

# Impedance study of the interfaces between lithium, polyaniline, lithium-doped $\text{MnO}_2$ and modified poly(ethylene oxide) electrolyte

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## Abstract

Impedance study was carried out for the interfaces between lithium, polyaniline (PAn), lithium-doped  $\text{MnO}_2$  and modified poly(ethylene oxide) (PEO) electrolyte under various conditions. The interfacial charge-transfer resistances  $R_{ct}$  on PEO/PAn,  $R_{ct}$  on PEO/ $\text{LiMn}_2\text{O}_4$  increase with depth-of-discharge and decrease after the charge of the cell containing modified PEO as electrolyte. The charge-transfer resistance  $R_{ct}$  on PEO/PAn is higher than  $R_{ct}$  on PEO/ $\text{LiMn}_2\text{O}_4$  under the same condition, since inserted species and mechanism are different for both cases. In the case of PAn, an additional charge-transfer resistance might be related to the electronic conductivity change in discharge/charge potential range, as it was evident from a voltammetry curve. With increasing cycle numbers, the charge-transfer resistance increases gradually. The impedance results also have shown that at low frequency the diffusion control is dominant in the process of the charge and discharge of Li/PEO/PAn or Li/PEO/ $\text{LiMn}_2\text{O}_4$  cell. The diffusion coefficients have been calculated from impedance data.

## Introduction

In recent years, considerable attention has been devoted to the investigation of all solid-state secondary lithium batteries [1–3]. In many cases, conducting polymers, like polyaniline (PAn) and inorganic intercalated compounds like Li-doped  $\text{MnO}_2$  are used as cathode and Li foil as anode, respectively. The interfacial phenomena that have been widely studied seem to be important factors in determining the charge/discharge process in all solid Li battery. In this paper, the interfacial behavior between Li, PAn, Li-doped  $\text{MnO}_2$  and modified PEO electrolyte have been studied by a.c. impedance method. The results of voltammetry on above interfaces are also presented.

## Experimental

Modified PEO electrolyte film was obtained by casting of a solution containing  $\gamma$ -radiated cross-linked PEO dissolved in propylene carbonate (PC) solution of 1.0 M  $\text{LiClO}_4$ , and was dried under vacuum at 50 °C for 20 h. The film thickness was about 100–150  $\mu\text{m}$ . The ambient conductivity, measured from ion-blocking electrode config-

uration, was as high as  $1.33 \times 10^{-4} \text{ S cm}^{-1}$ . Noncrystalline peaks were observed on differential scanning calorimetry curves for cross-linked PEO [4]. PAN was prepared by electrochemical polymerization in 1.0 M  $\text{HClO}_4$  solution containing 0.2 M aniline [5].  $\text{LiMn}_2\text{O}_4$  was obtained by heat treating of the mixture of  $\text{Li}_2\text{CO}_3$  and  $\text{Mn}_2\text{O}_3$  at atomic ratio Li:Mn. The cathode was made of powder PAN (or  $\text{LiMn}_2\text{O}_4$ ) with 15% acetylene black and 2% Teflon binder pressed on an about  $1.5 \text{ cm}^2$  nickel screen.

The assembly of the experimental cells was carried out in a dry box (VAC company) for the a.c. impedance study of the separated interfaces a three-electrode cell was used, as shown in Fig. 1. A two-electrode cell also was used for the impedance measurement of whole cell. The reference and counter electrodes were Li foils.

Impedance measurements were taken on 5208 Lock-in analyzer in combination with a PAR 273 potentiostat controlled by an IBM/XT computer. The frequencies used were between  $0.1\text{--}10^5 \text{ Hz}$ . Cyclic voltammetry was conducted on PAR 273 potentiostat.

## Results and discussion

Figure 2 shows the impedance spectra of a Li/modified PEO/Li cell obtained at different storage times at room temperature. A progressive extension of the low frequency semicircle can be easily noticed. According to its equivalent circuit, the diameter of the semicircle is the interfacial resistance between PEO electrolyte and

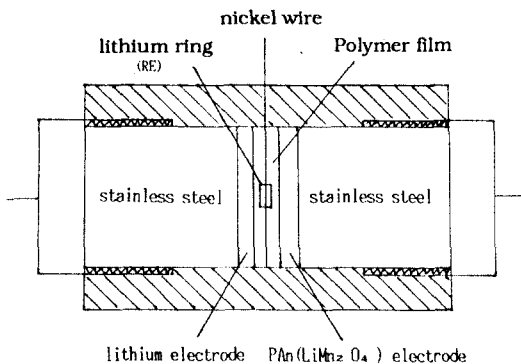


Fig. 1. Essential lithium cell configuration.

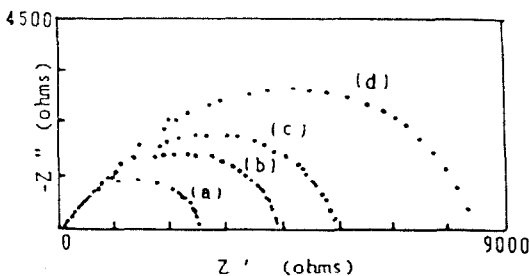


Fig. 2. Impedance plots for a Li/PEO/Li cell at  $20 \text{ }^\circ\text{C}$  taken at progressive storage times, (a) 0 h, (b) 15 h, (c) 27 h, and (d) 48 h.

Li electrode. Therefore, the interfacial resistance increased with storage time of the cell. This probably was associated with the formation of corrosive layer [6].

The impedance spectra of a Li/PEO/PAN cell, with Li as reference electrode and PAN as working electrode at different doping extent of  $\text{ClO}_4^-$  in PAN which are corresponding to different depth-of-discharge, are illustrated in Fig. 3. On the basis of the equivalent circuit (also shown in Fig. 3) the high frequency intercept with the real axis is related to the solid-electrolyte resistance ( $R_e$ ). The diameter of the semicircle represents the interfacial resistance ( $R_{ct}$ ) between PEO electrolyte and PAN electrode. The straight line at the low frequency showed an existence of ion diffusion resistance during PAN doping process. It can be seen that the charge-transfer resistance at the PAN/PEO interface increased (from 31 to 72  $\Omega$ ) gradually with the increase of the depth-of-discharge. However, after charge the impedance value again decreased to a certain extent.

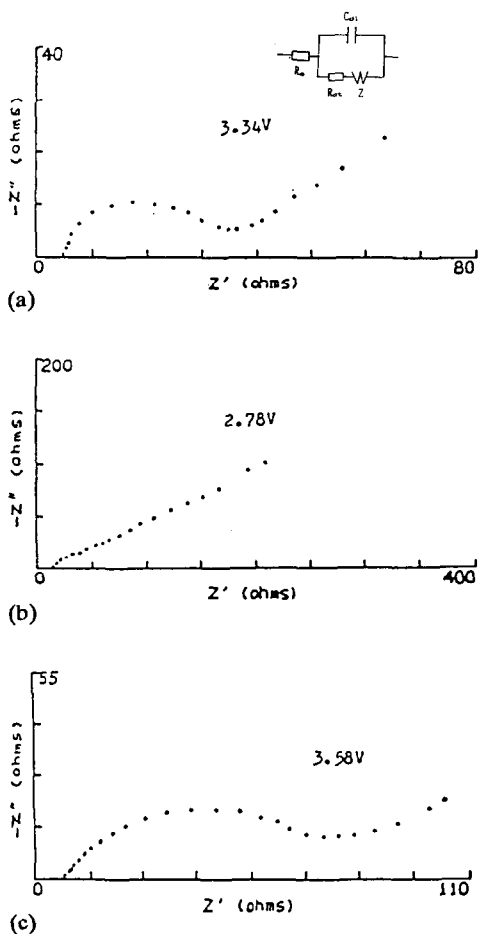


Fig. 3. Impedance spectra of the Li/PEO/PAN cell (a, b) at different discharge, and (c) charge voltages at 22 °C.

The impedance spectra of the Li/PEO/LiMn<sub>2</sub>O<sub>4</sub> cell with Li foil as reference electrode and LiMn<sub>2</sub>O<sub>4</sub> as working electrode, shown in Fig. 4, were similar to that of the PAN/PEO interface. Comparing Fig. 4 with Fig. 3, one may know that the charge-transfer resistance at PAN/PEO interface is greater than that at LiMn<sub>2</sub>O<sub>4</sub>/PEO interface, as shown in Fig. 5. The reason may be related to different mechanism of the intercalation or doping/undoping process. Generally speaking, the charge-controlled kinetics became more difficult as more Li is added to the lattice as in the case of LiMn<sub>2</sub>O<sub>4</sub>. But, conducting organic linear polymer, such as PAN have fibrous structure,

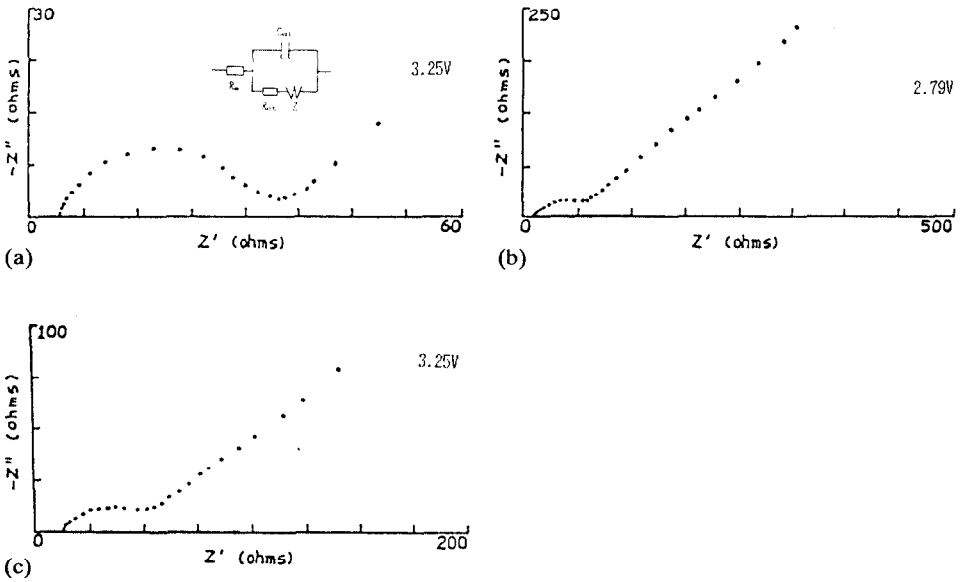


Fig. 4. Impedance spectra of the Li/PEO/LiMn<sub>2</sub>O<sub>4</sub> cell (a, b) at different discharge, and (c) charge voltages at 22 °C.

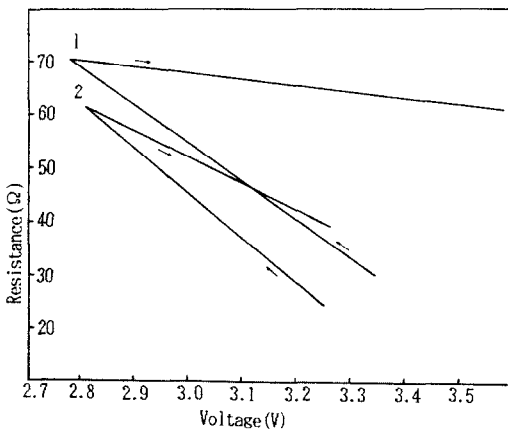


Fig. 5. The charge-transfer resistances at PEO/PAN and PEO/LiMn<sub>2</sub>O<sub>4</sub> interfaces vs. open-circuit voltage at 22 °C; (1) Li/PEO/PAN, and (2) Li/PEO/LiMn<sub>2</sub>O<sub>4</sub>.

in which anions could be doped and undoped. Figure 6 shows cyclic voltammetry curve of the PAn electrode in contact with a modified PEO electrolyte at room temperature. The anodic peak and the cathodic peak indicated doping and undoping of  $\text{ClO}_4^-$  anions, respectively. The oxidation charge or reduction one was about 2.0 Q, which shows a good reversibility of charge/discharge reaction of PAn. As it is well known that during doping process PAn is converted to the conductive state and become less conductive in reduced state. An additional charge-transfer resistance associated with electron conductivity change should be considered in case of PAn [7].

With increasing cycle numbers of the Li/PEO/PAn cell, the impedance spectrum, as shown in Fig. 7, shifted toward the real axis, the interfacial charge-transfer resistance also increased gradually.

The impedance spectrum of Li/PEO/LiMn<sub>2</sub>O<sub>4</sub> cell, Li/PEO and Li/LiMn<sub>2</sub>O<sub>4</sub> interfaces were shown in Fig. 8. It is clear that the shape of impedance spectra of the whole cell is similar to the impedance spectrum of Li/PEO interface except a small difference in the low-frequency region. This implies that the main contribution to the total impedance of the whole cell came from the charge-transfer resistance on Li/PEO interface.

The chemical diffusion coefficients calculated from the straight line of impedance spectra [8] is listed in Table 1.

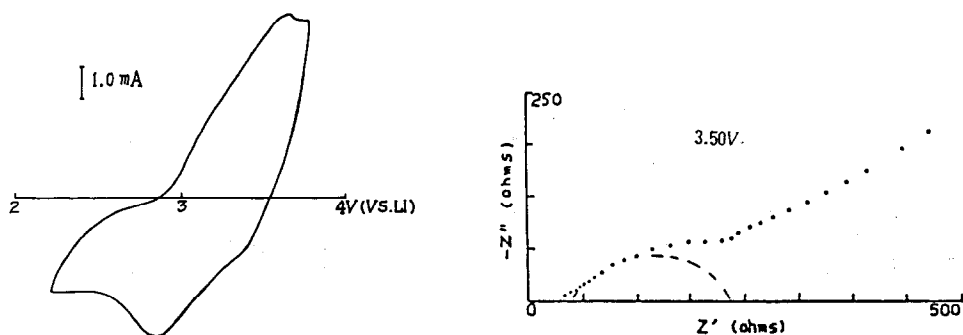


Fig. 6. Cyclic voltammetry of the Li/PEO/PAn cell at 22 °C; scanning rate: 2.0 mV s<sup>-1</sup>.

Fig. 7. Impedance spectrum of the Li/PEO/PAn at state-of-charge (3.50 V) after 17 cycles at 22 °C.

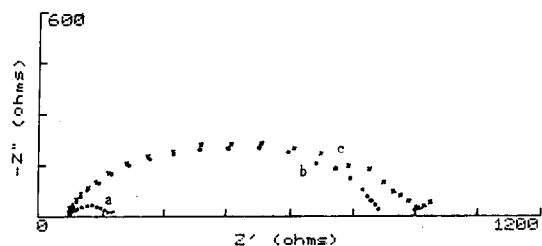


Fig. 8. Impedance responses of the Li/PEO/LiMn<sub>2</sub>O<sub>4</sub> at 18 °C; (a) PEO/LiMn<sub>2</sub>O<sub>4</sub>, (b) Li/PEO, and (c) Li/PEO/LiMn<sub>2</sub>O<sub>4</sub>.

TABLE 1

The diffusion coefficients of Li and  $\text{ClO}_4$  in  $\text{LiMn}_2\text{O}_4$  and PAN, respectively; temperature: 18 °C

$x$ in $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$	OCV (V)	$D$ ( $\text{cm}^2 \text{S}^{-1}$ )	$x$ in $\text{PAN}(\text{ClO}_4)_x$	OCV (V)	$D$ ( $\text{cm}^2 \text{S}^{-1}$ )
0.05	3.25	$3.18 \times 10^{-11}$	0.056	3.25	$2.13 \times 10^{-13}$
0.15	3.10	$8.03 \times 10^{-12}$	0.168	3.12	$9.1 \times 10^{-14}$
0.74	2.90	$2.28 \times 10^{-12}$	0.42	2.93	$5.2 \times 10^{-15}$

## Conclusions

1. The charge-transfer resistances of PAN/PEO and  $\text{LiMn}_2\text{O}_4$ /PEO interface increased with discharge and decreased after charge of all solid-state cell. In addition,  $R_{ct}$  of PAN/PEO was higher than that of  $\text{LiMn}_2\text{O}_4$ /PEO.

2. With increasing cycle numbers, the charge-transfer resistance increases gradually.

3. The main contribution to the total impedance of the whole cell came from the charge-transfer resistance at the Li/PEO interface.

4. In the low-frequency region of impedance spectra charge and discharge process is controlled by ion diffusion and the diffusion coefficients have been calculated.

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