

IMPEDANCE SPECTROSCOPY STUDY ON THE REACTIVITY OF PVDF/HFP-BASED GEL POLYMER ELECTROLYTES TOWARDS A LITHIUM ELECTRODE

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ABSTRACT

The reactivity of poly(vinylidene-co-hexafluoropropylene) (PVdF/HFP)-based gel polymer electrolytes towards a lithium electrode was studied by AC impedance spectroscopy technique. PVdF/HFP-based gel polymer electrolyte (GPE) was formed by immobilizing the lithium hexafluorophosphate (LiPF_6) in a mixture of ethylene carbonate-dimethyl carbonate (EC-DMC) liquid electrolyte in the copolymer matrix. The impedance measurement was run during 10 days storage of a cell of Li/gel polymer electrolyte/Li. Results obtained were used to identify charge-transfer resistance, double layer capacitance and properties of passivation films. Ceramic filler of SnO_2 was introduced in the system in attention to improve the transport properties as well as to reduce the reactivity towards lithium electrode.

INTRODUCTION

Lithium metal demonstrates a remarkably low electrochemical equivalent and the most negative redox potential of all metallic elements. The main drawbacks of lithium anode is the degradation of cycle life due to the formation of dendritic deposits which causes the isolation of active lithium metal and also leads to short circuit with the cathode. The second reason is the formation of an interfacial layer between lithium metal and electrolyte with a low ionic or electronic conductivity. It is well known that lithium metal reacts spontaneously once in contact with electrolyte material, with the formation of a passivating films on its surface [1]. When the film reaches a certain thickness, it will block the active metal surface from further reactions with the electrolyte and thereby passivate it. Thus, the Li surface becomes an insulator for electron transfer. However, as all the above surface species are Li salts, they are Li ion conducting. Hence, a series of electrochemical Li deposition and dissolution may take place through these surface films.

The electrochemical processes occurred between the lithium electrode and gel polymer electrolyte always reflects several time constants. Impedance spectroscopy technique is one of the most appropriate techniques for the electrochemical studies of the reactivity between gel polymer electrolyte and lithium electrode. This technique allows a straightforward analysis of the time constants related to the various stages in the electrochemical response by modeling and simulation procedure followed by fitting equivalent circuit analogs to the experimental results [2-4]. The electrical equivalent is expressed in terms of different time constants resistance-capacitance (RC) which contains information related to rate constants,

surface layer composition and thickness, diffusion parameters and transport numbers of moving charged species [5].

In this paper we report the results of the investigation on the lithium/ (PVdF/HFP)-based gel polymer electrolyte interface. In particular, the investigation was focused on the interfacial stability of electrolytes toward the lithium metal as a function of time.

EXPERIMENTAL DETAILS

PVdF/HFP-based gel polymer electrolyte was prepared by immobilizing a non-aqueous electrolyte in a copolymer of poly (vinylidene fluoride-*co*-hexafluoropropylene) (PVdF/HFP) matrix. In order to obtain homogenous samples, particular care was devoted to the synthesis procedure. Non-aqueous electrolyte of 1M LiPF₆ in mixture of Ethylene Carbonate (EC) and Dimethyl Carbonate (DMC) (w/w 1:1) (Mitsubishi Chemical) which is stored in the glove box has been used without any purification. Copolymer PVdF/HFP (Aldrich, reagent grade) was dried by heating under vacuum at 100 °C for 24 h prior been used. The copolymer was completely dissolved in tetrahydrofuran (THF) at 50 °C for 2 h. Then the polymer solution was mixed with the battery electrolyte and stirred for 3 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. All the synthesis procedure was done in an argon-controlled environment, where H₂O and O₂ levels were maintained below 1 ppm.

Impedance measurement was performed using a Solartron SI 1255 High Frequency Response Analyzer coupled with Solartron SI 1286 Electrochemical Interface under an oscillation potential of 200 mV over a frequency range from 1 M to 0.1 Hz. The Li/electrolyte interfacial characteristic was obtained by monitoring the time dependence of the impedance of symmetrical Li/electrolyte/Li cell. Simulation and modeling of data obtained was performed via Z-View software (Scribner Inc.) based on the CNLS software written by MacDonald [6].

RESULTS AND DISCUSSION

Fig. 1 and 2 show the typical impedance responses of symmetrical Li/(PVdF/HFP)-based gel polymer electrolyte/Li cells. The spectra show a slight difference shape of the impedance response with electrolyte composition. In general, all cells showed a slightly depressed semicircle, associated with the lithium/gel polymer electrolyte (GPE) interfacial processes, followed by more complicated features at lower frequency which is related to diffusion phenomena into the electrolyte. The high frequency intercept of the semicircle with the real axis is inversely related to the gel polymer electrolyte ionic conductivity. The observed slight shift toward higher impedance values of the high frequency intercept was probably due to modification of the electrolyte thickness upon storage via composition changes through significant reactions with the lithium electrode [7-8]. The diameter of the semicircle is related with the overall interfacial impedance. A progressive expansion of the semicircle associated to a continuously growing of a resistive layer on the electrode surface clearly indicates that the lithium electrode is passivated when in contact with the electrolyte.

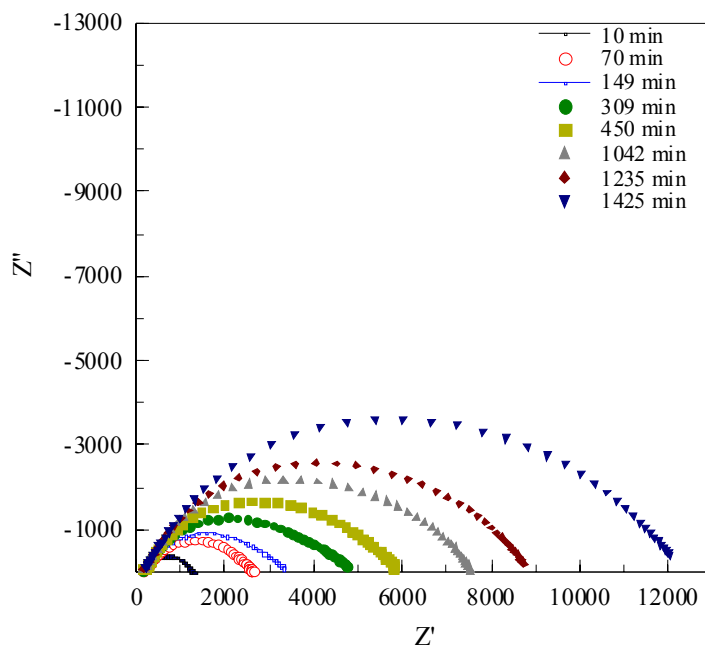


Figure 1: Time evolution of the impedance spectra of the Li/GPE/Li cell under open circuit at room temperature

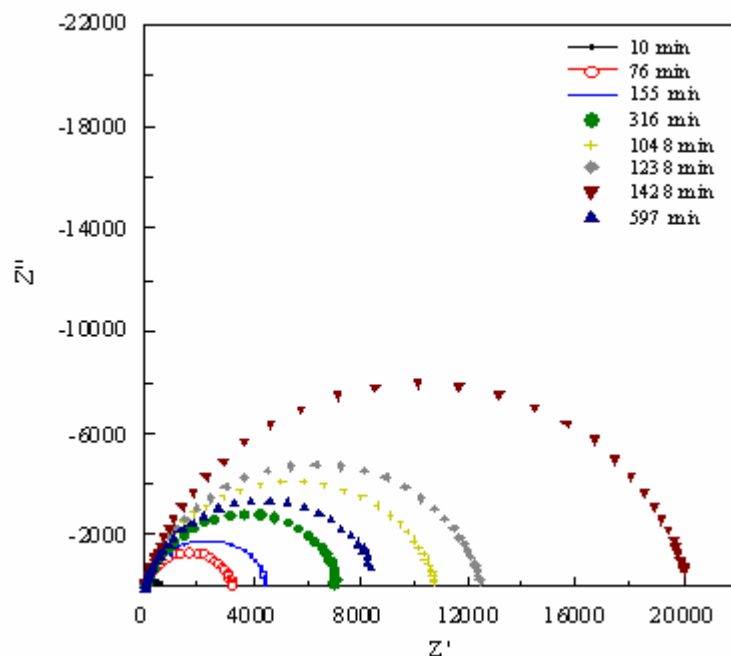


Figure 2: Time evolution of the impedance spectra of the Li/GPE-1% SnO₂/Li cell under open circuit at room temperature

Various impedance parameters contributed in the responses illustrated in Fig. 1 and 2 could be separated using an equivalent circuit analog to the experimental results. In this way, one may represent the time evolution of the lithium interfacial resistance as given in Fig. 4 and 5. The behavior of interfacial resistance shall be explain by assuming that the morphology of the passivation film changes with time. In designing the equivalent circuit, three electrochemical processes should be taken into account as describe in the following:

- a. The charge-transfer reaction that takes place at the gel polymer electrolyte/lithium interface which is represented by a parallel network of a resistor (R_{ct}) and a double-layer capacitor (C_{dl}).
- b. The passive layer spontaneously forming on the lithium electrode by reaction with the electrolyte, assumed to be as an ionically conductive layer represented by a resistor (R_f) and a capacitor (C_f) associated with the passive film ionic resistance and geometric capacitance.
- c. The diffusion process of lithium taking place in the gel polymer electrolyte at very low frequencies, represented with a typical Warburg impedance element (Z_w).

As reported [7,9], due to the difficulty in discriminate the two interfacial processes (ionic conduction through the passive layer and electrode charge-transfer) contribution even using a constant phase element (CPE) instead of capacitor, a simplified equivalent circuit has been proposed as illustrated in Fig. 3. In this equivalent circuit, the large semicircle is represented by a parallel combination of a generic interface resistance (R_{int}) and double-layer capacitance (Q_{dl}) which is associated with the total interface impedance. While the intercept of the semicircle at the high frequency side on the Z' -axis gives the ohmic resistance of the cell associated with the resistance of the electrolyte (R_b).

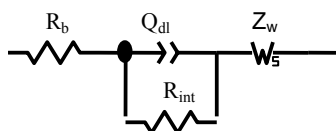


Figure 3: Proposed equivalent circuit used to fit the impedance results of Li/(PVdF/HFP)-based GPE/Li cell.

The impedance spectra were fitted into the equivalent circuit using the Z-View software (Scribner, Inc.). This program enables the fitting to be quantified using the sum of square errors and chi-square of standard deviation (χ^2) via non-linear least square method [10]. As a general rule, the fitting result only accepted when the fitting χ^2 parameter was $\leq 5 \times 10^{-4}$. It takes into account the charge-transfer of lithium at the interface as well as the additional impedance associated with the growth of a passivation layer at such an interface.

The depressed semicircle observed which is represented by the constant phase element (CPE) parameter (Q_{dl}) is related to the interfacial capacity. The deviations of such behavior from a pure capacitor have been associated with several physical causes [6]. In

the studied system, this behavior should be regarded to the growth of a compact (non-rough) passive layer at the interface between the gel polymer electrolyte and the lithium electrode [11,12].

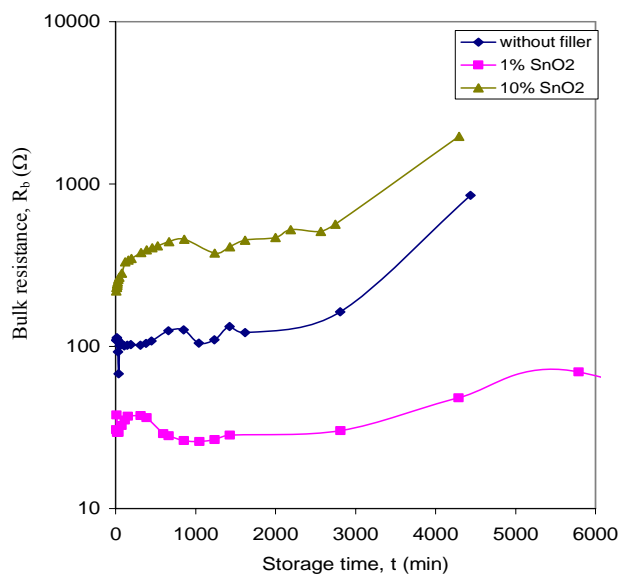


Figure 4: The bulk resistance, R_b calculated from impedance measurement of Li electrode as a function of storage time

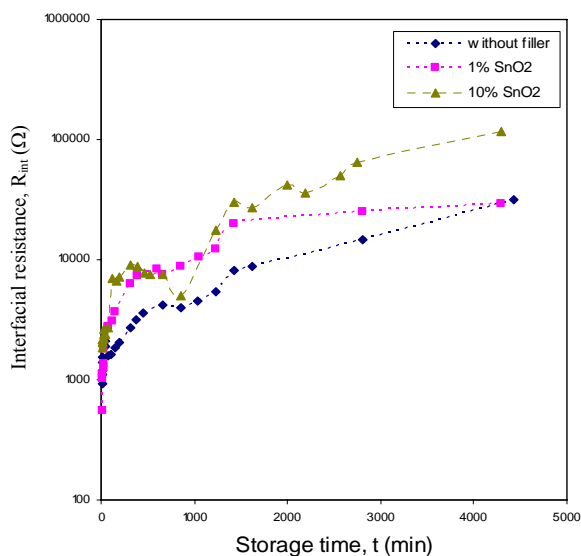


Figure 5: The interfacial resistance, R_{int} calculated from impedance measurement of Li electrode as a function of storage time

Fig. 4 and 5 show the changes of resistances, R_b and R_{int} respectively as a function of time. The small changes observed in R_b was assumed to reflect the surface reaction between the active metal and electrolyte species that may change the composition of the electrolyte, either by consumption of electrolyte components, or by dissolution of electrolyte reduction products [13]. The observed initial rapid increase of R_{int} can be explained as being caused by the growth of a passivation layer on the lithium electrode surface as a result of its progressive reaction with the electrolyte. However, it is difficult to assign a particular chemical species for the reaction since all the components of the electrolyte can react with the lithium electrode. The subsequent decay observed at longer storage time may associate to the occurrence of morphological changes which lead to a more compact and uniform layer on the electrode surface. Generally, the resistance for the lithium-ion migration, R_{int} through the surface film is determined by the thickness and specific lithium ion conductivity of the surface film.

The addition of ceramic filler to the gel polymer electrolyte may reduce the growth rate of the lithium passivation in particular due to their ability to trap traces of residual impurities such as water. It was reported that utilizing of ceramic filler also favors the formation of compact thin passivation layers on the lithium electrode surface [14]. Although the interfacial resistance value of filler added GPE a little bit higher but it shown a slower growth rate at longer storage time that indicates an improve in interfacial stability.

CONCLUSION

The Li/(PVdF/HFP)-based gel polymer electrolyte interface shows a progressive growth of a passivation layer on the lithium electrode surface even in a short period of storage time. The used of suitable ceramic filler due to its ability to trap residual impurities may help to reduced the growth rate in longer storage time, then improve the interfacial stability.

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