

## Characteristics of a thin film lithium-ion battery using plasticized solid polymer electrolyte

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### Abstract

Synthesis was performed on a three-dimensional cross-linked material comprising principal chains of a random copolymer made of ethylene oxide and propylene oxide as a solid polymer electrolyte, which was plasticized by an organic solvent. This solid polymer electrolyte has an ionic conductivity of  $1.5 \times 10^{-3} \text{ S cm}^{-1}$  at 20°C and good temperature properties. The solid polymer electrolyte is high in mechanical strength and thermal stability because of the three-dimensional crosslinking. We have manufactured successfully a lithium-ion battery of film form and card size with a thickness of 0.45 mm by using this solid polymer electrolyte. Positive electrodes of the battery use  $\text{LiCoO}_2$  as an active material, and negative electrodes use a less highly graphitized carbon material. The battery has an average voltage of 3.6 and a discharge capacity of about 100 mAh. In a 0.3C cycle test at 20°C, the battery was shown to have retained a capacity of about 90% of the initial capacity at the 300th cycle.

**Keywords:** Lithium-ion batteries; Electrolytes/solid polymer

### 1. Introduction

In association with the rapid progress in size and in thickness reduction of electronic devices and development of multi-media industries in recent years, demand has been increasing for small-size electronic devices, including cellular phones and PDA. With this situation as the background, the battery industry has a very important role to play. Replacement of conventional batteries with nickel/metal hydride and lithium-ion types is progressing, particularly in cellular phones and the like, while a primary lithium battery which is small in size and large in capacity is drawing attention. Lithium-ion batteries currently available commercially are cylindrical or prismatic in shape and use non-aqueous solvent-based electrolytes.

On the other hand, studies on the solid polymer electrolyte (hereinafter abbreviated to SPE) started upon its discovery by Wright et al. [1] in 1973. Its application as a battery electrolyte has become active in recent years as a result of proposals made by Armand et al. [2]. The use of SPE as a battery electrolyte would make the fabrication of highly safe batteries possible, allow use of printing techniques, and fabrication of a thin film battery feasible. However the SPE has indicated a problem in that its ionic conductivity is low at

room temperature, being different from the electrolytes which have been used conventionally. It is known that lithium-ion movements depend on segmental motion of polymers [3], so improving movement of the polymer is one of the problems to be solved for its application in lithium batteries.

Methods to solve this problem have been proposed by a number of research teams, including such methods as to crosslink polymers [4] and to introduce polymers into side chains to make them a comb shape [5]. Watanabe and co-workers [6] have achieved recently  $10^{-4} \text{ S cm}^{-1}$  at 30°C with a copolymer of 2-(2-methoxyethoxy)ethyl glycidyl ether and ethylene oxide with LiTFSI.

Propositions to add plasticizers have been made by a large number of researchers. Organic electrolyte itself has been used as a plasticizer, and is referred to as a gel electrolyte. Such research has been carried out since 1973 [7]. The SPE prepared by using organic electrolyte as a plasticizer has a high ionic conductivity,  $10^{-3} \text{ S cm}^{-1}$  or higher at room temperature. A number of reports have been given recently on electrolytes using PAN [8–10], PMMA [11–13] and PVdF [14] as the main chains. Such research is actively elucidating ionic migration mechanisms, as well as improving the conductivity of the electrolyte and its stability under a battery driving condition. These plasticized SPEs or gel electrolytes, which use as their network PAN and PVdF

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whose main chains themselves have no ionic conductivity, may be largely classified into two kinds of crosslinked structures in terms of gelation. One is a physically crosslinked gel whose crosslinking point is presented by the van der Waals' binding, as represented by the foodstuff jelly. The other is a chemically crosslinked gel made by covalent binding. The former gel is prepared generally by dissolving the polymer in solution at elevated temperatures, and then lowering the temperature. This type of gel has low stability against temperature, and may cause a case of hysteresis to occur against a thermal history. On the other hand, the latter chemically crosslinked gel is stabler than the former gel since a strong network has been formed as a result of the covalent binding.

In battery applications, gels should preferably have a wide operating temperature range and must be reversibly stable during thermal variations. Furthermore, if an electrolyte layer is formed by gel alone without using a separator, the gel must be stable structurally in addition to being mechanically strong.

## 2. Experimental

### 2.1. Preparation and measurement of properties of plasticized solid polymer electrolyte

Synthesis was performed on a precursor composed of a random copolymer of ethylene oxide and propylene oxide to form an SPE network, to which was added copolymerizing functional groups. This precursor was dissolved in electrolyte, and copolymerized by using a photo-crosslinking reaction. A solvent made of a mixture of propylene carbonate and ethylene carbonate was used for the electrolyte, and  $\text{LiBF}_4$  was used as the lithium solute. In order to investigate the properties of the prepared plasticized SPE, DSC and ionic conductivity measurements were conducted. The DSC measurement, using a sealed aluminum pan, was started at room temperature, going to a lower temperature at a scanning rate of  $10 \text{ K min}^{-1}$ . Measurements from  $-150$  to  $80^\circ\text{C}$  were repeated over three cycles. For reference,  $\alpha$ -alumina sealed in the aluminum pan was used. The apparatus used was a DSC220C made by Seiko Electronics. The ionic conductivity measurement was performed by using a Ni blocking electrode and the a.c. impedance method. The measurement was carried out from 1 Mhz to 0.1 Hz at  $20^\circ\text{C}$ . The apparatus used was the electrochemical interface 1286 and frequency response analyzer 1255 made by Solartron, which were controlled by a personal computer.

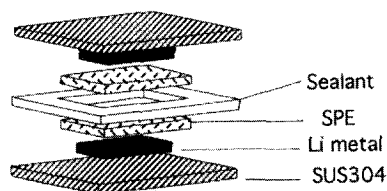


Fig. 1. Schematic representation of an Li/solid polymer electrolyte/Li cell.

Half-cells using lithium as electrode, as shown in Fig. 1, were fabricated and subjected to gas-phase cold/heat shock tests over ten cycles, each composed of  $-20^\circ\text{C}$  for 10 min and  $80^\circ\text{C}$  for 10 min, using a thermal shock chamber TSA-40L made by Tabai-Espec Corporation. Measurements were taken before and after each cycle to determine any change in impedance.

### 2.2. Fabrication and characterization of a 0.45 mm card size film-form lithium-ion battery

A negative electrode using less highly graphitized carbon as an active material was formed on a copper collector. A positive electrode made by mixing  $\text{LiCoO}_2$  as an active material with carbon to aid electron conduction was formed on an aluminum collector, having been processed in various ways. In order to form a plasticized SPE layer on the positive electrode, a solution made by mixing electrolyte composed of  $\text{LiBF}_4$  dissolved into a solvent mixture of propylene carbonate and ethylene carbonate with precursor polymers was printed, crosslinked, and copolymerized. The positive electrode, SPE layer and negative positive electrode were put together, and sealed by an adhesive made of modified polypropylene applied around the above assembly to form a battery.

The fabricated battery was given charge/discharge tests to investigate its rate, temperature and cycling characteristics. The tests were all performed at constant current and with cut-off voltages of 4.2 for the upper limit and 2.7 for the lower limit. The battery charge and discharge tests described in this paper were all performed without applying external pressure to the cell.

## 3. Results and discussion

### 3.1. Properties of plasticized solid polymer electrolyte

The prepared SPE is in the form of a transparent and flexible film. Arrhenius plots for the ionic conductivity of this

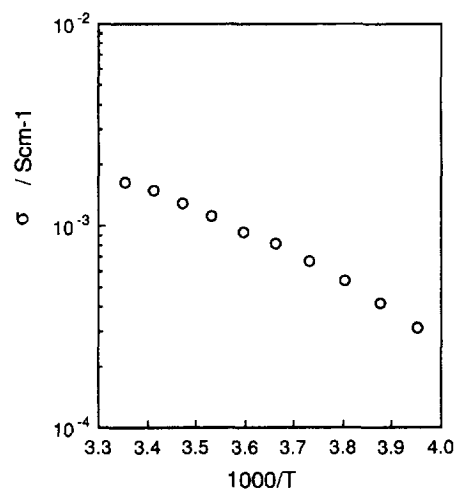


Fig. 2. Arrhenius plot of ionic conductivity for a solid polymer electrolyte.

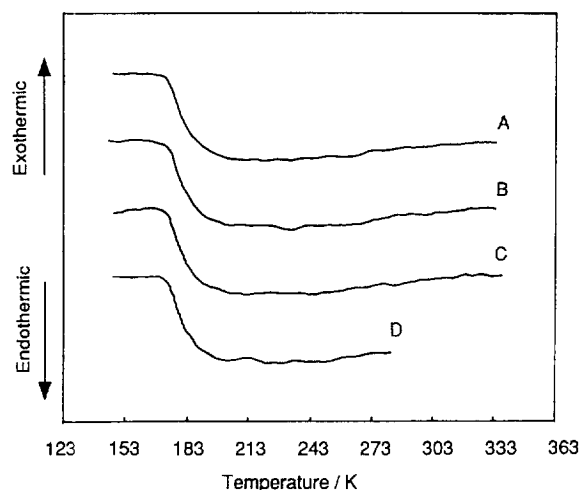


Fig. 3. DSC curves for solid polymer electrolyte. A: 1st cycle; B: 2nd cycle; C: 3rd cycle; D: 4th cycle. Scanning rate: 10 K/min. Operating temperature ranges: 123–353 K for A, B and C; 123–293 K for D.

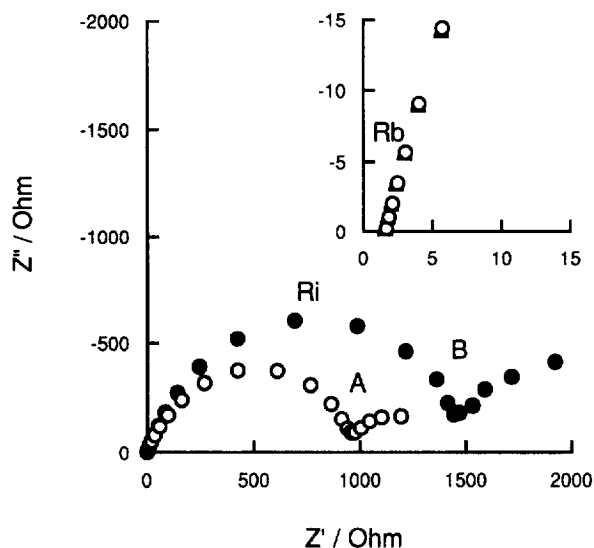


Fig. 4. Impedance measurements in the lithium half-cells.

SPE are shown in Fig. 2. The ionic conductivity showed the good characteristic of  $1.5 \times 10^{-3} \text{ S cm}^{-1}$  at  $20^\circ\text{C}$ . Activation energy when taken from a straight line between room temperature and  $-20^\circ\text{C}$  is  $23 \text{ kJ mol}^{-1}$ . The plots shifted from the straight line at lower temperatures, forming a gradual curve. For a more strict definition, it would have been more appropriate to have fitted the plots to an VTF equation.

The result of the DSC measurements is shown in Fig. 3. While  $T_g$  of the polymers can be recognized in the vicinity of

$173 \text{ K}$ , it can also be seen that the material is very stable thermally. The DSC curves show the temperature rising in different temperature cycles, but present no heat absorption peaks that would be associated with dissolution of the plasticizer. Each cycle has come up with nearly the same curve. This means that the material is stable against the thermal history, and no change in properties due to heating of the electrolyte is recognized in the measured temperature range.

As a result of measuring impedance in the lithium half-cells used in the cold/heat shock tests, it can be seen in Fig. 4 that resistance changes very little in the bulk  $R_b$ , which reflects the ionic conduction. The  $R_i$ , corresponding to the resistance of the interface with lithium, grew to about 1.5 times larger than the initial value. The capacitor component,  $C_p$ , showed no change, remaining at about  $2.8 \mu\text{F}$ . This suggests that the resistance increased monotonously. As the battery was cycled at temperatures as high as  $80^\circ\text{C}$ , corrosion reaction has progressed on the surface of lithium, which should have increased the surface resistance. The corrosion could be caused by a reaction between the electrolyte and lithium.

Stability during the thermal history is because the network of polymers is formed firmly as a result of chemical crosslinking and is in a stable swelling region. The fact that no large change has been recognized in the impedance, particularly in the bulk section, indicates that no phase segregation has occurred in association with such a change as syneresis. Therefore, it could be said that the material has a very low possibility of exhibiting deterioration in its characteristics and developing short circuits caused by temperature change if it is used as a battery electrolyte.

### 3.2. Battery characteristics

Fig. 5 shows the battery construction. It is a card-form battery with a thickness of  $0.45 \text{ mm}$ . The electrodes and electrolyte can be made easily because a printing process can be used for fabrication. With respect to its shape, the area can be either reduced or increased easily.

Fig. 6 shows the variation in behavior of the battery at various rates of charge and discharge. The capacities of the batteries used were  $105 \text{ mAh}$  for the battery used in the charge test and  $100 \text{ mAh}$  for the battery used in the discharge test. Discharge and charge voltages change gradually because less highly graphitized carbon material is used in the negative electrode. The battery has good charge/discharge characteristics, showing the capability of charging and discharging at about 85% of the nominal capacity at the  $0.5\text{C}$  rate.

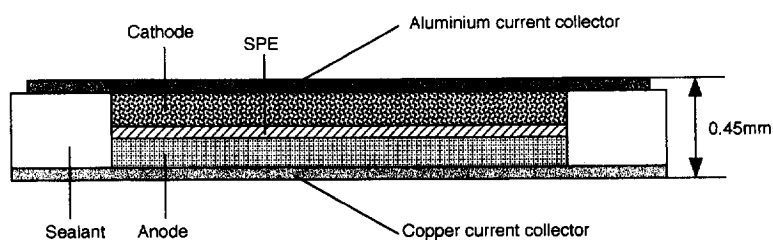


Fig. 5. Cross-sectional view of a 'film ion' cell.

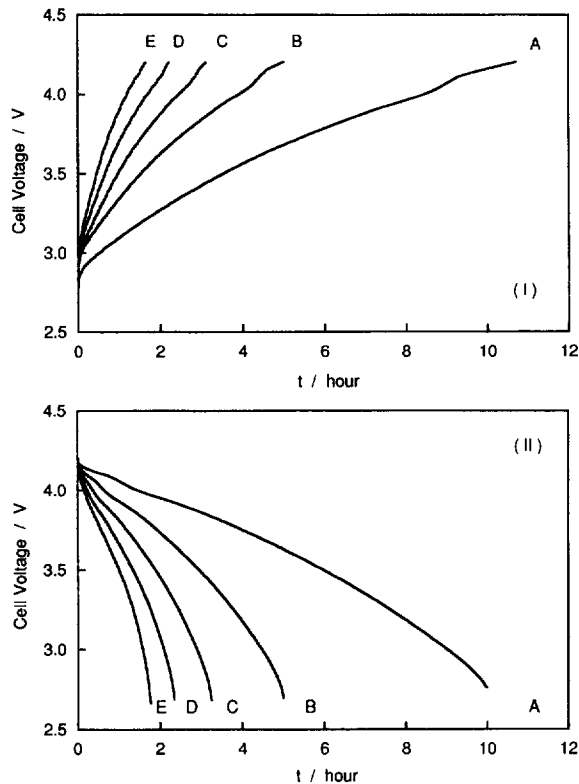


Fig. 6. Charge and discharge curves for a 'film ion' cell at 20°C. Upper figure: charge characteristics, with all discharges at 10 mA. Lower figure: discharge characteristics, with all charges at 10 mA. In both figures, currents (mA) were: A, 10; B, 20; C, 30; D, 40; E, 50.

Fig. 7 shows discharge curves at 10 mA from 20 to  $-10^{\circ}\text{C}$ . The discharge capacity at  $-10^{\circ}\text{C}$  was approximately 74% of that at 20°C.

Fig. 8 shows the cycling characteristics. The battery retained 90% of initial capacity after 300 cycles during constant current charge and discharge at 30 mA at 20°C. The charge/discharge efficiency remained nearly at 100% throughout cycling. Deterioration in the capacity is thought to have been caused by isolation of the active material during the cycling. The characteristics may be regarded as good because the result was obtained without applying any external pressure. No abnormality such as gas generation during the cycling was seen.

### 3.3. Safety test

Different types of safety tests were given to batteries manufactured using the same design as used in the electrical experiments.

#### 3.3.1. Overcharge test

A fully discharged battery was connected to a power supply in the charge direction, at a voltage of 12 V and a current equivalent to 1C. After the charge had continued for 2 h, the terminal voltage has risen to 4.9 V, but no rupture or ignition occurred. The battery temperature rose by 2°.

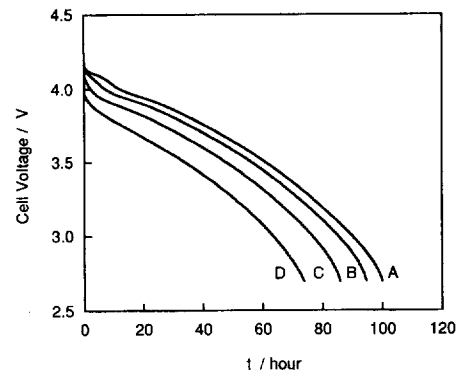


Fig. 7. This shows discharge curves at 10 mA: A, 20; B, 10; C, 0; D,  $-10^{\circ}\text{C}$ .

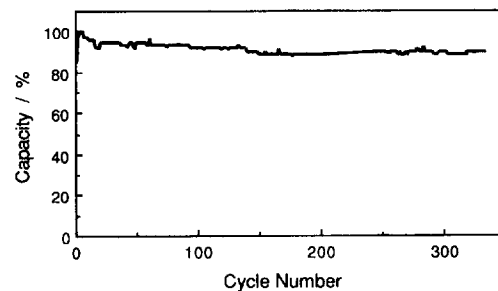


Fig. 8. This shows the cycling characteristics at 30 mA at 20°C.

#### 3.3.2. Over-discharge test

A fully charged battery was connected to a power supply in the discharge direction, at a voltage of 12 V and a current equivalent to 1C. During the 2 h discharge, the terminal voltage decreased to a maximum of  $-6$  V. No rupture or ignition was seen. The battery temperature rose by 4°.

#### 3.3.3. External short-circuit test

A fully charged battery, placed in a constant temperature tank maintained at 60°C, was shorted by using a 1.5 mm diameter copper wire. A maximum momentary short-circuit current of 8.5 A was seen, but no ignition, rupture or change in the battery appearance was observed. The battery temperature rose by 2°.

## 4. Conclusions

Plasticized SPE, having as the main skeleton a three-dimensionally crosslinked structure comprising a random copolymer of ethylene oxide and propylene oxide as the main chain, has excellent ionic conductivity and shows good characteristics, including thermal stability. This is because the polymer network is structured by strong covalent binding and the crosslinking point does not change in association with molecular motions including dissolution of polymers. When solid electrolyte or gel electrolyte is used to separate a positive electrode and a negative electrode, no physical alteration and chemical alteration should occur from viewpoints of safety and reliability.

As this plasticized SPE is stable, it is suitable for battery use. Lithium-ion batteries using SPE showed excellent

cycling characteristics. Charges and discharges were completed with good results. It is thought that because thermal capacity is small because the battery is thin, this will make for high safety.

As a battery design has been realized that has a thickness as thin as 0.45 mm, it is possible to arrange such a battery in spaces within electronic device casings or in the liquid crystal panel in a notebook-type personal computer. This battery leads to an expectation that electronic devices could be further reduced in weight, thickness and length.

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