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J. Description/Abstract

During this program we have synthesized and characterized several novel cathode and anode materials for application in Li-ion batteries. Novel synthesis routes like chemical doping, electroless deposition and sol-gel method have been used and techniques like impedance, cyclic voltammetry and charge-discharge cycling have been used to characterize these materials. Mathematical models have also been developed to fit the experimental result, thus helping in understanding the mechanisms of these materials.

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SYNTHESIS, CHARACTERIZATION AND TESTING OF NOVEL
ANODE AND CATHODE MATERIALS FOR LI-ION BATTERIES**

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EXECUTIVE SUMMARY

During this program we have synthesized and structurally and electrochemically characterized a wide range of chromium based materials ($m\text{CrO}_{2.85}$, $\text{Co}_{0.2}\text{CrO}_{2.85}$ and $\text{V}_{0.1}\text{CrO}_{2.85}$). These materials are stable intercalation hosts for lithium and exhibit higher capacity than any prominent positive electrodes in secondary lithium batteries. They were found to be reversible in the entire intercalation range (2.0–4.2 V vs. Li/Li^+). Estimated energy density of these materials for the first 90 cycles was approximately 750 Wh/kg (capacity of 270 mAh/g with an average voltage of 3.1 V). A small amount of Co or V added as dopants in “in house” synthesized $m\text{CrO}_x$ provided greater stability for the host and helped in improving the high rate behavior of these oxides.

Chromium oxides and lithiated chromium oxides^a were synthesized by thermal decomposition of chromium trioxide (CrO_3) at high temperature and oxygen pressure. Synthesis temperature and pressure markedly affect the performance of these cathode materials. It was found that high pressure leads to a higher O/Cr ratio and fewer impurities in the final product. These materials are stable intercalation hosts for lithium, and exhibit a higher capacity than any of the prominent positive electrodes used in the secondary lithium batteries. Chemically modified $m\text{CrO}_x$ has a capacity of 255 mA/g, while $m\text{LiCrO}_x$ has a capacity of 210 mAh/g. the average voltage of these cells is 3.0 V vs. Li/Li^+ that gives an average energy density of approximately 650 Wh/Kg. These compounds have different properties than CrO_3 . They are neither hygroscopic nor soluble in water thus are not biohazards. The electrode prepared from $m\text{CrO}_x$ exhibited negligible capacity fade when cycled between 2.0 and 4.2V at a current density of 0.1 mA/cm². This material can be used as a positive electrode with lithium or lithiated carbon as a negative electrode in secondary lithium cells. Charge and discharge studies indicated that $m\text{CrO}_x$ is stable and reversible over the entire intercalation range with an initial capacity of 210 mAh/g. This material can be used as a positive electrode with a carbon negative electrode in the Li-ion cell.

Cobalt doped chromium oxides^b $\text{Co}_{0.2}\text{CrO}_x$ synthesized using procedure developed in our laboratory exhibited an initial capacity of 290 mAh/g with an average discharge voltage of 3.0 V. The lithiated $\text{Co}_{0.2}\text{CrO}_x$ was found to be reversible in the entire intercalation range (2.0–4.2 V). A small amount of Co as dopant in the chromium oxides provided greater stability to the structure of CrO_x and helped in improving the high rate behavior of these oxides. The capacities estimated for $\text{Co}_{0.2}\text{CrO}$ at 0.65 C discharge rate were 85% compared with 55% of the total capacity estimated for CrO_x . Lithiated and non-lithiated Co doped CrO_x can be used as positive electrodes on secondary lithium batteries with carbon and lithiated carbon as negative electrodes, respectively.

$\text{V}_{0.1}\text{CrO}_x$ was synthesized in our laboratory by thermal decomposition of chromium trioxide (CrO_3) in presence of NH_4VO_3 at high temperature and oxygen pressure and under atmospheric conditions^c. We found that this material is a stable intercalation host for lithium, and exhibits a higher capacity than any of the prominent positive electrodes used in secondary lithium batteries. Partial substitution of Cr in $m\text{CrO}_x$ with V ($\text{V}/\text{Cr}=0.2$ in molar ratio) stabilizes

^a P. Arora, D. Zhang, B. N. Popov, R. E. White, *Electrochem. Sol. State Let.*, **1**(6), 249 (1998).

^b D. Zhang, B. N. Popov, Y. M. Podrazhansky, P. Arora, R. E. White, *J. Power Sources*, **83**, 121 (1999).

^c D. Zhang, B. N. Popov and R. E. White, Abstract No 52, The Electrochemical Society Meeting, Extended Abstracts, Vol. 98-1, San Diego, CA, May (1998).

its structure, and makes possible to prepare $V_{0.1}CrO_x$ under low oxygen pressure and atmospheric conditions. The V doped CrO_x has good rate capability and cyclability. This compound delivers a discharge capacity of 160 mAh/g even at 1.5 C, and maintains a reversible capacity of 220 mAh/g over 100 cycles.

Besides chromium oxides, in view of its economic and environmental advantages, spinel has demonstrated to be the most promising positive electrode material for lithium-ion batteries. However, the final issue regarding the acceptance of the spinel commercially is its performance (storage life and cycle life) at elevated temperatures. Spinel electrodes suffer from irreversible capacity loss during cycling and in storage at temperatures higher than 50°C. It was shown in our studies that spinel doped with chemically modified $mCrO_x$, $LiCr_{0.1}Mn_{1.9}O_4$ completely stabilized the structure at room temperature. The results obtained in our laboratory showed that after 30 cycles, $Li_4Cr_yMn_{5-y}O_{12}$ delivers a capacity of 170 mAh/g with cutoff voltage 2.2-3.6 V at discharge rate of 0.5 C.

Quaternary spinels doped with chemically modified chromium oxides^d ($mCrO_{2.65}$) $LiCr_yMn_{2-y}O_4$ with $y=0.02, 0.05$ and 0.1 were prepared in our laboratory with completely stabilized spinel structure. Cyclic voltammograms of pure spinel exhibit high irreversibility compared with that obtained initially. The observed decrease of the volume shrinkage of $Li_{0.3}Cr_{0.1}Mn_{1.9}O_4$ contributes to the stability of the spinel structure. $LiCr_{0.1}Mn_{1.9}O_4$ increases the exchange current density and facilitates the charge transfer reaction of the active material. The spinel doped with chemically modified chrome oxide $mCrO_x$ causes the peak separation to decrease contributing to the electrochemical reversibility of the doped cathode materials. Negligible shift of the peak potentials was observed for these cathodes. Chromium dopant enhances the mass transfer of Li^+ in the active material. The Li^+ diffusion coefficient in $LiCr_{0.1}Mn_{1.9}O_4$ estimated from an analysis of the Warburg impedance is two orders of magnitude higher than in pure spinel. The $mCrO_x$ precursor in $LiCr_{0.1}Mn_{1.9}O_4$ forms a passive film, which has lower resistance than the film, formed on pure spinel. Potentiostatic experiments carried out to determine the cumulative capacity loss of pure spinel, and $mCrO_{2.65}$ doped spinel showed the lowest capacity loss.

We synthesized a wide range ($y=0.05-0.33$) of Co doped $LiCo_yMn_{2-y}O_4$ spinel that showed improved capacity and retention over pure spinel^e. Electrochemical impedance spectroscopy and the linear polarization resistance technique were used to determine the transport and electrochemical kinetic parameters of Co doped spinel. The presence of Co in spinel increases the exchange current density and facilitates the charge transfer reaction of the active material. The lower self-discharge observed for Co-doped spinel was attributed to their low surface areas. The cumulative capacity loss estimated for pure spinel resulting from self discharge was 3 to 6 times larger than those estimated for Co-doped spinels with $y=0.05$ and $y=0.16$ in $LiCo_yMn_{2-y}O_4$, respectively.

A mathematical model is presented for the lithium intercalation of a single spinel particle as a microelectrode under the stimulus of a cyclic linear potential sweep^f. The model includes both lithium diffusion within the particle and kinetics at the particle/electrolyte interface. The model is used to predict that peak current densities depend linearly on the scan rate to a certain power with a constant term, which is different from the predicted peak current density for a conventional redox system.

^d D. Zhang, B. N. Popov, R. E. White, *J. Power Sources*, **76**, 81 (1998)

^e P. Arora, B. N. Popov, R. E. White, *J. Electrochem. Soc.*, **145**, 807 (1998)

^f D. Zhang, B. N. Popov, R. E. White, *J. Electrochem. Soc.*, **147**, 831 (2000)

We developed a complex impedance model for spherical particles, which was used to determine the lithium diffusion coefficient in graphite as a function of the state of charge (SOC) and temperature^g. In this study, the conventional electrochemical methods, i.e., the PITT and Warburg impedance approaches were evaluated and the results were compared with our modified EIS method. The Li^+ diffusion coefficients estimated using the PITT and Warburg impedance methods were two orders of magnitude lower than those obtained using the modified EIS approach and the dependence on the SOC was much less in the later technique. The observed differences in the Li^+ diffusion coefficients resulted from uncertainties in the estimation of the parameters that were required in the PITT and Warburg impedance approaches such as (dE_{oc}/dx) , C^o and C_R , V_m , and A . In contrast only ω and R are required in the modified EIS method, which gives rise to less uncertainty compared to the PITT and conventional Warburg impedance approaches.

We carried out extensive studies with an objective to develop superior graphite (carbon) anodes for Li ion cells by a surface modification treatment based on electroless plating of ultra-thin films of Ni, Co Sn, and SnOx. These films contained microscopic pores and defects that allow Li^+ to intercalate into the underlying carbon, but prevent solvent from accessing the carbon surface. Sn and SnOx systems were of particular interest because tin can alloy with Li, thus providing another way for intercalation while protecting the underlying carbon from solvent. The one-step electroless deposition of SnOx developed in our laboratory on carbon shows an enormous promise for application in Li-ion batteries.

The specific objective was to eliminate the initial irreversible capacity loss of graphite to increase the lithium charge transfer rate and to enhance the lithium diffusion in the anode. Also, we expected the film to act as a barrier film for protecting the surface from reduction and to increase the electrical and thermal conductivity. Synthetic graphite (KS-10) was chemically modified with Ni^h and Pd^i , which resulted in substantial improvements in discharge capacity, cyclability and almost a complete suppression of the initial irreversible capacity loss. Coating KS-10 with an alloy of Ni-P alloy (procedure developed in our laboratory) resulted in a dramatic decrease of the initial discharge capacity from 740 to 350 mAh/g. The charge discharge efficiency increased from 38.8% to 91% when coated with a thin layer of Ni-P alloy. The XRD studies indicated that lithium ion forms a thin layer of LiP on the carbon surface, which is a main constituent of the SEI. The cyclic voltammograms and the galvanostatic charge discharge curves indicated that the Ni-P layer and LiP suppress completely the co-intercalation of solvated lithium ions and the reduction of the solvent thus improving the first charge-discharge reversibility. We used modified EIS technique to study the properties of SEI formed on bare carbon and Ni encapsulated graphite^j. The results indicated that a remarkable enhancement of the Li intercalation and de-intercalation has been obtained on carbons encapsulated graphite with Ni. Also, a simple theoretical model has been used to simulate the galvanostatic discharge behavior of the Ni-composite graphite electrode^k. The discharge profiles predicted by using a constant diffusion co-efficient (CDC) and by a varied diffusion co-efficient (VDC) have been compared. Exchange current and diffusion co-efficient for the lithium diffusion have been predicted using this model.

^g P. Yu, B. N. Popov, J. A. Ritter, R. E. White, *J. Electrochem. Soc.*, **146**, 8 (1999)

^h P. Yu, J. A. Ritter, B. N. Popov, R. E. White, *J. Electrochem. Soc.*, **147**, 1280 (2000)

ⁱ P. Yu, J. A. Ritter, B. N. Popov, R. E. White, *J. Power Sources*, **91**, 107 (2000)

^j P. Yu, J. A. Ritter, B. N. Popov, R. E. White, *J. Electrochem. Soc.*, **147**, 2081 (2000)

^k V. R. Subramanian, P. Yu, B. N. Popov, R. E. White, *J. Power Sources*, **96**, 396 (2001)

Further, we found that it was advantageous to combine the tin oxide system with carbon in order to produce electrodes with superior characteristics. Sn and SnO are of particular interest because tin can alloy with Li, thus providing another way of intercalation while protecting the underlying carbon from the electrolyte. Tin-graphite composites have been developed as an alternate anode material for Li-ion batteries using an autocatalytic deposition technique¹. The specific discharge capacity, coulombic efficiency, rate capability behavior and cycle life of Sn-C composites has been studied using a variety of electrochemical methods. The amount of tin loading and the heating temperature have a significant effect on the composite performance. The synthesis conditions and Sn loading on graphite have been optimized to obtain the maximum reversible capacity for the composite electrode. Apart from higher capacity, Sn-graphite composite possesses higher coulombic efficiency, better rate capability and longer cycle life than the bare SFG10 graphite. Also, pyrrole was polymerized onto the Sn-C composite to decrease the irreversible capacity associated with such composites^m. The decrease in the irreversible capacity loss is due to the reduction in the thickness of the SEI layer formed.

The capacity fade of Li-ion cells has been analyzed using cyclic voltammetry, impedance spectroscopy and electron probe microscopic analysis EPMAⁿ. The surface resistance at both the positive LiCoO₂ and negative carbon electrodes were found to increase with cycling. This increase in resistance contributes to decreased capacity. Impedance data reveal that the interfacial resistance at LiCoO₂ electrode is larger than that at the carbon electrode. The impedance of the positive electrode LiCoO₂ dominates the total cell resistance initially and also after 800 charge-discharge cycles. EPMA analysis on carbon electrodes taken from the fresh and cycled cell show the presence of oxidation products in the case of cycled cells. No change in the electrolyte resistance is seen with cycling.

¹ B. Veeraraghavan, A. Durairajan, B. Haran, B. Popov, R. Guidotti, *J. Electrochem. Soc.*, **149**, A675 (2002).

^m B. Veeraraghavan, J. Paul, B. Haran, B. Popov, *J. Power Sources*, **109**, 377 (2002).

ⁿ D. Zhang, B. S. Haran, A. Durairajan, R. E. White, Y. Podrazhansky, B. N. Popov, *J. Power Sources*, **91**, 122 (2000).

RESULTS AND DISCUSSION

1. INTRODUCTION

1.1 Current State of Technology of Cathode Materials for Li Secondary Batteries.

The commonly used cathode materials¹⁻¹⁰ for Li-ion cells are: LiCoO_2 , LiNiO_2 and LiMn_2O_4 . These materials have capabilities of intercalating lithium ions at high voltage, but they suffer from high cost (LiCoO_2 \$220/kg for small quantities or \$65 for large quantities*). LiNiO_2 costs \$160/kg for small quantities or \$45/kg for large quantities* and also has safety concerns and temperature dependent rate capability. The spinel, LiMn_2O_4 , is by far the least expensive - \$120/kg for small quantities or \$30/kg for large quantities.* The cost of manganese (IV) oxides for small quantities is \$15.6 (Aldrich, 1998). However apart from low intrinsic capacity and poor long-term stability this material has a difficult preparation procedure. In this study, we propose to develop novel cathode materials based on chromium, vanadium and manganese oxides that will have increased specific capacity and improved storage and cycle life at elevated temperatures as compared to LiCoO_2 , LiNiO_2 and LiMn_2O_4 (Table 1).

Chromium oxides have been studied to a limited extent as cathode materials in primary and rechargeable Li-cells.¹¹ Varta developed a primary Li/CrO_x cell which has a practical specific energy of 270 Wh/kg and an energy density of 675 Wh/l at low drain rates.¹² Toyoguchi et al.¹³ developed coin-type LiCr_2O_5 secondary batteries with an energy density of 170 Wh/l and a cycle life of over 400 cycles.

According to Yamamoto¹⁴ the best performance of the chromium oxide cathode was obtained with amorphous Cr_3O_8 cathodes due to the high surface roughness of the amorphous cathode. Primary $\text{Li/Ag}_2\text{CrO}_4$ cells, utilizing organic electrolytes are manufactured by SAFT. They are generally used for low rate applications and yield specific energies of 200-290 Wh/kg and very high volumetric energy density of 400-880 Wh/l. CrO_3 was repeatedly claimed to be a suitable cathode material for organic electrolyte batteries.¹⁵

CrO_3 intercalated in graphite was proposed for rechargeable batteries with a solid aluminae or organic electrolyte.¹⁶ Rechargeable cathodes based on $\text{Li}_2\text{Cr}_x\text{Mn}_{2-x}\text{O}_4$ have been suggested in literature.¹⁷ Bessehard et al.¹⁸ studied chromium oxides as cathodes for secondary high energy density lithium batteries. Desilvestro and Haas¹⁹ in their review of metal oxide cathode materials for electrochemical energy storage state that chromium compounds offer one of the highest theoretical energy densities when used as solid cathodes in Li cells.

1.2 Current State Of Technology Of Anode Materials For Li-Ion Cells

Intercalation electrodes, wherein lithium can be inserted and removed from a metal many times hold tremendous interest for lithium ion batteries. Intercalation carbon electrodes have emerged as the promising anodes for rechargeable Li-based batteries for portable electronic devices. For lithium ion batteries most investigations focus on graphite, disordered carbons, various cokes, carbon fibers, aerogels and pyrolytic carbons. However most of these studies are concerned with the exploration of new carbon materials or modification of existing carbons with dopants such as P, B, and N rather than focussing on the carbon surface.

The disadvantage of using carbon as the anode material arises due to the following reasons:

* Japanese Sources

1. The charge storage capacity of lithium seen in practical carbon based electrodes lies below the theoretical predicted value. The theoretical intercalation capacity of graphite carbons (one carbon per six carbon atoms), corresponding to a specific capacity of 372 mAh/g has not been fully utilized.²⁰

2. The intercalation of lithium in carbon results in an increase in the lattice parameters and can cause swelling of the anode materials and loss of active material.

3. There exists a substantial irreversible capacity loss between the first discharge and subsequent charge/discharge cycles. It has been suggested that the irreversible capacities associated with the co-intercalation of solvent into the carbon. Also, chemical properties (functional groups) of the carbon surface contribute to the observed irreversible capacity loss in the first cycle. Various carbon materials have been synthesized and even though some are less sensitive to this problem, there exists a problem of irreversibility in the first cycle.

The electrochemical reaction takes place at the interface between the carbon and the electrolyte and hence no sufficient improvement in performance is expected even for carbons with high capacity unless the interfacial properties are improved.

There have been several attempts to coat the surface of carbon anodes with protective films.²¹⁻²³ The protective films apart from metallic coatings include polymer films.²⁴ However, the polymer coating introduces a new surface that has higher interfacial and polarization resistance, which decrease the lithium charge transfer rate and lithium diffusion in the anode. Wei *et al.*²¹ and Takamura *et al.*²² reported a decrease of the initial capacity loss of graphite anode through a surface modification based on the electroless plating of Ag and Au, respectively. In this recent study,²⁵ a thin film of gold, vacuum deposited on carbon, was found to increase the doping/undoping current peaks. Both the vacuum deposition technique and the choice of gold for the surface coating are limited by the prohibitively high cost.

Also, an alternative system based on an inorganic amorphous anode system containing oxides of tin has been proposed.²⁶⁻²⁸ From our studies and literature data one can conclude that tin could reversibly alloy with lithium.²⁹⁻³⁴ However, the capacity degrades very quickly because of the volume change associated with metal going from Sn to Li_xSn.^{27,28} Recently Fuji Film Celtec Co.Ltd.³⁵ has announced a new Li ion cell with an amorphous tin oxide as the anode. Tin alloys extensively with lithium,³² forming various Li_xSn_y type compounds giving rise to a theoretical capacity of 991 mAh/g. However, tin, when used alone as an anode material, loses capacity rapidly. The reason for this is the large volume change associated with the formation of different Li-Sn phases.³⁶ Tin expands as much as 259% when alloying with lithium.³⁶ During cycling, this large expansion and contraction leads to disintegration of the anode material, thereby resulting in rapid capacity decay during normal cycling. It has been suggested that reducing the particle size of the Li⁺ storage material or reducing the extent of alloying may improve the situation.³⁶ Whitehead *et. al.*³⁷ have shown that reducing the particle size of Sn leads to better reversibility. Li and Martin³⁸ have used sol-gel template synthesis to prepare thin films of SnO₂ nanofibers, which show very high capacity and better capacity retention, even at high discharge rates. On the other hand, Idota *et. al.*³⁹ have shown that amorphous Sn based materials show better cycling behavior. In general, present research is focused on developing amorphous Sn particles with small particle size.

2. STUDIES ON NOVEL CATHODE MATERIALS

Rechargeable lithium ion batteries based on chromium oxides as the active cathode material are of considerable interest because of the very high specific energies of these compounds, e.g., 1200 Wh/kg for Cr_3O_8 . The objective of this work was to synthesize and electrochemically characterize chromium oxides, lithiated chromium oxides, Co doped CrO_x , lithiated Co doped CrO_x , V modified CrO_x , and V modified lithiated CrO_x . They were synthesized by thermal decomposition of chromium trioxide (CrO_3) at high temperature and oxygen pressures. The product was leached with distilled water five times and then dried at 100°C in vacuum oven for 24 hours. Synthesis temperature and pressure markedly affect the performance of these cathode materials. Higher pressures leads to higher O/Cr ratio and less impurities in the final product. These materials are stable intercalation hosts for lithium, and exhibit a higher capacity than any of the prominent positive electrodes used in secondary lithium batteries. CrO_x has different properties than CrO_3 .

Figure 1. Schematic of T-Cell

It is neither hygroscopic nor soluble in water and thus is not a biohazard. $\text{Co}_{0.2}\text{CrO}_x$ was prepared by heating a mixture of CrO_3 , $\text{Co}(\text{C}_2\text{O}_4)$ and small amount of additive in an autoclave for 24 hours. $\text{V}_{0.1}\text{CrO}_x$ was synthesized by thermal decomposition of CrO_3 in presence of NH_4VO_3 at high temperature and oxygen pressure and under atmospheric conditions. The chemical lithiation of pure, and Co and V doped CrO_x was carried out from active LiI dissolved in acetonitrile. A roller-pressed, round thin film cathode was prepared from active powder material, carbon black and binder PTFE in a weight ratio 1:0.1:0.05. Electrochemical characterization of the cathode materials was carried out using a Swagelok™ three-electrode cell (T-cell shown in Fig. 1).

Fig. 2. O/Cr ratios as a function of weight loss observed during TGA analysis

Fig. 3. Cyclic voltammograms of CrO_x at 0.05 mV/s after 50 cycles.

The anode and the reference electrode were discs of lithium foil, and the separator was a sheet of WhatmanTM glass fiber membrane. The electrolyte used in this study was 1 M LiPF_6 in a

1:1:3 mixture of PC/EC/DEC. The O/Cr ratio vs. weight loss for each sample obtained by TGA is shown in Fig. 2. The best electrode material obtained in this study has O/Cr atomic ratio values close to Cr_3O_8 . As shown in Fig. 3, the structure of this cathode material is very reversible over the entire intercalation range with a very small capacity fade. The structural change during intercalation was avoided by not allowing Cr(VI) to reduce to Cr(III), which may result in structural breakdown. Fig. 4 shows the first discharge curves for various chromium oxides prepared at different temperatures and pressures. Sample D and chemically modified CrO_x were prepared at higher pressures compared to samples B and C. The initial capacity of chemically modified m- CrO_x is 255 mAh/g. The oxides prepared at lower pressures have impurities, which result in a small plateau at the start of discharge. As shown in Fig. 4, the length of the plateau decreases by increasing the pressure. Also, the average voltage depends on the synthesis temperature and pressure of the active material. It increases from 2.5 V to 3 V by increasing the oxygen pressure. Fig. 5 shows that the capacity of m- CrO_x after 50 cycles is still 210 mAh/g. The charge-discharge curves for LiCrO_x when cycled between 2.0 and 4.2 V at the rate of 0.5 mA/cm² are shown in Fig. 6. The initial capacity of LiCrO_x was 210 mAh/g.^{2,3} Cobalt was substituted in m- CrO_x in order to increase the stability and high rate behavior of chemically modified chromium oxides. The Co content in CrO_x was optimized as shown in Fig. 7. $\text{Co}_{0.2}\text{CrO}_x$ exhibited highest capacity (ca. 290 mAh/g) when cycled at the rate 0.5 mA/cm². The discharge capacity of $\text{Co}_{0.2}\text{CrO}_x$ as a function of cycle number is shown in Fig. 8. The capacity after 70 cycles is 210 mAh/g. The cells were cycled at 0.5 mA/cm² between 2.0 and 4.2 V. The first discharge capacity of $\text{LiCo}_{0.2}\text{CrO}_x$ is close to 230 mAh/g.

Fig. 4. First discharge curves of various chromium oxides

Substituting a small amount of Co dramatically improves the stability and rate behavior of these oxides. $\text{Co}_{0.2}\text{CrO}_x$ and $\text{LiCo}_{0.2}\text{CrO}_x$ exhibit more than 85% and 75% of initial capacity at 0.65C rate as shown in Fig. 9.

Fig. 5. Capacity vs. cycle number for various chromium oxides and other cathode materials

Fig. 6. Charge-discharge curves for lithiated CrOx. The numbers on the graph refer to cycle numbers.

Figure 7. The first discharge capacity and open-circuit potential as a function of cobalt content in chromium oxides.

Figure 8. Discharge capacity of $\text{Co}_{0.2}\text{CrO}_x$ as a function of cycle number.

Figure 9. The discharge capacity as a function of various discharge rates.

Partial substitution of Cr in CrO_x with V ($\text{V/Cr} < 0.2$ in molar ratio) stabilizes its structure, and makes possible to prepare $\text{V}_{0.1}\text{CrO}_x$ under low oxygen pressure and atmospheric conditions. The V-doped CrO_x has good rate capability and cyclability: it delivers a discharge capacity of 160 mAh/g even at 1.5C, and maintains a reversible capacity of 220 mAh/g over 100 cycles. Figure 10 shows the variation of the discharge capacity of $\text{Li/V}_y\text{CrO}_x$ ($y=0.05, 0.10, 0.20, 0.30, 0.40$, and 0.50) cell as a function of cycle number. $\text{V}_{0.1}\text{CrO}_x$ shows larger capacity and better cycling behavior than the first of the V_yCrO_x compounds. This is in agreement with the XRD data which indicated that $\text{V}_{0.1}\text{CrO}_x$ is a new single phase compound. $\text{V}_{0.1}\text{CrO}_x$ appears to be a promising cathode material for 3 V lithium secondary batteries. Fig. 11 shows the discharge capacity of $\text{Li/V}_{0.1}\text{CrO}_x$ cell at different discharge rates as a function of cycle number. The cell exhibits excellent capacity retention at all applied discharge rates. The discharge capacity drops from 240 mAh/g at 0.25C to 160 mAh/g at 1.5C.

LiCrO_x , $\text{LiCo}_{0.2}\text{CrO}_x$, and $\text{LiV}_{0.1}\text{CrO}_x$ can be used as the positive electrode with any carbon negative electrode in a lithium-ion cell, while CrO_x , $\text{Co}_{0.2}\text{CrO}_x$, and $\text{V}_{0.1}\text{CrO}_x$ can be used with lithium or lithiated carbon as the negative electrode in lithium secondary cells.² Chemically modified chromium oxide and lithiated chromium oxides have been found to be promising cathode materials for lithium ion batteries. They are stable intercalation hosts for lithium ions and exhibit higher capacity than any of the prominent positive electrodes used in secondary lithium batteries. The insertion/de-insertion process is reversible in the entire intercalation range (2.0-4.2 V vs. Li/Li^+) and exhibit high charge/discharge capacity.

Figure 10. Variation of discharge capacity of Li/V doped CrO_x as a function of cycle number. V doped CrO_x samples were prepared with different V/Cr ratios.

Figure 11. Cycle behavior of Li/V0.1CrO_x cell at different rates between 2.0 and 4.2 V.

3. STUDIES ON CHROMIUM DOPED SPINELS

In this work an attempt was made to stabilize the spinel structure by modifying the oxygen stoichiometry, the manganese valence state and the lattice constants using $m\text{-CrO}_{2.65}$ as a precursor. A range of $y=0$ to $y=0.1$ of $m\text{-CrO}_{2.6}$ doped spinels ($\text{LiCr}_y\text{Mn}_{2-y}\text{O}_4$) were synthesized and electrochemically characterized. The results were compared with those obtained for stoichiometric pure spinel LiMn_2O_4 . The capacity fade of all cathode materials was studied and the active materials loss during cycling was determined. Also the effect of Cr content in the spinel on its self-discharge was investigated.

Fig. 12 shows the initial cyclic voltammograms and those obtained after the 100th cycle of pure spinel and $m\text{-CrO}_{2.65}$ doped spinel, $\text{LiCr}_y\text{Mn}_{2-y}\text{O}_4$ with $y=0.02, 0.05$ and 0.1 . The experiments were performed using a sweep rate of 0.1 mV/s . As shown in Fig. 12a, after 100 charge-discharge cycles, the pure spinel exhibits high irreversibility when compared with the cyclic voltammogram obtained initially during the first cycle. The anodic peak shifts approximately 0.26 V in anodic direction, while the cathodic peak shifts 0.12 V in cathodic direction compared to the initial values. Also, the peak currents drop to half of those observed in the first cycle. The observed shift of the peak potentials contributes to the increased instability of the electrolyte, which results in higher capacity fade of pure spinel. Figs 12b-d indicate that $m\text{-CrO}_{2.65}$ doped spinel, $\text{LiCr}_y\text{Mn}_{2-y}\text{O}_4$ cathodes with $y = 0.02, 0.05$ and 0.1 are completely stabilized. Negligible shift of the peak potential and consequently negligible reduction of the initial capacity was observed for these cathodes. As shown in Fig. 13, $m\text{-CrO}_{2.65}$ doped spinel $\text{LiCr}_{0.1}\text{Mn}_{1.9}\text{O}_4$ showed the best cycle performance. Even using a seven times higher discharge rate (0.7 mA/cm^2 or $\text{C}/2$) than that for the pure spinel, the capacity of $m\text{CrO}_x$ doped spinel remains almost the same after 200 cycles as the initial capacity.

Figure 12. Cyclic voltammograms of pure and doped spinels before and after cycling.

Figure 13. Capacity of pure and doped spinels as a function of cycle number.

Figure 14. Capacity loss during self-discharge for pure and doped spinels.

Fig. 14 shows the cumulative capacity loss during a 100 hour period for pure spinel, and m-CrO_{2.65} doped spinel. The results indicated that m-CrO_{2.65} doped spinel stabilizes the spinel structure and inhibits the passivation process at the interface from the electrolyte decomposition.

4. STUDIES ON COBALT DOPED SPINELS

Substitution of Co in spinel LiMn_2O_4 increases the particle size and decreases the total surface area of the spinel by 50% which is beneficial for good capacity retention properties of the cathode. After the initial reduction of the surface are observed for $y=0.05$ in $\text{LiCo}_y\text{Mn}_{2-y}\text{O}_4$, the spinel surface area remained independent on the Co content in the oxide. Increasing the Co content in the spinel from $y=0$ to $y=0.05$ and 0.06 respectively, resulted in an increase of the capacity. With a Co content in the spinel of $y=0.160$ a small reduction in the initial capacity was observed as shown in Fig. 15. However, after the initial decrease in the capacity, the $y=0.160$ sample capacity line crosses the capacity decay lines 0.060 and 0.050 after 12 and 30 cycles, respectively.

Figure 15. Capacity vs. cycle no. for pure and Co doped LiMn_2O_4

Cyclic voltammograms obtained for samples with $y=0.16$ and 0.06 in $\text{Li}_x\text{Co}_y\text{Mn}_{2-y}\text{O}_4$ after the 2nd and 85th cycles are shown in Fig. 16a and 16b. The observed decrease in the peak height and estimated capacity as a function of Co content are in agreement with the observed capacity loss observed during galvanostatic charge-discharge profiles presented in Fig. 15. The cumulative capacity losses for pure and Co-doped spinels are shown in Fig. 17. The capacity loss estimated for pure spinel resulting from self-discharge in the first 30 hrs is 3 and 6 times larger than those for cobalt doped spinel with $y=0.06$ and 0.16 , respectively.

The electrochemical parameters were determined for pure and cobalt doped spinels. The charge transfer resistance values for both the pure spinel and Co doped spinel were independent of SOC. The average exchange current densities estimated for Co doped spinel ($y=0.160$) and pure spinel are $1.73 \times 10^{-6} \text{ A/cm}^2$ and $6.59 \times 10^{-6} \text{ A/cm}^2$. The presence of Co increases the charge transfer

Figure 16a. Cyclic voltammograms for sample with $y=0.16$ in Co doped spinel after 2nd and 85th cycle

Figure 16b. Cyclic voltammogram obtained for $y=0.06$ in Co doped spinel after the 2nd and 85th cycles.

resistance and facilitates the charge transfer reaction in the active material, which is favorable for battery operation. The surface resistance values, R_{sl} were independent of SOC and increased during charging. The observed increase of the resistance was due to the slow growth of the passive film on the surface of the cathode as a function of time. The observed increase of R_{sl} values is in agreement with the estimated decrease of C_{sl} from 3.26 F up to 1.9 F and 8.16 to 6.4 F for pure and cobalt doped spinel, respectively. The Li diffusion coefficient (D_{Li+}) for Co doped spinel was estimated to be in the range of 2.4×10^{-12} to $1.4 \times 10^{-11} \text{ m}^2/\text{s}$ as a function of SOC and was found to be higher than the value estimated for the pure spinel (9.20×10^{-14} to $2.6 \times 10^{-12} \text{ m}^2/\text{s}$). The Li^+ partial conductivity estimated in Co doped spinel (in the range between 8×10^{-5} to $1.85 \times 10^{-4} \text{ S/cm}$) was higher than that estimated for pure spinel (1.2×10^{-5} to $7.2 \times 10^{-5} \text{ S/cm}$). The higher particle size of Co doped spinel resulted in lesser contact between the active material and the electrolyte contributing to the decrease of the rate of the electrolyte and the electrode decomposition and consequently to a smaller initial cumulative capacity loss.

Figure 17. Cumulative capacity loss during self-discharge for pure and Co doped spinels.

5. SYNTHESIS AND CHARACTERIZATION OF HIGH PRESSURE OXYGEN TREATED LiNiO_2

LiNiO_2 has been found to be promising cathode material for lithium-ion batteries. Its high rate performance and stability at ambient and high temperatures has slowed its commercialization. In order to increase the stability and to increase the specific capacity, LiNiO_2 and $\text{LiCo}_{0.2}\text{Ni}_{0.8}\text{O}_2$ were synthesized by a conventional process by treating them at high temperature and pressure under oxygen environment. Fig. 18 shows discharge capacity vs. cycle number for pressure treated and untreated LiNiO_2 . The cells were cycled at 0.7 mA/cm^2 between 3 and 4.3 V. The discharge capacity of temperature and pressure treated LiNiO_2 showed a capacity of 190 mAh/g compared to a capacity of 170 mAh/g for untreated samples. Temperature and oxygen pressure treated $\text{LiCo}_{0.2}\text{Ni}_{0.8}\text{O}_2$ showed a capacity of 180 mAh/g compared to a capacity of 160 mAh/g before the treatment as shown in Fig. 19. As shown in Fig. 20, $\text{LiCo}_{0.1}\text{Ni}_{1.9}\text{O}_2$ showed better cycling performance than LiNiO_2 or $\text{LiCo}_{0.05}\text{Ni}_{0.95}\text{O}_2$. The cells were cycled at 0.7 mA/cm^2 between 2.8 and 4.2 V. Structural studies indicated that the LiNiO_2 hexagonal lattice parameters became larger after the treatment, which is favorable for lithium diffusion in the material. Electrochemical Impedance Spectroscopy studies showed that the growth of the surface layer was slower for pressure treated samples resulting in lower capacity fade for these samples.

Fig. 18. Comparison of discharge capacity vs. cycle number for LiNiO_2 cathodes

Figure 19. Comparison of cycling performance of $\text{LiCo}_{0.2}\text{Ni}_{0.8}\text{O}_2$.

Figure 20. Comparison of cycling performance of treated $\text{LiCo}_y\text{Ni}_{1-y}\text{O}_2$ at low cutoff voltages

6. CAPACITY FADE STUDIES OF SEALED LI-ION BATTERIES

The capacity fade of Sony 18650S Li-ion cells has been analyzed using cyclic voltammetry; impedance spectroscopy and electron probe microscopic analysis (EPMA). After 800 cycles, the discharge capacity of the Sony 18650S cell drops to 840 mAh from 1200 mAh, a large capacity loss occurring after extended cycling. Cyclic voltammetry and impedance spectroscopy have been used to study the decay in performance of the batteries with cycling. CVs of LiCoO_2 and carbon electrodes indicate an increase in the interfacial resistance with cycling. It is seen that LiCoO_2 deteriorates more severely than the carbon electrode during cycling.

Electrochemical Impedance Spectroscopy (EIS) was used to determine the impedance parameters as well as ohmic resistance of Sony 18650 sealed lithium ion batteries cycled up to 800 cycles. The results showed that the interaction between the electrode and electrolyte in the cell result in the formation of a solid electrolyte inter-phase (SEI). Both the anode and the cathode contributed to the capacity fade of the battery. The thickness of the SEI increases during cycling and results in an increase of the anode interfacial resistance, which increase from 23.6 m Ω estimated after the first cycle up to 62.7 m Ω after 800 cycles. The interfacial resistance of LiCoO_2 electrode/electrolyte increases almost linearly with the cycle number. The initial interfacial resistance was estimated to be 0.117 m Ω and increased up to 0.298 m Ω after 800 cycles.

Figure 21a. Nyquist plots for electrodes at discharged state. The electrodes and separator are from the fresh Sony US18650S cell.

Fig. 21a and 21b shows the Nyquist plots for both electrodes taken from fresh and cycled cells. The total cell resistance varies significantly with SOC, with resistance being higher at the discharged state. It is also seen that the impedance of the positive electrode dominates the total cell resistance. No significant change in the electrolyte resistance is seen with cycling. However,

both the positive and negative electrode resistance increases with cycling thereby increasing the total cell impedance. Finally, the positive electrode (LiCoO_2) contributes more to the capacity fade of the lithium ion cells, when compared to the negative electrode. This increase in impedance of LiCoO_2 electrode with cycling is attributed to an increase in surface resistance due to oxidation.

Figure 21b. Nyquist plots obtained using a T-cell at discharged state. The electrodes and separator are from the Sony US18650S cell after 800 charge-discharge cycles.

Pulse reversal charging (the experiments were carried out at Advanced Charger Technology, Inc, Norcross, GA) results in a discharge capacity of 1.05 Ah, compared to 0.86 Ah with DC charging. Obviously the SEI grows slower by pulse charging. The cyclic voltammograms (CV) showed that after 800 cycles the cell with pulse charging exhibits higher current peaks than that with DC charging. Fig. 22 shows discharge capacity as a function of cycle number for two different charging protocols. The observed higher capacity in case of pulse charging can be explained by taking into account that during pulse reversal Li metal formed on the surface of the negative electrode oxidizes to Li^+ instead to react with the solvent irreversibly. Pulse reversal charging also causes the SEI to grow at slower rate which dramatically decreases the interfacial resistance and the voltage drop at the electrode/electrolyte interface.

Summary Of Capacity Fade Studies:

1. The rate capability of the cells continues to decrease with cycling and this decrease in rate capability can be attributed to increased resistance at both electrodes.
2. Impedance measurements for both full and half-cells show an overall increase in the cell resistance with cycling and temperature.
3. Cyclic voltammetric studies reveal the decrease in the magnitude of peak currents and vanishing of the lithium intercalation and de-intercalation peaks with cycling.
4. Charge-discharge studies on individual pellet electrodes show a reduced tendency for lithiation for both LiCoO_2 and carbon.

5. XRD studies of the LiCoO_2 electrode shows a decrease in the lithium stoichiometry with cycling.
6. Both primary (Li^+) and secondary active material (LiCoO_2) is lost during charging.
7. Thus, capacity fade in 18650 Li-ion cells is attributed to oxidation of cathode during overcharge and repeated SEI layer formation on anode during charge.
8. The higher capacity fade for the cell cycled at elevated temperatures can be due to repeated film formation over the surface of anode, which results in increased rate of primary active material loss.

Figure 22. Comparison of discharge capacity as a function of cycle number with different charging protocols for Sony cells.

7. DETERMINATION OF LITHIUM ION DIFFUSION COEFFICIENT IN GRAPHITE

Several electrochemical techniques have been developed to determine the diffusion coefficient of the lithium-ion in carbon, such as potential intermittent titration technique (PITT), current pulse relaxation (CPR), potential step chronoamperometry (PSCA), cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS). Reported values of the diffusion coefficient of the lithium ion in various carbon materials using these techniques vary greatly. In this work, the focus is on determining the lithium-ion diffusion coefficient in graphite by novel modified impedance method and comparing it with values obtained from other conventional methods.

Figure 23. Li⁺ ion diffusion coefficients in graphite determined by the modified EIS method as a function of SOC at various temperatures.

A complex impedance model for spherical particles was used to determine the lithium ion diffusion coefficient in graphite as a function of the state of charge (SOC) and temperature. The values obtained range from 1.12×10^{-10} to 6.51×10^{-11} cm²/s at 25°C for 0 and 30% SOC, respectively, and for 0% SOC, the value at 55°C was 1.35×10^{-10} cm²/s. The values of the Li⁺ diffusion coefficient determined by the modified EIS method estimated at two different temperatures and at various SOC are presented in Fig. 23. It was found that the diffusion coefficient is independent of state of charge (0 – 40%). The values obtained from the Warburg method are presented for comparison.

Figure 24. Li^+ diffusion coefficient as a function of the SOC determined by PITT and Warburg impedance approaches.

The conventional potentiostatic intermittent titration technique (PITT) and Warburg impedance approaches were also evaluated, and the advantages and disadvantages of these techniques were exposed. Fig. 24 compares the value of diffusion coefficients obtained by PITT technique and by conventional Warburg impedance approach. The diffusion coefficients determined using the PITT technique ranged from 1.03×10^{-13} to $9.3 \times 10^{-14} \text{ cm}^2/\text{s}$, and they decrease with an increase in SOC from 9 to 57%. The Li^+ diffusion coefficient estimated using the PITT and Warburg impedance methods were two orders of magnitude lower than those obtained using the modified EIS approach and the dependence on the SOC was much less in the latter technique. The observed differences in the Li^+ diffusion coefficients resulted from uncertainties in the estimations of the parameters that are required in the PITT and Warburg Impedance approaches such as (dE_{oc}/dx) , C^0 and C_R , V_m , and A . In contrast only ω and R are required in the modified EIS method, which gives rise to less uncertainty compared to the PITT and conventional Warburg impedance approaches in estimating the Li^+ diffusion coefficient in carbon materials.

8. STUDIES ON MICROENCAPSULATED CARBON MATERIALS AS ANODE FOR LITHIUM-ION BATTERIES

The objective of this work is to develop superior graphite (carbon) anodes for lithium-ion cells by a surface modification treatment based on electroless plating of ultra-thin metal films of Ni, Co, Sn or Ag on different graphite powders. Currently, Li-ion anodes made from synthetic graphite (For *e.g.*, MCMB) have 80% coulombic efficiency for the first charge/discharge cycle with irreversible capacity loss of 65-70 mAh/g. Graphite coated with a thin film of Ni or Sn will provide a low-cost option with 90% coulombic efficiency and irreversible capacity less than 30 mAh/g. The Ni microencapsulated graphite has higher charge transfer rate, better stability, higher capacity, and higher rate for lithium diffusion compared to MCMB1028.

Figure 25. Cyclic voltammograms of Ni-Co-P coated graphite (KS-10) in comparison with bare KS-10 and MCMB

Synthetic graphite (KS-10) was chemically modified with Co and Ni, which resulted in substantial improvements in discharge capacity, cyclability and almost a complete suppression of the initial irreversible capacity loss. Coating KS-10 with an alloy of Ni-Co-P alloy (procedure developed in our laboratory) resulted in a dramatic decrease of the initial discharge capacity from 740 to 350 mAh/g. This is seen clearly in Fig. 25 where the capacity loss in the first cycle for graphite (KS-10) is absent in the subsequent cycles. The performance here is similar to that of MCMB and has been achieved at a much cheaper cost. Figure 26 presents the charge-discharge curves of modified KS-10 in comparison with MCMB and bare graphite. The charge discharge efficiency increased from 38.8% to 91% when coated with a thin layer of Ni-Co-P alloy.

Figure 26. Charge-discharge curves of Ni-Co-P coated graphite (KS-10) in comparison with bare KS-10 and MCMB

The XRD studies indicated that lithium ion forms a thin layer of LiP on the carbon surface. This is a main constituent of the SEI. The cyclic voltammograms and the galvanostatic charge discharge curves indicated that the Co-Ni layer and LiP suppress completely the co-intercalation of solvated lithium ions and the reduction of the solvent thus improving the first charge-discharge reversibility. Current studies are focussed on stabilizing this material further by modifying the treatment procedure.

We have also developed composite carbon-metal oxides (Sn) using an aqueous thin film deposition technique. The advantage of this process is in obtaining uniform deposits of desired metals on the surface of carbon substrates in amorphous form. The existence of tin in amorphous form with small particle size ensures the good cyclability of tin particles.. Synthetic graphite (commercially known as SFG10 graphite, obtained from Timcal® America) was chosen as the substrate. Sn particles were embedded on the host graphite surface by using an autocatalytic process. Subsequent to deposition, the Sn composite material was prepared and heated in air at four different temperatures namely 100° C, 200° C, 300° C and 400° C. Based on the XRD data, starting from 200°C the degree of crystallinity increases with increase in heat treatment temperature. New peaks appear close to 42° and 46°. No changes in structure are seen at other angles. This confirms that the synthesis route leads to the formation of thin amorphous films of metal oxide on the surface of graphite.

Figure 27 shows the effect of increasing tin loading on the discharge capacity of the composite. The discharge capacity increases with increase in tin content, reaches a maximum and then decreases. The initial increase can be expected due to the increased reaction between tin and lithium. It is seen from the plot that the rise in the specific capacity reaches a maximum at 15-wt% Sn and the specific discharge capacity begins to decrease with further increase in tin composition. 20-wt% Sn on graphite shows a lower specific capacity of 381.7 mAh/g than that of 15% Sn composite electrodes (433.2 mAh/g). Since a small amount of Sn has been incorporated into carbon the thickness of the surface film is very small. This leads to better utilization of the active material as compared to bulk Sn particles. However, increasing the tin content beyond 15% can lead to agglomeration of tin, thereby resulting in poor utilization of the tin particles. This could explain the drop in specific capacity with continued increase in Sn content.

Figure 27. Change in Specific Capacity with Sn Loading for Sn-Graphite Composites

Figure 28 shows the cyclic voltammogram of Sn encapsulated graphite composite. The cyclic voltammogram performed on the bare graphite has also been shown for comparison. Sweeping the potential from 1.2 V to 0 V results in lithiating the composite. According to Dahn *et. al.*³⁶, cycling bulk SnO between 1.3 V to 0.4 V gives a reversible capacity of approximately 300 mAh/g. In our case, integrating the area under the cathodic curve in Fig. 3 from 1.2 V to 0.4 V we obtain a charge of 40 mAh/g. This is much lower than that reported by Dahn *et. al.*³⁶. Hence it is clear that Li alloying with Sn in the composite differs significantly from that reported previously for the bulk material. During de-intercalation (sweeping the voltage from 0 to 1.2 V) two characteristic peaks appear at the same voltage for both the bare graphite and the composite. However the magnitude of the peak current is larger for Sn coated graphite as compared to the bare material. The plot also shows an increase in the area of the i-V curve for the coated carbon.

This serves as an additional support for the increase in the capacity due to tin coating seen in charge-discharge studies. However, no discernible peak corresponding to the reaction of Sn with Li are seen, suggesting that the lithiation reactions with Sn occur in the same potential range as that of carbon. Lower Li-Sn alloy phases (Li_5Sn_2 , $\text{Li}_{13}\text{Sn}_5$, Li_7Sn_2 , $\text{Li}_{22}\text{Sn}_5$) have been observed at a potential range of 0.23 V-0.10 V.³⁶ This corresponds to the potential range in which lithiation is seen in the case of the composite. Finally, comparison of the ratio of charges under the anodic and cathodic sweeps reveals a higher coulombic efficiency for the Sn encapsulated sample.

Figure 28. Comparison of Cyclic Voltammograms of Bare and 15-wt% Sn Coated Graphite

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