

Short communication

Studies on PVdF-based gel polymer electrolytes

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Abstract

A complex of polymer, plasticizer and lithium salts can be used as a solid gel polymer electrolyte in lightweight and rechargeable lithium batteries. Considerable research has been directed towards the development of a gel polymer with high conductivity at room temperature. In this work, a gel polymer electrolyte using polyvinylidene fluoride (PVdF)-1000 (KF), a plasticizer of 1:1 ethylene carbonate (EC) and propylene carbonate (PC), and LiBF₄ salt is optimized. Gel electrolytes have high ionic conductivity, good mechanical stability, a wide electrochemical stable window, and a stable lithium interface. The results of preliminary charge–discharge of cells are discussed in detail. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Gel polymer; Plasticizer; Ionic conductivity

1. Introduction

Polymer composite electrolyte, developed at the end of 1970s, has been widely used in solid-state batteries with high specific energy. Among the most promising, highly conducting, new-generation polymers are gel-type systems, e.g., those obtained by immobilizing in a PAN matrix Li salt solvates in organic solvent mixtures, such as an ethylene carbonate (EC) + propylene carbonate (PC) mixture [1]. Gel polymer electrolytes, which were originally described by Feuillade and Perche [2] and further characterized by Abraham and Alamgir [3,4], are dimensionally stable and have a room temperature conductivity in the range 10^{-3} S cm⁻¹. Some of the results clearly demonstrated that the lithium electrode undergoes serious passivation in contact with gel electrolytes [5,6]. In the present study, gel polymer electrolyte films which consist of polyvinylidene fluoride-1000 (KF), EC, PC and a lithium tetrafluoroborate are prepared by a solvent casting technique. The physical and electrochemical properties of the gel polymer electrolyte films (such as thermal stability, crystallinity, conductivity, mechanical stability and electro-

chemical stable window, lithium gel electrolyte interface and charge–discharge behaviour) are characterized.

2. Experimental

2.1. Preparation of gel polymer electrolyte films

Gel polymer electrolyte films were prepared by heating a mixture of PVdF-1000 (KF), and high purity plasticizers. EC, PC and LiBF₄ were weighed in an appropriate proportion and mixed in a pyrex bottle. The mixture was heated at 160–175°C for 60–75 min. The viscous solution was poured on a PET sheet and then the desired thickness was made using a doctor blade. The cast film was dried in a dry room for 3–4 h. A dimensionally stable and solvent-free polymer electrolyte film with a thickness of 50 μm was obtained.

2.2. Preparation of composite cathode

Composite cathodes were prepared by the addition of 50% LiCoO₂, and 15% graphite (KS-15) to a mixture of suitable composition of 35% gel polymer electrolyte consisting of polymer and plasticizers. Powders were added to the gel polymer while hot and mechanically blended. The

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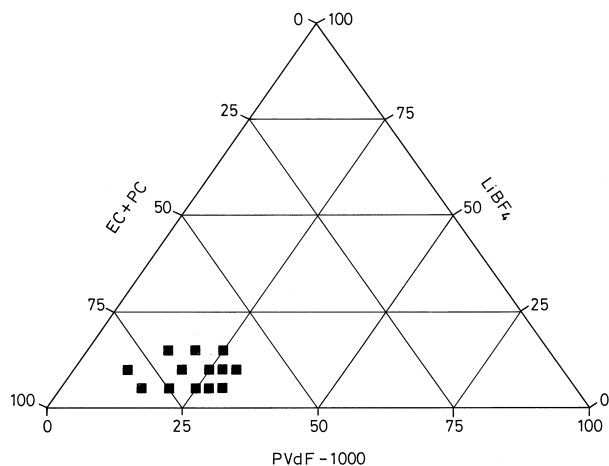


Fig. 1. Composition diagrams for gel polymer electrolytes containing PVdF-1000 (KF), EC+PC and the LiBF_4 in various ratios by weight.

blended paste was poured onto an aluminium foil and spread uniformly using a doctor blade. Composite cathodes were dried at 130°C for 24 h. The area and thickness of the electrodes were 2 cm^2 and $75\ \mu\text{m}$, respectively.

2.3. Measurements of physical properties

X-ray diffraction patterns of PVdF, LiBF_4 and the gel polymer were obtained by means of a Rigaku X-ray diffractometer using $\text{Cu-K}\alpha$ radiation. The thermal stabilities of PVdF, LiBF_4 and gel polymer electrolytes were studied using a differential scanning calorimeter (DSC) in an argon gas flow. The heating rate was $10^\circ\text{C}/\text{min}$ and the samples were scanned from $30\text{--}300^\circ\text{C}$. The weight loss of the gel polymer electrolyte was determined by thermogravimetric analysis (TGA) under a flow of argon, and the weight change was monitored as a function of time.

2.4. Measurements of electrochemical properties

The gel polymer electrolyte film of particular size was sandwiched between two stainless-steel electrodes. The conductivity was obtained by analyzing the impedance spectrum which was measured with a Solartron SI 1286 electrochemical interface coupled to an SI 1260 impedance gain phase analyzer over the frequency range 1 Hz–100 kHz at room temperature and a 0.01 V a.c. signal. All the experiments were repeated in order to obtain reproducible values. The electrochemical interface stability of a gel polymer electrolytes containing PVdF, EC + PC and LiBF_4 was studied by means of cyclic voltammetry of a symmetric cell $\text{Li}/\text{gel polymer}/\text{Li}$, as a function of lithium plating and stripping in the potential range of -1.0 to 1.0 V and monitoring the corresponding cell impedance. Thin lithium rechargeable batteries, Li/LiCoO_2 with gel electrolyte were assembled and the charge–discharge studies were carried out at room temperature.

3. Results and discussion

The gel polymer electrolyte films were prepared, examined for their homogeneity, and dimensional stability and the preparation conditions were optimised. The gel polymer viscous film results can be summarized in the form of a triangular composition diagram, as shown in Fig. 1. Electrolytes are taken to consist of three components, namely, PVdF, EC + PC and LiBF_4 salt. Homogeneous electrolyte films are formed only for particular ratios of the polymer, plasticizer and Li salt. In this case, the viscosity of the gel polymer electrolyte solution was affected by the lithium salt concentration. In general, the higher the salt concentration, the more viscous the gel electrolyte solution [7]. Homogeneous and thin-film, solid gel polymer electrolytes are obtained only if the amount of salt concentration is below 10% LiBF_4 . Above this ratio, gels which contained polymer, plasticizer and salt remain heterogeneous. However, the gel polymer containing more than 30% PVdF-1000 (KF) was strong and those containing less than 27.5% PVdF 1000 (KF) were weak and fragile. Therefore, gel polymer electrolytes containing 27.5%–30% PVdF combined with 60%–67.5% EC + PC and 5%–10% LiBF_4 exhibit good dimensional stability and homogeneity and can be isolated as free standing films. X-ray diffraction patterns of the gel polymer electrolytes are presented in Fig. 2. In general, PVdF is highly crystalline and it is difficult to make it fully amorphous by adding organic solvents [8]. Fig. 2(a) and (b) are characterized by sharp diffraction peaks at $2\theta = 20.3^\circ$ and 18.6° (PVdF), 26.6° (LiBF_4). The X-ray diffractograms shown in Fig. 2(c) and (d) reveal clearly that the gel polymer electrolyte is generally amorphous and its crystallinity is depressed greatly by the addition of 67.5% EC + PC with 5% LiBF_4 . It is slightly more amorphous than after the addition of 60%

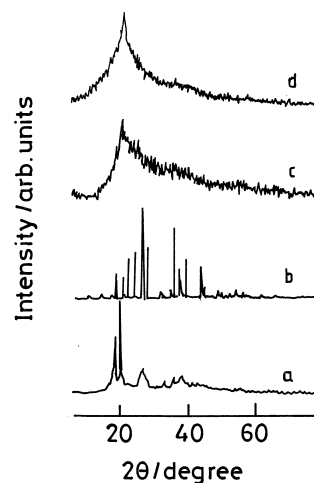


Fig. 2. X-ray diffraction patterns of: (a) PVdF-1000 (KF); (b) LiBF_4 ; (c) 27.5% PVdF–67.5% EC+PC–5% LiBF_4 ; (d) 30% PVdF–60% EC+PC–10% LiBF_4 .

EC + PC with 10% LiBF_4 . This change to an amorphous nature is due to the interaction between the polymer and the low molecular weight organic solvents of EC and PC and lithium salts. DSC plots for PVdF-1000 (KF), LiBF_4 and gel electrolytes in the temperature range 30–300°C are shown in Fig. 3. There is an endothermic peak between 150 and 175°C (Fig. 3(a)) which is attributed to the melting point of PVdF. The sharp endothermic peak in Fig. 3(b) represents a loss of hydration by water molecules. The addition of 60% EC + PC with 10% LiBF_4 (Fig. 3(d)) results in endothermic broad peaks which are due to the phase transition of EC and PC, i.e., the boiling point of organic solvents. By contrast, the endothermic peaks for boiling points of EC and PC are not identified in Fig. 3(c) by the addition of 67.5% EC + PC with LiBF_4 . The disappearance of the phase transition of EC + PC is due to the segments of polymer chain and lithium salts.

TGA plots for 20% PVdF-1000 (KF)–65% EC + PC–15% LiBF_4 at constant temperatures of 40, 50 and 70°C under a flow of argon are shown in Fig. 4. The electrolyte started to lose weight as soon as it was exposed to a flowing argon gas (Fig. 4(a),(c)). After 2 h, the gel polymer electrolyte lost 13, 17 and 22.5% of its total weight at 40, 50 and 75°C, respectively. Most of the weight loss may be due to gel polymer preparation by the solvent-casting technique in which some of the organic solvents are lost during evaporation in a dry room.

The conductivity data for gel polymer electrolytes containing different weight ratios of PVdF, EC + PC and

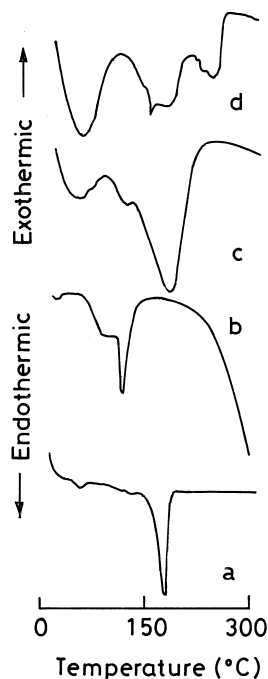


Fig. 3. DSC curves of: (a) PVdF-1000 (KF); (b) LiBF_4 ; (c) 27.5% PVdF–67.5% EC + PC–5% LiBF_4 ; (d) 30% PVdF–60% EC + PC–10% LiBF_4 .

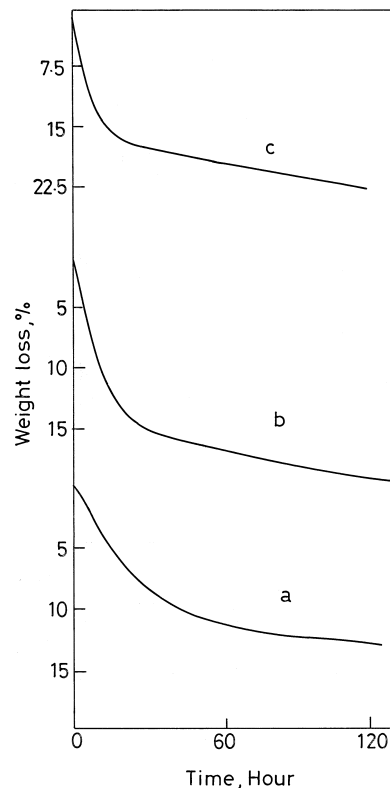


Fig. 4. TGA plots for 20% PVdF–65% EC + PC–15% LiBF_4 at constant temperature of: (a) 40°C; (b) 50°C; (c) 70°C. (All under a flow of argon.)

LiBF_4 salt are given in Table 1. The conductivity and the mechanical stability of the gel polymer electrolyte vs. polymer PVdF 1000 (KF) composition at the room temperature is presented in Fig. 5. The data in Table 1 show that the polymer increased from 15 to 35 wt.% as the plasticizer decreased from 80 to 60 wt.% and the lithium salt to 5 wt.% in all the composition ratios. Generally, the conductivity of the gel polymer electrolyte is determined mainly by the weight ratio of polymer to plasticizer. The

Table 1
Composition (wt.%) and conductivity of PVdF-1000 (KF), EC + PC and LiBF_4 gel polymer electrolytes

Sample no.	PVdF-1000	EC	PC	LiBF_4	Conductivity (S cm^{-1})
A	15	40	40	05	0.00640
B	15	37.5	37.5	10	0.00640
C	15	35	35	15	0.00059
D	20	37.5	37.5	05	0.00221
E	20	35	35	10	0.00162
F	20	32.5	32.5	15	0.00095
G	25	35	35	05	0.00155
H	25	30	30	15	0.00053
I	27.5	33.75	33.75	05	0.00105
J	27.5	31.25	31.25	10	0.00090
K	30	30	30	10	0.00079
L	35	30	30	05	0.00021

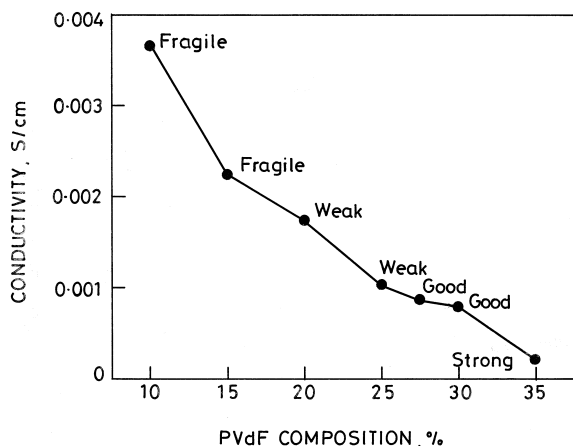


Fig. 5. Conductivity and mechanical stability of gel polymer electrolytes containing EC + PC, LiBF_4 and PVdF-1000 (KF) at room temperature.

higher this weight ratio, the lower the mobility of the charge carriers and, hence, the lower is the conductivity. The conductivity of a gel polymer containing 15% PVdF–80% EC + PC is $6.4 \times 10^{-3} \text{ S cm}^{-1}$ and that of 35% PVdF–60% EC + PC is $2.1 \times 10^{-4} \text{ S cm}^{-1}$. Also, as the

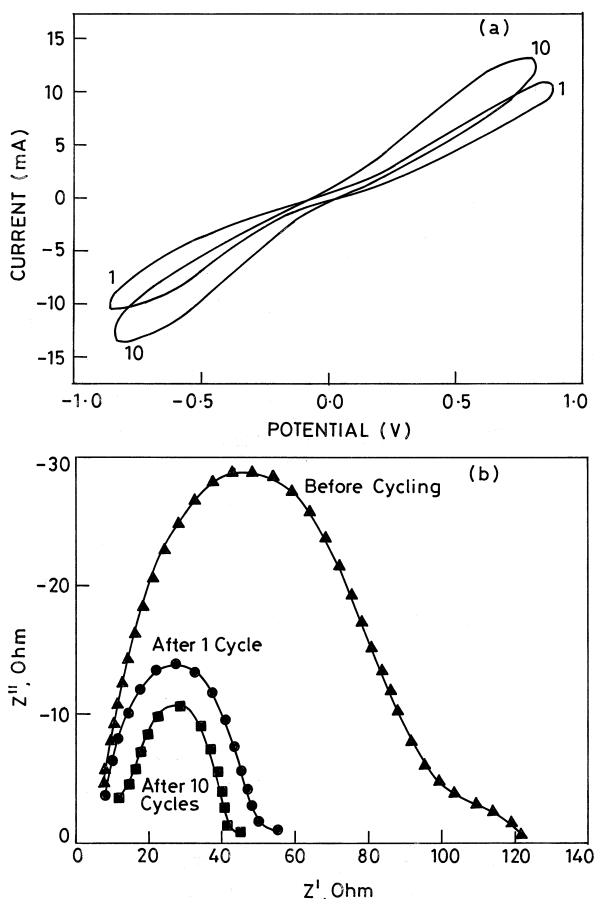


Fig. 6. (a) Cyclic voltammograms of 27.5% PVdF–67.5% EC + PC–5% LiBF_4 gel electrolyte in an Li/Li cell. (b) Corresponding cell impedances.

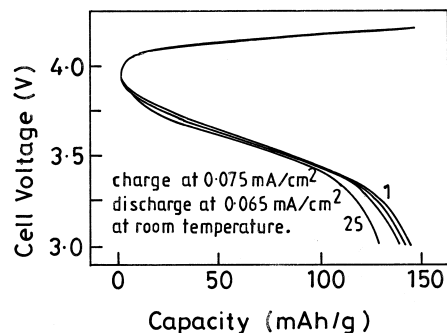


Fig. 7. Charge–discharge curves of Li//27.5% PVdF–67.5% EC + PC–5% LiBF_4 //LiCoO₂ cell.

polymer content increases, the mechanical stability increases and the conductivity of gel polymer decreases (Fig. 5). The stability of the PVdF-EC + PC- LiBF_4 electrolytes in contact with lithium electrode was studied by means of a.c. impedance (Fig. 6(b)) and cyclic voltammetry (Fig. 6(a)). Before subjecting the cell to cyclic voltammetry, the impedance spectrum showed a large semicircle, displaced from the origin by the amount of the electrolyte resistance. The semicircle results from a parallel combination of the geometric capacitance and charge-transfer resistance at the lithium electrodes. The impedance spectrum after the first voltammogram displays a lower interfacial charge-transfer resistance which is continued by the reduction in the diameter of the impedance semicircle.

The impedance spectrum continued to decrease with further cycling. This decrease can be attributed mostly to the removal of the passivating film which is present initially on the lithium electrode and the renewal of the lithium surface with repeated cycling. The gel polymer electrolytes were further tested with Li as the anode and LiCoO_2 as the cathode by charge–discharge examination. The charge–discharge cycles of a typical prototype are presented in Fig. 7. The voltage profile develops along the expected values and the cycling efficiency is high (i.e., 95%). After 25 cycles, the charge–discharge efficiency of the cathode capacity is around 85%. The preliminary results reported in this work provide a promising basis for further studies of 27.5% PVdF–67.5% EC + PC–5% LiBF_4 gel polymer electrolytes for the fabrication of lithium rechargeable polymer batteries.

4. Conclusions

1. Gel polymer electrolytes using 27.5%–30% polymer (PVdF- 1000 (KF)), 60%–67.5% plasticizer (EC + PC) and 5%–10% lithium salt (LiBF_4) provide a highly solvent-free standing film (I, J and K, Table 1).

2. The gel electrolytes have favourable electrochemical properties such as high ionic conductivity, mechanical stability, and wide electrochemical stability.

3. Among the various compositions of gel polymer electrolyte samples produced (A–L, Table 1) the above compositions (I, J and K) appear to be the most stable with respect to the lithium electrode interface.

4. The I, J and K gel polymer films are candidates for thin layer, rechargeable, lithium polymer batteries.

5. A prototype of such cells gives an indication of good voltage performance, and good charge–discharge efficiency.

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