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New gel electrolytes for batteries and supercapacitor applications

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Abstract

The thermal behaviour, ionic conductivity and electrochemical stability of two new gel electrolytes synthesised by gelling (433 K, 5 min) polyacrylonitrile (PAN) and poly(vinylidene fluoride) and hexafluoropropylene (PVDF-HFP) (KF2801) polymer matrixes in a solution of LiCF_3SO_3 in ethylene carbonate– γ -butyrolactone (EC– γ BL) solvent mixture are reported. The high ionic conductivity obtained, together with the good electrochemical stability (the current onset is detected around 4.7 V versus Li/Li^+ for the PAN-based gel, and 4.5 V versus Li/Li^+ for the PVDF-HFP gel, make this membranes of definite interest for practical applications in lithium batteries and supercapacitors technology. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Gel-type polymer electrolytes are currently receiving a great deal of attention because of their proposed large scale applications in secondary lithium batteries and electrochemical supercapacitors [1–3]. The membranes, in which a liquid electrolyte has been immobilised by incorporation of a matrix polymer, combine the high conductivity of the liquid solution with the mechanical properties of the host polymer and with a wide electrochemical stability window, which allows their use in high voltage electrode couples. A variety of polymers, ranging from polyacrylonitrile, poly(vinyl chloride), poly(methyl methacrylate), poly(vinyl sulfone), poly(vinylidene fluoride), etc. have been used as polymer matrixes [3,4]. In practice, the choice of the individual components of the gel membrane is crucial; their chemistry and compatibility among them and with the electrodes will affect both the mechanical and electrochemical properties of the material [5–8]. In this work, we report on the thermal behaviour, ionic conductivity and electrochemical stability of gel electrolytes based on polyacrylonitrile (PAN) and a commercially available copolymer of poly(vinylidene fluoride) (PVDF) and hexafluoropropylene (HFP) as polymer matrices, being the liquid electrolyte a solution of lithium trifluoromethanesulfonate (LiCF_3SO_3) in a mixture of ethylene carbonate (EC) and

γ -butyrolactone (γ BL). PAN has been used as polymer matrix in gel electrolytes, as nitrile substituents are well known for their high dipole moment. On the other side, PVDF has a high dielectric constant ($\epsilon = 8.4$), which should assist in greater ionisation of lithium salts, providing a high concentration of charge carriers. The effect of copolymerization with hexafluoropropylene is traduced in a reduction in the melting temperature and the crystallinity together with an increase in the level of swelling by the EC and γ BL solvents.¹

2. Experimental

Polyacrylonitrile (PAN), EC, γ BL and LiCF_3SO_3 were purchased from Aldrich. Kynar 2801, a copolymer of vinylidene fluoride and hexafluoropropylene (PVDF-HFP) was obtained from Elf-Atochem. γ -Butyrolactone was dried by means of a 4 Å molecular sieve prior to use. All other materials were dried at 393 K under reduced pressure along 48 h.

The gel electrolyte membranes were prepared by gelling (433 K, 5 min) PAN and PVDF-HFP (KF2801) polymer matrixes in a solution of LiCF_3SO_3 in EC– γ BL solvent mixture. The composition of the membranes (wt.%) was PAN/PVDF-HFP 12.5, LiCF_3SO_3 11, EC 56.3, γ BL 20.2. All operations and handling were made inside an argon-filled glove box with a humidity level below 1 ppm.

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¹ Elf-Atochem Kynar PVDF for lithium batteries technical brochure.

The DSC data were obtained by using a Mettler TA4000 scanning calorimeter operated under nitrogen. Samples were heated to 498 K (289 K for EC and γ BL) at 10°K^{-1} , then cooled down at 10°K^{-1} to 173 K, and reheated to 498 K (289 K for EC and γ BL) at 10°K^{-1} . Glass transition and melting temperatures were measured in the second heating cycle thermograms to avoid any inference from thermal history.

Complex impedance measurements were carried out at frequencies from 10 to 10^7 Hz by using a Hewlett-Packard 4192 A impedance analyser coupled to a computer for data acquisition and handling. Samples (6 mm diameter, 0.3 mm thickness) were sandwiched between two stainless steel ion-blocking electrodes in a sealed PTFE cell.

Cyclic voltammetry measurements were performed at room temperature by using a Radiometer VoltaLab32 potentiostat operating at a 10 mV s^{-1} scan rate, in the potential range of 0 to 5 V against lithium. The gel electrolytes were sandwiched between two steel electrodes with a lithium foil as negative electrode, and located in a sealed PTFE cell. The electrode area was 1.13 cm^2 .

3. Results and discussion

Fig. 1 shows the second heating cycle DSC thermograms of the liquid electrolyte $\text{LiCF}_3\text{SO}_3\text{-EC-}\gamma\text{BL}$ and those corresponding of the two gel membranes. The thermogram of the $\text{LiCF}_3\text{SO}_3\text{-EC-}\gamma\text{BL}$ liquid electrolyte shows two melting regions, the one at higher temperatures with two melting transitions located at 253.8 and 289.2 K, which have been associated to the melting of EC coordinated and non-coordinated with the lithium salt, and a second region appearing at lower temperatures, which shows again two peaks at 208.1 and 214.1 K, associated to γ BL coordinated and non-coordinated γ BL, together with a recrystallisation region centred at 233.1 K. It must be pointed out at this time, that there exists a displacement towards lower temperatures of the melting temperatures of EC and γ BL relating to that obtained for EC and γ BL under the same experimental

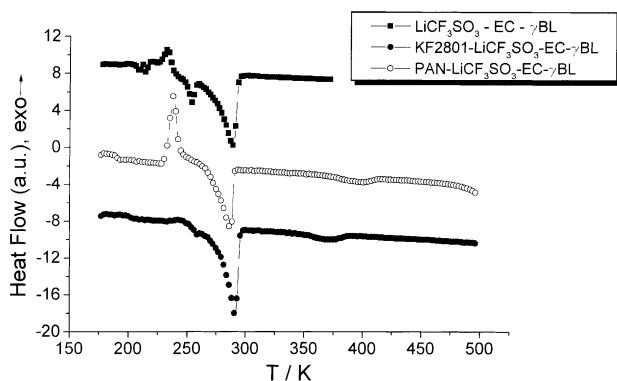


Fig. 1. DSC thermograms of the $\text{LiCF}_3\text{SO}_3\text{-EC-}\gamma\text{BL}$, and the gel electrolytes $\text{PAN-LiCF}_3\text{SO}_3\text{-EC-}\gamma\text{BL}$ and $\text{KF2801-LiCF}_3\text{SO}_3\text{-EC-}\gamma\text{BL}$.

conditions (312 and 234.4 K measured as melting points of EC and γ BL, respectively).

Relating to the gel electrolytes, it has to be remarked that both samples were thermally stable up to 498 K, showing melting transitions located at 287.5 K (PAN gel) and 290.1 K (KF2801 gel), which based on enthalpy values were associated to the EC, and a second melting region centred at 399.7 K (PAN gel) and 370.4 K (PVDF-HFP gel). This melting region at high temperatures is associated to the melting of crystalline EC or γ BL- LiCF_3SO_3 complexes, even the low enthalpy values allow us to consider both membranes as amorphous materials at room temperature. Glass transition temperatures, measured at the inflection point in the C_p jump, are 188.7 K for the PAN-based gel and 201.7 K for the KF2801-based gel electrolyte, values well below that of the pristine polymers (358.2 and 236.2 K, respectively), the displacement being explained in terms of the plasticizing effect of EC and γ BL solvents.

Fig. 2 shows the ionic conductivity of the membranes. The KF2801 gel exhibit slightly higher conductivities, values of the order of $10^{-3} \text{ S cm}^{-1}$ being measured at temperatures higher than 318 K for PAN gel membranes and 305 K for the KF2801-based ones. It has to be pointed out that the experimental ionic conductivity data are in the range of those reported in the literature for polymer gel-type electrolytes [8,9].

The temperature dependence of the ionic conductivity of both gel membranes can be described in both cases by the Vogel-Tamman-Fulcher equation [10–12]

$$\sigma = AT^{1/2} \exp \left[\frac{-B}{T - T_0} \right]$$

where A and B are constants related to the number of charge carriers and the activation energy for ion conduction, respectively, and T_0 is the temperature below which there is no further entropy loss resulting from configurational changes of the polymer, which according to the Adams-Gibbs analysis [13] was taken as $T_g + 50 \text{ K}$. Values of A and B obtained from the linear fit of the representation of $\sigma T^{1/2}$ versus $1000/(T - T_0)$ are compiled in Table 1. Results

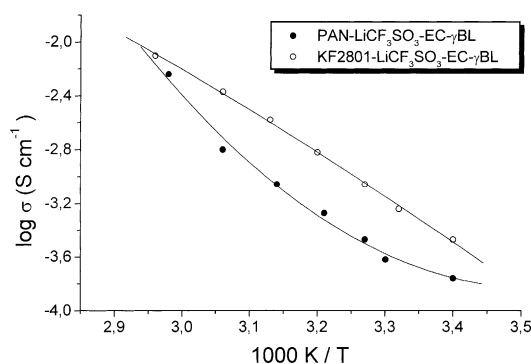


Fig. 2. Arrhenius conductivity plot for $\text{PAN-LiCF}_3\text{SO}_3\text{-EC-}\gamma\text{BL}$ and $\text{KF2801-LiCF}_3\text{SO}_3\text{-EC-}\gamma\text{BL}$ gel electrolytes.

Table 1
Best fit VTF parameters for electrical conductivity data

Gel electrolyte	A ($\text{K}^{1/2} \text{ S cm}^{-1}$)	B (K)	T_0 (K)
PAN-LiCF ₃ SO ₃ -EC- γ BL	3.73	990	139.2
KF2801-PAN-LiCF ₃ SO ₃ -EC- γ BL	3.28	778	151.7

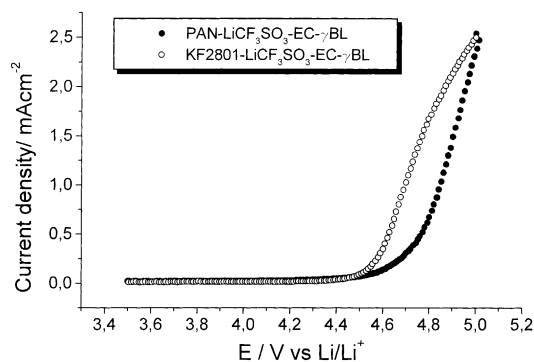


Fig. 3. Sweep voltammetry of a stainless steel electrode in PAN-LiCF₃SO₃-EC- γ BL and KF2801-LiCF₃SO₃-EC- γ BL cells. Counter electrode: Li; scan rate 10 mVs⁻¹; room temperature.

indicate that the number of carrier ions as well as the value of the apparent activation energy are higher for the PAN-based than that obtained for the KF2801-based membrane.

The breakdown voltage of the PAN and KF2801-based gel electrolytes was evaluated by running sweep voltammetry on a cell using a stainless steel and a lithium counter electrode, taking the irreversible onset of the current in the anodic region as the given electrolyte breakdown voltage. Voltammograms are plotted in Fig. 3, showing that the current onset is detected around 4.7 V versus Li⁺/Li for the PAN-based gel, the KF2801 gel practically being stable up to 4.5 V versus Li⁺/Li. This voltage is high enough to allow the safe use of both membranes in secondary batteries where the insertion/desinsertion at the cathode typically take place around 4 V versus Li⁺/Li. Regarding to the variation of the electrochemical stability on cycling, it has to be pointed out that, independently of the current density values, these suffer a large decrease after the first cycle, after that the profiles of the voltammograms seems to be practically identical independently of the cycle number.

4. Conclusions

Two new gel electrolytes synthesised by gelling (433 K, 5 min) PAN and PVDF-HHP (KF2801) polymer matrixes in a solution of LiCF₃SO₃ in EC- γ BL solvent mixture are proposed. DSC analysis show that even some crystallinity was detected, its low enthalpy value allow as to consider both gels as amorphous at room temperature. The high ionic conductivity of the membranes (values of the order of 10⁻³ S cm⁻¹ being measured at temperatures higher than 318 K for PAN-based gel membranes and 305 K for the KF2801-based ones), together with the good electrochemical stability (the current onset is detected around 4.7 V versus Li/Li⁺ for the PAN-based gel, and 4.5 V Li/Li⁺ for the KF2801-gel) make those membranes of definite interest for practical applications in lithium batteries and supercapacitor technology.

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