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Ionic conduction and electrochemical properties of new poly(acrylonitrile-itaconate)-based gel polymer electrolytes

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Abstract

A new copolymer polyacrylonitrile-co-bis[2-(2-methoxyethoxy)ethyl]itaconate (abbreviated as PANI) was synthesized in the hope of getting a polymer host having a better ability of trapping organic solvent to overcome the drawbacks of polyacrylonitrile (PAN) system gel polymer electrolytes. Blend of PAN and PANI was complexed with organic solvents, ethylene carbonate (EC) and γ -butyrolactone (BL), and LiClO₄ salt. The highest room temperature conductivity of $1.9 \times 10^{-3} \text{ S cm}^{-1}$ was found for a film of 25PAN–10PANI–50EC/BL–15LiClO₄. The PANI was found to effectively trap organic solvents and, therefore, greatly enhance the miscibility of polymer host and solvents, possibly due to ion chelating ability of itaconate unit. The PAN–PANI blend gel-electrolyte, as compared with pristine PAN-based electrolyte, had better electrochemical stability and was more stable toward lithium electrode, though it exhibited slightly less mechanical rigidity caused by amorphization of the PAN matrix. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Poly(acrylonitrile); Poly(acrylonitrile-itaconate); Gel polymer electrolytes; Ionic conductivity

1. Introduction

The performance of polyacrylonitrile (PAN)-based gel polymer electrolytes is still less than desirable to fit the requirements of lithium polymer battery [1–3], since the compatibility with the electrode materials is not satisfactory [1,4]. Therefore, it is desirable to find out a suitable polymer host having an enhanced ability of trapping aprotic organic liquid electrolytes. In this regard, a new gel polymer electrolyte based on the modified PAN, a polyacrylonitrile-co-bis[2-(2-methoxyethoxy)ethyl]itaconate (abbreviated as PANI) copolymer was synthesized. Since the PANI as a host polymer did not form a free standing film, PANI and PAN blend was complexed with organic solvents, ethylene carbonate (EC) and γ -butyrolactone (BL), and LiClO₄ salt. Measurements of ionic conductivity, differential scanning calorimetry, interfacial resistance, voltammetry and mechanical strength have been carried out for various compositions.

2. Experimental

A new polymer host PANI was synthesized. First, bis[2-(2-methoxyethoxy)ethyl]itaconate (MEEIt) was synthesized

by reacting itaconic acid, 2-(2-methoxyethoxy)ethanol, toluene, and *p*-toluenesulfonic acid. Copolymer of acrylonitrile with MEEIt was synthesized as follows: a mixture of acrylonitrile, comonomer MEEIt and initiator α, α' -azobisisobutyronitrile dissolved in dimethylformamide (DMF) were placed in a glass ampoule. The solution was degassed by Freeze-Thaw method. The sealed glass ampoule was heated at 65°C and maintained for 24 h. The polymerized mixture was precipitated into a large amount of ethyl ether. The produced white precipitate was dissolved in DMF and again precipitated into *n*-hexane. The solid powdery product was dried at 50°C for 12 h under vacuum.

PANI was dissolved in the organic solvent mixture of EC and BL (1:1 mole ratio). LiClO₄ and PAN were then dissolved in the resulting mixture and stirred at 80°C. The final transparent solutions were dispersed on a Teflon plate and dried at 60°C for more than 5 days to evaporate off the excess solvents in Ar atmosphere until the actual solvent concentration in the films reached to a predetermined value. All compositions cited in this paper are in weight ratio.

The ionic conductivity was determined by measuring the complex impedances of cells formed by sandwiching a given electrolyte sample between two blocking stainless-steel (SS) electrodes using a HP model 4192A LF impedance analyzer in the frequency range from 100 Hz to 1 MHz. To investigate the stability between lithium electrode and polymer electrolyte, the interfacial resistance of symmetrical Li/electrolyte/

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Li cells was measured in the frequency range from 0.01 Hz to 1 MHz utilizing an Eco Chemie PGSTAT20 frequency response analyzer at 30°C. Thermal analysis was performed by using a Shimadzu differential scanning calorimeter (DSC-50) at a heating rate of 10°C min⁻¹ from -110 to 250°C. The electrochemical stability of the electrolytes and the reversibility of lithium deposition/stripping process were determined by running linear sweep voltammetry and cyclic voltammetry using a three-electrode Li/electrolyte/SS cell with Li reference electrode using an Eco Chemie PGSTAT20 potentiostat/galvanostat, respectively. The mechanical strength of the gel-electrolytes was measured from strain–stress tests using an Lloyd materials testing system (model LR10K).

3. Results and discussion

Fig. 1 shows the DSC thermograms obtained in the heating cycle for PAN–PANI–EC/BL–LiClO₄ gel-electrolytes. The melting peak of salt-dissolved BL-rich phase appears at around -50°C, and that of EC-rich phase appears at around between 5 and 15°C. There exist solvent-rich domains as crystalline solids at low temperature, which were separated on quenching. Each melting temperature is lower than that of respective pure solvent ($T_m(\text{EC}) = 37^\circ\text{C}$ and $T_m(\text{BL}) = -45^\circ\text{C}$). When PANI is introduced, the volume of solvent-rich phases gradually decreases. For 20PAN–15PANI–50EC/BL–15LiClO₄ film, there are no endothermic peaks below 125°C, indicating that the solvents are thoroughly mixed with polymer host. This reveals that the PANI greatly enhances the miscibility of polymer host and solvents. Since the ionic groups of itaconate, mainly oxy-

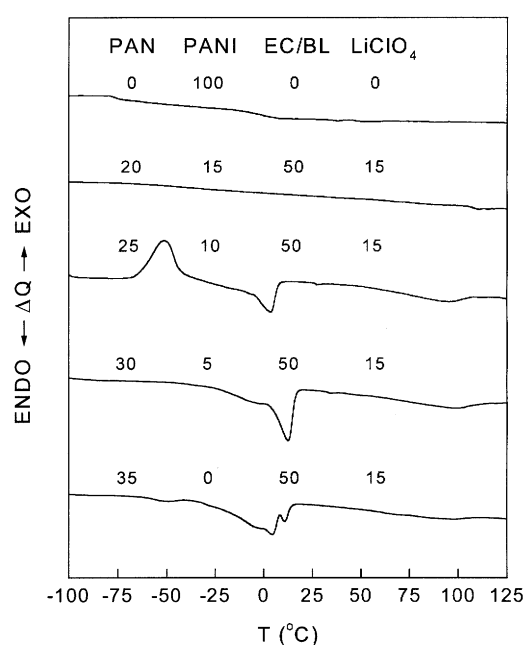


Fig. 1. DSC thermograms of PAN–PANI–EC/BL–LiClO₄ gel electrolytes.

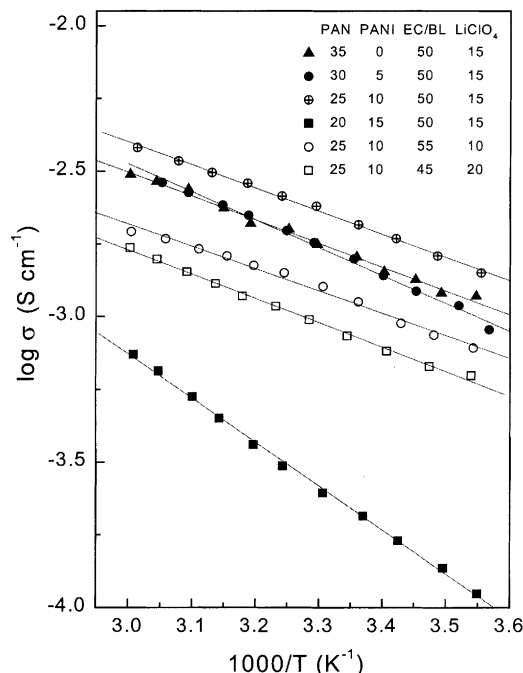


Fig. 2. Arrhenius plots of ionic conductivity for PAN–PANI–EC/BL–LiClO₄ gel electrolytes with varying PAN/PANI ratios (solid) and salt/solvent ratios (open).

gens, have ion chelating ability as well as the itaconate unit consists of double comb-like structure, the PANI seems to effectively trap organic solvents. For 25PAN–10PANI–50EC/BL–15LiClO₄ polymer electrolyte, a recrystallization peak appears at around -50°C. The recrystallization heat was almost equal to the melting heat. Since the volume of solvent-rich domains of above composition is smaller than that of the other compositions, they might be surrounded in stiffer environment consisting of PAN/PANI matrix. Consequently, the crystallization of the EC-rich domains might be difficult to occur during the quenching process.

The temperature dependence of the ionic conductivity for some of PAN–PANI–EC/BL–LiClO₄ electrolytes with varying PAN/PANI ratios and varying salt/solvent ratios is shown in Fig. 2. It shows that the conductivity is well described by the familiar Arrhenius equation. The replacement of PAN by PANI has some effect to enhance the conductivity, most likely due to the reduction of crystalline solvent domains and, therefore, the increase in the number of charge carriers. As the PANI content increases more than 10 wt.%, the ionic conductivity decreases, even though the solvent-rich domains completely disappear. The chelating ability of the itaconate group in PANI may enhance microscopic viscosity and, therefore, reduce ionic mobility. Hence, at higher PANI content, the increase in the number of charge carriers may be offset due to the decrease in the mobility of the charge carriers. As the salt/solvent ratio changes, an increase of the salt concentration increases the concentration of the charge carriers and also increases the viscosity of the electrolyte which will lower the mobility of charge carriers

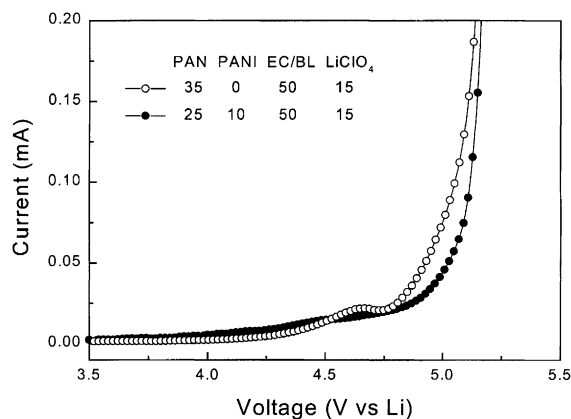


Fig. 3. Current–voltage responses of Li/electrolyte/SS cells at 30°C.

[5,6]. Optimum concentration of salt is determined via the competition between the number of charge carriers and their mobility. The highest room temperature conductivity of $1.9 \times 10^{-3} \text{ S cm}^{-1}$ was found for a film of 25PAN–10PANI–50EC/BL–15LiClO₄.

The current–voltage response of a stainless steel electrode of a Li/electrolyte/SS cell was measured at room temperature. The result is shown in Fig. 3. The onset of current flow is associated with the electrolyte decomposition. The anodic limit of PAN–PANI blend film is about 5.0 V versus Li and slightly higher than that of PAN-based film. For pristine PAN-based film, a small current peak appears at about 4.65 V, which can be attributed to oxidation of water molecules or impurities. It further proves that the blending of PANI enhances the ability of trapping water molecules as well as organic solvent.

The enhanced ability of trapping liquid solvent is expected to give an enhanced compatibility of the PAN–PANI gel-electrolyte with lithium electrode. The lithium interfacial resistance of the PAN–PANI blend gel-electrolytes, which can be attributed to the formation of a passivation layer due to the reactivity of the lithium electrode [7,8], was proved to be lower than that obtained with pristine PAN-

based film. The reversibility of the lithium deposition/stripping process is also found to be quite good, even though, however, the mechanical strength of the PAN–PANI gel-electrolytes decreased gradually with the increasing amount of PANI due to a weakening effect caused by amorphization of the PAN matrix.

4. Conclusions

The addition of PANI as a host polymer in the PAN-based gel electrolytes has beneficial effects, such as higher ionic conductivity, better thermal and electrochemical stability, better ability of trapping organic solvent and better interfacial stability to the lithium electrode, though it exhibits less mechanical rigidity. The PAN–PANI blend gel-electrolytes are considered to be a promising candidate for the solid electrolytes of lithium polymer batteries.

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