

ELECTROCHEMICAL STUDIES OF PVdF-HFP-BASED GEL ELECTROLYTES

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ABSTRACT

The electrochemical properties of PVdF-HFP-based gel electrolytes formed by immobilizing of commercial battery electrolytes in a copolymer poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) have been determined. The ionic conductivity, interaction with lithium metal and Li^+ ion transference number of gel electrolytes, which are examined by the impedance spectroscopy and the dc polarization of cells are evaluated and discussed. Particular attention is devoted to the phenomena occurring at the interface between this gel and the lithium metal electrode.

INTRODUCTION

Gel-type polymer electrolytes (commonly known as gel electrolyte) receiving a great deal of attention because of their proposed large scales applications in secondary lithium batteries and electrochemical supercapacitors[1-3]. Compared to solid polymer electrolyte, gel electrolytes are much closer to actual applications because they inherited the major properties from the liquid electrolytes, including ion conduction, electrochemical stability on both carbonaceous anode and various metal oxide cathode materials, safety and tolerance against mechanical and electrical abuses. Gel electrolyte system in which a liquid electrolyte has been immobilized by incorporation of a matrix polymer combine the high conductivity of the liquid solution with mechanical properties of the host polymer and with a wide electrochemical stability window.

A variety of polymers such as polyacrylonitrile (PAN), poly(methyl methacrylate) (PMMA), poly(vinyl chloride) (PVC) and poly(vinylidene fluoride) (PVdF) have been used as a polymer matrix [3-4]. In practice, the choice of the individual components of the gel electrolyte 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 electrochemical performance of gel electrolyte based on a commercially available copolymer of poly(vinylidene fluoride-co-hexafluoropropylene)

(PVdF-HFP) as a polymer matrix and being the liquid electrolyte a solution of lithium hexafluorophosphate (LiPF_6) in a propylene carbonate (PC).

EXPERIMENTAL

Preparation of PVdF-HFP-based gel electrolyte involved the immobilization of a commercial battery electrolyte in a copolymer poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVdF-HFP) matrix. In order to obtain homogenous samples, particular care was devoted to the synthesis procedure. Battery electrolyte of 1M LiPF_6 in Propylene Carbonate (PC) (Tomiyama Chemical) which is stored in the glove box has been used without any purification. Copolymer poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVdF-HFP) (Aldrich, reagent grade) was dried by heating under vacuum at 100 °C for 24 h. The copolymer was completely dissolved in tetrahydrofuran (THF) at 50 °C for 3 h. Then the polymer solution was mixed with the battery electrolyte and stirred for 2 h until the homogenous solution with 20 wt% of copolymer was obtained. The solution was casting into propylene dish and THF was allowed to evaporate slowly. The obtained film then was final dried in the vacuum oven at 60 °C to evaporate the solvent residue. All the synthesis procedure was done in an argon-controlled environment, where H_2O and O_2 levels were maintained below 1 ppm.

The conductivity of the electrolyte was measured via AC impedance analysis by sandwiching the samples between two stainless steel blocking electrode. The measurement were performed using a Solartron SI 1260 Impedance/Gain-Phase Analyzer and Solartron SI 1287 Electrochemical Interface under an oscillation potential of 10 mV over a frequency range from 1 M to 0.01 Hz.

The cyclic voltammograms were recorded by using a EG&G 273 Potentiostat/Galvanostat controlled by CorrWare software at room temperature. The electrochemical stability of the electrolyte was determined by running a sweep voltammetry on cell having stainless steel working electrode, lithium counter and lithium reference electrode.

The lithium ion transference number, t_{Li^+} of the gel electrolytes was measured by sandwiching the samples between two symmetrical Li electrode, utilizing the combination of impedance spectroscopy and *dc* polarization method as described by Bruce and Vincent [9-11]. The polarization current was monitored using Solartron SI1287 Electrochemical Interface and Solartron SI1260 Impedance/Gain-Phase Analyzer for the impedance measurements. The impedance was measured under an oscillation potential of 10 mV over a frequency range from 1 M to 0.001 Hz.

The Li/electrolyte interfacial characteristic was obtained by monitoring the time dependence of the impedance of symmetrical Li/electrolyte/Li cell utilizing the same instrument used in the case of the conductivity measurement.

RESULT AND DISCUSSION

The measurement of the electrochemical stability window of the electrolyte is an important test for the determination of its compatibility with high-voltage cathodes, such as the lithium transition metal oxides, e.g. LiCoO_2 , LiNiO_2 or LiMn_2O_4 . The electrochemical stability range is generally determined by running a linear sweep voltammetry of an inert electrode such as stainless steel or platinum in the given electrolyte [12]. Fig. 1 illustrate the current-voltage curve obtained by sweeping a stainless steel (SS) electrode in cells of SS/PVdF-HFP-LiPF₆-PC gel electrolyte/Li at a scan rate of 1 mV/s. The anodic limit obtained for this electrolyte was up to 4.4 V vs. Li, suggesting that the electrolyte is compatible with the cathode materials operating under this limit. The onset of the current in the anodic high voltage range is assumed to result from a decomposition process associated with electrode. [13]

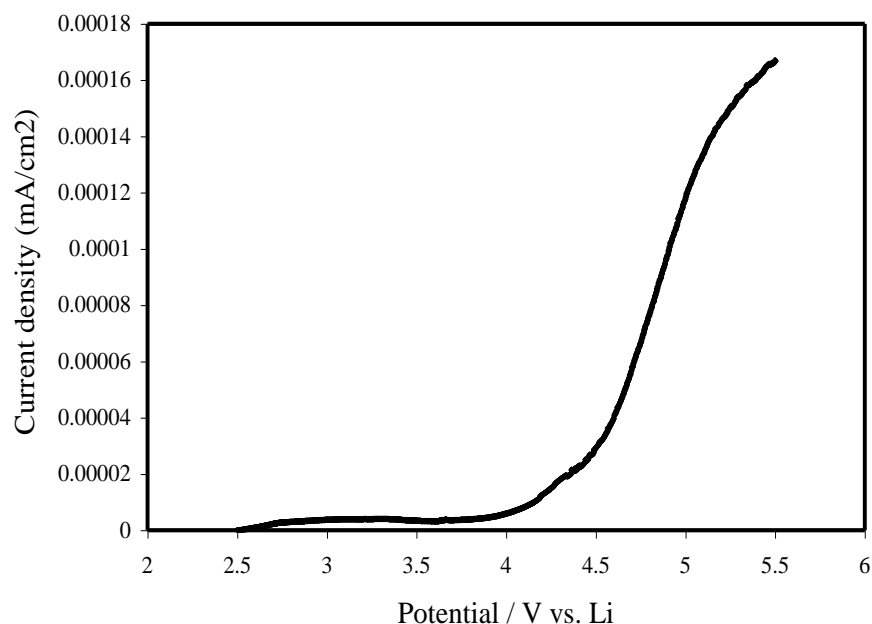


Figure 1: Current-voltage response of a stainless steel electrode in PVdF-HFP-LiPF₆-PC electrolyte cell. Scan rate: 1 mV/s

Since the electrochemical process of the electrodes consists of the intercalation and deintercalation of lithium ions throughout the host compound lattice, electrolytes with Li^+ transference number approaching unity ($t_{\text{Li}^+} \rightarrow 1$) are desirable for avoiding concentration gradient during the charge and discharge cycles. Therefore, the evaluation of this parameter is of great importance for the characterization of electrolyte materials designed for battery application.

Bruce and Vincent [9-11] have recently shown that a method based on a combination of *dc* polarization and *ac* impedance may effectively provide reproducible and reliable result compared with other method such as *dc* polarization, *ac* impedance spectroscopy, potentiometric analysis and classical Tubandt gravimetric analysis,^[14]. Basically, the

method consists of measuring by *ac* impedance and by *dc* polarization, respectively the resistance of and the current across a symmetrical Li/electrolyte/Li cell polarized by a *dc* voltage pulse, *V*. The measurements are taken at the initial time of the applied *dc* voltage pulse ($t=t_0, R=R_0, I=I_0$) and under steady state conditions ($t=t_s, R=R_s, I=I_s$). By using these values, the t_{Li+} is given by the following expression:

$$t_{Li+} = \frac{I_s (V - I_0 R_0)}{I_0 (V - I_s R_s)} \quad (1)$$

where *V* is the value of the *dc* voltage pulse applied to the cell for the polarization analysis. Figure 2 and 3 show respectively, the response of the cell current monitored with time until a steady-state current was reached and the impedance plot of the symmetrical cell Li/electrolyte/Li before and after *dc* polarization. The cells were also left at open circuit for 100 h to permit the concentration gradient to disperse prior to the polarization procedure being repeated to test the repeatable result. The calculation of lithium transference number obtained for the PVdF-HFP-LiPF₆-PC gel electrolyte was 0.42.

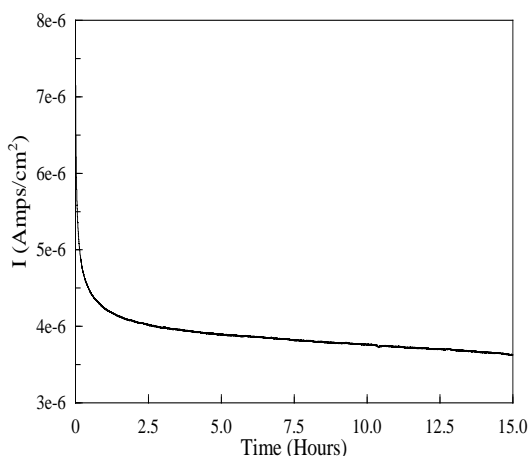


Figure 2: Variation of current with time during polarization with applied potential of 10 mV.

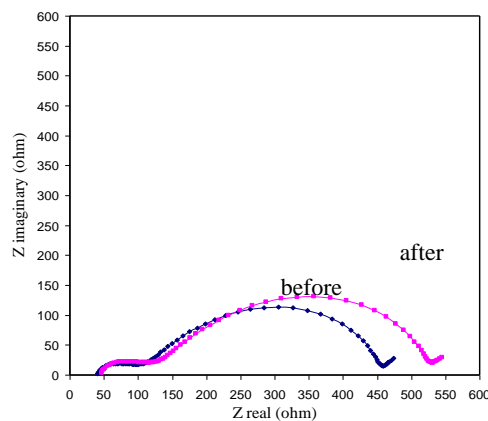


Figure 3: Cole-cole plot of the complex impedance before and after the

High conductivity, high lithium transference number and wide electrochemical window, although desirable properties, are not sufficient to make an electrolyte completely useful in practical term. The compatibility with the electrode materials is also an essential parameter to guarantee acceptable performance in electrochemical devices, especially when cyclability and reliability are considered. It is well known that critical factors of lithium rechargeable batteries are the lithium interface resistance (R_i) and its stability over time. A detail impedance analysis of symmetrical cell of the Li/electrolyte/Li stored at open circuit condition has been carried out with particular attention devoted to Li/electrolyte interface properties.

Fig. 4 shows the time evolution response of the impedance of a Li/PVdF-HFP-LiPF₆-PC/Li cell kept continuously under open circuit conditions at room temperature. The plots reveal a progressive expansion of the middle frequency arc with time, which is typically attributed to interfacial phenomena [15-16]. The expansion of the arc may be ascribed to a resistive layer continuously growing on the lithium electrode surface, indicates that the lithium electrode is passivated once in contact with the PVdF-HFP-based gel electrolyte. This behavior is due to some the electrolyte components such as PC, which is known lithium corrosive agents. As previously discussed by Abraham & Alamgir [17] these components may diffuse from the bulk of the gel electrolyte to reach the lithium interface, thus inducing the observed passivation effects. The growth of this resistive layer will increasingly prevent Li-ion transport and thus block the flow of current through the cell [13].

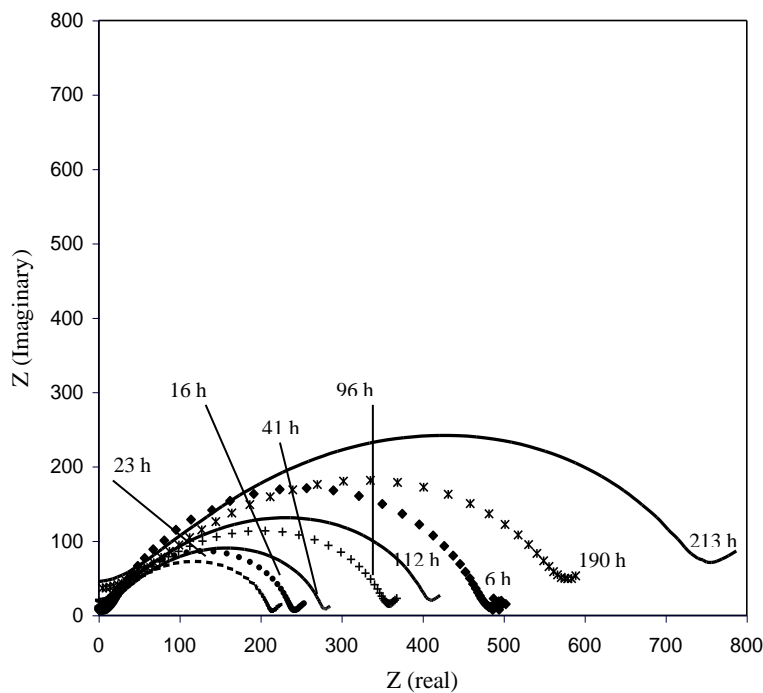


Figure 4: Time evolution of the impedance of Li/PVdF-HFP-LiPF₆-PC/Li cell stored under open circuit conditions at room temperature.

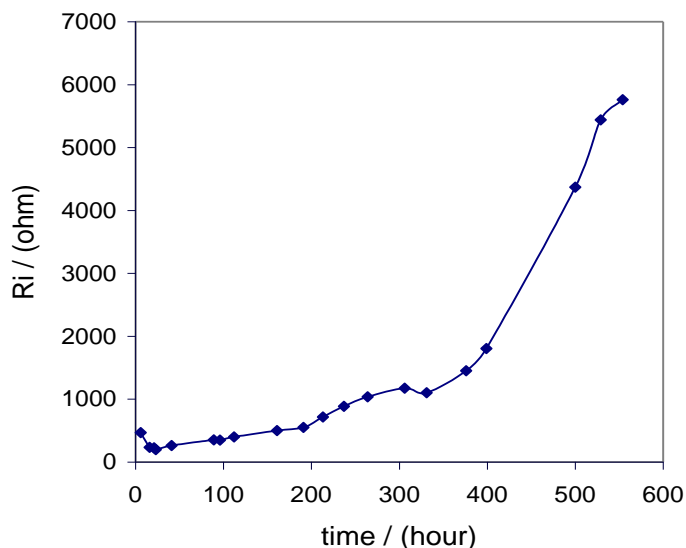


Figure 5: Time evolution of the interfacial resistance, R_i of the lithium electrode in the PVdF-HFP-LiPF₆-PC gel electrolyte at room temperature

By using a model circuit which may be representative of the equivalent of the lithium electrode interface ^[15], it is possible to separate the various impedance parameters which contribute to determine the response illustrated in Fig. 4. Fig. 5 represents the time evolution of the lithium interfacial resistance, R_i . Increases in obtained R_i values are associated with the growth of a passivation layer on the electrode surface. As shown, the rate of passivation is slow at the initial stage but then becoming progressively much faster.

The kinetic of the lithium plating-stripping process:



from PVdF-HFP-based gel electrolyte on stainless steel substrate was determined by cyclic voltammetry. Fig. 6 illustrates a voltammogram obtained in cell using PVdF-HFP-LiPF₆-PC electrolyte. As shown, a single anodic stripping peak follows a single cathodic deposition (plating) peak. The voltammetric response also been monitored (shown in Fig.6) with progressive time interval to determine the effect of the corrosion phenomenon at the lithium interface. The voltammetric response of aged cell shows that the reversibility of the lithium plating-stripping process decreases upon cycling over time. This is an indicative of a progressive deterioration of the interface most probably due to passivation phenomena at the lithium electrode surface.

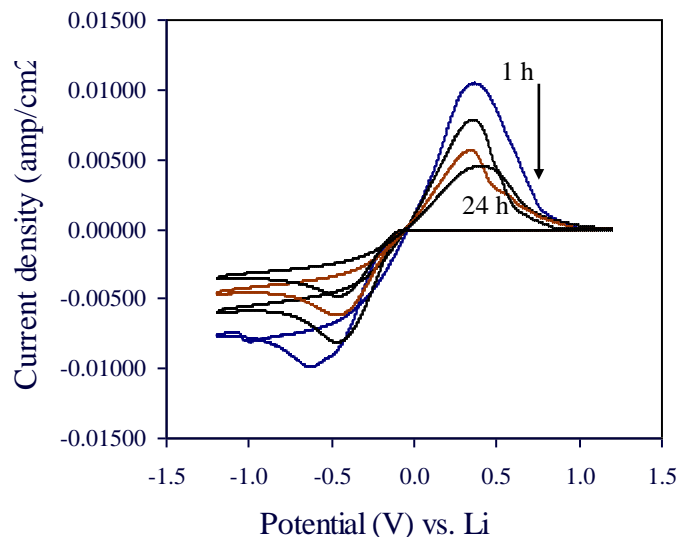


Figure 6: Cyclic voltammetry of a stainless steel electrode in PVdF-HFP-LiPF₆-PC electrolyte vs. Li reference electrode. Scan rate 1 mV/s.

CONCLUSION

The PVdF-HFP-LiPF₆-PC gel electrolyte exhibit wide electrochemical stability window up to 4.4 V vs. Li, which is compatible with high-voltage cathodes, used in lithium battery. The transference number of 0.42 also comparable to other gel electrolyte system. However this gel electrolyte display a growth of passivation film on the surface of lithium as shown by the increasing interfacial resistance over time. Further investigation on improving the interfacial stability with the lithium electrode is in progress. In addition the use of different types of battery electrolyte for PVdF-HFP-based gel electrolyte is also in progress.

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