Improved Charge/Discharge Behaviors of Li/γ-FeOOH(an) Cell with Poly(vinyl chloride)-based Electrolyte

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PVC를 기초로 고분자 전해질을 활용한 Li/γ-FeOOH(an) 전지의 충·방전 성능 개선

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Abstract

The electrochemical characteristics of Li/γ-FeOOH(an) cell with PVC, poly(vinyl chloride)-based electrolyte were studied. A new electrolyte of this class showed the quite high ionic conductivity, wider electrochemical stability window, and adjustable lithium ion transference number(t_{Li^+}) in the solid polymer electrolyte (SPE). Moreover, as the N,N-Dimethylaminomethylferrocene(DMAMF) was added in the SPE, the improved stability of the lithium/SPE interface and the cyclability of the discharge/charge process, compared with others using the PVC-based electrelyte, have been developed.

1. Introduction

SPE(solid polymer electrolyte) has been known as excellent materials for secondary battery due to their flexibility and good adherence on lithium electrode and other specific characteristics. The polymeric conductor has been the subject of several researches, because it is the most environmentally stable, inexpensive and relatively simple synthesis. Also, solid polymer electrolyte offers potential applicability to lithium polymer batteries for commercial products. Wright[1] reported that polymeric complexes of poly(ethyleneoxide)(PEO) with salts of alkali metals lead to the development of solid polymer-based electrolytes.

We reported that the conductivities of PVC-based polymer electrolytes, plasticized with solutions of lithium salt, lithium perchlorate($LiClO_4$), in low molecular weight organic solvents such as propylene carbonate(PC), ethylene carbonate(EC), and 3-methyl-2-oxazolidinone(MEOX) were varied as $10^{-3} \sim 10^{-4}$ $\Omega^{-1} \cdot cm^{-1}$ at room temperature.

In this paper, the improved electrochemical properties and the stability of the lithium/SPE interface were studied. Especially, we report that the cyclability of the discharge/charge process of a Li/γ-FeOOH(an) cell was improved by adding DMAMF(N,N-Dimethylaminomethylferrocene) in SPE.

2. Experimental Procedure

In this research, The sample R_1 which is plasticized by PC, EC organic solvent was developed by the method of Abraham et al.[2] The sample R_2 and R_2F were prepared by adding MEOX and DMAMF in R_1, respectively. The compositions of these samples are as follows : (R_1) ; 15 w/o PVC : 40 w/o PC : 40 w/o EC : 5 w/o LiClO4, (R_2) ; 15 w/o PVC : 33 w/o PC : 32 w/o MEOX : 7 w/o LiClO4, (R_2F) ; 12.6 w/o PVC : 28 w/o PC : 29.5 w/o EC : 11.5 w/o MEOX : 6.4 w/o LiClO4 : 12 w/o DMAMF.

PVC(low molecular weight, Aldrich) and $LiClO_4$(Aldrich) were dried before use at 50℃ and 130℃, respectively, under vaccum for 12 hr. EC and PC (Mitsubishi) were dried over molecular sieves. MEOX, DMAMF, and tetrahydrofuran(THF) were used without further purification. The preparation of these sample involved the immobilization of the selected organic solution of $LiClO_4$ in PVC matrix. The entire preparation procedure was carried out in argon-filled dry box.

The ionic conductivities of these electrolytes were determined at 5℃ ~ 55℃ by measuring the impedance response of cells formed by sandwiching a given electrolyte sample between stainless steel(S.S) blocking electrodes. Potentiostat/Galvanostat(EG &G PAR, Model 273A) and Lock-in amplifier(EG &G PAR, Model 5210) were used for the measurements. The frequency range of impedance spectroscopy was 0.1 Hz to 100 kHz. The lithium ion transference number(t_{Li^+}) of the samples was measured by the impedance method described by Bruce and Vincent[3].

The electrochemical stability window was determined by running sweep voltammetry on a three electrode cell where S.S plate and lithium rod were used as a working electrode and counter electrodes, respectively and a lithium strip placed between two adjacent layers of electrolyte was served as the reference electrode. The kinetics of the lithium deposition/stripping process was evaluated by cyclic voltammogram obtained in three electrode SPE cells. The stability of the Li/SPE interface was investigated by monitoring the time dependance of the impedance of symmetrical Li/SPE/Li cells.

The Li/γ-FeOOH(an) cell were assembled in argon-filled dry box by pressing into an appropriate case in a sequence of Li rod anode, the selected SPE membrane, and cathode film. The latter was based on a amorphous γ-FeOOH(an)[4] as the Li-intercalatable material blended with acetylene black(a.b.) and with the selected SPE used as polymer binder. The composition of γ-FeOOH(an), a.b., and SPE in this cathode film is in the range of 42 : 8 : 50 w/o ratio. The cyclability of the charge/discharge process of the cells were investigated using the Battery tester(Arbin).

3. Results and Discussion

3.1 Electrochemical Characteristics

Abraham et al.[2] reported that the ionic conductivity of R_1 was $1.2\times10^{-3}\ \Omega^{-1}\cdot\mathrm{cm}^{-1}$ at 20℃. The ionic conductivities of R_2 and R_2F were $1.63\times10^{-4}\ \Omega^{-1}\cdot\mathrm{cm}^{-1}$ and $7.42\times10^{-5}\ \Omega^{-1}\cdot\mathrm{cm}^{-1}$ at 25℃, respectively. Although these values of R_2 and R_2F were smaller than the value of R_1, it was quite high, compared with the PEO-based electrolytes. The conductivity of R_1 was increased remarkably at temperatures above 25℃. This temperature was the glass transition temperature, T_g, which was identified by differential scanning calorimetry. The R_2F obeyed the Arrhenius behavior. This result is due to adding the DMAMF.

Figure 1(a) shows a typical sweep voltammetry curve. The oneset of current flow in the type of Li/SPE/SS cell may be associated with the decomposition voltage. Thus, figure 1(a) provides the evolution of the anodic electrochemical stability. The anodic stabilities of R_1 and R_2 were 4.6 V and 4.8 V, respectively. This result indicates that the stability window was hardly related to the composition of plastizers. Figure 1(b) shows that the addition of DMAMF palys a important role on the overcharge protection.

The lithium ion transference numbers of R_1, R_2, and R_2F were 0.533, 0.331, and 0.332, respectively. This result illustrates that the diffusion of Li ion was controlled by plasticizers. Therefore, the role of PVC is simply acting as porous solid matrix for the liquid($LiClO_4$ in plasticizers) solution.

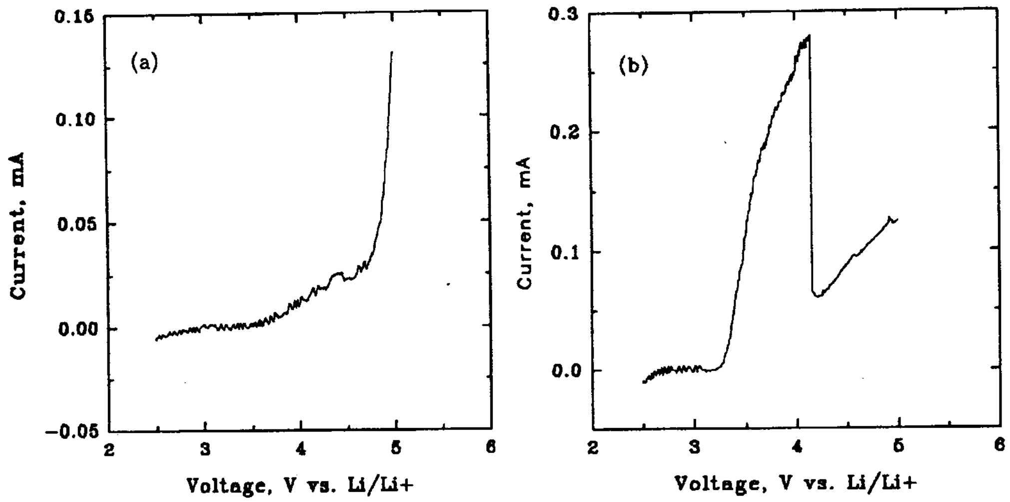

Figure 1. Current-voltage of Li/SPE/SS cells at room temperature. Scan rate : 2 mV/s. S.S :Stainless steel. Electrode surface : 1.327 cm^2. (a) ; $LiClO_4$-PC/EC/MEOX-PVC (sample R_2), (b) ; LiClO4-PC/EC/MEOX/DMAMF-PVC (sample R_2F)

3.2 Improved Stability and Cyclability

A high conductivity, a wide electrochemical stability window and an acceptable lithium transference number, although being important properties, are not sufficient to make a given electrolyte suitable for battery application. Also compatibility with the electrode materials is a crucial requirement for cyclability of battery. First of all, we tested this important aspect by investigating the impedance of Li/SPE/Li cell.

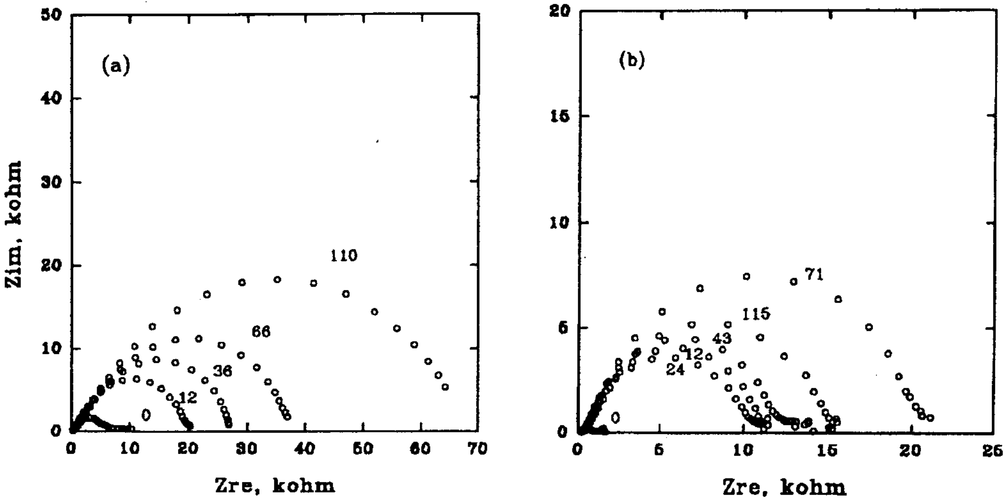

Figure 2. Time evolution of the impedance of a Li/SPE/Li cell stored at room temperature (a) ; $LiClO_4$-PC/EC/MEOX-PVC(sample R_2), (b) ; $LiClO_4$-PC /EC/MEOX/DMAMF-PVC(sample R_2F). The number of progressive hours of storage is indicated in the figure.

Figure 2(a) and (b) show the impedance responses obtained with a cell using R_2 and R_2F as selected electrolytes, respectively. The Nyquist plot shows a progressive expansion of the middle frequency semicircle. In fact, the expansion of the semicircle may be generally ascribed to a resistive layer (i. e., Li_2O) continuously growing on the lithium electrode surface. This is due to the poor physical properties of PVC-based electrolyte occurred from the aspect of adherence, and water contamination from solvent. But the improvement of the Li/SPE interface stability was achieved by the addition of DMAMF.

The kinetics of the lithium deposition/stripping process in PVC-based electrolyte were investigated by cyclic voltammetry. The process occurred with fast kinetics, but reversibility was bad. We prepared the Li/γ-FeOOH(an) cell by using more reversible R_2 than R_1. The OCV(open circuit voltage) and current of this cell were 3.109 V and 0.609 mA, respectively. Its discharge/charge process was presented on figure 3(a). The discharge/charge current densities were 0.1 mA/cm^2. The 1st discharge capacity was 1.75 mAh, and so good, but charge process shows the bad trend. The DMAMF was added into the R_2F electrolyte for the overcharge protection. The OCV and current of this cell were 2.764 V and 3.49 mA, respectively. As shown in figure 3 (b), the cell performance was better than that of the cell composited with R_2. The cell was overcharged at the end of each cycle, with the plateau time-limited to be ~ 0.04 mAh. Therefore, the cell using R_2F shows a good cyclability due to the 2nd discharge process having prolonged time and higher voltage plateau than that of the 1st one.

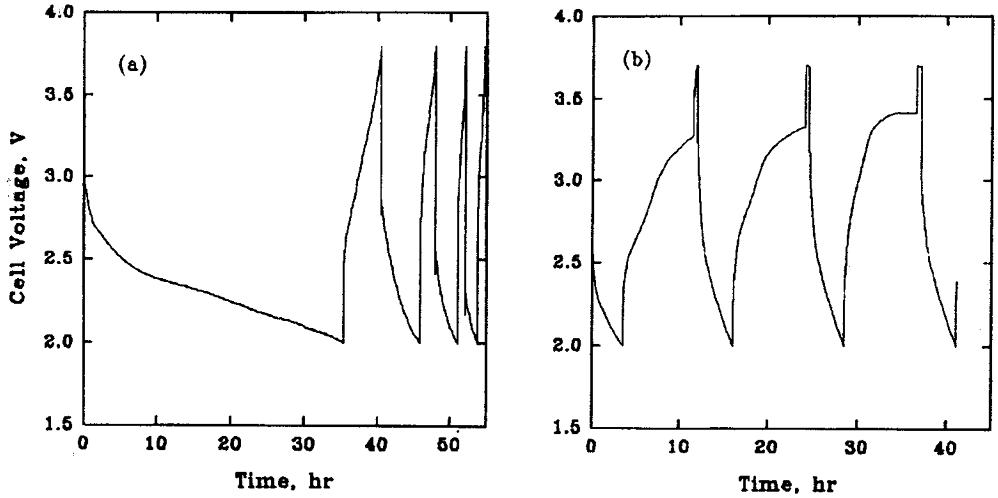

Figure 3. Cycling curves for Li/SPE/γ-FeOOH(an) cell. (a) ; $LiClO_4$-PC /EC/MEOX-PVC (sample R_2) cell. Discharge/charge current density = 0.1 mA $/cm^2$. (b) ; $LiClO_4$-PC/EC/MEOX/ DMAMF-PVC (sample R_2F) cell. The cell was overcharged at the end of each cycle. Discharge current density = 0.1 mA/cm^2, Charge current density = 0.05 mA/cm^2.

To improve the discharge/charge behaviors of Li/γ-FeOOH(an) cell with PVC-based solid polymer electrolyte, we are currently under the test for the change of composite cathode/SPE interface of Li/γ-FeOOH(an) cell on the discharge/charge process.

4. Conclusion

PVC-based eletrolyte is hybrid electrolyte, because the polymer component does not influence the short-range lithium ion mobility. The addition of DMAMF plays important roles of the increase of the stability of Li/SPE interface and the overcharge protection. In the case of the Li/γ-FeOOH(an) cell with R_2F, the OCV was 2.764 V, and the discharge capacity was about 20 mAh/g. If the proporton of DMAMF as the additive and the composition of cathode film are improved, we'll get the higher discharge capacity.

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