

Solid polymer electrolytes for lithium cells

Syuichi Izuchi, Seijiro Ochiai, Ken-ichi Takeuchi

Yuasa Corporation, Central Laboratory, 6-6, Josai-cho, Takatsuki-shi, Osaka 569, Japan

Accepted 13 January 1997

Abstract

This paper reports on ionic conductivity, mechanical characteristics, thermal stability, and electrochemical stability of solid polymer electrolytes (SPEs) that use a cross-linked poly(ethylene oxide) and a cross-linked ethylene oxide copolymer both containing a plasticizer. We obtained the SPEs that have a high ionic conductivity of $2.4 \times 10^{-3} \text{ S cm}^{-1}$ at 20 °C, a mechanical strength that creates no problems in practical use, and higher thermal stability than liquid electrolytes. Batteries using these SPEs were manufactured and submitted to various tests. The results showed that the low-temperature and rate characteristics of these batteries were comparable with those of liquid electrolyte batteries. The results of loading, bending and twisting tests indicated that no internal shorting of the batteries occurred. These batteries did not swell at high temperatures at which liquid electrolyte batteries usually do. © 1997 Elsevier Science S.A.

Keywords: Solid polymer electrolytes; Ionic conductivity; Mechanical characteristics; Thermal stability; Lithium cells

1. Introduction

The history of the solid polymer electrolyte (SPE) development started in 1975 when Wright [1] developed an SPE. The polymers used since then have a structure containing mainly poly(ethylene oxide) (PEO) in the skeleton because of its easy orientation versus alkali metal ions. In the first years of the developmental history, PEO with a high molecular weight was used at temperatures higher than the melting point [2]. In order to improve the conductivity at temperatures lower than room temperature, many investigations have been made in order to inhibit crystallization. Some improvements in conductivity have been made at low temperatures and one of the improvements was attained, for example, by introducing side chains of PEO into polyphosphazene chains [3]. Presently, however, it is very difficult to increase the ionic conductivity of SPEs below room temperature in order to realize their practical use taking into consideration the ionic conductivity mechanism. More specifically, the current concept commonly known is that the ionic conductivity is obtained by the segment motion of polymer chains [4]. As long as the SPE development is carried out under the above concept, it will be difficult to raise the ionic conductivity at temperatures below room temperature to the same level as that of organic liquid electrolyte systems. For this reason, two methods have been adopted presently. One is a method to operate a battery at high temperatures of 40 to 100 °C [5]. The other method is to raise the ionic conductivity by includ-

ing a plasticizer(s) in the SPE. Reports have been given on lithium batteries using a solid polymer electrolyte made using this latter method [6].

The authors commenced research on the method of adding plasticizers, and applied their results to lithium batteries. In these studies, cross-linked polymers using mainly an ethylene oxide (EO) as a base have been employed, and including the plasticizer in these polymers made it possible to attain a large improvement in ionic conductivity. This paper introduces the characteristics of SPEs described above, and their application in batteries.

2. Experimental

2.1. Materials

Lithium battery-grade prepolymers, plasticizer and salts were used, and SPEs prepared in dry air. The prepolymers used were reactive PEO and reactive copolymers of EO with other monomers. The weight ratio of polymers in the SPEs was made identically in all the SPE systems. The plasticizer used was propylene carbonate and the fluoro-type lithium salt used was lithium perfluoroalkane sulfonimide.

2.2. Electrochemical measurements

The ionic conductivity was measured by using a Solartron 1255 HF frequency analyser and a Solartron 1286 electro-

Table 1
Polymers used in plasticized SPEs

Polymers		Relative density of cross-linking ^a
Cross-linked PEO1	network of EO homopolymer	10
Cross-linked PEO2	network of EO homopolymer	1
Cross-linked PEO3	network of EO homopolymer	0.36
Cross-linked EO copolymer	network of copolymer between EO and other monomer	2.5

^a These values were determined by calculation on a unit weight basis from the number of functional groups that are effective for the cross-linking of prepolymers.

chemical interface. The ionic conductivity was measured by using a cell with an SPE film which was set between two platinum plates with a diameter of 13 mm, and the cell was placed in a thermostatted tank to keep the temperature constant.

Cyclic voltammograms were measured and recorded using an EG&G Princeton Applied Research potentiostat/galvanostat, Model 273. The cell used for this measurement was made from the platinum working electrode and lithium metal counter and reference electrodes.

2.3. Measurement of mechanical characteristics

A test piece used for a tensile strength test had a width of 10 mm and a length of 70 mm, and the measurement was carried out at a pulling rate of 10 mm/min by using Shimadzu Autograph DCS-2000 and Data Letty 401.

In the compression test, a test piece was subjected to a static load, and its thickness obtained in the loading process was read on Citizen Digimetric Counter DGM-C2 and DGM-0501B Thickness Gauge. To describe more specifically, a circular and flat stainless-steel contact part having a diameter of 5 mm was placed on a ~ 3 cm² sample that was placed on a flat stainless-steel plate to measure the distance between the pressed contact part and the flat stainless-steel plate.

2.4. Differential scanning calorimetry

Differential scanning calorimetry (DSC) measurements were performed using Seiko Instrument DSC 220C. The cell used for the measurement was a stainless-steel can with an inner diameter of 4 mm, which was placed in an argon gas atmosphere.

2.5. Battery tests

Film primary batteries with positive electrodes of manganese dioxide and negative electrodes of metallic lithium were assembled to a card size or a CS3603 size, and subjected to various tests.

3. Results and discussion

3.1. Construction of polymers

Polymers used for the SPE were those with cross-linked PEO (homopolymer type) and those with cross-linked EO copolymer (copolymer type). Structural differences in the SPEs may be seen from the difference in cross-linking density given in Table 1. The relative cross-linking densities were determined by calculating, on a unit weight basis, the number of functional groups that are effective for cross-linking of prepolymers, with the cross-linking density of the cross-linked PEO2 being set as '1', and the results thus obtained are given in Table 1.

3.2. Ionic conductivity

Fig. 1 shows the relationship between the ionic conductivity and the salt concentration in the SPE, which provides the highest ionic conductivity when 1 M lithium perchlorate is included in the plasticizer.

A comparison of the ionic conductivities for two different types of lithium salts with different dissociability is given. In

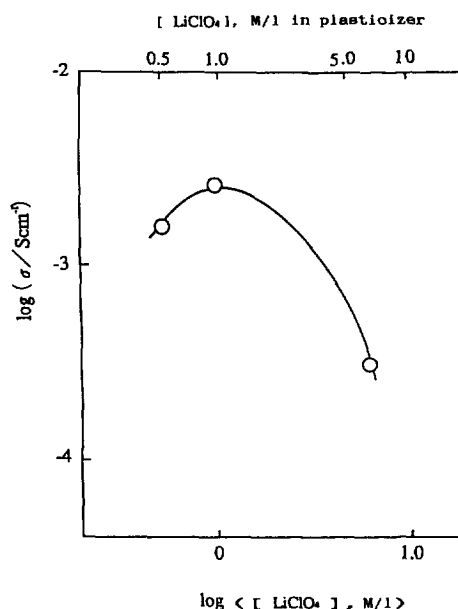


Fig. 1. Relationship between ionic conductivity and salt concentration, cross-linked PEO/LiClO₄, temperature: 25 °C.

Table 2
Mechanical performance of plasticized SPEs

Polymers	Tensile strength (kg/cm ²)	Tensile strain (%)	Compression strength (kg/cm ²)	Bending (180°)
Cross-linked PEO1				cracking
Cross-linked PEO2	0.38	28	> 7.7	no cracking
Cross-linked PEO3	0.70	200		no cracking
Cross-linked EO copolymer	3.2	85	> 9.5	no cracking

Salt: LiClO₄ (1 M/l in plasticizer).

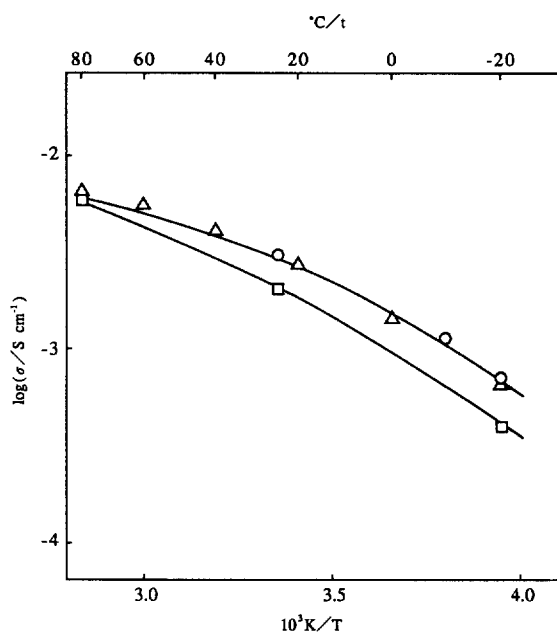


Fig. 2. Temperature vs. conductivity for salts using in plasticized SPE and 1 M salt in plasticizer: (○) cross-linked PEO2/fluoro-type salt; (□) cross-linked PEO2/LiClO₄, and (△) cross-linked EO copolymer/fluoro-type salt.

Fig. 2, the fluoro-type lithium salt shows higher ionic conductivity than lithium perchlorate even at low temperatures because of the higher salt dissociability.

Ionic conductivities of the homopolymer-type polymers and the copolymer-type polymers showed very little difference, see Fig. 2.

3.3. Mechanical performance

Table 2 shows the different mechanical characteristics. Comparison of the tensile strengths reveals that the copolymer-type polymers are stronger than the homopolymer-type polymers. This may be inferred from the difference in cross-linking density.

The compression strength is 9.5 kg/cm² or more for the copolymer-type polymers, whose compression force versus compression rate curve is shown in Fig. 3. When a static pressure up to 5 kg/cm² was applied and then removed slowly, the material was restored to its original thickness. The plasticized network is estimated to have little local fracture

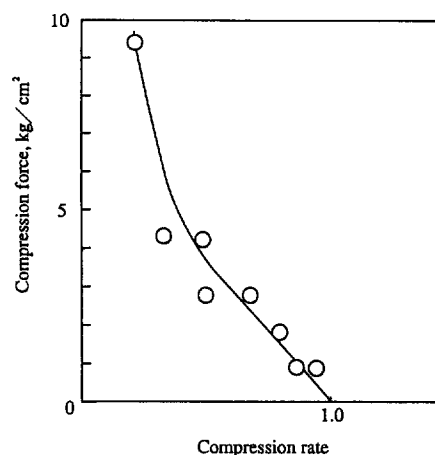


Fig. 3. Compression force vs. compression rate for plasticized SPE: polymer: cross-linked EO copolymer, and salt: 1 M LiClO₄ in plasticizer.

of the polymer network when the pressure of 5 kg/cm² was applied or less at least for a short period of time.

In addition, when an SPE was bent 180°, cracks developed on the SPE using the polymers (cross-linked PEO1) of which the relative cross-linking density was ten times higher than that of the cross-linked PEO2 among the polymers shown in Table 1. However, SPEs using other polymers did not crack (Table 2). This indicates that an SPE is fragile when the relative cross-linking density of polymer in SPE is too high.

3.4. Thermal stability

Fig. 4 shows a DSC curve with regard to thermal stability of the copolymer-type SPE when it is in contact with metallic lithium. The plasticizer (propylene carbonate) had its exothermic peak at 266 °C, and the copolymer at 390 °C. As a result of adding the plasticizer, the exothermic peak for the polymer shifted to the low-temperature side, and the quantity of heat decreased. In contrast, the exothermic peak for the plasticizer shifted to the high-temperature side and the quantity of heat decreased. Adding a proper quantity of the plasticizer may improve the ionic conductivity, but may also cause a problem of decreasing the thermal stability of the polymer. However, its stability would be higher than that of the liquid electrolyte.

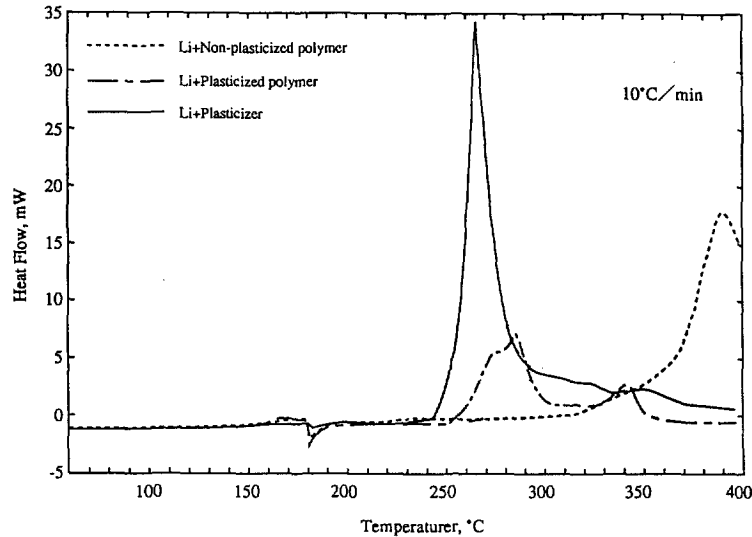


Fig. 4. DSC spectra of various materials for SPE brought into contact with lithium; polymer: cross-linked EO copolymer.

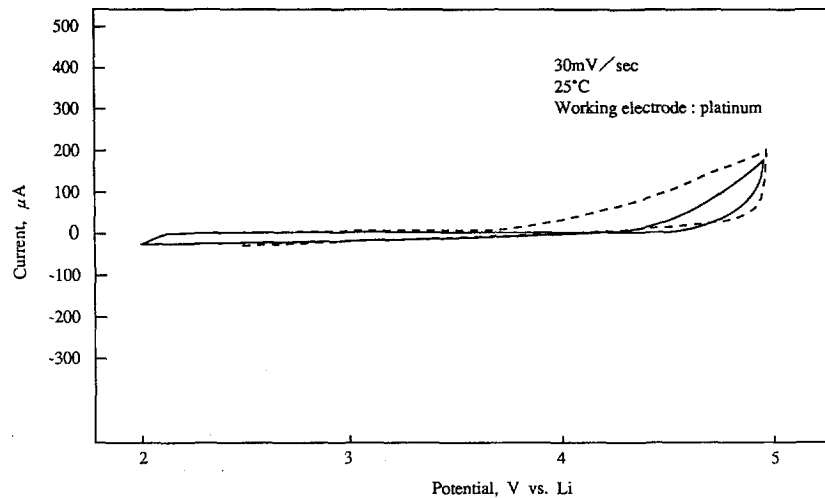


Fig. 5. Cyclic voltammograms of SPEs: (---) plasticized SPE, salt: 1 M fluoro-type salt in plasticizer; (—) non-plasticized SPE; salt: fluoro-type salt (O/Li = 30/1), and polymer: cross-linked EO copolymer.

3.5. Electrochemical stability

Fig. 5 shows a cyclic voltammogram of an SPE. It can be seen that the oxidation potential decreased from 4.3 to 3.8 V against lithium in comparison with a system containing no plasticizer (propylene carbonate). The electrochemical stability depends on the plasticizer used, hence its selection is important.

3.6. Application of SPEs to lithium batteries

The characteristics of the SPEs described above when applied to lithium batteries are very interesting. Using the feature of SPEs being easy to handle in the battery production process, the authors have been working on the development of batteries that are as thin as 0.2 to 0.3 mm. Fig. 6 shows examples of the battery shapes.

Improvement in the SPE ionic conductivity has led to an expectation of a significant improvement in temperature char-

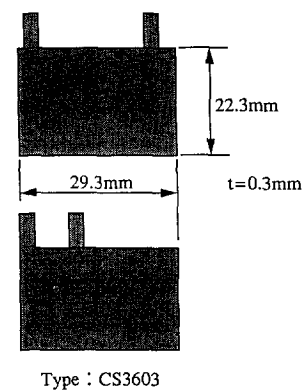


Fig. 6. Film-like primary lithium battery.

acteristics of lithium batteries and their practical application at temperatures below room temperature, as compared with SPEs containing no plasticizer. Fig. 7 shows the rate characteristics at various temperatures [7].

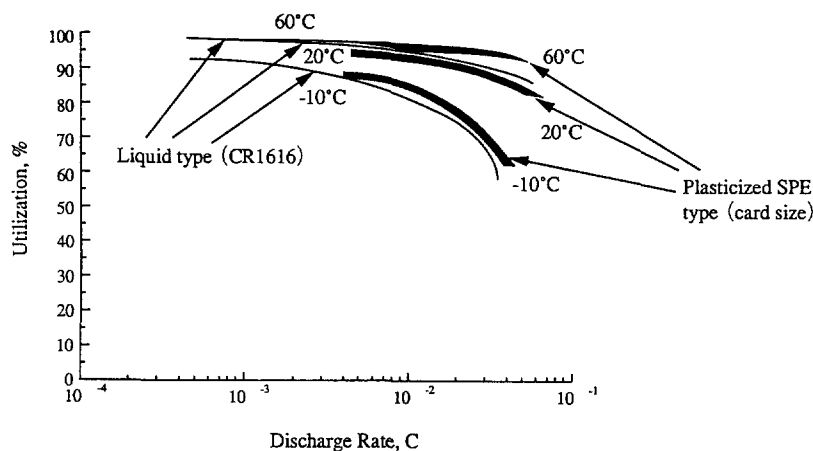


Fig. 7. Discharge characteristics at various temperatures for the film-like primary battery.

Table 3
Mechanical test results of film-like primary battery

Test methods	Pressure (kg/cm ²)				Bending ^a <i>R</i> = 90 mm, 10 000 times	Twist ^b Both sides 30°, 1000 times
	50	50	100	500		
Temperature (°C)	60 ^a	100 ^a	R.T. ^{b,c}	R.T. ^{b,c}	R.T.	20
Results	no shorting	shorted	no shorting	shorted	no shorting	no shorting

^a CS 3603-type cell.

^b Card size cell: 86 × 54 × 0.2 mm.

^c R.T.: room temperature.

Table 4
Results of various heating tests for film-like primary battery

Type	Swelling test	Oven exposure test 93 °C, 20 days	Combustion test
SPE type ^a	swelled at 100 °C	no fire, no explosion	emitted flame up to 5 cm
Liquid type ^b	swelled at 80 °C		exploded and scattered fragments

^a CS 3603-type cell.

^b Coin-type cell (CR 2016).

Table 3 summarizes the test results on the mechanical properties of batteries using SPEs. No batteries have caused shorting even at 60 °C against a load of 50 kg/cm² applied to the battery front surface. The test results for repeated bending done at *R* = 90 mm have ascertained that no shorting was observed even for more than 10 000 bendings, indicating that a battery with a satisfactory strength and flexibility may be provided by using SPEs.

Table 4 summarizes the thermal stability tests of batteries that use SPEs. While the batteries using a liquid electrolyte swell at 80 °C, the batteries using SPEs did not show such swelling below 100 °C. Furthermore, the latter batteries have neither caused ignition nor explosion when stored in an oven at 93 °C for 20 days. In addition, the combustion test results

revealed that the batteries using SPEs are free of explosive burst that may happen on coin-type batteries using a liquid electrolyte. Thus, it has been ascertained that the lithium batteries using SPEs are thermally more stable than batteries using liquid electrolytes.

4. Conclusions

An SPE containing a plasticizer showed an ionic conductivity of 2.4×10^{-3} S cm⁻¹ at 20 °C, and when applied to lithium batteries, it showed a level performance as that of batteries using a liquid electrolyte, both at low temperatures and the same rate characteristics. Its mechanical properties

showed that SPE has excellent strength and flexibility qualities when used in batteries even if it contains a plasticizer. This SPE has also an excellent thermal stability. It is an obvious advantage that the batteries using SPE do not swell even at high temperatures at which liquid electrolyte batteries normally do. Furthermore, the former batteries did not cause any explosion although they burnt, whereas batteries using a liquid electrolyte exploded in some conditions.

Thus, it has been verified that primary lithium batteries using SPE-containing plasticizers have outstanding basic characteristics.

References

- [1] P.V. Wright, *Br. Polym. J.*, 7 (1975) 319.
- [2] M. Gauthier, D. Fauteux, P. Ricoux, D. Muller and M.B. Armand, *J. Electrochem. Soc.*, 132 (1985) 1333.
- [3] P.M. Blonsky and D.F. Shriver, *J. Am. Chem. Soc.*, 106 (1984) 6854.
- [4] D.F. Shriver and G.C. Farrington, *Chem. Eng. News*, (20 May) (1985) 42.
- [5] T. Ono, H. Mishima, S. Izuchi, P. Wang and K. Takeuchi, *Proc. Int. Workshop on Advanced Batteries, Osaka, Japan, 1995*.
- [6] T. Noda, S. Kato, Y. Yoshihisa and K. Takeuchi, *J. Power Sources*, 43–44 (1992) 89–99.
- [7] K. Murata, *Electrochim. Acta*, 40 (1995) 13–14; 2177.