Journal of Applied Electrochemistry **34**: 1211–1214, 2004.
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Study of lithiated Nafion ionomer for lithium batteries

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Received 19 January 2004; accepted in revised form 26 May 2004

Key words: ionomer, lithium batteries, Nafion membrane, polymer electrolyte

Abstract

Lithiated Nafion 112 ionomer was characterized by FT-IR spectroscopy, AC impedance, and cyclic voltammetry. The ionomer swollen with mixed solvents of propylene carbonate (PC) and ethylene carbonate shows ionic conductivity of 8.18×10^{-5} S cm^{-1} at 25 °C and good electrochemical stability to allow operation in Li/ionomer/LiCoO$_2$ cells. The discharge capacity of the first cycle is 126 mAh g^{-1}. Significant capacity loss occurs during cycling due to the presence of PC. AC impedance shows that the passive layer formed at the Li/ionomer interface dominates the cycling performance of the cell.

1. Introduction

Ionomers have many advantages, such as lack of corrosive anionic species, simplicity of the system, unity transference number etc. [1, 2]. They have received much attention with regards to producing single ion conductors to inhibit the concentration polarization in electrochemical applications [3, 4]. Recently, Thomas et al. [5] compared lithium batteries with polymer electrolytes with unity and nonunity transference number and found that though the ionic conductivity of an ionomer membrane is an order of magnitude smaller than that of a binary salt separator, lithium batteries can achieve similar performance since the transference numbers are dramatically different.

Nafion® membrane is a well-known perfluoro ionomer. It has excellent mechanical, chemical and thermal stability. The membranes have been widely used as separator and solid electrolyte in a variety of electrochemical systems, such as sensors, fuel cells, batteries, and electro-organic synthesis [6, 7]. However, there has been little work [6, 8] on the application of perfluoro ionomer in lithium batteries due to its lower conductivity in nonaqueous media. Recently, Doyle et al. [9, 10] summarized previous work on the applications of Nafion ionomers in nonaqueous solvents and studied the ionic conductivity and swelling behavior of lithiated Nafion® ionomers in a wider range of nonaqueous solvents. The ionic conductivity of lithiated Nafion® 117 ionomer reaches 1.00×10^{-4} S cm^{-1} if it is swollen with a mixture of propylene carbonate and ethylene carbonate without the use of a lithium salt. Sachan et al. [11] proposed that perfluoro ionomers may be used in rechargeable lithium polymer batteries if the ionic conductivity exceeds 1×10^{-4} S cm^{-1}. The aim of this work is to study lithiated Nafion® 112 ionomer for use as a polymer electrolyte in rechargeable lithium batteries.

2. Experimental

2.1. *Materials*

Nafion® 112 membrane and Nafion® solution were purchased from DuPont. Battery grade carbonate solvents propylene carbonate (PC), ethylene carbonate (EC) and ethylmethyl carbonate (EMC) were supplied by Yingpai Inc. and contained less than 30 ppm water. All the solvents were used without further purification.

2.2. *Membrane pretreatment*

The membrane was first converted to —SO$_3$H form as follows. After boiling in deionized water for 4 h, the membrane was put in H$_2$O$_2$ (10 wt %) at 80 °C for 3 h and rinsed in boiling deionized water. Then, it was immersed in a solution of 1 M H$_2$SO$_4$ for 3 h and finally washed with deionized water.

A lithium ion exchange procedure was carried out in a solution of 2 M LiOH in 1:2 volume ratio of ethanol and deionized water for 2 h at 80 °C under strong stirring. The ionomer was then rinsed and washed in boiling deionized water to remove the remaining salt and organic solvent. After vacuum drying at 80 °C for several days, it was transferred into an argon-filled glove box.

2.3. *IR characterization*

The FT-IR absorption spectra were recorded on a JASCO FT/IR-660 Fourier transform IR spectrometer over the range 1800–800 cm^{-1}. For each IR spectrum 40 scans were recorded and averaged. The resolution was set to 4 cm^{-1}.

2.4. *Electrochemical measurement*

The ionic conductivity was determined using a conventional AC impedance method with two electrodes. The impedance was measured with a Solartron 1255B Frequency Response Analyzer interfaced with an Electrochemical Interface Solartron 1287 operating in the frequency range 1–1 MHz. Two blocking stainless steel (SS) electrodes were employed. The cyclic voltammetry (CV) was carried out on a Solartron 1287 Electrochemical Interface with lithium foil (99.9%) as both the counter and reference electrodes and SS as the working electrode. All the test cells were assembled and sealed in the glove box.

2.5. *Cell assembly*

The Nafion solution contain 10% perfluorosulfonic acid was neutralized to Li$^+$ form by adding 2 M aqueous lithium hydroxide until the pH rose to 7. The solution was rotary evaporated to form Li-Nafion gel. Mixed solvents of ethanol and butanol (1:2 by volume) were then added to form homogenous liquid. The Li-Nafion content was controlled to 10% to be used as a binder.

The Cathode was fabricated with lithium cobalt oxide ($LiCoO_2$), black carbon and Li-Nafion binder in weight ratios of 80:10:10. The homogenous slurry was cast onto one side of the lithiated Nafion 112 ionomer. After vacuum drying 24 h at 80 °C, the composite membrane was transferred into the glove box and immersed in PC/EC solvent for 1h at room temperature. Lithium foil was used as anode. The charge–discharge performance was evaluated by cycling the cells between 4.25 and 2.5 V at room temperature with a Neware Battery Test System.

3. Results and discussion

Nafion is commonly hydrolyzed in dimethyl sulfoxide (DMSO) for its excellent swelling behavior [9]. However, DMSO is very difficult to remove completely. The residue DMSO will cause a mixed solvent effect and influence the electrochemical properties of the membrane [11]. Here, ethanol was used as swelling agent as developed by Sachan et al. [11]. By comparison, the membrane was also hydrolyzed in a solution of 0.5 M LiOH in a 1:1 volume ratio of DMSO and deionized H_2O for 2 h at 60 °C.

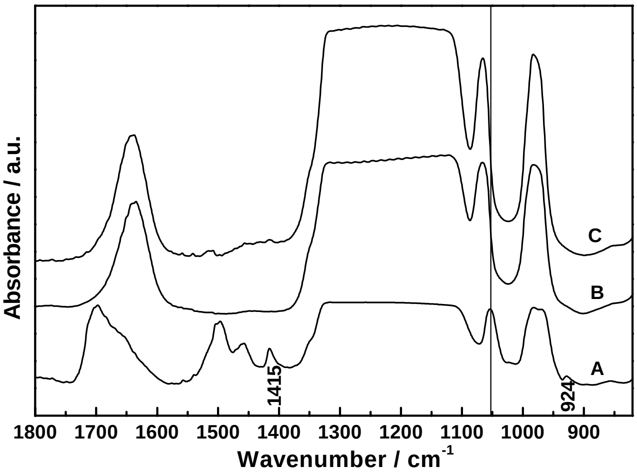

Fig. 1. FT-IR spectra of the Nafion 112 ionomers in different forms: (A) H$^+$ form membrane, (B) Li$^+$ form membrane hydrolyzed in ethanol and (C) Li$^+$ form membrane hydrolyzed in DMSO.

The IR behavior of Nafion ionomers in different cationic forms has been extensively studied [12–16]. FT-IR spectra can be used to identify the membrane in H$^+$ or Li$^+$ forms. Figure 1 shows the FT-IR spectra of the ionomers in H$^+$ and Li$^+$ forms. Due to the thickness of the membrane, the vibrational modes of the membrane cannot be observed between 1400 and 1100 cm^{-1}. The band at 1052 cm^{-1} of spectrum A is assigned to the $-SO_3^-$ symmetric stretch of H-Nafion [12, 13]. It shifts to high frequency in the spectrum of Li-Nafion due to the interaction between Li$^+$ and oxygen. The absorption at 1702 cm^{-1} of spectrum A is attributable to the bending band of protonated water in H-Nafion. This band disappears and vibration of the water molecule appears at about 1630 cm^{-1} in the spectrum of Li-Nafion [14–16]. The middle intensity band at 1415 cm^{-1} and the weak band at 924 cm^{-1} of spectrum A are assigned to S═O and S─OH stretching modes of the undissociated $-SO_3H$ groups in H-Nafion [12]. These bands are absent in the spectrum of Li-Nafion since H$^+$ has been exchanged with Li$^+$. As shown in spectra B and C, the band at 1052 cm^{-1} shifts to 1065 cm^{-1}, the bands at 1702, 1415 and 924 cm^{-1} disappear and a new

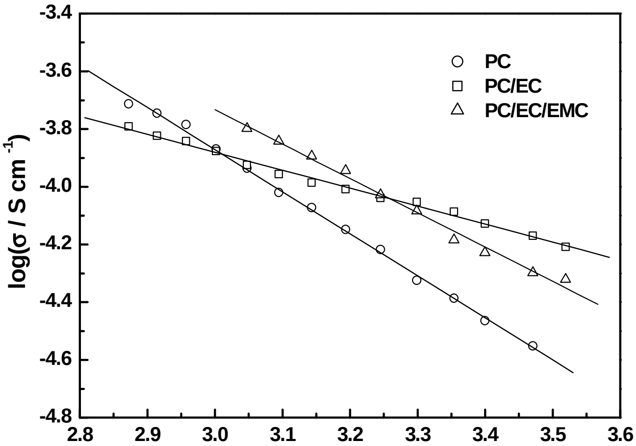

Fig. 2. Arrhenius plots of ionic conductivity for Li-Nafion 112 ionomers swollen in ○ PC, □ PC/EC, △ PC/EC/EMC.

band appears at 1636 cm^{-1}. These indicate [11] that hydrolysis has been carried out completely in the ethanol solution as well as DMSO solution.

Temperature-dependant conductivities and swelling behavior were studied for the Li-Nafion 112 ionomers swollen in PC, PC/EC and PC/EC/EMC. For all measurements, the membrane was initially immersed in excess pure liquid solvent or solvent mixtures (equal volumes) at 25 °C for 2 h and was then dried with filter paper to remove surface solvent. The weight uptake and thickness increase were calculated based on the percentage of the dry membrane. Figure 2 shows the Arrhenuis relationships of the ionic conductivities (σ) vs. the reciprocal temperature ($1/T$) for the Li-Nafion 112 ionomers. The temperature dependence of the conductivity of the swollen membranes agrees well with the Arrhenuis equation over the temperature range studied. The activation energies of the ionomers swollen in PC, PC/EC and PC/EC/EMC are 27.92, 11.93 and 22.79 kJ mol^{-1}, respectively. The result is different from those of Doyle et al. [10] who suggested that the temperature-dependent conductivities agree with Vogel law rather than the Arrhenuis equation if the lithiated Nafion 117 ionomers is swollen with PC or PC/EC. This may be due to their different solvent uptake, an important factor in determining the ionic conductivity [10] of membranes swollen with nonaqueous solvents. The solvent swelling behavior and ionic conductivities of the Li-Nafion 112 ionomers are shown in Table 1. The weight uptake is lower and the thickness increase is higher than those of Li-Nafion 117 reported by Doyle et al. [9, 10]. The conductivity of the ionomer swollen with PC/EC is 8.18×10^{-5} S cm^{-1} and higher than the others at 25 °C. Since Nafion 112 is much thinner, it can potentially be used in lithium batteries.

The electrochemical stability of the Li-Nafion 112 ionomer was investigated using cyclic voltammetry at 25 °C as shown in Figure 3. The membranes were swollen in PC/EC and cycled from −0.6 to 5 V (Li^+/Li) at a sweep rate of 10 mV s^{-1}. The onset of deposition of Li was found at −0.15 V and the stripping peak of Li is at 0.3 V. The Li plating-stripping process is reversible and there are no other oxidation peaks up to 4.25 V. The electrochemical stability of the ionomer is sufficient for use as a separator in lithium batteries.

Table 1. Solvent swelling behavior and ionic conductivities of Li-Nafion 112 membranes swollen in PC, PC/EC and PC/EC/EMC (equal volume)

Solvent	Solvent uptake /wt %	Thickness increase /%	Ionic conductivity at 25 °C /S cm^{-1}
PC	51	36	4.11×10^{-5}
PC/EC	56	30	8.18×10^{-5}
PC/EC/EMC	50	30	6.53×10^{-5}

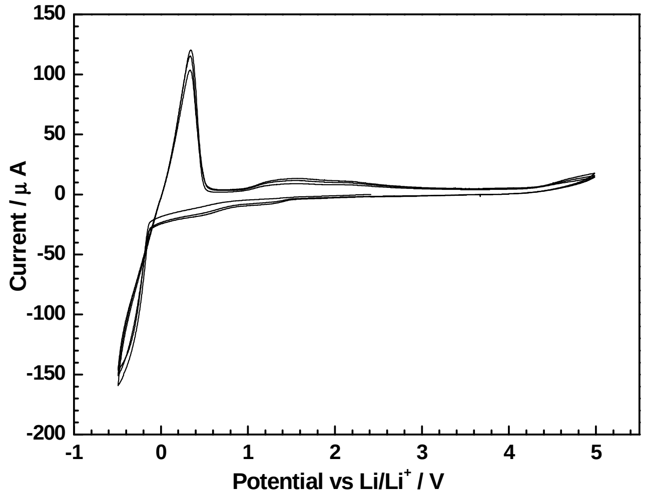

Fig. 3. Cyclic voltammogram for Li-Nafion 112 ionomer swollen in PC/EC with stainless steel as working electrode, Li foil as reference and counter electrodes (scan rate = 10 mv/s; T = 25 °C).

To confirm this, the ionomer composite with $LiCoO_2$ was assembled in a lithium-ion half-cell with a lithium counter electrode. The cycling test was carried out at C/10 and C/5 rate between 2.5 and 4.25 V. The current density was about 0.05 and 0.1 mA cm^{-2}. Figure 4 gives the first charge and discharge curves of the cell at a current density of 0.05 mA cm^{-2}. The specific discharge capacity as a function of cycle numbers is given in Figure 5. The first charge and discharge capacity is 150 and 126 mAh g^{-1}, respectively. The discharge capacities decrease from 126 mAh g^{-1} in the first cycle to 100 mAh g^{-1} in the tenth cycle at C/10. The large irreversible capacity in the first cycle and the comparatively fast decrease in capacity can be explained [17] by the formation of a passive film on the surface of the lithium electrode, which results from the presence of PC solvent. This can be explained by AC impedance spectra of the Li/ionomer/$LiCoO_2$ cell before and after several cycles as shown in Figure 6. The large semicircle at middle frequency is associated with the interfacial resistance at the lithium electrode. And the straight line represents Warburg diffusion impedance between the

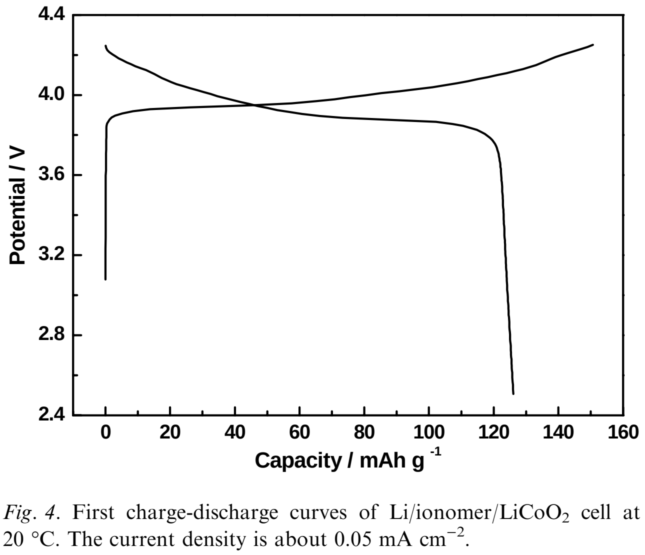

Fig. 4. First charge-discharge curves of Li/ionomer/$LiCoO_2$ cell at 20 °C. The current density is about 0.05 mA cm^{-2}.

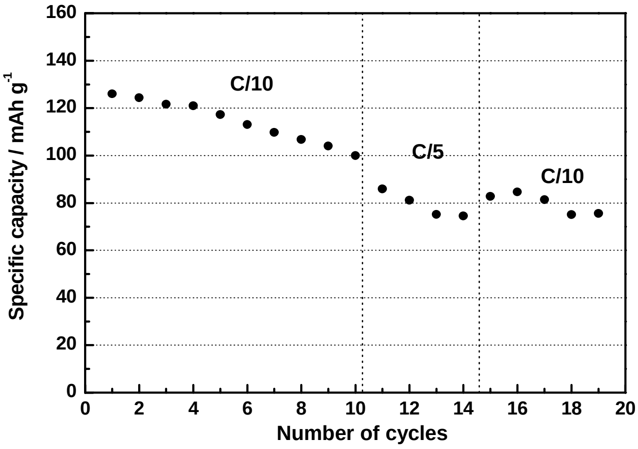

Fig. 5. Evolution of discharge capacity with the number of cycles. The cutoff voltage is from 2.5 to 4.25 V.

electrode and electrolyte. After the first charge–discharge cycle, the interfacial resistance on the Li surface increases greatly, and then decreases to a lower value in the later cycles. In further cycling, the middle-frequency semicircle increases as the cycle number increases and this semicircle is deformed by Warburg diffusion impedence. This result is as the same as that of Wen and Chen [17]. They suggested that the reaction between PC and lithium metal results in a passive layer, which causes capacity loss on cycling due to degradation of the Li/ionomer interface. The passive layer formed at the Li/ionomer interface dominates the rechargeable ability of cells. Therefore, optimizing the electrode formulation and improving the interface properties is expected to improve the cycling performance.

4. Conclusion

Lithiated Nafion 112 ionomer has been studied for use as a polymer electrolyte in lithium batteries. The conduction performance of the ionomers swollen with PC based solvents agrees well with the Arrhenuis equation. The conductivity of the ionomer swollen with PC/EC is 8.18×10^{-5} S cm^{-1} at 25 °C. Cyclic voltammetry shows that the ionomer possesses good electrochemical stability in the range 2–4.25 V. The ionomer is potentially useable in Li/ionomer/$LiCoO_2$ cells. The first charge and discharge capacity is 150 and 126 mAh g^{-1}, respectively. The discharge capacities of the cell decrease from 126 mAh g^{-1} in the first cycle to 100 mAh g^{-1} in the tenth cycle due to the presence of PC. The rechargeability of the cell is determined by the passive layer formed at the Li/ionomer interface.

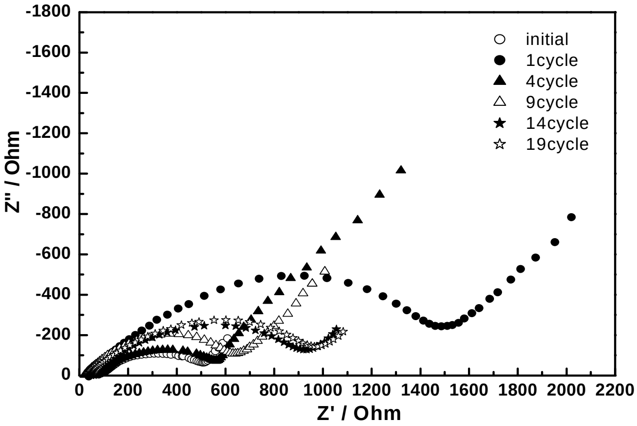

Fig. 6. AC impedance spectrum of the Li/ionomer/$LiCoO_2$ cell at different cycles.

Acknowledgement

The authors acknowledge financial support of the National Key Basic Research and Development Program (2002CB211803).

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