AN ABSTRACT OF THE THESIS OF


Abstract approved:

Michael M. Lerner

This thesis details (1) the simple synthetic methods for incorporating organocations into transition metal oxide hosts to form nanocomposites and (2) the electrochemical characterization of polypyrrole and polypyrrole/clay nanocomposites and the results obtained are described. A brief introduction to and motivation for the work is dealt in chapter 1.

The first project deals with the intercalation chemistry of Cobalt and Nickel oxides. A simple chemical method is reported for the intercalation of layered nickel and cobalt oxides with organocations. Compounds containing anilinium, dodecyl-trimethylammonium, octadecyl-trimethylammonium, or distearyl-dimethylammonium cations are obtained by reaction of lithiated hosts with aqueous persulfate, followed by treatment with desired organocation. Basal repeat distances, calculated from x-ray data, indicate that the arrangements of organocations are similar to those seen with other layered hosts, with bilayers of alkylammonium ions, or a single layer of anilinium, in the pillared galleries. Thermogravimetric and elemental analyses are used to estimate compound stoichiometries, and indicate the partial exchange of organocation for lithium. The
anilinium compound contains oligomeric cations, and is unstable when treated with polar solvents. Open circuit measurements indicate that the materials contain Co in an oxidation state of 3+, or higher.

The second project focuses on extending the electrochemistry of chemically synthesized polypyrrole and polypyrrole/clay nanocomposite. Polypyrrole is known to be intercalated into layered host lattices both by \textit{in situ} polymerization and by latex-colloid interaction methods. The behavior of the chemically synthesized polypyrrole and the polypyrrole/clay nanocomposite is reported here. The electrochemical methods employed in this characterization, cyclic voltammetry and chronopotentiometry, confirm the distinct electrochemical behavior of the polymer and the nanocomposite. The as-prepared polymer exhibits redox peaks at already reported potentials whereas the intercalated polymer exhibits a redox potential shifted negative by 1 V. This is predicted to be due to the electron-donating effect of the negatively-charged aluminosilicate sheets within which the polymer is intercalated. Cyclic voltammetric studies of the nanocomposite showed no evidence of the redox peaks at normal potentials of the polymer (at \(-200\) mV and \(-500\) mV vs Ag/Ag+) but well-defined were observed at much negative potentials of \(-1200\) mV and \(-1500\) mV. The distinct electrochemical was confirmed by chronopotentiometry. The conducting polymer-clay composite shows promise for both coatings and electrochemical capacitor applications.
Synthesis and Characterization of Novel Materials for Electrochemical Devices

by

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I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request.

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Kartik Ramachandran, Author
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Dr. Michael M. Lerner was involved in the analysis and writing of each manuscript. Dr. Oriakhi was involved in the synthesis of aniline-intercalated LiCoO$_2$ and Dr. Koch helped in collecting the electrochemical data for the intercalated cobalt and nickel oxide samples.
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DEDICATION

To my mother and father,
for their blessings, love and faith

To my brother, Bharat and sister, Harini
for their love, affection and prayers
Chapter 1

INTRODUCTION

1.1 General Introduction

This thesis has been organized as follows: Chapter 1 introduces the motivation behind the enormous research being pursued in the field of lithium rechargeable batteries. The chapter also reviews some of the promising cathode materials, anode materials and non-aqueous electrolytes that have been examined. Some of the recent advances in the field of conducting polymers and the widespread research being pursued on the applications of these polymers are also outlined. Finally, an outline of our research goals and strategies and motivation for this work and also the prospective applications of the materials under study are described. Chapter 2 describes in detail the work carried out in the incorporation of large cations in layered metal oxides, of stoichiometry LiMO$_2$, and the characterization of these compounds by x-ray diffraction and thermogravimetric methods. Chapter 3 concentrates on the electrochemical characterization of polymer intercalated layered clay lattices and their electrochemical applications. Detailed electrochemical studies include cyclic voltammetry and charge-discharge characteristics. Chapter 4 summarizes the overall results and concludes the work being done.
1.2 Introduction to Batteries

The many and varied requirements for battery power and the different environmental and electrical conditions under which they must operate necessitate the use of a number of different types of batteries and designs, each having superior performance under certain operational conditions. Although many advances have been made in battery technology in recent years, there is still no one 'ideal' battery that gives optimum performance under all operating conditions. As a result, many electrochemical systems and battery types have been and are being investigated and promoted. However, a relatively small number have achieved wide popularity and large production and sales. The less conventional systems are typically used in military and industrial applications requiring the specific capabilities offered by the special batteries.

Batteries are becoming increasingly important part of our society. Recent advances in portable electronics, laptop computers, and wireless communication have resulted in significant growth in the need for small, high energy, reliable power sources. This has spurred a surge in the research of new battery materials, optimization of existing electrochemical couples, and the marriage of electronic circuits with batteries to form hybrid systems that can extend battery life significantly.

The 'ideal' electrochemical cell or battery is obviously one that is inexpensive, has a high energy density, defined as the ratio of the energy available from the battery to the volume (Wh/L) or weight (Wh/Kg) can provide high power levels, can operate over the full range of temperature and environmental conditions, has unlimited shelf life, and is completely safe.
In practice, energy storage limitations do exist as materials are consumed during the discharge of the battery, shelf life is limited due to chemical reactions and physical changes that occur, albeit slowly in some cases, during storage, and temperature and discharge rate affect performance. The use of energetic component materials and special designs to achieve high energy and power densities increases cost and requires precautions during use to avoid electrical and physical abuse. The selection of the most effective battery and the proper use of this battery are important in an application to achieve optimum performance.

Owing to the present exponential development of portable consumer electronics and to the increasing concern about the environment, new energy sources are required that provide more energy in the same volume and/or mass. Within a short period of time, many changes in the area of rechargeable batteries for the consumer market have occurred, along with the emergence of several new technologies. The ubiquitous Ni-Cd cells, which are environmentally unfriendly because of the toxicity of cadmium, will be replaced by Nickel-metal hydride, rocking-chair lithium (or lithium ion), and lithium polymer electrolyte rechargeable cells.

1.3 What is a Battery?

A battery is a self-supporting energy storage system that converts chemical energy into electrical energy. It is comprised of two electrodes separated by ion conducting medium called an electrolyte. Figure 1.1 shows the basic structure of a battery. Connecting the electrodes to an external load results in an electron flow in the external leads and an ion flow
Figure 1.1 Electrochemical Operation of a Cell - Charge (above) and Discharge (below).
through the electrolyte. The charge flows result from the electrochemical (or redox) reactions at the electrodes that involve chemical species and electrons and occur at different voltages. Batteries are classified as primary or secondary. In a primary battery, the redox reactions cannot be reversed and the system can only be discharged once. Primary batteries, hence can only be of one time use only but are relatively inexpensive and simple in their design. On reversal of polarity, parasitic reactions such as electrolyte decomposition occur. Since primary batteries are disposable, environmental concerns exist about their contribution to solid waste.

Secondary batteries, can be cycled between the charged and discharged state several times. The redox reactions are reversible, leading to a system that be discharged and recharged many times. The number of cycles available from a secondary battery before its capacity degrades to some prespecified value defines its cycle life. The life of a secondary battery also depends on the conditions under which it is recharged. Most battery recharge reactions occur rapidly, with little polarization and current efficiencies approaching 100%.

Batteries are devices that convert the energy released by spontaneous chemical reactions to electrical work. This conversion process occurs because of the redox character of the reactions involved. By placing electrical insulators (separators) between the electrodes, the flow of electrons from one electrode to the other is only permitted through an external circuit. Internally, the electrical circuit is completed by ion transport through an electrolyte. Electrical energy from battery is generally expressed in watt-hour (Wh) because of the large amount of energy available. Often, only 20 to 30% of the theoretical energy content of a battery reaction is realized in practice. The amount of electrical energy that can be actually recovered during a discharge depends on the voltage difference between the two electrodes, the rate at
which the electrochemical reactions occur, and the length of time for which the reaction can proceed.

Batteries using water-based electrolytes (called aqueous batteries), deliver output voltages limited by the electrochemical stability of water - theoretically in the range of 0.9 V for basic solutions to 1.6 V for acidic solution. Electrochemically, aqueous $\text{H}_2\text{SO}_4$ is stable up to 1.7 V but is stable up to 2.2 V in practice (as in lead-acid batteries) due to overpotential effects. The use of lithium metal as the negative electrode together with a non-aqueous, Li$^+$ conducting electrolyte (lithium reacts with water even in trace amounts) can lead to much larger output voltages (up to 4.5V), due to the highly reducing character of lithium. In addition, a higher specific energy density and better performance per unit weight can be achieved because of the low atomic weight of lithium.

Battery technology has been developed during the past 100 years. In the early stage of investigation, a large number of inorganic and organic materials, like binary oxides, ternary oxides and conducting polymers to name a few, have been examined in aqueous solutions and the possible candidate materials were selected. Cathode materials which are still used and will not be ruined in batteries are (1) manganese dioxide ($\text{MnO}_2$) in primary batteries such as zinc-carbon (Leclanche), zinc chloride, and primary alkaline cells; (2) nickel oxyhydroxide ($\text{NiOOH}$) in secondary alkaline batteries i.e. Ni/Cd or recent Ni/metal hydride cells; and (3) lead dioxide in lead acid batteries. These batteries are used all over the world. However, any dramatic increase in energy densities for these systems is almost hopeless in the current form because of the thermodynamic limitations of water (1.23V of decomposition voltage at 25°C).
At the beginning of the 1980's, research on secondary lithium batteries intensified, using as the positive electrode, an intercalation material with the ability to reversibly incorporate lithium ions in its structure. Layered chalcogenides, such as TiS₉, were intensively studied, but, more recently, attention is being focused on oxides, which allow higher operating voltages and consequently higher energies. The development of secondary lithium cells has been slowed by safety problems, arising from the simultaneous use of lithium metal and a liquid organic electrolyte, and because of dendritic regrowth of lithium on the anode upon cycling, which eventually causes the cell to short circuit.

Two approaches were proposed early in 1980 to overcome the safety problem. The first consisted of using a solid polymer electrolyte, which is less reactive with lithium leading to all solid-state lithium metal rechargeable batteries. The second way to eliminate the problem associated with lithium metal is to replace the lithium metal with a material able to intercalate lithium ions reversibly at very low voltage, leading to the so-called "lithium-ion" or "rocking-chair" lithium rechargeable batteries. Unlike lithium plating and stripping as in conventional systems, the electrochemical process at the negative side of such a cell is the uptake of lithium ions during charge and their release during discharge.

The demand for high energy batteries stimulates the materials research for new non-aqueous lithium batteries. Several materials have been proposed and some of them have been already demonstrated. The success in primary lithium batteries, Li/(CF)ₙ and Li/MnO₂, as power sources for electronic devices in the early 1980's is a milestone in high energy density lithium batteries. The rechargeable lithium batteries, such as Li/TiS₂, Li/MoS₂, Li/NbSe₃, Li/MnO₂, Li/Vanadium oxides, etc have been advanced and already demonstrated in
prototype cells. An innovative secondary system called the lithium-ion (or shuttle cock) cell or rocking chair cell has been developed and commercialized as power sources for handy video cameras, wireless telephones and other electronic devices. The cell consists of LiCoO$_2$ as cathode and carbon as anode electrode materials.

In summary, batteries are complex systems involving highly independent thermodynamic and kinetic factors. As users, people like them to be small, lightweight devices that supply large amounts of energy, last for a long time, and cost little. There is an ongoing effort in the area of nonaqueous battery chemistry to develop a high energy rechargeable system, capable of many thousands of charge/discharge cycles. Much effort is being expended worldwide on new lithium ion battery systems. The major effort is being directed towards the carbon anode and the metal oxide cathode.

1.4 Role of Lithium rechargeable nonaqueous battery systems

Small, but highly efficient, batteries are needed today to power popular devices such as cellular phones and computers, where the high degree of sophistication of the electronic circuitry is contrasted by a still inadequate battery package. High-energy density rechargeable batteries are also needed for the development of long range electric vehicles in order to improve the air quality. For versatile uses the availability of an ambient-temperature rechargeable battery is the main goal. The most promising approach in reaching this goal has been the effort directed towards the production of non-aqueous lithium battery systems, i.e. batteries based on a lithium metal or lithium ion source anode, a lithium-ion conducting
electrolyte, and a lithium-ion accepting cathode material. The latter is generally an open-structured compound capable of accepting and releasing lithium-ions into and out of its crystal lattice. Open structured materials are broadly classified as three-dimensional lattices or channels, two-dimensional or layered lattices (metal chalcogenides like TiS$_2$, MoO$_3$) and one-dimensional or chain lattices (zeolites). The choice of these lithium batteries is motivated by the fact that lithium metal has a higher specific capacity than any other practical negative electrode and that the preferred Li-intercalation positive electrode offers advantages of highly reversible electrochemical processes. The theoretical energy content of lithium batteries significantly exceeds that of more conventional electrochemical systems, such as lead-acid, nickel-cadmium, or even systems of more recent developments such as nickel-metal hydride.

In the earlier section, chemical/electrochemical process for batteries in general were outlined. The discharge process of lithium batteries involves the electrochemical dissolution of lithium to generate lithium ions, and their migration across the electrolyte and insertion into the crystal lattice of the host cathode material. Meanwhile, electrons travel in the external circuit to the electronic band structure of the same host cathode to compensate for the action charges [fig 1.2]. The charging process is just the reverse. The overall battery process may be described as the insertion-extraction of both mobile lithium ions and compensating electrons into the rigid host structure. The former induces reversible spatial modifications (e.g., expansion or contraction of the host lattice), while the latter induces reversible changes
Figure 1.2 Schematic illustration of the electrochemical process of a lithium-ion rechargeable battery.
in the oxidation state of the transition metal atom. Therefore, any liquid or solid lithium ion conducting medium may be used as a suitable electrolyte. If maintained within the structural limits of the host compounds, the driving process of the lithium batteries is highly reversible and the lithium batteries are in principle capable of delivering very long cycle life.

1.5 Selection of Battery Components

Considering the general design, which involves a positive lithium-source electrode combined with a negative lithium-accepting electrode and the related nature of the electrochemical driving process, a successful operation for a rocking chair battery and its effective competition with a metal lithium system requires some crucial conditions that should be fulfilled by the selected insertion electrodes.

The conditions that need to be considered are outlined as follows. The lithium activity in the negative electrode must be close to 1 in order to assume open circuit voltages approaching those obtainable with pure lithium. The equivalent weight of both electrodes must be low in order to assure specific capacity values of practical interest. The voltage changes upon lithium ion uptake and release must be small in both electrodes to limit fluctuations during charge and discharge cycles. Both the ion-source and the ion-sink electrode must be easy to fabricate and based on non-toxic compounds, to assure low cost and environmental control. Insertion compounds must be selected to meet these conditions satisfactorily and with properties consistently different from those normally used for the conventional lithium batteries.
1.5.1 **Anode Materials**

Carbon has been shown to be a good candidate for negative electrodes in lithium secondary batteries. At present, extensive efforts have been dedicated to the research and development of different carbonaceous materials that are able to deliver high specific capacity, high cyclic efficiency, and long cycling life. The structure of the carbon is a major factor in the how much lithium can be intercalated and at what voltage.

By using carbon materials as an anode for lithium ion rechargeable batteries, carbon can be lithium doped/undoped during charging/discharging without morphology change at the surface. The reaction of Li-CIC (Carbon-Intercalation Compound) during charge-discharge can be expressed as the following equation:

\[ \text{Li}_x \text{C} = \text{Li}_{x+dx} \text{C} + dx \text{Li}^+ + dx e^- \]

Carbon can be classified as graphitic and non-graphitic carbon. Compared with graphitic carbon, non-graphitic carbon has low density, porous surface, small crystallites, relatively random orientation of crystallites and long interplanar spacing. Since graphitizable carbon is similar to graphite with respect to crystallinity, lithium intercalation into graphitizable carbon seems to be preferable to that of non graphitizable carbon. Lithium doping/undoping capabilities depend strongly on the species of carbon materials. Even though the same carbon precursor is selected, the carbon obtained by heat treatment with various temperatures yields numerous kinds of structures, depending on the carbonization processes. The various forms of carbon available range from natural graphite, pitches, cokes, pyrolitic carbon to the fullerenes that have been reported recently. Furthermore, the capacity is considered to be...
affected by the characteristics of structures such as stacking structure and/or alignment of crystallites.

1.5.2 Cathode Materials

The choice of cathode is as flexible as that of anode materials, since various materials can in principle assure the electrochemical balance for the overall lithium battery process. In this respect, an element $A_y$ can be selected if it is capable of reacting directly with lithium to form a lithium compound $LiA$. The less the extent of bonding and structure modifications of the selected cathode material, the more likely it is that rechargeable, long-cyclable battery systems will be developed successfully. The most suitable materials in this respect are the so-called insertion compounds - namely, $A_2B_y$ compounds having an open structure capable of accepting and releasing $x$ number of lithium ions per $A_2B_y$ mole, as the results of a reversible electrochemical reaction of the type

$$x Li^+ + A_2B_y + xe^- \rightarrow Li_xA_2B_y$$

This reaction induces the formation of metastable phases accompanied with minor and reversible modifications in the structure of the host oxide $A_2O_y$. Such a topotactic or topochemical reaction is usually called a lithium insertion or intercalation process and is described in detail in earlier sections.

The combination of a lithium metal or Li-CIC (Lithium-Carbon Intercalation compound) anode with a layered host cathode in a $Li^+$-ion-conducting electrolyte gives rise to an electrochemical cell characterized by the process where the $Li^+$ ions rock back and forth
between two intercalation materials. There has been considerable research and development activity targeted towards the commercial manufacture of battery systems based on lithium insertion cathodes and metallic lithium anodes. Lithium metal free lithium batteries have been known for several years and were originally termed as 'rocking chair batteries' by Armand. Shortly after, the rocking chair battery concept was demonstrated using transition metal compound anodes and cathodes. In 1990, Sony Energytech Inc announced the commercial availability of their "lithium ion rechargeable battery" based on a carbon (non-graphitic) anode and a LiCoO₂ cathode.

A number of different electrode materials are arbitrarily divided into LiMO₂ (e.g. LiCoO₂, LiNiO₂ and LiMnO₂) compounds, manganese oxides (e.g. LiMn₂O₄) and other materials. These compounds are characterized by their high electrode potentials and as such reversibly intercalate lithium ions above 3V versus Li. For layered transition metal oxides LiMO₂ (M=Co, Ni, Mn) and spinel manganese oxide LiMn₂O₄, electrode potentials become higher than 4V vs Li/Li⁺ by extracting lithium from these oxides electrochemically in non-aqueous electrolyte solutions. It is found that lithium intercalation/deintercalation into/from these oxides takes place at the potential around 4V. Particularly in the case of LiCoO₂, the polarization is smaller and the capacity is larger compared with other transition metal oxides. It is necessary to employ a transition metal oxide with high capacity and high electrode potential, such as LiCoO₂, as a cathode in order to attain the higher energy density. Although this is a relatively expensive material, its favorable electrochemical properties mean it is continuing to find applications. LiNiO₂ is comparatively inexpensive but is much more difficult to prepare in the electrochemically active form. Only the first row transition metal oxides
are considered because of the relatively low insertion potentials (versus Li) of the LiMO$_2$ compounds of the heavier transition metals, e.g., LiWO$_2$, LiMoO$_2$ and LiRuO$_2$.\textsuperscript{23}

The layered metal oxides of the type LiMO$_2$ (where M= Co, Ni and Mn) have a rhombohedral structure\textsuperscript{24-26} where lithium and transition metal atoms are ordered in alternate (111) planes in a distorted cubic-close-packed oxygen ion lattice. The layered framework provides a two-dimensional interstitial site which allows for relatively facile extraction and insertion of lithium ions.

Rocking chair batteries do not require stringent manufacturing environments because the starting electrode materials (i.e. lithiated oxides and carbon) are stable in ambient atmosphere. The cell is assembled in its discharged state, where the output voltage is close to 0V and, consequently, can be handled before use without any fear of irreversible degradation due to short circuit. The battery is activated during the first charge. This is similar to the well-known and widely used Nickel-Cadmium batteries that need to be charged prior to their first use. The lithium-ion cell delivers its capacity between 4.1- 4.3V and 2.5V, with an average voltage of 3.5-3.7 V and can be discharged reversibly down to 0 V. The carbon-based rocking-chair batteries are environmentally safe, possess higher specific (mass) energies and energy densities (volume energies) than Ni-Cd and Ni-metal hydride cells, and exhibit good rate capability and long cycle life.
1.5.3 Electrolytes

Most liquid or solid conducting materials characterized by fast lithium ion transport can be employed as an electrolyte medium for these batteries but other requirements like their electrochemical stability limit their effective use in commercial cells. Common examples of liquid electrolytes are solutions of lithium salts LiX (e.g., LiClO₄, LiAsF₆, LiPF₆, etc) in aprotic organic solvents (e.g., Propylene Carbonate (PC), dimethoxyethane (DME), etc.) or their mixtures (PC-DME). Crystalline or glassy compounds having vacancy or interstitial defects energetically favorable for Li⁺ transport may act as solid electrolytes. Some examples of these electrolytes are LiI.A1₂O₃ composite powders or LiI-Li₅PₓO₁₀Sₓ chalcogenide glasses. ²⁸

Although no work was directed on identifying suitable electrolyte systems, a brief summary of the most efficient electrolytes employed is reported. Earlier reports on the behavior of lithium metal at the overcharging potential range revealed that the electrolyte system using LiPF₆ as a lithium salt showed good performances. ²⁷⁻²⁸ In rechargeable batteries with high voltage, it is also required that the electrolyte solution remain stable at a voltage higher than 4V, in the temperature range of approximately -20 to +60 °C. It was found that these requirements could be met by using Propylene carbonate(PC)+Diethyl carbonate (DEC)/LiPF₆. ²⁹ The lithium ion rechargeable battery using PC-DME (Dimethyl Carbonate)/LiPF₆ exhibits the excellent cycle performances around 23°C. The cycle performance becomes worse with increasing temperature. On the other hand, PC-DEC/LiPF₆ exhibits a smaller decrease in retention of the discharge capacity even at a moderate high
temperature (45°C). Theoretical studies conclude that the cycle performance could be improved using the electrolyte solution with electrochemical stability such as PC+DEC/LiPF₆.

1.6 Introduction to Synthesis of LiCoO₂ and LiNiO₂

The lithium cobalt oxide, LiCoO₂, was among the lithium insertion compounds first described by Mizushima et al.¹⁸ in 1980, and is currently the most extensively used cathode material for rocking chair batteries. LiCoO₂ is isostructural with the rhombohedral R3m α-NaFeO₂ layered structure. The structure is an ordered rocksalt structure with edge sharing CoO₆ octahedra linked to form CoO₂ sheets. The CoO₂ sheets are separated by sheets of octahedrally coordinated lithium ions. The sheets of positively charged lithium ions effectively screen and stabilize opposing negatively charged CoO₂ sheets. The lithium ions have unobstructed two-dimensional pathways which result in the reversible deintercalation attributes (fig 1.3). The removal of the electrostatic repulsions of the CoO₂ sheets results in the subsequent expansion of the hexagonal lattice in the c direction. It is due to this binding effect of lithium that it has been believed that removal of lithium to concentrations less than 0.5 mole results in structural instabilities.

LiCoO₂ is prepared by both the high temperature and the low temperature route.¹⁸,³¹ The former is prepared by heating a stoichiometric mixture of Li₂CO₃ and CoCO₃ in air at 900°C for 24 hours. The low-temperature LiCoO₂ is prepared by reacting stoichiometric quantities of Li₂CO₃ and CoCO₃ at about 400°C. In the high temperature route LiCoO₂, the octahedral sites, 3a and 3b, are solely occupied by lithium and cobalt ions, respectively. The low-
Figure 1.3  Structure of LiCoO$_2$ emphasising the layered structure of the material. (●)Co, (•)Li, and (○)O.
temperature LiCoO$_2$ was reported to have a rocksalt structure in which the 3z and 3b octahedral sites were occupied by both lithium and cobalt ions. However, the open-circuit voltage was around 3.6 V for the low-temperature oxide and about 4V for the high-temperature analog. Lithium can be extracted chemically from these compounds to yield samples with various lithium contents. Removal of lithium corresponding to $x=1$ in Li$_x$CoO$_2$, is equivalent to a theoretical capacity of about 274 mAh/g. Due to structural restrictions, rearrangement, when $x<0.4$, to form Li$_{0.4}$CoO$_2$ decreases the reversible capacity of the compound. Hence, lower amounts of lithium may be removed and inserted reversibly. The LiNiO$_2$ compound appears to be more difficult to synthesize than the corresponding cobalt oxide, in a modification which is able to reversibly insert lithium to any significant extent. Contrary to LiCoO$_2$, which is be prepared by sintering a mixture of almost any Li, Co and O sources under proper conditions, the LiNiO$_2$ compound needs to be prepared under strongly oxidizing conditions. It can be prepared by the dry heat treatment of a mixture of the NiO with LiOH or by the conventional procedure by annealing mixtures of Ni (II) hydroxycarbonate and lithium carbonate at 875°C for 18 h under constant O$_2$ flow-rate. The flow-rate of oxygen has a direct effect on the oxidation state of nickel in the final product and hence the maintenance of strong oxidizing conditions is required.

The experimentally realized capacity of LiCoO$_2$ falls in the range of 120-130 mAh/g, and the compound is most suitable as a cathode material as it is highly crystalline. The cyclability is dependent on the amount of lithium removed from the structure. Deep discharge to $x<0.33$ results in irregular structural changes and lowers the capacity significantly. The capacity is fairly independent of the preparation method.
1.7 Research Goals and Strategies

The development of lithium-ion rechargeable batteries of high energy density has relied on the successful development of high energy density intercalation compounds. The reaction of LiCoO₂ in a lithium-ion cell is well known to be lithium-ion extraction from and insertion into a layered cobalt dioxide matrix by varying the interlayer distance. The rechargeable capacity of the cell fades rapidly for deep charge/discharge cycles of x > 1/ in Li₁₋ₓCoO₂. The chemical oxidation of LiCoO₂ can be carried out using acids³⁶, Cl₂ or Br₂³⁷ and other oxidants such as NO₂⁻ salts or MoF₆. The cationic intercalants into the cobalt and nickel layer (nickel layers in LiNiO₂) structures have been limited to alkali metals and H⁺ ³⁹,⁴⁰. Given the technological importance of these oxides, an effort to expand the intercalation chemistry for these hosts was attempted. Intercalation of several organocations within the layered CoO₂ and NiO₂ structures were carried out. Pillared structures were obtained and were characterized by XRD, thermogravimetric, and elemental analyses. The open-circuit voltage measurements confirmed the increased oxidation state of the Co and Ni metal ions. Future work will be directed towards the intercalation of conducting polymers into these layered structures.

1.8 Introduction to Conducting Polymers - Applications and Research Goals

Since the discovery of the conducting organic polymers⁴¹ and the electropolymerization under controlled conditions, the physicochemical properties of polypyrrole and other conducting polymers have been the subject of many investigations. Possible applications of
conducting polymers are in the following areas: battery technology and energy storage, corrosion protection, electromagnetic shielding, antielectrostatic coatings, electronic and electrochromic devices and modified electrodes for biological and chemical sensor applications. Polypyrrole has been widely studied for its high conductivity, stability in the oxidized form, and the ability to be electrochemically switched between the conducting and insulating states.

One of the most interesting aspects of conducting polymers is the coupling of electron transfer reaction and exchange of counter ions during the electrochemical oxidation and reduction process of the polymer. For polypyrrole, this can be described in the formula:

\[ \text{ppy}^+ + \text{e}^- \leftrightarrow \text{ppy} + \text{A}^- \]

The corresponding electrochemical investigations have mainly been restricted to measurements on polymer film coated electrodes. A great deal of work has also been directed towards the electrochemical preparation of a number of polypyrroles leading to a new class of multi component materials with controllable electrical, electrochemical and catalytic properties.

Polypyrrole and other conducting polymers have been reported to have the potential advantage of improving the rate of slow oxidation process - by virtue of their very large, solvent-reagent accessible internal surface areas while suppressing corrosion. Further improvement in the polypyrrole system can be achieved with additional molecular-level surface chemistry.
Of some of the major applications of conducting polymers and their nanocomposites are in microelectronics. The techniques of microfabrication used in the manufacture of solid-state electronic devices have been combined with electrode modification techniques to prepare analogs of solid state transistors. Figure 1.4 illustrates the kind of transistor device that has been made by surface modification of a pair of closely spaced gold microelectrodes\textsuperscript{52,53}. The key is that the redox polymer spanning the gap between the two microelectrodes has a conductivity that depends on its redox potential. Possible applications are likely in the sensor field, where molecular materials may present superior ways to detect and amplify chemical signals.

Electrocatalysis is a process of great industrial interest. The aim is to drive selective oxidations or reduction of substrates efficiently at modest potentials. Recent developments in the electrochemistry of polypyrrolic coating have allowed laboratory scale electrosynthesis to be carried out. A large part of this development is attributable to the high chemical stability of polypyrrole films and the possibility to immobilize very efficient and selective functional groups and transition-metal complexes catalysts into this polymer.

Another potential application recently suggested for conducting polymers is that of the electrode-active material in electrochemical capacitors, which are high power, energy storage devices\textsuperscript{54-56}. An electrochemical capacitor is very much the same as a battery except that the nature of charge storage in the electrode active material is capacitative, i.e., the charge and the discharge processes involve only translation of ionic and electronic charges through electronically or ionically conducting domains, respectively. Although energy densities of electrochemical capacitors are lower than those of advanced batteries, their main application
Figure 1.4 Microelectrochemical transistor based on polymers.
is targeted as a power storage device in electric vehicles (EV) operating in parallel with the EV battery.

Conducting polymers possess the advantage of potentially low materials cost. It can be anticipated that electrodes of relatively simple conducting polymers, such as polypyrrole, polyaniline and polythiophene, can be fabricated at a cost comparable with that of noble metal oxide electrodes. It is the combination of low materials cost and high energy density that makes conducting polymers attractive potential active materials for use in electrochemical capacitors. Most conducting polymers can be p-doped and undoped, and these processes generally take place at electrode potentials that are accessible in aqueous solutions. Conversely, only a limited number of conducting polymers can be reversibly n-doped and hence most works have been concentrated on the p-doping of stable conducting polymers such as polypyrrole and polyaniline. Reliance on p-doping/undoping alone in a single type of active material limits the overall voltage window of a device to about 1V. For this reason, various efforts are being pursued for other configurations of capacitors based on conducting polymer active materials, which would provide an increased voltage window, and hence an increased energy density. A number of configurations have been explored so far but only a few of them have been found to have some interesting properties.

In one case of electrochemical capacitor configuration (fig. 5), the active components of the two electrodes comprise of two identical, p-dopable polypyrrole films. When the capacitor is fully charged, one of the films will be in the undoped form and the cell voltage is typically 1V. Upon discharge, the undoped film oxidizes (become undoped) while the
doped film reduces (dedopes), until both are half doped and the cell voltage is zero. Hence, the charge released on discharge is only one half of the full doping charge.

In another type of configuration for the electrochemical capacitor, two different p-dopable conducting polymers, polypyrrole and polythiophene, are used as the active material on the two electrodes. These polymers are selected by virtue of the difference in potential ranges over which they become doped. This results in an increase of the voltage of the fully charged capacitor to 1.5V, and also allows a greater proportion of the total doping charge to be released on discharge.

Conducting polymers and their nanocomposites thus represent an attractive class of materials for use as active components in electrochemical capacitors. The voltage of the device can be extended higher than 3V by employing n- and p-dopable polymers and their nanocomposites in non-aqueous electrolytes. Optimization of these types of materials, and of electrolyte will result in significant improvement in the extent and reversibility of charging in both p- and n-doping modes.

Modified electrodes have been extensively used in the last decade by electrochemists attempting to control the direction and extent of electrode reactions. One of the attractive features of clays for use in electrode modification is the high reactivity of the clay surface with organics. This feature has already been exploited to localize and organic substrate in close proximity to the electrode to enhance an electrochemical process. Clay-modified electrodes have been used to support RuO₂ near the electrode surface and clay by itself can participate in a redox reaction by the addition of a charge shuttle, like Ru(NH₃)₆³⁺.
1.9 Research Goals and Strategies

Extensive studies have been carried out on the characterization of polypyrrole and polypyrrole derivatives. It has already been reported that the redox potential of the surface polymer shifts significantly more negative compared to the value of the pure polymer. The substitution of electron-withdrawing groups, like Br, I or Cl, on the polymer chain make the polymer more difficult to oxidize and shift the redox potentials more positive with respect to the pure polypyrrole. These types of materials have been known to have wide applications.

In our effort to modify the polypyrrole system, polypyrrole was incorporated within clay sheets and were characterized for their electrochemical behavior. The polypyrrole used in our study was chemically polymerized from monomeric pyrrole. Colloidal polypyrrole was prepared by using the method described by DeArmitt and Armes and the nanocomposite prepared by the method outlined by Oriakhi and Lerner.

1.10 Experimental

1.10.1 Characterization Techniques

1.8.1.1 X-ray powder diffraction

X-ray powder diffraction data were collected on a D5000 Siemens powder diffractometer (CuKα radiation) with modified sample holder designed to contain an inert atmosphere at 0.02° 2θ sec⁻¹ between 2 and 70°.
1.8.1.2 Thermal analysis

Thermogravimetric analysis data were obtained using a Shimadzu TGA-50 in flowing air (50mL/min) at 10°C/min.

1.8.1.3 Elemental analysis

Atomic absorption spectroscopy data for Co or Li content in samples were obtained on a Buck Scientific 200 analyzer or a Varian Techtron AA6 atomic absorption spectrophotometer. Standard analytical procedure was used for instrument settings and preparation. Elemental analyses were performed by Desert Analytical (Tucson, AZ).

1.8.2 Electrochemical Measurements

A two compartment cell with a coarse glass frit separator was used for all the electrochemical studies (fig 1.6). Working electrode films, from polypyrrole and polypyrrole-clay nanocomposites dispersions in acetonitrile, were cast on Pt foils and were air-dried for a few hours. The counter electrode used was Pt mesh and the reference electrode was SCE in the case of aqueous electrolytes and Ag/Ag+ for non-aqueous electrolytes. The electrolytes used were NaCl for aqueous studies and lithium perchlorate in propylene carbonate (LiClO₄-PC) and tetrabutyl ammonium perchlorate in propylene carbonate (TBAP-PC) for non-aqueous studies. The concentrations were 1 M solutions in all the cases. The electrode areas were about 0.8-0.9 cm² and the weight loading about 1.8-2.4 mg for the active material. Cells
Figure 1.6 Two-compartment cell employed for electrochemical measurements.
were assembled under dry N₂ and an airtight seal was maintained during the experiment. All electrochemical measurements were carried out using PAR 270 software on an EG&G 372 potentiostat/galvanostat.
1.11 References

1. Guymard, D. and Tarascon, J. *Advanced Materials* 1994, 6, 408


Chapter 2

Intercalation Chemistry of Cobalt and Nickel Dioxides:
A Facile Route to New Compounds Containing Organocations

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(Materials Research Bulletin - in press)
2.1 Abstract.

A simple chemical method is reported for the intercalation of layered nickel or cobalt dioxide with organocations. Compounds containing anilinium, dodecyl-trimethyl-ammonium, octadecyl-trimethyl-ammonium, or distearyl-dimethyl-ammonium cations are obtained by reaction of lithiated hosts with aqueous persulfate, followed by treatment with the desired organocation. Basal-repeat distances for the intercalated products indicate that the arrangements of organocations are similar to those seen with other layered hosts, with bilayers of alkylammonium ions, or a single layer of anilinium, in the pillared galleries. Thermogravimetric and elemental analyses are used to estimate compound stoichiometries, and indicate the partial exchange of organocation for lithium. The anilinium compound contains oligomeric cations, and is unstable when treated with polar solvents. Open circuit measurements indicate that the materials contain Co in an oxidation state of 3+, or higher.

Keywords: A. Layered compounds, A. Oxides, B. Intercalation reactions
2.2 Introduction.

The application of lithium cobalt and nickel oxides towards reversible energy storage has been suggested since the first description of the reversible oxidation and delithiation of LiCoO$_2$ and practical secondary batteries based on this chemistry have been realized in the past few years.

The chemical oxidation of LiCoO$_2$ has been reported using acids, Cl$_2$ or Br$_2$, and other oxidants such as NO$_2^+$ salts or MoF$_6$. When acids are employed, delithiation is accompanied by a partial exchange of Li$^+$ for H$^+$. The cationic intercalants into the cobalt and nickel layer structures have been limited to alkali metals and H$^+$. There have also been relatively few reports of organocation insertion into other layered dioxides, although the incorporation of alkylammonium and other cationic species into birnessite (Na$_4$Mn$_{14}$O$_{26}$·9H$_2$O) has been noted. Given the technological importance of these oxides, it should be useful to establish a broader intercalation chemistry for these hosts.

We report here the intercalation of several organocations within layered CoO$_2$ and NiO$_2$. These compounds are easily derived in a one or two-step reaction under ambient conditions, mainly in aqueous media. Pillared structures including anilinium (basal repeat ~ 12 Å), dodecyldimethylammonium (~ 27 Å), octadecyltrimethylammonium (~ 34 Å), and distearyldimethylammonium (~ 41 Å) between oxide layers are characterized by XRD, thermogravimetric, and elemental analyses.
2.3 Experimental:

2.3.1 Materials and Methods

LiCoO₂ and LiNiO₂ powders were prepared and supplied by Covalent Associates, Inc (Woburn, MA). LiCoO₂ (0.200 g, 2.02 mmole) was stirred in aqueous (NH₄)₂S₂O₈ (1.14 g, 5.00 mmole) for 24 h. In order to prepare the intercalation compound containing anilinium, the amorphous black solid was isolated, washed with water to remove residual persulfate, and air-dried. A solution containing anilinium, prepared by acidification of neat aniline (2 mL, 20 mmole) with conc. HCl to pH ~ 1-2, was reacted with the product (0.21 g). The resulting black intercalation compound was isolated by centrifugation and dried in vacuo at 80 °C for 24 hrs.

The other intercalation compounds were obtained from LiMO₂ in a single step by addition of the organic salt to the persulfate reaction mixture. For example, C₁₂H₂₅N(CH₃)₃Cl (0.944 g, 3.00 mmole) was dissolved into the solution and stirred for 24 hours. The resulting solid was isolated by centrifugation, washed several times with warm water - until no trace of alkylammonium chloride was observed by XRD - and air-dried. Intercalation compounds were prepared using a similar method with C₁₈H₃₇N(CH₃)₃Br (1.18 g, 3.00 mmole) and (C₁₈H₃₇)₂N(CH₃)₂Cl (1.78 g, 3.00 mmole).

The intercalation reactions with LiNiO₂ and products obtained, were similar, although shorter interaction times with persulfate are required. Stirring with excess ammonium persulfate for 24 h. brings about complete dissolution of the nickel oxide.
All reagents were of analytical grade and used without further purification. Distilled, deionized water was used in all preparations.

2.3.2 Characterization

X-ray powder diffraction data were collected on a Siemens D5000 powder diffractometer, using CuKα radiation, at 0.02° 2θ sec⁻¹ between 2 and 60°. Thermogravimetric analyses (TGA) of powdered samples (10 - 20 mg) were carried out at 10 °C / min in flowing air (50 mL / min) using a Shimadzu TGA-50. Lithium contents were determined by atomic absorption spectroscopy using standard methods. CHN analyses were performed at Desert Analytics (Tuscon, AZ). Open circuit potentials were determined using a three-electrode configuration with Li foil counter and reference electrodes in a 1 M LiClO₄ / propylene carbonate electrolyte.

2.4 Results and Discussion

The XRD powder data obtained on solid products (Figure 2.1) show that the (003) peak for LiCoO₂ (2.1a), indicating a basal-repeat spacing of 4.69 Å, disappears after the persulfate reaction. When a 5-fold excess of aqueous ammonium persulfate is employed, the black product shows no diffraction peaks (2.1b), indicating that the stacking coherence dimension has decreased below the detectable limit for XRD (~ 50 Å). SEM of the amorphous, lamellar solid revealed a reduced particle size (approx. 1 - 2 μm). Subsequent treatment with aqueous alkylammonium, or neat anilinium, results in the regeneration of an
Figure 2.1 XRD powder diffraction data of LiCoO$_2$ (a), and products obtained by reaction of LiCoO$_2$ with excess (NH$_4$)$_2$SO$_4$ (b), and subsequent reaction with C$_6$H$_5$NH$_3$Cl (c), C$_{12}$H$_{25}$N(CH$_3$)$_3$Cl (d), or C$_{18}$H$_{37}$N(CH$_3$)$_3$Br (e).
ordered layer structure with intercalated organocations between oxide sheets.

The initial treatment with persulfate is essential in order to incorporate all these organocations: no new products are observed when LiCoO$_2$ is reacted directly with aniline, anilinium, or the aqueous ammonium salts. Reactions with a smaller excess of ammonium persulfate, or with a solution containing the less-soluble potassium persulfate, do not produce an intermediate amorphous phase, but are effective for generating the organocation intercalation compounds. The ion exchange process thus appears to require partial oxidation of the cobalt layers. This might be related to enhanced intercalation kinetics associated with the vacant cationic sites and disordered structure that results from the oxidation. A similar situation arises in the formation of alkylammonium complexes by ion exchange in Li$_x$MS$_2$, which proceeds only when $x < 1$.\textsuperscript{11}

The basal-repeat distances observed for the C$_{12}$H$_{25}$N(CH$_3$)$_3$\textsuperscript{+} (approx. 26.5 Å) and C$_{18}$H$_{37}$N(CH$_3$)$_3$\textsuperscript{+} (approx. 34 Å) are similar to those obtained by incorporation of dodecyl ammonium and octadecylammonium into buserite (27 Å and 32 Å, respectively).\textsuperscript{10} (Table 2.1)

These dimensions suggest a bilayer structure for the intercalated species, with significant overlap of the alkyl chains at the gallery center. The interpenetration of these chains is not surprising in these materials, due to the larger diameter of the substituted trimethylammonium headgroup, as well as the relatively low ratio of organocation to Co. (vide infra). The expansion in the anilinium intercalate (7.6 Å) is somewhat larger than those reported in MoS$_2$ (6.7 Å)\textsuperscript{12} and fluorohectorite (5.3 Å)\textsuperscript{13}, but consistent with the
<table>
<thead>
<tr>
<th>R</th>
<th>M</th>
<th>Basal-repeat</th>
<th>Δd</th>
<th>FWHM (2θ)</th>
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<tr>
<td></td>
<td>Co</td>
<td>4.687</td>
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<td>0.087 (18.9)</td>
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<td>Ni</td>
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<td>C₆H₄NH₃</td>
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<td>7.58</td>
<td>0.139 (7.19)</td>
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<tr>
<td>C₁₂H₂₅N(CH₃)₃</td>
<td>Co</td>
<td>26.54</td>
<td>21.85</td>
<td>0.055 (3.32)</td>
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<tr>
<td></td>
<td>Ni</td>
<td>26.93</td>
<td>22.20</td>
<td>0.082 (3.30)</td>
</tr>
<tr>
<td>C₁₂H₂₅N(CH₃)₃</td>
<td>Co</td>
<td>34.04</td>
<td>29.35</td>
<td>0.068 (2.60)</td>
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<tr>
<td>C₁₈H₃₇N(CH₃)₃</td>
<td>Ni</td>
<td>34.36</td>
<td>29.65</td>
<td>0.081 (2.55)</td>
</tr>
<tr>
<td>(C₁₈H₃₇)₂N(CH₃)₂</td>
<td>Co</td>
<td>41.25</td>
<td>36.56</td>
<td>-</td>
</tr>
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</table>
incorporation of a single layer of intercalate, with conjugated plane perpendicular to the plane of inorganic layers. The sharp (00l) peaks obtained for the intercalation compounds indicate that in each case these consist of coherently stacked arrays with large domain lengths. In contrast, the interaction of the persulfate-treated oxide with symmetrically-substituted alkylammonium species RN₄⁺ (R = methyl to pentyl) does not result in an ordered product.

TGA and elemental analyses, along with the derived compound stoichiometries are provided in Table 2.2.

The amorphous solid obtained by reaction with persulfate contains only a small residue of ammonium ion, but shows delithiation to Li/Co of approximately 0.2. Earlier reports on the oxidation of LiₓCoO₂ also indicate that the material becomes amorphous for x < 0.33.¹ TGA, and H analysis, indicate that this material is a hydrate, with the water content of at least 0.4 H₂O / Co. The high temperature of water loss, combined with the low electrochemical potential, suggest the product contains hydronium species. The alkylammonium intercalates show good correlations between C, H, and N content and weight loss between 250 - 600 °C, with organocation contents of 0.4 - 0.5 / Co in each case. Li analyses give similar ratios, so that these compounds have exchanged about 50 % of Li with organocations. The open circuit potentials are significantly higher than that of the fully lithiated compound, which indicates that Co is partly oxidized and the total cation / Co ratio is somewhat less than 1 for these intercalated products.

As prepared, the anilinium compound contains excess aniline, as evidenced by the weight loss below 200 °C. Attempts to remove the aniline with solvents were unsuccessful, treatment with water, THF, or propylene carbonate all resulted in the dissolution of a purple
### Table 2.2

Elemental and thermogravimetric analyses of intercalation compounds of cobalt dioxide.

<table>
<thead>
<tr>
<th>Weight Percents: Observed and (Calculated)</th>
<th>Stoichiometry</th>
<th>OCV vs Li/Li⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>H</td>
<td>N</td>
</tr>
<tr>
<td>0.19 (0.0)</td>
<td>0.91 (1.1)</td>
<td>0.95 (1.0)</td>
</tr>
<tr>
<td>39.99 (40.0)</td>
<td>8.17 (7.6)</td>
<td>3.22 (3.1)</td>
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<tr>
<td>48.60 (49.0)</td>
<td>9.08 (9.0)</td>
<td>2.88 (2.7)</td>
</tr>
<tr>
<td>48.30 (48.0)</td>
<td>4.22 (5.3)</td>
<td>9.26 (9.2)</td>
</tr>
</tbody>
</table>

a) only 29.6 % loss above 200 °C is ascribed to intercalated anilinium
species (anilinium oligomers or polyaniline) and deintercalation of the organocation. The oxidation of anilinium by the cobalt oxide is not surprising given that the $E_{1/4}$ oxidation potential for anilinium has been reported to be 4.1 V vs Li/Li$^+$ which is close to the OCV recorded for the amorphous product. The open circuit potential of the intercalated product (3.0 V) indicates that all the Co is reduced to 3+ after reaction with excess anilinium chloride.

It seems likely, therefore, that this intercalated species is also oligomeric or polymeric, although this question will require further study. An approximate compound stoichiometry can be derived from the separate weight loss event above 200 °C, and indicates that the polyaniline may not be in a highly-protonated form within the oxide structure.

2.5 Acknowledgment.

K.R., C.O., and M.L. gratefully acknowledge supporting grant DMR-9322071 from the National Science Foundation.
Figure 2.2  Thermogravimetric analyses of LiCoO$_2$ (a), and products obtained by reaction of LiCoO$_2$ with excess (NH$_4$)$_2$S$_2$O$_8$ (b), and subsequent reaction with C$_{12}$H$_{25}$N(CH$_3$)$_3$Cl (c), C$_{16}$H$_{33}$N(CH$_3$)$_3$Br (d), C$_6$H$_5$NH$_3$Cl (e), or (C$_{13}$H$_{37}$)$_2$N(CH$_3$)$_2$Cl (f). Data were collected at 10 °C / min in flowing air.
2.6 References.


Chapter 3

Electrochemical Characterization of chemically synthesized Polypyrrole and Polypyrrole/Clay nanocomposite.

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(To be Submitted)
3.1 Abstract

Polypyrrole is known to be intercalated into layered host lattices both by \textit{in situ} polymerization and by latex-colloid interaction methods. Here, we report the behavior of the chemically synthesized polypyrrole and the polypyrrole/clay nanocomposite as electrode material. The electroanalytical techniques used in this characterization, cyclic voltammetry and chronopotentiometry, confirm the distinct electrochemical behavior of the polymer and the nanocomposite. The as formed polymer exhibits normal electrochemical behavior with redox peaks at reported potentials whereas the intercalated polymer exhibits a redox potential shifted negative by 1 V. This may be attributed to be due to the electron-donating effect of the negatively-charged aluminosilicate sheets within which the polymer has been intercalated. Cyclic voltammetric studies of the nanocomposite showed no evidence of the redox peaks at the normal potentials of the pure polymer (at -200mV and -500mV vs Ag/Ag+) but well-defined redox peaks were observed at much negative potentials of -1200mV and -1500 mV (vs Ag/Ag+). The distinct electrochemical behavior was confirmed by chronopotentiometry. The conducting polymer-clay composite shows promise for both coatings and electrochemical capacitor applications.
3.2 Introduction

Polypyrrole has been widely studied for its high conductivity, stability in oxidized form, and the ability to be electrochemically switched between the conducting and insulating states.\textsuperscript{1-5} A great deal of work has been directed towards the electrochemical and chemical preparation of a number of polypyrroles with controllable electrical, electrochemical and catalytic properties.\textsuperscript{3-7} One of the most interesting aspects of polypyrrole, and that of other conducting polymers, is the coupling of electron transfer reaction and exchange of counter ions during the electrochemical oxidation and reduction process of the polymer. For polypyrrole, the process can be described as

\[
[ \text{ppy}^+ \text{A}^- ] + e^- \leftrightarrow [ \text{ppy} ] + \text{A}^-
\]

There has been limited information in the literature on the electrochemistry of polymer intercalated nanocomposites. A survey of the literature\textsuperscript{8-13} revealed that most of the electrochemical investigations are mainly restricted to both the chemically and electrochemically synthesized polymer and derivatives of the polymer. Electropolymerization of aniline intercalated in clay sheets and electrical characterization of PEO intercalated in MoO\textsubscript{3} are the only reports available on the electrochemistry of polymer nanocomposites. Polypyrrole may be chemically prepared by a very simple one step oxidation of the monomer by a strong oxidant, such as ammonium persulfate or potassium persulfate, in aqueous solutions\textsuperscript{14,15}. This chemically synthesized polypyrrole is a black and conducting powder which has properties similar to those of the electrochemically synthesized polymer\textsuperscript{16}. 
Conducting polymers possess the advantage of potentially low materials cost. It has been reported that electrodes of relatively simple conducting polymers, such as polypyrrole, polyaniline and polythiophene, can be fabricated at a cost comparable with that of carbon capacitor electrodes and much lower than that of noble metal oxide electrodes like RuO$_2$. Although, the charge and energy densities observed for the noble metal oxides are slightly higher than those obtained at conducting polymer electrodes, it is the combination of low materials cost and high energy density that makes conducting polymers attractive potential active materials for use in electrochemical capacitors.

The electrochemical p-doping (oxidation) of conducting polymers take place by oxidation of the polymer backbone and concurrent incorporation of a anion from solution to counterbalance the positive electronic charge. (Fig. 3.1) The electrochemical n-doping (reduction) of conducting polymers proceeds by an opposite reaction. Electrons are delocalized along the polymer backbone, and cations enter the polymer from the solution phase in order to maintain overall charge neutrality. Most conducting polymers can be reversibly p-doped, and this reaction generally take place at electrode potentials that are accessible in aqueous solutions. Conversely, only a limited number of conducting polymers can be reversibly n-doped, all at reducing electrode potentials which require cathodically stable and relatively pure non-aqueous systems. The reliance on p-doping/undoping alone in a single type of active material limits the overall voltage window of a device to about 1V. For this reason, various efforts are being pursued for other configurations of capacitors based on conducting polymer active materials, which would provide an increased voltage window,
Figure 3.1  Schematic representation of the charging and discharging processes at conducting polymer electrodes associated with (a) p-doping and (b) n-doping.
and hence an increased energy density. A number of configurations have been explored so far but only a few have been found to be of potential interest.

It is the aim of the present investigations to expand the polypyrrole system, study the electrochemical behavior of the polypyrrole-clay nanocomposite and compare with that of pure polypyrrole using different electrochemical techniques.

Electrochemical investigations on chemically synthesized polypyrrole and electrochemically prepared polypyrrole have been described previously. The redox potentials in each case are reported to be similar with the anodic peak near -200 mV and the cathodic peak at -500 mV vs Ag/Ag⁺.

The redox potentials of the polymers is modified by the addition of either an electron withdrawing or electron donating functional group on the pyrrole ring prior to polymerization. The functionalization of polymer with electron withdrawing groups like Cl₂, Br₂ or I₂ shift the redox potentials more positive to +800 mV (vs Ag/Ag⁺). Alternatively, when the polymer is functionalized with an electron donating group like CH₃ or C₂H₅, the redox peaks are shifted negative as compared to the pure polymer. This shift in the peak oxidation potentials of the series of substituted pyrrole and thiophenes are dependent on three parameters: namely, their polar, steric and mesomeric effects, which are exerted by the substituents and is described by the Hammett-Taft equation:

\[ E = \rho_\pi \sigma + S \]
\[ \rho_\pi \sigma = \text{polar-mesomeric parameters} \]
\[ S = \text{steric factor} \]

The mesomeric effect, which occurs in conjugated systems with \( \pi-\pi \) or \( p-\pi \) overlap, expresses the influence of a substituent on the movement of an electron pair. Since the
substituent constant $\rho_T$ has a positive sign in the equation, higher the electrophillicity of the substituent, more the difficulty in oxidizing the monomer. The less the electronegative the monomer, the more easily it is oxidized. This can be identified with the incorporation of the polymer in an electron-rich environment, like aluminosilicate sheets. The negatively charged clay sheets function as highly nucleophilic substituent on the monomer ring.

X-ray diffraction of polypyrrole/clay provide a basal repeat distance of 15.1 Å, the distance between clay sheets, 5.5 Å is greater than in anhydrous Na-montmorillonite has already been reported$^{35,39}$. An expansion of 5-6 Å is suggestive of an edge-on orientation of the polymer conjugated plane to clay basal surface (fig 3.2). The negatively charged clay sheets thus tend to behave like an electron-donating group on the monomer ring and appear to make the polymer more easy to oxidize. The research stems from an expectation that some of the electrochemical and catalytic properties of exchangeable clays can be coupled with the electrochemical and electronic properties of conducting polymers.

Polypyrrole has been intercalated into clay by the following two methods. The first by the intercalation of a monomeric precursor followed by in situ polymerization within the host$^{35-38}$ and the other by latex-colloid interaction$^{39}$. In the former route, reaction of clay with excess pyrrole yields an intercalated layered material with an expanded d-spacing. The intercalated pyrrole is then polymerized inside the clay sheets by addition of suitable oxidant.

In the present paper, the polymer/clay nanocomposite has been synthesized by the latter route, latex-colloid interaction. Electrochemical studies on these materials include running cyclic voltammetry and chronopotentiometry. The systematic study of each cell, both for the polymer and the nanocomposite, by cyclic voltammetry and chronopotentiometry techniques
Figure 3.2  Schematic illustrating the orientation of polypyrrole in Na-montmorillonite
(Top) Polypyrrole (Bottom) polypyrrole intercalated in Clay
were employed in correlating the distinct electrochemical behavior of the polymer and the nanocomposite.

3.3 Experimental

3.3.1 Synthesis.

Preparation of Polymer Latexes: Colloidal polypyrrole was prepared using the method described by DeArmitt and Armes\textsuperscript{40}. Sodium dodecylbenzenesulfonate (SDBS, 10.0 g, Aldrich, technical grade) and ammonium persulfate (7.85 g, Aldrich, 98\%) were codissolved in 200 mL of deionized water at room temperature to give a turbid solution. Pyrrole (2.0 mL, Aldrich, 99\%) was injected quickly via syringe into the reaction vessel. The solution was stirred for several hours and the resulting black, viscous colloidal dispersion was centrifuged to produce a black solid. This black solid was redispersed in deionized water by mechanical stirring and was stripped of the residual SDBS, persulfate and other soluble components via repeated centrifugation and redispersal in deionized water.

Preparation of Polymer/Clay Nanocomposites: The nanocomposite was synthesized as follows: 1 g of Na-montmorillonite (SW\textsubscript{y}-1, Source Clay Repository) was purified\textsuperscript{41}, exfoliated in water and then stirred with the above prepared polymer (20 mL solution, 1 mL containing 0.01 g of polymer). Upon mixture of these solutions, nanocomposite particles flocculate from the solution within 1-2 hours. The mixture was typically stirred for 12-24 h, and nanocomposite isolated by centrifuging, washing and drying for at least 24 hours \textit{in vacuo}.
3.3.2 Characterization

Experiments aimed at evaluating the electrochemical behavior of the conducting polymer and the nanocomposite materials were performed in an electrochemical cell of the design described in figure 3.3. The two-compartment cells were assembled under dry N₂ and airtight seal maintained throughout the experiment. Working electrodes were fabricated by coating 50 μm thick films of the pure polypyrrole or polypyrrole-clay from a dispersion in acetonitrile, onto well polished, smooth Pt foils connected to Pt wires. Active electrode area varied between 0.75 cm² to 0.96 cm² and the weight loading was between 1.8 mg to 2.5 mg of the active material. Electrochemical measurements were done after the films were air-dried overnight to remove residual CH₃CN. XRD analysis of the films confirmed that the sheet structure of the starting materials was not affected. The counter electrodes for both the cyclic voltammetry and cycling experiments were Pt mesh. Standard Calomel electrode (SCE) was used for aqueous electrolytes. Due to the stability limitations of aqueous solutions, non-aqueous electrolytes systems were investigated in order to study the electrochemical activity of the nanocomposite over a wider voltage window. In the case of non-aqueous electrolytes, the reference electrode was made up of a silver wire immersed in 0.01M AgNO₃. A 1M NaCl (Mallinckrodt, 99.7%) was used as electrolyte for aqueous studies and 1M LiClO₄ in propylene carbonate (PC, Aldrich, 99.9% and purged with N₂) and 1M tetra butyl ammonium perchlorate (TBAP, Fluka, 99.99% electrochemical grade) in PC were used as electrolytes for non-aqueous studies.
Reference electrode

Glass cell
Electrolyte
Working electrode

Vicor plug
Glass frit
Counter electrode

Figure 3.3 Two-compartment cell used for electrochemical measurements
Cyclic Voltammetry: Cyclic Voltammetry was performed with a PAR 173 potentiostat under computer control. The scan rates employed were typically 20-200mV/s. The voltage window examined depended on the electrolyte used; the voltage window was limited between -800mV to +400mV vs SCE for aqueous electrolyte and between -2000mV and +400mV vs Ag/Ag+ for non-aqueous solutions. The voltage window upper limit was +400mV vs Ag/Ag+ in both the cyclic voltammetry and cycling experiments as polymer degradation occurs above this potential. Within the potential range examined, polypyrrole can be cycled several times without degradation.

Chronopotentiometry: Charge-Discharge cycles were performed, using same instrumentation under galvanostatic conditions: a current of 50 µA for the pure polymer films and 10 µA for the nanocomposite films was used. Samples were cycled 5 times between the charged and discharged state. Experimental values of faradaic charge stored, energy densities and values of number of monomer repeat units are calculated.

3.4 Results and Discussion.

Cyclic Voltammetry: Cyclic voltammetry provides both qualitative and quantitative information on electrode processes. A reversible, diffusion-controlled reaction exhibits an approximately symmetrical pair of current peaks. In order to determine the parameters for this technique, we have followed the evolution of the voltammograms with the scanning speed (fig 3.4). The available cyclic voltammetry data for the chemically synthesized polypyrrole and the clay nanocomposite in the different electrolytes are compared in Table 3.1. With the exception of peak current values, the reduction and oxidation potentials of the pure polymer...
Figure 3.4  Plot of scan rate, \( v^{1/2} (\text{mV/s})^{1/2} \) vs peak current, \( i_\text{p} \) (mA)
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<th>( v ) (mV/s)</th>
<th>( i_p ) (mA)</th>
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<th>( E_a - E_c )</th>
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Table 3.1  Summary of Cyclic Voltammetry data for Polypyrrole and Polypyrrole/Clay in 1M NaCl, 1M LiClO4/PC and 1M TBAP/PC at different scan rates.
are identical in the different electrolytes. In fig 3.5, typical voltammograms of chemically synthesized polypyrrole and the nanocomposites in 1M NaCl is reported. Well defined reduction and oxidation peaks for the polymer films are observed with $V_{p,n} = -320$ mV and $V_{p,c} = -500$ mV (vs SCE). In contrast, the nanocomposite film displays no peaks in this voltage range and $H_2$ evolution occurs at more negative potentials which is confirmed by a similar behavior in the case of running a blank Pt foil in the same electrolyte.

Fig. 3.6 shows typical voltammograms of the polymer and the nanocomposite in 1M LiClO$_4$/PC. The redox peaks of the polymer are well formed in the characteristics potentials as reported by others$^{17,18}$. The oxidation peak appears at -280mV and the reduction peak at -490mV vs Ag/Ag$. The most striking feature of the voltammogram is that the nanocomposite does not exhibit any electrochemical activity at the normal peak potentials of the pure polymer, but well defined redox peaks are observed at more negative potentials. The anodic peak is observed at -1100mV and the cathodic peak at -1450mV. Table 3.1 compares the redox potentials and the peaks currents for the polymer and the nanocomposite in different electrolytes.

A control experiment, using a film obtained from a physical mixture of polypyrrole and clay, and not the nanocomposite (which was confirmed by XRD), as the working electrode was run to verify that the redox peaks were due to the polymer intercalated in montmorillonite. Fig 3.7 shows the voltammogram for the polymer-clay mix. The redox peaks observed are similar to those obtained for the pure polymer and not for the nanocomposite. The peaks are much broader and reduced in the intensity of peak currents because the polymer surface is not fully accessible to the solvent. It supplements the earlier results that
Figure 3.5  Cyclic voltammogram for (a) polypyrrole and (b) polypyrrole/clay nanocomposite films in 1M NaCl. (scan rate 100 mV/s)
Figure 3.6  Cyclic voltammogram for (a) polypyrrole and (b) polypyrrole/clay nanocomposite films in 1M LiClO$_4$. (scan rate 100 mV/s; 1st, 2nd and 5th cycles)
Figure 3.7  Cyclic voltammogram for polypyrrole-clay mix film in 1M LiClO$_4$
(scan rate 100 mV/s, 1st, 2nd and 5th cycles)
the redox potential of the polymer has been shifted due to its presence inside clay sheets and not on the surface. Intercalation, thus appears to result in the polymer becoming more resistant to reduction with a corresponding negative shift in the reduction potential.

Voltammetric scans in 1M Tetra butyl ammonium perchlorate (TBAP)/PC (fig 3.8) show broader and less intense as compared to those in 1M LiClO₄, although the peak positions were at the same potentials for both the cathodic and anodic scans.

**Chronopotentiometry**: The results of cyclic voltammetry reveals the essentialness for the understanding of the chronopotentiometry experiments. The experimental values of \( Q_F \) (amount of faradaic charge stored), \( E \) (the energy density) and \( n \) (number of monomer repeat units) are calculated from Fig. 3.9 and 3.10 and are listed in Table 3.2. \( Q_F \) varies between 1.02 C to 1.29 C, \( E \) varies between 134 to 170 Ah/kg, and \( n \) values range between 2.5 to 2.9 in the case of the pure polymer. The values for the nanocomposite, which contain 20 % by weight of the polymer, are calculated per kilogram weight of the polymer (active material in the electrode). The values, based on the amount of active material, are in agreement with expected values if all the intercalated polymer are involved in the redox process.

Novak et al (1987) \(^4\) and Mermilliod et al (1986)\(^6\) reported \( n \) values of 2.5 to 2.9 correspond to energy density values between 162 Ah/g and 140 Ah/kg. The experimental values, calculated from the curves in fig. 3.9 and 3.10, range between 2.4 and 2.9 and correspond to calculated energy density values of 143 Ah/kg to 169 Ah/kg. These values are in good agreement with the reported values.
Figure 3.8  Cyclic voltammogram for (a) polypyrrole and (b) polypyrrole/clay nanocomposite films in 1M tetrabutyl ammonium perchlorate (scan rate 100 mV/s, 1st, 2nd and 5th cycles)
Table 3.2

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<th>Experimental</th>
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<th>Energy Density (Ah/kg of ppy)</th>
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Table 3.2 Charge-Discharge characteristics for Polypyrrole and Polypyrrole/Clay.
Figure 3.9 Charge-Discharge characteristics for polypyrrole film in 1M LiClO$_4$/PC
Figure 3.10 Charge-Discharge characteristics for polypyrrole/clay film in 1M LiClO₄/PC
The charge and discharge curves for the first two cycles are shown. The charge stored in the second cycle is slightly less than the first, 159 Ah/kg for the second cycle as compared to 169 Ah/kg in the first. In the case of the nanocomposite, calculated values for the successive cycles are comparatively much lesser than the first as indicated in Table 3.2.

Galvanostatic charge/discharge cycles in 1M TBAP/PC for the polymer and the nanocomposite, as shown in figures 3.11 and 3.12 respectively, confirm the reproducibility in different electrolytes. The calculated values for the charge stored, energy density and n, agree well with those for the LiClO4/PC.

This supports our proposed mechanism for the oxidation of the intercalated and non-intercalated polymer. The oxidation of the pure polymer agrees well with other reported values both in terms of the redox potentials and the energy densities. The proposed mechanism of oxidation of the polymer, hence is described as:

\[ \text{Ppy} + \text{An}^{-} \rightleftharpoons \text{Ppy}^{+} \text{An}^{-} + \text{e}^{-} \]

Since the behavior of the intercalated polymer is similar in the different electrolytes under study, LiClO4 and TBAP, we infer that the redox process is not dependent on the cation and is directly related to the anion and the polymer. It appears that the oxidation of the intercalated polymer is similar to that of the pure polymer but inside the negatively charged aluminosilicate sheets.
Figure 3.11 Charge-Discharge characteristics for polypyrrole film in 1M tetrabutylammonium perchlorate
Figure 3.12 Charge-Discharge characteristics for polypyrrole/clay film in 1M tetrabutly ammonium perchlorate
3.5 Conclusion

The above results indicate that conducting polymer-clay nanocomposites do possess many characteristics of both the polymer and the clay host. A thin film of polypyrrole-clay appears suitable for use as an alternate cathode in an electrochemical capacitor. The redox potential of the composite has been shifted by a 1 V negative. This indicates that the field of study can be extended to similar compounds like polythiophene/clay and polythiophene/LDH. Although the electrochemical capacity is lower than that of the pure polymer, long-term behavior of the cells is much better in the case of the nanocomposite. The low-cost of this material coupled with ease of preparation can give rise to interest as electrodes in electrochemical capacitors.

3.6 Acknowledgments

The authors gratefully acknowledge supporting grant DMR-9322071 from the National Science Foundation.
3.7 References


Purification to remove the major portion of colloidal impurities such as quartz and feldspar was achieved by dissolving clay (15 g) in 1 liter of deionized water and allowing it to stand for several hours. The suspension was decanted and the sediment discarded. This procedure was repeated. Homoionic Na-montmorillonite was prepared by stirring an aqueous suspension of the clay with 0.5 M NaCl solution for several days. The clay was washed repeatedly with deionized water until free of chloride then freeze-dried. The product was further vacuum-dried at 200 °C for few hours. X-ray diffraction confirmed that the clay was in the sodium form (basal repeat = 9.6 Å).

Sample calculation for faradaic charge stored and energy density.

\[ m = 2.11 \text{ mg} \; \text{number of moles of ppy} = \frac{0.0021 \text{ g}}{65 \text{ g/mol}} = 30.46 \mu \text{mol} \]

\[ \text{time} \times \text{t under the plateau region} = 25750 \text{s} \; \text{current} = 50 \times 10^{-6} \text{ A} \]

Charge, \( Q_F = I \times t = (50 \times 10^{-6} \text{ A}) \times (27500 \text{s}) = 1.29 \text{ C} \]

Energy Density = \( \frac{Q_F}{\text{weight}} = \frac{1.25 \text{ As}}{(2.11 \times 10^{-6} \text{ kg} \times 3600 \text{ s/h})} = 169 \text{ Ah/kg} \)
Chapter 4

4 Summary

This thesis described the synthetic routes towards intercalation chemistry of transition metal oxides and the electrochemical techniques employed to characterize chemically synthesized polymer and polymer/clay nanocomposite. Newer compounds have been synthesized in the former case and electrochemistry of polypyrrole has been extended for its nanocomposites in the latter.

A simple chemical method is reported for the intercalation of organocations in layered nickel or cobalt dioxide. Earlier studies were restricted to intercalation of alkali metal cations and water. Compounds containing anilinium, dodecytrimethylammonium, octadecyltrimethylammonium, or distearyldimethylammonium cations are obtained by direct reaction of lithiated CoO₂ and NiO₂ hosts with aqueous ammonium persulfate, followed by treatment with the desired organocation. Basal-repeat distances, obtained from the x-ray data, for the intercalated products indicate that the arrangements of organocations are similar to those seen with other layered hosts, with bilayers of alkylammonium ions, or a single layer of anilinium, in the pillared galleries. Thermogravimetric and elemental analyses are used to estimate compound stoichiometries, and indicate the partial exchange of organocation for lithium. The anilinium compound contains oligomeric cations, and is unstable when treated with polar solvents. Open circuit measurements indicate that the materials contain Co in an oxidation state of 3+, or higher.
The behaviour of the chemically synthesized polypyrrole and the polypyrrole/clay nanocomposite as electrode material has been reported. Polypyrrole is known to be intercalated into layered host lattices both by in situ polymerization and by latex-colloid interaction methods. The electrochemical techniques used in this characterization, cyclic voltammetry and chronopotentiometry, confirm the distinct electrochemical behaviour of the polymer and the nanocomposite. The as formed polymer exhibits normal electrochemical behaviour with redox peaks at reported potentials whereas the intercalated polymer exhibits a redox potential shifted negative by 1 V. This may be attributed to be due to the electron-donating effect of the negatively-charged aluminosilicate sheets within which the polymer has been intercalated. Cyclic voltammetric studies of the nanocomposite showed no evidence of the redox peaks at the normal potentials of the pure polymer (at -200 mV and -500 mV vs Ag/Ag+) but well-defined redox peaks were observed at much negative potentials of -1200 mV and -1500 mV (vs Ag/Ag+). The distinct electrochemical behaviour was confirmed by chronopotentiometry. Further studies are necessary to characterize the application properties of the composite material in coatings and electrochemical capacitors. Also, electrochemical characterization should be extended to similar compounds like polythiophene/clay and conducting polymer/layered double hydroxides.
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