SECONDARY LI BATTERY INCORPORATING 12-CROWN-4 ETHER

Inventors: Ganesan Nagasubramanian, La Crescenta; Salvador DiStefano, Alhambra, both of Calif.

Assignee: The United States of America as represented by the Administrator of the National Aeronautics and Space Administration, Washington, D.C.

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Field of Search 429/192, 198; 252/62.2

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Primary Examiner—Stephen Kalafut
Attorney, Agent, or Firm—Thomas H. Jones; John R. Manning

ABSTRACT
The conductivity is increased an order of magnitude and interfacial charge transfer resistance is substantially decreased by incorporating a minor amount of 12-Crown-4 ether in a polyethylene oxide-lithium salt solid electrolyte film.

12 Claims, 3 Drawing Sheets
FIG. 1

- ● = +12 CROWN ETHER (1.5 mM)
- ▼ = +12 CROWN ETHER (3 mM)
- □ = +12 CROWN ETHER (6mM)
- ○ = REF 8
- ■ = PEO + LiClO₄ + 12 CR₄ (0.3 mM)
- △ = PEO₅CF₃SO₃Li

\[
\sigma (\Omega^{-1} \text{cm}^{-1}) = \frac{1}{kT}
\]

- \( k \) is the Boltzmann constant
- \( T \) is the temperature in Kelvin

Temperature range: 2.6 to 3.8 \( \frac{1}{kT} \times 1000 \)
FIG. 3(a)

FIG. 3(b)
SECONDARY LI BATTERY INCORPORATING 12-CROWN-4 ETHER

DESCRIPTION

1. Origin of the Invention
The invention described herein was made in the performance of work under a NASA contract, and is subject to the provisions of Public Law 96-517 (35 USC 202) in which the Contractor has elected not to retain title.

2. Technical Field
This invention relates to secondary, lithium polymeric electrolyte batteries and, more particularly, this invention relates to a rechargeable, lithium battery utilizing a lithium salt-polyethylene oxide solid electrolyte having increased conductivity and reduced interfacial charge transfer resistance.

BACKGROUND OF THE INVENTION

Rechargeable, lightweight batteries are desired as miniaturized power sources for use in microelectronic devices in consumer, space, transportation and military applications. Solid state, high specific energy batteries are under development based on use of alkali metal-ionic polymeric complexes. Most of these batteries are based on lithium since it has such a low atomic weight and is highly electronegative. Lithium batteries based on liquid solvent containing electrolytes are unstable and present leakage problems. Molten electrolytes require high temperature environments.

The lifetime and number of discharge-charge cycles demanded of a lithium battery place stringent requirements on the components of the battery. The battery components also have mechanical, thermal and electrochemical constraints arising from the conditions of service. The electrolyte is subjected to the most stringent requirements since it provides several functions. The polymeric electrolyte must function as a lithium ion carrier, a separator and a binding agent for the positive electrode such as a titanium disulfide or cobalt oxide composite electrode. Solid state lithium-ion conducting polymeric electrolytes provide good adhesion, are deformable and have good elasticity.

Polyethylene oxide has been found to be the most satisfactory solid polyelectrolyte for use in thin film lithium batteries due to the formation of complexes with lithium salts and the ability to be recharged. Batteries containing polyethylene oxide (PEO) films are compatible with other components of the battery and exhibit the mechanical properties required for a thin film battery. However, the PEO salt films exhibit low conductivity at room temperature and low cation transport.

Approaches to improving the conductivity of PEO-lithium salt electrolyte films include adding inert fillers such as Al₂O₃ and plasticizers such as glyme to PEO or other polymeric electrolytes (2,3) or mixing the PEO with another polymer such as propylene oxide (PPO), poly(bis-(methoxyethoxy ethoxide)-phosphazene) and the like (4).

STATEMENT OF THE PRIOR ART

List of the Prior Art


STATEMENT OF THE PRIOR ART

The ionic conductivity of alkali metal-polyethylene oxide (PEO) was discovered by Fenton et al (1). The very low ionic conductivity (<10⁻⁶ S cm⁻¹) of this electrolyte has been enhanced by use of polypophosphate as the polymer (2a) addition of inert fillers such as alumina (2) to the Li salt-PEO complex, use of mixed polymers such as PEO-polyurethane (4a) or methoxyethoxyethoxide (MEEP)-PEO (4b) or modification of the cathode material such as cobalt bronze, Li₄CoO₄ (5). Crown ethers have been added to poly (vinylene carbonate)-lithium salt complexes and other polymers to increase conductivity (2b,7,9). The addition of 12CR4 both kinetically and thermodynamically favored in the polymer electrolyte of the invention. An order of magnitude increase in bulk conductivity results in 100 fold increase in power density. Battery efficiency is increased and the temperature of operation is decreased in batteries utilizing the improved polymeric electrolyte of the invention.

The polymeric electrolyte of the invention comprises a thin film of a solid polyethylene oxide complexed with a minor amount of a lithium salt containing an amount of 12-Crown-4 ether (12CR4) effective to increase ionic conductivity by a factor of at least 5. The addition of 12CR4 also results in a reduction of interfacial charge transfer resistance by a factor of at least 3 in one polyethylene oxide-lithium salt complex to a factor of over 25 with other polyethylene oxide-lithium salt complexes. The improvement in conductivity and the lowering charge transfer resistance has been demonstrated with several lithium salt polymer complexes.
The solid electrolyte is formed by dissolving the PEO, lithium salt and 12CR4 ether in a solvent such as acetonitrile with stirring. The mixture is placed in a mold and the solvent allowed to evaporate to form a thin film having a thickness from about 1 to 10\(\mu\)m. The cathode is usually an insertion type cathode such as CoO2 or TiS2 dispersed in a polymer matrix.

The invention will now be illustrated by the following experiments:

**EXPERIMENT**

Polyethylene oxide (M.W. = 4 \times 10^6), lithium triflate (LiCF3SO3) and lithium perchlorate (LiClO4) were dried under dynamic vacuum (\(>10^{-5}\) Torr) for 48 hours. Solvent acetonitrile (MeCN) and 12-Crown-4 ether (12CR4) were used as received. Thin film casting was done inside an argon-filled glove box. Appropriate amounts of PEO and either LiCF3SO3 or LiClO4 were weighted, to yield an oxygen to lithium ratio of 5:1, and transferred to a Teflon beaker to which a predetermined volume of 12CR4 was added. To this mixture was added 100-150 ml of MeCN and was stirred overnight, after which the viscous liquid was transferred to Teflon molds and the solvent was allowed to evaporate. This procedure yielded ~ 100 \(\mu\)m thick films. The films were vacuum dried at 100° C. for 48 hours. An electrochemical cell designed to hold a sample in a fixed geometry and with a known cross-sectional area was used. Standard electrochemical equipment was used to make the measurements. Polymer thin films are denoted as follows:

- PEO/LiCF3SO3: A
- PEO/LiCF3SO3/12CR4: A-12CR4
- PEO/LiClO4: B
- PEO/LiClO4/12CR4: B-12CR4

**RESULTS AND DISCUSSION**

**A. DC Measurements**

In Fig. 1 is shown the plot of the ionic conductivity as a function of temperature for A, B, A-12CR4 (three different concentrations of 12CR4) and B-12CR4 (one concentration of 12CR4). Literature values (8) for PEO/LiClO4 are also plotted for comparison. The conductivity (\(\sigma\;\text{Scm}^{-1}\)) values were determined from the resistance values at 100 kHz obtained with the polymer film sandwiched between two Li foils which are in turn pressed against the Ni electrodes. The plots demonstrate the following features:

- The conductivity of the PEO-salt film is comparable to that reported in literature.
- The increase in conductivity is not monotonic with increasing 12CR4 concentration.
The presence of 12CR4.

Compared to A, B has a higher σ for B-12CR4 (−3 mM).

In FIG. 2 the cyclic voltammetric behavior of plating and stripping of Li at Ni electrodes in A, A-12CR4, and B-12CR4 at approximately 70°C. The following observations are evident:

As shown, plating/stripping occurs at a potential closer to Li+/Li for 12CR4 incorporated samples than those without.

Of the two salts (LiCF3SO3 and LiClO4), studied, the plating/stripping occurs at a potential closer to Li+/Li for B-12CR4 than for A-12CR4.

The complex impedance behavior of both A and A-12CR4 are shown in FIG. 3 at approximately 65°C. Both polymer electrolytes exhibit two poorly resolved semicircles followed by a straight line corresponding to a diffusional process. The charge transfer resistance (Rct), which is the diameter of the semicircle at the lower frequency, determined from these plots are about ~58 kΩ cm² for A and 16 kΩ cm² for A-12CR4.

Similar behavior was observed for B-12CR4 with a Rct of approximately 1 kΩ cm².

An electrochemical cell containing a PEO LiBF4 electrolyte was prepared having an oxygen to lithium ratio of 5:1. The 12CR4 ether concentration was 3 mM. The films were cast utilizing 100 to 150 ml of MeCN solvent at a thickness of 1 to 2 pm. The films were vacuum dried at 100°C for 48 hours. An electrochemical cell designed to hold a sample in a fixed geometry, with a known cross-sectional area and equipped with a provision to maintain either a static or dynamic ambient atmosphere was used. Standard electrochemical equipment was used to make the measurements. Polymer films are denoted as follows:

A1: PEO, LiBF4 without 12CR4
A2: PEO, LiBF4 with 12CR4

Dc cyclic voltammogram of the electrolytes (A1 and A2) sandwiched between two well polished stainless steel electrodes were obtained. Both electrolytes appear stable with very little leakage/breakdown current in the potential range 3.5–5.5 V vs. Lithium. In both cases the electrolytes used are ~100 μm thick and 1 cm² in area. Below 3.5 V slight irreversible reduction takes place in both electrolytes, the origin of which is not yet known. The perceptible reduction current may be due to the reduction of the residual impurities either in the PEO or in the LiBF4. In most cases measurements were made positive of 3. V.

An electrochemical cell comprising Li/electrolyte/-Li2O2 was assembled inside an argon-filled glove box at this temperature. The cell was raised to the desired value (60°C) and the cell was allowed to equilibrate before the open circuit voltage (OCV) was measured. The OCV of a freshly assembled cell thus measured is ~3.8 V.

The dc cyclic voltammetric curves as a function of scan rates respectively for Li/A1/Li2O2 and Li/Al/CoO2 demonstrate the following features:

At slower scan rates >2 mV/sec there are well defined cathodic and anodic peaks. These peaks are very poorly defined and are absent at faster scan rates. The peak splitting is smaller with 12CR4 in the electrolytes than without indicating a greater reversible behavior. This again is due to a decrease in charge transfer resistance (Rct) in the presence of 12CR4.

At a particular scan rate, the current is higher with the 12CR4 additive incorporated in the electrolyte.

These measurements were repeated at 70°C and 80°C, and found to be equivalent to the scans at 60°C.

The OCV of a freshly assembled Li/Polymer electrolyte/Li2O2 with and without 12CR4 additive is ~3.8 V. The dc cyclic curves indicate that the peak splitting is smaller and the current is higher for cells with 12CR4 than without.

The values of the charge transfer kinetic parameters are summarized in the following table:

<table>
<thead>
<tr>
<th>Electrolyte System</th>
<th>Charge Transfer Resistance, Rct</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO/LiSO4:CF3</td>
<td>58.00</td>
</tr>
<tr>
<td>PEO/LiSO4:CF3-12CR4</td>
<td>16.00</td>
</tr>
<tr>
<td>PEO/LiClO4:12CR4</td>
<td>1.00</td>
</tr>
<tr>
<td>PEO/LiBF4</td>
<td>48.50</td>
</tr>
<tr>
<td>PEO/LiBF4-12CR4</td>
<td>1.75</td>
</tr>
</tbody>
</table>

The interfacial charge resistance is reduced by a factor of about 3 in the presence of 12CR4 ether and is as low as 1.0 kΩ in the case of PEO/LiClO4. The order of magnitude increase in conductivity and exchange current density results in a 100 fold increase in power density. The charge transfer and conductivity effects are consistently shown in several lithium salt electrolytes. The concentration of 12CR4 appears to be critical and limited to amounts below 6 mM preferably, below about 3 mM. Dc cyclic curves indicate that the peak splitting is smaller and the current is higher for cells having PEO electrolytes containing 12CR4.

Batteries containing the improved electrolyte of this invention permit operation of the battery at a lower temperature with improved efficiency. In addition to electrochemical devices the 12CR4 containing PEO-Li salt complex may find use in electrochromic devices and ion selective electrodes.

It is to be realized that only preferred embodiments of the invention have been described and that numerous substitutions, modifications and alterations are permissible without departing from the spirit and scope of the invention as defined in the following claims.

We claim:

1. A solid electrolyte comprising in combination: a solid polyethylene oxide matrix; a dispersion of a lithium salt in the matrix, the ratio of oxygen to lithium in the polyethylene oxide matrix being from 1 to 10 to 1; and further including 12 Crown-4 ether in an amount effective to increase conductivity.

2. A polyelectrolyte according to claim 1 in which the ratio is about 5 to 1.

3. A polyelectrolyte according to claim 2 in which the lithium salt is selected from LiBF4, LiCF3SO3, LiClO4 and LiAsF6.

4. A polyelectrolyte according to claim 3 in which the lithium salt is LiClO4.

5. A polyelectrolyte according to claim 1 in which 12-Crown-4 ether is present in the polyelectrolyte in an amount from about 1 mM to about 6 mM.

6. A polyelectrolyte according to claim 5 in which the 12-Crown-4 ether is present in the polyelectrolyte in an amount of less than about 3 mM.

7. A battery comprising in combination: a thin film of electrolyte according to claim 1; a lithium anode in contact with one face of the film;
a cathode in contact with an obverse face of the film; and
a first terminal in electrical communication with the anode, and
a second terminal in electrical communication with the cathode.

8. A battery according to claim 7 in which the cathode is an insertion cathode.

9. A battery according to claim 8 in which the cathode includes TiS₂ or CoO₂.

10. A method of forming a solid electrolyte comprising the steps of:
   dissolving a solid polyethylene oxide polymer in vaporizable solvent to form a solution;
   dispersing a lithium salt and 12-Crown-4 ether in the solution;
   casting the solution into a thin film; and
   removing the solvent from the thin film.

11. A method according to claim 10 in which the film is in the form of a disc.

12. A method according to claim 11 in which the film has a thickness from 1 μm to 1000 μm.