It was found that the voltammetric performance of the electrodes was hardly influenced by the addition of ethanolamine into the electrolyte, however, the stability of the electrolyte containing water could be improved by ethanolamine. The contents of H_2O and HF changed from 101.3ppm and 9.5ppm to 3.2ppm and 205.1ppm in electrolyte without ethanolamine, but to 65.6ppm and 92.7ppm in the electrolyte containing 0.1% ethanolamine, respectively, after storing the electrolytes at 45℃ for 24hr. The cyclic stability of C/$LiCoO_2$ battery using water containing electrolyte was improved to a great extent.

Two kinds of sultones were used as SEI forming additives. The electrochemical reduction of sultones, the composition of the formed SEI films and the performance of the batteries with the application of the additives were investigated. The reduction of the additives took place at the potential more positive than those of solvents. Sulphur was detected in the SEI films formed on graphite in electrolyte containing sultones. The discharge performance of batteries was improved with the application of sultones under either low or higher temperature.

Cyclohexylbenzene (CHB) was used as an over-charging inhibitor. The cyclic voltammogram of platinum electrode, the charging-discharge curve of $LiMn_2O_4$ electrode in electrolyte containing CHB, and the voltage and the inner resistance of the battery using CHB containing electrolyte were measured. It was found that the decomposition of solvents at high potential could be inhibited by CHB. The charging and discharge performance of $LiMn_2O_4$ electrode was hardly influenced by CHB. The voltage of the battery was hardly changed but the inner resistance of the battery increased sharply with charging time when CHB was used.

Key words: Additives, Electrolyte stabilizer, SEI film forming additive, Over-charging inhibitor.

Electrode materials for supercapacitors with ionic liquid electrolytes

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Supercapacitors of high specific power play a crucial role in the development of electric vehicles where they can be coupled with lithium batteries or fuel cells to provide power peaks during acceleration as well as for energy recovery during braking. The typical operating temperature for these applications are higher than RT. Thus, in order to develop high voltage supercapacitors operating above RT we are pursuing the strategy of using ionic liquids (ILs) as “solvent-free” electrolytes of high thermal stability, wide electrochemical stability window and good conductivity. We already demonstrated the viability of this strategy in activated carbon (AC) // poly(3-methylthiophene) (pMeT) hybrid supercapacitors: when a high purity and hydrophobic IL such as N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide was used these supercapacitors provided maximum cell voltages higher than 3.4V as well as long cycling stability over 15,000 cycles at 60 °C [1]. Furthermore, this very interesting result was achieved with commercial electrode materials and we demonstrated that improvements of such IL-based hybrid supercapacitors are feasible via optimization of the affinity of electrode materials for the ILs [2].

Here we present and discuss results on the development of materials with morphologies and surface chemistry tailored for operation at 60°C in hydrophobic ILs. Particularly, data on mesoporous cryogel carbons and pMeT synthesized in the frame of the ILHYPOS “Ionic Liquid-based Hybrid Power Supercapacitors” UE Project are reported and discussed.

Acknowledgements
Research funded by ILHYPOS EC Project (Contract Number 518307).

1. A. Balducci, W.A. Henderson, M. Mastragostino, S. Passerini, P. Simon, F. Soavi, Electrochim. Acta, 50 (2005) 2233-2237.
2. A. Balducci, F. Soavi and M. Mastragostino, Appl. Phys. A, 82 (2006) 627-632.

Ionic Mass Transfer of Li^+ Ion near the Li Ion Battery Electrode

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Li ion battery is now widely used as power sources of mobile electronic devices. It is also expected for the power supply of the electronic vehicles. However, a new negative electrode material must be developed, because the capacity of graphite material as the negative electrode has almost reached the theoretical limit.

Li metal is an attractive candidate for the negative electrode, because it has highest energy density. The dendrite growth of Li metal during the charging operation however, introduces a fatal problem. Generally speaking, the dendritic growth of metal is influenced by the ionic mass transfer phenomena. Therefore, it is indispensable to understand the coupling phenomena between ionic mass transfer phenomena and the dendritic growth of Li metal. On the other hand, Sn based alloys provide promising materials for the negative electrode. Many researchers have focused on the cycle efficiency and the mass transfer inside the electrode materials. The ionic mass transfer in the electrolyte has not been examined.

In this study, the mutual diffusion coefficients of $LiClO_4$ and $LiPF_6$ in PC electrolyte are measured by the Moiré Pattern method. However, the ionic mass transfer rate during the electrodeposition or electrochemical dissolution of Li metal (or charging to Sn based alloy) was in-situ measured by the holographic interferometry technique. The horizontal installed working electrode is facing downward in order to restrict the natural convection induced by the electrodeposition.

Figure 1 shows the transient behaviour of the electrode surface concentration accompanied with the electrodeposition of Li metal (circle) and insertion of Li^+ into Ni-Sn alloy (triangle)in the $LiClO_4$-PC electrolyte solution.

In case of the electrodeposition of Li Metal, "incubation period" explicitly appears before the interference fringes starts to shift. This phenomena may be caused by the formation of SEI layer on the electrodeposited Li metal surface.

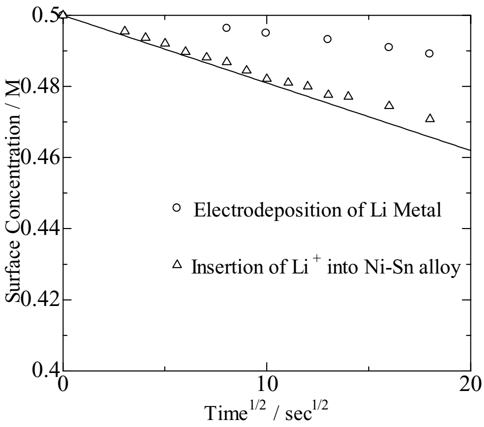

Figure 1: Transient Behavior of Surface Concentration of Li^+ Ion (at 0.5mA/cm^2)

The hydrogen evolution and recombination kinetics in sealed rechargeable NiMH batteries

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The hydrogen evolution and recombination kinetics in NiMH batteries have been investigated under temperature-controlled, steady-state, overdischarging conditions within a temperature range of 10 and 50 °C and at discharging currents of 1 to 350 mA (0.0009 to 0.3 C-rate). *In situ* Raman spectroscopic analyses of the gas phase showed that hydrogen is the only gas evolving inside the battery during overdischarge at the above-mentioned conditions. The pressure increase could be very critical at low temperatures, leading to opening of the safety vent at relatively low discharging currents, for example, only 220 mA at 10 ^{0}C. The polarisation parameters for the hydrogen evolution reaction, such as Tafel slopes and exchange currents were determined at the different temperatures (see Eq. (1) and Fig. 1) as well as the parameters for the recombination process (see Eq. (2) and Fig. 2). The reaction mechanism and the rate-determining steps will be discussed. For modelling NiMH batteries this is highly valuable information as they are directly obtained from the system of interest. Furthermore, the obtained results make battery simulations more realistic by minimising the number of parameters involved and making the correct assumptions.

$$ln(I_{her,Ni}) = ln(I^{0,ref}_{her,Ni}) - (1-\alpha_{her})\frac{nF}{RT}\left(E_{Ni} - E^0_{H_2}(T)\right) \tag{1}$$

$$I_{hrr,MH} = I^{0,ref}_{hrr,MH}\left(\frac{p_{H_2}}{p^{ref}_{H_2}}\right)^{x_{hrr}} exp\left(\alpha_{hrr}\frac{nF}{RT}\left(E_{MH} - E^0_{H_2}(T)\right)\right) \tag{2}$$

Fig. 1. Tafel slopes for the hydrogen evolution kinetics.

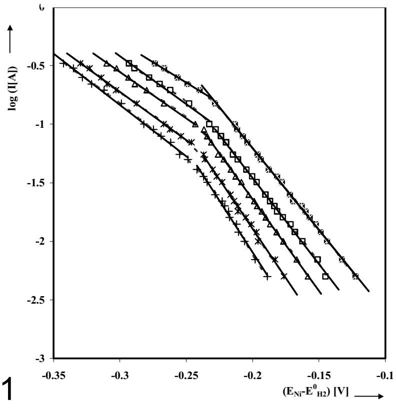
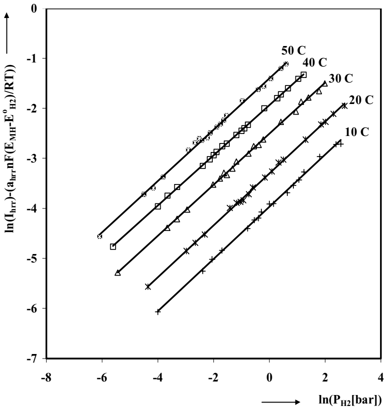


Fig. 2. The hydrogen recombination kinetics.



In situ analysis of interfaces in nonaqueous electrochemical systems

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The high energy density available from lithium-ion batteries is the reason for their key importance in both the current high-end consumer electronics and the development of hybrid vehicles. In such batteries both the negative and positive electrodes are made from electronically conductive matrix materials which are able to reversibly accommodate (insert) variable quantities of lithium ions. So far, electroactive insertion materials used in commercial lithium-ion cells are based on lithiated carbon (LiC_6) and lithium transition metal oxide $LiMO_2$, typically on the basis of cobalt, nickel, and manganese. Several new, alternative electroactive materials like nano-silicon are also promising for application in rechargeable lithium-ion batteries.

In the contribution basic scientific questions will be discussed, principally related to the surfaces' electrocatalytic activities. The challenge here is the understanding of how the structure and composition of these materials are correlated with their electrochemical properties, in particular with their specific charge, cycling stability, and rate and mechanism of side reactions.

The electrode potential of most of the electroactive materials is far beyond the thermodynamic stability window of the most commonly used organic electrolytes. Hence reductive and oxidative electrolyte decomposition occurs. Typically propylene, ethylene, hydrogen, and (in a few electrolytes) CO_2 are generated during electrochemical electrolyte reduction. On oxide positive electrodes, carbon dioxide and occasionally oxygen are characteristic gaseous reaction products. Gas evolution increases the cell internal pressure, which may result in raised safety risks and reduced cycle stability. Fortunately a protective layer called the Solid Electrolyte Interphase (SEI) forms normally at the surface of negative electrode materials, preventing further reductive electrolyte decomposition. A similar protective film is also reported for positive electrode materials such as $LiMn_2O_4$ and $LiCoO_2$.

In the contribution results of several advanced *in situ* methods, like FTIR- and Raman spectroscopy, as well as *post mortem* Scanning Electron Microscopy (SEM) will be discussed. Emphasis will be given to the Differential Electrochemical Mass Spectrometry (DEMS).

Parts of this work were performed within the European project CAMELiA and the European network of excellence ALiSTORE. We acknowledge the materials and contributions from TIMCAL and Degussa.

Electrochemistry of naphthalene derivatives with disulfide bonds and their application to cathode materials for lithium secondary batteries

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Electrochemical behaviors of dithionaphthalene(DTN) and tetrathiolenes(TTL) such as tetrathionaphthalene(TTN), tetrachlorotetrathionaphthalene(TCTTN), tetrathiotetracene(TTN) and bis(phenylenedithio)tetrathionaphthalene(PDTTN) have been investigated. It is expected that these molecules would undergo reversible multi electron transfer reactions at S-S bond, which is active center in energy storage (1)(2) . All molecules are planar with highly delocalized π systems but the HOMO in these molecules changes dramatically upon replacement of the hydrogens at some positions of naphthyle ring with sulfur and halogen (3). Therefore, the redox potentials of compounds would change dramatically. Below 2.5 V vs. Li/Li^+, an S-S bond ring in these molecules was accepted to reduce with one or two electrons. Above 2.8 V vs. Li/Li^+, the ring was oxidized to stable cationic radical. The cyclic voltammetric responses demonstrated good possibility as cathodic materials with high energy density, as shown in Fig.2. The cell performance will be reported.

References:

(1)N.Oyama, et.al., *Nature(London)*,373,598(1995)

(2)T.Inamasu et.al., *J. Electrochem.Soc.,*150(1),A128-A132(2003)

(3) B.K. Teo et.al.,*Inorg. Chem*.,18,1490(1979)

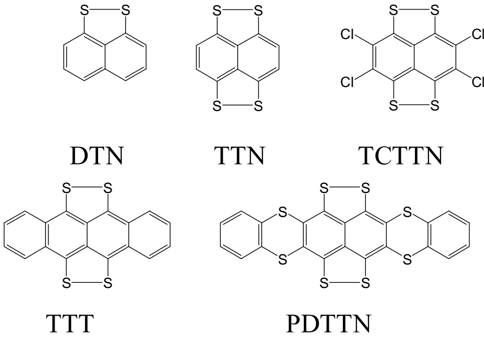

Fig.1 Structures of the compounds

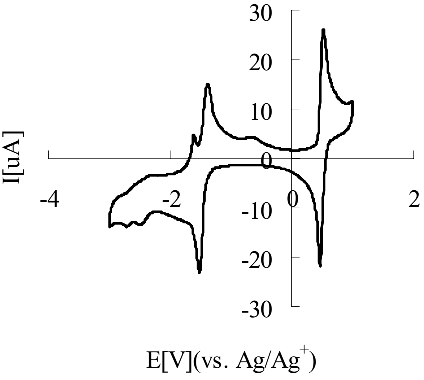

Fig.2 Cvclic voltammogram of 0.5mM DTN in 0.1M Et_4NBF_4/AN at GCE. Scan rate : 100mV/s.

Insertion of hydrogen in palladium films examined by combining EQCM and electroacoustic measurements.

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Palladium can offer interesting potentialities for hydrogen storage and can be used as a model for understanding the metal hydride systems [1,2]. Hydrogen dissolves and occupies interstitial sites in the host metal. The mechanism of insertion is not very well understood and this insertion is accompagnied by an expansion of the crystal lattice where strain and stress fields results.

The aim of this investigation is to characterize the hydrogen absorption by combining classical electrochemical measurements with acoustic transducer measurements used in different modes: active mode (EQCM), time resolved mode (*ac*-electrogravimetry) and passive mode (electroacoustic impedance).

Palladium films were electrodeposited onto one of the gold electrodes of a quartz resonator working at 9 MHz. Classical EQCM measurements were realised with a home made oscillator set-up and *ac*-electrogravimetry measurements with high stable frequency/voltage electronic converters. They allow fast measurement with a high frequency resolution and the mass-potentiel transfer function were estimated. In parallel, electroacoustic impedances were carried out on the same samples. All the measurements were performed in sulfuric acid 0.1M.

Thus, one interesting parameter i.e. the mass/charge ratio can be estimated according to different approaches. On the one hand, during voltage cycles, the mass was estimated through EQCM measurements during a complete cycle. On the other hand, the mass/charge ratio was directly calculated at certain potentials by using the mass-potential transfer function. If for small overvoltages this ratio is around one for higher overvoltages, the ratio becomes higher and differs from the hydrogen molar weight. This problem is certainly due to stress effects which occured during hydrogen insertion. To corroborate this effect motional resistance of the equivalent circuit of the resonator were measured by using electroacoustic impedance analysis. A change of this resistance is correlated to the stress increase shown by means of a laser beam deflection technique [3].

References

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[1] M. Baldauf et D.M. Kolb, Electrochimica Acta, 38 (1993) 2145.
[2] A. Czerwinski, R. Marassi et S. Zamponi, J. Electroanal. Chem, 316 (1980) 211.
[3] J. N. Han, S.I. Pyun and D.J. Kim, Electrochim. Acta, 44(1999)1797.

High Throughput Positive Electrode Material Studies Using Post Synthesis Array Transfer Techniques

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In recent years high throughput methods for the discovery of new materials for lithium batteries has grown in popularity. Several groups have demonstrated parallel synthesis and screening for the study of lithium battery negative and positive electrode materials, e.g. Si-Al-Mn alloys [1, 2] and $LiCoO_2$ [3].

This paper reports a study investigating the performance of $LiFePO_4$ [4] when coated with different amounts of carbon. This will showcase a new high throughput approach referred to as post synthesis array transfer (PoSAT). Details of the technique will be outlined and comparisons will be drawn to alternative methods.

The PoSAT approach uses an array of 64 quartz tubes in which precursor solutions are mixed before high temperature synthesis to produce the active materials. During the preparation materials can be homogenised using a rotating glass-bar attached to a drill. After sintering the materials are then ground to a powder and composite inks are prepared in the quartz tubes by the addition of acetylene black and PVDF binder. Electrode films are then deposited on an array of 64 aluminium current collectors for parallel electrochemical testing and high throughput XRD measurement. The advantages of this technique are accelerated material screening, its similarity to bulk synthesis and the use of composite electrodes is similar to the industrial standard. Further advantages are the freedom in preparation conditions, e.g. atmosphere, synthesis temperature, and the addition of mixing steps.

The scatter in the current density and specific capacity have been reduced by accurately measuring the active material mass for each of the electrodes in a time efficient way. This has been achieved by weighing the composite electrodes prepared using the PoSAT technique with a computer connected balance followed by TGA of the 64 composite inks. This has allowed the determination of the effect of precursor [4] composition on the electrode performance. It was found that percolation of the electronic conduction path required a sucrose to $LiFePO_4$ molar ratio of 0.24 ± 0.012.

Results showing the application of the PoSAT method to investigate solid solutions such as $Li_{1-2x}Mg_xFePO_4$, $LiFe_{1-x}Mg_xPO_4$ and $LiFe_{1-x}Co_xPO_4$ will also be reported at the meeting.

References

[1] M.D. Fleischauer, J.R. Dahn, J. Electrochem. Soc. 151 (2004) A1216.
[2] M.D. Fleischauer, T.D. Hatchard, A. Bonakdarpour, J.R. Dahn, Meas. Sci. Technol.16 (2005) 212
[3] K. Takada, K. Fujimoto, T. Sasaki, M. Watanabe, Appl. Surf. Sci. 223 (2004) 210.
[4] A.D. Spong, G. Vitins, J.R. Owen, J. Electrochem. Soc. 152 (2005) A2376.

In situ Raman and XRD studies of carbons for supercapacitors

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Energy storage in electrochemical double-layer capacitors (EDLCs), also referred to as supercapacitors, is based on charge separation at the interface between an electronic conductor and an electrolyte solution with ionic conductivity. Energy is stored in the electric field established in the double-layer comprising electronic charges in the electrode and the according counter-ions in the electrolyte. The use of high surface area carbon electrodes leads to a significant charge storage capability and therefore to high specific capacitances and power densities. When the energy storage occurs solely via double-layer charging and discharging, the lifetime of an EDLC device is expected to be considerable.

However, it can be shown that processes other than those related to double-layer effects may readily occur under working conditions. In particular, ion intercalation may lead to degradation of the carbon electrodes, which can be anticipated to reduce the lifetime of EDLCs. We demonstrate how *in situ* Raman microscopy, X-ray diffraction (XRD), and atomic force microscopy (AFM) provide information on the intercalation of electrolyte species into carbon electrodes in EDLCs.

Using *in situ* Raman microscopy, we could show the insertion of $(C_2H_5)_4N^+$ into graphite for the negative electrode at an onset potential of +1.1V *vs.* Li/Li^+, while BF_4^- was shown to intercalate into the positive graphite electrode positive to +4.5V *vs.* Li/Li^+. These results were confirmed by *in situ* XRD measurements performed at the Swiss Light Source (SLS) and also by *in situ* AFM investigations on highly oriented pyrolytic graphite (HOPG) model electrodes.

These new findings complement earlier results from electrochemical dilatometry measurements [1], and the role of ion intercalation into carbon electrodes in EDLC systems is discussed on the basis of these methods with an emphasis on lifetime limitations and increased capacitor voltage for the optimization of today's EDLCs.

[1] M. Hahn, O. Barbieri, F. P. Campana, R. Kötz, R. Gallay, Appl. Phys. A **82**(4) (2005), 633-638.

Charge Storage Mechanism of Nanostructured RuO_2 and Fabrication of Highly Functional RuO_2 Nanosheet Electrodes

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Electrochemical capacitors based on ruthenium oxides have attracted increased interest owing to their capability of providing higher energy density than conventional electric double-layer capacitors that employ carbon-based electrodes.[1,2] Specific capacitance of 600-800 F g^{-1} can be achieved by using nanostrucutred RuO_2 such as hydrous RuO_2, layered $H_{0.2}RuO_{2.1}$ (HRO), and $H_{0.2}RuO_{2.1}$ nanosheets (HROns) as electrode material.[3,4] The hydrous regions within the nanoparticles allow facile electrolyte permeation for efficient charge storage while the interconnected ruthenium oxide regions accounts for the electronic conduction. The key is to design electrode materials with high mixed electronic-ionic conductivity, large electrochemically active surface area, and practical electrochemical stability, at a reasonable price. Here, we discuss the charge storage mechanism of various ruthenium oxides. Results on the use of ruthenium oxide nanosheets for advanced functional applications will also be presented.

The charge storage mechanism of nanostructured ruthenium-based oxides (anhydrous RuO_2, hydrous RuO_2, layered HRO, HROns) was evaluated by various electrochemical techniques (CV, RDE, CA, impedance). The overall capacitance could be deconvoluted into three major contributions; namely, the electric double layer capacitance (C_{dl}), adsorption related charge (C_{ad}), and charging of the grain boundaries (C_{irr}). C_{ad} is strongly dependent on the structure of material. Layered HRO and HROns exhibit large C_{ad}, whereas it is not as obvious in hydrous RuO_2. C_{irr} was not observed in hydrous materials such as hydrous RuO_2, HRO and HROns, which is attributed to the lack of charging of the grain boundary. The hydrous state is a key factor in terms of both energy and power density. Ionic conduction via hydrous micro and mesopores, or interlayer seems to dominate the capacitive behavior.

HROns electrodes were fabricated on various substrates by electrophoretic deposition. Transparent or flexible electrodes could be fabricated by using ITO electrodes as the substrate. The deposited amount of material could easily be controlled by the extent of deposition, which was confirmed from the linear increase in specific capacitance as a function of the deposition time. Capacitance in the order of mF to F cm^{-2}(geometric) could be achieved using such HROns electrodes.

1. B.E. Conway, *Electrochemical Supercapacitors*, Kluwer Academic Pub., (1999).
2. Y. Takasu, Y. Murakami, *Electrochim. Acta*, **45**, 4135 (2000).
3. J.P. Zheng, et al, *J. Electrochem. Soc.*, **142**, L6 (1995) ; **142**, 2699 (1995).
4. W. Sugimoto, H. Iwata, Y. Yasunaga, Y. Murakami, Y. Takasu, *Angew. Chem. Int. Ed.*, **42**, 4092 (2003).

Propionic acid assisted sol-gel synthesis of $LiCu_xMn_{2-x}O_4$ ($0.025 \geq x \leq 0.10$) as 5V cathode materials for lithium rechargeable batteries

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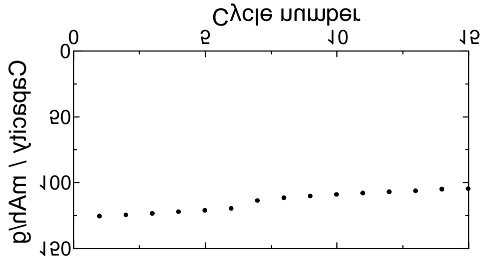
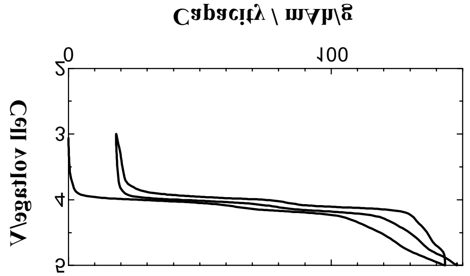
Spinel $LiCu_xMn_{2-x}O_4$ (0.025 – 0.1) has been synthesized using propionic acid as chelating agent by a sol-gel method to obtain sub-micron sized particles, good surface morphology, better homogeneity, good agglomeration and better crystallinity involving short heating time. X-ray diffraction (XRD), scanning electron microscopy (SEM), fourier transform infrared spectroscopy (FT-IR), thermo gravimetric and differential thermal analysis (TG/DTA) were carried out for the physical characterization of the synthesized powder. The XRD patterns of $LiCu_xMn_{2-x}O_4$ show the single-phase spinel product, which is in good agreement with JCPDS Card (35-782). SEM pictures show a decrease in particle size with increase in copper stoichiometry in the spinel product. Electrochemical cycling studies of the compound was carried out between 3–5V to understand the redox behaviour of Cu^{2+} ions. Further, the charge discharge characteristics reveal that 10% substitution of manganese by copper enhances the electrochemical reactivity of the spinel.





Nano Size Holes at the Basal Plane of Graphite Active Material Play an Important Role in Li-Ion Battery Anode

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The most common active material for the anode of Li-ion batteries is spherical shape graphitized material (**Fig. 1**). Since Li has been understood to be able to permeate into the interior of graphite only from the edge plane of the graphite structure and not from the basal plane, it seems unlikely for Li to be inserted easily from the outside of the rounded shape active material whose outer sphere is comprised of basal plane. But actually, the rounded material accepts Li very easily. For the purpose of elucidating this perplexing problem we propose the presence of nano-size holes at the surface of the basal plane of the active material, and Li can permeate easily into the interior of the active material through the holes. In this paper we would like to show the presence of the holes by TEM images for several graphitized samples (**Fig.2**).

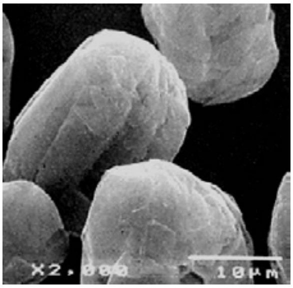

Fig. 1 (left) Round shaped graphite active material.

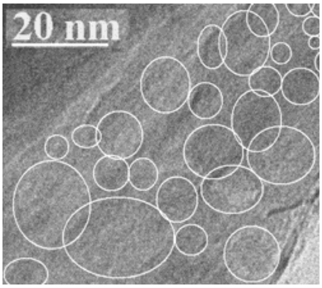

Fig. 2 (right) TEM image showing the presence of nano-holes at the graphite surface (in the white circle)

The graphite samples examined were natural graphite powder, and commercially available three different types of round shape active materials (An example is shown in **Fig.1**). The evaluation was performed for electrochemical performance (cyclic voltammetry and constant current insertion/deinsertion cycle test), XRD, SEM, Raman spectra and TEM images.

A sample giving an excellent electrochemical performance revealed the presence of a number of holes on the TEM image as shown in Fig. 2, while a sample having an inferior performance exhibited a limited number of small size holes.

Pristine natural graphite revealed the holes as well, implying the crystallite is not perfect but has many defects although the XRD pattern shows no evidence of imperfection. A rather stable cycle performance was obtained with natural graphite for Li insertion and extraction reaction, which can be attributed to the presence of a number of nano holes at the surface.

Effect of lithium salt addition on a C-2 substituted imidazolium ionic liquid

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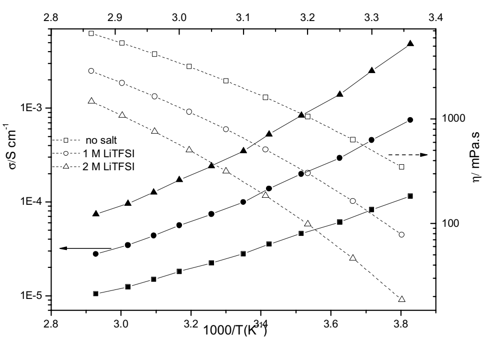
Various organic solvent-based solutions have been used as solvent in lithium batteries. However, the organic solvents are flammable and volatile, which makes the batteries that employ them a safety risk. One promising solution is to use a non-flammable, non-volatile electrolyte, such as room-temperature molten salts. Ionic liquids consist of solely of ions and these ions are typically not electroactive in lithium batteries thus requiring the addition of a suitable LiX salt[1,2]. Herein, we have studied the effect of a lithium salt (LiTFSI) on a new ionic liquid, called 1,2-dimethyl-3-n-butylimidazolium bis(trifluoromethanesulfonyl)imide (BMMITFSI).

BMMITFSI was synthesized by the ion exchange reaction of the corresponding imidazolium bromide with LiTFSI in water. This colorless liquid was characterized by FTIR, NMR and elemental analysis. We also have determinate the density, viscosity and ionic conductivity in different temperatures. The electrochemical window was estimated by cyclic voltammetry as 5 V.

The LiTFSI/BMMITFSI solutions were prepared by the addition of the lithium salt on the ionic liquid, followed by heating. The graphs of viscosity and ionic conductivity measurements plotted against the content of solute salts have shown an inverse behavior. While the addition of LiTFSI increases the viscosity of the solution, the ionic conductivity decreases (Figure 1). The only considerable reason for the decrease of conductivity by the addition of salt is the formation of ion pairs, which do not contribute for charge conduction in solution and the consequent increase of viscosity. Raman spectra of these solutions have shown the decrease of the peak intensity at 742 cm^{-1} and the increase of another one at 760 cm^{-1} when the LiTFSI concentration increases. This result confirms the formation and the increase of ion pair concentration with the LiTFSI addition, since the peak fragment at 760 cm^{-1} is attributed to the existence of strong interaction between cations and anions.

Figure 1



[1] H. Sakaebe, H. Matsumoto, Electrochem. Commun. 5 (2003), 594.
[2] P.C. Howlett, D.R. MacFarlene, A.F. Hollenkamp, Electrochem. Solid-State Lett. 7 (2004) A97.

Lithium Ion Batteries for Hybrid Applications

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The development of high-performance rechargeable batteries for power tools or hybrid vehicles has proved to be an extremely challenging task because of the need to simultaneously meet multiple battery performance requirements, like high energy (watt-hours per unit battery mass or volume), high power (watts per unit battery mass or volume), long life (5-10 years and some hundreds of deep charge-discharge cycles), low cost (measured per unit battery capacity), resistance to abuse and operating temperature extremes, perfect safety and minimal environmental impact. Despite years of intensive worldwide R&D, no battery can meet all of these goals. The use of lithium ion batteries in power tools, vehicles or other applications were high amounts of energy have to be stored in the battery are limited because of safety risks and the lack of safety mechanisms.

A wider use of lithium ion batteries for power tools or hybrid vehicles requires safer battery materials and intelligent battery packaging concepts. The required physical and electrical properties and safety of the lithium ion batteries are supposed to be achieved by the introduction of new materials, e.g. alternative electrode materials and electrolytes. The focussed applications require new designs for the electrode contact deposition, for the heat management and the combination of the single cells into battery modules.

In this paper we will focus on two points. At first, the possibilities to improve safety and high temperature performance of lithium ion batteries will be discussed. The focus will be on electrode materials and alternative electrolytes, especially ionic liquids. Ionic liquids are the ideal material for use as an electrolyte because they are non-volatile and flame resistive. Second, we will discuss possible designs of battery packages in terms of thermal management and safety.

Kinetic Studies of the V^{4+}/V^{5+} Red/Ox – system in Sulphuric Acid

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A Vanadium red/ox flow battery is a hybrid between a regenerative fuel cell and a rechargeable battery. The coulombic efficiency is excellent, 90 to 100 % and the energy efficiency is high, 70 to 90 % (1). Main problems have been low stability and solubility of the 4 and 5 valent species defined as VO^{2+} and VO_2^+(2). Raman spectroscopy shows very complex ions in the V(V) system in sulphuric acid solution (3). We have studied the kinetics of the positive red/ox electrode with V(IV) and V(V) ions in concentrated sulphuric acid.

Experiments were performed with a rotating disk electrode in sulphuric acid solutions with V(V) and V(IV) ions in equal concentrations ranging from $10^{-2.5}$ to $10^{-1.25}$ M. The concentration of H_2SO_4 varied between 0.4 and 4 M. Electrode materials tried were Pt, Au and Glassy carbon (GC). Both metallic electrodes showed a time dependency which could be related to changes in the complexes in solution interfering with oxides on the electrodes. GC gave stable current/potential curves.

Anodic and cathodic polarisation curves were obtained at different concentrations for a GC electrode. The polarisation curves were corrected for diffusion control, using the relation $i_k = i_m\ (i_d/ i_d - i)^p$. Here i_k is the kinetic cd, i_m the measured cd and i_d is the diffusion limited cd. p is the reaction order of the reduced and oxidized species, respectively. The polarisation curves show Tafel behaviour at low cds. At increased cds an almost symmetrical increase in potential for both directions, relative to the Tafel line, is observed.

The kinetic parameters are rather symmetrical for the GC electrode showing a one electron rate determining step in both directions with a chemical step taking over at higher rates. In the case of Au the process is different with a lower cathodic Tafel gradient and a semi-passive behaviour in the anodic direction. The following kinetic parameters were found; *GC electrode*: b_a = 133mV/dec.; b_k= - 108mV/dec.; α_a = 0.45; α_k= 0.55; k^o = 5.61E10^{-8} cm s^{-1}; *Au electrode*: b_k = - 65 mV/dec.

The diffusion coefficient for the V(V) species is $(2.7 \pm 0.2) \times 10^{-6}$ cm^2s^{-1} determined with both electrodes. For the V(IV) species more or less the same value is found on GC. This indicates that the same type of species is diffusing in both processes.

References

(1) Lotspeich C. and Santo Y. , Liquid Electrisity: Flow Batteries expand Large-scale Energy Storage Markets EB for DE-18 June 2002, E-source/Platt A Division of McGraw Hill
(2) Skyllas-Kazacos M., Menictas C., Kazakos M., J. Electrochem. Soc. 143 (1996) L86- L88
(3) Kausar N., Howe R., Scyllas-Kazacos M., J. Appl. Electrochem. 31 (2001), 1327-1332

Soluble lead redox flow cell for electrochemical energy conversion

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Large scale and efficient energy storage is important for applications such as load levelling, standby power supplies, strategic power distribution and vehicle propulsion. Redox flow batteries have several advantages over traditional energy storage systems and commercial technologies are currently being developed.

Typically, redox flow batteries, such as the all vanadium or bromine/polysulfide technologies, rely on an ion exchange membrane to separate the anolyte and catholyte. However, considerable engineering and chemical challenges need to be overcome when using two electrolytes separated by a membrane.

Performance data and technical aspects for the design and testing of a membrane-less redox flow cell are presented. The system is based on an electrolyte containing soluble lead:

Positive electrode $Pb^{2+} + 2H_2O - 2e^- \leftrightarrow PbO_2 + 4H^+$
Negative electrode $Pb^{2+} + 2e^- \leftrightarrow Pb$

Charge/discharge characteristics and deposit formation/dissolution (Pb and PbO_2) at the electrode surface will be discussed along with electrode selection and selected aspects of the design for a laboratory test rig.

In-M (M = Ni, Cu) Film Electrodes for the Anode in Lithium Secondary Batteries

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The lithium alloy materials (Si, Sn, Al, In) have attracted much attention as an alternative to the commercialized graphite anode for lithium secondary batteries. In spite of their high theoretical capacity, however, their practical application is still hindered due to a severe volume change upon cycling. As one of the approaches to solve this problem, the alloy materials have been prepared as the active/inactive intermetallics.[1] Some of the active/inactive intermetallics are reported to be inactive for alloying reaction at room temperature even though the reaction is thermodynamically allowed.[1,2] The kinetic problems encountered with these materials have not been fully understood until now.

In this study, the anodic performance of In-M (M = Ni, Cu) film electrodes was examined. The reaction mechanism was studied using *in-situ* and *ex-situ* XRD analysis. Both In-Cu and In-Ni electrodes were active for the alloying reaction at elevated temperature, but with different onset temperature. It is found that the In-M bond is broken during the alloying reaction, thereby the reaction kinetics is controlled by the bond strength of In-M. The onset temperature of In-Ni was higher than that of In-Cu, which must be the direct result of bond strength difference. The bond strength of In-Ni (271 kJ mol^{-1}) is known to be higher than that of In-Cu (147 kJ mol^{-1}).[3]

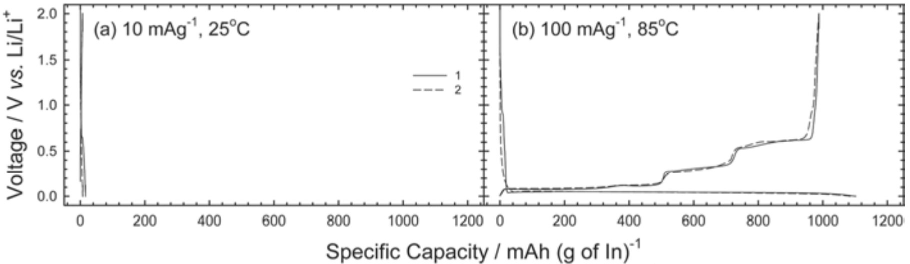

Fig. 1. Voltage profiles of Li/In-Cu cell: (a) 10 mAg^{-1} at 25°C and (b) 100 mAg^{-1} at 85°C.

References

[1] D. Larcher, L. Y. Beaulieu, O. Mao, A. E. George, and J. R. Dahn, J. Electrochem. Soc., 147 (2000) 1703.
[2] M. D. Fleischauer, M. N. Obrovac, J. D. Mcgraw, R. A. Dunlap, J. M. Topple, and J. R. Dahn, J. Electrochem. Soc., 153 (2006) A484.
[3] A. R. Miedema and K. A. Gingerich, J. Phys. B, 12(1979) 2255.

Hydrous Ruthenium Oxide Electrode for Non-aqueous Proton-Conducting Gel Electrolyte

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Electrochemical capacitors (ECCs) based on hydrous metal oxides, such as $RuO_2{\cdot}xH_2O$, $MnO_2{\cdot}xH_2O$, are expected to provide higher energy density than conventional electric double layer capacitors. ECCs reqire a proper proton (H^+) conductor as an electrolyte, and an aqueous solution of sulfuric acid is usually applied as the electrolyte of ECCs. We previously reported the poly(ethylene oxide)-modified polymethacrylate (PEO-PMA)-based, poly(vinyliden fluoride) (PVdF)-based and poly(vinyliden fluoride-co-hexafluoropropylene)-based gel electrolytes as the proton conductor for electrochemical capacitors[1, 2)]. We found that the gel consisting of PVdF-HFP dissolving trifluoromethanesulfonic acid (CF_3SO_3H) act as the proton conductor for $RuO_2{\cdot}xH_2O$ electrode at ambient temperature. In this paper, we have optimized the $RuO_2{\cdot}xH_2O$ composite electrode suitable for non-aqueous proton-conducting gel electrolyte based on PVdF-HFP for improving the characteristics of the ECCs with gel electrolytes.

The proton-conducting gel electrolyte was prepared by thermal casting method as described previously[2)]. The electrochemical properties of $RuO_2{\cdot}xH_2O$ prepared by a sol-gel method[3)] was investigated in the proton-conducting polymeric gels.

Fig. 1 shows the discharge capacitance of $RuO_2{\cdot}xH_2O$ symmetric cells at room temperature. The discharge capacitance of the electrode containing a gel component was higher than that of the electrode consisting of $RuO_2{\cdot}xH_2O$ and a binder (PVdF). About 300 F g^{-1} of the discharge capacitance (per mass of single electrode) was obtained at 5 mA cm^{-2}, although some pre-cycles were required to obtain the constant capacitance.

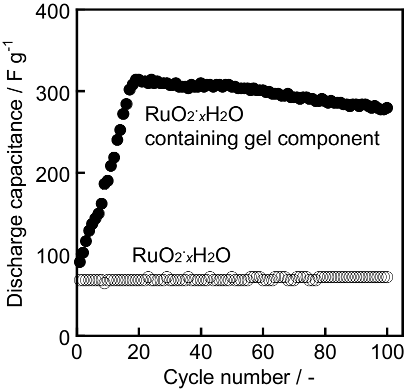

Fig. 1 Discharge capacitance of $RuO_2{\cdot}xH_2O$ symmetric cell at room temperature.
Electrolyte:PVdF-HFP/0.5 M CF_3SO_3H (DMF)
Current density : 5 mA cm^{-2}

References
1. M. Morita, J.L. Qiao, N. Yoshimoto, M. Ishikawa, *Electrochim. Acta*, **50**, 837 (2004).
2. M. Morita, N. Ohsumi, N. Yoshimoto, M. Egashira, 2nd International Conference on Polymer Batteries and Fuel Cells, Las Vegas, Nevada, USA (2005).
3. J.P. Zheng, P.J. Cygan, T.R. Jow, *J. Electrochem. Soc.*, **142**, 2699(1995).

Performance of Asymmetric *$Ni(OH)_2$ – Carbon* Supercapacitors

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An asymmetric supercapacitor typically consists a battery type electrode (usually a *faradaic* or intercalating metal oxide) and an electrochemical capacitor type electrode (high surface area carbon). In such an arrangement, the battery electrode has a greater capacity than the carbon electrode, resulting in twice the energy storage capability of a comparable symmetric carbon based supercapacitor. The battery electrode is selected such that the potential is near either the low or high end of the potential window, which can maximize the operational voltage as well as the energy density of the cell. As the voltage swing of the cell during charge/discharge occurs mainly across the carbon, the battery electrode experiences a relatively low depth of discharge and provides the conditions required for high cycle life. Results on the electrochemical characteristics and the performance of a 14 Wh/kg (and 2000 W/kg) packaged nickel hydroxide - carbon asymmetric device are presented. This device has the potential to offer both high power and high energy in a single long cycle life device.

High Throughput Evaluation of Polymer Electrolytes

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This work aims to use the combinatorial array techniques reported earlier for the evaluation for the composition dependence of ionic conductivity, and other properties of polymer electrolytes. These materials are particularly suited to the combinatorial approach because they generally consist of three or more components, e.g.

- matrix polymer, responsible for structural stability
- salt
- co-solvent or plasticizer
- other additives, e.g. fillers

The ionic conductivity of lithium based solid polymer films prepared from polyvinylidene fluoride hexa-fluoropropylene (PVDF-HFP) and lithium bis(trifluoromethane)sulfonimide (LiTFSI) with varying compositions of plasticizer propylene carbonate (PC) and ethylene carbonate (EC) were measured sequentially by AC Impedance Spectroscopy and then adapted to a 64 electrode combinatorial array. Conductivity values of 10^{-3} S cm^{-1} were observed in films with high plasticizer compositions which could be attributed to an enhancement in conduction pathways formed by the coordination of the lithium ions with the ester linkages in the plasticizer.

Results to be reported at the meeting, will include conductivity plots for the above lithium systems as well as studies on Nafion-based polymers and other compositions used as membranes in fuel cells and other applications.

Nanostructured Vanadium Oxide Prepared Hydrothermally as a Cathode Material for Lithium Batteries

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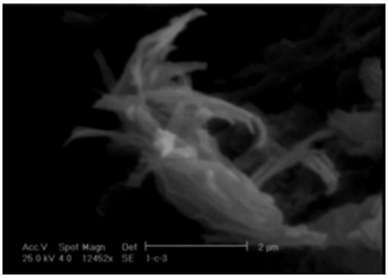
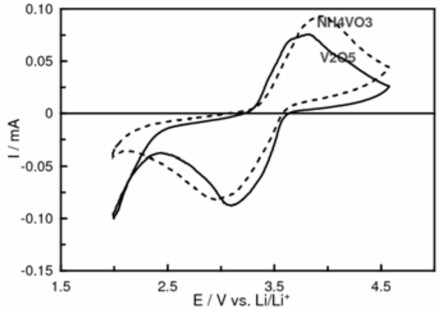
By decreasing the crystal dimensions, the solid-state Li^+ diffusion in lithium batteries is progressively replaced by surface-confined Li-storage [1]. Thus, synthesis of nanostructured materials is of particular interest, and hydrothermal route would be the most common method for this purpose. Nanostructured vanadium oxides provide high surface area which is considerably favorable for practical applications as a cathode material in lithium-ion batteries. Here, we report a simple hydrothermal method for the synthesis of these nanostructered materials. The physical and chemical as well as morphological aspects of these oxides are particularly investigated from both fundamental and applied points of view. This method results in the formation of bunches of nanofibers as illustrated in the SEM. Although the nanostructured vanadium oxides prepared by this method generally show a good electrochemical performance for lithium battery application, it was found that experimental conditions also play an important role in the electrochemical properties of the product. For instance, as can be seen in the illustrated CV, the electrochemical behaviors of two vanadium oxide samples prepared under similar conditions but using different vanadium sources namely V_2O_5 and NH_4VO_3 are significantly different. Thus, a particular attention should be paid to this issue to choose the most appropriate experimental conditions.





References

[1] A. Eftekhari, F. Molaei, P. Jafarkhani, F. Moztarzadeh, 56th Annual Meeting of the International Society of Electrochemistry, 25-30 September, 2005, Busan, Korea, Abstract# S43-031-O.

Development of poly(acrylonitrile) / Poly(vinyl acetate) - pan/pva - based gel Electrolytes for lithium ion batteries

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Polymeric gel electrolytes have been extensively studied for application in lithium ion batteries, since the electrolyte can be fabricated as a thin film that leads to major performance improvements. This is mainly due to the higher ionic mobility and the higher concentration of charge carriers, yielding ionic conductivities of about 10^{-3} $S.cm^{-1}$ at room temperature and sufficient mechanical strength. PAN-based gels have been studied together with a wide range of plasticizers and tested in lithium batteries systems with excellent results. Based on these results, we developed PAN-based gels with EC/PC and EC/DMC mixtures as plasticizers, $LiClO_4$ or $LiBF_4$ as the ionic salt and the copolymer PAN-PVA as the polymer matrix to be used as separator and electrolyte in lithium ion batteries. The choice of the copolymer was made due to its hydrophobic properties, low cost and easy access, since it is well used in textile industries as precursor for acrylic fibers manufacture. These new electrolytes were characterized by electrochemical techniques such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) to determine their stability window and conductivity. The charge/discharge performance of the PAN-PVA based gel electrolytes was investigated, by the galvanostatic battery test, for two different systems: a Li/gel/$LiMnO_2$ and an all polymeric system made of Ppy/gel/Pani (Ppy = polypirrol and Pani = polyaniline). FT-IR analyses showed that PAN-PVA is not a passive polymer host but an active component in the gel, were Li^+ ions are located close to C=O groups from plasticizers and CN groups of PAN. In addition to ionic conductivities between 10^{-3} and 10^{-4} $S.cm^{-1}$, these gels presented excellent electrochemical and chemical stabilities, which means a slight increased performance compared to only PAN-based gels, and suitable charge/discharge profiles.

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Effect of surface functional groups in the electrochemical behaviour of porous carbon materials: their relevance in supercapacitors

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The main object of this work is to study the electrochemical behaviour of activated carbons with different surface chemistry properties.

For this purpose, microporous activated carbons were obtained from an anthracite by chemical activation using both KOH and NaOH as activating agents. As a result, activated carbons with high BET surface area (2300-2900 m^2/g) have been obtained. In order to obtain porous carbon materials with different amounts of surface oxygen complexes, the former samples were oxidized with HNO_3 and thermally treated in N_2 flow at different temperatures.

On the other hand, the activated carbons were doped with nitrogen using a novel method based on the reaction of aniline with surface oxygen groups. Thus, this procedure consists on condensation reactions as a result of which oxygen functionalities are replaced by nitrogen ones. With this method, an amount of nitrogen close to 4 wt% can be introduced in the sample

The surface chemistry of the materials was systematically characterized by TPD experiments and XPS measurements. Galvanostatic and voltammetric techniques were used to deepen into the electrochemical behaviour of the modified porous carbon materials. The combination of both, chemical and electrochemical methods provides unique information.

The contribution of oxygen and nitrogen functionalities to the electrochemical behaviour of porous carbon materials is of relevance to optimise their use as electrochemical capacitors. Oxygen functionalities present a twofold contribution to capacitance. On one hand, these groups increase the accessible surface area improving carbon wettability and on the other, they promote pseudocapacitance, since some oxygen complexes undergo redox processes. Dealing with nitrogen functionalities, the role of the nitrogen-doping to increase the potential stability window will be discussed.

Structural and electrochemical properties of the doped spinels $Li_{1.05}M_{0.02}Mn_{2-y}O_{4-0.02}N_{0.02}$ ($M = Ga^{3+}, Al^{3+}, Co^{3+}$; $N = F^{-}, S^{2-}$) for use in lithium batteries

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In previous ~~εγ~~studies[1] we showed that the spinel $Li_{1.05}Mn_2O_4$ can be easily obtained by a solid-state reaction from ε-MnO_2 (with more structural defects than the γ-form), using only one heating step in the thermal treatment. Aiming at improving the capacity performance, in the present work doped spinels were obtained by a solid state reaction at 750 ºC for 72 h between the precursors ε-MnO_2, LiOH and the respective oxide/salt of ±the doping ions. In order to control the particle size, all the spinels were milled in a ball milling for 30 min. Mechanical milling, associated or not to further calcination, was also used to obtain the pure spinel. The obtained spinels were characterized by the average manganese valence (*n*), X-ray diffractometry, scanning electron microscopy, particle size distribution and specific superficial area. From the X-ray diffractograms, spinels of single cubic phase belonging to the *Fd3m* space group were identified. The values of the unity cell parameter (*a*) calculated for all the doped spinels (8.221 Å – 8.229 Å) were always lower than that for the pure one (8.234 Å), decreasing in the following order: $a(Li_{1.05}Ga_{0.02}Mn_{1.98}O_4) > a(Li_{1.05}Co_{0.02}Mn_{1.98}O_4) > a(Li_{1.05}Al_{0.02}Mn_{1.98}O_4) > a(Li_{1.05}M_{0.02}Mn_{1.98}O_{3.98}S_{0.02}) > a(Li_{1.05}M_{0.02}Mn_{1.98}O_{3.98}F_{0.02})$. The values of *n*, determined by Vetter´s method, for the doped spinels (3.56 – 3.50) were higher than that for the pure spinel (3.53 ± 0.01), decreasing in the following order: $n(Li_{1.05}Ga_{0.02}Mn_{1.98}O_4) > n(Li_{1.05}Co_{0.02}Mn_{1.98}O_4) > n(Li_{1.05}Al_{0.02}Mn_{1.98}O_4) > n(Li_{1.05}M_{0.02}Mn_{1.98}O_{3.98}F_{0.02}) > n(Li_{1.05}M_{0.02}Mn_{1.98}O_{3.98}S_{0.02})$. Mechanical milling with further calcination changed the spinel particles, since formation of nanometric particles, generation of lattice strain and partial oxidation of the Mn ions occurred. The pure spinel obtained using only mechanical milling presented nanometric particles, a highly disordered lattice structure and a high number of structural defects. In the charge and discharge tests, the cathodes of the doped spinels presented values of the specific discharge capacity decreasing in the following order:

$C(Li_{1.05}Al_{0.02}Mn_{1.98}S_{3.02}O_{3.98}) > C(Li_{1.05}Al_{0.02}Mn_{1.98}F_{3.02}O_{3.98}) >$
$C(Li_{1.05}Ga_{0.02}Mn_{1.98}S_{3.02}O_{3.98}) > C(Li_{1.05}Ga_{0.02}Mn_{1.98}F_{3.02}O_{3.98}) >$
$C(Li_{1.05}Co_{0.02}Mn_{1.98}S_{3.02}O_{3.98}) > C(Li_{1.05}Co_{0.02}Mn_{1.98}F_{3.02}O_{3.98})$.

Although the $Li_{1.05}Al_{0.02}Mn_{1.98}S_{3.02}O_{3.98}$ cathode presented the highest initial capacity (126 mA h g^{-1}), the $Li_{1.05}Ga_{0.02}Mn_{1.98}S_{3.02}O_{3.98}$ cathode presented the lowest capacity fading (from 120 mA h g^{-1} to 115 mA h g^{-1}) after 300 charge-discharge cycles.

Acknowledgements to FAPESP (grant # 01/09685-9) and CNPq.

[1] Ferracin, L. C.; Amaral, F. A. & Bocchi, N., *Solid State Ionics*. 130 (2000) 215.

Solvent-Solvent and Ionic Liquid-Solvent Mixtures for Lithium Batteries

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In order to enhance lithium ion batteries performances, and particularly at low temperatures, the formulation of the electrolyte is critical. A new trend in the batteries research is the search of binary or ternary mixtures of solvents thermodynamically stable at low temperature (below -20°C). For this purpose, few of studies deal with phase diagrams of mixtures of organic dipolar aprotic solvents. For example, the phase diagrams of mixtures of cyclic ethylene carbonate (EC) and linear carbonates as dimethylcarbonate (DMC) or ethylmethylcarbonate (EMC) have been studied by Ding [1]. The obtained phase diagrams are simple and characterised by an eutectic point which is close to the compound having the lowest melting point. Moreover, there is no miscibility gap in the liquid state whereas in solid state there is no mutual solubility.

In this work, Differential Scanning Calorimetry (DSC) and X-Ray diffraction (XRD) have been performed to investigate the thermal behaviour at low temperature (between -120°C to 20°C) of solvent-solvent and ionic liquid-solvent binary mixtures. These mixtures are made up of gamma-butyrolactone (BL), DMC, EC as organic solvents and 1-butyl-3-methyl-imidazolium hexafluoroborate ($BMIPF_6$) and tetrafluoroborate ($BMIBF_4$) as ionic liquids.

Phase diagrams of BL-DMC and BL-EC are as simple as alkylcarbonates binary mixtures. They are characterised by an eutectic point at x_{EC}=0.12 and T=-57.5°C for BL-DMC mixtures and x_{EC}=0.10 and T=-56.3°C for BL-EC mixtures.

Phase diagrams of ionic liquid-solvent binary mixtures evidenced the apparition of a vitreous phase when the mole fraction in ionic liquid is higher than a critical mole fraction (x_{critic}). This means that all solvent molecules, embedded in the amorphous phase, belong to the solvation shell of the imidazolium salts. From the value of the critical mole fraction, it is possible to calculate the number of solvent molecules in the solvation shell of BMI^+. In $BMIBF_4$-BL and $BMIPF_6$-BL systems the number of solvent molecules is respectively 4 and 5. The difference in the number of solvent molecules in the solvation shell of BMI^+ may be explained by the presence of one BF_4^- in the solvation shell of the imidazolium ion in $BMIBF_4$-BL and no PF_6^- anion in the solvation shell of BMI^+ in $BMIPF_6$-BL.

Charge-discharge capacities at a graphite electrode of these binary mixtures in presence of lithium salts such as lithium tetrafluoroborate and lithium hexafluorophosphate are also presented in this work.

[1]: M.S.. Ding, K. Xu, and T.R. Jow, J. Electrochem.Soc 147 (2000), 1688

The iron electrode revisited

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The alkaline metal hydride/Ni oxide secondary cells have superseded in most applications the old Fe/Ni battery.

However the negative Fe electrode when coupled with a positive air electrode is still attractive since combining good energy density (75 W h kg^{-1}) with robustness, low cost and high environmental safety.

The development for this battery of the air electrode can now take advantage from the alkaline fuel cell technological progress, but for Fe, in spite of the active investigation from the beginning of last century till the late '70s, several points are still questioned. For instance, the importance of Li^{+} in the electrolyte for the reduction of Fe oxides has only recently been clarified, whereas unanswered questions concerns:

•the discharge pathway, generally assumed to involve the successive Fe □ Fe^{II} and Fe^{II} □ Fe^{III} oxidations;

•the fact that at room temperature or below, only a minor fraction of the large theoretical capacity (960 A h kg^{-1}) can be exploited;

•whether and how the depth of discharge affects the electrode performances, etc.

The present paper shows that poor Fe utilization and two stage oxidation both correlate with resistance phenomena: in fact by using Fe/TiO_2 or Fe/ZnO composite electrodes the full theoretical capacity is exploited within a single Fe □ Fe^{II} oxidation pathway. Deep discharges seem furthermore important to inhibit Fe activation towards the hydrogen evolution reaction. With respect to this latter point the compatibility of mixing active Fe with intermetallic compounds (IMCs) as hydrogen buffers is eventually discussed.

Correlation of ac-impedance and in situ X-ray spectra of $LiCoO_2$

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We report in this presentation *in-situ* X-ray and AC-impedance spectra obtained simultaneously during the deintercalation of lithium from $LiCoO_2$ using a specially designed electrochemical cell. The AC-dispersions have been correlated with the cell parameters obtained from the X-ray spectra. The correlation confirms previous hypothesis on the interpretation of the AC-dispersions in terms of an equivalent circuit comprising an element that relates the change of the intrinsic electronic conductivity, occurring at the early stages of deintercalation, to the semiconductor to metal transition caused by the change of the cell parameters.

Study on Conductive Bipolar Plates for Vanadium Redox Flow Battery

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Vanadium redox flow battery used for energy storage system provides several favorable characteristics in energy distribution. Good conductivity, stress intensity, imperviousness, and antioxidant capability are required to the bipolar plate. Two kinds of bipolar plates, composite imperforate graphite plate and conductive carbon-plastic plate, were prepared and studied in this article.

The composite imperforate graphite plates were prepared by infusing the fine-structured graphite plates (ϱ= 1.84g/cm^3) into the resin, and then were sintered in high-pressure inert gas at high temperature to carbonify the resin. The conductivity of composite graphite plates of thickness 3mm is $1*10^{-3}\Omega\cdot$cm. And the feather test showed that they have good impermeability. Cyclic voltammetry was used to test the graphite plates being infused and carbonified and to compare with the one without dealing. The working electrode was the tested graphite plate. The reference electrode was a Hg/Hg_2SO_4(in saturated K_2 SO_4) electrode. A platinum plate was used as a counter electrode. The electrolyte was a $1.5MVOSO_4+1.5MH_2SO_4$ solution. The sweep rate was 100mv/s. The cyclic voltammograms showed that the graphite plate after modification got a lower current peak both of oxidation and reduction. The vanadium redox battery of 8 cells with the composite graphite bipolar plates was discharged at 120 mA/cm^2 and output a satisfying power density of 125mw/ cm^2. The battery output a stable power and the columbic efficiency achieved 84% with the modified graphite plate. After enlarging the area of composite graphite plate from 256 to 961 cm^2 and increasing the number of cells from 8 to 15, the battery kept the same efficiency. The power of vanadium redox battery with composite graphite plates achieved 1000w.

More cheaper carbon-plastic plates were prepared too. The composition of this material are 50~60% polymer and conductive additives such as carbon black and graphite particles about 40~50%. The conductive additives and the resin were mixed to be the composite, and the admixture was extruded to be composite particles, then these particles were injection-molded to form the carbon-plastic plates (thickness was 2.5mm, surface area was 961 cm^2). The conductivity of the carbon-plastic plates is $0.20\Omega\cdot$cm. The test of carbon-plastic plates in the vanadium battery of 10 cells showed that the battery run well at the 40A of charging and discharging current (the current density was 50mA/ cm^2).

Electrochemical behavior of lead foam negative electrode in spiral VRLA batteries

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Besides having the merits of conventional flat VRLA batteries, spirally VRLA batteries possess special advantages, such as, good charge acceptances and high instantaneous output powers, which can ensure their reliability and validity [1]. The use of thin lead foil and lead fiber as the current collectors of spirally VRLA batteries has been reported [2]. However, there have been few reports about lead foam being used as the negative grid material and the behaviors of lead foam negative electrodes in spirally VRLA batteries. The present paper deals with the effects of lead foam on the electrochemical behaviors by comparison with those of lead foil.

Spirally VRLA batteries were prepared by using lead foam as the negative current collector material. The electrochemical behaviors of a lead foam negative electrode in sulfuric acid were studied by means of chronoamperometry, cyclic voltammetry (CV), electrochemical impedance spectrometry (EIS) and charge-discharge tests.

The real surface area of a lead foam negative electrode is larger than that of a lead foil negative electrode, while the overpotential of the lead foam negative electrode is lower. Compared with those of a lead foil negative electrode, the mass specific capacities of a lead foam negative electrode are 25.9%, 30.0 % and 48.2% higher at 10h, 5h and 2h discharge rates, respectively. So the test results of the discharge performances of the spirally VRLA batteries show that for a lead foam negative electrode, both the utilization efficiency of the negative active material and the mass specific capacity of the negative electrode are higher. Besides, the observation of SEM shows that the active material on the lead foam negative electrode has smaller crystals and higher porosity. Compared with that of a lead foil negative electrode, the electrochemical reaction resistance R_{ct} and Warburg resistance (Z_w) of lead-foam negative electrode are obviously lower at the same state of charge, while the exchange current density i^0 [3] is higher, which means that the charge-discharge reactions of a lead foam negative electrode can proceed relatively more easily. This is probably due to the fact that the electric conductivity of lead foam grids is better than that of lead foil grids and lead foam grids have a three-dimensional net structure. Therefore, lead foam grids have larger contact areas of an negative active material, and the reaction of the negative active material is more uniform on lead foam grids. The $PbSO_4$ film is thinner and the ions transfer is more easily on a lead foam negative grid; accordingly, the electrochemical reaction resistance of at a lead foam electrode is obviously lower than that at a lead foil electrode. In a word, when used as grids of spiral VRLA batteries, lead foam has advantages over lead foil.

[1] J. Wang, H. K. Liu, S. X. Dou, S Zhang, Y Zhu and C Fu. J. Power Sources. 113 (2003) 241.
[2] D. John. J. Power Sources. 64 (1997) 153.
[3] G. Lindbergh. Electrochimica Acta. 42 (1997) 1239.

Synthesis and electrochemical polymerization of 3, 6-bis (2-thienyl)-n-carbazole

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The most important topics of the rapidly developing field of conducting polymers especially on carbazole containing ones are reported recent literatures [1]. The carbazole family have been extensively studied for the different applications due to their good hole transport, luminescent and electroactive properties [2].

Since the first reports on the electrochemistry of polythiophene films several reviews appeared on the electrical conductivity and other physical properties [3].

Obtaining electrically conductive and redox active polymers by electropolymerization of a heterocyclic monomer depends on the oxidation potential of the monomer. In the case of a monomer such as thiophene, having a high oxidation potential compared to the polymer, the high applied potential causes some degradation of the polymer. This problem can be overcome by extending the conjugation of the monomer by introducing different monomers, resulting in a significant reduction in the oxidation potential. Organometallic polycondensations mediated by organotransition metal complexes have been used to obtain such materials [4]. Recently, we have been reported the preparation of 3, 6-bis (2-thenyl)-N-ethylcarbazole having low oxidation potential due to extended conjugation that underwent facile electrochemical polymerization to form stable electroactive polymers [5]. This type of polymers gives rise to an array of different colors, which is dependent upon an electrochemical potential, making these polymers effective in such applications as electrochromic devices/windows.

Therefore, in this study, we report synthesis and electropolymerization of Th-Cz-Th, co-monomer and the properties of polymeric films compared with poly (Th-ECZ-Th). The properties of electrochemically obtained polymer films from this monomer were characterized by simultaneous voltammetric and spectrophotometric measurements. EIS measurements on Pt/P (Th-Cz-Th) film electrodes were carried out in monomer free solution in dependence of , thickness, supporting electrolyte concentration, polarization potential. Capacitance properties, the ionization potentials I_p, electron affinity E_a, optical band gap E_g, peak potentials, E_p, and doping degree y, of polymer films were calculated from these measurements.

[1]. Inzelt G., Pineri M., Schultze J.W., Vorotyyntsev M.A., Electrochim. Acta 45 (2000) 2403

[2]. Chevrot C, Ngbilo E, Kham K, Sadki S. Synth Met. 81 (1996) 201–4.

[3]. Strohriegl P, Grazulevicius JV. Photoconductive polymers. In: Nalwa HS, editor. Handbook of organic conductive molecules and polymers,vol. 1. New York: Wiley; 1997. p. 553–620.

[4]. Yamamoto T., Synlett, 4,2003,425

[5]. Sezer E., Van Hooren M., Saraç A.S. and Hallensleben M.L., J. Polym. Sci.: Part A: Polym. Chem., 37, (1999) 379–381.

Research of improvement the circulation performance of zinc electrode

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The zinc alloy powder as the active material of zinc electrode was prepared by the electrolysis way. Through the Linear Sweep Voltammetry(LSV), Chronoamperometry(CA) and charge and discharge test, ect. The results indicate that the corrosion intensity of zinc electrode in the lye is reduced about 60% by using the electrolytic alloy zinc powder, and it has higher electrochemical activity, the initial capacity reaches 277 mAh/g. The electrolytic ternary alloy Zn-Bi-In is best in synthesis performances. According to the working environment that the zinc electrode is used in, organic additives were added into the electrolyte, in order to improve electrodeposition shapes of the zinc in the course of charge and discharge. Through LSV, CA and charge and discharge test, ect. The results indicate that, the electrodeposition shapes of the zinc is improved effectively by adding the organic additive ZFD in the electrolyte, the growth of zinc dendriteic is restrained, and the circulation performance of zinc electrode is improved. The circulation performance of zinc electrode can also be improved remarkably by micro capsule processing on the zinc powder surface. The crystalloid nuclear positions of zinc electrodeposition might be provided by the membrane structure, at the same time reduced the discharge product to dissolve and diffuse in the electrolyte , restrained corrosion of zinc electrode in electrolyte. Through the Cyclic Voltammetry, AC Impednace and charge and discharge test, The results show that the best way to improve the circulation performance of secondary zinc electrode is adoption dark passivation of copper salt for 5 minutes in zinc powder surface. The electrolytic alloy zinc powder, the additive of electrolyte and surface modifiability of zinc powder were combined together, and the zinc electrode performances were investigated. After 40 times charge and discharge circulations, electrode capacity loss is 18.4%; But the zinc electrode of no optimized capacity loss is 49.6%.

Suppressive Effect of Ag-coating on Decomposition of PC on the Surface of Graphite

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Lithium ion batteries are widely used in many fields. Researchers have focused on improvement of low temperature performance. Propylene carbonate (PC)-based electrolytes are more desirable than ethylene carbonate (EC)-based electrolytes because of their low-temperature characteristics. Unfortunately, PC is not used in commercial lithium-ion batteries due to its cointercalation and graphite exfoliation. Here we found that coating carbonaceous mesophase spherules (CMS: an artificial graphite) with Ag could prevent the decomposition of PC, which shows promising of PC-based electrolytes in practical applications.

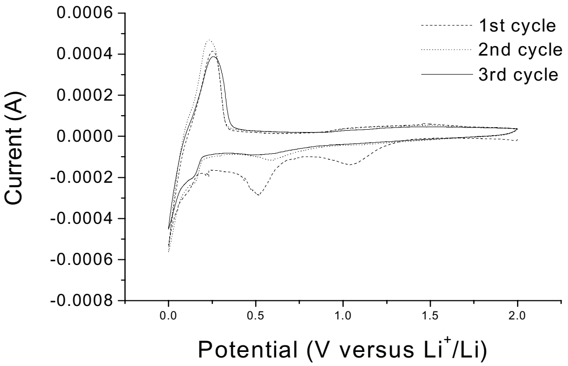

Fig. 1. Cyclic voltammogram of Ag-coated CMS electrode in 1M $LiClO_4$ /PC:DMC(1:1.86 by volume) at a scan rate of 0.1 mV/s.

Fig. 1 shows the cyclic voltammogram of an Ag-coated CMS electrode in 1M $LiClO_4$ /PC:DMC (1:1.86 by volume). At the first scan, there are two irreversible peaks at 0.5 and 1.1 V versus Li^+/Li, respectively, which can be attributed to the decomposition of the electrolyte to build up the SEI film. These irreversible peaks disappear gradually with repeated scanning. The peak near 0.8V corresponding to the decomposition of PC is not observed. The anodic peak corresponding to lithium deintercalation is very strong at every scan. These results indicate that a stable SEI film can be formed on the surface of CMS coated with Ag in PC-based electrolyte. Consequently, continuous decomposition of PC is effectively suppressed by Ag coating.

Acknowledgment

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The effect of Co on the electrochemical characteristics of nickel-rich layered $LiCo_XMn_YNi_{1-X-Y}O_2$

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Nowadays, $LiCoO_2$ is the prevalent cathode material and many reports address the problem in synthesizing a lower cost, higher-capacity, and safer cathode material than $LiCoO_2$[1]. $LiCo_XMn_YNi_{1-X-Y}O_2$ is the most studied material. $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ could be one of the promising cathode materials, but its unstable cycling performance results in gradual capacity fade, especially when charged to higher voltage.

Venkatraman et al. [2] have showed that oxygen loss from layered metal oxide cathodes becomes significant above 4.25V.This may contribute to observed cycling losses and limits the achievable practical capacities that can be obtained, unless steps are taken to reduce oxygen activity. The decline in cycle ability of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ could be related to the chemical instability of the $Co^{3+/4+}$ redox couple due to its significant overlap with the top of the O^{2-}:2p band. Experiments shows that oxygen loss from nickel-rich layered $LiCo_XMn_YNi_{1-X-Y}O_2$ becomes more serious with the amount of Co increasing ,especially at higher voltage. While, Dahn et al found that transition metal atoms especially Ni^{2+} have a tendency to enter the Li layers when the Co content is low in the material. Experiments indicates that Co can stabilize the structural of nickel-rich layered $LiCo_XMn_YNi_{1-X-Y}O_2$ as the influence of Co on the structural stability of $LiNiO_2$.Its rate performance is improved with the rising Co content, which is probably caused by reducing the propensity of transition metal atoms to enter Li layers. So the amount of Co in the nickel-rich layered $LiCo_XMn_YNi_{1-X-Y}O_2$ is detrimental to its performance and safety .

[1] A.R.Armstrong,P.G.Bruce. Nature. 381(1996)499
[2] S.Venkatram,A .Manthiram.Chem.Mater.15(2003)5003.

Electrochemical behavior of nickel-rich layered $LiCo_{1/4}Mn_{1/4}Ni_{1/2}O_2$ cathode material

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Recently, layered $LiCo_XMn_YNi_{1-X-Y}O_2$ was adopted and studied to overcome the drawback of $LiNiO_2$,$LiMnO_2$ and $LiCoO_2$. $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ is amongst the most studied material for higher capacity and lower cost. But the unstable cycling performance of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ results in gradual capacity fade, especially when charged to higher voltage [1]. Concluded from previous chemical experiments shows that the chemical instability of material arising from an overlap of metal:3d band with the top of oxygen:2p band and the consequent tendency to lose oxygen from the lattice decreases in the order $Co^{3+/4+}>Ni^{3+/4+}>Mn^{3+/4+}$.So nickel-and manganese-rich compositions have higher reversible capacities than cobalt-rich compositions. But experiments show that manganese-rich compositions with a large irreversible anodic peak at 4.5V, while nickel-rich compositions with a good stability when charged to higher voltage.

$LiCo_{1/4}Mn_{1/4}Ni_{1/2}O_2$ cathode material was synthesized by sol-gel method in air, successfully. The cyclic voltammogram curve of $LiCo_{1/4}Mn_{1/4}Ni_{1/2}O_2$ showed two couples of peaks at 4.06V/3.63V and 4.29V/4.26V, respectively. There isn't any irreversible peak at higher voltage until the value of voltage is higher than 4.75V, which may indicate that $LiCo_{1/4}Mn_{1/4}Ni_{1/2}O_2$ is stabile when charged to 4.75V.The cycling performance test operated in the voltage range of 2.95~4.75V of $LiCo_{1/4}Mn_{1/4}Ni_{1/2}O_2$ testified this point : $LiCo_{1/4}Mn_{1/4}Ni_{1/2}O_2$ showed stable cycleability after some capacity loss during the initial cycle; it maintained the discharge capacities larger than 220 mAh g^{-1} even after the 100th cycle; the capacity of its first cycle was 246.3 mAh g^{-1}.Venkatraman et al. [2] have shown that oxygen loss from layered metal oxide cathodes becomes significant above 4.25V .This may contribute to observed cycling losses and limits the achievable practical capacities that can be obtained, unless steps are taken to reduce oxygen activity. Obviously, the oxygen loss of $LiCo_{1/4}Mn_{1/4}Ni_{1/2}O_2$ at higher voltage is restrained effectively.

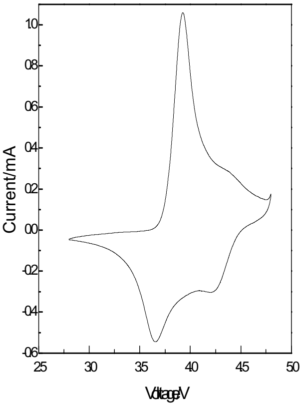

Fig.1.cyclic voltammogram curve of $LiCo_{1/4}Mn_{1/4}Ni_{1/2}O_2$

Reference
[1] K.M.Shaju,G. V. Subba Rao, B.V.R Chowdari.Electrochim.Acta.48(2002)145.
[2] S.Venkatram,A .Manthiram.Chem.Mater.15(2003)5003.

Stannum Doping of Spherical Spinel $LiMn_2O_4$

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Rechargeable Li-ion battery, with high energy density and long life, has been applied successfully in portable electronic appliances such as mobile telephones and laptop computers, and is also considered to be a promising alternative for application in electric vehicles (EV) and hybrid electric vehicles (HEV). But conventional $LiCoO_2$ has the shortage of cost and thermal safety problems, significant efforts have been made by many groups in recent years to develop a cheaper, higher capacity, and safer cathode material to replace $LiCoO_2$. $LiMn_2O_4$ and its derivatives, have been studied extensively as possible substitution due to the safety issue.

In this study, stannum is used to dope spherical spinel $LiMn_2O_4$ at first time. The doping can improve the performance of the spinel. The preparation is as follows[1]. The spherical $MnCO_3$ was firstly synthesized by controlled crystallization of $MnSO_4 \cdot H_2O$, $NH4HCO_3$ and $NH_3 \cdot H_2O$. The spherical Mn_2O_3 precursor was then obtained by heat treatment of $MnCO_3$. A mixture of Mn_2O_3 and Li_2CO_3 was calcined to produce $LiMn_2O_4$. A mixture of SnO_2, Mn_2O_3 and Li_2CO_3 was calcined to produce Sn doped spinel $LiMn_2O_4$.

Fig. 1 shows the cycling performance of the test cell. It indicates the doping of stannum can improve the performance of the spinel.

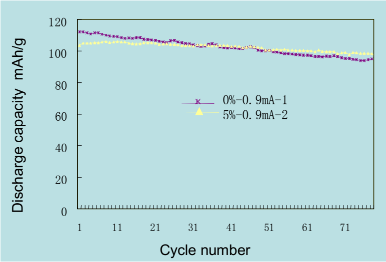

Fig 1 Cycling performance of Sn doped spinel $LiMn_2O_4$

References

[1] X.M. He, J.J. Li, Y. Cai, Y.W Wang, J.R. Ying, C.Y Jiang, C.R. Wan, J. Solid State Electrochem, 2005, 9 (6): 438-444.

$Li_{2.6}Co_{0.4}N$ Composite of Hard carbon for Its Initial irreversible Capacity Improvement

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The outstanding merit of hard carbon is large discharge capacity, but the first irreversible capacity is too large, leading to very low initial efficiency. We believe that the micro pores (2nm-5nm) in the hard carbon inhibit lithium-ion to de-intercalate. On the other hand, $Li_{2.6}Co_{0.4}N$ cannot be directly treated as being in the delithiated state and lithium must be extracted from the structure in an initial anodic oxidation by either chemical or electrochemical ways. So we put forward the idea to constitute composite anodes based on hard carbon and $Li_{2.6}Co_{0.4}N$ for lithium ion batteries.

The electrochemical performance of hard carbon as an anode for lithium ion batteries was investigated. SEM, XRD and the constant-current charge-discharge properties of hard carbon and the composite were studied. Results showed that the composite demonstrated a high first cycle efficiency at 104.8%. A large initial discharge capacity of ca. 435.9 m Ah g^{-1} (Fig1) is achieved after the composite.

The discharge capacity of the composite remained higher than hard carbon even after 20 cycles. So the cycling performance of hard carbon can be greatly improved.

The composite appears to be a promising anode material for lithium ion batteries. This work may contribute to an effective way to compensate the high irreversibility capacities of the $SnSb_X$, SnO and SiOx based electrodes in the first cycle for lithium ion batteries.

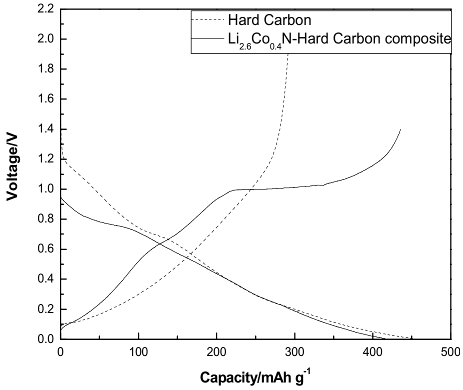

Fig. 1. Charge and discharge curves of the $Li_{2.6}Co_{0.4}N$-Hard Carbon composite and the Hard Carbon electrodes at the first cycle.

Electrochemical Studies of Electrode Material for Sealed Ni-MH Battery

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Nickel metal hydride (Ni-MH) battery is attracting much attention for the application in electric devices and emission-free electric vehicles because of their several advantages such as high energy density and environmentally acceptable components. Ni-MH battery is consisted of a hydrogen absorbing alloy for a negative electrode and a nickel hydroxide for a positive electrode. However, when charge and discharge cycles are repeated, a gas absorbing performance and charge efficiency at the negative electrode is reduced due to oxidation of hydrogen absorbing alloy. Therefore, there have been such problems as a rise in battery inside pressure, which is increase a loss of electrolyte and a lowering of battery performance. It is intended to improve the service life of negative electrode by adding additive elements to the nickel hydroxide. A potential difference (η value) between an oxidation potential and an oxygen evolution potential of the nickel hydroxide correlates with the charge efficiency, and it is expected that charge efficiency has a tendency to become large with an increase in the η value. When the additive elements such as Ca, Sn, Cd, Zn etc. are added to the nickel hydroxide, oxygen evolution potential of nickel hydroxide shifted to the noble side. we reported on the electrochemical properties of a single particle of spherical nickel hydroxide treated with some additive elements. The electrochemical measurements were done by a microelectrode technique.

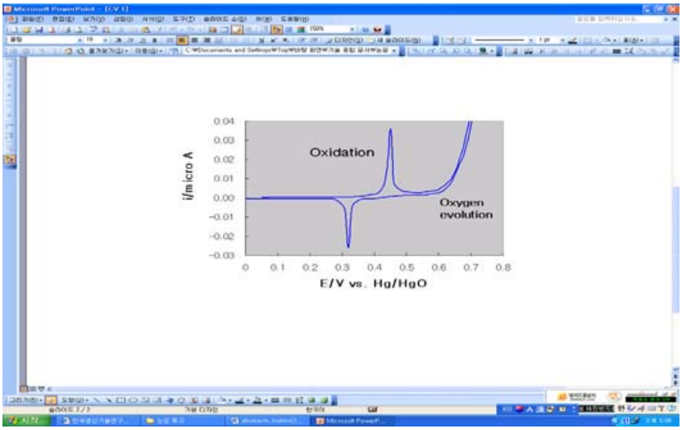

Fig. 1 Cyclic voltammogram for a single particle and a composite film electrode of nickel hydroxide in 5M KOH solution. Scan rate was 1mV/s.

Li Reaction Behavior of GaP Nanoparticles Prepared by Sodium Naphthalenide Reduction Method

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Recently, transition metal phosphides, such as CoP_3, MnP_4, FeP_2, Sn_3P_4, VP_4, and Cu_2P have been investigated as possible candidates for anode materials in Li-ion batteries and can be categorized into two groups depending on transition metal and phosphors bonding stability upon lithium reaction. MnP_4, Cu_2P, and VP_4 showed the topotactic lithium insertion without breaking bonds between transition metal and phosphor, and overall reaction can be written as follows:

$M_xP_y \rightarrow Li_tM_xP_y \rightarrow Li_tP + M_xP_y \leftrightarrow Li_zM_xP_y$ (1).

For instance, Kim et al. reported that VP_4 reacted with lithium through topotactic reaction, phase transformation from monoclinic Li_3VP_4 into cubic Li_6VP_4 phase, and decomposition to form Li_3P and VP followed by lithium insertion into VP phase.
On the other hand, Sn_3P_4, FeP_2, CoP_3 showed the direct decomposition of metal phosphide into metal and lithum phosphide, and lithium phosphide and transition metal can participate in the lithium reaction. For instance, Li reaction in CoP_3 can be written as:

$CoP_3 \rightarrow Li_3P + Co \leftrightarrow 3LiP + Co$ (2)

In case of CoP_3, initial uptake of Li forms highly dispersed cobalt clusters embedded in matrix of Li_3P; extraction of Li from this ion-conductive matrix on charge yields nano-particles of LiP, with no oxidation of Co. However, when an active transition metal was formed from the decomposition reaction, lithium can reversibly react with the active metal. Sn_3P_4 was formed in a final reaction:

$Sn + LiP$ and $Sn \rightarrow Li_4Sn$, $LiP \rightarrow Li_3P$ (3).

In reactions (1,2 and 3), since LiP is an insulator, and once Li_3P changed into LiP, it is detrimental effect on reversibility of the phosphorous electrode. As long as electrochemical window is limited below 0.72 V, the Li_3P matrix is believed to be relatively stable. However, above 0.75 V, capacity fading was severe and showed ~ 0mAh/g after 30 cycles. However, preparation method for metal phosphides described above used ball-milling or high temperature solid-state reactions mostly.
In this study, we report lithium reaction behavior of the GaP nanoparticles with different particle sizes produced by sodium naphthalenide reduction of $GaCl_3$ in ethylene glycol dimethyl ether (glyme), and concurrent reaction with P at 390°C without pressured condition.

A novel composite solid-state polymer electrolyte of methyl group-functionalized SBA-15 for rechargeable lithium batteries

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Since the idea that some polyether-based polymer with alkali metal salts was presented by Wright [1,2] and Armand [3], the development of polymer electrolytes with high ionic conductivity has become one of the objectives in polymer research due to their potential application in electronic devices such as all-solid-state rechargeable batteries. The polyethylene oxide (PEO)-based system is the most comprehensively investigated because of the unique properties of PEO to form 'polymer solutions' of good ionic conductivity. The system, however, still suffers from inadequate room temperature ionic conductivity ($< 10^{-7}$ S cm^{-1} at 25°C). Extensive research efforts have been made to optimize the properties of polymer electrolytes to satisfy the need of all-solid-state lithium-polymer electrolyte battery [4,5].

In this study, molecular sieve SBA-15 was functionalized via trimethylchlorosilane, which was used as inorganic filler in a poly (ethyleneoxide) (PEO) polymer matrix to synthesize composite solid-state polymer electrolytes (CSPEs) for rechargeable lithium batteries using $LiClO_4$ as the doping salts. The methyl group-functionalized SBA-15 powder possesses hydrophobic pore surfaces that facilitate the combination between SBA-15 filler and PEO matrix, which improves its compatibility with the polymer matrix. The methods of linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC) were employed to study the electrochemical properties and interfacial stability of the CSPEs. The experimental results illustrated that the incorporation of ~5% functionalized SBA-15 yields a stable and homogeneous CSPE with the maximum ionic conductivity (1.87×10^{-6} S cm^{-1}) at room temperature. Addition of functionalized SBA-15 with high concentration (~15%) leads to nevertheless a decrease in the ionic conductivity of the CSPE. Emission FTIR spectroscopy at different temperature was first used to explore the temperature dependent of structure of polymer, and experimental results show that the existence of amorphous phase induces a great contribution to the ionic conductivity. Combining with other experiments we have set up a mechanism of ion conducting. Furthermore, the addition of functionalized SBA-15 has improved also the electrochemical stability window of CSPEs.

The study was supported by grants from natural science foundation of China (20021002, 90206039) and Special Funds for Major State Basic Research Project of China (2002CB211804).

[1] D.E. Fenton, J.M. Parker, P.V. Wright, Polymer, 14 (1973) 589.
[2] P.V. Wright, Br. Polym. J., 7 (1975) 319.
[3] J.-M. Tarascon, M. Armand, Nature, 414 (2001) 359.
[4] J.Y. Xi, S.J. Miao, X.Z. Tang, Macromolecules, 37 (2004) 8592.
[5] H. M. Kao, Y. Y. Tsai, S.W. Chao, Solid State Ionics, 176 (2005) 1261.

Nano-Scale $LiFePO_4$/C Composites Doped by Ti as Cathode Materials of Lithium Ion Battery

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Ordered olivine structure material $LiFePO_4$ is a very attractive cathode material with the advantages of low cost, environmental benignity, high cycle stability, and high theoretical capacity. But in practice $LiFePO_4$ has not been used extensively due to its low electric conductivity and low electrochemical diffusion kinetics. In this paper, $LiFePO_4$ was synthesized using $LiOH·H_2O$, $FeC_2O_4·2H_2O$, and $NH_4H_2PO_4$. Three kind samples were prepared under high rotary ball-milling: mixed with carbon (as $LiFePO_4$/C) ; doped with low amount Ti (as $Li_{0.99}Ti_{0.01}FePO_4$), and treated with both ways (as $Li_{0.99}Ti_{0.01}FePO_4$/C composite).

The SEM image in Fig.1 presents the morphology of $Li_{0.99}Ti_{0.01}FePO_4$/C. The nano-particles were coated by carbon. The composition of samples influences the charge/discharge cycle performance obviously， as shown in Fig.2. $Li_{0.99}Ti_{0.01}FePO_4$/C composite presents the best behavior (curve a) with the initial capacity of 154.5mAh/g. And after 120 cycles it maintains 92% of initial capacity. It can be attributed to the improving diffusion character by Ti doping and conductivity between particles by carbon mixing. The sample treated only by carbon mixing presents also good cycle stability (curve b), but the discharge capacity is much lower than that of $Li_{0.99}Ti_{0.01}FePO_4$/C. A sharp capacity decrease was observed for the sample only doped with Ti (curve c).

Acknowledgments

This work was supported by National Nature Science Foundation of China.

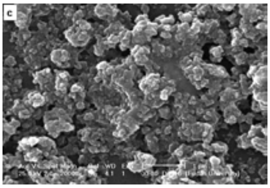

Fig.1

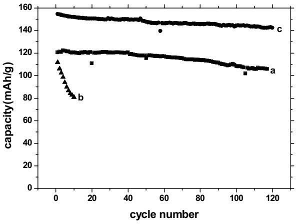

Fig.2

Reference: A. K. Padhi, K. S. Nanjundaswamy, and J. B. Goodenough, *J. Electrochem. Soc.* 144, 1188(1997).

Determination of Li^+ solid diffusion coefficient of $LiCoO_2$ by capacity intermittent titration technique (CITT)

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Investigation on the solid diffusion process of Li^+ within Li insertion-host materials plays an important role in improving properties of electrode materials and optimizing designs of lithium-ion batteries because the diffusion process is the key step for the energy storage and output. By the capacity intermittent titration technique (CITT), the Li^+ solid diffusion coefficients within $LiCoO_2$ have been determined at different voltages and different charge-discharge cycles. Results show that the Li^+ solid diffusion coefficient(D) values vary non-linearly from 10^{-12} $cm^2 \cdot s^{-1}$ to 10^{-13} $cm^2 \cdot s^{-1}$ in the voltage range from 3.9V to 4.3V, with a minimum at E=3.95V. During charge-discharge cycles, the variation of Li^+ solid diffusion coefficient come through three steps because of the crystal structure changes. The XRD and FTIR were used to describe the structure changes during charge-discharge cycles.

Preparation of porous carbon using surfactant and its rate capability in electric double-layer capacitor

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The electric double-layer capacitor (EDLC) has been considered as a promising high power energy source for digital communication devices and electric vehicles. EDLC electrode materials should have a large surface area for charge storage, and an appropriate pore structure for electrolyte wetting and rapid ionic motion.

In this work, porous carbons were prepared *via* resorcinol-formaldehyde polymerization [1-3] and carbonization, where a surfactant was added after a certain period of pre-curing. The prepared carbons possess two different types of pores; one inside carbon spheres (intra-particle pores) and the other at the interstitial sites made by carbon spheres (inter-particle pores). The surface area developed at the intra-particle pores is much larger than that at the inter-particle pores, such that the EDLC performance is predominantly determined by the pore structure of the intra-particle pores. The size of carbon spheres decreases with an increase in the pre-curing time, thereby the length of intra-particle pores is shortened. The carbons comprising smaller spheres show a better rate capability due to a smaller pore resistance and higher ion penetrability.

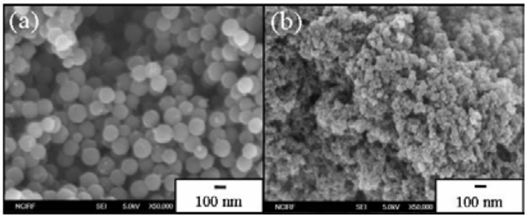

Fig. 1. FE-SEM images of carbons as a function of pre-curing time: (a); 0 min and (b); 90 min.

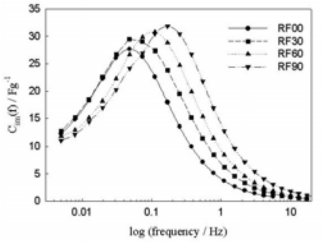

Fig. 2. Imaginary capacitance plots derived from impedance data.

Reference

[1] R. W. Pekala, J. Mater. Sci. 24 (1989) 3221.

[2] X. Lu, M. C. Arduini-Schuster, J. Kuhn, O. Nilsson, J. Fricke and R. W. Pekala, Science 225 (1992) 971.

[3] A. Al-Muhtaseb and J. A. Ritter, Adv. Mater. 15 (2003) 101.

[4] K. T. Lee and S. M. Oh, Chem. Commun. 21 (2002) 2722.

Synthesis, phase composition and structure of spinel type catode materials based on manganese compounds for Li-ion batteries

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Lithium manganese spinel represents promising cathode materials for rechargeable lithium and lithium ion batteries. However lithium manganese spinels obtained by conventional solid state method are characterized by relatively low specific capacity and capacity fading during cycling. The method of obtaining pure phase, high dispersal, homogenous samples of cathode materials from solutions is considered at present as the most promising.

Series of modified $Li_xMn_{2-y}Me_yO_4$ spinels, where Me = Ni, Co was obtained by a simplified method as compared with the sol-gel method. Appropriate initial mixtures of Li, Mn, Ni, Co - containing reagents were obtained directly from homogenous solutions by heating and evaporation without using special complex formation agent. Lithium hydroxide was used as Li- containing reagent, and as Mn, Ni, Co – containing reagents nitrates and acetates were used. It was established that it is possible to use nitrates as initial Mn, Ni, Co- containing reagents formation of $Li_xMn_{2-y}Me_yO_4$ type samples with Me=Co, Ni, $1 \le x \le 1.2$ and $y = 0.1$ unit formula. Formation of pure phase, superlithiate, doped cubic spinels with parameter $a = 8.180 \pm 0.004$Å and dispersion ~ $2{\cdot}10^{-7cm}$ takes place as a result of corresponding initial batch heating at 600°C during 6 hours. Using manganese and nickel nitrates as initial reagents leads to formation of pure phase samples with cubic singony, lattice parameters $a = 8.186 \div 8.208 \pm 0.03$Å and dispersion ~ 10^{-7cm}. Simplified method allows for obtaining of high dispersal samples of $Li_xMn_{2-y}Me_yO_4$, $1 \le x \le 1.2$ and $y = 0.1$, at 450°C ($\tau = 6$h). High dispersion and homogeneity, relatively low temperature and minimum time of cathode material synthesis as well as samples doping with Co or Ni and creating lithium excess in spinel structure provides for increased electrochemical performance and cycleability of cathode materials, and subsequently of lithium-ion battery.

Evaluation of Anodic 0xidation Durability of PAN Based Carbon Fibers

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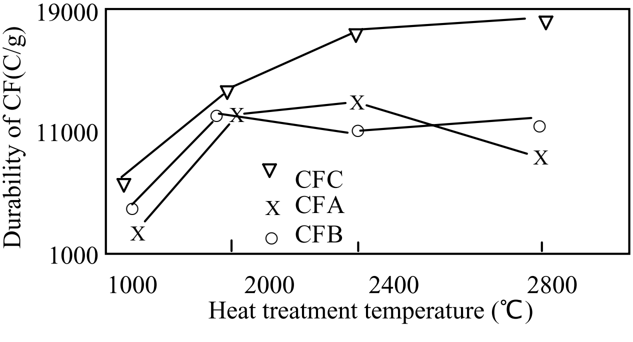
In the early time, carbon materials were used for many types of batteries including a Ni-H secondary battery as conductive materials. However, because of the weakness against the anodic oxidation, carbon materials were not used as electrodes, especially for Ni-H secondary battery. So, a new conductive carbon material, which has high durability against both over discharge and charge is strongly required.

It seems to be that there are a few exact investigations about the durability of anodic oxidation of carbon materials with wide range of heat-treatment temperature in high-concentration (6N) alkaline solution. On this background, we tried to improve the durability of carbon fiber in the anodic oxidation conditions. Three kinds of PAN based carbon fibers produced by different makers, namely, CFA: 3 micron meter diameter, epoxy sized 12K filaments. CFB and CFC:7 micron meter diameter, epoxy sized 12K filaments were examined. Thebundles of these CF were heat-treated at 2000℃ and 2400℃ in the vacuum furnace under N_2 gas atmosphere. Heating ratio was 100℃/hr. Holding time at the maximum temperature was 5 hrs. Heat treatment of 2800℃ was performed in the small Acheson furnace under self-atmosphere. Heating ratio was 280℃/hr. Holding time at the maximum temperature was 4 hrs. All fiber bundles were heat-treated in the graphite crucible (under no stress). As the results were shown in Fig.1, the durability of CF (electricity was passed until the cut off of CF) in the anodic oxidation was remarkably increased by heat treatment.



Electrochemical capacitors based on highly porous carbon prepared by chemical treatment

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Activated carbon was activated with chemical treatment to attain high surface area with porous structure. We have been considered activated carbon is the ideal material for high voltage electric double layer capacitor due to their high specific surface area, good conductivity and chemical stability. In this study we found that increase in electrochemical capacitance due to activated carbon. Also chemically activated carbon and water treatment have resulted larger capacitance and also exhibits better electrochemical behavior, and is about 15% more than in untreated state. The structural change in activated carbon through chemical treatment activation was investigated by using SEM and XRD. In this study, the dependence of the activation behavior with KOH in the micro structure of host materials will be discussed. Furthermore, the relation to the electric double layer capacitance, especially the specific capacitance per unit area, is also discussed.

The treated activated carbon was obtained by KOH solution and activated carbon (YP-17) mixed warm up in a double boiler at 60°C for 12h. The resultant materials were washed repeatedly with 0.1M solution of HCl and distilled water to remove chloride ions and next were dried at 110 □C for 6 h. The BET surface area of carbons was measured from N_2 adsorption isotherms at 77K with asorptiometer. Two-electrode capacitors were built from the KOH activated carbon samples and 1 mol l–1 H_2SO_4 and 10M KOH solution was an electrolytic solution. The electrodes consist of 80% of carbon, 5% of polyvinylidene fluoride(PVDF) and 15% of super-P.

The electrochemical behavior of treated activated carbon was characterized by cyclic voltammogram as shown in Fig. 1. A voltammogram close to the ideal rectangular shape was observed treated activated carbon.

The isotherms of N_2 adsorption at 77K for the KOH activated carbons are presented in Fig. 2. The highly developed surface area of KOH activated carbons with a suitable particle size seems to be a primary reason of the exceptionally high capability charge accumulation in electric double layer of such carbon.

Synthesis and electrochemical characterization of activated carbon/metal oxide thin film electrodes for micro electric capacitor applications

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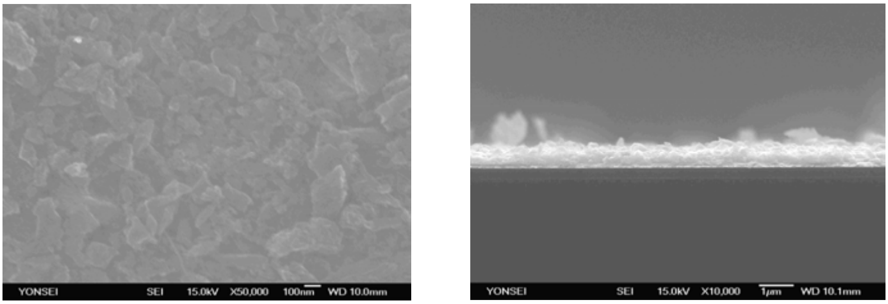
Activated Carbon is most popular materials for EDLCs (Electrical double layer capacitors) owing to its characteristics of large surface area, good conductivity and chemical stability. Nowadays, there has been considerable interest in carbon–metal oxide composites to improve specific capacitance of carbon based electrode materials. There are two typical approaches ; development of new class of carbon based materials and modification of existing carbon based materials with transition metal oxides and conducting polymers.

For micro electrochemical capacitors, a very thin layer of electroactive materials need to be prepared and conventional slurry coating technology may face technical difficulties in its preparation. We have reported metal oxide thin films, CNT thin films and metal oxide/CNT nanocomposite thin films for electrochemical capacitor applications using electrostatic spray deposition (ESD) technique.

In this study, we report on the synthesis of Activated Carbon thin film electrodes and Activated Carbon/Metal oxide thin film electrodes without any additives using electrostatic spray deposition (ESD) technique. Morphological, structural and electrochemical studies were performed with SEM, TEM, XRD and Cyclic voltammetry, and charge-discharge tests. Detailed results and discussion will be presented in the meeting.



(a) (b)

Fig.1. SEM images of activated carbon thin film (a) planer view and (b) cross sectional view

SnO_2 Filled Mesoporous Tin Phosphate: High Capacity Negative Electrode for Lithium Secondary Battery

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SnO_2 filled mesoporous tin phosphate was prepared by impregnating an Sn melt into the mesopores of hexagonal mesoporous tin phosphate with a pore size of 3 nm at 300°C under vacuum. Although Sn was oxidized to SnO_2 via a reaction with the oxygen ions consisting of one of tin phosphate porewall frameworks at 300°C, the porewall material remained amorphous without showing any other phases. The electrochemical results revealed significant improvement of the reversible capacity to 805 mAh/g from 400 mAh/g after the mesopores were filled with SnO_2. This was because the SnO_2 not only added capacity but also decreased high BET surface area of the mesoporous tin phosphate that caused the large irreversible capacity.

Lithium Insertion/Extraction Characteristics of Carbon Nanofibers Formed from PAA using Porous Template

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Nanocarbon materials, including carbon nanotubes, have attracted much attention due to their wide spread applications. The some of the authors have prepared carbon nanofibers by liquid phase carbonization of polyvinyl chloride (PVC) and polyvinyl alcohol (PVA) in pores of the porous anodic alumina template. By using this template technique, the carbon nanofibers of controlled diameter can be produced. The carbon nanofibers thus prepared have a platelet structure, in which graphene layers are normal to the fiber axis. The nanocarbon materials of this type are of great interest as an anode material with high rate capability for lithium ion batteries, since the diffusion path of intercalated lithium ions is short. In fact, the authors have found the good rate capability of the carbon nanofibers prepared at 1000°C. PVC and PVA are classified as soft carbon materials. However, hard carbon materials are known to have higher capacity than soft carbon materials at heat treatment temperatures around 1000°C. Thus, in the present study, carbon nanofibers have been prepared from polyacrylamide (PAA), which is one of hard carbon precursors and porous template.

The templates used were porous anodic alumina with pore diameters of about 30 and 200 nm. A mixture of PAA powders and the template were heated in a stream of high purity argon gas to 600°C. Then, the template was dissolved and fibrous carbon precursors were obtained. The precursors were further heated to 1000 and 1500°C. The anodes were prepared by coating a mixture of carbon nanofilaments, acetylene black and polyvinylidene fluoride on porous nickel sheets. A liquid electrolyte of 1.0 mol dm^{-3} $LiClO_4$ dissolved in EC+DEC (1:1 by volume) was used.

The carbon nanofibers with the diameter corresponding to the pore diameter of the template were obtained successfully. TEM observations revealed that the carbon nanofibers had a platelet structure. Apparent gas bubbles are present in the carbon nanofibers, possibly associated with the high viscosity of the liquid formed during the carbonization process.

The charge-discharge curves of the carbon nanofibers were similar to those of typical hard carbon materials. As expected, the reversible capacity was larger than those prepared from PVC, being ~400 mA h g^{-1} at a current density of 50 mA g^{-1} for the carbon nanofibers heat-treated at 1000°C. The beneficial effect of smaller diameter of the carbon nanofibers on the reversible capacity at high current densities up to 2 A g^{-1} was also found. The rate capability of the carbon nanofibers prepared from PAA was as high as that prepared from PVC.

Electrochemical Impedance Spectroscopy of Poly(3,4-ethylenedioxythiophene) films: effects of electrolyte composition and film thickness

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The EIS responses of p-doped poly(3,4-ethylenedioxythiophene) (PEDOT) modified electrodes were investigated in acetonitrile and propylenecarbonate solutions, containing different counter-ions (ClO_4^-, PF_6^-, BF_4^-). The polymer films of various thickness were obtained on platinum electrodes by galvanostatic polymerization of 0.05 – 0.1M monomer in acetonitrile in the presence of 0.5 M $LiClO_4$.

For all experimental conditions two characteristic parts of spectra are observed in Nyquist plots: at high frequencies a semicircle due to a parallel RC-element and at low frequencies a nearly vertical capacitive response. The EIS data were analyzed on the basis of a homogeneous film model. It was found that the low-frequency capacitance was independent on the $LiClO_4$ concentration (0.05-1.0 M) and slightly dependent on the nature of counter-ions. The C_{LF} values were linearly dependent on the charge consumed during the electrosynthesis, i.e. were proportional to the film thickness. The parameters of RC-element were derived from semi-circle and analyzed as functions of experimental variables.

The electrochemical behaviour of PEDOT films was compared to that of poly-3-alkylthiophenes (PAT). PEDOT films show more stable electrochemical response (CV, EIS) in comparison with PATs which show noticeable degradation of electrochemical properties at positive potentials (1 – 1.2 V vs. Ag/AgCl). The possible reasons of difference in electrochemical behaviour of PEDOT and PAT films will be discussed.

Financial support from the Russian Foundation for Basic Research (grant N 05-03-33262) is gratefully acknowledged.

Lithium diffusion in thin-film amorphous silicon electrodes

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The electrochemical lithium intercalation into amorphous hydrogenated silicon (a-Si:H) thin-film electrodes is studied by chronopotentiometry, cyclic voltammetry, and electrochemical impedance spectroscopy. The electrodes with thickness from 0.25 to 1.35 µm were obtained from SiH_4 by a method of high-frequency glow discharge on stainless-steel substrates at 250 °C. 1 M $LiClO_4$ in a mixture of propylene carbonate with dimethoxyethane was used as an electrolyte.

The cyclic voltamograms contain cathodic peaks of lithium insertion and corresponding anodic peaks of lithium extraction. The peak current density i_p is proportional to square root of potential scan rate v. The lithium diffusion coefficient D was calculated by the following formula:

$D^{1/2} = i_p \,/\, (2.69\ 10^5\ n^{3/2}\ c_{Li}\ v^{1/2})$,

where n is the number of electrons transferred per one diffusing particle, c_{Li} is the lithium concentration in the intercalate calculated by the integration of the cathodic curve taken at the smallest potential scan rate. For the a-Si:H electrodes D came to 10^{-13} cm^2/s.

Frequency dependencies of impedance were obtained at different potentials at different charge-discharge cycles in a range $2.5*10^{-2}$ to 10^5 Hz. An equivalent circuit of the electrodes is suggested, which comprises the electrolyte resistance and three chains in series, each chain being a parallel connection of a resistance and a constant-phase element (CPE). The phase shift of the first CPE is close to $\pi/2$, and this CPE relates to charge transfer at the silicon/electrolyte interface. The second CPE relates to charge transport in the passive film on silicon. The phase shift of the third CPE is some more than $\pi/4$, and this CPE relates to lithium diffusion in the silicon film with finite thickness. With the potential cycling in progress, the most significant changes are observed in the chain relating to the passive film. The Li diffusion coefficient in a-Si:H was calculated from impedance data at not very low frequencies according equation

$$D = \frac{(dE/dQ)^2}{2\rho^2 W^2}$$

where W is Warburg constant, dE/dQ is a slope of quasi-equilibrium galvanostatic charging curve, and ρ is a-Si:H density (2.2 g/cm^3). D values calculated from impedance is very good coincides with that estimated from cyclic voltammetry.

Acknowledgement. The work was supported by the Russian Foundation for Basic Research, project No. 05-08-18109a.

Synthesis of mesoporous manganese oxide/carbon nanocomposites for pseudocapacitor applications

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There have been an increasing number of reports about high rate electrochemical energy devices for possible applications as auxiliary power sources for hybrid electric vehicles and fuel cell vehicles. Current technology of secondary batteries, which have high energy density, does not appear to meet the high power requirements for hybrid electric vehicles and fuel cell vehicles. Electrochemical capacitors are attractive energy storage systems, particularly for applications involving high power requirement, however, their energy density is far less than one tenth of secondary batteries.

Since the discovery of M41S silica molecular sieves in 1992, mesoporous materials, possessing remarkably large internal surface area and narrow pore size distribution, have attracted considerable attention because of their potential applications ranging from catalysts, absorbents, gas sensors to batteries and electrochemical capacitors. Mesoporous metal oxides are expected to be an ideal solid-pore architectured material which could improve power density of secondary battery materials or energy density of pseudocapacitor materials because of their large surface area, their thin wall thickness which is equivalent to a short diffusion length and their interconnected nanopores for easy ion transport.

In this study, we report on the surfactant-assisted synthesis and electrochemical properties of mesoporous manganese oxides electrodes for supercapacitor applications. In order to increase the energy density and high rate capability of the materials, the mesoporous manganese oxide electrodes including carbon materials as conducting agent were fabricated by electrodeposition in the presence of surfactants. Rate capability and specific capacitance were estimated with cyclic voltammetry and charge/discharge tests in aqueous solutions.

More details will be presented at the meeting

Structural Characterization of the Surface Modified $Li_xNi_{0.9}Co_{0.1}O_2$ Cathode Materials by MPO_4 Coating (M = Al, Ce, SrH, and Fe) for Li-ion Cells

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Structural characterization of surface modified $Li_xNi_{0.9}Co_{0.1}O_2$ cathodes (x = 0.3 and 0.15) using a MPO_4 coating (M = Al, Ce, SrH, and Fe) were investigated for their potential applications to Li-ion cells. MPO_4 nanoparticles that were precipitated from metal nitrate and $(NH_4)_2HPO_4$ in water at pH = 10 were coated on the cathodes via mixing and heat-treatment at 700°C. The $CePO_4$ and $SrHPO_4$-coated $Li_{0.3}Ni_{0.9}Co_{0.1}O_2$ cathodes heat-treated at 300°C were mainly made up of the rock-salt phase (Fm3m) while $AlPO_4$ and $FePO_4$-coated cathodes showed disordered $[Li_{1-x}(Ni,Co)_x]_{3b}[(Ni,Co)_y]_{3a}O_2$-type hexagonal structure (R-3m) with a cation-mixing. However, when x value decreased from 0.3 to 0.15, bare and coated cathodes which had a spinel (F3dm) or hexagonal structure (R-3m) at x = 0.3 were transformed into a NiO-type rock salt structure. Structural changes of the coated cathodes at 300°C was influenced by the coating materials, depending on x value in $Li_xNi_{0.9}Co_{0.1}O_2$. Among the bare and coated samples, $AlPO_4$-coated sample exhibited lowest degree of oxygen generation after 300°C annealing at x = 0.15, indicating the highest thermal stability among the bare and coated cathodes.

Capacitance of the Solid Electrode -Ionic Liquid Double - Layer

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Ionic liquids (IL) - salts characterized by low melting points, have been studied extensively during the last decade. These liquid salts may be used as solvents as well as electrolytes in electrochemical devices. At the same time double-layer electrochemical capacitors, based on carbon materials having very high-surface area, have also been studied with very promising results. Both aqueous and various non-aqueous liquid electrolytes as well as polymer electrolytes have been applied there in, including ionic liquids. There are only a few publications about double layer capacity measured at well defined electrode/electrolyte surface. Except the report on ionic liquids based on the chloroaluminate ion [1], a paper about specific capacitance for glassy carbon (GC), mercury and a commercial carbon as electrode materials and four ionic liquids based on 1-ethyl-3-methyl imidazolium cation can be found in the literature [2]. The general aim of this work was to examine the differential capacity at the solid electrode/IL interface for a number of ionic liquids.

Differential capacity at the electrode/IL interface (electrode material was: glassy carbon (GC), Pt or Au) was measured applying (i) chronoamperometry (ii) cyclic voltamperometry and (iii) ac impedance measurements. The chronoamperometric measurements were done in a two electrode system. The working (GC, Pt or Au) electrode was charged by superimposing a ± 10, 20, 30, 50 up to 90 mV potential dc signal, U, and the current flowing during electrode charging or discharging was recorded as a function of the time. The charge Q accumulated at the electrode was obtained by integrating the $I = f(t)$ curves and the capacity was obtained directly from the slope of the $dQ = C\, dU$. The impedance spectra were measured in a three compartment cell over a frequency range from 0.01 Hz to 99 kHz with an ac potential amplitude of 10 mV. The double layer capacity at the GC/IL interface, obtained from chronoamperometry, is at the level of ca. 10-25 microF/cm^2 at potentials close to the open circuit potential, while the corresponding values for the Pt/IL and Au/IL systems were significantly lower, typically at the level of 1-8 microF/cm^2. This difference is probably due to possible faradaic reactions that can take place at the GC electrode.The capacity value was approximately constant within a broad potential range (of ca 3V).

[1] R. J. Gale, R. A. Osteryoung, Electrochim. Acta, 25 (1980) 1527
[2] C. Nanyundiah, S.F. McDevitt. and V.R Koch, J.Electrochem. Soc., 144 (1997) 3392

Impacts of surface conversion on determination of hydrogen diffusion coefficient in hydrogen storage alloys

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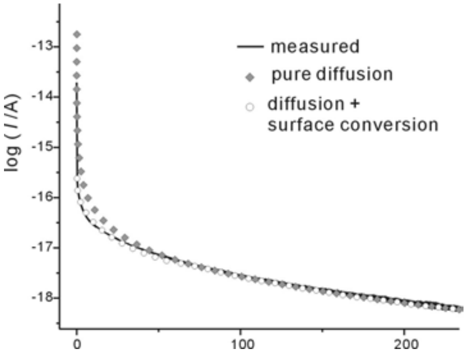
As an important parameter characterizing hydrogen storage alloys, the hydrogen diffusion coefficient (D) has attracted much research interest. However, the data reported in literature are largely scattered (10^{-7}~10^{-13} cm^2/s). Moreover, while most researchers claimed D increasing with decreasing SOC (state of charge), some others reported D being independent of SOC. This paper will show that these controversies are due by large to the difference in dealing with the surface conversion process.

The surface conversion is a chemical step converting the hydrogen stored in the surface layer of the alloy to the hydrogen adsorbed on the alloy surface, and only the adsorbed hydrogen is able to be oxidized during discharge. According to this model, the diffusion coefficient deduced from transient measurements without correction for the surface conversion effect will be an apparent diffusion coefficient D_{app} in stead of D:

$$D_{app} = D\{1-(D/\delta)/[(1-\theta)\,k+(D/\delta)]\} \qquad (1)$$

where δ is the effective diffusion layer thickness (a function of time), k the surface conversion rate constant, θ the surface coverage of adsorbed hydrogen (decreasing with increasing potential and approaching zero at sufficiently positive potentials). Most of the reported D values are actually D_{app} values. Most of the works claiming "SOC dependent D" used different potentials (influencing θ) and time scales (influencing δ) according to SOC values, resulting in an apparent (NOT intrinsic!) correlation between D_{app} and SOC and this correlation was unfortunately mistaken as the causality between D and SOC changes. In this presentation, individual cases in the literature will be critically reviewed in the light of Eq. 1 to support the above statement.

Reasonable approaches must take into account the surface conversion step properly, as exemplified by Fig. 1. The chronoamperometry for a single spherical particle $LaNi_5$ (ϕ30 μm) can be well simulated only if the surface conversion is considered. The results obtained from Fig. 1 are $D = 6\times10^{-10}$ cm^2/s, $kf = 8\times10^{-6}$ cm/s (f is the roughness factor of the particle surface). The long range linearity (corresponding to SOC=0.3 to 0) in the insert of Fig. 1 also serves additional evidence of SOC independence for D.



Studies on Structure and Electrochemical Properties of Pillared M-MnO$_2$ (M = Ba^{2+}, Sr^{2+}, ZrO^{2+})

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Supramolecular pillared oxides M-MnO$_2$ (M = Ba^{2+}, Sr^{2+}, ZrO^{2+}) were prepared through the intercalation of M^{2+} cations into MnO$_2$ host matrix by the method of ion exchange between the precursor δ-K$_x$MnO$_2$ and the corresponding guest. The materials M-MnO$_2$ crystallize in the hexagonal system, the same structure as the precursor, with a larger interlamellar spacing. In the case of ZrO-MnO$_2$, extended X-ray absorption fine structure (EXAFS) determination indicates that Zr atom locates between the MnO$_2$ layers forming a stable octahedral interlayer complex. Compared with the precursor, the cycling property of M-MnO$_2$ was improved distinctly, while the capacity decreased to some degree due to the strong interaction between pillars and the host matrix. Among these pillared materials, ZrO-MnO$_2$ has a reversible capacity of 161.5 mAh·g^{-1} and rather stable cycling behavior compared with the precursor.

Keywords: Layered M-MnO$_2$; Cathode materials; Lithium secondary batteries; Intercalation; Electrochemical properties

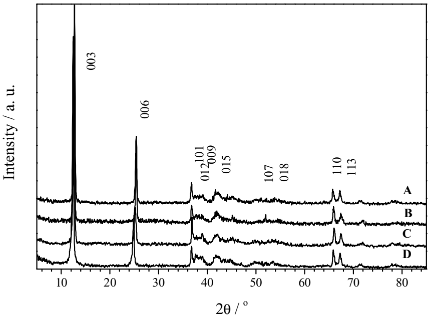

Fig. 1 XRD patterns for the precursor and the products M-MnO$_2$ (M = Ba^{2+}, Sr^{2+}, ZrO^{2+})
A. the precursor K$_x$MnO$_2$; B. Ba-MnO$_2$; C. Sr-MnO$_2$; D. ZrO-MnO$_2$

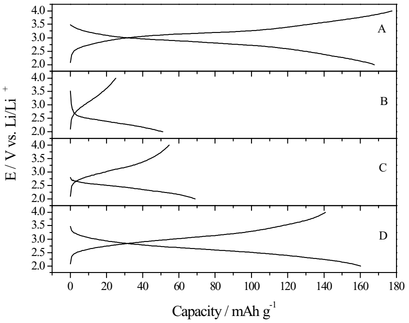

Fig. 2 Charge-discharge curves of the precursor and M-MnO$_2$ used as cathode materials
A. the precursor K$_x$MnO$_2$; B. Ba-MnO$_2$; C. Sr-MnO$_2$; D. ZrO-MnO$_2$

Synthesis of Nanostructured carbon and Sulfonate polysulfone Ionomer for Solid-State Supercapacitors

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An ordered mesoporous carbon material has been synthesized and used together with solid polymer electrolyte (SPE) to realize a solid-state supercapacitor (SC). The synthesis of carbon consisted in the preliminary preparation of highly ordered mesoporous silica (SBA-15), used as a template material, that in a second step was impregnated with sucrose that after thermal treatment at 850 °C was transformed in carbon. The so prepared carbon is know as CMK-3 type carbon. The solid polymer electrolyte was synthesized using trimethyl silyl chlorosulfonate as sulfonating agent in homogeneous polymer solution of chloroform. The silyl sulfonate polysulfone is modified in the sulfonate form by reaction with sodium methoxide. The membranes were prepared by casting method. The prepared membranes were washed with water, dried and converted in protonic form for immersion in HCl solution before their characterization. Two samples of sulfonated polysulfone membrane (SPSf) were employed as electrolyte in the fabrication of solid-state supercapacitors. The former sample contained only the SPSf, whereas the second was in composite form being SPSf filled with 5% of SBA-15 silica. The electrodes for the supercapacitors was prepared with CMK-3 mesoporous carbon and Nafion ionomer. The latter had both the functions of binder and ion conductor. The structures of nanostructured silica template and carbon material was evaluated by transmission electron microscopy (TEM) small angle X-Ray diffraction (XRD) and BET analyses. The solid-state supercapacitors based on carbon electrodes and solid polymer electrolytes were characterized by cyclic voltammetry (CV), galvanostatic charge/discharge measurements and, electrochemical impedance spectroscopy (EIS) analyses. As a result, it was found that the supercapacitor with the composite SPSf membrane exhibited higher specific capacitance (105 F/g) compared to that with the membrane containing only SPSf (86 F/g). Further results on the structural features of synthesised nanostructured carbon, on the proton conductivity of the polymeric membranes and, on the effect of filler on supercapacitor performance will be shown during the presentation.

Preparation, Structure and Electrochemical Properties of $Li_2Na_4V_{10}O_{28}$ as a New Cathode Material in Li-ion Battery

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It is well known that $LiCoO_2$ is commercially used as cathode material for lithium-ion batteries. Nonetheless, cobalt has economic and environmental problems. Among the alternative candidates, Lithium vanadium oxide is considered as a promising material based on its lower price and higher specific capacity compared to $LiCoO_2$[1]. In this work, new material, $Li_2Na_4V_{10}O_{28}$ was prepared by using hydrothermal synthesis and annealing method.

$\{[LiNa_2(H_2O)_9]2_{10}O_{28}\}_2\}_n$ single crystal has been firstly synthesized as reported in Ref.[2] . The as-prepared sample was placed into a furnace to anneal at 513K for 5h in N_2 gas, and then was pulverized to fine powder with ball milling after cooling to room temperature. $Li_2Na_4V_{10}O_{28}$ sample was obtained. The structures of this sample, $Li_2Na_4V_{10}O_{28}$, were determined by XDR with $CuK\alpha$ radiation resources and SEM. A half-cell composed of lithium foil as anode and cathode made of $Li_2Na_4V_{10}O_{28}$ powder was used to check the electrochemical properties. The electrolyte was 1M $LiPF_6$ in EC/DMC (1:1) solution. The cathode was prepared by pasting a mixture of the prepared lithium vanadium oxides, acetylene black and PVdF binder (weight ratio: 85:5:10) onto Al substrate. The size of the testing cathode was around 1.0 cm^2, and the weight of active material in the electrode was around 1.45 mg. Galvanostatic charge / discharge cycling studies were carried out at 0.03mA/cm^2 rate in a voltage range 1.5 to 4.5 V.

Experimental result shows that there is a long path in a, b, c orientations in structure of the sample respectively, and its size of cross section is around 5.9456Å×5.3165Å; 5.9456Å×4.2693Å; 4.2693Å×5.3165Å. The three paths communicate each other. It would be helpful to the movement of lithium ion during charge/discharge process.

It has been noticed that the material exhibits high OCV, around 3.43V (vs. Li/Li^+) and high discharge capacity, around 350 mAh/g. The electrode made of $Li_2Na_4V_{10}O_{28}$ sample shows good electrical conductivity and electrochemical reversibility during charge/discharge process, which maybe be attributed to the novel structure of the three paths. All the results show that this new cathode material would be a promising alternative material for lithium secondary batteries.

[1] H. Y. Xu, H. Wang, el at., Electrochimica Acta, 49, (2004), P349
[2] C. A. Ma, A. L. Xie and L. B. Wang, Acta Crystallographica Section E, 61(7), Pi185

Synthesis and characterization of birnessite nanorods on carbon nano tube (CNT) for electrochemical capacitor applications

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Manganese oxide is a promising electrode material for pseudocapacitors on account of its pseudocapacitive behavior, low cost and environmental compatibility. CNTs have been continuously studied as electrode materials for electrochemical capacitors, as additives to improve the electrode performance of conducting polymers and metal oxides or as deposition substrates for metal oxide particles and conducting polymers for pesudocapacitors because of their chemical stability, good conductivity and large surface area. In addition, CNTs are strongly entangled, providing a network of open mesopores.

Lately, several studies on the synthesis of manganese oxide / CNT composites have been carried out with the aim of improving the electrochemical utilization of manganese oxide and the high rate capability. Previous approaches to the synthesis of manganese oxide / carbon composite include various methods such as physical mixing, thermal decomposition, ball milling, electrodeposition, sonochemical synthesis, and redox reaction.

Because the pseudocapacitive reaction of manganese oxide is known to be a surface reaction, only the surface or a very thin surface layer can participate in the pseudocapacitive reaction. Therefore, in the synthesis of manganese oxide / CNT composites, it is ideal to deposit a very thin layer (~ nm) of manganese oxides onto CNT with a large surface area in order to improve the electrochemical utilization of manganese oxide. An increase in the effective interfacial area between the manganese oxide and an electrolyte can lead to a higher electrochemical utilization of manganese oxide in the manganese oxide / CNT composites. Greater chemical contact and increased contact area between the manganese oxide and CNT can improve the electric conductivity of the electrode on account of the high electric conductivity of CNT.

In this study, we report on the synthesis of birnessite nanorods of manganese oxide spontaneously deposited onto CNT at the nanometer scale by the simple immersion of CNT into aqueous potassium permanganate solution for electrochemical capacitor application and on the synthesis mechanism of the heterogeneous nucleation of manganese oxide on CNT using in situ monitoring of the solution chemistry.

More details on the synthesis and characterization of birnessite nanorods on CNT will be presented at the meeting.

Electrochemical characterization of spontaneously deposited manganese oxide on carbon nano tube (CNT) for electrochemical capacitor applications

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Electrochemical capacitors (ECs) are energy storage devices that possess higher energy and power density than conventional dielectric capacitors and batteries, respectively. According to the mechanism of energy storage, ECs can be categorized into two classes: electrochemical double layer capacitor (EDLC) and pseudocapacitor. EDLC is based on double layer capacitance due to charge separation at the electrode/ solution interface, and pseudocapacitor is based on the pseudocapacitance of faradaic redox reactions at active electrode materials. The electroactive materials of supercapacitors are conducting polymers and transition-metal oxides.

Among the various transition metal oxide materials for pseudocapacitor, amorphous and hydrated ruthenium oxide exhibits remarkably high specific capacitance (~720 F/g) compared with other oxides. However, its commercial use is limited by its high cost. Therefore, a great effort has been devoted to identifying alternative and inexpensive metal oxide electrode materials with acceptable electrochemical properties. In this sense, manganese oxide is a promising electrode material for pseudocapacitors on account of its pseudocapacitive behavior, low cost and environmental compatibility.

Various carbonaceous materials, with their large specific surface areas and good conductivity, can serve as promising candidates for high surface area substrates. Among them, the carbon nanotubes (CNTs) are attractive substrate materials for the metal oxide due to their chemical stability, good conductivity, and large surface area. CNTs have uniform diameters of several tens of nanometers, and they have unique properties such as entanglement and mesoporous character.

In this paper, we report the preparation and electrochemical characterization of spontaneously deposited manganese oxide with various morphologies on carbon nano tube (CNT) for electrochemical capacitors.Permanganate ions were reduced to manganese dioxide by CNT as reducing agent. Its morphology was controlled by a change in pH of a potassium permanganate solution.

More details on the electrochemical properties of manganese oxide on CNT will be presented at the meeting

Pseudocapacitive behaviors of hydorothermally synthesized nano $Ni(OH)_2$/CNT composites

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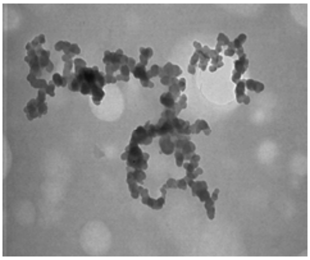
Research on nanoparticles synthesis, characterization and applications continues unabated as the nanomaterials make a revolution in macrosystems. The major advantage of nanoparticle assembly over conventional materials is the high surface area to volume ratio. For instance, a nanocrystalline metal oxide may have an internal surface area approximately 1000 times greater than the geometric area which answers for the better capacitances and electronic conductance on exposure to a conducting electrolyte solution. The existence of such size effects offers a new pathway to regulate reactivity, either chemically or electrochemically or both by controlling the particle size. Electrochemistry plays a key role in nanoparticle science as it paves a way for coupling particle activity to external circuitry.

To increase the performance of electrochemical capacitors in terms of energy density and high rate capability, nano metal oxy/hydroxides of nickel in combination with carbon nano tubes were investigated in our present work. The metal oxide/CNT composite electrodes utilize both advantages of double layer capacitance and pseudo-capacitance. Phase pure alpha nickel hydroxide is synthesized by a hydrothermal method using urea and nickel nitrate in an autoclave. Composites are made by wet impregnation and controlled precipitation of metal oxide on CNT. Metal oxide to CNT ratio is optimized based on the electrochemical studies. Characterization techniques like XRD, SEM/TEM, BET surface area, XPS etc. were used to study the physical and chemical properties of the materials. Individual as well as the composites of nickel oxide and CNT were subjected to electrochemical characterization both in aqueous and non-aqueous electrolytes. Composites of metal oxide/CNT showed better energy density and high rate capability when compared to individual metal oxides and CNTs. In an aqueous electrolyte, specific electrochemical capacitance of Ni(OH)2/CNT composite was ~ 1000 Fg-1, compared to 289.8 Fg-1of pure α-Ni(OH)2.



Spherical nano $Ni(OH)_2$

Mesoporous NiO/CNT composites : potential electrode material for pseudocapacitor applications

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Recently, efforts are being made to improve the energy density of the EDLC by increasing the effective surface area of carbon-based materials, although the resulting densities are still too low. The major bottlenecks to be addressed are a) optimization of particle size of active materials; b) high cycle life during the rapid charge–discharge process; and c) increase the electronic conductivity of the electrode materials. For an ideal double layer capacitor, the charge is transferred into the double layer and there are no Faradaic reactions between the solid material and the electrolyte. In this case, the capacitance is constant and independent of voltage. On the other hand, for capacitors that use metal oxides, pseudo-capacitance due to Faradaic reactions between the solid material and the electrolyte arises and it is voltage dependent. The double layer capacitance has a typical value of 10–40 μF cm−2 for a real surface, while pseudo-capacitance may be 10–100 times greater. The metal oxide/CNT composite electrodes utilize both advantages of double layer capacitance and pseudo-capacitance. Prototypes made of ruthenium and tantalum oxides have been highly successful and are commercialized. As these oxides are highly expensive, alternative metal oxides are explored.

In order to increase the performance of electrochemical capacitors in terms of energy, power and voltage, ordered mesoporous NiO in combination with carbon nano tubes were investigated in our present work. Due to high surface area of both electroactive and conducting materials, we expect better specific capacitance compared to nonporous oxide active materials. Many approaches have been presented in literature to synthesize ordered mesoporous transition metal oxides which have yielded in mixed results. Our aim is to prepare mesoporous NiO by a) using cationic and neutral surfactants as templates; b) using SBA-15 as hard template; and c) in situ generation of mesoporous silica followed by mesoporous NiO. We have followed very simple aqueous hydrothermal route to prepare mesoporous NiO and also its composites with CNT. The materials were characterized by XRD, SEM, TEM, BET surface area and XPS. These nanomaterial were immobilized on paraffin impregnated graphite electrode by abrasive transfer technique and the electrochemical behavior was studied in aqueous electrolytes employing techniques like cyclic voltammetry, charge–discharge and impedance spectroscopy

Effect of Substrate on Synthesis and Electrochemical Behavior of Manganese Oxide for Lithium Battery Application

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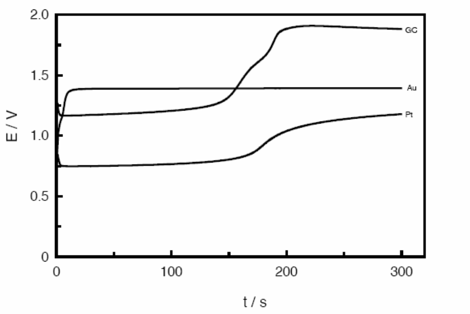
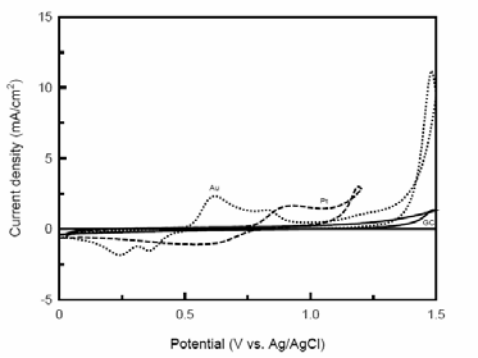
Manganese oxide is very interesting as a positive electrode material for lithium-ion batteries due to its superior electrochemical performance, environmentally friendly nature and low cost [1]. Since electrodeposition is an efficient approach for the preparation of stable films of electroactive materials on substrate surfaces [2], we have chosen this method and investigated the effect of three different substrates (platinum, gold and glassy carbon) on the synthesis and electrochemical performance of manganese oxide. We found that the addition of a small amount of carbon nanotubes to electrodeposition bath (at low current densities) causes the improvement of electrochemical performance of manganese oxide for lithium battery application, because nanostructures minimize the Li$^+$ diffusion path in solid state diffusion. According to the value of the potential in galvanostatic deposition, various types of manganese oxide can be formed on the substrate surfaces. For Pt, two plateaus are observed at potentials of ca. 0.8 and 1.0 V corresponding to the formation of manganese oxides based on Mn^{3+} or Mn^{4+}. In other two cases, higher valances of Mn can be generated as a result of higher electrodeposition potentials. In their corresponding CVs, no peaks are observed for the film electrodeposited on GC electrode; while in the case of Au, two distinct redox couples are observable. In CV of the manganese oxide electrodeposited on Pt, one redox couple related to Mn^{3+}/Mn^{4+} transformation is observed, which makes it a suitable cathode for 4V lithium batteries.





References

[1] H.Y. Lee, J.B. Goodenough, J. Solid State Chem. 144 (1999) 220.

[2] A. Eftekhari, J. Electrochem. Soc. 151 (2004) A1816.

Polyaniline nanofibers as electrodes for electrochemical supercapacitors

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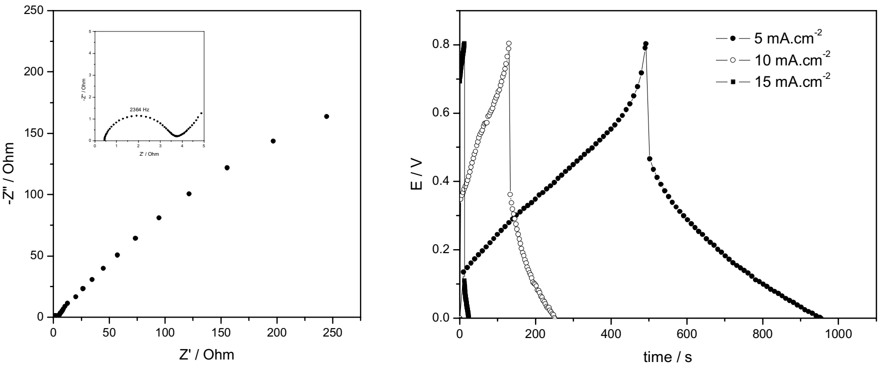
Electronically conducting polymers such as pyrrole, aniline, thiophene, etc, are attractive materials for lightweight rechargeable batteries and electrochemical supercapacitors, due to their good high conductivity, good redox reversibility, ease of synthesis and relatively low prize.

During the last decade, many attempts have been devoted to the synthesis of high porosity, high surface area, micro and nanostructured conducting polymers, resulting from their potential application in areas such as catalysis, optics, drug-deliver, microelectronics, etc. In the present work we report on the synthesis of acid-doped polyaniline nanofibers without the use of templates, via an interfacial polymerization process at an aqueous/organic interface, and their application as active electrode material in electrochemical supercapacitors.. Symmetric supercapacitors were assembled from two 12 mm diameter, 50 mg weight polyaniline composite electrodes (70 wt% PANI, 20 wt% Super P carbon and 10 wt% KF2801 binder) that were kept apart by a glass paper soaked in a 1M solution of the same acid used in the PANI synthesis as electrolyte. The specific capacitance of the supercapacitors was evaluated by means of cyclic voltamnetry, impedance measurements and galvanostatic charge-discharge tests (Figure 1).



Electrochemical impedance spectra (0.8 cell voltage after 300 s 0.8V) and galvanostatic charge/discharge curves for a SO_4H_2-doped PANI-based symmetric supercapacitor

The results obtained indicate that both polyaniline morphology and electrical conductivity depends on the chemical nature of the acid dopant. Regarding to specific capacitance and efficiency, the calculated values obtained are strongly dependent on the nature of the acid dopant and the electrolyte used.

Sonochemical assisted oxidation of pbo to nanostructured lead dioxide and its use as cathodic material of lead – acid battery

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In recent years, an increasing interest has been focused on the preparation and application of nano-structured materials (e.g. metal oxides) [1]. Various techniques have been used for the preparation of nano-structured materials [2]. Recently, a sonochemical method has been used to generate materials of nanometer dimension [3, 4] which show improved properties such as better energy storage [5].

In our previous work, we used electrochemically prepared nano-structured PbO_2 as the active material of lead acid batteries [6]. In this work, we report on the ultrasonically assisted synthesis of lead dioxide. Here, PbO_2 nano-powder was synthesized from an aqueous dispersed PbO solution. In the presence of the ultrasonic irridation, the oxidation of lead oxide was initiated with addition of $(NH_4)_2S_2O_8$ (ammonium persulfate) as an oxidant. The effect of various parameters such as the amount of lead oxide and ammonium persulfate, temperature and pulse amplitude was investigated on the particle size and phase structure of the prepared lead dioxide. The oxidation of lead oxide was completed with increasing the amount of ammonium persulfate and temperature after 2 h of solution ultrasonication. A dark brown powder was obtained after centrifuge of the solution. The resulting PbO_2 nano-powders were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The PbO_2 particles were composed of aggregated nano-structured lead dioxide, the size of which was found to be in the range of 50-100 nm. The XRD pattern shows that, when the reaction is completed, only the crystalline β -PbO_2 was obtained, while in the case of incomplete reaction, both $PbSO_4$ and β-PbO_2 were observed in the texture. The prepared lead dioxide was used as a cathodic material of lead- acid battery. Energy storage abilities of the battery including discharge capacity, specific energy and power were investigated.

[1] M. Cao, C. Hu, G. Peng, Y. Qi, E. Wang, J. Am. Chem. Soc., 125(2003)4982.
[2] B. D. Gates, Q. Xu, M. Stewart, D. Ryan, C. G. Willson, G. M. Whitesides, Chem. Rev., 105(2005)1171.
[3] M. K. Mishra, B. Tyagi, R. V. Jasra, Ind. Eng. Chem. Res., 42(2003)5727.
[4] L. Jiang, G. Sun, Z. Zhou, S. Sun, Q. Wang, S. Yan, H. Li, J. Tian, J. Guo, B. Zhou, Q. Xin, J. Phys. Chem. B 109(2005)8774.
[5] Zhou, Z. Zhou, Solid State Ionics 176(2005)1909.
[6] S. Ghasemi, M. F. Mousavi, H. Karami, M. Shamsipur, S. H. Kazemi, Electrochim. Acta, accepted for publication (2006).

Change in morphology of polyaniline/graphite composite: a fractal dimension approach

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Investigation of surface roughness is an important issue in surface science. Electrode surface characteristics are exceptionally important for all electrochemical process because they can determine the adsorption and ion exchange behavior of the electrode [1]. Fractal geometry is a mathematical concept that describes objects of irregular shape. Some natural geometrical shapes, that can be irregular, tortuous, and rough or fragmented, can be described using concepts of fractal geometry as long as the requirement of self-similarity is satisfied [2]. Moreover, fractal geometry provides a powerful opportunity to investigate surface roughness via geometrical models [3,4]. Fractals have been characterized by several methods that can be classified as physical, chemical and electrochemical. Electrochemical methods have been supported by mathematical simulations and experimental evidences and are one of the most useful and reliable methods for the determination of fractal dimension of surfaces [5].

In the present work, graphite (G) particles with different sizes were incorporated in polyaniline (PANi) matrix to form polyaniline/graphite composites by repeated potential cycling at the Pt electrode from – 0.20 to 0.85 V for 100 cycles at a sweep rate of 50 mVs^{-1} in a stirring solution containing 1.0 M hydrochloric acid, 0.1 M aniline, 5.0×10^{-3} M SDS and 4% of graphite in suspension. SDS was used as an additive in order to suspend of graphite particles and to improve the stability and electroactivity of the resulting films [6]. The surface morphology of PANi/G composites with different graphite particle sizes were studied by using the fractal dimension concept. The fractal dimensions evaluated from the cyclic voltammetry and electrochemical impedance spectroscopy measurements do indeed coincide. The results obtained from both these methods are in good agreement indicating the reliability of the estimated fractal dimension (D_f).

As shown by using SEM and fractal dimension, the PANi/G composites possess more porous structure with an increase in graphite particle size. The results indicated that the electrochemical methods described in this work could be used as a simple tool for analyzing the fractal structure of conducting polymers and their composites.

[1] S. Neves, C. Polo Fonseca, Electrochem. Commun. 3 (2001) 36.
[2] B. B. Mandelbort, D. E. Passoja, K. S. Feinberg-Ringel, Nature 308 (1984) 721.
[3] B. B. Mandelbort, Fractal Geometry of Nature, Freeman, San Francisco, 1983.
[4] F. Family, T. Vicsek, Dynamics of Fractal Surfaces, World Scientific, 1991.
[5] P. J. McMahon, S. P. Moss, J. App. Cryst. 32 (1999) 956.
[6] J. M. Pernaut, R. C. D. Peres, V. F. Juliano, M. A. De Paoli, J. Electroanal. Chem. 274 (1989) 225.

Electrodeposition and Characterization of Chromium-Containing Manganese Oxide Films for Electrochemical Capacitors

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Amorphous hydrous manganese oxide has received attention as a new supercapacitor electrode candidate. Advantages of manganese oxide are the lower cost for raw materials and the fact that manganese-based capacitors are environmentally benign in the point of view that they can operate in neutral electrolyte. Incorporation of other transition metals into MnO_2 compounds is a common strategy to improve their charge-storage capability. Hence, the development of a simple procedure for the synthesis of Mn-based mixed oxides in a thin film form will provide a breakthrough to fabricate electrode materials for supercapacitors. Herein, we describe a new electrochemical route to construct manganese and chromium mixed oxide films. The process includes anodic oxidation of aqueous Mn^{2+} ions in the presence of chromate anions. This method is similar to what we previously reported for the formation of V- and Mo-containing Mn oxide films.[1,2)]

A Mn/Cr mixed oxide film was prepared on a Pt plate electrode by applying a constant potential of +0.7 V versus Ag/AgCl in a 2 mM $MnSO_4$ aqueous solution with 20 mM $(NH_4)_2CrO_4$. The resulting Pt-supported film was characterized by FE-SEM, XRD, and CV in a 0.5 M Na_2SO_4 solution at a scan rate of 20 mVs^{-1}.

A FE-SEM image of the deposited film is depicted in Fig. 1, presenting spherical particles with high porosity that were not observed for the film prepared without CrO_4^{2-}. XPS revealed that the deposit is composed mainly of Mn oxide with minor amount of Cr^{3+}. The reduced state of Cr indicates the involvement of chemical reduction of Cr^{6+} in the electrodeposition process. Fig. 2 shows voltamograms of the Mn/Cr oxide film when cycled repeatedly in 0.5 M Na_2SO_4 electrolyte, yielding a roughly rectangular shape characteristic of capacitor behaviour. The voltammetric charge was much larger than that of pure Mn oxide and kept constant during repetitive cycles.

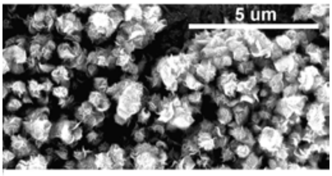

Fig. 1 FE-SEM images of the electrodeposited film.

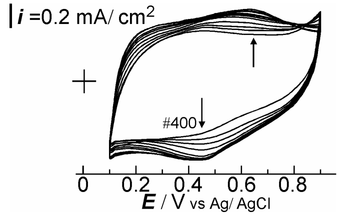

Fig. 2 CV of the film-coated electrode in 0.5 M Na_2SO_4.

References

1. M. Nakayama, M. Nishio, K. Ogura, *J. Mater. Res.* **2003**, *18*, 2364.
2. M. Nakayama, A. Tanaka, Y. Sato, T. Tonosaki, S. Konishi, K. Ogura, *Langmuir* **2005**, *21*, 5907.

Activation Energy of the Lithium Diffusion in Graphite

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Various modifications of graphite and other carbonaceous materials have been used as the negative electrode materials for lithium-ion batteries. Due to a slow solid-phase diffusion rate such batteries can operate only at relatively low discharge rates. Values of diffusion coefficient D of lithium in graphite are documented in numerous references but quantitative data on the effect the temperature exerts on D are scarce and refer to narrow temperature ranges. The present work is devoted to studying the effect of temperature on the rate of lithium diffusion in graphite FG-A [1].

The values of D were obtained by switch-on-curves method in the temperature range from –40 to +40 ^{o}C. Experiments were run in three-electrode cells with Li counter and reference electrodes and with 1M $LiClO_4$ in a 7:3 mixture of propylene carbonate and dimethoxyethane.

Before embarking on pulse chronopotentiometric measurements, a quasi-equilibrium curve for Li intercalation and deintercalation were registered to obtain the quantitative correlation between electrode potential E and charge Q corresponding to amount of intercalated Li.

Galvanostatic switch-on curves were registered at potentials of 0.09–0.10 V. The initial portions of the curves were linear in the E, $\sqrt{t}$ coordinates, and the slope $dE/d\sqrt{t}$ (here t is time from switching current) was proportional to current density i. These facts confirm that conditions of semi-infinite diffusion were fulfilled. Values of D were calculated according to equation

$$D = \frac{4}{\rho^2 \pi}\left(\frac{dE}{dQ}\right)^2 / \left(\frac{d^2E}{di\, d\sqrt{t}}\right)^2$$

Here ρ is the graphite density.

The slope $d^2E/di\, d\sqrt{t}$ happened to equal 3.27 ohm·cm^2·s$^{-1/2}$. The slope of quasi-equilibrium curve dE/dQ is equal to $1.78 \cdot 10^{-4}$ V·g·C^{-1} at the potential 0.1 V. The D values amounted to $2.5 \cdot 10^{-12}$, $1.9 \cdot 10^{-11}$, $4.5 \cdot 10^{-11}$, $1.2 \cdot 10^{-10}$, and $2.7 \cdot 10^{-10}$ cm^2 s^{-1} at –40, –15, 0, +23, and +40 ^{o}C, relatively. Such temperature dependence of D is well obeys to Arrhenius equation, activation energy being equal to 35 kJ·mole^{-1}.

Reference:
1. Russian Patent No. RU 2198137, 26.04.02.

Electric double layer capacitor with acidic polymer hydrogel electrolyte

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Many studies on polymer gel electrolytes have been made for use in electric double layer capacitors (EDLCs). Previously, we prepared a new acidic polymer hydrogel electrolyte with high ionic conductivity, ca. 0.2 S cm^{-1} at 25°C, from 1 M H_2SO_4 aqueous solution, poly(vinyl alcohol) (PVA) and glutaraldehyde (GA) aqueous solution. However, from the practical viewpoint, it is essential that the polymer hydrogel electrolyte is prepared from H_2SO_4 aqueous solution of much higher concentration. Therefore, in this study, we tried to prepare the polymer hydrogel electrolyte from 4 M H_2SO_4 aqueous solution, PVA and GA aqueous solution. As a result, the polymer hydrogel electrolyte containing 4 M H_2SO_4 aqueous solution could be successfully obtained as homogeneous and transparent self-standing membrane under an adequate condition. The electrolyte exhibited higher ionic conductivity, ca. 0.6 S cm^{-1} at 25°C, than the previous one containing 1 M H_2SO_4 aqueous solution. An EDLC was assembled using the electrolyte membrane and two activated carbon electrodes. As can be seen from charge-discharge curves in Fig. 1, the cell with the electrolyte prepared in this study worked successfully as an EDLC, and its capacitance was higher than that for the previous one.

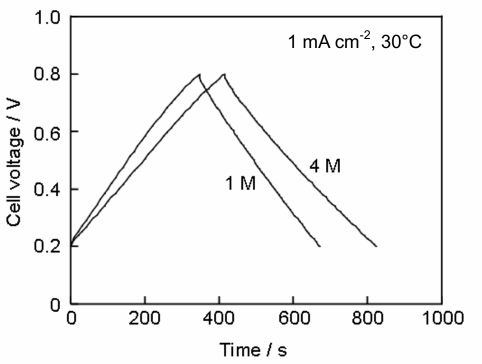

Fig. 1 Charge-discharge curves of EDLC cells with the polymer hydrogel electrolytes containing 4 M and 1 M H_2SO_4 aqueous

Capacitance and Pore Resistance Distribution Within Carbon Supported Ruthenium-Oxide Thin Porous Layers

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Carbon supported ruthenium-oxide composite pretends to be an excellent supercapacitive material, since its high capacitance is represented as the sum of double-layer capacitance of high surface area carbon blacks and oxide pseudocapacitance [1-3]. Composite capacitive performance and charging/discharging behavior strongly depends on morphology and physicochemical properties of composite itself, but also of carbon black and oxide as its constituents. In this work, the capacitive characteristics of carbon/RuO_2 composites, prepared by the impregnation of Black Pearls 2000® (BP) and Vulcan® XC-72R (XC) carbon blacks with oxide colloidal dispersion obtained by forced hydrolysis of Ru chloride, were investigated by electrochemical impedance spectroscopy (EIS). The ageing of oxide sol and oxide solid phase concentration strongly influence the composite capacitive response.

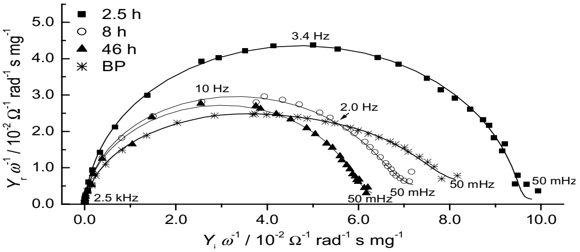

Fig. 1. Admitance complex plane plots of BP/RuO_2 composites (!,–,7), prepared from the sols of indicated ageings, and of BP ( ). EEC simulations are given by lines.

Fig. 1 shows the admitance complex plane plots registered for BP/RuO_2 composites, which are prepared from differently aged sols, and for BP support itself. The capacitive loops are seen as overlapped semicircles, which indicates capacitance distribution within the porous composite layer according to de Levie transmission line model [2]. The data of equivalent electrical circuits are represented by lines in Fig. 1. The distribution of capacitance and pore resistance within composite layer, obtained by simulation of EIS data, showed the absence of the impregnation of inner BP surface (within porous BP grains) if the sols of longer ageings are used.

References

1. M. Ramani, B. Haran, R. White, B. Popov, J. Electrochem. Soc. 148 (2001) A374.
2. B. Conway, "Electrochemical Supercapacitors – Scientific Fundamentals and Technological Applications", Plenum Publishers, New York, 1999.
3. V. Pani, , T. Vidakovi, , S. Gojkovi, , A. Dekanski, S. Milonji, , B. Nikoli, , Electrochim. Acta 48 (2003) 3789.

Performance improvement of $LiCoO_2$ paste electrodes for all solid state lithium ion microbattery

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A thick film cathode has been fabricated by the screen-printing technique using the $LiCoO_2$ paste to improve the discharge capacity in all solid state lithium ion micro-batteries. The $LiCoO_2$ thick film (about 6 μm) was obtained by screen printing using the ethyl cellulose based $LiCoO_2$ paste. Since the adhesion force between printed cathode and substrate was very weak, however, the delaminating was observed during sputtering of LIPON electrolyte on the cathode. In order to enhance the adhesion force, the small amount of epoxy was added in the ethyl cellulose based $LiCoO_2$ paste. The electrical conductance of the printed cathode much increased by coating $LiCoO_2$ powders with pyrolized carbon of resorcinol and the ion conductance was improved via adding lithium ion conducting glass. The printed cathode developed in this work showed the typical discharge curve of $LiCoO_2$ cathode with the high discharge capacity. The average and maximum values of surface roughness of printed $LiCoO_2$ films reduced effectively from 0.8 to 0.49 and from 14.3 to 5.46 μm, respectively, via controlling the composition of $LiCoO_2$ paste.

A better way to improve the electrochemical performance of the Li-secondary battery with $LiMn_2O_4$ cathode

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A simpler method to improve the electrochemical properties of Li-secondary batteries with $LiMn_2O_4$ cathode is suggested. By investigating the electrochemical properties of the batteries produced by different routes of adding ZrO_2, we found that the presence of the ZrO_2 in the electrolyte also improved the performance of the Li-batteries, suggesting the possibility of simple mixing of ZrO_2 in the electrolyte to achieve enhanced electrochemical properties rather than coating the cathode with ZrO_2. In this study, $LiMn_2O_4$ was produced using a sol-gel method followed by heat treatments in oxygen atmosphere. As a conventional method to produce cathodes, 2 wt % ZrO_2 was mixed in the slurry before cast to examine the effect of ZrO_2. We also fabricated the cells containing various amounts of ZrO_2 suspended in the electrolyte (EC:DMC = 1:1 with 1M $LiPF_6$) to compare with celles with the $LiMn_2O_4$ cathode coated with ZrO_2. Charge-dischage experiments showed that the ZrO_2 added cathode decreased its initial capacity while it tended to be good capacity retention. On the other hand, certain amounts of ZrO_2 mixing in the electrolyte enhanced capacity retention without decreasing initial capacity. Based on these findings, detailed mechanism of the role of ZrO_2 on the electrochemical properteis of the Li-batteries with $LiMn_2O_4$ cathode is discussed in this paper.

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Preparation of P (AN-MMA) Microporous Gel Electrolyte for Li-ion Batteries

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Gel polymer electrolyte (GPE) has been attractive for developing plastic Li-ion batteries. Owing to its unique hybrid network structure, its possess simultaneously both the diffusive transport properties of liquid electrolyte and cohesive properties of solid electrolyte. The lithium batteries based on a lithium metal anode and GPE have high ionic conductivity and free of leakage. The energy density, reliability and safety of the batteries have been much more improved than that the performance of the conventional Li-ion batteries based on carbonaceous anodes and liquid electrolytes

In this study, both in-situ nano SiO_2 composition and phase inversion process were used to prepare poly (acrylonitrile-methyl methacrylate) based microporous gel electrolyte for Li-ion batteries. The poly (acrylonitrile-methyl methacrylate (P (AMMA)) was synthesized by suspension polymerization and was dissolved into N, N-dimethylformamide (DMF) to form a uniformity solution, then tetraethyl orthosilicate (TEOS) was added into the solution according to weight ratio of copolymer/SiO2 = 85/15 and stirred for 6 h. TEOS was hydrolyzed by catalysis of alkali ammonia solution to form SiO2. The solution was cast onto a glass plate using a doctor blade, and exposed to humidified atmosphere produced by ultrasonic humidifier, followed by washing, rinsing and drying, successively. The gel electrolyte was obtained by putting the P (AMMA) microporous membrane in a liquid electrolyte for 30 min. The gelled microporous membrane sucked with 755 wt% of liquid electrolyte vs. the dried membrane. It had a prosirity of 70 %, about 1~5um of pores and presented an ionic conductivity of 2.52×10^{-3} S/cm at room temperature. Electrochemical stability window of the porous polymer electrolyte was determined by running a linear sweep Voltammetry. The decomposition voltage of the polymer electrolyte exceeds 4.5V versus Li, indicating that the addition of nano silica improves electrochemical stability of gel polymer electrolytes. The coin test battery with the microporous gel electrolyte showed a good cycling performance. The discharge capacity retention was above 87% at 0.1C rate at the 45th cycle.

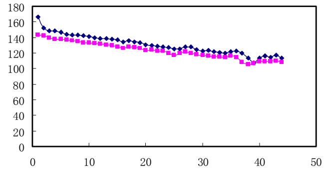

Fig 1 Cycling performance of LiCoO2/C test cell with P(AN-MMA)-based gel electrolyte

Ionic Conductivity in Acrylate Based Polymer Gel Electrolytes

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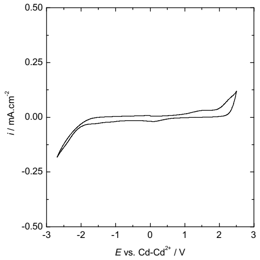
New polymer electrolytes with poly(ethyl methacrylate) PEMA and poly(2-ethoxyethyl methacrylate) PEOEMA with immobilised solution of $LiClO_4$ in propylene carbonate (PC) were prepared by direct UV initiated radical polymerisation. Prepared samples exhibit long-term stable mechanical and chemical properties. Our work in based on previously reported PMMA-based polymer electrolytes [1-3].

Influence of monomer composition, salt concentration, level of the polymer cross-linkage and the salt-solvent ratio on the electrolyte conductivity were investigated [4]. Temperature dependent conductivity measurements showed, that both PEMA and PEOEMA electrolytes exhibit suitable conductivity above -20 °C. The composition of the material was fluently optimised and the best samples exhibited high ionic conductivity up to ca. 0.23 mS/cm at 20 °C. Significant possitive effect of the polymer cross-linkage on conductivity was observed in PEMA-PC electrolytes [4]. Voltammetrical measurements showed the accessible potential window over 4 V. Recently we attempt to immobilise other solvents like dimethyl carbonate.



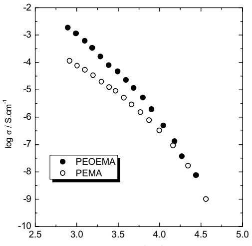


Fig. 1 (left) - Cyclic voltammogram of PEOEMA-PC-$LiClO_4$ on the glassy carbon.
Fig. 2 (right) - Arrhenius plot of the specific conductivity of PEOEMA-PC-$LiClO_4$ (41.2/37.5/21.3 mol. %) and PEMA-PC-$LiClO_4$ (58.1/38.6/3.3 mol. %) electrolyte.

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References

1. J. Vondrák, M. SedlaIíková, J. Reiter, T. Hodal, Electrochim. Acta 44 (1999) 3067.
2. J. Reiter, J. Vondrák, Z. Mi-ka, Electrochim. Acta 50 (2005) 4469.
3. J. Vondrák, J. Reiter, J. Velická, B. Klápšt1, M. SedlaIíková, J. DvoIák, J. of Power Sources 146 (2005) 436.
4. J. Reiter, J. Michálek, J. Vondrák, D. Chmelíková, M. PIádný, Z. Mi-ka, J. of Power Sources (in press).

Preparation and Electrochemical Properties of Chemically Synthesized Polyindole

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Polyindole(PI) is an electroactive polymer, which can be usually obtained by electrochemical oxidation of indole in various electrolytes and chemical polymerization by oxidants like $FeCl_3$ and $CuCl_2$. The doping and dedoping of PI are possible by proton, similar to the case of polyaniline(PANI). This material can be used as electrochromic material, proton conductor, and sensor material. Especially, it has been used as electrode materials in proton battery due to the advantage that the redox window of PI is wider than that of PANI. In this work, we synthesized the PI by chemical oxidation polymerization of indole monomer in solutions of $FeCl_3$ dissolved $CHCl_3$+H_2O mixture. The polymerization of PI was confirmed by FT-IR range from 4000 to 400 cm^{-1}. The dc conductivity was measured using a four-probe method. Brucker ESP300 spectrometer (X-band) was used to obtain the ESR spectra. We have measured the electrochemical properties of the unit cell, which was composed of PI based cathode, lithium metal anode, the glass filter separator, and EC:DMC:$LiPF_6$ (1:1v/v, 1M) as electrolyte solution. The cathode was prepared from the PI, poly(tetrafluoroethylene) binder, and carbon black conductor powder (Super P, MMM Carbon Co.) (6:1:3 in weight). These were sequentially accumulated like a sandwich by using a test cell holder in a dry box. The cells were tested using a galvanostatic charge/discharge cycler in the cut-off voltage range from 2.0 to 4.0V with constant current density of 0.1mA/cm^2. The specific discharge capacity value of these compositions was saturated after 10th cycle as ~58mAh/g.

An investigation of structural changes of silicon during lithiation and de-lithiation by using raman spectroscopy

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The structural changes during lithiation and de-lithiation of Si thin film electrode have been investigated by using Raman spectroscopy. Two different Si samples were prepared by rf-sputtering and ion beam assisted deposition (IBAD) methods. The Raman spectrum obtained from as-deposited IBAD silicon thin film shows broad peak ranging from 450~500cm^{-1}, indicating a typical amorphous structure. On the other hand, rf-sputtered Si thin film is speculated to consist of nano-sized Si crystallites dispersed in amorphous phase from sharp Raman peak around 490 cm^{-1}. The spectral studies in complement with morphological analysis during lithiation and de-lithiation imply that amorphous silicon thin film undergoes abrupt structural transition, resulting in excessive volume expansion and contraction. The distinct potential plateaus during lithiation and de-lithiation clearly confirms the structural phase transformation in amorphous Si thin film. On the contrary, thin film consisting of nano-sized Si crystallite shows mild structural change. From the experiment results, it is concluded that initial structure of Si plays a key role in determining the cycle life of the Si thin film electrode.

Sol-gel Synthesis and Electrochemical Behaviour of 5V $LiCo_{0.25}Ni_{0.25}Mn_{1.5}O_4$ for use as cathode material for lithium rechargeable batteries

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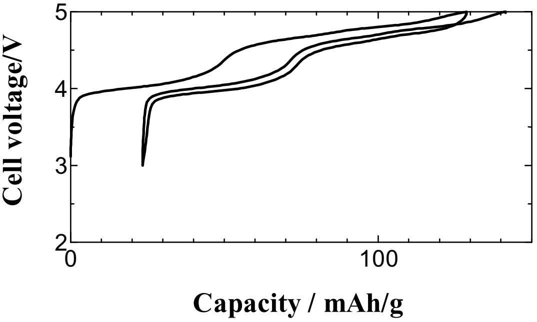
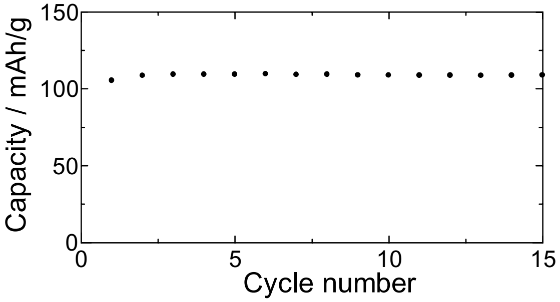
$LiCo_{0.25}Ni_{0.25}Mn_{1.5}O_4$ has been synthesized using sol-gel technique involving different chelating agents viz., acetic acid, oxalic acid and maleic acid. Physical characterization of the synthesized powder were carried out using X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), thermo gravimetric and differential thermal analysis (TG/DTA). The XRD patterns reveal crystalline single-phase spinel product, which is in good agreement with JCPDS Card (35-782). SEM photographs indicate good agglomeration. Electrochemical studies have been carried out using the synthesized powder as cathode material in a 2032 type coin cell configuration. The anode used was lithium foil and the cells were cycled in the voltage range 3 to 5V in a non-aqueous electrolyte solution. Results indicate that a capacity of 110 mAh/g has been obtained in the case of oxalic acid as a chelating agent and remains constant even after 15 cycles.





Alkaline cation intercalation into graphite used as a conducting material in nickel electrode of aqueous secondary batteries

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The discharge voltage profile of aqueous secondary batteries, such as nickel-cadmium and nickel-hydrogen with a metal hydride negative electrode consists of a voltage plateau at approximately 1.2 V mainly involving the β-$Ni(OH)_2$ /β-NiOOH redox couple corresponding to the useful operating voltage of these batteries. Moreover, these batteries are known to frequently show a discharge plateau at about 0.8 V. This phenomenon has already been reported as the second low voltage plateau 1) and is likely to be related to the positive electrode behavior.

In order to clarify the origin of the second low voltage plateau, we first reviewed the papers on this phenomenon and noticed that the effect of the conducting materials added to the Ni electrodes such as graphite. We found that the secondary low voltage plateau appeared only in the Ni electrode containing graphite as the conducting material. The discharge capacity of second low voltage plateau depends on the quantity of graphite added in Ni electrode and its maximum capacity is about 200 mAh/g-graphite. From the ^{7}Li-NMR spectra of charged or discharged Ni electrode containing graphite, it was found that Li^+ ions, i.e., also K^+ ions remaining in the Ni electrode intercalate into graphite in contact with NiOOH during the discharging process. Although the K^+ direct intercalation from an aqueous solution into graphite is hard to occur, the K^+ intercalation from NiOOH into graphite coexisting with NiOOH may be possible, where K^+ seems to be dissolved in solid electrolyte like NiOOH. This situation is similar to the case of Li^+ insertion into graphite during the charging process of Li^+ batteries, where Li^+ is dissolved in organic electrolytic solutions. K^+ and Li^+ intercalation into graphite may be the cause of the second low voltage plateau2).

1. N. Sac-Epee, M. R. Palacin, B. Beaudoin, A. Delahaye-Vidal, T. Jamin, Y. Chabre, and J-M. Tarascon, *J. Electrochem. Soc.*, **144**, 3896 (1997).
2. M. Morishita, K. Kobayakawa, and Y. Sato, *Electrochemical and Solid-Sate Letters*, **8**, A539 (2005).

A Novel Surface Modification Method on Hydrogen Storage Alloy of Ni/MH Batteries

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It is very important to develop electric vehicles for protecting environment, saving energy and improving energy structure. With enhancement of consciousness of environment protection and increasing exhaustion of oil resources, countries and groups all over the world have draw up development projects of electric vehicles (EV) and hybrid electric vehicles (HEV). However, the final acceptance of electric vehicles will depend strongly on the electrochemical performances of the battery and on its acquisition price and maintenance costs. Ni/MH is presently the most promising battery system for electric vehicles in the short and mid-term, which has many advantages such as high specific energy, high specific power, safety and no poisonous elements.

The performance of Ni/MH battery closely depends on the characteristic of negative MH electrode, and the active material of MH electrode is commonly the hydrogen storage alloy. Therefore, the electrochemical performance of alloy greatly affects battery properties. In present study, in order to improve the performances of the hydrogen storage alloy and to optimize the treating process, a new method of surface modification on the hydrogen storage alloy is studied. The hydrogen storage alloy is treated in $CuCl_2$ solution with HF acid as a catalyst. The optimal condition for the reaction is investigated, and the mechanism of this surface modification is probed. The modified alloys show improved electrochemical performance such as superior high rate discharge-ability, better charge acceptance ability, and longer cycle life, compared with unmodified one. EIS results reveal decreased contact resistances and charge transfer resistances of modified alloys, which indicates the high electronic conductivity and electrochemical activity of alloy after modification. The surface modification method employed in our study has many advantages such as low cost and simple process, and points to an effective way of improving electrochemical performances for hydrogen storage alloys.

A microcalorimetric investigation of pulse charging Ni/MH batteries under high rates

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Microcalorimetric technique was adopted to investigate the effects of pulse charge on the heat evolved from the cylindrical 1.3-Ah Ni/MH Ni/MH batteries by comparison with the conventional galvanostatic charge. The battery charged by pulse current exhibits a slower rise in heat generation rate at the same charge rate.

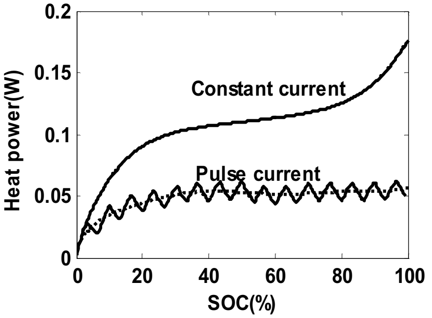

Fig. 1 Heat generation rate at 2C charge

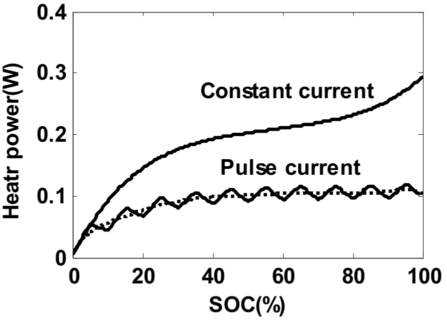

Fig. 2 Heat generation rate at 3C charge

All the experimental was carried out on the Tian-Calvet microcalorimeter. Fig.1 and Fig.2 compared the differences of heat generation rate between the pulse charge and galvanostatic charge. At the end of charge, the generated heat at the galvanostatic charge attains 0.3W at 3C rate charge and 0.17W at 2C rate charge ,respectively ,while the values at pulse charge are only 0.05W at 2C rate charge and 0.1W at 3C rate charge respectively, namely, the generated heat drops about 66% .Furthermore, the generation rate of heat rises more quickly at the galvanostatic charge, while the rise in heat generation rate holds to be rather even at the pulse charge, which is indicated from the plateaus of heat generation rate in the figures. The plateaus extending from 10% SOC to 100% SOC indicate that heat evolution is rather uniform under all cases in the pulse charge regime.

Modeling of current and temperature distribution in a lithium-polymer battery

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The lithium-polymer battery is a preferred candidate as a power source for hybrid electric vehicle (HEV) and electric vehicle (EV) due to its outstanding characteristics such as high energy density, high voltage, low self-discharge rate, and good stability among others. However, much larger lithium-polymer batteries than those available in the market for consumer electronics are required for HEV and EV applications. Because the primary challenge in designing larger lithium-polymer batteries is safety, thermal stability problems must be overcome. The main concern with the thermal behavior of lithium-polymer battery is the possible significant temperature increase during high power extraction, which may cause battery degradation and thermal runaway. Thermal modeling can play a vital role to maintain the operating temperature and temperature uniformity of lithium-polymer battery within a suitable range.

In this work, a two-dimensional modeling is performed to calculate the potential and current density distribution on the electrodes of a lithium-polymer battery comprising a $Li[NiCoMn]O_2$ cathode, a graphite anode, and a plasticized electrolyte. The modeling of the potential and current density distribution on the electrodes is validated by the comparison between experimental and modeling discharge curves obtained at room temperature with various discharge rates from 1C to 10C. Then, the thermal modeling of the lithium-polymer battery is carried out, which accounts for the ohmic heating and the heat generated due to charge transfer at the electrode/electrolyte interface. The heat generation rate is computed by using the calculated results of the modeling of potential and current density distribution.

Electrochemical properties of the carbon-coated and doped $LiFePO_4$

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In recent years, the demand for developing new cathode materials for high performance lithium ion batteries has increased much. Among them lithium iron phosphate is known as a promising candidate for low-cost lithium batteries due to its moderate capacity (170 mAh/g) and excellent safety. However, its low diffusivity and poor electrical conductivity lead to poor electrochemical performance. Much effort has been made to improve these inferior properties since the first report from Goodenough et al. [1-3]. In order to circumvent the low electronic conductivity of the lithium iron phosphate, conductive carbon was incorporated into the $LiFePO_4$ and also doped the $LiFePO_4$ with equi- or supervalent elements. The samples $LiFe_{1-x}M_xPO_4/C$ (M=Mg, Cr, and Zr, x=0~0.05) were prepared from Li_2CO_3, $FeC_2O_4 \cdot H_2O$, $(NH_4)_2HPO_4$, doping agent, and carbon by ball milling [4], followed by calcination at 600~800°C. X-ray diffraction analysis and scanning electron microscopy observations revealed fine crystalline $LiFe_{1-x}M_xPO_4/C$ particles. The electrochemical performance of the $LiFe_{1-x}M_xPO_4/C$ was tested under various conditions. Results showed that the $LiFe_{1-x}M_xPO_4/C$ showed higher specific capacity and better capacity retention compared to the bare $LiFePO_4$. The improved capacity retention during cycle tests was attributed to the reduced $LiFePO_4$ particle size and enhanced electrical conductivity by carbon-coating and doping.

This work was supported by the Core Technology Development Program of the Ministry of Commerce, Industry and Energy (MOCIE).

1. A. K. Padhi, K. S. Nanjundaswamy, C. Masquelier, S. Okada, J.B.Goodenough, J. Electrochem. Soc. 144 (1997) 1609
2. H. Huang, S. Yin.,L. F. Nazar, Electrochem. and Solid-State Lett. 4 (2001) A170
3. S. Y. Chung, J. T. Blocking, Y. M. Chiang, Nature Materials, 1 (2002) 123

Novel polymer electrolytes based on poly(epichlorohydrin-co-ethylene-oxide)

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Since Wright *et al*. first reported the ionic conduction of poly(ethylene oxide) (PEO), solid polymer electrolytes (SPEs) have been intensely studied because of their potential application in solid-state primary and secondary batteries and other electrochemical devices [1- 3].

In this presentation the results of the preliminary studies of a novel electrolyte based on poly(epichlorohydrin-co-ethylene-oxide) ($-(CH_2-CH(CH_2Cl)-O-CH_2-CH_2-O)-$ and lithium salts, are described. Electrolytes compositions were represented as $p(EEO)_nLiX$ and produced with lithium salt compositions of n between ∞ and 0.5 (where *n* indicates the number of epichlorohydrin-co-ethylene-oxide repeat units per mole of Li^+ ions). Compositions were prepared by co-dissolution of the guest salt and host polymer in tetrahydrofuran. The solvent casting technique was used to prepare thin, free-standing films. Electrolytes were characterized by conductivity measurements, cyclic voltammetry at a gold microelectrode and thermal analysis.

[**1**] B. E. Fenton, J. M. Parker, P. V. Wright, *Polymer* **14**, (1973) 589.
[**2**] C. G. Granqvist, *Solid State Ionics* **53 – 56** (1992) 479.
[**3**] F. M. Gray, in Solid Polymer Electrolytes: Fundamentals and Technological Applications, VCH Publishers, Inc. (1991)

Electrochemical Properties of Carbon Black Electrodes

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This work is dedicated to the memory of Professor Aleksandar Despić

Application of carbon black, for battery and fuel cell electrodes as well as in electrochemical supercapacitors, boosted scientific interest in their electrochemical properties [1,2]. In this work, the morphology and capacitive properties of the electrodes, made of commercial carbon blacks, Black Pearls 2000® (BP) and Vulcan® XC-72 R, (XC) were investigated by scanning electron microscopy (SEM), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The electrodes were examined in the form of a thin layer applied from water suspensions of BP and XC onto Au disk.

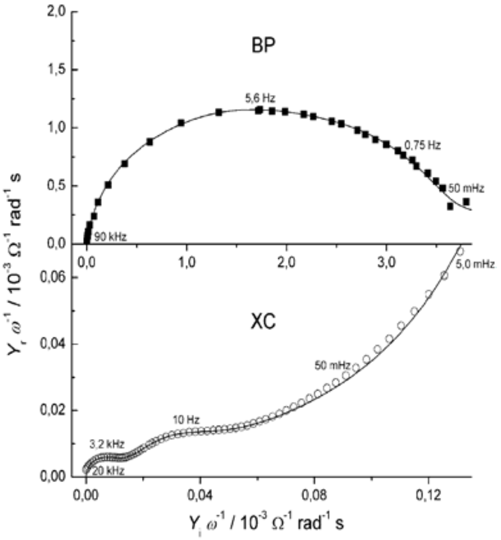

Fig. 1. Complex plane admittance plots for BP and XC carbon black electrodes, obtained at 0.55 V_{SCE} in 0.50 mol dm^{-3} H_2SO_4. Simulations by equivalent circuits are represented by lines.

As expected, voltammetric charges were found to depend on the sweep rate, *v*. Dependence of total charge as well as overall capacitance on the sweep rate is commonly explained by the existence of less accessible surface in the porous electrodes [3]. Complex plane admittance plots for prepared carbon black electrodes are shown in Fig. 1. Overlapped capacitive loops are seen for both BP and XC electrodes. The plot for XC electrode indicates the appearance of a charge transfer resistance at low frequencies. EIS data were fitted by de Levie model of transmission line equivalent electrical circuit [2]. Structure of applied equivalent circuits, as well as capacitance and resistance values obtained by simulations of EIS data enabled estimation of capacitance and resistance profile throughout carbon black porous electrodes. The results of EIS investigation are correlated with the results obtained by SEM and CV measurements.

References

1. K. Kinoshita, "Carbon-Electrochemical and Physicochemical Properties", Wiley, N.Y., 1988.
2. B. Conway, "Electrochemical Supercapacitors – Scientific Fundamentals and Technological Applications", Plenum Publishers, N. Y., 1999.
3. S. Ardizzone, G. Fregonara, S. Trasatti, Electrochim. Acta 35 (1990) 263.

Glycine-nitrate Method of Synthesis of $Li_{1+x}Cr_yMn_{2-x-y}O_4$ Spinels

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The largest improvement in preventing capacity fade of lithium manganate spinels, as potential cathode materials in lithium batteries, was achieved by substitution of some manganese by other metal cations. Chromium for manganese substitution gives one of the highest performance increases [1]. Doubly substituted spinels in which lithium ion as the second substitutional cation occupy not only tetrahedral but also octahedral crystallographic positions show even better charge-discharge characteristics [2]. These complex spinels are usually prepared by time and energy consuming solid state reaction.

In this work we applied rapid and simple glycine-nitrate method to synthesize complex Li1+xCryMn2-x-yO4 spinel compounds. This method we already used for preparation of lithium manganates [3,4]. Firstly metal nitrates and glycine were dissolved in water. The solution is gradually heated in a covered glass beaker up to 200oC. The evaporation of water was followed by spontaneous ignition. Resulting powder was collected and additionally heated in the furnace at 800oC for 4 h. XRPD measurements and Rietveld refinement confirmed the presence of pure spinel phase. For spinel with composition Li1.05Cr0.10Mn1.85O4 no capacity fade was observed after 20 charge-discharge cycles, but initial discharge capacity was reduced to 82 mAh g-1.

[1] M. C. Tucker, J.A. Reimer, E.J. Cairns, J. Electochem. Soc. **149(5)** (2002) A574
[2] Y. Shin, A. Manthiram, J. Electochem. Soc. **151(2)** (2004) A204
[3] D. Jugović, N. Cvjetićanin, V. Kusigerski, S. Mentus, Journal of Optoelectronics and Advanced Materials **5(1)** (2003) 343
[4] I. Stojković, A. Hosseinmardi, D. Jugović, M. Mitrić, N. Cvjetićanin, Solid State Ionics, in press

Syntheses of $LiCoO_2$ for cathode materials of secondary batteries at low temperature by the high-frequency microwave

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The use of microwaves for solid-state synthesis is a fairly new development but promises advantages in speed and energy efficiency. Synthesized $LiCoO_2$ by the high-frequency microwave is investigated in this paper. Used the superfine Co_3O_4 powders as start material, acquired $LiCoO_2$ at 400-500℃ in 1 hours. Experimented the factor affect the process. $LiCoO_2$ has well-crystallized with the layered structure. The consequences in terms of the phase purity, crystallization, and particle sizes are described. The charging capacity is up to 185mAh/g, and both the platform charging curve and time for charging/discharging demonstrate the electrochemical activity of the microwave synthesized $LiCoO_2$.

Key words: tricobalt tetraoxygen, fine particles, super-high-frequency microwave

1. Introduction

$LiCoO_2$ have been studied as cathode materials in lithium secondary batteries because of their high operating voltage and energy density, large capacity, and long cycle life. Despite the highest cost among the candidate materials, $LiCoO_2$ is used most widely for its better thermal and structural stability during electrochemical operations. But $LiCoO_2$ powders are usually synthesized by solid state reactions at high temperature (HT) 800℃.

The low temperature synthesis reactions can acquire more uniform $LiCoO_2$ fine particle, it is benefit to the battery electrode materials. The high-frequency microwave (10^{9-11}GHz) can acquire the apex temperature do not surpass 500℃. Present investigation focuses on synthesizing $LiCoO_2$ at 400-500℃.

In order to realize syntheses of $LiCoO_2$ by the super-high-frequency microwave method at 400-500℃, we use superfine the superfine Co_3O_4 powders as start material.

2. Experimental

2.1 Raw material Co_3O_4 characterization.

The structure of $LiCoO_2$ is the Li+ implanting in the Co_3O_4 crystal. However, the structure of Co_3O_4 crystal is key factor for the $LiCoO_2$ crystal. The raw material were identified by X-ray powder diffracto-metry (D/Max-Ra,Cu K_α, 40kv,40ma)Fig1. The particles size distribution was identified by the SEISHIN LMS-30. Fig2 is the SEM photography of Co_3O_4 fine particles Fig3 the SEM photography of traditional Co_3O_4 particles. The fine particles are globular; the traditional Co_3O_4 particles are rodlike. The difference is obvious. The traditional Co_3O_4 particles size distribution, D50 is about 27 μm. The Co_3O_4 fine particles size distribution D50 is 2.4 μm. In the experiment, using the

Charge-discharge characteristics of rechargeable alkaline manganese dioxide-zinc batteries with nickel hydroxide additive

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The rechargeable alkaline manganese dioxide (RAM^{TM}) battery is an environmentally benign, low cost battery system that can be used for all applications where primary cells (e.g. alkaline-manganese dioxide and zinc-carbon) are being used. In addition, the worldwide licensed RAM^{TM} technology has the capability to replace Ni-Cd or Ni-MH batteries, especially in applications where charge retention at higher temperature and intermittent usage are important issues. The cathode and anode formula of the RAM^{TM} battery was significantly improved during the last few years (XL Rechargeable Alkaline Battery) [1] and a few prototypes of flat plate design were successfully developed [2].

In this work we studied the charge-discharge characteristics of cylindrical RAM^{TM} batteries (AA type) with nickel hydroxide as cathode additive. Due to its high power density, good cycling behaviour and relatively low price, nickel hydroxide is widely used as active material of alkaline rechargeable batteries, e.g. Ni-Cd, Ni-MH and Ni-Zn batteries [3]. RAM^{TM} batteries that were prepared with an admixture of nickel hydroxide (approx. 20 %) to manganese dioxide show two sloping steps during discharge: (i) NiOOH to $Ni(OH)_2$ and (ii) MnO_2 to MnOOH, resulting in a benefit of higher cell voltage and discharge current compared to batteries without additive. But the gelled zinc anode needs to be properly adjusted to cathode composition, as nickel hydroxide requires an equivalent amount of zinc oxide at the negative electrode, in order to yield excellent battery performance.

Charging of these batteries has to be carried out at higher voltage (up to 1.9 V) and is done with constant voltage (CV), constant current (CC) or with a combined mode (CC-CV charging). Battery cycling can either be started with the discharge procedure (reduction of MnO_2) or a capacity-limited charging procedure (NiOOH formation). This work mainly focuses on proper balancing of cathode/anode composition as well as on developing a suitable charging procedure to improve the charge-discharge characteristics and cycling performance of RAM^{TM} batteries containing nickel hydroxide.

[1] J. Daniel-Ivad, XL Rechargeable Alkaline Batteries, in: The 23rd Internat. Battery Seminar and Exhibit, Ft. Lauderdale, Florida, March 13-16, 2006.
[2] A. Stani, W. Taucher-Mautner, K. Kordesch, J. Daniel-Ivad, J. Power Sources 153 (2006) 405-412.
[3] W. Taucher-Mautner, K. Kordesch, J. Power Sources 132 (2004) 275-281.

Synthesis and electrochemical polymerization of nonconductive poly(n-vinly carbazole methly ethyl ketone formaldehyde -resin)

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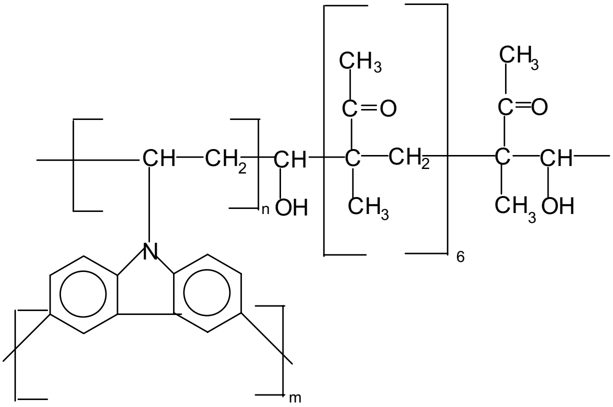
Recently, carbazole, based polymer systems have received considerable attention, which is amply justified in view of the unusual electrical, photoelectric, thermal and other relevant properties of these materials [1]. The electrochemical copolymerization of N-vinly carbazole(NVCz) with MEKF-R have been reported [2].

In this study synthesis of conductive NVCz and methly ethyl ketone formaldehyde-resin (MEKF-R) copolymer has been reported. Non- conductive poly (N-vinly carbazole methly ethyl ketone formaldehyde-resin) [p(NVCz/MEKF)] was synthesized via the vinyl groups by electroinduced copolymerization system in the presence of a catalytic amount of the cerium ion in a separated anode compartment [3].

Conductive p[(NVCz/MEKF-R)] was synthesized by electrochemical polymerization.The solubility of polymers was compared with homopolymer. The characterization of homopolymer and copolymer films was performed by polarization curves and cyclovoltammetric measurements, solid state conductivity measurements and spectrophotometric methods comparatively. From these measurements, ionization potentials I_p, electron affinity E_a, optical band gap E_g, peak potentials, E_p, and doping degree y, of polymer calculated. Impedance spectroscopy of monomers and polymers for electrochemical capacitors are described.A possible sheme for the conductive copolymer has been suggested.



Scheme 1: Conductive p(NVCz/MEKF)

References

1- M. Biswas and S.K. Das, *polymer* 23, 1713(1982)
2- B. Ustamehmeto lu, N. Kızılcan, A. S. Saraç, A. Akar, , *International Journal of Polymeric Materials*, 53. 1-12 (2004)
3- B. Ustamehmeto5lu*, A. S. Saraç, N. Kızılcan and A. Akar, *Polym. Adv. Technol.* 15:1-7 (2004)

Stability of an Ionic Liquid as Electrolyte for Lithium Ion Cells

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Poor electrochemical stability of 1-ethyl-3-methyl imidazolium cation (EMI^+) salts at cathodic potentials currently impedes lithium insertion/de-insertion in graphite. Therefore several studies have been made in an effort to identify additives that extend the cathodic limit.[1] This work investigates a microelectrode technique for the study of the effects of addition of water and bromide ions on both cathodic and anodic stability of EMI^+TFSI^- (EMITFSI).

EMITFSI was synthesised according to the procedure described in earlier publications[2], The product was dried for 12 hours at 0.2 mbar, 120 ˚C. For electrochemical measurements, platinum, copper and tin microelectrodes were used as the working electrode of a two-electrode cell containing the test electrolyte. A $Li_{1.5}Mn_2O_4$/carbon composite was used as the reference and counter electrode. Linear Sweep Voltammetry (LSV) and Cyclic Voltammetry (CV) were performed. Li salts or water were added to EMITFSI up to various concentrations and cathodic and anodic behaviour were investigated.

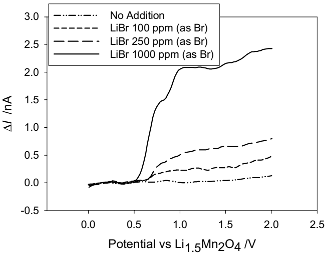

Fig. 1 Anthodic LSV of EMITFSI with LiBr

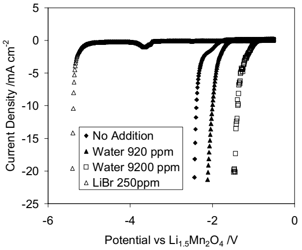

Fig. 2 Cathodic LSV of EMITFSI with LiBr or water

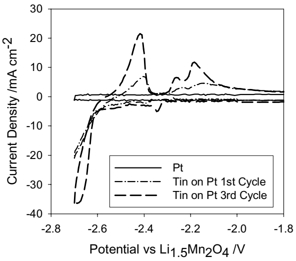

Fig. 3 CV of EMITFSI with LiTFSI on tin

With LiBr addition, anodic currents were observed above 0.5 V vs $Li_{1.5}Mn_2O_4$ (3.5 V vs Li), as shown in Fig. 1. The anodic limiting currents varied linearly with the concentration of Br^- according to a diffusion coefficient Br^- in EMITFSI of 2.4×10^{-7} cm^2/s. Although no cathodic current can be generated from LiBr until lithium is plated, the potential corresponding to the rise in cathodic current at the stability limit of EMITFSI was shifted negative as shown in Fig. 2. The effect of added water on the cathodic stability limit is also shown in Fig. 2. It is suggested that the potential shift is due to an increase in the rate of reduction of EMI according to a water-catalysed EC' mechanism. Fig. 3 shows a preliminary result for lithium insertion into a tin electrode from this electrolyte.

References

[1] M. Holzapfel, C. Jost, A Würsig, H. Buqa, P. Novák et al. Carbon, 43, 1488 (2005)
[2] P. Bonhote, Ana-Paula Dias, Michael Grätzel et al. Inorg. Chem., 35, 1168 (1996)

Effect of Ce(III) additive on crystal orientation and morphology of electrodeposited cobalt

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The structure and morphology of thick cobalt coatings on copper substrate by electrodeposits from mixture of sulfate and chloride electrolytes, either without or with addition of cerium sulfate, are investigated. From the SEM observation, the surface morphology of the electrodeposited cobalt obtained from the electrolytes with Ce(Ш) additive is the dependence of the amount of additive. The XRD analysis also indicates that the texture of electrodeposited cobalt was changed with the variety of the content of Ce(Ш) in the electrodeposited solution.

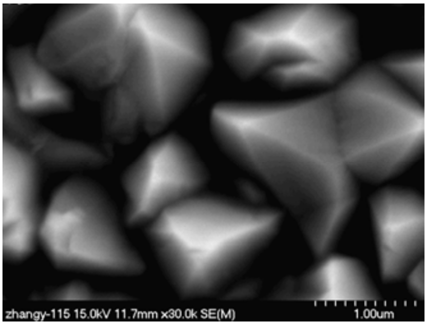

Fig.1 SEM of electrodeposited Co from 0.6M $CoSO_4$ + 0.2M $CoCl_2$ at 50°C with 5A·dm^{-2} pH=5

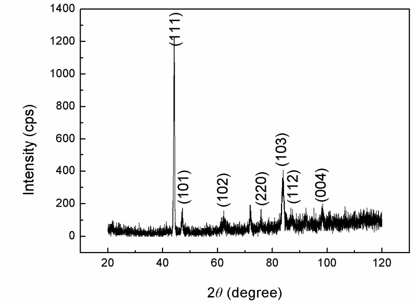

Fig.2 XRD of electrodeposited Co from 0.6M $CoSO_4$ + 0.2M $CoCl_2$ at 50°C with 5A·dm^{-2}pH=5

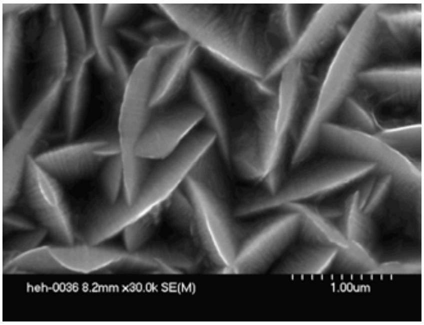

Fig.3 SEM of electrodeposited Co-Ce from 0.6M $CoSO_4$ + 0.2M $CoCl_2$ + 3.0gL^{-1} $Ce_2(SO_4)_3$ at 50°C with 5A·dm^{-2} pH=5

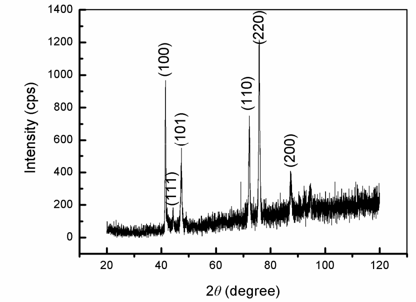

Fig.4 XRD of electrodeposited Co-Ce from 0.6M $CoSO_4$ + 0.2M $CoCl_2$ + 3.0gL^{-1} $Ce_2(SO_4)_3$ at 50°C with 5A·dm^{-2} pH=5

The research on surface behavior of pasted nickel electrodes with electrodeposited Co-Ce on the substrate

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MH/Ni battery of electro motion vehicle has become a hot point of studies. In this paper, electrodepositing Co-Ce alloys on the nickel substrate in order to enhance the MH/Ni battery's discharging performance at high rate modifies the pasted nickel electrode substrate. The results of CV, SEM, XPS, XRD indicated that (1) after nickel electrode formation, the film containing the CoOOH and $Co(OH)_2$ was formed on the substrate surface with electrodeposited Co-Ce; (2)the CoOOH on the electrodeposited Co-Ce alloys substrate increased combine intensity between substrate and active materials, electron conductivity, electricity transmission ability and performance of charging and discharging at high rate.

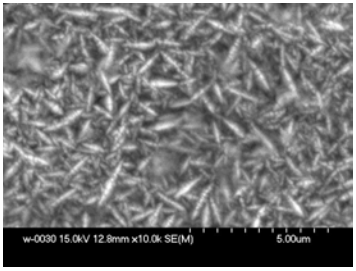

Fig.1 SEM of SOC on the Co-Ce substrate

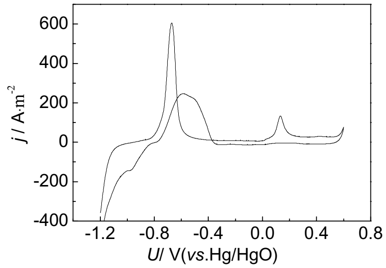

Fig.2 The CV curve of nickel substrate with electrodeposited Co-Ce

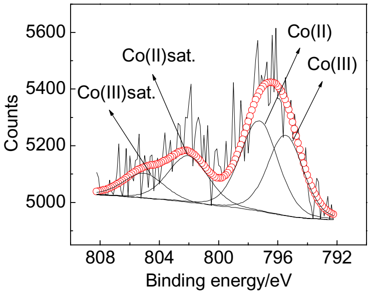

Fig.3 XP detailed spectra of $Co2p_{1/2}$ region for the SOC on the electrodeposited Co-Ce substrate

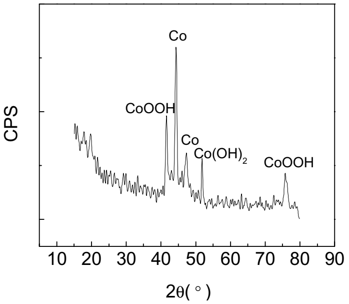

Fig.4 The XRD spectra of electrodeposited Co-Ce substrate at SOC

Study of Degrade Mechanism of Alloy Negative Materials for Li-ion Batteries

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Lithium-ion batteries have been commercially used in popular portable devices, such as mobile telephone, notebook computer and digital camera. The development of modern electric devices and electric vehicle requires more compact batteries with higher energy density. New energy materials have been extensively and deeply studied [1]. Sn-based Li storage alloy materials have been focused on because of high specific gravimetric (994mAh/g) and volumetric capacity (7200mAh/cc) than that of carbon (372mAh/g, 800mAh/cc) in Li-ion batteries. However, large volume and structure changes occur associated with the reversible reaction of Li-insertion and extraction, which results in poor cycle life. It is believed that particle cracking of electrode resulting from volume expansion and phase transition is responsible for the poor cycle performance of Sn-based alloy electrode [2].

In our work, Sn thin film was deposited by magnetron sputtering technique in Cu foil. The electrochemical properties of Sn film have been investigated using a coin cell with a Li metal counter electrode in 1M $LiPF_6$/EC:DMC(1:2 volume ratio) solution. Experimental result showed that the volume expansion of Sn film electrode during charging was around 200%, not so large compared with the theoretical calculation value, 370%. But most of the volume expansion, around 150% was resulted from the decomposition of electrolyte catalyzed by the alloy materials; only 50% could be attributed to Li insertion and phase transition. These results suggested that a novel electrolyte was necessary for the purpose of application of Sn-based alloy materials in Li-ion batteries.

Acknowledgemeng: This work was supported National Natural Science Foundation of China (No.20506024) and Zhejiang Natural Science Foundation (No. (Y405496).

[1] Besenhard J O, Yang J, Winter M. Will, J. Power Sources, 1997, 68:87-90
[2] C. Wang, A.J. Appleby, F.E. Little, *J. Power Sources* 93, (2001)174

Passivation Phenomena on the Graphite Electrode/ Electrolyte Interphase in Li-ion Cells Containing Silicon Di- and Tripodands

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Passivation phenomena occurring on the graphite electrode surface during first reduction in aprotic solvents are a matter of great importance for proper functioning of lithium-ion (Li-ion) batteries, including rate capability and cyclic life. Present common solutions, based on the application of ethylene carbonate as film-forming component, are not fully satisfactory. This is primarily due to its high melting point, being an obstacle in operating the batteries in very low temperatures. Because of this, there is a tendency among battery researchers and engineers to return to propylene carbonate (PC) as electrolyte solvent. However, because of the phenomenon of solvent co-intercalation followed by its decomposition associated with destructive particle exfoliation, propylene carbonate is known to be inherently incompatible with most of the graphitic anodes. Therefore applying this solvent requires adding certain chemical species to the electrolyte, or pre-treatment of the graphite surface, both approaches aiming at preventing solvent intercalation, thus enabling creation of stable and good-quality passive layer on the graphite surface. Very recently we have found that certain peculiar silanes, belonging to the class referred to as silicon tri-podands, can serve as effective additives for propylene carbonate-based electrolytes for Li-ion cells. We proved that addition of vinyl tris-2-methoxyethoxy silane to PC prevented the graphite flake exfoliation and we attributed this phenomenon to a protective barrier formed by silane molecules self-assembled on the electrode surfaces. In the present contribution we continue this research by examining various di- and tripodands differing in the nature of functional groups, as well as the length and number of polyoxaethylene chains capable of complexing lithium cations. We consider two different strategies for studying the influence of examined Si-podands on the passivation phenomena. In the first approach the compound is added to PC-based electrolyte solution. In the second approach we pre-treat the graphite electrodes in the examined compound and then test such electrodes in electrochemical cells containing PC as electrolyte sole solvent. The passive layer formation was studied using galvanostatic charging/discharging in half-cells with metallic lithium counter electrode and cyclic voltammetry experiments. Structure of the passive layer was investigated by means of FTIR, SEM and other techniques.

Active Material for Li-ion Batteries and Supercapacitors Fabricated from Waste Car Tyres

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Utilization of waste car tyres is a matter of great practical importance in terms of economy and environmental impact. Recent legal regulations force more intensive works on fuller recycling of tyres, so that less amount of dangerous substances pollute the environment. In the course of processing of waste tyres large amounts of substances are produced, consisting mainly of low-crystalline carbonaceous materials with an important mineral impurities content. This low-temperature carbonizate has found application as a precursor for adsorbents and fillers. Taking into account the scale of the problem there is a need for searching for other possible industrial applications of carbon-based materials from recycling of waste tyres. Electrochemical industry has been utilizing a large variety of carbon materials for a long time, mainly as active electrode materials for various types of batteries, including lithium-ion batteries, but also as inactive additives for electrode mixtures. Very recently there has arisen a new prospective area of applications as electrode materials for the so-called supercapacitors.

The aim of the presented work is to demonstrate the possibility of applying the low-temperature carbonizate from processing of waste car tyres as active alectrode material for Li-ion batteries and supercapacitors. The starting material was obtained by pyrolysis of pre-treated tyres in rotary kiln at 500°C. After milling in a ball-mill the material was subjected to chemical purification to increase the carbon content. Finally carbonization at 1000°C in the flow of argon was applied aiming at elevating the crystallinity degree. At each step of processing the sample crystal structures were controlled by means of XRD technique and the lithium insertion/deinsertion behaviour was followed by constant current charging/discharging in the electrochemical cells, as well as other electrochemical techniques.

Changes of Anode Material during Extended Cycling of Lithium Ion Battery

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Efficient use of energy and natural sources is becoming more and more important with the continuous growth of population. In the case of lithium ion battery, its cycling behavior is excellent and more advantageous than the other rechargeable batteries. However, its cycling is still urged to be extended to meet the requirements of electric vehicles so that its cost can be decreased much. As to the capacity fading of lithium ion batteries, there are some reports. However, most of the authors did not produce the lithium ion batteries by themselves. As a result, the real reason as to capacity fading cannot be well understood. Here we reported a lithium ion battery manufactured in our laboratory and the changes of anode material during extending cycling.

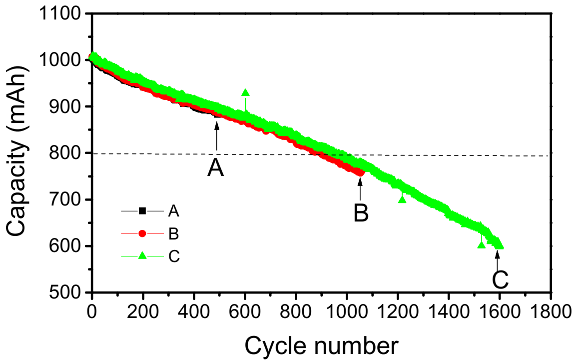

Fig. 1 Cycling behavior of three 063450 cells

Fig. 1 shows the cycling of three 063450 cells: A, B and C, which were manufactured by home made $LiCoO_2$ and graphite as cathode and anode. They were terminated at 500, 1060 and 1600 cycles, respectively. X-ray diffraction does not show much change of the graphitic structure. However, at the surface of the graphite more and more spots were produced, which were from the decomposition of electrolytes, consistent with the results from X-ray photoelectron spectroscopy. The impedance measurement also shows that the resistance increases with cycling. The reversible capacity also fades with cycling.

The above results show that the surface structure of anode materials is very important to extending cycling. A good anode material should not react with the electrolytes again after formation, which provides a next direction to achieve excellent cycling of lithium ion batteries.

Acknowledgment

Financial supports Shanghai Committee of Science & Technology (04QMX1406) and Humboldt Foundation are greatly appreciated.

Electrochemical Performance of Aqueous Rechargeable $LiV_3O_8/LiCoO_2$ cell

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Rechargeable lithium ion battery using aqueous electrolytes can overcome some disadvantages of the commercial lithium ion batteries such as high cost and safety problem, and it was regarded as the promising power for electric vehicles. $LiCoO_2$ and LiV_3O_8 have been well investigated as electrode materials in lithium ion batteries. Here we reported the electrochemical performance of an aqueous rechargeable lithium battery using LiV_3O_8 as anode, $LiCoO_2$ as cathode material and 1M $LiNO_3$ as aqueous electrolyte.

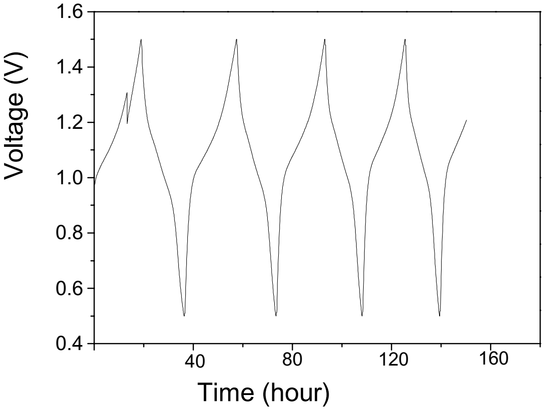

Fig.1. Charge and discharge profiles of aqueous rechargeable $LiV_3O_8/LiCoO_2$ cell.

Both LiV_3O_8 and $LiCoO_2$ were synthesized in our laboratory by using solid state reaction. The charge and discharge curves of the $LiV_3O_8/LiCoO_2$ cell in aqueous electrolyte are shown in Fig.1. It can be seen that the first discharge capacity of $LiV_3O_8/LiCoO_2$ cell is 59.8 mAh/g based on the weight of the cathode, and the charge capacity 65.4 mAh/g. The coulomb efficiency in the first cycle is 91.3%. The discharge capacity in the second cycle is 54.9 mAh/g. After the second cycle the cycle performance of the cell becomes stable. The structural changes of the electrode materials were investigated, and the results show that there is much space for the improvement of the structural stability. However, it presents the promise of the aqueous rechargeable lithium batteries as practical application.

Acknowledgment

Financial supports from Natural Science Foundation Committee of China (50573012), Shanghai Committee of Science & Technology (04QMX1406) and Humboldt Foundation are greatly appreciated.

Preparation and characterization of multiwalled carbon nanotube-supported platinum and ruthenium for methanol electrooxidation

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Multi-walled carbon nanotube-supported PtRu (PtRu/MWCNTs) catalysts were prepared by colloid method. The PtRu/XC-72 were prepared by the same method too. We compared the structures and the properties between PtRu/XC-72 and PtRu/MWCNTs catalysts. By measurements of transmission electron microscope(TEM) and X-ray photoelectron spectroscopy (XPS) on MWCNTs oxided in mixed acid, we find that most MWCNTs are isolated, nearly there is not carbon nanoparticle agglomeration and the ultrasonic makes MWCNTs orter and the port of tube are opened abundantly. At same time a high density of oxygen containing species are produced on the surface of carbon nanotubes, for example carboxyl, hydroxy and carbonyl. TEM images of catalysts show that the spherical PtRu metal particles on the PtRu/MWCNTs catalysts have a high and homogeneous dispersion and the particles are distributed in a narrow range of 3-6nm which is consistent with the value of 4.2nm obtained from the X-ray diffraction(XRD) calculation. XPS tests were used to characterize electronic properties and chemical state of catalysts. The results indicate that most of Pt and Ru exhibits oxidized phase of PtO and $RuO(OH)_2$, respectively. We find that there is interaction between PtRu and MWCNTs in PtRu/MWCNTs catalysts, and because of this interaction, the outer-shell electrons of Pt transfer to MWCNTs. XRD of catalysts show that every diffraction peaks in the power XRD patterns of PtRu/XC-72 and PtRu/MWCNTs catalysts is boardening to some extent. The phenomenon shows the presence of a significant mass-fraction of much larger crystallites, i.e.PtRu has high dispersion on those both carriers. Meanwhile we find each diffraction peaks of PtRu/MWCNTs catalysts are moved to higher value of 2θ and the parameters of crystal lattice get smaller. This phenomenon shows that Ru and Pt form alloy by a part of Ru entering the crystal structuren of Pt The electron effect of Pt produced by Ru can weaken the absorption of the middle intermedia products produced by methonal oxidation on Pt. During the oxidation of methonal, the remainder Ru existed in oxid provides enough oxygen to neighbour Pt which is available to the desorption and oxidation of the intermedia products. By a series of electrochemistry tests, the PtRu/MWCNTs catalysts display significantly higher performance than the PtRu/XC-72 catalysts for mathnol electrooxidation. The better catalytic performance of the MWCNT-supported catalysts is attributed to the high dispersion of PtRu on the MWCNTs as well as the existence of the PtRu alloy and Ru oxidation in PtRu/MWCNTs, i.e. on the effect of PtRu/MWCNTs catalysts, during the oxidation process of methonal two mechanisms foregoing stated exist at same time. According to the foregoing results of experience, we give the figures of the oxidation process of MWCNTs and the synthesis of PtRu/MWCNTs.

S1·P-78

Structural and electrooxidation performance of Pd/CeO_2-γ-Al_2O_3 catalysts

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CeO_2 possesses the fluorite structure, which consists of a cubic close packed array of Ce cations with all tetrahedral holes occupied by oxygen. Three-way catalysts (TWC) compositions usually include up to CeO_2 in the component, it is also associated with thermal stabilization of the alumina support, and dispersion of the active noble metal phase. The Pd/CeO_2-Al_2O_3 nanocomposites were prepared by double impregnation method. Studied the influence of the amount of Ce for the structure and performance of catalysts by the test of XRD analysis, BET and XPS.XRD of catalysts show that along with the content of CeO_2 increasing, the diffraction peak of CeO_2 increase obviously. The diffraction peak of`γ-Al_2O_3 become weaken, especially the (111) crystal face of γ-Al_2O_3. CeO_2 was added largely changed the structure of crystal face of γ-Al_2O_3. The diffraction lines are broad and the crystallite sizes calculated by using the Debye–Scherrer method are in the range of 9–25 nm. Diffraction lines due to Pd metal or any palladium oxides have not been seen. And when the percentage of Ce is 24%, catalysts has the smallest average crystal diameter it shows ceria dispersing on the carrier of `γ-Al_2O_3 is good, making for Pd disperse on the suface equality. Having tested the ratio surface area and average aperture cubage for the carrier with different of the amount of Ce by BET. And when the percentage of Ce is 24%, the ratio surface area and average aperture cubage of catalysts is the most of all. The result accord with the result of XRD. And XPS of $Pd_{3d2/5}$ shows most of Pd is metal state. Concerning Ce 3d, the strong peaks at 886.4eV(ν’) and 904.1eV u’ are typical for Ce^{3+}, while the main features of Ce^{4+} are at 883.5eV(ν), 889.2eV(ν”), 899.2eV(ν’”), 901.6eV(u), 908.4eV(u’’) and 917.4eV(u’”). And the Ce^{3+} showed a part of Ce^{4+} were deoxidized, in other word,Ce was existed on multivalence state in catalysts. And the XPS curve of O_{1s} describe that the 529.2 eV peak may belong to CeO_2 and the 531.5 eV peak refers to Ce_2O_3. It shows that the most part of Ce are existed on oxide state. Through the electrochemistry testing in H_2SO_4 electrolyte , It shows that when the percentage of Ce is 24%, the electrocatalyse action of Pd/CeO_2-γ-Al_2O_3 is best of all. And the preferable electrocatalyse action owe to the CeO_2 have the upper decentralization on γ-Al_2O_3 ,and the abundant oxygen in Ceria help to oxidation the adsorption hydrogen Pd.

The synthezise and polymerization of carbazole and methyl ethyl ketone formaldehyde resin comonomer

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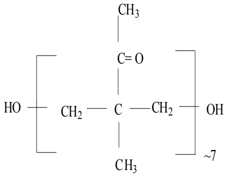
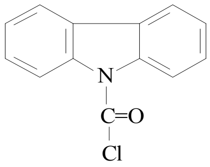
Among the various conducting polymers polycarbazole exhibits interesting electroactive characteristics [1]. Researches have continued for important properties of carbazole polymers by means of chemical modification or copolymerization [2]. Chemical copolymerization of pyrrole and electrochemical polymerization of carbazole in the presence of methyl ethyl ketone formaldehyde resin (MEKF-R) were reported [3,4]. In this study, carbazole (Cz)/ (MEKF-R) comonomer will be synthesized and oxidative polymerization with ceric ammonium nitrate (CAN) will be investigated. The characterization of products will be compared with homopolymer of carbazole and copolymer of Cz/MEKF-R. The concentration of Cerium (IV), MEKF-R and comonomer on polymerization will be investigated. Characterization of products will be realized with UV-visible, NMR, FT-IR and floresans spectrofotometric measurements, DSC, elementel and SEM analyses and 4.probe solid conductivity, cyclic voltammogram, impedance, photoconductivity and viscosity measurements.

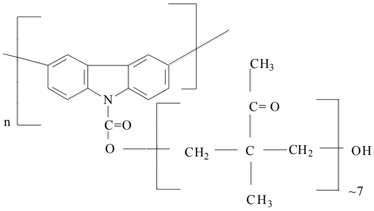


MEKF-R (Metil-Etil-Keton-Formaldehit Reçinesi)



Cz-9-Carbonyl Chloride

Cz-9-Carbonyl Chloride + MEKF-R _ Cz / MEKF-R (comonomer) $\overset{e^-}{\_}$ Poly Cz/ MEKF-R



Preparation and performance of 5 V $LiNi_{0.5}Mn_{1.5}O_4$ cathode materials by ultrasonic-assisted solution method

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In recent years, $LiNi_{0.5}Mn_{1.5}O_4$ material has received much attention for its high redox potential at around 4.7 V and shows good performance. In this paper, we synthesized single phase $LiNi_{0.5}Mn_{1.5}O_4$ material by ultrasonic-assisted solution method which has superior capacity retention upon cycling.

$LiNi_{0.5}Mn_{1.5}O_4$ powders were synthesized by reacting a stoichiometric mixture of $LiNO_3$, $Ni(NO_3)_2\cdot 6H_2O$ and $Mn(NO_3)_2$ (50% solution). The above chemicals were mixed at a predetermined molar ratio, and then in distilled water. The pH of the mixed solution was maintained 8.0. After constantly shocked at 80 ºC for 5 h in a homemade mini ultrasonic cleaner (50W, 28 kHz) to remove excess ammonia and water. The metal precipitate so formed was dried in vacuum drying oven for 12 h at 110 ºC. Then the precursors were heat treated at 850 ºC for 24 h at ambient condition, and then air-cooled to the room temperature, yielding dark powders. The complete coin cell compromises a cathode, a celgard 2300 as the separator and lithium foil anode. 1M $LiPF_6$ dissolved in a mixture of EC and DMC (1:1 by volume) was used as the electrolyte.

Discharge profiles of the firste cycle were obtained from different coin cells with $LiNi_{0.5}Mn_{1.5}O_4$ cathode as shown in Fig. 1. Both curves were obtained at about C/3 discharge and charge rate.

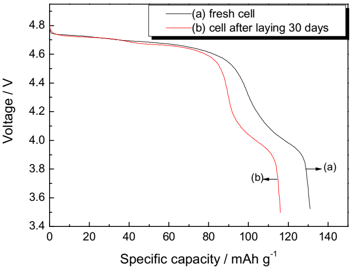

Fig.1 Discharge curve of different $LiNi_{0.5}Mn_{1.5}O_4$ cells

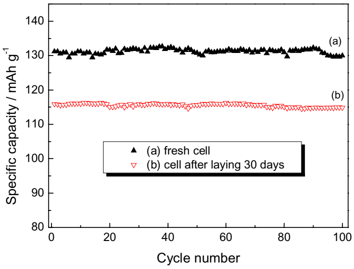

Fig.2 Cycle ability curve of different $LiNi_{0.5}Mn_{1.5}O_4$ cells

All discharge curves have two potential plateaus at 4.0 V and 4.7 V. A bonding energy of electron in e_g level of Mn and Ni ions are estimated to be 1.5-1.6 eV and 2.1 eV, respectively, with respect to that in t_{2g} level of Mn^{3+} ion. This leads to a higher discharge potential. The initial discharge capacity of fresh $LiNi_{0.5}Mn_{1.5}O_4$ cell is 131.2 mAh g^{-1}, and the cell laying 30 days also reaches 116.0 mAh g^{-1}. Fig. 2 exhibits capacity retention of the two kinds of cell. The capacity retention of the fresh and layed $LiNi_{0.5}Mn_{1.5}O_4$ cells exceed 99% after 100 cycles. Both cells have superior capacity retention upon cycling. All of above-mention indicates that ultrasonic-assisted solution method is a good method to prepare high performance $LiNi_{0.5}Mn_{1.5}O_4$ material.

The effect of different sintered temperatures on elecrochemical behavior of spinel $LiMn_2O_4$

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Lithium manganese oxide spinel $LiMn_2O_4$ is an interesting and promising cathode material for rechargeable lithium batteries. In this study, $LiMn_2O_4$ was synthesized by adipic acid-assisted sol-gel method. The main interest of this paper is to investigate the effects of different sintered temperatures on elecrochemical behavior of spinel $LiMn_2O_4$.

Manganese acetate and lithium acetate were dissolved in distilled water to give a saturated solution. A saturated aqueous solution of adipic acid was then added at 1:1 molar ratios with the total metal ions. The pH of the mixed solution was maintained 6.0, and then heated at 80°C to remove excess water. The metal adipate precipitate so formed was dried in vacuum drying oven for 12 h at 110°C. After drying, the precursors were calcined at 350°C ~900°C for 15 h in air.

The cycle ability curves for $LiMn_2O_4$ sintered at different temperatures for 15 h are presented in Fig.1.

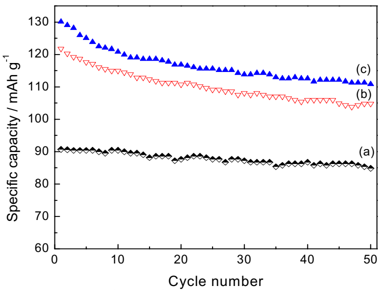

Fig.1 Cycle ability curves for $LiMn_2O_4$ calcined at different temperature in 50 cycles (a) 350°C, (b) 700°C and (c) 800°C

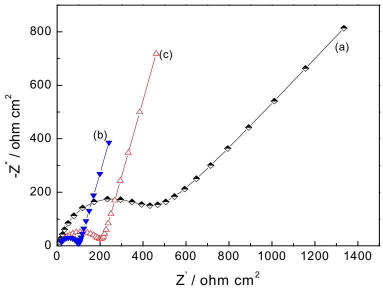

Fig. 2 Niquist plots for the $LiMn_2O_4$ samples calcined at (a) 350℃, (b) 800℃, (c) 900℃ at 100% discharge state after 20 cycles

The result show that $LiMn_2O_4$ powders calcined at higher temperatures has high discharge capacity and capacity loss, and $LiMn_2O_4$ powders calcined at lower temperatures has low discharge capacity and high capacity retention. EIS result of $LiMn_2O_4$ samples after 20 cycles with diffirent calcined temperatures at 100% discharge state (discharged to 3.3 V) is given in Fig.2. $LiMn_2O_4$ powders calcined 800 °C has the smallest R_t (electrochemical reaction impedance), which indicates that this samples have better discharge capacity; however, $LiMn_2O_4$ powders calcined 350 °C and 900 °C has the bigger R_t, which leads that these samples have small discharge capacity. It may be that $LiMn_2O_4$ powders calcined too high or low temperatures exit much lattice defect, which leads to the lattice distortion during the cycles.

Electrochemical Characteristics of $Ti_{0.32}Cr_{0.43}V_{0.25}$ Alloy Ball-milled with LM $Ni_{4.1}Al_{0.25}Mn_{0.3}Co_{0.65}$ Alloy as a New Anode Material for Ni-MH Secondary Battery

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In recent days, oil price maintains at a high level. The high price of oil makes the cost-effective hybrid electric vehicle (HEV), which contains an electrically charged battery pack coupled with an internal combustion engine, more attractive. Consequently, Ni-MH battery for HEV is now in great demand.

The Ti-Cr-V alloy with bcc crystal structure has been considered as a promising new anode material for Ni-MH battery on account of its excellent hydrogen storage capacity over 2 wt% and proper plateau pressure for hydrogen. The alloy, however, is hardly activated during charging due to the formation of stable oxide layer on the alloy. Therefore, the measured discharge capacity of the alloy is much smaller than the theoretical value.

To improve the surface activation of bcc-type Ti-Cr-V alloy, the alloy powder was mixed with AB_5 type alloy powder, which can be activated more easily and thus can possibly provide paths for hydrogen diffusion on the electrode surface. The mixture of the bcc-type $Ti_{0.32}Cr_{0.43}V_{0.25}$ alloy powder and the AB_5 type $LmNi_{4.1}Al_{0.25}Mn_{0.3}Co_{0.65}$ alloy powder was ball-milled by varying the ball-milling time and the proportion of $LmNi_{4.1}Al_{0.25}Mn_{0.3}Co_{0.65}$ alloy.

The discharge capacity of the electrode of $Ti_{0.32}Cr_{0.43}V_{0.25}$ alloy ball-milled with the $LmNi_{4.1}Al_{0.25}Mn_{0.3}Co_{0.65}$ alloy was significantly improved compared with the electrode of $Ti_{0.32}Cr_{0.43}V_{0.25}$ alloy without $LmNi_{4.1}Al_{0.25}Mn_{0.3}Co_{0.65}$ alloy. The greatest discharge capacity of 310 mAh g^{-1} was obtained when 20 wt% $LmNi_{4.1}Al_{0.25}Mn_{0.3}Co_{0.65}$ alloy had been added to the $V_{0.25}Ti_{0.32}Cr_{0.43}$ alloy and ball-milled for 20 min.

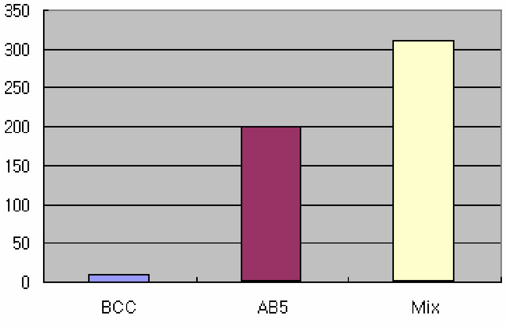

Fig. 1. Discharge capacity of the Ti-Cr-V and the AB5 alloy after ball milling

The Reasonable Fe(III) Compounds for Selective Electro-generation of Ferrate

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Ferrate, excellent super-oxidant[1,2], has been focused[3,4] recently for the appearance of super-iron battery [5]. However, complicacy of Fe(VI)/Fe(III) system[1] and OER play obstructive and harmful roles in research and the realization of secondary super-iron battery. The ferrite was made from the main component of the open-hearth dust of Inner Mongolia [6], Fe_2O_3. The electrochemical behavior of different Fe(III) compounds was investigated by the technique of powder microelectrode[7] . The XRD profile of the roasted mixture of NaOH and Fe_2O_3, was presented in **Fig.1**. It proves that the molecular formula of the product is $NaFeO_2$. The electrochemical results indicated that $NaFeO_2$ is the most reasonable Fe(III) compound for selective electro-generation of ferrate and Fe_2O_3 is an inert compound for the same electrochemical reaction from 293K to 333K in 12~14 mol/L NaOH solutions.

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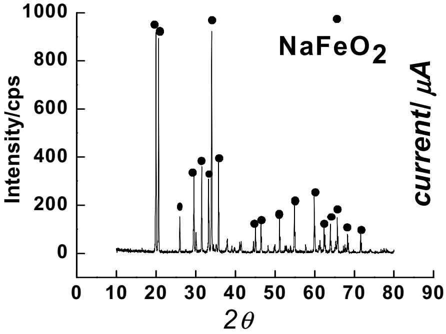

Fig. 1 The XRD results of sodium ferrite

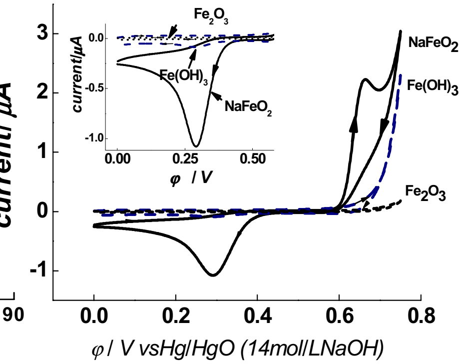

Fig. 2 The cyclic voltammetric curves of three Fe(III) compounds

Reference:

1. V. K. Sharma, *Advances in Environmental Research,* **2002**, (6), 143.
2. L. Delaude, P. Laszlo, *J. Org. Chem.,* **1996**, 61, 6360.
3. M. D. Koninck, D. Bélanger, *Electrochim. Acta.,* **2003**, 48, 1425.
4. C. Z. Zhang, Z. Liu, F. Wu et al. *Electrochem. Comm.,* **2004**, (6), 1104.
5. S. Licht, B. H. Wang and Susanta Ghosh. *Science,* **1999**, 285, 1039.
6. A. J. Xu, S. C. Liu, *J. Inner Mongolia Normal University*, **2003**, 32(3), 388.
7. C. S. Cha, M. C. Li and H. X. Yang et al. *J. Electroanal. Chem.,* **1994**, 368, 47.

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Modified Natural Graphite Anode Materials for Lithium-ion Batteries

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Modified natural graphite is made by surface-coating and graphitizing process. The modified natural graphite is examined with a view to improve discharge capacity and coulombic efficiency on the first charge-discharge cycle. It processes superior cycleability. Modified process results in a marked improvement in electrochemical performance. These are investigated by means of X-ray power diffraction, scan electron microscopy, and measurement of electrochemical capacity. The proportion of rhombohedral crystal structure was reduced by the heat treatment process. The modified natural graphite exhibits 40 mAh/g reduction in the first irreversible capacity while the reversible capacity increased by 16 mAh/g in comparison with pristine graphite electrode. Also, it has an excellent capacity retention of about 94% after 100 cycles and about 87% after 300 cycles .

The natural graphite used in this experiment was SG18 (from BTR Energy Materials Co.). Surface modified graphite(MSG) was prepared as follows: SG18 was first dispersed in a solvent that contains the precursor of nongraphitic carbon and then the solvent was evaporated. Finally, the residue was treated at 3000℃ for 4 hours to 15 days. SEM images indicate that the surface of the modified graphite particles appears smoother than that of the SG18 particles. Some of the micrpores are filled with nongraphitic carbon.

The specific capacities of SG18 and MSG were listed in Tab.1. The modified graphite provides a very high discharge capacity of 358.7mAh/g (i.e. close to the theoretical value of 372 mAh/g based on LiC_6) and a perfect coulombic efficiency of 95.6%, the irreversible capacity is decreased to 16.7mAh/g, the irreversible capacity loss of the modified graphite electrode on the first charge-discharge process is only 4.4%, whereas the pristine graphite electrode suffers a capacity loss of 14.8%. From the first charge/discharge profiles, it is almost invisible for the plateau at about 0.75V, which is ascribed to the irreversible charge. On the other hand, the rhombohedral crystal structure has been eliminated to the maximum extent. All of them result in the improvement of the electrochemical performance of the anode.

Tab. 1 First charge/discharge test results

Sample	Discharge Capacity (mAh/g)	Charge capacity (mAh/g)	Irreversible capacity (mAh/g)	Efficiency (%)
SG18	402.4	342.7	59.7	85.2%
MSG	375.4	358.7	16.7	95.6%

The Effect of Mg Content on the Phase Structure and Electrochemical Properties of the Ml-Mg-Ni-based Hydrogen Storage Alloys

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Due to the demand for novel electrode materials with much higher hydrogen storage capacity is very urgent, the new kind R-Mg-Ni-based AB_3-type alloys with higher hydrogen storage capacity are regarded as one of promising candidates for electrochemical hydrogen storage materials. However, their cycle stability are unsatisfied. The main reason is the oxidation of La and Mg element in alkaline solution, which causes the electrode to lose activity. For improving the cycle stability of R-Mg-Ni-based hydrogen storage alloys, we used Ml instead of pure La element in A-sites and multi-component alloying in B-sites simultaneity to prepare the $Ml_{1-x}Mg_x(Ni\text{-}Co\text{-}Mn\text{-}Al)_{3.5}$ ($x = 0.05, 0.10, 0.20, 0.30$) alloys, and the effects of variable Mg content on the phase structure and electrochemical properties of Ml-Mg-Ni-based hydrogen storage alloys were studied in this paper. The results of XRD reveal that all the alloys consist mainly of $LaNi_3$ phase with the rhombohedral $PuNi_3$-type structure and $LaNi_5$ phase with the hexagonal $CaCu_5$-type structure. With the increasing of x, the intensity of $LaNi_3$ diffraction peaks increases gradually, the maximum capacity and low temperature dischargeability of the alloy electrodes increase first and then decrease. Moreover, when x is 0.20, the discharge capacity of the alloy electrode reaches 363 mA h/g at 293 K and 216 mA h/g at 233 K, respectively. The HRD of the alloy electrodes increases with the increasing of x. At the discharge current density $I_d = 1200$ mA/g, the HRD of the alloy electrodes increases from 16.2% to 43.3% with x from 0.05 to 0.30. The cycle stability of the alloy electrodes decreases gradually with the increase of Mg content.

Investigation on the Performance of Nano-scale β-$Ni(OH)_2$ Prepared at Different Transformation pH

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Nano-scale $Ni(OH)_2$ is a new kind of batteries material. It exhibits many superior electrochemical performance, such as bigger proton diffusion coefficient and higher electrochemical reaction activity, and so on, so much interest has focused on investigation of nano-scale $Ni(OH)_2$. But a majority of researchers have laid their emphasis on the discoveries of new preparation methods, few investigation is against the systematical research on the effects of preparation conditions on the performance of nano-scale $Ni(OH)_2$, especially the electrochemical behaviour.

In this study, we have prepared a series of nano-scale $Ni(OH)_2$ under different transformation pH. The influence of transformation pH on the morphology and performance of nano-scale $Ni(OH)_2$ were investigated.

The measurement results indicate that the prepared nano-scale $Ni(OH)_2$ isβ(II)-phase, and the crystal lattice parameters of nano-scale $Ni(OH)_2$ prepared at different transformation pH is different; Transformation pH exerts a great influence on the agglomeration degree of nano-scale $Ni(OH)_2$. With the increase of transformation pH, the agglomeration of nano-scale $Ni(OH)_2$ becomes obvious. CV and EIS measurement results show that transformation pH affects the proton diffusion coefficient (D) and charge-transfer resistance (Rct) of the material, and the discharge performance of electrodes depends on both D and Rct, so the kinetics characteristics that electrodes reaction is controlled by both mass-transfer step and charge-transfer step was put forward.

[1] M. Meyer, A. Bee, D. Talbot, J. of Colloid and Interface Science, 277 (2004) 309
[2] X. H. Liu, L. Yu, Materials Letters, 58(2004) 1327
[3] P. Jeevanandam, Y. Koltypin, A. Gedanken, Nano Letters, 1 (2001) 263

Room temperature lithium metal batteries based on elctrospun PVDF-based nanofibrous separator

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The Li-ion batteries generally employ polyolefin separators. These commercialized polyolefin separators have good mechanical properties. On the other hand, they exhibit poor compatibility with liquid electrolytes due to their hydrophobic property. It usually gives rise to resistance increases, which is responsible for the shortening of the battery lifetime and severely affect the battery performance, e.g., cycle life [1]. In order to overcome this disadvantage, it is possible to use more wettable polymer with liquid electrolytes. Electrospun PVDF-based membranes (EPMs) have been previously reported as a polymer matrix in lithium ion battery [2, 3].

In this study, we prepared EPMs for battery separators applications and mainly investigatate the characteristics of interface between lithium metal and EPM separator. The Crystal structure and chain conformation of the EPMs also were investigated by differential scanning calorimetry (DSC), and wide-angle X-ray diffraction (WAXD). Due to soften PVDF fibers in high temperature, the thermal treated EPMs can form an interconnected web structure, which greatly improve physical properties. Compared that with Celgard^{TM} 2400 (PP separator), the cell with EPM shows good cycling performance with little capacity loss after 50 cycles.

From Fig.1, the cell with EPM showed the better cycling behaviour than that with PP separator. Structure properties of the EPMs, such as a fully interconnected open pore structure, a great deal of nano-scale fibers, enhanced the degree of PVDF swelling in polymer electrolyte. The gel phase can greatly improve interface affinity to lithium metal. Additionally, uniform pore distribution and low pore tortuosity of EPMs can be factors that suppress mechanically Li dendrites on lithium metal surface. The results of CV imply that EPMs could provide an effective approach to smoothing lithium deposition and improving battery cycle-ability.

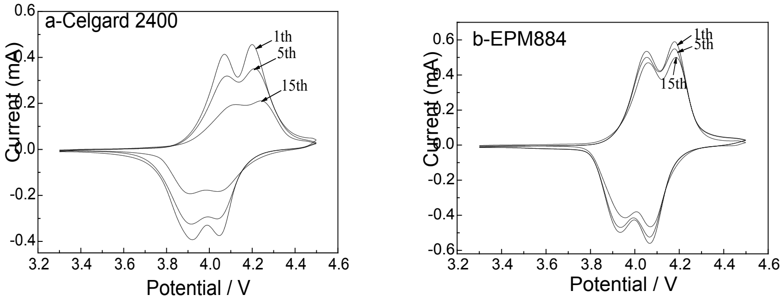

Fig.1 Cyclic voltammorgrams for the cells with (a) Celgard^{TM} 2400 and (b) EPM884 at sweep rate 0.1 mV·s^{-1}.

[1] K.M. Abraham, M. Alamgir, J Electrochem Soc. 142 (1995) 683.
[2] S.W. Choi, S.M. Jo, W.S. Lee, Y.R. Kim, Adv. Mater. 15 (2003) 2027.

Effects of methanol contaminant in electrolyte on the performance of graphite electrodes for Li-ion batteries

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Commercial lithium-ion batteries with high energy density and good cycleability usually consist of a carbon-based negative electrode, a positive lithium metal oxide electrode, and a separator soaked with an organic electrolyte. Despite of the high level of development of the batteries, there are still unsolved problems remaining. One of them is the irreversible charge loss occurring during first charging of the carbon electrodes. It is generally accepted that this charge loss is mainly due to reductive decomposition of electrolyte on negative electrode. The resulting protective film, called solid electrolyte interphase (SEI), allows lithium-ion transfer but prevents electron transfer. The SEI formation mechanism is rather complex and not yet completely understood.

Methanol was a common impurity in the organic electrolyte. In this study, the electrochemical performance of graphite electrode cycled vs. Li in1MLiPF$_6$–EC:DEC:DMC(1:1:1,v/v/v) electrolyte solution, containing different concentrations of methanol, was investigated by cyclic voltammetry and electrochemical impedance spectroscopy in the process of first lithiation. It has been demonstrated that methanol contaminant caused the deterioration of the electrochemical performance of graphite electrodes, and this effect is depends markedly on the concentration of methanol. Based on experimental results and analysis, a mechanism of methanol contaminant causing the deterioration of the electrochemical performance of graphite electrodes was proposed, in which methanol was reduced to lithium methoxide, deposited on the graphite electrode surface to form initial SEI at the potential near 2.0V(as shown in Fig.1). Such process resulted in ethylene carbonate excess decomposition and poor passive ability of SEI ultimately formed on the graphite electrode surface.

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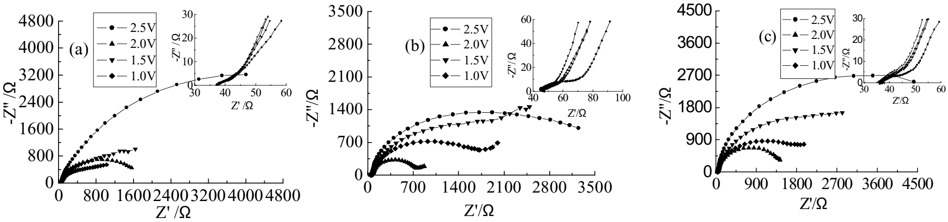

Fig.1 Nyquist plots of graphite electrodes at 2.5, 2.0, 1.5 and 1.0 V in 1MLiPF$_6$-EC:DEC:DMC (1:1:1,v/v/v) electrolyte solutions. Frequency range10^5~10^{-2}Hz, concentrations of methanol: (a)0%, (b) 0.5% ,(c) 0.1%(v/v). The insets show the spectra enlarged over a 10^5Hz–10^2Hz frequency range.

Electrochemical studies of the Si-C composites as anode materials for rechargeable lithium ion batteries

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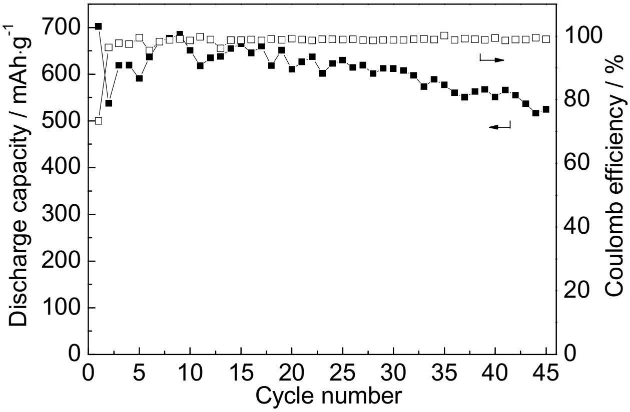
Silicon/carbon composites have so far been investigated extensively as anode materials for rechargeable lithium ion batteries because of their high specific capacity[1,2]. We succeeded to attain a Si/C composite with a high capacity and good cycle performance by pyrolysis of phenol-formaldehyde resin embedded with graphite and silicon powders.

In this study, the preparation of the Si/C composite was as follows: The phenol-formaldehyde resin (PFR) was dissolved into ethyl acetate. Silicon particles and graphite were added into the PFR solution and homogeneously mixed and the weight ratio of silicon: PFR: graphite was 5:12:5. The ethyl acetate solvent was evaporated under stirring to get a solid blend. The mixture was heated at 900 °C in an Ar atmosphere for 2 h at a heating rate of 10 °C min^{-1} and allowed cool down to room temperature normally. The products before sieved were further treated by high-energy mechanical milling in a sealed bowl in Ar at a rotational speed of 200 rpm for 2–10 h.

A coated electrode was prepared by mixing the composite material with PVdF binder, coated on a Cu sheet, and dried at 120 °C for 14 h under Ar. Fig.1 shows the good cycle performance and reversible capacity of this material. The initial discharge capacity of the composite was 702 mAh·g^{-1}, the reversible capacity after 45 cycles being 525 mAh·g^{-1}.



References

[1] Wen Z S, Yang J, Wang B F, et al. Electrochemistry Communications, 2003, 5: 165-168.

[2] K. Hanai, Y. Liu, N. Imanishi, et al. Journal of Power Sources 146 (2005) 156–160

Capacitance of the double-layer formed at the solid electrode – ionic liquid interface

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Ionic liquids (IL) have been investigated intensively due to their specific properties which makes them a good material as a electrolyte especially in Electric Double Layer Capacitors (EDLC) applications where wide electrochemical stability window is needed. Energy in EDLC's is stored in the double layer formed at electrode/electrolyte interfaces. Energy, E stored in EDLC strongly depends on applied potential, V therefore, it depends on electrochemical stability of electrolytes $E = QV^2/2$

Both aqueous and various non-aqueous liquid electrolytes as well as solid polymer electrolytes have been applied in EDLC, including ionic liquid [1]. There are only a few publications about double layer capacity measured at well defined electrode/electrolyte surface [2, 3].

The main aim of this work was to examine the differential capacity at the solid electrode|ionic liquid interface for a number of ionic liquids.

Differential double layer capacity at the electrode/ionic liquid interface (electrode: glassy carbon (GC), Pt, Au), was measured using chronoamperometry and *ac* impedance technique. Measurements were done in a two electrode system and made for 18 ionic liquid.

Dependencies of double layer on the potential were determined using *ac* impedance in a three electrode system with Ag/Ag+ electrode in dimethyl sulfoxide solution as a reference electrode.

The double layer capacity (by chronoamperometric method) at the GC/IL interface, was at the level of ca. 10-25 μF/cm^2 at potentials close to the open circuit potential, while the corresponding values for the Pt/IL and Au/IL systems were significantly lower, typically at the level of 1-8 μF/cm^2.

Evaluating double layer capacitance C_{dl} from impedance plots two equivalent circuits were taken into account. Constant phase element (CPE) exponent were usually in range 0,77 - 0,82 and shows that it is not pure capacitor-like behavior. Values determined by *ac* impedance technique are of 4-5 times higher than obtained by chronoamperometric method.

The capacity value was approximately constant within a broad potential range (of ca 3V).

References

1 Hiroyuki Ohno (Ed.), Electrochemical Aspects of Ionic Liquids, Wiley-VCH, Weinheim, 2005)
2 R. J. Gale, R. A. Osteryoung, Electrochim. Acta, 25 (1980) 1527
3 C. Nanyundiah, S.F. McDevitt, V.R Koch, J.Electrochem. Soc., 144 (1997) 3392

Discharge Characteristics of Polypyrrole/Silver Vanadium Oxide Composite Used for Lithium Primary Batteries

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Silver vanadium oxide (SVO), $Ag_2V_4O_{11}$, shows high gravimetric/volumetric energy densities. It also provides an electrode potential curve with multiple plateaus, which allows accurately to predict the lifetime of the battery. Therefore, SVO has generated commercial interest in the arena of medical devices, and has become the cathode of choice in lithium primary batteries used to power implantable cardioverter defibrillators (ICDs).

In an ICD, a Li/SVO cell performs most of the time at low power and occasionally delivers one or more high power pulses. It should be capable of delivering about 50 J within 5 to 10 s and in case of a continuous current drain on the order of microamperes for at least 5 years [1]. However, low utilization of SVO is typically attained, especially during pulse discharges with high rates. The internal cell resistance drastically increases with progressing discharge, resulting in a poor power capability of a Li/SVO cell.

In this work, a hybrid composite of polypyrrole (PPy)/SVO was synthesized by an oxidative polymerization of pyrrole monomer on the SVO surface in an acidic medium. Galvanostatic discharge experiments indicated that the composite electrode exhibits higher discharge capacity and better rate capability as compared with the pristine SVO electrode. The utilization study suggested that the improvement in electrochemical performance of the composite electrode is due to PPy which accommodates lithium ions and also enhances the SVO utilization.

In order to demonstrate the feasibility of the PPy/SVO composite system in an ICD, the pulse discharge characteristics were investigated at 38 ^{o}C under conditions that simulate battery operation inside an ICD [2]. The kinetic parameters which govern pulse discharge performance of the composite electrode (e.g. interfacial charge transfer resistance and chemical diffusion coefficient of lithium) were estimated as a function of depth of discharge, and compared with those parameters obtained for the pristine SVO electrode.

References
[1] K.J. Takeuchi, A.C. Marschilok, S.M. Davis, R.A. Leising, E.S. Takeuchi, Coordin. Chem. Rev., 219-221 (2001) 283.
[2] R.P. Ramasamy, C. Feger, T. Strange, B.N. Popov, J. Appl. Electrochem., 36 (2005) 487.

SYNTHESIS AND ELECTROCHEMICAL POLYMERIZA 4-[2-THIOPHENYL]INDOLE

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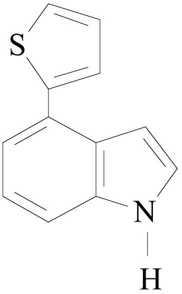
The copolymerization of heteroaraomatics was of interest since the beginning o electrochemical polymerization leading to conducting polymers. The main advantages of co gradually changeable physical properties. In particular, functionalisation of the thiophene r substituents changes dramatically both physical and chemical properties of the resulting polym have appeared on chemical synthesis of new monomers and on chemical and electrochemi characterization of the relevant polymers, often dealing necessarily with peculiar aspects of [1,2]

In this study we report the synthesis of 4-[2-thienyl]indole (4,2 THIN) by Stille (Sheme 1) and the product was characterized by common techniques such as NMR, F spectrophotometry and elemental analysis. Electropolymerization of (4,2 THIN) wer potantiodynamically and potantiostatically. Results were compared with the homopolymers and indole (IN). Evaluation of electroactivity of polymeric films by different techniques, impedance spectroscopy, and charge/discharge characteristics was also discussed.



Sheme 1. 4-[2-thienyl]indole (4,2 THIN)

References

[1] G. Zotti, G. Schiavon, Synth.Met. 31 (1989) 347.
[2] C. Visy, J. Kankare, J. Electroanal. Chem. 442 (1998)