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Highly conductive and electrochemically stable plasticized blend polymer electrolytes based on PVdF-HFP and triblock copolymer PPG-PEG-PPG diamine for Li-ion batteries

Diganta Saikia[a], Hao-Yiang Wu[b], Yu-Chi Pan[a], Chi-Pin Lin[a], Kai-Pin Huang[c], Kan-Nan Chen[d], George T.K. Fey[c], Hsien-Ming Kao[a,*]

[a] *Department of Chemistry, National Central University, Chung-Li 32054, Taiwan, ROC*
[b] *Department of Neurological Surgery, Tri-Service General Hospital, National Defense Medical Center, 325, Sec. 2, Cheng-Kung Rd, Taipei 11490, Taiwan, ROC*
[c] *Department of Chemical and Materials Engineering, National Central University, Chung-Li 32054, Taiwan, ROC*
[d] *Department of Chemistry, Nano-Tech Research Center, Tamkang University, Tamsui 251, Taiwan, ROC*

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ABSTRACT

A new plasticized poly(vinylidene fluoride-co-hexafluoropropylene (PVdF-HFP)/PPG-PEG-PPG diamine/organosilane blend-based polymer electrolyte system has been synthesized and characterized. The structural and electrochemical properties of the electrolytes thus obtained were systematically investigated by a variety of techniques including differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), tensile test, Fourier transform infrared spectroscopy (FTIR), ^{13}C and ^{29}Si solid-state NMR, AC impedance, linear sweep voltammetry (LSV) and charge–discharge measurements. The FTIR and NMR results provided the information about the interaction among the constituents in the blend polymer membrane. The present blend polymer electrolyte exhibits several advantageous electrochemical properties such as ionic conductivity up to 1.3×10^{-2} S cm^{-1} at room temperature, high value of Li$^+$ transference number ($t_+ = 0.82$), electrochemical stability up to 6.4 V vs. Li/Li$^+$ with the platinum electrode, and stable charge–discharge cycles for lithium-ion batteries.

1. Introduction

The ever increasing pace for the development of storage systems for sustainable energy supplies make the lithium ion battery technology one of the most promising future energy resources as it has tremendous scope to be used in many applications from modern hi-tech devices to hybrid electric vehicles [1–5]. In that context, ion-conducting polymer electrolyte membranes have attracted considerable interests as components for rechargeable lithium-ion batteries [4–16]. General requirements for the membrane materials are high ionic conductivity, good mechanical stability and processing of ultrathin films to allow fast loading processes. Currently, a liquid electrolyte along with a separator is used for fabrication of batteries. However, the possibility of internal shorting, leakage problems and highly reactive nature of such electrolytes towards the electrode surfaces necessitate the protective enclosures, which increase the size of the battery. An ideal way to get a light-weight, leak proof and flexible battery is to use polymer electrolyte serving as a separator as well as an electrolyte. Solid polymer electrolytes (SPEs) have received attention for several decades because they typically possess the mechanical properties and structural integrity required for battery applications [6–10]. However, they have inherently lower conductivities due to the more restricted motion of the polymer molecules and thus make them inadequate for practical use. Due to this reason, much attention has turned to gel or plasticized polymer electrolytes, which can be regarded as an intermediate state between typical liquid electrolytes and dry solid polymer electrolytes [11–15]. Nevertheless, plasticized electrolytes also exhibit drawbacks, such as reactivity of polar solvents with lithium electrode, poor mechanical properties at high degree of plasticization, and solvent volatility.

Polymer blending is another approach to improve the properties of plasticized polymer electrolytes. The main advantages of blend-based polymer electrolytes are simplicity of preparation and easy control of physical properties by changing the composition of blended polymer matrices. In addition, mechanical properties can be controlled in polymer blend systems [16,17]. Typically, the blend polymer electrolyte is composed of at least two polymers, one that absorbs the active elements of the electrolyte and the other that is tougher and comparatively inert, which enhances the mechanical integrity of the blend polymer [18,19]. Among various polymers, poly(vinylidene fluoride-co-hexafluoropropylene (PVdF-HFP) has

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[*] Corresponding author. Tel.: +886 3 4275054; fax: +886 3 4227664.
E-mail address: hmkao@cc.ncu.edu.tw (H.-M. Kao).

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been extensively investigated because of its excellent mechanical strength and electrochemical stability with respect to nonaqueous electrolyte and electrode materials [20–23]. Moreover, the high dielectric constant ($\varepsilon \approx 9.4$–10.6, Aldrich data) and strong electron withdrawing functional group (–C–F–) of PVdF-HFP make it favorable as polymer matrix [24–26].

With the aim of developing a highly conductive polymer electrolyte, herein a triblock copolymer poly(propylene glycol)-*block*-poly(ethylene glycol)-*block*-poly(propylene glycol) bis(2-aminopropyl ether) (PPG-PEG-PPG diamine, H_2N-PPG-PEG-PPG-NH_2, denoted as ED2000) is blended with PVdF-HFP copolymer to synthesize the blend polymer electrolytes. The presence of soft segment in ED2000 (ester carbonyls or ether oxygens) makes it more flexible to trap enough amount of electrolytes. Besides, the PPG segment of ED2000 is miscible with PVdF-HFP [27]. An organosilane plasticizer, 2-methoxy(polyethylenoxy)propyl trimethoxysilane (MPEOP), is also used as the presence of PEG tails in MPEOP helps in the decrease of T_g values [28]. The blending of ED2000 with MPEOP not only improves the miscibility between the organic and inorganic entities, but also guarantees the amorphous behavior of the hybrid electrolytes. Also PEG/PPG part of ED2000 and PEG part of MPEOP may help in the segmental movement of the chain to carry lithium ions. Blending of ED2000 and MPEOP with PVdF-HFP would thus provide a matrix which is flexible as well as mechanically stable. A series of blend polymer electrolytes has been synthesized by varying the weight ratio of PVdF-HFP and ED2000. The structural and electrochemical properties of the electrolytes thus obtained were systematically investigated by a variety of techniques including differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), ^{13}C and ^{29}Si solid-state NMR, AC impedance, linear sweep voltammetry (LSV) and charge–discharge measurements.

2. Experimental

2.1. Preparation of blend polymer electrolytes

The copolymers PVdF-HFP (Aldrich, $M_w = 400{,}000\ \mathrm{g\,mol^{-1}}$) and $H_2N\text{-}(PPG)_a(PEG)_b(PPG)_c\text{-}NH_2$ (Aldrich, $M_w = 2000\ \mathrm{g\,mol^{-1}}$, containing $a + c = 3.5$ and $b = 40.5$ units, commercially designated by Jeffamine ED2000) were dried at 70 °C for 24 h under vacuum (<10^{-3} Torr) prior to their use. In a typical synthesis, ED2000 was dissolved in small amount (10 mL) of dried THF and stirred at 60 °C. MPEOP ($CH_3O\text{-}(CH_2CH_2O)_n\text{-}(CH_2)_3Si(OCH_3)_3$, $n = 6$–9, Gelest Inc.) was then added to the above solution and continuously stirred for 2 days at 60 °C. MPEOP, consisting of a PEG segment with an average molecular weight of 375, is uniformly mixed with ED2000 because of its possible interactions with the ED2000 chain. Separately, PVdF-HFP was dissolved in dried THF by stirring at 60 °C. Both the PVdF-HFP and ED2000 solutions were then added together, stirred, and heated at 60 °C for 24 h. The resulting viscous solution thus obtained was cast onto Teflon dishes and the solvent was slowly evaporated at room temperature for 2 days. Finally, the materials were heated at 80 °C under vacuum for another 24 h to get crack-free membranes. This procedure gave homogenous and mechanically strong membranes. The membranes were then stored in a glove box (VAC, MO 40-1) under argon atmosphere for further measurements. The thickness of the membranes was controlled to be in the range of 50–70 μm. Polymer electrolytes were obtained by soaking blend membranes in liquid electrolytes consisting of either 1 M $LiClO_4$ in ethylene carbonate (EC)/propylene carbonate (PC) (1:1, v/v, chemicals obtained from Aldrich) or 1 M $LiPF_6$ in EC/diethyl carbonate (DEC, Tomiyama Chemicals, Japan). The nomenclatures of the blend polymer electrolyte membranes with different compositions in weight ratios are given in Table 1.

2.2. Characterization methods

The blend polymer membrane was dipped in an electrolyte solution of 1 M $LiClO_4$ in EC/PC (1:1, v/v) for measurements of the extent of swelling. The percentage of swelling was determined by $(W - W_0)/W_0 \times 100\%$, where W and W_0 are the weights of the wet and dry blend polymer membrane, respectively. Alternate current (AC) impedance measurements of the blend polymer electrolytes were performed using an Autolab/PGSTAT 302 frequency response analyzer over a frequency range of 10 Hz to 1 MHz with an amplitude of 10 mV. All the specimens were sandwiched by two polished stainless steel blocking electrodes in argon atmosphere inside a glove box for conductivity tests. Scanning electron microscopic (SEM) images were taken on a Hitachi S-3500N electron microscope.

As the lithium perchlorate is a strong oxidizing agent, the use of $LiClO_4$ in battery testing may explode the cell. Because of this safety concern, the electrochemical testing (e.g., LSV and charge–discharge tests) of the cell was carried out with 1 M $LiPF_6$ in EC/DEC as the electrolyte to soak the blend polymer membrane and a standard 2032 coin-cell hardware was used for cell fabrication. The blend polymer membrane was dried overnight at 70 °C in an oven and placed into an argon-filled glove box that contained < 1 ppm oxygen and moisture, to soak in the electrolyte solution for 5 h. The electrochemical stability of the blend polymer electrolytes was determined by LSV using stainless steel (SS) and platinum (Pt) as a working electrode and lithium as counter and reference electrodes for a Li/plasticized blend polymer electrolyte/SS(Pt) cell at a scan rate of $1\ \mathrm{mV\,s^{-1}}$ from an open circuit potential to 9 V vs. Li/Li^+. The interfacial resistance between electrolyte and lithium electrode was evaluated by AC impedance method using Autolab/PGSTAT 302 impedance analyzer for a Li/plasticized blend polymer electrolyte/Li symmetric cell. Charge–discharge studies were carried out with Maccor^{TM} multichannel battery tester (S4000). Lithium metal (Alfa Products) was used as the anode. The cathode used commercially available FMC cathode powder of $LiCoO_2$ by blade-coating a slurry of 85 wt.% active material with 10 wt.% conductive carbon black and 5 wt.%

Table 1
Ionic conductivities and percentage of swelling of plasticized blend polymer electrolytes with different compositions.

Sample	Compositions in wt. ratios			Conductivity at 30 °C ($\mathrm{S\,cm^{-1}}$)	Swelling (%)
	PVdF-HFP	ED2000	MPEOP		
PED-1	0.5	3.5	0.92	1.1×10^{-2}	229
PED-2	1	3	0.92	1.3×10^{-2}	259
PED-3	2	2	0.92	5.5×10^{-3}	158
PED-4	3	1	0.92	2.8×10^{-3}	102
PED-5	1	3	0	8.3×10^{-3}	186
PED-6	4	0	0.92	1.3×10^{-3}	87
PED-7[a]	1	3	0.92	8.2×10^{-3}	–

[a] Sample is activated with 1 M $LiPF_6$ in EC/DEC, others are activated with 1 M $LiClO_4$ in EC/PC.