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ABSTRACT

A new class of polyethers has been prepared by the Mitsunobu coupling of poly(4-vinyl phenol), P4VP, with low molecular weight poly(ethylene glycol)methyl ether. These comb-like polymers, having ca. 20-30% residual phenols, were characterized by IR, DSC, and TGA. Results of thermal analysis on the polymers suggest thermal stability to at least 300°C and a glass transition temperature in the range -30 to -40°C. Complexes with $LiPF_6$ gave conductivities of ca. 1×10^{-5} S/cm at room temperature. The polymers were blended with plasticized poly(vinylidene fluoride) (PVDF) to prepare porous films and subsequently infiltrated with lithium salts and ethylene and ethyl methyl carbonate. Ionic conductivities of these hybrid films were measured from –20°C to 40°C. Conductivities as high as 2.4×10^{-3} S/cm are observed at room temperature. The electrochemical stability of hybrid materials was studied by cyclic voltammetry.

INTRODUCTION

There has been much recent focus on the development of suitable materials for lithium secondary cell components. The potential functions of these materials

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in this context are varied: they may be employed as separators, as binder material for the anode, or as the source of a form of "disordered carbon" for use as an intercalation host within the cell. Polymer electrolyte materials to be employed as separators must possess (1) the ability to solvate inorganic salts and (2) mechanical and electrochemical stability at the cell's operating conditions. The ease of migration of lithium ions during the course of cell discharge is predicated on the ionic conductivity of the polymer electrolyte, and is therefore a key characteristic of any new material to be employed as cell separator [1]. The structural attributes believed to enhance ionic conductivity include large free volume, the ability of the polymer chains to engage in segmental motion, and the presence of donor atoms such as oxygen to coordinate to the lithium ion [2, 3]. Large free volume is most readily incorporated in polymer structure by increasing the number of chain ends in the molecule. The concept of "hyperbranching" has met with some success in this regard [4]. Segmental motion of chains can be accomplished by the inclusion of polyether chains, which have the further advantage of providing donor oxygen to the polymer structure. A recent report by Gramain and coworkers suggests that materials possessing an aromatic backbone with pendant polyether chains to form comb-like structures show promise as ion conductors [5].

There remains a need for new electrolytes that are easily synthesized and processed yet afford acceptable properties as battery electrolytes and/or electrode binder materials. Toward that end, we report here the synthesis, characterization and preliminary ionic conductivity and electrochemical analysis of a new polymer electrolyte (PHS-MPEG) depicted in Scheme 1, derived from poly(4-vinyl phenol), P4VP, and poly(ethylene glycol)methyl ether (MPEG) via the Mitsunobu[6] etherification using triphenyl phosphine (PPh$_3$) and diethylazo dicarboxylate (DEAD). This is a random copolymer with m/n of about 3:1, and x in this work was, on average, about 7.

We have used this approach to modify other polyphenols (e.g., the polyphenol derived from enzyme-catalyzed polymerization of 4-phenyl phenol [7]), although we focus here on the poly(4-vinyl phenol) derivatives. Our approach represents a useful alterative to oligoether-modified polymers discussed in recent related work, namely the polymerization of phenols with pendant oligoethers by enzymatic catalysis, [8] the synthesis of polystyrene-PEO graft copolymers, [9]
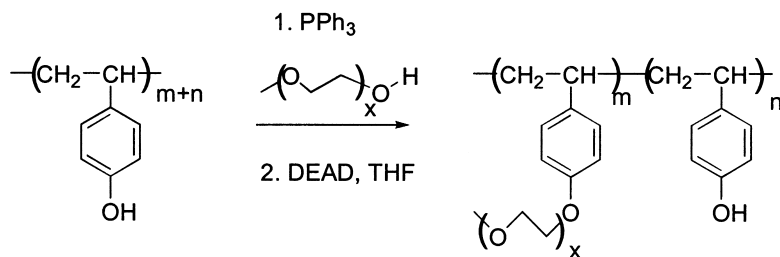
Scheme 1. Synthesis of P4VP-MPEG.

and the use of poly(4-hydroxystyrene) as a multifunctional initiator for grafting of poly(ethylene oxide) [10].

EXPERIMENTAL

Synthesis

All reagents used in the syntheses were purchased from Aldrich Chemical. Preparation of P4VP-MPEG: P4VP (1.2 g, 1 equivalent, M_n = 20,000 g/mol, used as received), poly(ethylene glycol)methyl ether [M_n = 350 g/mol; density = 1.089 g/mL] (8.23 mL, 1.2 equivalents), and triphenyl phosphine (3.14 g, 1.2 equivalents) were stirred together in dry THF under N_2 atmosphere. Diethylazodicarboxylate [DEAD] (2.4 mL, 1.5 equivalent) in 10 mL of dry THF was placed in an addition funnel, flushed with nitrogen, and then added dropwise over a 20-minute interval to the reaction mixture. Diethyl ether was added to the mixture after 1 hour. The THF/ether layer was decanted from the white precipitate, which was washed two more times with ether and then with methanol and dried. Yield: 6 g (approximately 60%).

Thermal Analysis

DSC and TGA measurements were made on a Perkin-Elmer Pyris 1 Differential Scanning Calorimeter and Thermal Gravimetric Analyzer. DSC measurements were carried out in aluminum pans with helium purge gas at 20 ml/min. and a scan rate of 10° C/min. TGA was carried out under nitrogen purge in platinum pans at a flow rate of 20 ml/min. and a scan rate of 10°C/min.

Spectroscopic Characterization

Infrared measurements were obtained on neat samples on a Nicolet Avatar FTIR with HATR multi-bounce accessory.

Colorimetric Titration

Fine, gel-like dispersions of P4VP-MPEG were titrated with tetrabutylammonium hydroxide in n-butylamine to colorimetric endpoint [11, 12] to determine the percentage of remaining unreacted phenols. We typically find that 25-30% of the phenol groups remain after etherification.

Measurement of Electrical Properties

P4VP-MPEG was dispersed in N-methylpyrrolidinone (NMP) and placed in Ni vessels and dried for 24 hours under vacuum. The polymer has limited solubil-

ity at room temperature, but dissolves in NMP at temperatures > 60°C. For the solid P4VP-MPEG (S series in Table 1; no ethylene carbonate or ethyl methyl carbonate added), the electrolytes employed were lithium hexafluorophosphate, $LiPF_6$ and lithium imide, $LiN(SO_2CF_3)_2$ designated LiTFSI. After dissolution, the solvent was evaporated and residues dried in vacuum. For liquid-based electrolytes (L series in Table 1), P4VP-MPEG was mixed with varying amounts of PVDF and SiO_2 and dissolved in a mixture of dibutyl phthalate (DBP) and acetone (frequently noted as the "Bellcore" approach) [13]. The resulting solution was doctor-bladed onto glass plates and the acetone allowed to evaporate to yield a thin DBP-plasticized film. Subsequent removal of DBP with methanol produces a porous film which is treated with an electrolyte solution of $LiPF_6$ (1 mol/dm³ concentration) in an ethylene carbonate (EC)/ethyl methyl carbonate (EMC) mixture (1 EC/3 EMC by mass). For conductivity measurements, a two-electrode configuration glass cell was used. Temperature control was maintained with a Tenny Environmental Chamber; temperature runs ranged from –40°C to 60°C. Impedance measurements for liquid-based electrolytes were carried out with a Gamry dc/ac potentiostat/galvanostat. SE electrolytes impedance measurements were completed with a Solartron 1286 Electrochemical Interface and 1255 Frequency Response Analyzer.

Measurement of Electrochemical Stability

Three-electrode cells were fabricated for these studies. For electrolyte reduction stability studies, cells were cycled at 10 mV/s over the potential range of around 3.0 (OCV) to 0.1 or 0.2 V vs. a Li/Li$^+$ reference. For electrolyte cathodic stability studies, cells were cycled at 10 mV/s over the potential range of around 3.0 (OCV) to 5.0 V vs. a Li/Li$^+$ reference electrode. We employed the blend composition that produced the most promising results in our conductivity studies—T1/PVDF/SiO$_2$ of 0.2/1.5/1.0 (mass ratio) for the CV scans. The concentration of electrolyte in solution used for all studies was 1 mol dm^{-3} LiPF$_6$ in EC/EMC (1/3 mass ratio).

Table 1. Specific Conductivities of Polymer Films (σ, S/cm)

Sample[a]	−40° C	−20° C	0° C	10° C	25° C	40° C
S-1	—	7.8×10^{-9}	5.5×10^{-7}	2.3×10^{-6}	1.0×10^{-5}	4.1×10^{-5}
S-2	1.34×10^{-8}	8.1×10^{-8}	5.4×10^{-7}	1.7×10^{-6}	5.47×10^{-6}	1.9×10^{-5}
L-1	—	—	—	4×10^{-5}	1.4×10^{-4}	—*
L-2	9×10^{-5}	3.6×10^{-4}	1.2×10^{-3}	—	1.9×10^{-3}	2.4×10^{-3}
L-3	2×10^{-4}	6×10^{-4}	1.2×10^{-3}	1.5×10^{-3}	1.9×10^{-3}	—*

[a]Sample S-1: P4VP/LiPF$_6$ (5/1 mass ratio); S-2: P4VP/PVDF/LiTFSI (1.5/1.5/1.0 mass ratio); L-1: P4VP/PVDF (0.4/1.0 mass ratio); L-2: P4VP/PVDF (0.6/0.3 mass ratio); L-3: P4VP/PVDF/SiO$_2$ (0.2/1.5/1.0 mass ratio).

RESULTS AND DISCUSSION

The Mitsunobu etherification of P4VP proceeds to a level of 70-77% as determined by colorimetric titration. IR spectroscopy shows the significant decrease of the phenolic -OH stretch at ca. 3500 cm^{-1} and growth of a band at ca. 1090 cm^{-1} ascribed to the C-O-C stretch in ether units. P4VP-MPEG is typically insoluble but swellable in many solvents at room temperature. This may be the result of light crosslinking from contamination of MPEG with small amounts of poly(ethylene glycol). However, the polymer appears to eventually dissolve in NMP at higher temperatures, suggesting that perhaps strong intermolecular hydrogen bonding between residual phenols and MPEG side chains is responsible for the poor low-temperature solubility. In fact, P4VP is known to form blends with many different polymers by virtue of strong intermolecular interactions [14]. We note that there exists IR data to support strong hydrogen bonding between P4VP and poly(ethylene oxide), PEO, [11,12] and that phenolic resins (novolaks) appear to disrupt crystallinity in PEO leading to a rise in conductivity [17]. These residual active hydrogens do not appear to interfere with electrochemical stability (discussed later), and may in fact be beneficial in facilitating good adhesion between electrolyte and electrodes. The residual phenols afford the opportunity to introduce additional, different functionality to P4VP-MPEG and to add ion
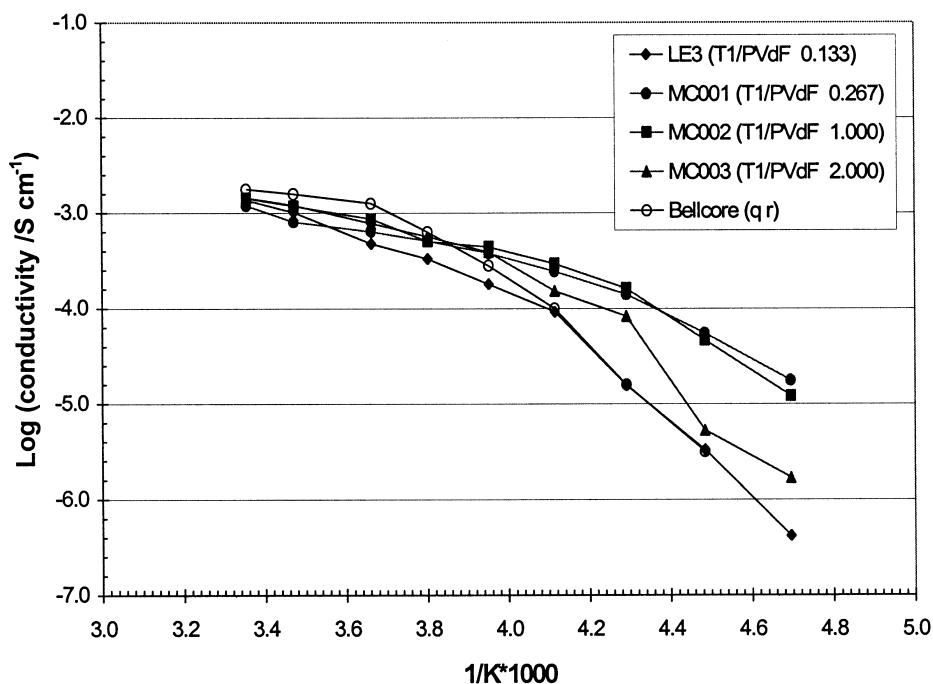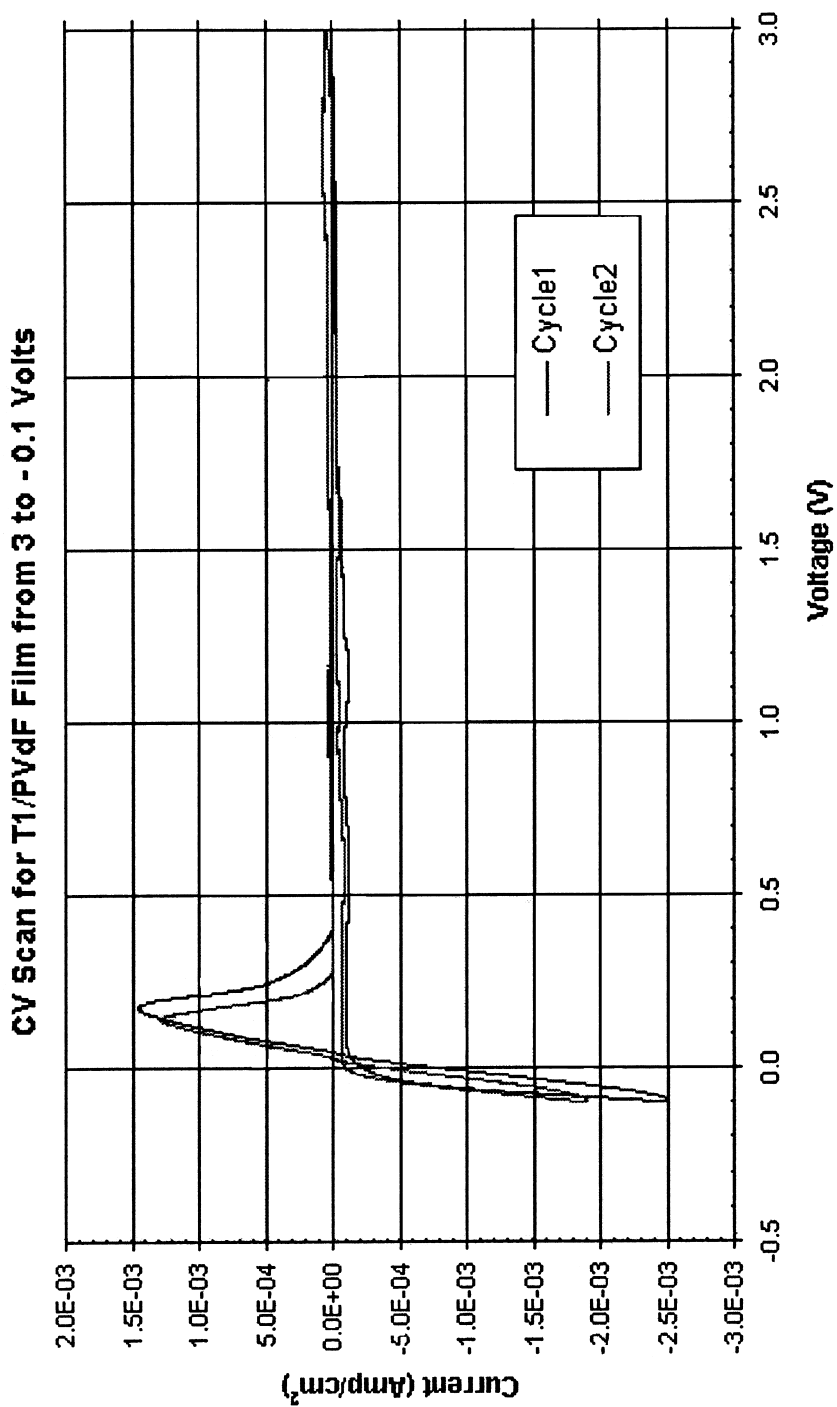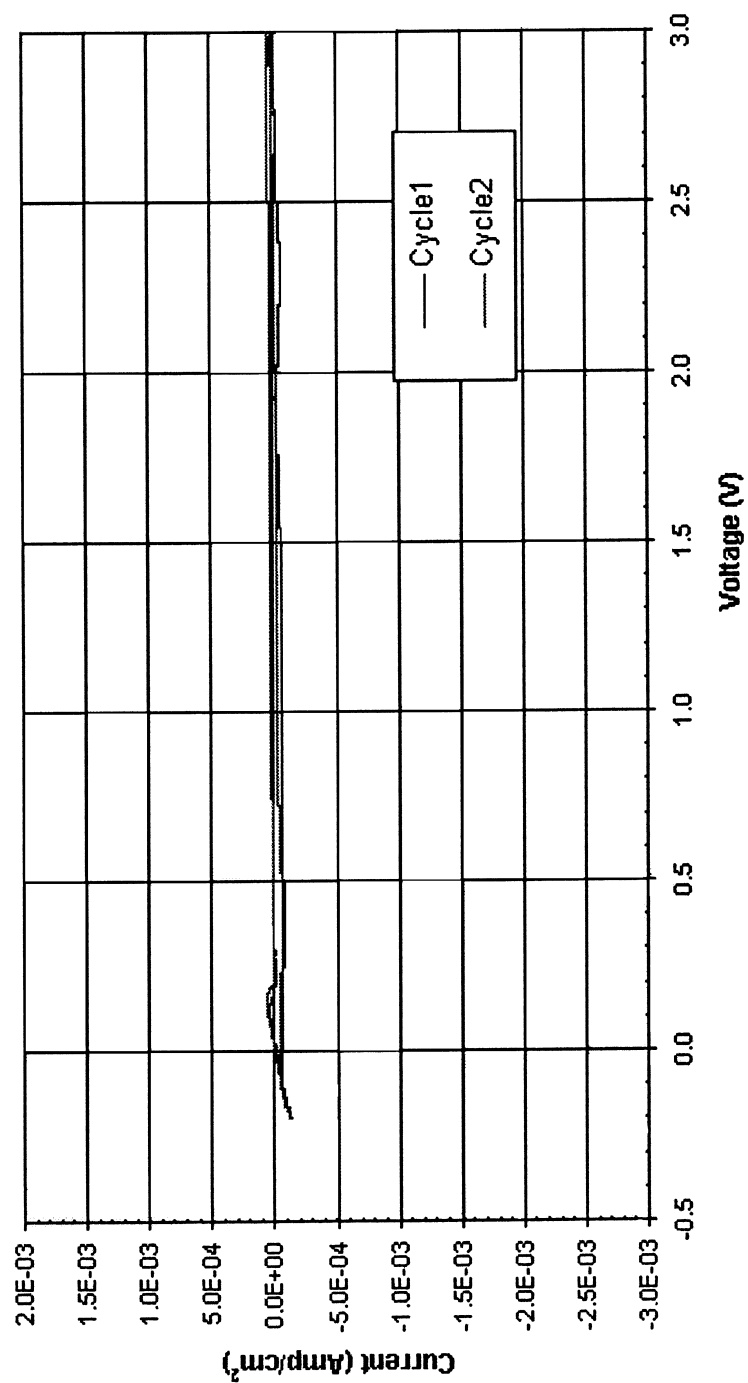

Figure 1. Conductivity vs. temperatures for L series materials and a "Bellcore-type" system.

CV Scan for T1/PVdF Film from 3 to - 0.1 Volts

Figure 2a. CV scan for L-1 film from 3 to –0.1 V.

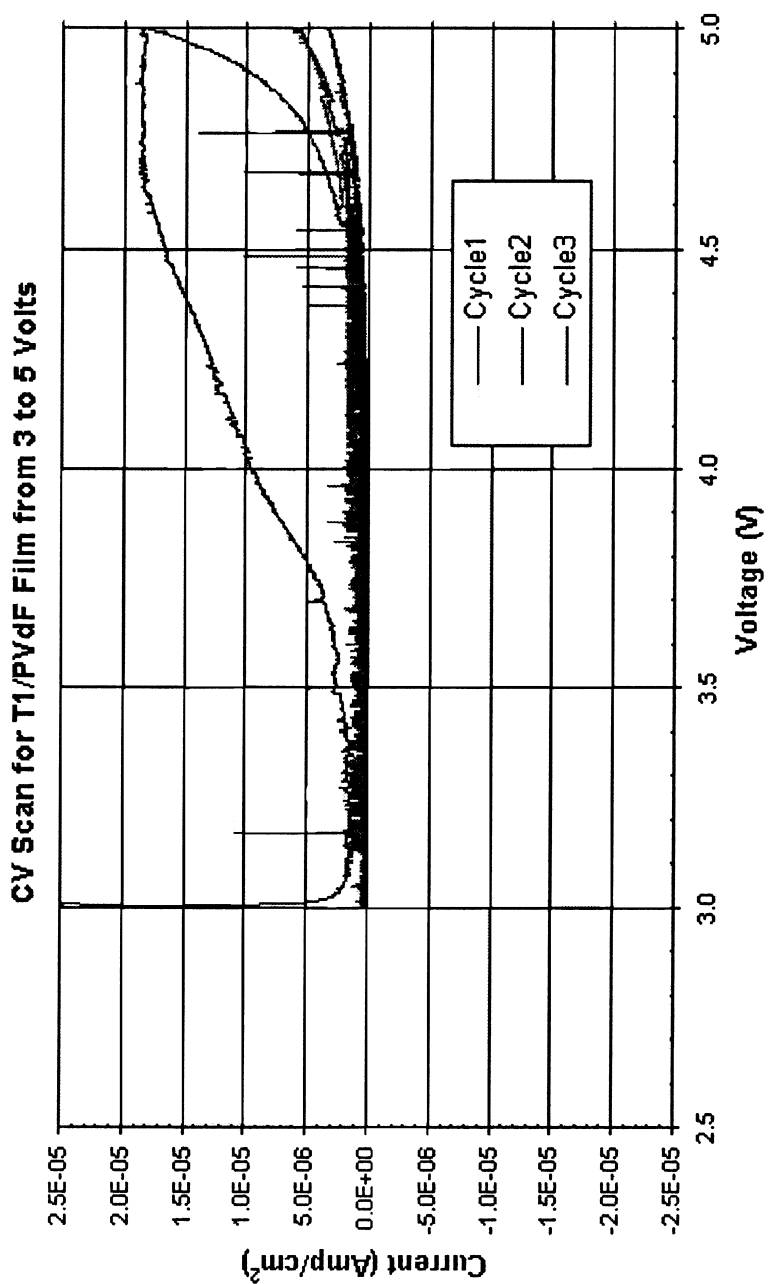***Figure 2b.*** CV scan for PVDF "Bellcore-type" film from 3 to –0.2 V.

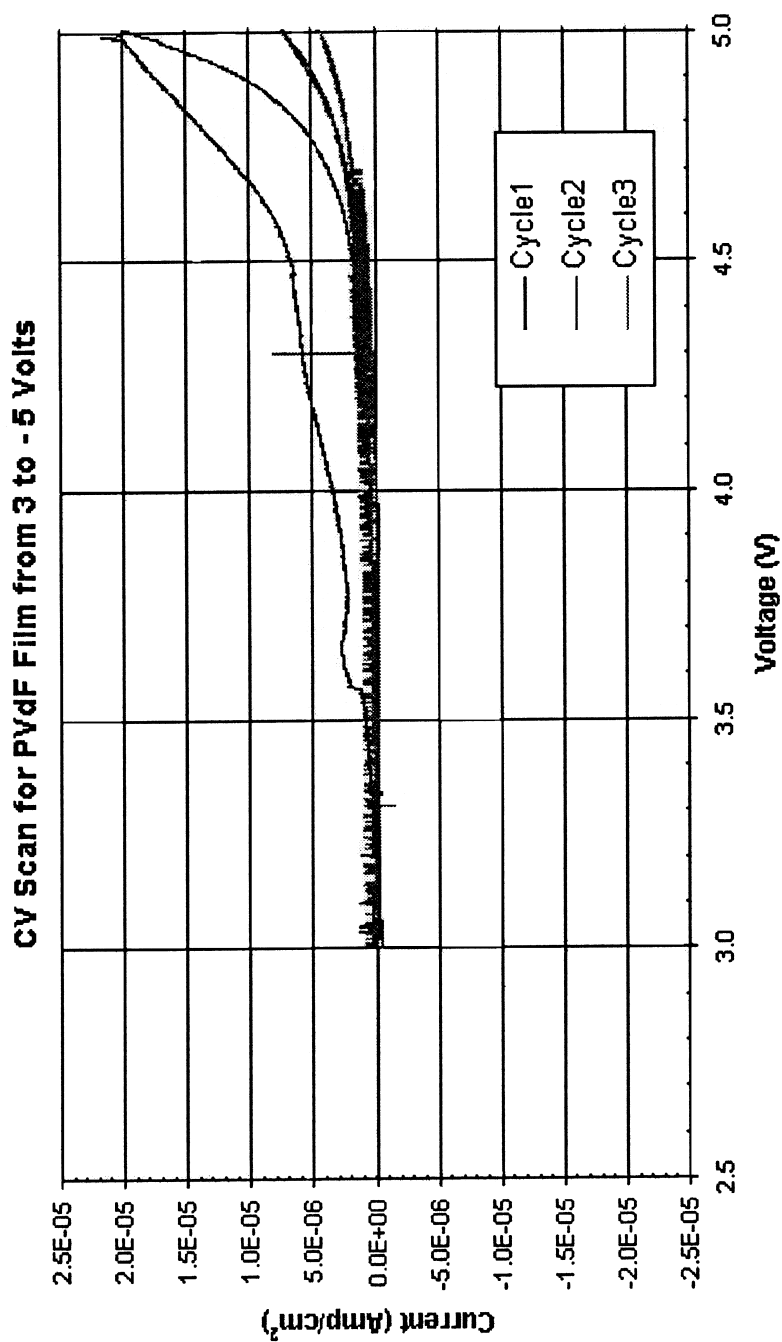*Figure 3a.*   CV scan for L-1 film from 3 to 5 V.

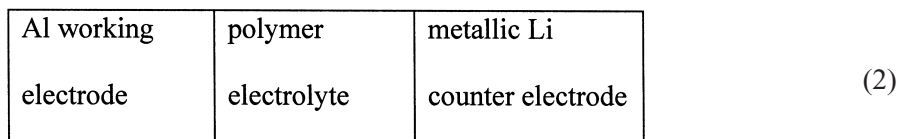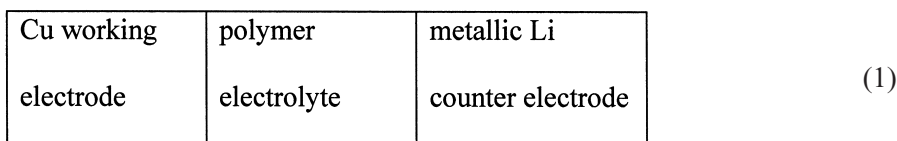*Figure 3b.*   CV scan for PVDF "Bellcore-type" film from 3 to 5 V.

content by generation of phenolate anions from residual phenols, although we have not yet attempted to exploit these prospects.

The glass transition temperatures of multiple P4VP-MPEG samples have been determined to be in the range -30 to -45°C by DSC, using a scan rate of 10°C/min. TGA studies (10°C/min) indicate that substantial mass loss begins at about 300°C.

Table 1 gives ionic conductivities for P4VP-MPEG containing $LiPF_6$ and a series of blends of P4VP-MPEG with PVDF containing EC and EMC along with $LiPF_6$. The conductivity of the P4VP-MPEG/salt complex is ca. 1×10^{-5} S/cm at room temperature, which is rather typical considering that the T_g of the polymer electrolyte is only about -40°C and most likely increases with added salt. However, the hybrid systems have conductivities approaching 2×10^{-3} S/cm, making them attractive candidates as electrolyte materials.

The ionic conductivities of several P4VP-MPEG/PVDF blends with $LiPF_6$ and EC/EMC are plotted vs. reciprocal temperature in Figure 1. Included in this plot are conductivities for a "Bellcore-type" electrolyte (i.e., without P4VP-MPEG) prepared under similar conditions. The data indicate that our hybrid systems compare well with the Bellcore-type material, and exceed the conductivity of the latter at low temperatures especially when the mass ratio of P4VP to PVDF is less than about 1.

The electrochemical stability of P4VP-MPEG was characterized by cyclic voltammetry. Specific concern regarding stability was increased due to the presence of a relatively high percentage (roughly 20-30%) of unreacted phenol sites as determined by our titration studies. Equations 1 and 2 summarize the cells used for the anodic and cathodic stability studies, respectively.

Cu working electrode	polymer electrolyte	metallic Li counter electrode

(1)

Al working electrode	polymer electrolyte	metallic Li counter electrode

(2)

We focused on the composition $P4VP\text{-}MPEG/PVDF/SiO_2$ of 0.2/1.5/1.0 (mass ratio) and examined conventional $PVDF/SiO_2$ "Bellcore-type" membranes for comparative purposes. The added SiO_2 gave improved mechanical integrity to the films without compromising conductivity (compare samples L-2 and L-3 in Table 1). Figures 2a and 2b compare the CV scans in the anodic direction. For our composite electrolyte in Figure 2a, a small reduction wave is seen for the first scan

at around 1.2 V vs. Li/Li$^+$ which is a common feature of all electrolytes, that is, it represents the formation of a passivating film on the working electrode surface. On carbon and graphite anode materials, this is the SEI. The solvent reduction wave is not observed on the second scan which indicates complete passivation. Lithium deposition (reduction) and oxidation are clearly seen on the figure at the lower potentials. The behavior confirms the anodic stability of P4VP-MPEG in that the CV scan features are essentially identical to those observed for the state-of-the-art PVDF polymer gel system as shown in Figure 2b.

Figure 3a shows the initial three CV scans for our composite electrolyte (equation [2]) in the cathodic direction. Starting at ca. 3.5 V vs. Li/Li$^+$, solvent oxidation is observed, but again on subsequent cycles, solvent oxidation disappears due to passivation of the Al working electrode. Since essentially identical behavior is observed for the state-of-the-art PVDF-gel electrolyte (Figure 3b), we conclude that the P4VP-MPEG-based electrolyte is stable, and that solvent oxidation on the initial scan is due to passivation of Al.

We note in passing that we have conducted preliminary studies using P4VP-MPEG as a binder in both anodes (carbon-based) and cathodes (LiCoO$_2$) affording electrodes of good integrity, and electrochemical characterization is in progress.

CONCLUSION

A new class of polymer electrolyte, P4VP-MPEG, has been synthesized and characterized with respect to ionic conductivity and electrochemical stability. This polymer, when used as a component in a gel-based electrolyte system, exhibits good conductivity down to -40°C and shows good electrochemical stability. Future work will focus on the use of different molecular weights and architectures of P4VP, MPEG, and related materials to optimize properties, and blends of P4VP with PEO and related materials as solid electrolytes.

ACKNOWLEDGMENT

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