

LITHIUM POLYMER BATTERIES



Edited by

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PROCEEDINGS OF THE SYMPOSIUM ON
**LITHIUM POLYMER
BATTERIES**

Editors

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Preface

This proceedings volume contains contributions to the Lithium Polymer Batteries Symposium held at the 190th Meeting of the Electrochemical Society, in San Antonio, Texas (October 6-11, 1996). All but three of the 37 papers presented are included here.

The Symposium drew papers which covered all aspects of lithium polymer batteries. Polymer materials were described which formed the basis of anodes and cathodes as well as the more commonly studied electrolyte formulations. New "true" electrolytes were describes as were "gel" and glass/polymer composite electrolytes. Cell construction, cell hardware, electrode pretreatments and life and performance are described. More fundamental measurements such as conductivity, interfacial impedance and transference numbers are also reported.

We would like to take this opportunity to thank the speakers, co-authors and chairpersons for their valuable contributions to the Symposium and this Proceedings volume. We would also like to thank the Headquarters Staff of the Electrochemical Society for their support, organization and understanding.

John Broadhead

Bruno Scrosati

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The Electrochemical Society, Inc., is an international, nonprofit, scientific, educational organization founded for the advancement of the theory and practice of electrochemistry, electrothermics, electronics, and allied subjects. The Society was founded in Philadelphia in 1902 and incorporated in 1930. There are currently over 7000 scientists and engineers from more than 60 countries who hold individual membership; the Society is also supported by more than 100 corporations through Patron and Sustaining Memberships.

The Technical activities of the Society are carried on by Divisions and Groups. Local Sections of the Society have been organized in a number of cities and regions.

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**Cyclability of Lithium/
Poly(methylmethacrylate)-Based Gel
Electrolyte/Polypyrrole Secondary Battery**

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Abstract

A new thin-film polymer electrolyte battery with a polymer cathode is described. At high current densities (0.5 mA cm^{-2}), the battery demonstrates a life of over 1000 cycles.

Introduction

In recent years, there have been strong demands for high energy and high power density secondary batteries for portable electric devices, load leveling systems and electric vehicles. The Li/polymer cathode battery system has been attracting attention because the energy density of the battery can be enhanced due to light weight of the polymer materials. Especially, the introduction of polymer electrolyte into the Li/polymer battery system should make a thin-layer, high energy density battery practicable. We have constructed a Li/polymer battery using poly(acrylonitrile) (PAN)-based gel electrolyte with polypyrrole (PPy) film as the cathode material. However, this battery showed poor shelf-life, which may be due to the chemical and/or electrochemical instability of PAN [1]. In this work, we employed a much more stable, poly(methylmethacrylate) (PMMA)-based gel electrolyte to construct a Li/PPy battery and investigated its characteristics.

Experimental

Polymer electrolyte used is PMMA-based gel electrolyte. The electrolyte consists of PMMA as a polymer matrix, LiClO_4 as ionically conducting salt, ethylene carbonate (EC) and propylene carbonate (PC) as organic solvents or plasticizers [2]. PPy cathode film was obtained by potentiostatic electropolymerization [3]. By using this gel

electrolyte, PPy cathode film, and Li metal anode, a two electrode, coin type cell was constructed.

The performance of the battery was investigated by cyclic voltammetry, ac-impedance measurement and galvanostatic charge-discharge tests at ambient temperature.

Results and Discussion

The battery performance of Li/PMMA gel/PPy was examined by galvanostatic charge-discharge tests at room temperature. Fig.1 shows the cycle performances of the Li/PMMA gel/PPy battery. Charge and discharge current densities of (a) 0.5, (b) 0.1 and (c) 0.05 mA cm⁻² and the cut-off voltages were 3.5V charging and 2.0V discharging. The battery shows about 90 to 100% of coulombic efficiency through all cycles at several current densities. This result demonstrates that the Li/PMMA gel/PPy system has sufficient electrochemical stability and reversibility. In Fig 1(a) at 0.5 mA cm⁻², the battery showed excellent performance with a constant discharge capacity up to almost 1000 cycles. On the contrary, in Fig 1(c) the capacity decreased suddenly after 10 cycles, followed by an increase and a decrease. The difference of cycle performance may be mainly due to the difference in the length of time required for charge and discharge at the two different current densities. We have investigated the interfacial stability of Li and PMMA gel electrolytes by ac-impedance measurements, which showed that the interfacial resistance increases with storage time. At low current densities, the length of time required to complete a cycle is longer than that at high current densities. Therefore, in the low rate operation, cycle performance is considerably affected by the increase in resistance. Furthermore, we believe that a relatively high current density is required to maintain conditions for reasonable ionic passage in the gel electrolyte. At 0.05 mA cm⁻², ionic passage in the electrolyte is less steady, hence cycle behavior becomes unstable in the early cycles. At 0.1 mA cm⁻², these phenomena occur only to a moderate extent, and the cycle performance observed (Fig. 1(b)) was intermediate between that at 0.5 mA cm⁻² (Fig. 1(a)) and that at 0.05 mA cm⁻² (Fig. 1(c)).

These results show that the Li/PMMA gel/PPy system can be operated with a long cycle life of greater than 1000 cycles at high current rate, which indicates another merit that the application of gel electrolyte prevents the dendritic deposition of Li, allowing Li metal anodes to be used in practical secondary batteries.

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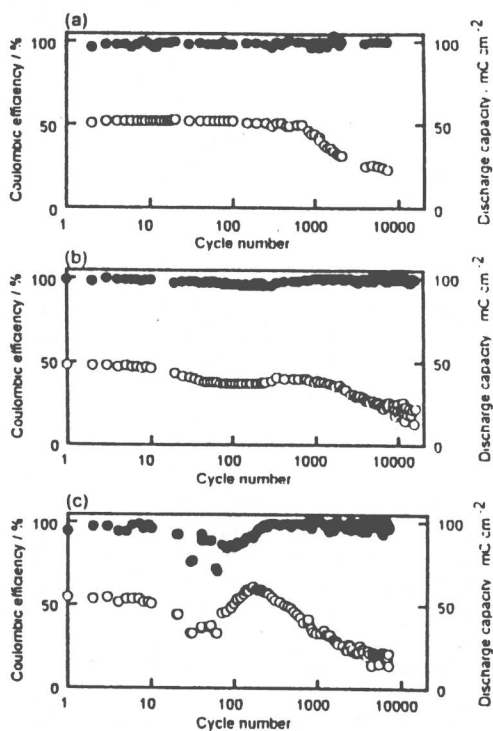


Fig. 1 Dependence of coulombic efficiency (●) and discharge capacity (○) of Li/PMMA gel/PPy battery on number of cycles. Charging and discharging current densities are (a) 0.5 , (b) 0.1 , (c) 0.05 mA cm^{-2}

Preparation of Functional Gradient Solid Polymer Electrolyte Thin-Films for Secondary Lithium Batteries

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Abstract

A new preparative technique to produce solid-state lithium batteries is described. The method uses functional gradient polymerization to fabricate ultra-thin film electrolyte from dimethyl-2-[(2-ethoxyethoxy)ethoxy]vinylsilane (DEVS). Initiation and polymerization is carried out by plasma and data are presented on characterization.

Introduction

Recently, a significant amount of work has been devoted to solid-state lithium batteries utilizing solid polymer electrolyte made from polymer complexes formed by complexation of lithium salts with polyethers, such as poly(ethylene oxide) and poly(propylene oxide). The ionic conductivity of these solid polymer electrolytes is considerably lower than that of liquid electrolytes. Because of the difficulty in decreasing their specific resistance, it is necessary instead to make use of these materials in the form of ultra-thin films. In previous papers, we have described the preparation of ultra-thin solid polymer electrolyte films using plasma polymerization techniques [1-4]. However, one problem to suppress a reaction between electrodes and the electrolyte, especially to suppress the dendritic growth of lithium during battery charging, remains to be solved for the development of the secondary solid-state lithium batteries of high performance. In this work, a novel concept of functional gradient solid polymer electrolyte was developed in order to solve the problem.

Experimental

A schematic diagram of the process for the synthesis of the functional gradient solid polymer electrolyte is shown in Fig. 1. Dimethyl-2-[(2-ethoxyethoxy)ethoxy]vinylsilane (DEVS) was selected as the monomer because this

substance contains ether, siloxane, and vinyl groups. First, composite cathodes (mixture of cathode active material and solid polymer electrolyte) was prepared by plasma-initiated polymerization.

As shown in Fig. 1a, a mixture of DEVS, lithium salt and cathode active material was used as substrate for the plasma-initiated polymerization. The DEVS in the mixture was polymerized by a chain propagation mechanism, Fig. 1b. Next, a thin layer of solid polymer electrolyte film was deposited on the composite cathode, Fig. 1c. DEVS and 1,1-difluoroethylene were used a monomer. The flow rate of 1,1-difluoroethylene was increased with time during plasma polymerization. On the other hand, flow rate of DEVS was decreased. This procedure resulted in the production of an ultra-thin ($\sim 1\mu\text{m}$) functional gradient solid polymer electrolyte film. The content of fluorine in the polymer is changed along its thickness. Finally, a lithium layer was deposited on top of the solid polymer electrolyte films using a thermal vapor-deposition technique, Fig 1d. A chemically stable layer, such as LiF, was formed by reaction between high fluorine content plasma polymer at the interface of the functional gradient solid polymer electrolyte film and the thermally deposited lithium layer [5].

The apparatus used to carry out the plasma polymerization consisted of a glass reactor equipped with capacitatively coupled inner electrodes to which an alternating voltage was applied at a frequency of 13.56 MHz. This reactor was incorporated into a vacuum system consisting of a diffusion pump, a rotary pump and a cold trap. The pressure in the reactor was monitored using a Pirani vacuum gauge.

Results and Discussion

The FT-IR spectra of the polymer in the composite cathode is very similar to that of DEVS, except for the complete absence of the characteristic peak for the olefin group. This results indicates that the DEVS in the cathode composite was polymerized by plasma-initiated polymerization which proceeds via a conventional chain propagation mechanism initiated by an ion, a radical, or highly energetic species in the plasma region.

Plasma polymers formed from DEVS have been prepared and characterized using SEM, ^1H NMR, XPS, and FT-IR. The ^1H NMR of the plasma polymer formed at 20 W and DEVS monomers were measured using CDCl_3 as the solvent. In the spectrum of the plasma polymer, the characteristic peaks of the olefin proton are completely absent. The FT-IR spectra of DEVS monomer (a) and its plasma polymer prepared at different RF power 20 W (b), 30 W (c), 40 W (d), and 50 W (e) are shown in Fig.2. At low RF power 20 W, the IR spectrum of the plasma polymer was similar to that of DEVS, except that the peak at 1600 cm^{-1} assigned to the olefin group disappeared. The higher the value of applied RF power, except for the regions of $1050\text{--}1250\text{ cm}^{-1}$ (corresponding to Si-O-Si, Si-O-C stretching vibrations), the strength of all the other peaks were decreased and the absorption peaks were broadened. These observations suggest that Si-O-Si cross-linking

reaction proceeds at high RF power as a result of the decomposition of monomer and ablation process of deposited plasma polymer.

The cross-sectional scanning electron micrograph shows that the solid polymer electrolyte of plasma-polymerized DEVS and lithium trifluoromethanesulfonate complexes had a thickness of about 1 μm and that at least from SEM observations, it was free of pinholes. The ionic conductivities of the solid polymer electrolytes are shown in Fig 3 as a function of $1/T$. The Arrhenius plots are not straight lines. This behavior is often observed for amorphous solid polymer electrolyte systems. It is well known that this type of temperature dependency is described by the Williams-Landel-Ferry (WLF) equation. The room temperature conductivity of $8 \times 10^{-6} \text{ S cm}^{-1}$ has been observed.

Conclusions

In conclusion, the composite cathode (mixture of the cathode active material and the solid polymer electrolyte) can be made by the plasma-initiated polymerization method. The plasma polymerized functional gradient solid polymer electrolytes, which were deposited on the composite cathode, were uniform and pinhole-free. The solid polymer electrolyte films are expected to be useful for lithium secondary batteries because of their low resistance and good chemical stability to lithium electrodes.

Acknowledgment

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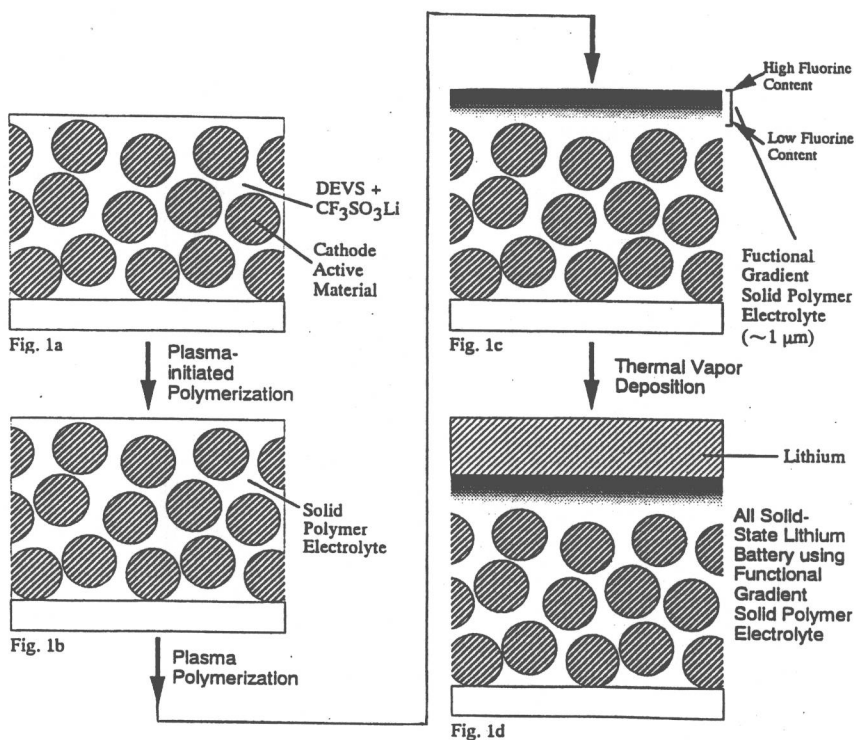


Fig. 1. Method for preparation of all solid-state lithium batteries using functional gradient solid polymer electrolyte plasma polymerization techniques.

Fig. 1a Mixture of DEVS, lithium salt and cathode active material.

Fig. 1b Polymerization of the mixture by chain propagation.

Fig. 1c Deposition of a thin layer of solid polymer electrolyte film on the cathode.

Fig. 1d Deposition of a thin layer of lithium by thermal vapor-deposition.

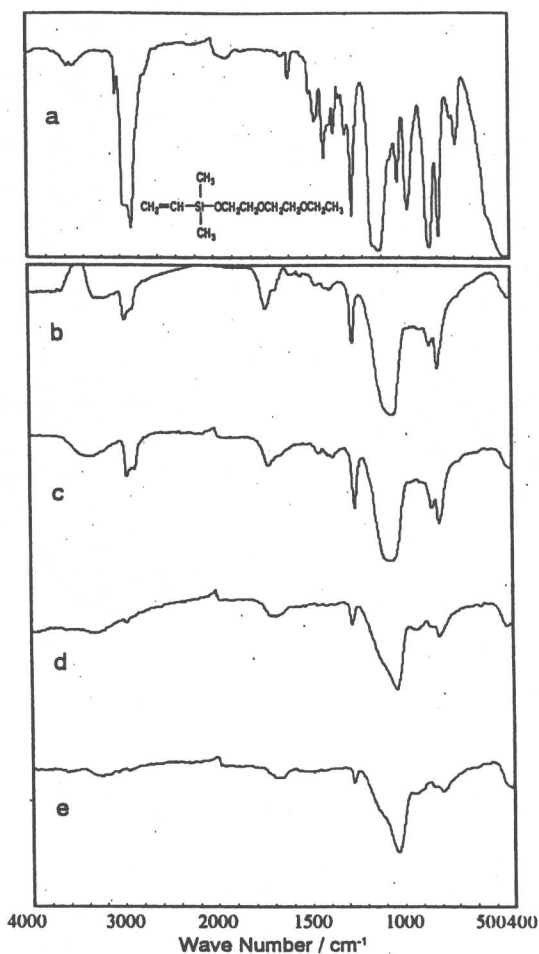


Fig. 2. FT-IR spectra of dimethyl-2-[(2-ethoxyethoxy)-ethoxy]vinylsilane (a), and its plasma polymers at RF powers of (b) 20W, (c) 30 W, (d) 40 W and (e) 50 W.