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SHORT COMMUNICATION

Ultraviolet radiation curing of acrylates for lithium polymer electrolytes

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1. Introduction

Lithium polymer electrolytes have attracted strong interest in applications for devices such as batteries and electrochromic devices, because polymeric solid electrolytes can have high reliability without leakage of the electrolyte, display high energy density, and can be made in ultrathin form.

A polymer electrolyte matrix can be obtained by the three dimensional crosslinking reaction of polyether having an acrylated reaction group. It is possible that in a short time the crosslinking reaction is completed by the application of radiation curing process [1, 2].

Lithium polymer electrolytes with ionic conductivities of approximately 10^{-4}–10^{-6} S cm^{-1} have been prepared by ultraviolet curing of the poly(ethylene glycol) acrylate–lithium salt-photoinitiator system [1, 2]. The kinetics of ultraviolet photopolymerization of poly(ethylene glycol)diacrylates was investigated by Kurdikar *et al.* [3]. Kono *et al.* [4] synthesized network polymer electrolytes based on poly(2-(2-methoxyethoxy)ethylglycidyl ether) and characterized their ionic conductivity, crosslinking density, and glass transition temperature, etc. It was concluded that EO/ME2GE (where EO is ethylene oxide and ME2GE is 2-(2-methoxyethoxy) ethyl glycedyl ether) = 70/30 (molar ratio) and Li/[–O–] = 0.02–0.03 in matrix were optimum compositions. The polymer electrolytes of poly(ethylene oxide)-poly(oxymethylene-oligo(oxyethylene)) were prepared by exposure to 254 nm radiation [5]. It was also observed that the formation rate of crosslinks was greatly enhanced by the presence of benzophenone and an average crosslink density up to 6 mol % of ethoxy units was possible after several hours irradiation.

In the present work solid polymer electrolytes were prepared by curing the mixture solution of the PEG-based acrylates, lithium salt, photoinitiator, and plasticizer under ultraviolet irradiation. The objective of this work is to characterize the effect of mixture compositions on the properties of the polymer electrolytes cured. Tensile tests, i.r. spectroscopy, thermal analysis, XRD and ionic conductivity investigations were performed on the samples.

2. Experimental details

Poly(ethylene glycol)methacrylate[Mn ~306], poly(ethylene glycol 400)dimethacrylate, and poly(urethane)acrylate[Mn ~2200] were employed as reagents for electrolyte matrix formation. $LiCF_3SO_3$ and propylene carbonate were used as lithium salt and plasticizer, respectively. 1-Hydroxy cyclohexyl phenyl ketone was employed as a photoinitiator.

The reagents were homogeneously mixed. The homogeneous and transparent mixture was coated on the patterned ITO substrate for impedance measurements, of which the schematic diagrams are shown in Fig. 1. The samples coated were irradiated using an u.v. processor (Aetek International). The samples were placed 10 cm distant from u.v. lamps and cured under radiation of power 800 mJ cm^{-2}. The atmosphere for curing was controlled by purging with nitrogen gas, which contributes to the enhancement of the surface crosslinking reaction of the electrolyte. The thickness of the polymer electrolyte cured was controlled at approximately 110 μm.

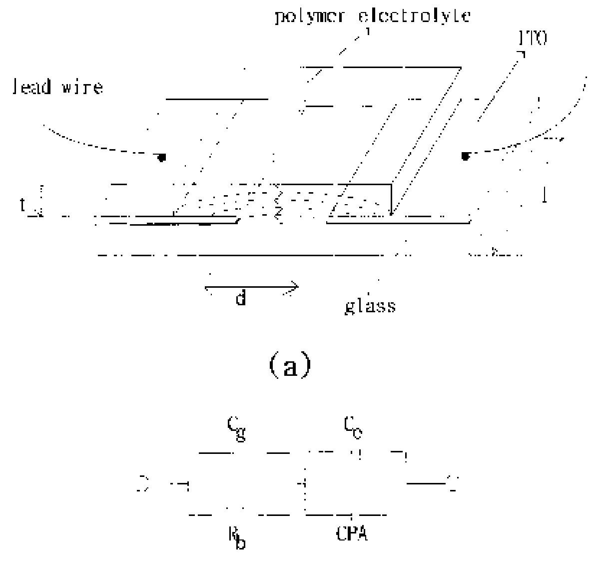

Fig. 1. Schematic diagram of (a) the cell and (b) the equivalent circuit for electrical conductivity measurements. (C_g) geometric capacitance, (C_e) electrode capacitance, (R_b) bulk resistance, (CPA) constant phase angle, (Γ) conductance $= 1/R = \sigma t\ l/d$.

Impedance spectroscopy was used to determine the total ionic conductivity of the polymer electrolytes. Measurements were carried out between 1 MHz and 100 mHz, at an amplitude of 100 mV peak to peak. Conductivity values were calculated from the electrolyte resistances determined from the intercept of the high frequency semicircle with the real axis in the complex impedance diagrams. The gel fractions of the electrolytes cured were measured by Soxhlet extraction process [6].

3. Results and discussion

3.1. *Chemical and physical properties*

Table 1 shows the reactant compositions of the PEGMA–PEGDA–PUA–PC–$LiCF_3SO_3$–1-HCHPK system. Figure 2 shows the infrared spectra of the samples u.v. cured from (a) S-1, (b) S-2, (c) S-3 and (d) S-4 systems. The spectra have C=O stretching vibration (1794 cm^{-1}) in the ester group, C=O stretching vibration (1722 cm^{-1}) in the acryl group, aliphatic–CH_2 group (1463 cm^{-1}), –CH_3 group (1390, 1354 cm^{-1}), C–O and C–O–C saturation linkage (1000–1300 cm^{-1}) in the ester and acryl groups, C–OH group (951 cm^{-1}) in the COOH, and C–H group (600–850 cm^{-1}) in the aliphatic alkane and alkene.

DSC analysis of the samples shows the weak endothermic peak near 60 °C and the weak exothermic peak over the range 18–22 °C, considered to be the glass transition temperature and the crystallization temperature, respectively. The crystallization temperature is consistent with that in the PEO–$LiClO_4$ system [7]. However, XRD analysis showed that no significant crystalline state existed in the matrix.

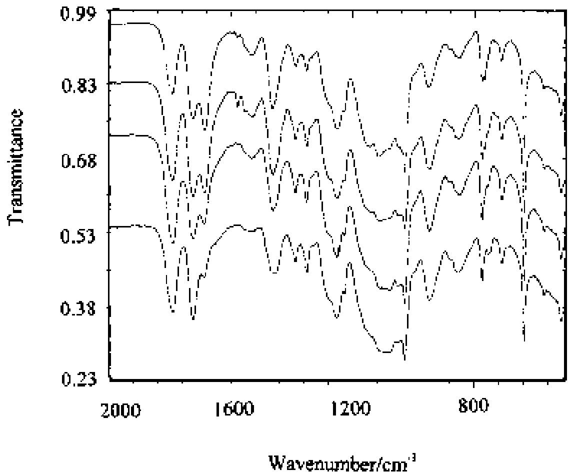

Fig. 2. Infrared spectra of the samples u.v. cured from (a) S-1, (b) S-2, (c) S-3 and (d) S-4 systems.

Table 2 shows the results of the tensile tests of the free–standing films prepared from the S-1, S-2, S-3 and S-4. As expected, the results indicate that the increased addition of polyurethane acrylate oligomer enhances the mechanical properties. This is because it causes an increase in crosslinking density.

3.2. *Electrochemical properties*

Figure 3 shows the ionic conductivities as a function of temperature. It is observed that the relative increase of the polyurethane acrylate oligomer in the formulated mixture causes a decrease in ionic conductivity. This is mainly because of the low segmental motion in the matrix.

The varied compositions of the PEGMA–PEGDA–PC–$LiCF_3SO_3$–1-HCHPK system are listed in

Table 1. Reactant compositions for the preparation of solid polymer electrolytes

Sample	*PEGMA* /%	*PEGDA* /%	*PUA* /%	*PC* /%	*$LiCF_3SO_3$* /%	*1-HCHPK* /%
S-1	18.3	18.2	36.5	14.6	2.9	9.5
S-2	22.8	22.8	27.4	14.6	2.9	9.5
S-3	27.4	27.4	18.2	14.6	2.9	9.5
S-4	32.0	31.9	9.1	14.6	2.9	9.5

PEGMA: poly(ethylene glycol)methacrylate (Mn ~306)
PEGDA: poly(ethylene glycol 400)dimethacrylate
PUA: poly(urethane)acrylate (Mn ~ 2200)
PC: propylene carbonate
1-HCHPK: 1-hydroxycyclohexyl phenylketone

Table 2. Tensile test of lithium polymer electrolytes

Sample	*Thickness* /μm	*Load at z-slip yield* /kg	*Stress at z-slip yield* /kg mm^{-2}	*Strain at z-slip yield* /%	*Load at autobreak* /kg	*Stress at autobreak* /kg	*Strain at autobreak* /%	*Young's modulus* /kg mm^{-2}
S-1	342	0.3141	0.0920	8.645	0.3141	0.0920	8.645	1.252
S-2	374	0.1980	0.0537	5.603	0.1980	0.0537	6.103	1.323
S-3	370	0.1221	0.0302	3.426	0.1973	0.0519	5.603	1.338
S-4	406	0.0242	0.0060	0.520	0.1396	0.0344	4.812	1.590

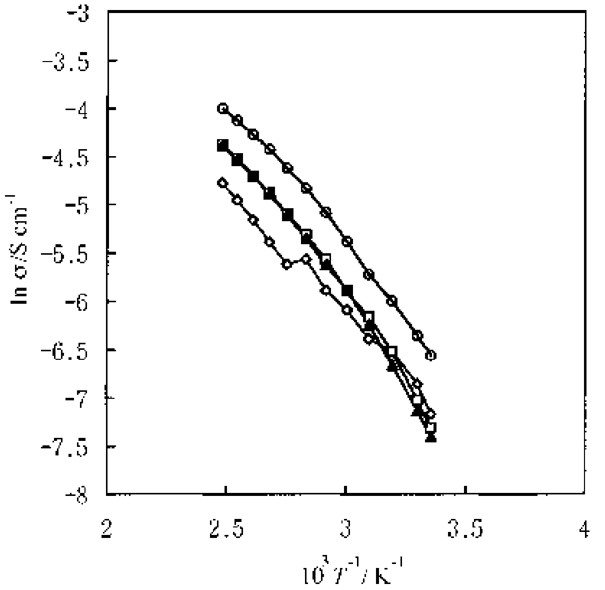

Fig. 3. Ionic conductivities as a function of temperature. Key: (◇) S-1; (□) S-2; (▲) S-3; (○) S-4.

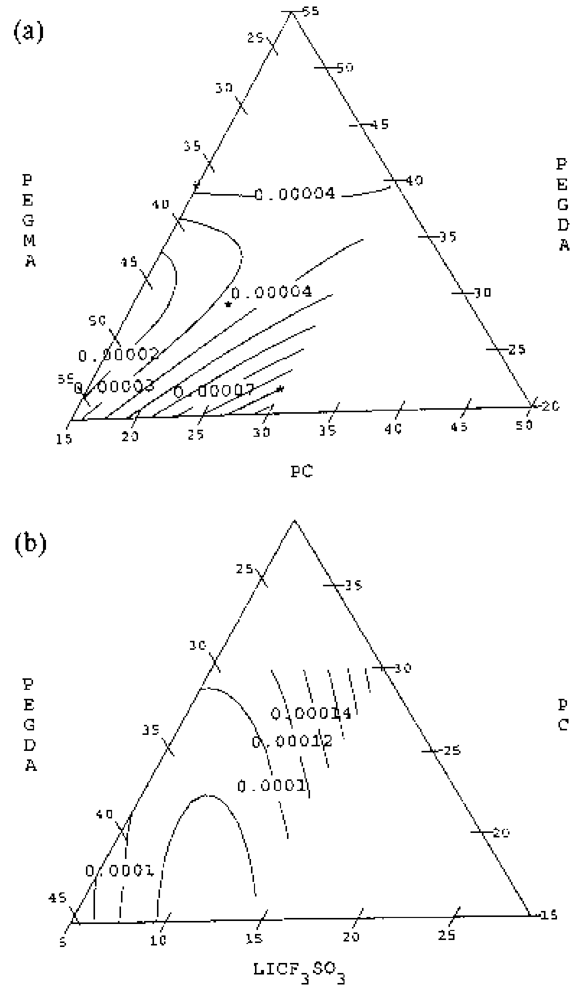

Fig. 4. a,b

Table 3. The controlled variation was determined by the experimental method of statistical data formulation and analysis. To analyse the responses of ionic conductivity to controlled variables such as PEGMA, PEGDA, PC and $LiCF_3SO_3$, the quadratic mixture model and D-optimal design were applied. These were performed using RS/1 software [8]. Figure 4 shows the contour plots for the ionic conductivity at 30 °C, in which (a) PEGMA, (b) PEGDA and (c) PC were chosen as a slack variable, respectively. The contour plots make it possible to predict the conductivity of simulated mixture. The results are as follows. The effect of propylene carbonate on conductivity is characterized to be linearly proportional. The increased addition of PEGDA in a formulated mixture decreases the electrolyte conductivity more significantly than in the case of PEGMA. On the other hand, the increase of $LiCF_3SO_3$ contributes to a sudden increase in conductivity only above about 7%.

Table 3. Experimental worksheet for the preparation of solid electrolytes

No.	*PEGMA* /%	*PEGDA* /%	*PC* /%	*$LiCF_3SO_3$* /%	*1-HCHPK* /%	*Conductivity* /S cm^{-1}	*Gel fraction*
1	20.0	40.0	21.5	14.0	4.5	1.53×10^{-4}	72.1
2	32.5	40.0	15.0	9.5	3.0	5.17×10^{-5}	70.0
3	39.0	20.0	30.0	5.0	6.0	7.43×10^{-5}	32.9
4	33.3	33.3	15.0	14.0	4.5	3.75×10^{-5}	74.1
5	20.0	40.0	23.0	14.0	3.0	5.89×10^{-5}	74.5
6	33.0	20.0	30.0	14.0	3.0	1.97×10^{-4}	36.9
7	32.2	32.2	24.7	5.0	6.0	4.32×10^{-5}	43.5
8	37.0	40.0	15.0	5.0	3.0	2.09×10^{-5}	42.8
9	40.0	34.0	15.0	5.0	6.0	2.23×10^{-5}	43.9
10	20.0	30.0	30.0	14.0	6.0	1.14×10^{-4}	60.2
11	22.0	40.0	30.0	5.0	3.0	5.09×10^{-5}	48.3
12	20.0	36.5	30.0	10.5	3.0	5.08×10^{-5}	55.8
13	40.0	22.0	30.0	5.0	3.0	1.01×10^{-4}	33.9
14	40.0	20.0	26.4	9.0	4.6	1.38×10^{-4}	43.7
15	40.0	28.0	15.0	14.0	3.0	3.48×10^{-5}	62.0
16	25.0	40.0	15.0	14.0	6.0	1.95×10^{-5}	71.5
17	20.0	40.0	24.5	9.5	6.0	2.27×10^{-5}	61.0
18	40.0	29.5	22.5	5.0	3.0	2.47×10^{-5}	28.7
19	20.0	39.0	30.0	5.0	6.0	4.73×10^{-5}	43.3
20	40.0	20.0	20.0	14.0	6.0	5.84×10^{-5}	62.0

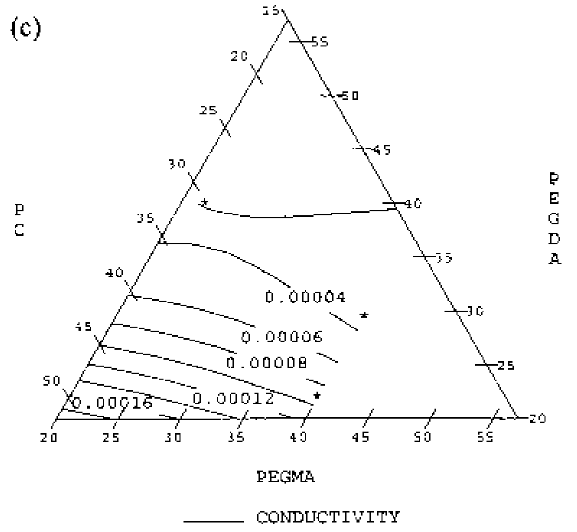

Fig. 4. Contour plots of ionic conductivity as a function of controlled factors [(a) $LiCF_3SO_3 = 5$ wt %, 1-HCHPK = 3 wt %, PEGMA (slack variable) = 92(wt %)–PC–PEGDA, (b) $LiCF_3$-$SO_3 = 5$ wt %, 1-HCHPK = 3 wt %, PC (slack variable) = 92(wt %) –PEGMA–PEGDA, and (c) PEGMA = 30 wt %, 1-HCHPK = 4.5 wt %, PEGDA (slack variable) = 65.5(wt %) –Li- CF_3SO_3– PC].

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