

APPLICATION OF ELECTROCHEMICALLY FORMED POLYPYRROLE IN LITHIUM SECONDARY BATTERIES: ANALYSIS OF ANION DIFFUSION PROCESS

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Summary

A long cycle-life has been obtained with an Li/LiClO₄-propylene carbonate (PC)/polypyrrole (PPy) battery when a PPy film formed in LiPF₆/PC by electro-oxidative polymerization is used in an LiClO₄/PC electrolyte after undoping PF₆⁻ anions. The apparent diffusion coefficients of anions within the PPy film and the impedance spectra for PPy film electrodes are strongly dependent upon the film formation conditions. Electrolyte anions used in the film formation, which influence the morphology of the polymer film, have been found to play an important role in determining the electrochemical process and the cycle life of the Li/PPy battery.

Introduction

The behaviour of electrochemically prepared polypyrrole (PPy) has been studied in detail [1 - 11]. As a result, battery industries have been paying considerable attention to the application of PPy as a possible positive electrode [12, 13]. Heterocyclic polymers, such as PPy, polyaniline and polythiophene, are expected to prove suitable as cathode active materials for polymer batteries [3] because of the following advantages:

(i) easy formation on various substrates [6] by an electro-polymerization method;

(ii) high film conductivity when doped with usual anions;

(iii) synchronous involvement of the anion doping-undoping reaction [1 - 4]. In particular, the electrolyte anion used for the film formation strongly influences the morphology of the resulting polymer film. A PPy film having a suitable morphology for battery material has been successfully obtained by using LiPF₆ in propylene carbonate (PC) [14, 15]. In this paper, frequency dispersions of electrode impedance and an apparent diffusion coefficient (D_{app}) of dopants for the PPy films formed in the presence of

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different electrolyte anions are measured and compared in an attempt to rationalize battery performance.

Experimental

Reagent grade PC was used as a solvent after purification by percolating through activated alumina [13]. PPy films were formed by potentiostatic electro-polymerization at 3.9 V or 4.2 V in $0.2 \text{ mol dm}^{-3} \text{ LiClO}_4/\text{PC}$, or $0.2 \text{ mol dm}^{-3} \text{ LiPF}_6/\text{PC}$ containing 0.2 mol dm^{-3} of pyrrole monomer. (Note, all the potentials are referred to the Li/Li⁺ electrode.) A platinum plate (0.25 cm^2) was used as the substrate for the PPy deposition and platinum wires served as the counter electrodes. The film thickness of PPy was controlled by monitoring the charge passed during polymerization. Electrochemical measurements were performed in $1.0 \text{ mol dm}^{-3} \text{ LiClO}_4$ or LiPF_6 in PC and in an Ar gas atmosphere.

An Li/LiClO₄-PC/PPy battery was assembled with a Pt/PPy cathode and a Ni-mesh/Li anode. Charging-discharging tests were conducted in $1.0 \text{ mol dm}^{-3} \text{ LiClO}_4/\text{PC}$ at a constant current density of 1.0 mA cm^{-2} , after undoping anions trapped in the PPy film during polymerization. The Li/PPy battery was charged up to 24% of the PPy doping level [15]. Discharging of the battery was terminated when the cell voltage reached 2.0 V. Electrode impedance was measured for frequencies from 0.1 Hz to 65 kHz by using a Solartron 1250 frequency response analyzer (current follower resistance: $R = 1000 \Omega$). The apparent diffusion coefficients (D_{app}) of dopants within the film were determined by potential-step chronoamperometry; the potential was stepped from 3.2 V to 1.5 V.

Results and discussion

Figure 1 shows cycle life tests of the Li/LiClO₄-PC/PPy batteries, where PPy films were formed in LiPF_6/PC (battery A) and LiClO_4/PC (battery B).

The cycle life of battery B is very short (~ 260 cycles) compared with that of battery A (>1800 cycles). The coulombic efficiency of battery A remains constant at about 92% between cycle numbers 4 and 1800. The initial drop in coulombic yield from 100% to 92% may be associated with the decomposition of PF_6^- anions by the oxidation/reduction process at the anode or the cathode. A slight decrease in the average discharge voltage is observed between cycles 750 and 800. The energy densities for these cycles were 85 W h kg^{-1} and 78 W h kg^{-1} , respectively.

In the case of battery B, the average discharge voltage falls from 3.1 V to 2.9 V at about cycle 210. The coulombic efficiency of battery B decreases sharply at about cycle 230. This dramatic change in battery performance (*i.e.*, cycle life, discharge voltage) could be due to the rougher morphology

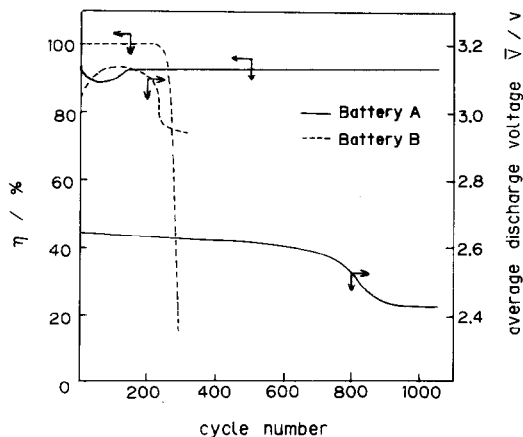


Fig. 1. Dependence of coulombic efficiency (η) and average discharge voltage on cycle life for Li/LiClO₄-PC/PPy batteries with PPy films formed at (A) 3.9 V in LiPF₆/PC (solid line) and (B) 4.2 V in LiClO₄/PC (dashed line).

of the PF₆⁻-formed PPy film [14, 15]. The manner in which PPy is differently polymerized with ClO₄⁻ and PF₆⁻ anions is still unclear at the present stage. However, the growth rate of PPy film which is closely associated with the stability of intermediate pyrrole radical, may be influenced by the different nucleophilicity of anions. It also seems likely that the decomposition of PF₆⁻ anions in some way influences the intermediate radicals generated at the surface, and thereby accelerates the growth rate of the PPy film.

Figure 2 presents the Cottrell plots obtained for the reduction (undoping) of the PPy electrodes. The D_{app} values determined for the PPy electrodes formed in LiClO₄/PC and LiPF₆/PC were $1.63 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ and

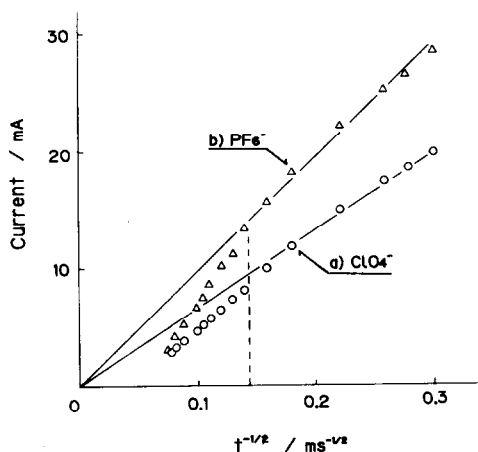


Fig. 2. Chronoamperometric Cottrell plots for PPy film electrodes (100 mC cm^{-2}) formed in (a) 0.2 mol dm^{-3} LiClO₄/PC and (b) 0.2 mol dm^{-3} LiPF₆/PC. Potential was stepped from 3.2 V to 1.5 V.

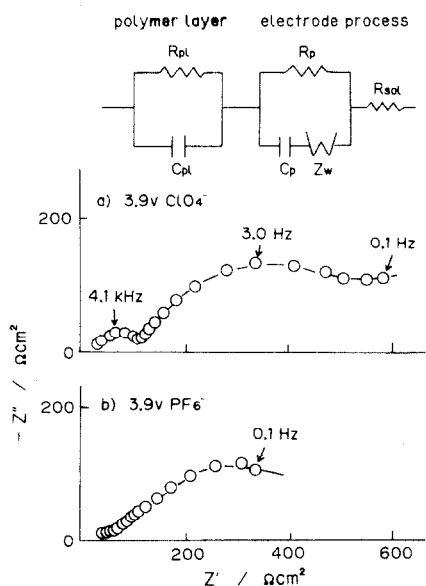


Fig. 3. Cole-Cole plots at 2.8 V for PPy film electrodes formed at 3.9 V in (a) $0.2 \text{ dm}^{-3} \text{ LiClO}_4/\text{PC}$ and (b) $0.2 \text{ mol dm}^{-3} \text{ LiPF}_6/\text{PC}$.

TABLE 1

Equivalent circuit elements of PPy electrodes (see Fig. 3)

	R_{sol} (Ω)	R_{p1} (Ω)	C_{p1} (μF)	R_{p} (Ω)	C_{p} (μF)	Z_{w} ($\Omega \text{ s}^{-1/2}$)
PPy(LiClO ₄)	40	50	10	450	1500	300
PPy(LiPF ₆)	40	10	10	450	1500	600

$3.97 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, respectively. The surface dopant concentrations in oxidized PPy films were calculated from the anodization charges in cyclic voltammograms recorded at slow scan rates (5 mV s^{-1}). Therefore, the dopant diffusion rate in the PPy film formed in LiPF₆/PC is about 2.4 times greater than that in the film formed in LiClO₄/PC.

Figure 3 shows Cole-Cole plots for the PPy electrodes used to produce the data in Fig. 2. Figure 3 also gives the equivalent circuit which fits the loci for these plots. This circuit model consists mainly of the impedance due to the polymer layer and the apparent electrode process. The first semi-circles at higher frequencies correspond to the impedance of the polymer layer, and the second semi-circles at lower frequencies represent the electrode process. The centres of these semi-circles are located in the inclined line below the Z' axis, indicative of the existence of a surface roughness impedance which may be incorporated in the C_{p} and R_{p} components. The circuit elements determined by digital simulation are listed in Table 1 for unit surface area (1 cm^2).

The diffusion component, Z_w , in the equivalent circuit is connected in series to C_p and in parallel to R_p . The C_p and R_p values represent the pseudo-capacitance and resistance due to doping or undoping. Z_w may reflect the diffusion of anions in the bulk of the polymer layer. A larger Z_w value contribution of the PF_6^- -formed PPy is associated both with the higher surface concentration of dopants and with the faster anion diffusion in the bulk of the PPy layer. In addition, the difference in the value of R_{p1} is in good agreement with the film conductivities of $\text{PPy}^+\text{PF}_6^-$ (ca. 130 S cm^{-1}) and $\text{PPy}^+\text{ClO}_4^-$ (ca. 50 S cm^{-1}), both of which were determined by the 4-probe method [15].

Studies of FT-IR spectra [15] show that there is little possibility of a difference in the chemical bonds between the PPy films formed in LiClO_4 and LiPF_6 . Therefore, only the morphology of the PPy film is considered to change.

Conclusions

The cycle life of an $\text{Li/LiClO}_4\text{-PC/PPy}$ battery was found to be markedly improved by using PF_6^- anions during PPy film formation. Potential step and a.c. impedance measurements showed that the diffusion rate of anions in a PPy film formed in LiPF_6/PC is faster than that in a PPy film formed in LiClO_4/PC . Hence, the electrolyte anions used in the preparation of PPy films are considered to strongly influence the performance characteristics of batteries.

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