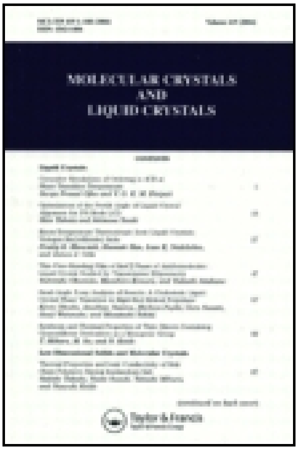

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Electrochemical Characteristics and Kinetic Parameters of Li/SPE/FeOOH(an) cell

Chong-Chul Ryu [a] , Kum-Sho Hwang [a] , Byung-Hyun Choi [a] , Do-Hoon Kim [a] & Jung-Soo Kim [a]
[a] Department of Chemistry, National Fisheries University of Pusan, Pusan, 608-737, Korea

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ELECTROCHEMICAL CHARACTERISTICS AND KINETIC PARAMETERS OF Li/SPE/FeOOH(an) CELL

CHONG-CHUL RYU, KUM-SHO HWANG, BYUNG-HYUN CHOI, DO-HOON KIM and JUNG-SOO KIM
Department of Chemistry, National Fisheries University of Pusan
Pusan 608-737, Korea

ABSTRACT The hybrid polymer thin film has been prepared by composing of poly(vinyl chloride), lithium salts and plasticizer and used as a solid polymer electrolyte(SPE). The phase transition temperature(Tg) was determined by differential scanning calorimetry (DSC). The ionic conductivities of the electrolyte at various temperatures have been investigated by a.c. impedance spectroscopy, and shown as $10^{-4} \sim 10^{-3}$ $ohm^{-1} \cdot cm^{-1}$ at room temperature. And a new secondary lithium cell, Li/FeOOH(an) employed with the prepared solid polymer electrolyte has shown the open-circuit voltage of 3.10 V, capacity of 69 mAh/g, and energy density of 179 Wh/kg, respectively.

In addition, the kinetic and impedance parameters and electrochemical characteristics of Li/SPE/FeOOH(an) cell at the discharge/charge process have been studied.

INTRODUCTION

Solid polymer electrolytes have a lot of applications in electrochemistry. Especially, SPE have specific characteristics in its application for the cell because of their flexibility and good adherence on electrode. This enables solid polymer electrolytes to be excellent alternative of liquid electrolyte which has liquid leakage problems. Also solid polymer electrolytes is one of lithium polymer batteries for the constituents of as a commercial application. In recent years, there has been an intensive research on the solid polymer electrolytes for lithium batteries.[1] Moreover, Abraham and Alamgir have reported that the ionic conductivity of poly(ethylene oxide) or poly(acrylonitrile) based on the solid polymer electrolytes can be improved as high as 10^{-4}~10^{-3} $ohm^{-1} \cdot cm^{-1}$ at room temperature .[2~3]

In the present, high Li^{+}ion conductivity of solid polymer electrolytes at the selected temperature and the discharge/charge characteristics of Li/FeOOH(an) cell using solid polymer electrolytes such as PVC-EC- PC-$LiClO_4$ were studied.

EXPERIMENTAL

Synthesis of Solid Polymer Electrolyte

PVC(Hanyang Co., average molecular weight 1.5×10^5), and lithium perchlorate($LiClO_4$) were used after drying at 50℃ and 130℃ for 12hr under vacuum, respectively. High purity ethylene carbonate (EC), propylene carbonate(PC)(Mitsubishi Petrochemical Co.) and tetrahydro-furan(99% THF, Aldrich) was used without any purification and treatment. All reagents were stored in a dry box under argon atmosphere. $LiClO_4$ was dissolved in the solvent mixture and the temperature of the liquid electrolyte was raised to 110℃ and followed by the slow addition of PVC. The mixture of PVC-EC-PC-$LiClO_4$(15 : 40 : 40 : 5 of weight ratio) was dissolved in THF. The resulted viscous solution was then stirred for 30min to avoid aggregation. The resulting solution was poured onto glass substrate. When the THF solvent was evaporated completely, the polymer thin film was formed. The film could be peeled off from the glass substrate easily by scratching out. The thicknesses of film were measured as 70~200 ㎛.

Composition of Lithium Cell and Measurements

In the present study, lithium metal was used as anode. The suspension of FeOOH(an)[4], acetylene black, and PTFE were prepared in a weight ratio of 80 : 15 : 5 and then used as cathode material. The synthesized polymer thin film was used as electrolyte and all the experiments were carried out 25℃ in an argon atmosphere. The conductivity of the electrolyte was determined using impedance spectroscopy in the frequency range of 0.1 Hz~100 KHz. An EG&G Princeton Applied Research(PAR) Potentiostat /Galvanostat Model 273A and M5210 Lock-in Amplifier Impedance System, interfaced with a personal computer, were used. And the phase transition were determined by DSC(Du pont Instruments, Model 910).

RESULTS AND DISCUSSION

Electrochemical Characteristics

The ionic conductivity to the temperature dependance of PVC-based solid polymer electrolytes determined with a.c. impedance spectroscopy at 10℃ to 45℃ is shown in Figure 1(a). The ionic conductivity of electrolytes was linearly increased with increasing temperature with an exceptionally steep increase at range of 40~45℃. The ionic conductivity at 10℃ and 45℃ was determined as 4.24×10^{-4} and 3.77×10^{-3} $ohm^{-1}\cdot cm^{-1}$, respectively.

The temperature dependance of the diffusion coefficient of PVC-based electrolyte obtained from the Warburg slope by a.c. impedance technique is shown Figure 1(a). As the temperature increases, the diffusion coefficient of the lithium ion in the PVC-based polymer electrolyte shows a linear increase from 3.94×10^{-13} cm^2/sec at 10℃ to 2.25×10^{-11} cm^2/sec at 45℃. Based upon these results, the concentration of the polymer electrolyte is determined as 3.46×10^{-3} by the weight ratio of the quantity of the lithium ion in

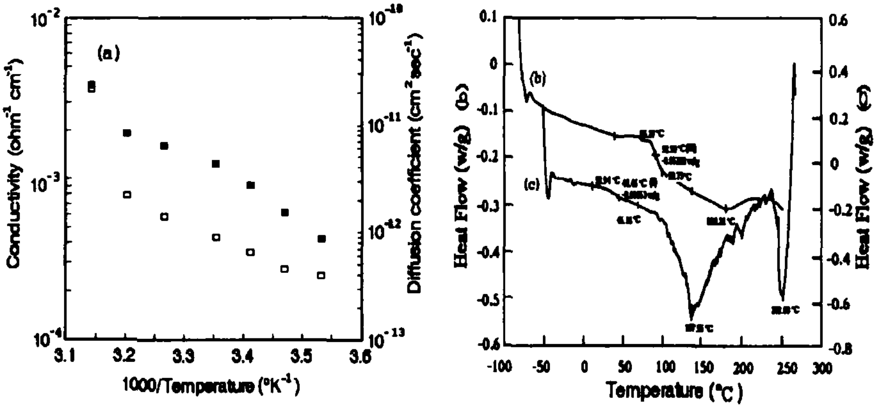

FIGURE 1 Temperature dependance of the ionic conductivity(■) and diffusion coefficient(□)of the lithium ion in the Li/SPE/FeOOH(an) cell, and DSC thermograms of pure PVC(b), and PVC-based EC/PC lithium salt polymer electrolyte(c).

the lithium salt/PVC-EC-PC. The phase transition of pure PVC shown in Figure 1(b) and was indicated to be occurred at about 95℃(Tg), but the phase transition temperature was about 45℃ in the hybrid polymer thin film electrolyte prepared by composing of poly(vinyl chloride), lithium salt, and plasticizer. The result from DSC thermogram in Figure 1(b) consistents with the trends of the ionic conductivity and diffusion coefficient of lithium ion in the hybrid polymer thin film.

Discharge and Charge Behavior of Li/SPE/FeOOH(an) Cell

The cyclic voltammetry (CV) of Li/SPE/FeOOH(an) cell in Figure 2(a) was obtained within a potential range of -1.2 to 2.8 V vs. Li^+/Li. The peak current of the discharge/charge(dc/ch) process gradually decreases as increasing the number of discharge/charge process. This indicates that the insoluble film was produced between PVC-based electrolyte and lithium electrode with increasing number of dc/ch process. Appeteccchi et al.[5] already reported that the passivation phenomena produced on the lithium electrode significantly influence the cyclability of lithium electrode in a poly(methylmethacrylate) PMMA-based gel electrolyte.

Figure 2(b) shows the dc/ch behavior of the Li/SPE/FeOOH(an) cell. The potential range of discharge/charge was 1.50~3.80V. And the

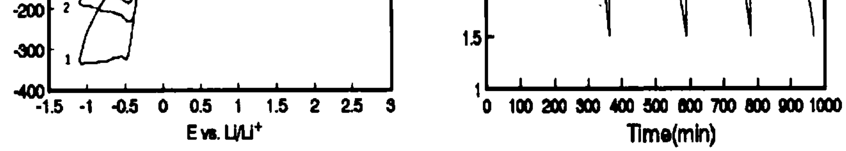

FIGURE 2 Cyclic voltammograms(a) of a Li/SPE/FeOOH(an) cell obtained before discharge/charge process, scan rate = 10 mVs^{-1}, and the discharge/charge curves(b) of a Li/SPE/FeOOH(an) cell at discharge current density, 0.10 mA/cm^2 and charge current density, 0.026 mA/cm^2.

TABLE I Kinetic parameters of lithium ion in a Li/SPE/FeOOH(an) cell.

Discharge/ charge	α	j (μA)	b (V)	R_{ct} (Ω)	Thickness of EEI(Å)	Jumping distance(Å)
Before dc/ch	0.12	3.73	0.22	284.9	292.0	78.4
After 1st dc	0.08	4.55	0.32	1615.4	74.8	13.8
After 1st ch	0.11	5.50	0.23	1307.1	66.4	17.1
After 2nd dc	0.07	4.64	0.37	2170.9	64.3	10.3
After 2nd ch	0.09	5.50	0.32	1944.5	62.1	11.5
After 3rd dc	0.07	5.34	0.37	2512.2	55.6	8.9
After 3rd ch	0.08	5.51	0.35	2355.1	56.1	9.5

discharge and charge current density was 0.1mA/cm^2 and 0.026mA/cm^2, respectively. The first discharge time is longer than later discharge time. Therefore, now, we are focusing on this problem our effect to have the improved cyclability over 100 cycles.[6]

Kinetic Parameters and Impedance Spectroscopy

Table1 shows the kinetic parameters of Li/SPE/FeOOH(an) cell obtained by current-potential method. The charge transfer resistance, R_{ct} after discharge/charge processes shows significant different value from that before discharge/charge processes. R_{ct} increases with the decreasing thickness of the electrode/electrolyte interface(L_{EEI}) as discharge/charge processes. The jumping distance decreases with the number of discharge/charge processes.

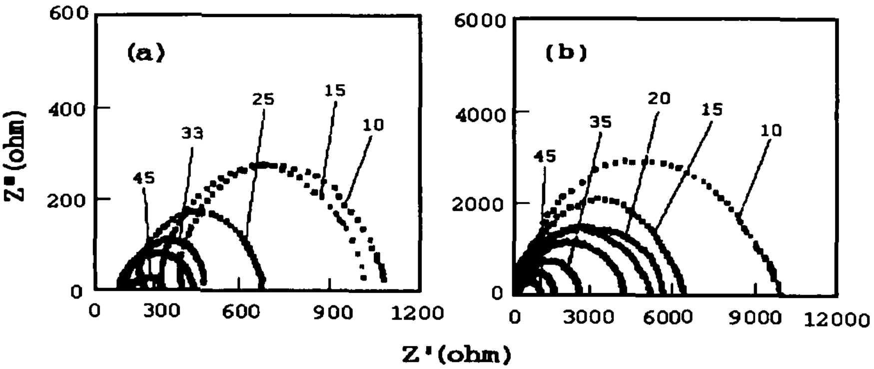

FIGURE 3 Temperature dependance of the impedance of Li/SPE/FeOOH(an) cell before discharge/charge(a) and after first discharge (b).

Figure 3 shows the comparative impedance data between the value before any discharge/charge and after the first discharge. Figure 3(a) shows the smaller resistance at lithium electrode/solid polymer electrolyte interface before any discharge/charge process than after the first discharge (Figure 3(b)). The expansion of the semicircle possibly is due to a continuously growing resistive layer on the lithium electrode surface. The impedance data indicates that the passivation increases as the number of discharge/charge process after the first discharge. The trends of R_{ct} in Table I consistent with CV data.

CONCLUSION

The hybrid polymer thin film has been prepared by composing of Poly(vinyl chloride), lithium salts and plasticizer and used as a solid polymer electrolyte. Its ionic conductivity at range of 10℃ ~45℃ were 4.24×10^{-4} to 3.77×10^{-3} $ohm^{-1}\cdot cm^{-1}$.

A new secondary lithium cell Li/SPE/FeOOH(an) using above solid polymer electrolyte had the open-circuit voltage(OCV) of 3.10V capacity of 69 mAh/g, and energy density of 179 Wh/kg, respectively.

However, the kinetic and impedance parameters and electrochemical characteristics of Li/solid polymer electrolyte/FeOOH(an) cell at the discharge/charge process have been obtained newly.

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