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Electrochemical and physical properties of poly(acrylonitrile)/poly(vinyl acetate)-based gel electrolytes for lithium ion batteries

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Abstract

Polymeric gel electrolytes have been extensively studied for application in lithium ion batteries, since the electrolyte can be fabricated as a thin film leading to major performance improvements. This is mainly due to the higher ionic mobility and the higher concentration of charge carriers, yielding ionic conductivities of about 10^{-3} S cm⁻¹ at room temperature and sufficient mechanical strength. PAN-based gels have been studied together with a wide range of plasticizers and tested in lithium battery systems with excellent results. Based on these results, we developed PAN-based gels with EC:PC and EC:DMC mixtures as plasticizers, LiClO₄ or LiBF₄ as the ionic salt and the copolymer PAN–PVA as the polymeric matrix to be used as separator and electrolyte in lithium ion batteries. The choice of the copolymer was made due to its hydrophobic properties, low cost and easy access, since it is widely used in textile industries as precursor for acrylic fibers manufacture. These new electrolytes were characterized by electrochemical techniques such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) in order to determine their stability window and conductivity. The charge/discharge performance of the PAN–PVA-based gel electrolytes was investigated for two different systems: Li/gel/LiMn₂O₄ and Li/gel/Pani (Pani = polyaniline). FT-IR analyses showed that PAN–PVA is not a passive polymer host but an active component in the gel, where Li⁺ ions are located close to C=O groups of the plasticizers and C=N groups of PAN. In addition to ionic conductivities higher than 10^{-3} S cm⁻¹, these gels presented excellent electrochemical and chemical stabilities, which means a slight increased performance when compared to PAN-based gels only, and suitable charge/discharge profiles.

Keywords: Gel electrolyte; Poly(acrylonitrile); Poly(vinyl acetate); PAN-based gel; Lithium ion battery

1. Introduction

The development of portable electric devices, especially mobile phones and notebook computers, has been remarkable in the last decade leading to a strong need of high-energy batteries. Among various types of batteries, lithium ion batteries are the most promising answer for this requirement. Actually, over 2 billion cells/year are produced and they have rapidly replaced nickel–cadmium and nickel–metal hydride in the consumer market [1–3].

In order to improve its performance, the lithium ion technology is presently aiming to the development of a new-design,

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high-energy, plastic-like power source system. By using a liquidelectrolyte configuration, the container should prevent electrolyte leakages. Moreover, a separator must be placed between cathode and anode to avoid short circuit in the cell. The weight of the container and volume occupied by the separator decrease the specific energy of the battery. On the other hand, using a solid polymer electrolyte (SPE) in a plastic-like container the weight will decrease and the whole system may assure modularity in design and reduction in production cost. Indeed, the replacement of common liquid electrolytes by an ionic polymer membrane is an important technological development for the lithium ion technology, since it provides the prospect of a favorable combination of high energy and long life [4]. One of the main requirements for a successful result is the availability of polymer electrolyte membranes having lithium ion conductivity approaching that of common liquid electrolyte to assure low

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ohmic drop and good interfacial compatibility with the electrode materials, *i.e.* a wide electrochemical stability window to allow the use of high voltage cathodes [5].

Solid polymer electrolytes (SPE), consisting of an ionic conductive polymer matrix and a supporting electrolyte salt, were firstly introduced by Fenton et al. [6]. By using a solid polymer electrolyte, a separator is unnecessary and the electrolyte can be prepared as a thin film, which enables to ensample an allsolid plastic-lithium battery of high energy. The first polymer studied as a matrix for SPE was poly(ethylene oxide) (PEO). However, these PEO-based electrolytes showed relatively lower ionic conductivity (ca. 0.1 μ S cm⁻¹) than liquid electrolytes (ca. $10 \,\mathrm{mS \, cm^{-1}}$) at room temperature. So, many attempts have been made to improve SPE ionic conductivity [7-10]. The addition of large quantities of liquid plasticizers (solvents) to a polymer host structure, leading to the formation of gel-polymer electrolytes, yielded the first practical plastic rechargeable Li-ion battery, known as the Bellcore battery [11]. This approach seems to be the most successful one [12].

Generally, a polymeric gel is defined as a system which consists of a polymer network swollen with solvent. Owing to their unique hybrid network structure, polymeric gels always possess, simultaneously, both the cohesive properties of solids and the diffusive transport properties of liquids. So, in this system, ion conduction occurs in the mobile solvent medium, and the polymer matrix is used for mechanical strength only [13]. In comparison to SPE systems, gel–polymer electrolytes have shown major performance improvements due to higher ionic mobility and higher concentration of charge carriers, yielding ionic conductivities of about 1 mS cm^{-1} at room temperature (high enough for portable electronic devices), while presenting sufficient mechanical strength [14].

A variety of polymers such as poly(acrylonitrile), poly(vinyl chloride) and poly(methyl methacrylate) has been used as polymer matrixes [15–17]. The choice of individual components for gel–polymer electrolytes is crucial; chemistry and compatibility among them and with the electrodes will affect both mechanical and electrochemical properties of the resulting material. Among the most studied polymer matrixes for gel electrolytes, poly(acrylonitrile) (PAN) seems to be the most successful attempt due to the formation of homogeneous hybrid films in which the salt and the plasticizer are molecularly dispersed [14]. Through Raman [18], FT-IR [19] and ⁷Li NMR [20] spectra, many authors have evidenced interactions between plasticizers and PAN matrix and, more interesting, between Li⁺ ion and

the nitrogen atom of the $C \equiv N$ bonds in PAN molecules and are responsible for high conductivity of these gel electrolytes, since the conductivity mechanism is improved [21,22].

PAN-based gel electrolytes have been investigated with various plasticizers such as ethylene carbonate (EC), propylene carbonate (PC) and dimethyl carbonate (DMC) [13,17,23]. The tests in lithium ion systems showed excellent results [24–26]. Based on these previous works, we investigated gel electrolytes formed by poly(acrylonitrile)/poly(vinyl acrylate) (PAN-PVA) as the copolymeric matrix, EC:PC and EC:DMC mixtures as plasticizers and LiClO₄ and LiBF₄ as ionic salt in lithium ion batteries. The PAN-PVA copolymer was chosen owing to its hydrophobic properties, low cost and easy access, since it is widely used in textile industries as precursor for acrylic fibers manufacture. These new gel electrolytes were characterized by thermal analysis and infrared spectroscopy. Electrochemical techniques such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used to determine their stability window and conductivity.

2. Experimental

All solvents, ethylene carbonate (EC; Acros, analytical grade), propylene carbonate (PC; Aldrich, analytical grade) and dimethyl carbonate (DMC; Aldrich, analytical grade) were kept in inert (Ar) atmosphere. Pure solid EC was added to distilled PC or DMC yielding the following solvent mixtures: 1EC:1PC (v/v), 1EC:1DMC (v/v) and 2EC:1DMC (v/v). Lithium tetrafluoroborate (LiBF₄, Aldrich, anhidrous) and lithium perchlorate (LiClO₄, Acros, 99.5%) were also kept in inert atmosphere. The poly(acrylonitrile)/poly(vinyl acrylate) copolymer (PAN–PVA 95%/5%, Radici Crylor of Brazil) was dried at 100 °C for 10 h.

The preparation of gel electrolytes was done according to the procedure already described for PAN-based gel electrolytes [17]. In a dry-box, lithium salt (LiClO₄ or LiBF₄) was dissolved in a given solvent mixture (1EC:1PC, 1EC:1DMC or 2EC:1DMC) at room temperature. Then, the PAN–PVA copolymer was added and dispersed in the mixture. The formed slurry was preheated at 90 °C and kept at this temperature for a short time for promoting a fast and complete dissolution. In order to favor gel formation, this solution was slowly cooled to room temperature. The composition of all PAN–PVA-based gel electrolytes prepared is shown in Table 1 (Section 3.4).

Thermal stability of the PAN–PVA powder was evaluated using a thermogravimetric analyser (TA Instruments, TGA 2050), under N_2 atmosphere, in a temperature range from room

Table 1

Composition, ionic conductivity and activation energy of PAN-PVA-based gel electrolytes

Gel composition polymer:solvent mixtures:lithium salt	Molar ratio	$\sigma \ ({\rm mS \ cm^{-1}}) \ ({\rm at \ 25 \ ^\circ C})$	$E_{\rm a}~({\rm eV})$
PAN–PVA:EC:PC:LiClO ₄	21:38:33:8	_	_
PAN-PVA:EC:DMC:LiClO ₄	20:28:45:7	1.10	1.241
PAN-PVA:2EC:1DMC:LiClO ₄	20:35:37:8	0.90	1.054
PAN-PVA:EC:PC:LiBF4	21:38:33:8	0.75	0.881
PAN-PVA:EC:DMC:LiBF4	20:28:45:7	1.47	1.247
PAN-PVA:2EC:DMC:LiBF4	20:35:37:8	1.07	1.054

temperature until 700 °C with a heating rate of 10 °C min⁻¹. Data of Differential Scanning Calorimetry (DSC) were obtained using a calorimeter (TA Instruments, DCS Q100) operating under N₂ atmosphere. Samples of the PAN–PVA powder and gel electrolyte were heated from -120 °C to 120 °C at 10 °C min⁻¹ for two heating cycles. The glass transition temperature was measured in the second heating cycle to avoid any inference from thermal history of materials.

Interactions between Li⁺ ion-solvent or Li⁺ ion-PAN–PVA copolymer, as well as their functional groups, were investigated by Fourier-transform infrared spectroscopy (FT-IR) for various samples: PAN–PVA powder; EC:PC or EC:DMC solvent mixtures + LiClO₄ and gel electrolytes themselves. FT-IR spectra were recorded in a Bomen MB-102 spectrophotometer in the region of 4000–550 cm⁻¹.

Electrochemical characterizations of the gel electrolytes were carried out using suitable cells assembled and kept in a dry box. The values of ionic conductivity were obtained by impedance spectroscopy by sandwiching the gel electrolyte between two stainless steel blocking electrodes in a button-type cell. The electrode surface area was 0.79 cm^2 ($\phi = 10 \text{ mm}$) and the thickness of gel membrane was 100 µm. The electrochemical impedance spectra were obtained in the temperature range 25-85 °C using an Autolab PGSTAT20 potentiostat/galvanostat from Eco Chemie coupled to a FRA2 module and controlled by the GPES software. The electrochemical stability of the gel electrolytes was evaluated by measuring the cathodic and anodic breakdown potentials. For this, cyclic voltammetries were run at 10 mV s^{-1} in the potential range of -0.50-5.50 V versus Li/Li⁺ in a three-electrode cell, using a blocking stainless steel as counter electrode and lithium as work and reference electrodes. The performance of the gel electrolytes was evaluated at constant current density in two different lithium ion systems: Li/gel electrolyte/Pani (Pani for polyaniline) and Li/gel electrolyte/LiMn₂O₄. While for the first battery the charge and discharge current densities were both 0.1 mA cm^{-2} , for the second they were 0.04 mA cm^{-2} and 0.08 mA cm^{-2} , respectively. An EG&G Model 263A potentiostat/galvanostat from PAR was used to obtain the charge and discharge curves. All testing cells were assembled in an environmentally controlled dry box.

3. Results and discussion

3.1. Thermal analysis

The thermal stability of the PAN–PVA powder was analysed by thermogravimetry at N₂ atmosphere, from room temperature to 700 °C at a heating rate of 10 °C min⁻¹. No mass loss was detected up to 197 °C, which means that no polymer degradation occurred in the temperature range used for the gel preparation (below 100 °C).

DSC thermograms of pure PAN–PVA copolymer and three PAN–PVA-based gel electrolytes are shown in Fig. 1. According to the upper curve of Fig. 1, pure PAN–PVA copolymer shows a glass transition at about 80 °C, considering that T_g of pure PAN is about 90 °C [27]. When plasticizers are added, PAN–PVA-based gel electrolytes present glass transitions at much lower

Fig. 1. DSC thermograms of pure PAN–PVA copolymer and PAN–PVA-based gel electrolytes with different solvent compositions.

temperatures (between -100 °C and -75 °C), indicating that the gel is amorphous at room temperature. Thermograms were obtained for different salt compositions and were similar to those presented in Fig. 1, indicating that neither the salt nature nor its composition affect the T_g of the gels. The same could be stated with respect to solvent composition and nature, although when PC is replaced for DMC a lower glass transition temperature is observed.

The T_g values obtained from DSC data indicated a completely amorphous nature for the gels above -75 °C. However, the values presented for gels prepared with the EC:PC solvent mixture (lower curve of Fig. 1) indicate a gel with less pronounced amorphousness, which may gel and may result in lower ionic conductivities.

3.2. FT-IR spectroscopy

FT-IR spectroscopy was used in order to analyse the interactions between atoms or ions in the various electrolyte systems and to investigate the role of the PAN-PVA polymer chain on the ionic conductivity of the gel. The FT-IR spectra of pure PAN-PVA copolymer and of 1EC:1PC and 1EC:1DMC solvent mixtures are shown in Fig. 2. For the PAN-PVA copolymer, characteristic vibrational bands of PAN [28]: (C=N at 2248 cm^{-1} and C–N at 1255 cm^{-1}) were observed. The vibrational bands at 2940 cm^{-1} , 2850 cm^{-1} and 1390 cm^{-1} are ascribed to CH₃ asymmetric stretching, symmetric stretching and symmetric bending vibrations, respectively, and the stretching frequency at 1740 cm^{-1} corresponds to C=O of PVA [29]. Bands observed near 1350 cm^{-1} and at 1070 cm^{-1} are ascribed to C-H and C-C bonds from PAN-PVA copolymer. On the other hand, for the solvent mixture spectra, the vibrational bands at near $1770 \,\mathrm{cm}^{-1}$ are ascribed to C=O asymmetric stretching in both solvent mixtures due to PC or DMC. Only a vibrational band at 1270 cm^{-1} in the spectrum for the 1EC:1DMC mixture can be seen, which is ascribed to the CH₃ symmetric stretching by inductive effect, since this is the only structural difference between both solvents (PC and DMC).





Fig. 2. FT-IR spectra of pure PAN–PVA copolymer and the solvent mixtures 1EC:1PC and 1EC:1DMC.

Since the structure of PAN involves only a simple C-C backbone and a high density of C=N groups, the change of the C=N vibration due to the presence of the salt and/or the solvent can provide an important information concerning the interaction between C≡N groups and Li⁺ [30]. Fig. 3 shows the FT-IR spectra for PAN–PVA-based gel electrolytes produced with 1EC:1PC and 1EC:1DMC solvent mixtures, enhancing the wavenumber region where the vibrational band of C≡N appears. It is possible to observe the broadening of the C=N vibrational band at about 2248 cm^{-1} in gels with the 1EC:1PC solvent mixture and the appearance of a new vibrational band in gels with the 1EC:1DMC mixture. These effects have already been assigned as an interaction between PAN molecules and LiClO₄ [19]. From these results, one may conclude that PAN-PVA is not a passive polymer host but an active component in the gel. This is in accordance with the proposed model for ionic conduction in



Fig. 3. FT-IR spectra for the PAN–PVA-based gel electrolytes in the region of $2100-2300 \text{ cm}^{-1}$.



Fig. 4. Cyclic voltammograms (first cycle) of PAN–PVA-based gel electrolytes, at 10 mV s^{-1} for stainless steal/PAN–PVA:EC:PC:LiBF₄/Li (straight line), and stainless steal/PAN–PVA:2EC:1DMC:LiBF₄/Li (dashed line).

PAN-based gel electrolytes, where Li^+ ions are located close to the C=O groups of plasticizers and the C=N groups of PAN [21].

3.3. Electrochemical window

The electrochemical stability range of the PAN–PVA-based electrolytes was determined by running a potential sweep through the system stainless steel/gel electrolyte/Li, in the potential range where the redox reactions for the Li-ion batteries occur. The cyclic voltammograms of the gel electrolytes presented in Fig. 4 are typical of liquid lithium salt/EC:PC or EC:DMC electrolytes. Cathodic and anodic peaks, appearing at around 0 V or 0.8 V, depending on the gel, correspond to the lithium redox processes according to Li⁺ + e⁻ = Li. Fig. 4 also shows a breakdown voltage of at least 4.5 V for both solvent mixtures and similar behavior was observed for the gel electrolytes with different salt nature. Therefore, the electrochemical stability window found for the proposed gels seems to be convenient for their applications in lithium ion batteries.

3.4. Ionic conductivities

The ionic conductivities of PAN–PVA-based gel electrolytes were evaluated from the ohmic resistance in the electrochemical impedance spectra, obtained by the intercept on the real impedance axis at the higher frequency regions. All the spectra (not presented here) were characteristic of a blocking electrode cell, presenting only a capacitive behavior. According to Panero and Scrosati [17], this behavior evidences good physical integrity of the gel electrolytes, since the presence of heterogeneities, as crystallization or phase separation, would generate semi-circles in the impedance spectra.

The ionic conductivities values at 25 °C for the PAN–PVAbased electrolytes are listed in Table 1. The conductivities at room temperature are higher than 10^{-3} S cm⁻¹, except for the gel prepared with the 1EC:1PC solvent mixture, as commonly found for gel electrolytes and required for good performance



Fig. 5. Arrhenius-type plot of different PAN-PVA-based gel electrolytes.

in battery electrolytes [19]. These values were stable even a month after the cell set up. The effect of the temperature on the conductivity of various PAN–PVA gel electrolytes is shown in Fig. 5. The conductivity of the gel electrolytes markedly increases with the rise in temperature. This implies that the conductivity is strongly dependent on the polymer backbone's segmental motion.

According to Croce et al. [18], when a small temperature range is investigated, an Arrhenius-type behavior could be observed above room temperature. This would lead to an erroneous interpretation of the conducting mechanism, since this plot behavior is attributed to a mechanism where the ionic conductivity is decoupled from the segmental movement of the polymer chains [31]. Since FT-IR data indicated strong interactions between lithium salts and PAN, a slight curvature was observed in the Arrhenius plots (Fig. 5), but the best fitting was achieved using the Vogel–Tamman–Fulcher (VTF) model, which can be interpreted by the free-volume model [32]. In this case, the ionic conductivity data for all the gel electrolytes should be fitted with the following equation:

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

where *A* and *B* are the constants related to the number of charge carriers and the activation energy for ion conduction, respectively. T_0 is taken as the idealized temperature corresponding to zero configurational entropy, according to Adam–Gibbs analysis [32]. In the temperature range analysed, the small values for the slopes estimated from Fig. 5 led to small activation energies for ion conduction (~1 eV, see Table 1), similar to other results for PAN-based gel electrolytes [19].

According to the FT-IR and ionic conductivity results, it is believed that the ionic conduction mechanism of PAN–PVAbased gel electrolytes is similar to those proposed for other PAN-based gels. Most proposed models assume that Li⁺ ions in the gel electrolyte appear to be solvated by both PAN (through CN groups) and the plasticizers. These mobile Li⁺ ions jump from one position to the next, while they move together with the chains of the polymer in the gel state [19,22,27]. For the



Fig. 6. Time evolution of the impedance response of Li/PAN–PVA:2EC: $1DMC:LiBF_4/Li$ cells at open circuit potential. Signal amplitude of 10 mV (rms) and frequency range of 10 kHz–10 mHz.

PAN–PVA-based gel electrolytes investigated in this work, the best interactions between Li⁺–PAN–PVA and Li⁺-plasticizers were achieved when employing LiBF₄ as the salt and EC and DMC as the solvent mixture.

3.5. Gel stability

Chemical stability of the gel electrolytes presenting higher conductivities was followed by impedance measurements. Fig. 6 shows the time evolution of electrochemical impedance spectra for the PAN-PVA:2EC:1DMC:LiBF₄ gel electrolyte in contact with Li electrodes, at open circuit potential. The spectra presented two semi-circles: one at higher frequencies whose diameter $(R_2 - R_1)$ increased with time evolution, and another at lower frequencies displaying a smaller and constant diameter $(R_3 - R_2)$. According to many authors [33–35], R_1 could be assigned as the electrolyte resistance, $R_2 - R_1$ as an increasing resistance due to the formation of a passive layer on the lithium electrode and $R_3 - R_2$ as the charge transfer resistance at the electrolyte/lithium interface. As no significantly variation was observed for R_1 values, it can be stated that the gel ionic conductivity is independent of time, which means a high chemical stability when in contact with lithium electrodes.

The semi-circle at higher frequencies is frequently attributed to the formation of a passive film, also referred to as the solid electrolyte interface (SEI) layer, on the lithium surface [33]. Matsuda et al. [34] already observed this behavior for other PAN-based gel electrolytes and concluded that the formation of this thin passive film does not affect the redox processes in the cell; actually it can even improve them, since it may inhibit side reactions between electrolyte and electrode.

The semi-circle describing the charge transfer resistance at the lithium/electrolyte interface was reported for PAN-based gel electrolytes [35]; the increasing values for this process was interpreted as due to solvent loss at the polymeric matrix. Fortunately



Fig. 7. Discharge curve of a Li/gel electrolyte/LiMn₂O₄ battery. Cutoff potentials of 3.3 V and 4.35 V. I_d = 80 μ A.

this phenomenon did not happen for the PAN–PVA-based gel electrolytes proposed in this work.

3.6. Discharge performance for two types of Li cells

Charge/discharge performance of the PAN–PVA-based gel electrolytes was investigated by the galvanostatic battery test. Two battery systems were analyzed: a Li/gel/LiMn₂O₄ and a semi-polymeric system made of Li/gel/Pani. However, although the optimized gel electrolyte was PAN–PVA:2EC: 1DMC:LiBF₄, it was not used in the Pani battery since it promoted the polymer dissolution; therefore, PAN–PVA:1EC: 1PC:LiBF₄ was used instead. Figs. 7 and 8 show typical discharge profiles for the LiMn₂O₄ and Pani systems, respectively. For the manganese oxide cathode (Fig. 7), the profile presented the well-known plateau for the Li ion intercalation in the 4 V region [36], typical for the spinel structure. The capacity for this electrode was 120 mAh g⁻¹, about the same value as when



Fig. 8. Discharge curve of a Li/gel electrolyte/Pani battery. Cutoff potentials of 2.5 V and 3.80 V. I_d = 100 $\mu A.$

a liquid electrolyte is used. On the other hand, Fig. 8 shows a different profile for polyaniline, which is characteristic for polymeric electrodes [37]. The capacity observed for this case was as high as 190 mA h g^{-1} and constant after many cycles, allowing to conclude that Pani did not undergo dissolution in this polymeric electrolyte. This result is similar to that one found in liquid electrolyte reported in a previous work [38]. For both batteries, the PAN–PVA-based gels were very efficient to maintain a stable ionic conduction mechanism during the electrochemical tests, without a significant increase of the passive layer on the lithium electrode.

4. Conclusions

PAN–PVA-based gel electrolytes were produced from a precursor commonly found in the Brazilian textile industry, obtained at low cost and having hydrophobic properties which are important requirements for their application in lithium ion batteries. The results presented in this paper show that the mechanisms for ionic conduction in the PAN–PVA gels can be understood similarly to the one in PAN-based gel electrolytes. In this sense, high ionic conductivities and good electrochemical and chemical stabilities were achieved.

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