Composite Polymer Positive Electrodes in Solid-State Lithium Secondary Batteries

Petr Novák

J. Heyrovsky Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, CS — 102 00 Prague 10, Czechoslovakia

Olle Inganäs and Robert Bjorklund

Laboratory of Applied Physics, IFM, University of Linköping, S-581 83 Linköping, Sweden

ABSTRACT

We have developed composite polymer electrodes for use in all solid-state batteries in combination with Li. The composite is formed from water soluble polypyrrole which is combined with the solid polymer electrolyte polyethylene oxide. The composite electrode shows enhanced coulombic capacity as compared to an electrode composed only of the electroactive material, polypyrrole. Coulombic efficiency is good (90-95%) and energy efficiency is acceptable (80-85%) in galvanostatic studies. Charge retention is rather poor due to self-discharge. We have obtained proof that the electroactivity is due to polypyrrole, through the use of in situ spectroelectrochemical studies. We have characterized the composite electrode using scanning electron microscopy and conductivity measurements, and conclude that the composite material consists of very small globules of electroactive material in a matrix of polyethylene oxide. Based on these results we argue that solid solutions of electroactive polymers in polymeric electrolytes offer interesting alternatives for solid-state batteries.

The application of organic electroactive polymers in secondary batteries has been widely studied since the first report (1) on these materials. Polycetylene is so far the most studied material, but other polymers like polyparaphenylene (2), polypyrrole (3), and polythiophene (4) are also under investigation for their applicability in energy storage.

Some of the major problems found in these systems are due to the difficulty of finding organic solvents that will be stable in combination with polymer positive electrodes and lithium negative electrodes. Other problems are a high rate of self-discharge and poor chemical stability under extended cycling (5). While the gravimetric energy density of these batteries is promising, the volumetric densities are of course much poorer. Both the gravimetric and volumetric densities are nonetheless partly wasted on the necessary separators that account for a major fraction of the weight and especially volume of the cells.

Several of these difficulties could possibly be solved by the use of solid polymer electrolytes (6). These ion conducting polymers, including polyethylene oxide (PEO), polypropylene oxide (PPO), and others are currently under investigation for use in secondary batteries based on a lithium negative electrode and different positive inorganic intercalation materials (7). The wide stability window of the polymer electrolytes suggests that some of the problems found in polymer electrode batteries could be solved by substituting a polymer electrolyte for the organic electrolyte. The preparation of the electrolyte gives a very thin film, which also serves as a separator, reducing the weight due to inactive structural materials.

Studies of the application of PEO in combination with electronically conductive, electroactive polymers have been reported by Chiang (8), who studied an all polymer battery using polycetylene both for the positive and negative electrode, with a PEO based electrolyte. Poor interpenetration of the two classes of polymers limited the performance of this structure.

Now that soluble electroactive polymers are available (9), we expect to be able to construct composite electrodes consisting of both electroactive polymers and solid polymer electrolytes. This should increase the interface area between the two phases, and thus enable us to obtain better performance. We decided to study composite electrodes formed from solutions of polypyrrole and polyethylene oxide, and obtained promising results.

Experimental

Colloidal solutions of polypyrrole were prepared by chemically oxidizing pyrrole monomer with FeCl₃ · 6H₂O in aqueous solutions of methyl cellulose and hydroxypropyl cellulose. The celluloses were dissolved in H₂O by standard techniques (10) and 1.25g FeCl₃ · 6H₂O were dissolved in 50 ml H₂O containing 0.04g cellulose. Pyrrole monomer was added slowly (0.25 m) and the solution was stirred for 5h. The product was washed by raising the temperature to 70°C so that the cellulose gelled (10) and the FeCl₃ solution could be decanted. After washing several times with hot water the product was redissolved in cold water and its polypyrrole concentration determined by visible absorption at 800 nm. Chemical analysis of the polypyrrole/methyl cellulose composite (methyl cellulose Mw 95,000, degree of substitution about 2) gave the following composition: calculated for (C₉H₇N₂O₅) (C₉H₅N)₉· Cl₃ · 0₆· C₉H₈O· 0₃· 0· 25· 8· FeCl₃· 6H₂O: C 52.98; H 4.13; N 12.58; Cl 6.36; O 23.94. Found: C 53.00; H 4.15; N 12.58; Cl 6.36; O 23.94; 0· 25· 8· FeCl₃· 6H₂O: C 52.86. The method of preparation of the composite polypyrrole (PPy)-polyethylene oxide (PEO) electrode was as follows: Polypyrrole oxide (BDH Chemical, Mw = 600,000) was dissolved in the aqueous solution of LiClO₄ (Ventron) at room temperature using magnetic stirring. The concentration used was 0.2 weight percent (w/o) and the molar ratio between salt and polymer was 1:8 (PEO₉, LiClO₄). This solution was mixed with the water solution of PPy in a desired ratio. The resulting mixture was used to form films by simple casting onto glass slides (for conductivity measurements), stainless steel coins (for electrochemical measurements and scanning electron microscopy), or indium tin oxide (ITO) conducting glass slides (for optical measurements). The water was allowed to evaporate in the atmosphere at room temperature. After that the sample was transferred to the glove box with a dry argon atmosphere and left there to dry at least overnight. Different ratios between PPy and PEO used in this study are listed in Table I.

The polyethylene oxide based solid electrolyte [composition (PEO₉, LiClO₄)] was prepared inside the glove box by casting the dry weight percent (w/o) solu-
tion of the solid electrolyte in acetonitrile (Merck) onto a PTFE plate. The solvent was allowed to evaporate to the box atmosphere at 25°C. The resulting film, ca. 100 μm thick, was allowed to dry at least one week in the dry argon environment of the glove box.

Electrochemical tests were performed using a hermetically sealed two-electrode arrangement. The freshly scraped lithium metal was pressed into a stainless steel die. The circular lithium surface was covered with two sheets of the solid electrolyte. The composite PPY-PEO electrode (geometric area 1.77 cm$^2$) on a stainless steel supporting coin was attached to the top of the structure (Fig. 1). The electrode assembly, spring loaded with ca. 1 kg/cm$^2$, was hermetically sealed and taken out from the glove box to perform electrochemical measurements.

All electrochemical measurements were done at 85°C using a Wenking PGS-81 Potenti-Galvano-Scan coupled with EG & G PARC Model 175 Universal Programmer or home built A/D-D/A interface with a Commodore 3008 computer. Curves were registered with a Watanabe WX 4401 recorder. In situ optical measurements at 85°C were performed using a Perkin-Elmer Lambda 9 Spectrophotometer. The epoxy-sealed electrochemical cell was constructed using an Alessi Industries four-point probe. Thickness was measured using a Dektak 3030 profilometer. SEM pictures were taken using a Cambridge Stereoscan microscope.

**Results and Discussion**

**Characterization.** The microstructures of both forms of PEO-PPy, based on the methyl cellulose and the hydroxypropyl cellulose, are similar as shown by scanning electron microscopy pictures (Fig. 2a, b). Small globules of approximately 200 nm diam can be observed in both materials. These are due to polypyrrole. In between these particles, which form an interconnected net-work giving electronic conductivity, we expect to find the ionically conducting polymer. We could not observe any heterogeneity of the material by optical microscopy. Furthermore, the use of polarizing light microscopy revealed that the material has no optical activity. As PEO as such is optically active, this result shows that the interpenetration is very efficient, and a major reorganization of PEO has occurred.

**Conductivity.**—The electronic conductivity of the composite material was measured at various levels of loading with polymer electrolyte. Four-point probe dc methods were used. At higher loadings of PEO, where a contribution of the ionic conductivity in the form of rapidly decaying currents was present, we waited for the steady state before registering data. The resulting conductivity/composition curve is given in Fig. 3. We see that the conductivity is not appreciably decreased at loadings below 40% of PEO. This is true both for hydroxypropyl cellulose polymerized polypyrrole as well as the methyl cellulose based material, but the absolute conductivity of the latter is two orders of magnitude higher. The conductivity of both types of polypyrrole is high enough for use as thick electrodes in batteries, without extra additives such as acetylene black for improving electronic conductivity.

**Electrochemical measurements.**—For the evaluation of coulombic efficiency of our composites we chose the galvanostatic method. From the preliminary experiments we deduced the potential limits 3.10 and 2.20V (vs. Li/Li$^+$. ) for cycling experiments. Above 3.10V slow degradation of the composite material occurs; it is possible to withdraw more capacity from the battery, but the cycle life of the electrode is decreased. Below 2.20V irreversible degradation of polypyrrole occurs, too. The nature of both the anodic and the cathodic degradation processes outside our 2.20-3.10V interval is not clear at present.

It is known that polypyrrole produced through electrochemical polymerization is not stable when extending the electrode potential beyond 0.5V vs. SCE (11). This degradation process may be similar to the one we induce when extending the potential of our material beyond 3.1V vs. Li, equivalent to ca. 0.14V vs. SCE. As the potential for the degradation process is quite different in the polymer electrolyte and the liquid electrolyte, we

<table>
<thead>
<tr>
<th>Additive</th>
<th>w/o PPy</th>
<th>w/o PEO</th>
</tr>
</thead>
<tbody>
<tr>
<td>A Hydroxypropyl cellulose</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>B Hydroxypropyl cellulose</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>C Methyl cellulose</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>D Methyl cellulose</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>E Methyl cellulose</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>F Methyl cellulose</td>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td>G Methyl cellulose</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>H Methyl cellulose</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

**Table I. Composition of different PPY-P(EO)$_8$·LiClO$_4$ composites**

![Fig. 1. The structure of the Li(P(EO)$_8$·LiClO$_4$)PPy + P(EO)$_8$·LiClO$_4$, composite cell.](image)

![Fig. 2 SEM pictures of (a, left) composite B and (b, right) composite F](image)
cannot identify them with each other. But we observe the redox potential of our material, as identified from poorly resolved peaks in the cyclic voltammogram shown in Fig. 4, to be located at 2.8 ± 0.1 V vs. Li which is equivalent to ca. −0.5 V vs. SCE. This is much lower than the redox potential found for electrochemically synthesized polypyrrole in organic electrolytes, at −0.2 V vs. SCE approximately (12). It must be noted that the temperature of our cell is 85°C, while most studies in liquid electrolytes are performed at room temperature, and therefore the comparison of redox potentials and degradation mechanisms is not straightforward.

The graphs in Fig. 5 show the coulombic capacity of our composite material as a function of the cycle number. (The current used was ±50 μA.) It is clear that the addition of PEO-based solid electrolyte increased the coulombic capacity noticeably (ca. five times for the composite with 30% PEO). The PPy utilization during first 30 cycles is between 40 and 25% of the theoretical capacity (based on 0.25 electrons per pyrrole ring) with a slight tendency to decrease during cycling. The coulombic efficiency during cycling is ca. 90%, the energy efficiency of the charge-discharge cycles is ca. 80%, and the mean discharge voltage of our Li/PPy cell is 2.45 V. If the cell is charged/discharged with ±20 μA, the accessible coulombic capacity is ca. 50% higher. The maximal coulombic capacity is reached using potentiostatic charging.

The decrease of the capacity during the first cycles may be correlated to the equilibration of Cl⁻ and ClO₄⁻ anions. As synthesized, the polypyrrole contains Cl⁻ anions, but these diffuse into the electrolyte during cycling. This process may also be reflected in the changes of voltammograms recorded for the first cycle and the one hundredth cycle (Fig. 4).

The cycle life of our composite material is remarkable. With composite B (Table I) we reached 170 cycles before the capacity was 60% of the original one. Using a very thin electrode giving 3.4 mC during first cycles we got 2.8 mC after cycle 700 using current ±50 μA and potential limits 2.20 and 3.10 V (13).

To obtain a better understanding of the system we studied the sources of polarization in our Li/PEO/PPy battery. We used the current interruption method to distinguish the source of polarization; both the ohmic potential drop and activation overpotential are negligible because the potential change was less than 20 mV after 1 s after current interruption (current 50 μA). Therefore, we performed some potentiostatic step measurements to investigate the role of diffusion. Figure 6 shows typical Cottrell plots of a thin PPy-PEO composite electrode. It is clear that the composite electrode is able to deliver current densities up to 500 μA/cm². The linear relationship between current and reciprocal square root of time indicates a rather pure diffusion limitation with diffusion time ca. 100 s. From the diffusion length ca. 100 nm (from SEM pictures) we can expect the diffusion coefficient of the order 10⁻¹² cm²/s. Because the diffusion coefficient of inorganic species in PEO is 10⁻⁷ cm²/s (14) we conclude that the diffusion limitation is in the polypyrrole particles (diffusion of ClO₄⁻ and/or Cl⁻ anions during doping/undoping of polypyrrole). The Cl⁻ anions are those incorporated into PPy during preparation of the material.

The self-discharge of this kind of battery is rapid. Charge is lost after only a few hours of waiting at open circuit between charge and discharge cycles. In one case we observed 50% to be lost over 4 h (in the case of a thick pellet), and total loss to occur over one day. The battery can then once more be recharged, with no loss of capacity.

The cause of self-discharge is not known. It has been observed that low self-discharge can be obtained when working with ultrapure electrolytes in combinations with polyanion electrodes (5). Self-discharge may thus be correlated to the chemical purity of the electro-
lyte. If this would be true also in our case, the first culprit would probably be water. We have no experimental evidence for this hypothesis at present. Actually, we find that one night of drying in a glove box (less than 10 ppm) to the spectrum of a polypyrrole electrode in liquid electrolyte when compensating for the presence of PEO shown in Fig. 7. The character of the spectrum is similar to that of the spectrum of a polypyrrole electrode in liquid electrolyte matrix. The difference is probably mainly due to the thickness of a polymer film as the characteristic length of diffusion, while we use the dimensions of the much smaller polypyrrole globules in the polymer electrolyte matrix. The difference is probably mainly due to this.

Optical measurements.—To confirm the nature of our composite electroactive material we carried out in situ optical measurements of the composite electrode. UV/VIS spectra of the oxidized and reduced electrode are shown in Fig. 7. The character of the spectrum is similar to the spectrum of a polypyrrole electrode in liquid electrolyte when compensating for the presence of PEO within the electrode, thus revealing that polypyrrole is responsible for the charge accumulation. The electrochromic behavior of the composite electrode was also observed, the oxidized (doped) form is black, the reduced (undoped) form is yellow.

Capacity estimates.—We estimated the gravimetric energy density to 55 Wh/kg of active material. We used data for the thirtieth galvanostatic discharge cycle between 3.1 and 2.2 V and found a mean voltage of 2.45 V at a discharge current of 20 mA. The theoretical energy density assuming the same discharge voltage and 0.25 electrons per pyrrole ring is 152 Wh/kg of positive electrode material.

Conclusions

We have demonstrated that solid solutions of electroactive polymers in solid polymer electrolytes offer interesting possibilities for construction of all solid-state secondary batteries. The ease of preparation of these materials, the flexible nature of the material, and the possibility of forming them in different geometries are advantages. We have demonstrated that the formation of the composite enhances the coulombic capacity of the electrode. We have also demonstrated a rather long cycle life, extending to several hundreds of cycles, in thin film electrodes. The coulombic and energy efficiencies are acceptable, 90 and 80%, respectively, depending on the current density. Charge retention is still rather poor, the source of this problem is not known. We found the system to be limited by diffusion within the polypyrrole phase, probably due to movement of anions in poly-pyrrole. The diffusion coefficient was estimated to approximately $10^{-10}$ cm$^2$/s at 85°C, from SEM pictures and Cottrell measurements. This value is two orders of magnitude lower than that found by chronocoulometry of polypyrrole electrodes in liquid electrolytes (at room temperature) (15). That estimate was obtained by using the thickness of a polymer film as the characteristic length of diffusion, while we use the dimensions of the much smaller polypyrrole globules in the polymer electrolyte matrix. The difference is probably mainly due to this.

The interpenetration of electroactive polymer and solid polymer electrolyte is very good. The material appears homogeneous under optical microscopy. The optical activity of the polyethylene oxide is lost in the composite. The SEM photographs show very small particles.

The electrochromic properties of polypyrrole are also clearly demonstrated in the in situ optical spectroscopy results, showing that polypyrrole is actually reduced and oxidized during battery cycling. We further wish to emphasize the possibilities of using this kind of technique, both in the UV/VIS/NIR region as well as the IR region for studies on the kinetics of electrode reactions in situ. We could also use this technique for characterization of different reaction products.

The fact that so many cycles of shallow charge and discharge can be performed indicates that the electroactivity is not destroyed, and that ion insertion and extraction is quite reversible. This is in marked disagreement with the reported results of studies of polypyrrole electrodes in combination with PEO electrolytes (16). These studies show a rapid loss of electroactivity, as observed by the absence of doping ions within the polypyrrole phase after successive cycling. We have not determined the elemental composition of our composite electrode during cycling, and can thus only note that our capacity is very stable.

In conclusion, we suggest that composites formed from electroactive conducting polymers and polymer electrolytes are interesting candidates for development of positive electrodes in secondary solid-state batteries. The rich variety of both classes of polymers suggests several areas for improvement. For instance, by using highly conducting electrolyte materials [e.g., polyphosphazene (17)] we could enable operation at ambient temperature. The energy density of the electroactive polymer can be enhanced through the use of polymers and copolymers of higher redox potential (18). Performance characteristics can be enhanced by enhancing the miscibility of the two phases. The structural material

Fig. 6. Typical Cottrell plots of PPy-PEO composite electrode. Composite B (Table I), temperature 85°C, electrode area 1.77 cm$^2$; potential steps between 2.20 and 3.00 V (vs. Li/Li$^+$).

Fig. 7. In situ optical spectra of oxidized and reduced composite F (Table I) in a Li/PEO/composite cell. Temperature 85°C.
used in our soluble polypyrrole can be removed, thereby increasing the concentration of electroactive material. We can also optimize the composition of the electrode material with respect to performance characteristics.

Acknowledgments

We gratefully acknowledge the SEM studies performed by Mr. Reine Lindwall and the assistance with polarizing light microscopy from Mr. A. Mohammadi. This work was supported by the National Swedish Board for Technical Development. Dr. Novak's stay at Linköping was made possible by an exchange program between the Czechoslovak Academy of Sciences and the Swedish Academy of Engineering Sciences.

Manuscript submitted July 7, 1986; revised manuscript received Jan. 7, 1987.

The University of Linköping assisted in meeting the publication costs of this article.

REFERENCES


**Li<sub>x</sub>Mo<sub>2</sub>O<sub>4</sub>**

A New Promising Cathode Material for Secondary Lithium Cells

J. M. Tarascon

Bell Communications Research, Red Bank, New Jersey 07701-7020

ABSTRACT

During the past decade the demand for high energy storage batteries has generated considerable interest in the study of rechargeable secondary lithium batteries and several new electrode materials with open structures, i.e., consisting of chains or layer of atoms, such as NbSe<sub>3</sub> or transition metal dichalcogenides, respectively, have been uncovered. In this paper we describe a novel synthetic route (ion exchange of Na<sup>+</sup> for Li<sup>+</sup> in Na<sub>x</sub>Mo<sub>2</sub>O<sub>4</sub>) to prepare for the first time crystallographically pure powdered Li<sub>x</sub>Mo<sub>2</sub>O<sub>4</sub> material in large amounts, and we report both the chemical and electrochemical behavior of this layered type compound with respect to lithium. The study of Li<sub>x</sub>Mo<sub>2</sub>O<sub>4</sub> electrochemical test cells shows that Li<sub>x</sub>Mo<sub>2</sub>O<sub>4</sub> turns out to be quite a promising electrode material. Li<sub>x</sub>Mo<sub>2</sub>O<sub>4</sub> can reversibly accommodate up to 1.7 lithium atoms per "Mo<sub>2</sub>O<sub>4</sub>" unit formula at an average potential of 3 V resulting in a theoretical energy density of 530 Wh/kg of cathode material, compared to 480 Wh/kg for TiS<sub>2</sub> cathodes. The above cells maintain their capacity over several cycles (7) and are able to sustain high current drains. Structural studies indicate that Li<sub>x</sub>Mo<sub>2</sub>O<sub>4</sub> is a multiphase intercalation system over the range of composition 0.3 < x < 2 with the presence of single phase domains at x < 0.3, 0.3-1, 1-1.35, and 2. These phases undergo hydration reactions leading to new compounds of formula Li<sub>x</sub>(H<sub>2</sub>O)<sub>y</sub>Mo<sub>2</sub>O<sub>4</sub>.

Secondary lithium batteries have been the subject of a large amount of work for use as energy storage sources (1-2). However, at the present time none of these batteries have been commercialized, mainly because of electrode problems such as poor cycling efficiency arising from the dendritic regrowth of metallic lithium on the anode. This problem has been overcome by using alloys based on lithium such as LiAl (3) or Li<sub>10</sub>Mo<sub>10</sub>Se<sub>4</sub> (4) instead of lithium metal. However, if this is done the overall cell capacity is lowered.

The smaller capacity of cells without metallic lithium can be compensated for by using cathode materials with high discharge/charge voltages. For this reason a great effort has been directed in recent years towards the search for new cathodes, and several new compounds such as V<sub>2</sub>O<sub>5</sub> (5) or Li<sub>5</sub>CoO<sub>2</sub> (6), which can take up lithium reversibly at high potentials, have been uncovered. The great ability of the above materials with respect to lithium insertion arises from their open crystal structure. For instance, V<sub>2</sub>O<sub>5</sub> has open channels while Li<sub>5</sub>CoO<sub>2</sub> is a layered compound, made up of Co<sub>2</sub>O<sub>3</sub> sheets separated by a van der Waals gap which can accommodate the lithium atoms.

We recently synthesized the layered oxide Na<sub>x</sub>Mo<sub>2</sub>O<sub>4</sub> (7) (whose structure consists of Mo<sub>2</sub>O<sub>4</sub> layers held together by van der Waals forces) as pure phases and have shown the ability of this compound to reversibly intercalate sodium atoms within the range of composition 0.55 < x < 1.9 at an average potential of 1.6 V. These promising results led us to embark on a program of synthesis and study of the chemical and electrochemical behavior of the homologue Li<sub>x</sub>Mo<sub>2</sub>O<sub>4</sub> phase. Within the same host structure, the higher oxidation potential of metallic lithium compared to metallic sodium would lead to the expectation that Li/Li<sub>x</sub>Mo<sub>2</sub>O<sub>4</sub> electrochemical cells should have a discharge/charge potential greater than the homologue sodium cells. The present work confirms this expectation and shows that the lithium intercalation/deintercalation process in Li<sub>x</sub>Mo<sub>2</sub>O<sub>4</sub> is taking place at an average potential of 3 V.