Li^+-Conductive Solid Polymer Electrolytes with Liquid-Like Conductivity

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Ever since the discovery of ionic conductivity in alkali metal salt complexes of solid polymers such as poly(ethylene oxide) (1), and the recognition of their technological importance for the construction of solid-state rechargeable batteries, electrochromic devices and sensors (2), identification of solid polymer electrolytes having conductivities of about 10^{-3} $ohm^{-1}\cdot cm^{-1}$ at room temperature remained an ambitious goal (3). We wish to report here the preparation and characterization of Li^+ conductive polymer electrolytes with ambient temperature conductivities up to ~$4x10^{-3}$ $ohm^{-1}\cdot cm^{-1}$, characteristic of some organic liquid electrolytes. They have been isolated as dimensionally stable, free-standing films. These electrolytes are composed of Li salt-solvates of certain organic solvents immobilized in a polymer network of polyacrylonitrile (PAN), poly(tetraethylene glycol diacrylate) (PEGDA) or poly(vinyl pyrrolidone) (PVP). A typical electrolyte comprises 38 mole-percent (m/o) ethylene carbonate (EC) and 33 m/o propylene carbonate (PC) containing 8 m/o $LiClO_4$ immobilized in 21 m/o PAN. It has conductivities of $1.7x10^{-3}$ $ohm^{-1}\cdot cm^{-1}$ at 20°C and $1.1x10^{-3}$ $ohm^{-1}\cdot cm^{-1}$ at -10°C. Conductivities we have measured for five different electrolyte films are listed in Table 1. A conductivity of about 10^{-3} $ohm^{-1}\cdot cm^{-1}$ in a solid polymer electrolyte at -10°C can be considered remarkable. Electrolyte No. 1 was prepared by dissolving PAN in an appropriate amount of EC/PC-$LiClO_4$ solution at 120°C and evaporating off the excess solvents in vacuum until a film is formed. Alternatively, electrolyte No. 3 could be prepared by adding PAN and tetraethylene glycol diacrylate (TEGDA) in the appropriate proportion to an EC/PC-$LiClO_4$ solution and UV-irradiating the solution to allow cross linking of TEGDA. Electrolytes No. 4 and 5 based in PEGDA and PVP, respectively, were also prepared by the UV-irradiation technique. Solid-state rechargeable Li/TiS_2 cells utilizing the novel electrolytes have been discharged with high capacities at rates as high as C/2 at room temperature. Detailed studies of solid-state secondary Li cells containing these electrolytes are presently underway. The utility of these solid-electrolytes as media for high-rate solid-state voltammetry at ambient temperatures has been demonstrated by cyclic voltammetry data for ferrocene on a glassy carbon electrode at room temperature (20°C) (Fig. 1). From this, a diffusion coefficient of $4x10^{-8}$ cm^2/s was calculated for ferrocene in electrolyte No. 3. This value in the PC/$LiClO_4$ (0.5M) liquid electrolyte at 20°C is $1x10^{-7}$ cm^2/s (4) and in the conventional polymer electrolyte of MEEP-$(LiCF_3SO_3)_{0.25}$ it is $7x10^{-8}$ cm^2/s at 50°C (5). A comparison of the conductivities of electrolyte No. 1 at different temperatures between -10 and 50°C with those of a MEEP/PEO-$(-LiClO_4)_{0.13}$ composite electrolytes we have prepared (6) and for PEO-$(-LiClO_4)_{0.13}$, given in Figure 2, illustrate the techological importance of these new electrolytes. Solid polymer electrolytes with conductivities between 10^{-3} and 10^{-9} $ohm^{-1}\cdot cm^{-1}$ at room temperature can now be tailor-made to satisfy a given application.

Previously, Watanabe et al. (7) prepared solid electrolytes comprising PC and $LiClO_4$ in PAN. They reported a maximum conductivity of $2x10^{-4}$ $ohm^{-1}\cdot cm^{-1}$. Others have reported even lower conductivities (8). The generality of the technique and the utilization of Li salt-solvates derived from mixtures of solvents of high dielectric constants to form electrolytes of high conductivity at room temperature and below are being demonstrated here for the first time.

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Table 1

Conductivities of Solid Polymer Electrolytes

Electrolytes	Conductivity ($ohm^{-1} \cdot cm^{-1}$)[1]			
	-10°C	0°C	20°C	50°C
1. 38%[2] EC/33% PC/21% PAN/8% $LiClO_4$	$1.1x10^{-3}$	$1.2x10^{-3}$	$1.7x10^{-3}$	$3.5x10^{-3}$
2. 42 EC/36 PC/15 PAN/7 $LiCF_3SO_3$	$4.0x10^{-4}$	$6.0x10^{-4}$	$1.4x10^{-3}$	$2.2x10^{-3}$
3. 62 EC/13 PC/16 PAN/1 PEGDA/8 $LiClO_4$	$4.0x10^{-4}$	$6.0x10^{-4}$	$1.2x10^{-3}$	$3.0x10^{-3}$
4. 68 EC/15 PC/3 PEGDA/14 $LiClO_4$	$1.2x10^{-3}$	$2.1x10^{-3}$	$4.0x10^{-3}$	$8.0x10^{-3}$
5. 35 EC/31 PC/24 PVP/10$LiCF_3SO_3$	$4.0x10^{-5}$	$1.3x10^{-4}$	$5.0x10^{-4}$	$1.0x10^{-3}$

[1]All conductivities were measured by the complex impedance technique (6).
[2]All are mole percentages.

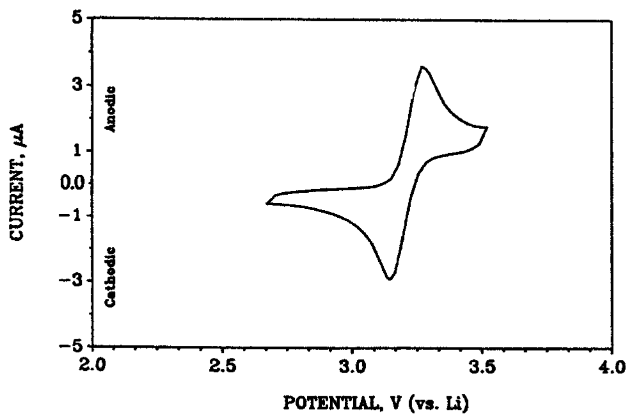

Fig. 1. Cyclic voltammogram of 3.3 mM ferrocene in EC/PC/PEGDA - $LiClO_4$ at room temperature. Sweep rate = 50 mV/s.

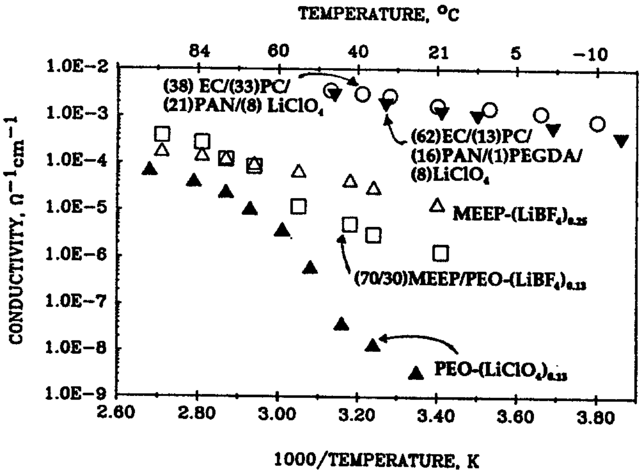

Fig. 2. Comparison of the conductivities of the new solid polymer electrolyte with PEO and MEEP-based electrolytes. The composition of the new electrolyte is given in mole percentage while that for the MEEP/PEO-$(LiX)_n$ is given as O/Li^+ ratios as previously (6).

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