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Polymeric Electrolytes for Ambient Temperature Lithium Batteries

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Polymeric Electrolytes for Ambient Temperature Lithium Batteries

Final Report

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A. Review of Research Results

Summary: Samples of a plasticized Li^+ polymer electrolyte having high conductivity at room temperature were prepared with mixed plasticizer compositions of ethylene carbonate (EC) and propylene carbonate (PC). The influence of EC:PC in varying proportions with 1M $LiAsF_6$ as the dissolved salt on the chemical and electrochemical properties of the electrolyte was studied. Electrolytes with mixed EC:PC compositions were found to have greater thermal stability, improved lithium and cathode (V_6O_{13}) interfacial properties, and superior mechanical properties compared to those prepared with pure EC and PC. The results of this work are relevant to possible uses of such electrolytes in energy storage technologies

A.1. Introduction

Considerable effort has been devoted to creating Li^+-conductive polymer electrolytes with high ambient-temperature conductivities for use in rechargeable Li batteries [1-5]. The goal has been a conductivity of about 10^{-3} S/cm at room temperature. Unfortunately, it has not yet been achieved with any electrolyte composition containing only polymer and dissolved Li salt. Pure polymer electrolytes, such as poly(ethylene oxide) (PEO) and related compounds, are at best considerably lower in conductivity at room temperature.

One of the most successful approaches to increasing the ionic conductivity of polymer electrolytes has been by the addition of various plasticizers. Some of the plasticizers that have been used include polyethylene glycol dimethylether (PEGDME) in PEO [6] which has produced an electrolyte with an ionic conductivity of about 10^{-4} S/cm at 40°C, and propylene carbonate in PEO [1]. Another approach [2] has involved encapsulating Li^+ salts dissolved in mixed organic solvents such as ethylene carbonate/propylene carbonate (EC/PC), EC/PC/tetraglyme within a polymer matrix such as polyacrylonitrile (PAN). Recent work has also shown it possible to prepare electrolytes with conductivities of 10^{-3} to 10^{-4} S/cm at ambient temperature by radiation induced polymerization of polyethers containing organic solvent plasticizers [3-5]. Some compositions retain conductivities as high as 10^{-4}S/cm to temperatures as low as 0°C [3].

Recent work [3,5,7] has shown that in polymer electrolytes prepared by radiation curing of ethylene oxide and acrylate oligomers, the plasticizer used strongly influences the physical, chemical, electrochemical and transport properties

of the polymer electrolyte. The type of Li salt used has a far smaller effect on those properties as has been reported in the 1991 Final Report from this project.

The polymeric electrolyte in this present report was prepared by radiation-induced curing of ethylene oxide/acrylate monomer such as ethylene glycol dimethacrylate and trimethylolpropane trimethacrylate. After curing, the polymer formed a rigid three dimensional structure which provided good mechanical properties for the electrolyte. High conductivity was realized by plasticizing the polymer with EC and PC. All compositions were prepared with a 1M concentration of $LiAsF_6$. In addition to the pure plasticizer, EC/PC mixtures in the ratios (wt%) 25:75, 50:50, and 75:25 were prepared.

A2. Material Characterization

Physical characterization included differential scanning calorimetry (DSC), thermogravimetry (TGA) and dynamic mechanical analysis (DMA). A DuPont 910 DSC/951 TGA and a DuPont 983 DMA equipped with low mass horizontal clamps designed to test thin or small specimens in a sheer mode were used. The DMA was controlled by a DuPont 2100 Thermal Analyzer. Polymer film conductivities and charge-transfer resistances (R_{ct}) were measured by complex impedance/admittance analysis from 10^{-2} Hz to 65 kHz. Electrochemical measurements were carried out with a BAS100 electrochemical analyzer (Bio-analytical Systems, Inc.). For the electrochemical studies, a laminate cell configuration with 9 cm^2 area and electrolyte thickness of 100 μm were used. Cells consisted of both symmetrical Li/SPE/Li and asymmetrical Li/SPE/Ni types.

A3. Results and Discussion

A3.1. Differential Scanning Calorimetry

DSC traces for some of the compositions are shown in Fig. 1. The electrolyte with pure EC has two melting peaks, one small peak Tm_1 around 26°C and a main peak Tm_2 around 39°C, indicating that the electrolyte is partially crystalline at room temperature. The Tg of this complex is -65°C. When 25% by weight PC is added to EC (composition 75:25), both the peak positions Tm_1 and Tm_2 shift to considerably lower values, to 8 and 15°C, respectively. The Tg also shifts to a lower value of about -75°C. Although the electrolyte is now amorphous at room temperature, it is still partially crystalline at sub-ambient temperatures. But when 50% by weight PC is

added (composition 50:50), both melting peaks Tm_1 and Tm_2 disappear completely, rendering the electrolyte amorphous from about -90 to 150°C and shifting the Tg to an even lower value of about -94°C. A further increase of the PC/EC ratio does not result in any further change in the DSC results. The electrolytes with mixed plasticizer compositions of 50:50 and higher PC content along with the pure PC are completely amorphous from -90 to 150°C with a low Tg of about -94°C. As will be seen later, the mixed compositions are thermally more stable than that of pure PC.

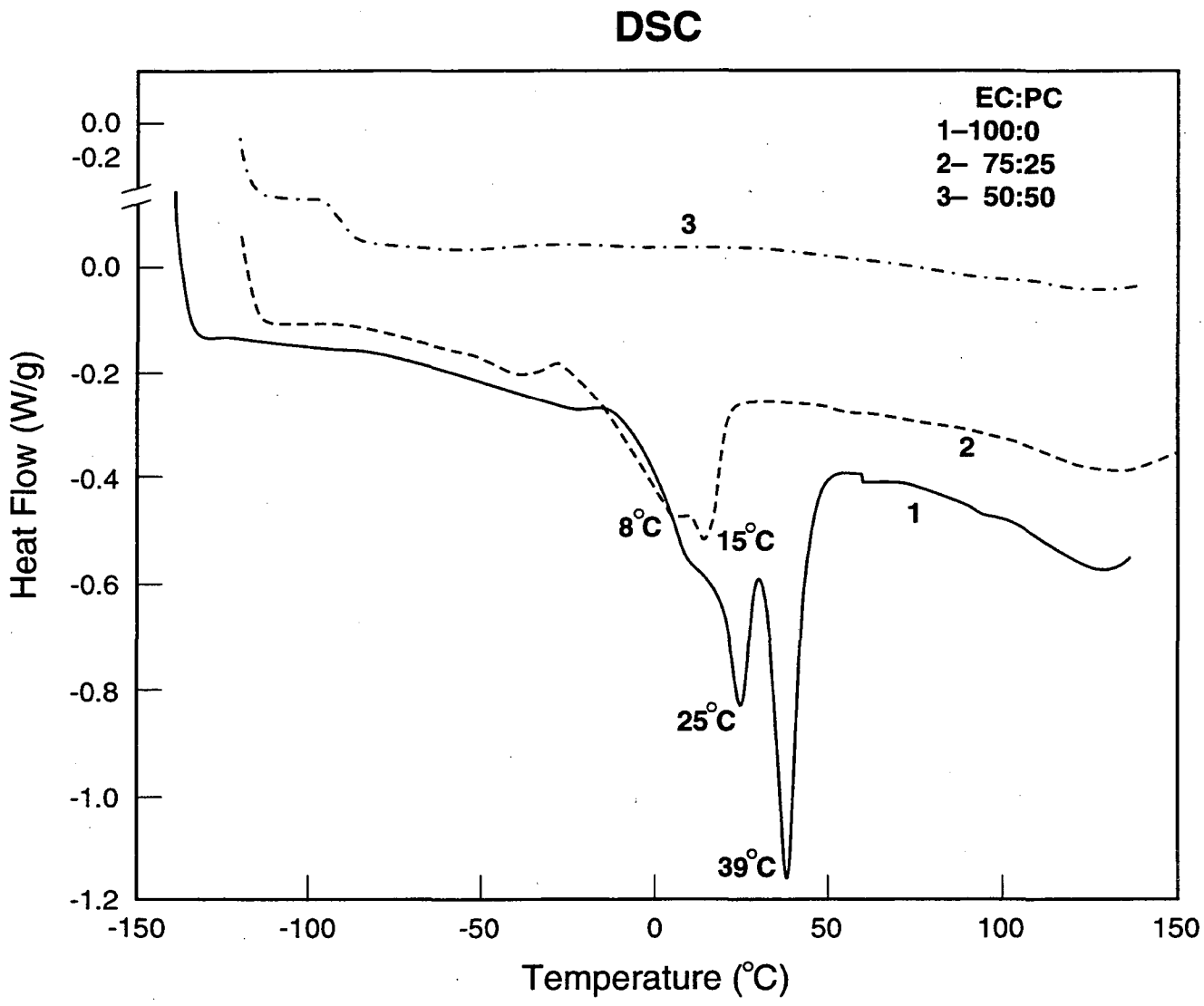


Figure 1. DSC trace of the polymer electrolytes with 1 M $LiAsF_6$ and EC:PC composition of (1) 100:0, (2) 75:25, (3) 50:50, at 10°C/min·

A3.1 Thermogravimetric Analysis

A TGA scan typical of electrolyte compositions containing mixed EC/PC is shown in Fig. 2. The particular composition in this case is EC/PC, 75:25. As can be seen, the decomposition of the electrolyte occurs in a two-step process. The maximum weight losses for the two processes occur at about 198 and 230°C, respectively. The weight loss at 100 and 150°C and the peak derivative temperature for each of the electrolytes are summarized in Table 1. It is evident that the 50:50 composition is thermally the most stable, with a weight loss of only 0.36% at 100°C; whereas pure PC is the least stable, with a 3.28% weight loss at the same temperature. The thermal stability of the 50:50 composition is comparable to that of an electrolyte containing Poly 500 [3].

Physically and mechanically the mixed compositions are completely transparent and rubbery, whereas those made with pure EC or PC tend to be slightly milky and brittle.

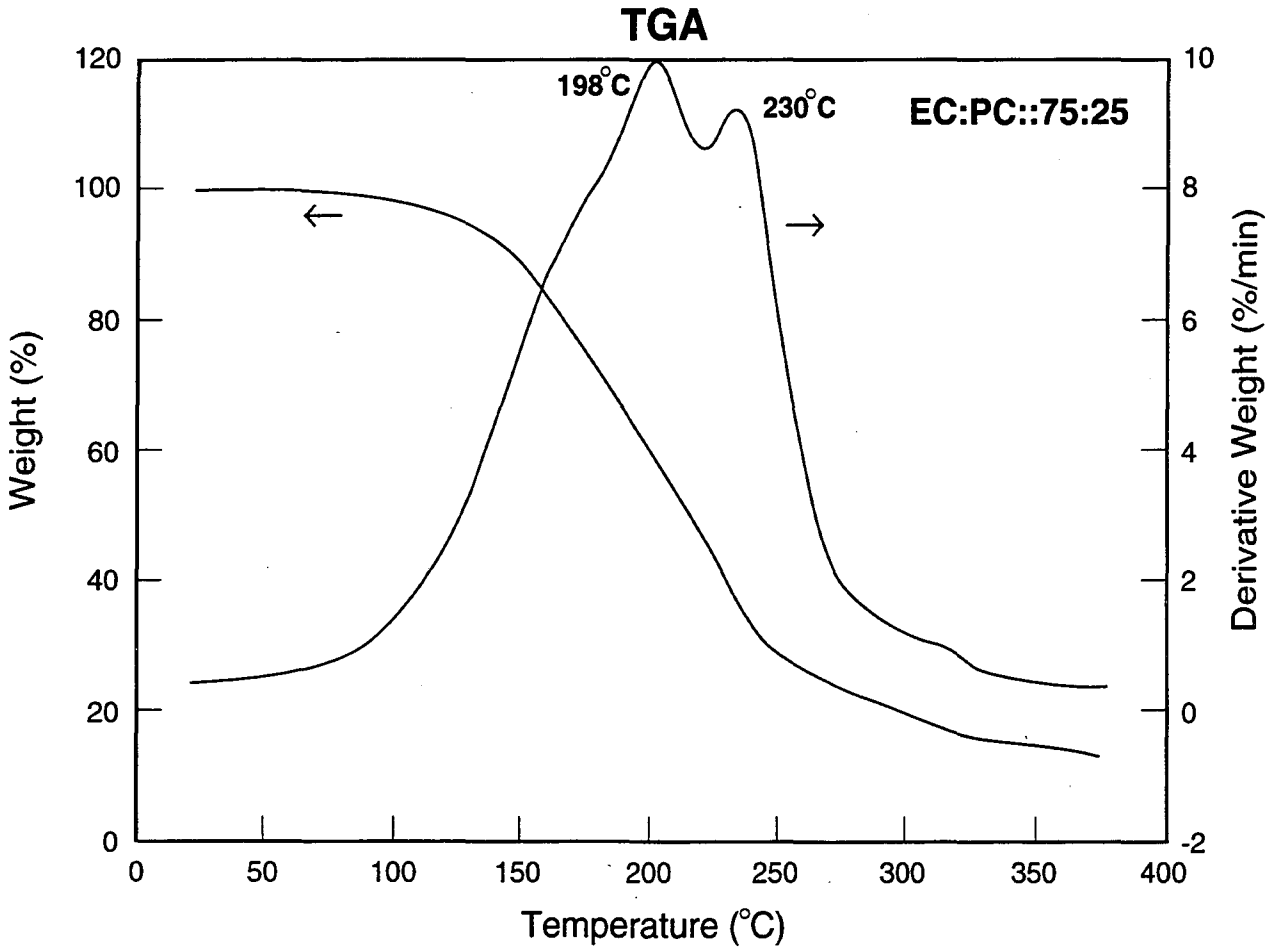


Figure 2. TGA trace of 1 M $LiAsF_6$ with EC:PC composition of 75:25 at 10°C/min.

Table 1. TGA Results 1 M $LiAsF_6$

Plasticizer Composition EC:PC	WT. loss at 100°C	Wt. loss at 150°C	Peak Temp1°C dWT/dT	PeakTemp2°C dWT/dt
100:0	1.78	8.03	202°	237°
75:25	1.84	12.14	198	230
50:50	0.36	6.86	214	238
25:75	2.30	11.07	203	216
0:100	3.28	21.06	160	----
*Poly 500	0.2	0.7	238	----

A.3.2 Conductivity Results

The room-temperature conductivities of the different compositions of the plasticizer containing EC/PC are summarized in Table 2, with the value for Poly 500 as the plasticizer is also included for easy reference [3]. The electrolyte containing 1 M $LiAsF_6$ with pure PC has the highest conductivities of about 2.3×10^{-3} S/cm. The electrolyte containing pure EC had the lowest conductivity, as expected, being partially crystalline at room temperature, although it is still pretty good with a value of about 5×10^{-4} S/cm. The conductivities of the mixed compositions are in between the two limits. The conductivities of 50:50 and higher PC content are only marginally lower ($\sigma > 8.0 \times 10^{-4}$ S/cm) than that of pure PC. As mentioned earlier the electrolytes with pure PC are not very thermally stable at temperatures above room temperature [3] and the dimensional stability is not as good either. Hence by incorporating EC in the mixture, we have been successful in maintaining the desirable properties of PC such as low Tg and a completely amorphous structure, for compositions 50:50 and higher PC content, while greatly improving the thermal and mechanical properties without much reduction in the conductivity. It will also be seen later that the Li cycling stabilities are better in the mixed compositions than with either pure PC or EC.

Table 2. Room Temperature Conductivity Results 1 M $LiAsF_6$

Plasticizer Composition EC:PC	Conductivity S/cm
100:0	5.0×10^{-4}
75:25	7.35×10^{-4}
50:50	8.43×10^{-4}
25:75	9.77×10^{-4}
0:100	2.25×10^{-3}
*Poly 500	1.95×10^{-4}

*Ref. 8

A.3.4 Interfacial Characteristics

Anode/Electrolyte Interface

The charge-transfer resistance, R_{ct}, was measured for a Li interface with the different polymer electrolyte compositions containing 1M $LiAsF_6$ in a cell of the type, Li/SPE/Li, using a.c. impedance measurements (same cell constant in all cases). The results, summarized in Table 3, show that the charge-transfer resistance is highest for the electrode when pure EC is used as the plasticizer and decreases with the addition of PC. This observation is not surprising since previous studies [4,8,9] have shown that Li reacts with the polymer electrolyte to form a complex passivating film. The interfacial charge-transfer characteristics are influenced by the nature of passivating film, the temperature of operation, and the thickness of the film at the interface.

Table 3. Change of charge-transfer resistance, R_{ct}, at lithium interface withplasticizer compositions

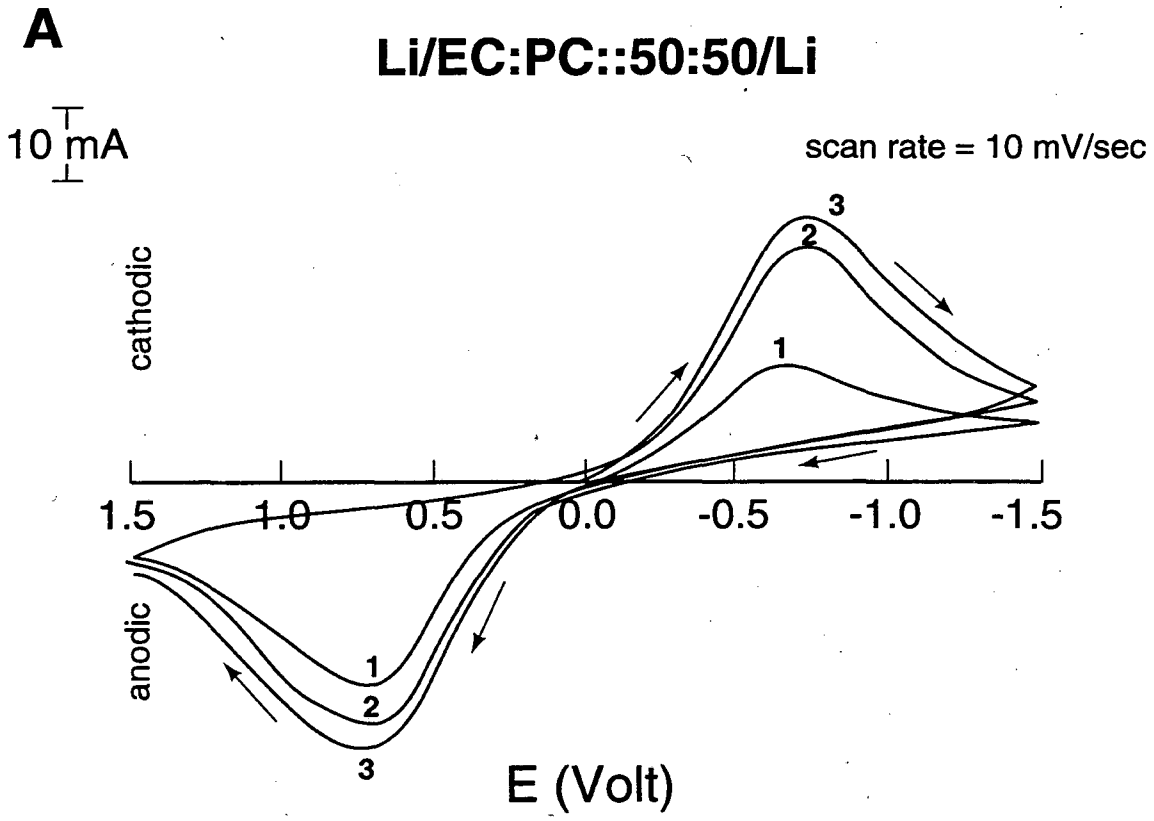
Plasticizer Composition EC:PC	R_{ct} (Ohm) Li /Li Cell
100:0	323
75:25	67
50:50	69
25:75	51
0:100	49

For all the compositions studied, it was found that the charge-transfer resistance decreased when a current is applied to the cell, indicating a typical behavior of an electrode surface covered with a thin film that is formed by reaction between the electrolyte and Li electrode.

The bulk electrolyte resistance increased minimally over a period of one month for all compositions. The charge-transfer resistance increased most with pure EC, less with pure PC, and least with compositions of EC:PC of 50:50 and 25:75, indicating that the mixed composition electrolytes are more stable in contact with Li and may show better Li cycle life in battery applications.

A.3.5 Lithium Cyclability

Cyclic voltammetry (CV) studies on symmetrical Li/SPE/Li cells show that all of the EC and PC electrolyte compositions are stable up to +4.0 V *vs.* Li/Li^+ [3]. Figure 3 shows a typical CV for two different compositions, 50:50 and 25:75 at 10 mV/sec and 2 mV/sec, respectively. The voltage ranges shown are +1.0 V and +1.5 V, but other experiments indicate that the electrolytes are stable up to +4.0 V. The only reaction observed is the result of Li plating and stripping. As can be seen from Fig. 3, the Li oxidation/reduction process is reversible and reproducible after the first cycle at scan rates of 1 to 10 mV/sec. The CV for an electrolyte with pure PC as the plasticizer is similar to that shown in Fig. 3. However, the voltammograms for electrolytes containing pure EC and a 75:25 EC:PC mixture are not reversible, as evident from the low ratio shown in Table 4. To evaluate the reversibility of the redox process in the various electrolyte compositions, the ratio of half peak anodic (HPk_a) and half peak cathodic (HPk_c) areas have been evaluated and are summarized in Table 4. The reversibility is poorest for pure EC ($HPk_a/HPk_c = 0.56$), excellent for 50:50 and 25:75 (HPk_a/HPk_c = nearly 1), and the value for pure PC is also very good. Hence, for Li cyclability mixed compositions of 50:50 and higher PC content are desirable.



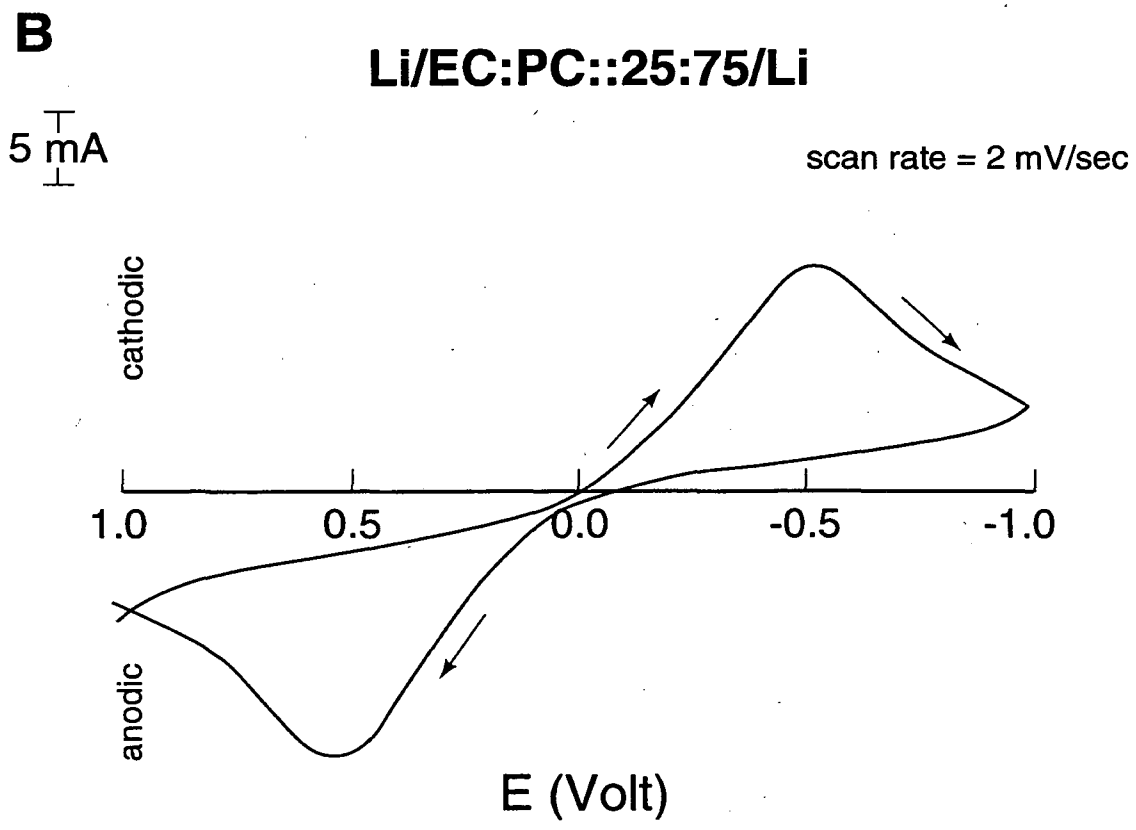


Figure 3. Cyclic voltammogram of Li/SPE/Li type cell at room temperature, area = 9 cm^2 (A) EC:PC::50:50 at scan rate of 10 mV/sec and EC:PC:: 25:75 at scan rate of 2 mV/sec.

Table 4. Reversibility of the lithium redox process and lithium plating/stripping efficiency at nickel substrate in various electrolyte compositions

Composition EC:PC	Ratio HPk_a/HPk_c	Li-plating/stripping Efficiency (%)
100:0	0.56	45
75:25	0.85	50
50:50	1.01	84
25:75	1.05	78
0:100	0.93	78

In a previous study of the Li cycling efficiency [10] in organic solvents such as EC, PC, EC:ether mixtures and EC:PC mixtures with $LiAsF_6$, it was reported that the maximum Li cycling efficiency was achieved at an equimolar ratio of PC and EC. The authors also established from SEM, FTIR and X-ray microanalysis that EC is reduced by Li to form a surface film that is quite different from that observed with PC and more homogeneously distributed on the Li surface. When EC is present as a co-solvent with PC, the Li cycling characteristics are improved. It appears that the EC in such mixtures dominates the film passivation process. Hence Li dissolution and deposition are more homogenous and less dendritic, and the Li cycling efficiency obtained in the mixtures containing EC is high. It is not surprising that radiation-cured polymer electrolytes containing EC:PC as the plasticizer behave similarly to the pure organic solvent system.

A.3.6. Lithium Plating and Stripping

The plating and stripping of Li from the electrolytes were investigated on a nickel substrate. When the Ni electrode in an asymmetric cell of the type, Li/SPE/Ni, was swept cathodically (1-5 mV/sec) in an electrolyte containing pure EC as the plasticizer, an irreversible reduction peak occurred around 1.3 V, which diminished with cycling (Fig. 4A) but did not disappear. The peak was followed by the plating of Li onto the Ni electrode beginning around -0.18 V. Reversing the scan, the stripping of Li was observed with the current peaking around 0.28 V; no other oxidation peak was observed up to +2.4 V *vs.* Li/Li^+. Note that the potentials reported here are all IR compensated.

The source of the irreversible peak around 1.3 V is not known. However, with increasing PC content it diminishes. For compositions containing 50% or higher PC (Fig. 4B), the irreversible peak was absent and Li plating and stripping peaks occurred between -0.4 and +0.4 V *vs.* Li/Li^+ (Fig. 4B). No other peaks appeared up to 3.2 V *vs.* Li/Li^+. Lithium plating and stripping in these cases are well defined and, as can be seen from Fig. 4B, quite reversible and reproducible. The characteristics of the peaks do not change appreciably with extended cycling after the first cycle. The efficiency of Li plating/stripping is quite high in electrolytes containing high concentrations of PC.

A.4. Conclusions

Of the polymer electrolyte compositions studied in this work, the one containing a 50:50 EC:PC plasticizer mixture is the most stable; the composition with pure PC is the least stable. Hence, by incorporating EC into the electrolyte, it has been possible to maintain the desirable properties of PC (*i.e.*, low Tg, completely amorphous), but eliminate the undesirable low thermal stability observed with pure PC.

The conductivities of the electrolytes containing a plasticizer of 50% PC and higher are only marginally lower ($\sigma > 8 \times 10^{-4}$ S/cm) than that of a pure PC electrolyte ($\sigma = 2.3 \times 10^{-3}$ S/cm). Unfortunately, electrochemical cells with pure PC electrolytes appear more prone to Li dendrite formation, hence shorter cycle life.

Lithium plating and stripping processes were more reversible with the electrolytes containing mixed EC:PC plasticizers and the Li cycling efficiency was quite high above 50% PC content. Lithium intercalation and de-intercalation reactions in V_6O_{13} composite cathodes were also found to be quite reversible.

Hence the properties of these mixed plasticizer compositions, especially those of 50% and higher PC content are very desirable and promising for the secondary Li battery applications over a wide range of temperatures (-60 to 100°C).

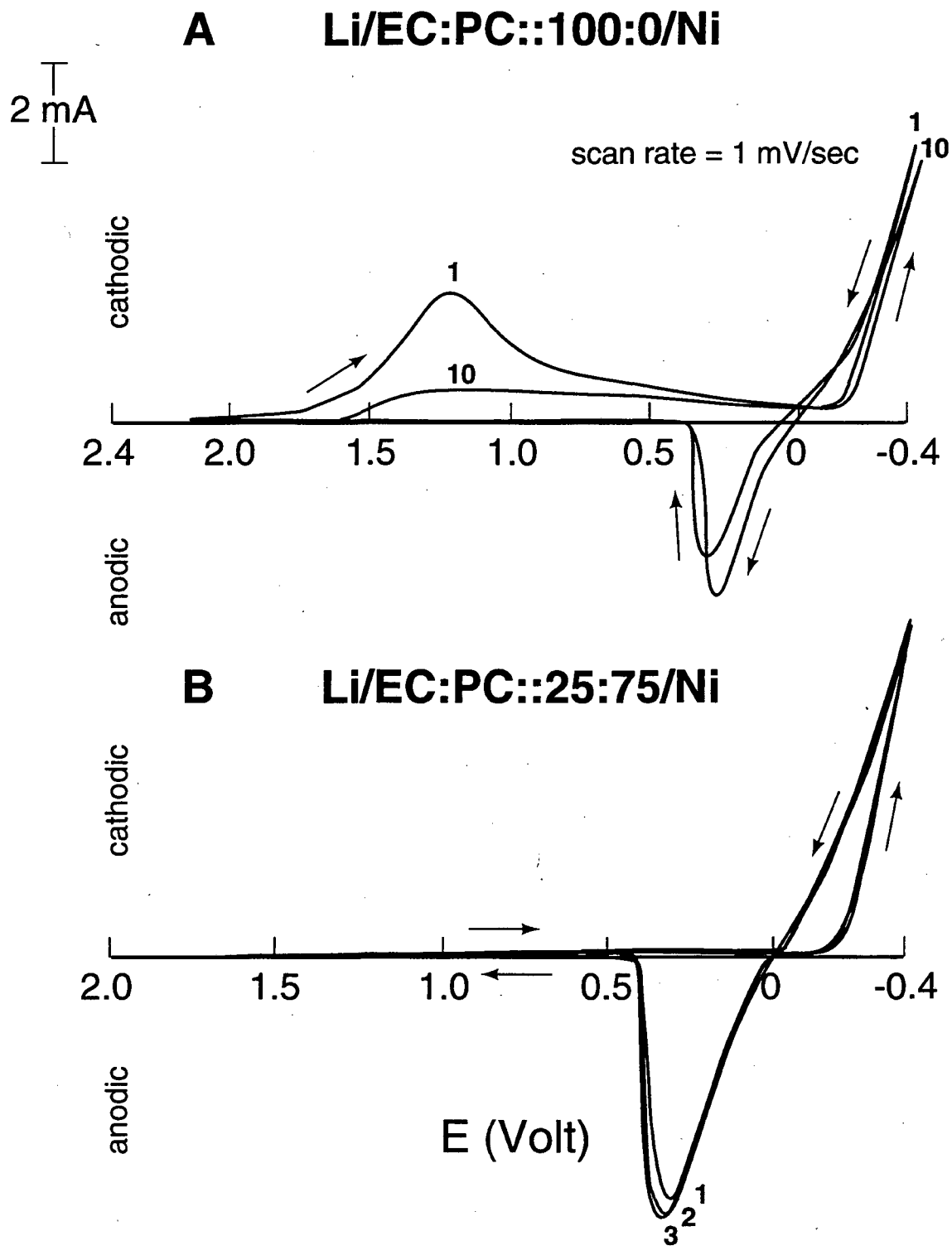


Figure 4. Cyclic voltammogram of Li/SPE/Ni asymmetric cell at room temperature, area = 9 cm^2 (A) pure EC at scan rate of 1 mV/sec. (B) EC:PC::25:75 at the same scan rate.

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