Impedance study for the interface and whole battery with PAN-based polymer electrolyte

Rongjian Xue*, Hong Huang, M. Menetrier** and Liquan Chen

Institute of Physics, Chinese Academy of Sciences, Beijing 100080 (China)

Abstract

The inhomogeneity of the interface and its effect on the whole battery is especially shown and discussed in terms of impedance spectrum. The constant-phase-element impedance, Z_{CPE} has been employed to analyse the inhomogeneous process. For Li/electrolyte interface, the growth of the interface layer is dominant, however, the composite cathode/electrolyte interface indicates a behaviour like in the corrosion environment on slightly cycle due to its more heterogeneity. The degradation of the electrolyte results in the big change in the interfaces and the decline of the battery property but the battery is still able to be used under limited condition.

Introduction

Several authors have paid attention to the interface in contact with polymer electrolyte [1–4]. However, they neglected the discussion on the depressed semicircle and non-Warburg behaviour in which inhomogeneous distribution characteristics involved in the IS. An empirical impedance, Z_{CPE} and Z_d [5] can be used to describe this behaviour.

This presentation will characterize the constant-phase-element (CPE) and the diffusion impedance (Z_d). Because of the heterogeneity in the system of hybrid polymer electrolyte and composite electrode, when a.c. current passes through them and their interface, it will cause different relaxation process corresponding to the distribution of single relaxation time. That means the appearance of a frequency-dependent element. Thus Z_{CPE} and Z_d will join normal resistance and/or capacitance in equivalent circuit to play an important role in different frequency regions.

Experimental

The polymer electrolyte, PAN–LiClO$_4$–PC/EC (PANLPE), was prepared as described in ref. 6. The composite cathode (V) consisted of Li$_{1+x}$V$_3$O$_8$ [2], carbon black and PANLPE. Three kinds of samples were constructed as following: (i) three-electrode battery, Li/PANLPE/V, with Li as reference (area: 1.2 cm^2, thickness: 0.25 mm);

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*Author to whom correspondence should be addressed.
**On leave from the Laboratoire de Chimie du Solide du CNRS and Ecole Nationale de Chimie et Physique de Bordeaux, France.

(ii) two-electrode cell, Li/PANLPE/Li and (iii) V/PANLPE/V (area: 1.0 cm^2, thickness: 0.15 mm).

The IS measurements were carried out in the frequency range from 0.1 to 100 000 Hz, at room temperature, by a Solartron model 1174 frequency response analyser linking to a Solartron 1186 electrochemical interface and an Apple II computer.

The constant capacity cycle was run for the three samples by a galvano-controlled instrument (made in our institute).

Result and discussion

Figures 1 and 2 show IS for both kinds of the samples from which the parameters can geometrically be taken out as below: R_e, electrolyte resistance; R_g, interface layer resistance; R_c, charge-transfer resistance; R_i, interface resistance and R_Ω, ohmic resistance for battery which includes electrolyte and electrode resistance; θ_g, θ_c, θ_i, and θ_d, correlating with $Z_{CPEg,c,i}$ and/or Z_{CPEd} or Z_d. Figure 3 gives the equivalent circuit for some of the IS. The parameters cited above for both interface and whole battery as a function of cycle are shown in Figs. 4 and 5 and Tables 1 and 2.

For Li/PANLPE interface, R_e, R_g and R_c have the same tendency to increase with the cycle, but with a θ value nearly constant. Since following relations:

$$Z_{CPE} = A_{(j\omega)}{}^{-a} \tag{1}$$

where $\omega = 2\pi f$, $a = 1 - 2\theta/\pi$, $w_0\,\tau = 1$ and $\tau = (AR)^{1/a}$, we consider A's meaning in different frequency regions.

The same discussion can be done for the V/PANLPE interface at the original by means of fractal interface and for the battery interface. By way of example, A's value which corresponds to R_g, to be called A_g, is related to diffusibility of moving species in interface layer and the same way, A_c, which corresponds to R_c, is related to the inhomogeneous factor of the interface. Thus, A_d and R_d are related to the diffusibility of species in cathode. The latter may be in parallel with capacitance C_d in the equivalent circuit to describe the Z_d.

If assuming $\tau = \tau_0 \exp(E/KT)$ represents distribution of the relaxation time τ_0 due to activation energy E, the E's distribution should be proportional to $\exp((1-a)-E_0/KT)$. Here $0 \leqslant a \leqslant 1$ and τ_0, E_0 are single relaxation time and single relaxation activation energy, respectively. Therefore both A and a are the reflection of inhomogeneity of a system, the former in morphology and the latter at an energy level.

Figure 6 demonstrates real physical interface between composite cathode and PAN-based electrolyte. It is easy to imagine that the corrosion and adsorption/desorption could appear in this interface during cycling. In the surface of the carbon, Li$^+$ may be adsorbed/desorbed to form or remove electrical double layer. The same thing may also happen for Li atoms in the insertion surface together with a redox reaction under different potential. For the PAN-based electrolytes which were enclosed in the vanadium oxide, the lithium atoms within the insertion compound may execute a redox reaction in progress of the cycle. Therefore, the morphology will change with the increasing cycle obviously in the complicated interface. Thus, after the first cycle, its IS shows an induction loop and anomalous diagrams (Fig. 1(ii), (a) and (b)). But for two identical electrode measurements (Fig. 2(ii), (a)), its IS also has a normal pattern. It may be attributed to the superposition effect of both interfaces. As one side progresses the oxidation, the other side gets reduction and so on, their overlapping offsets influence each other.
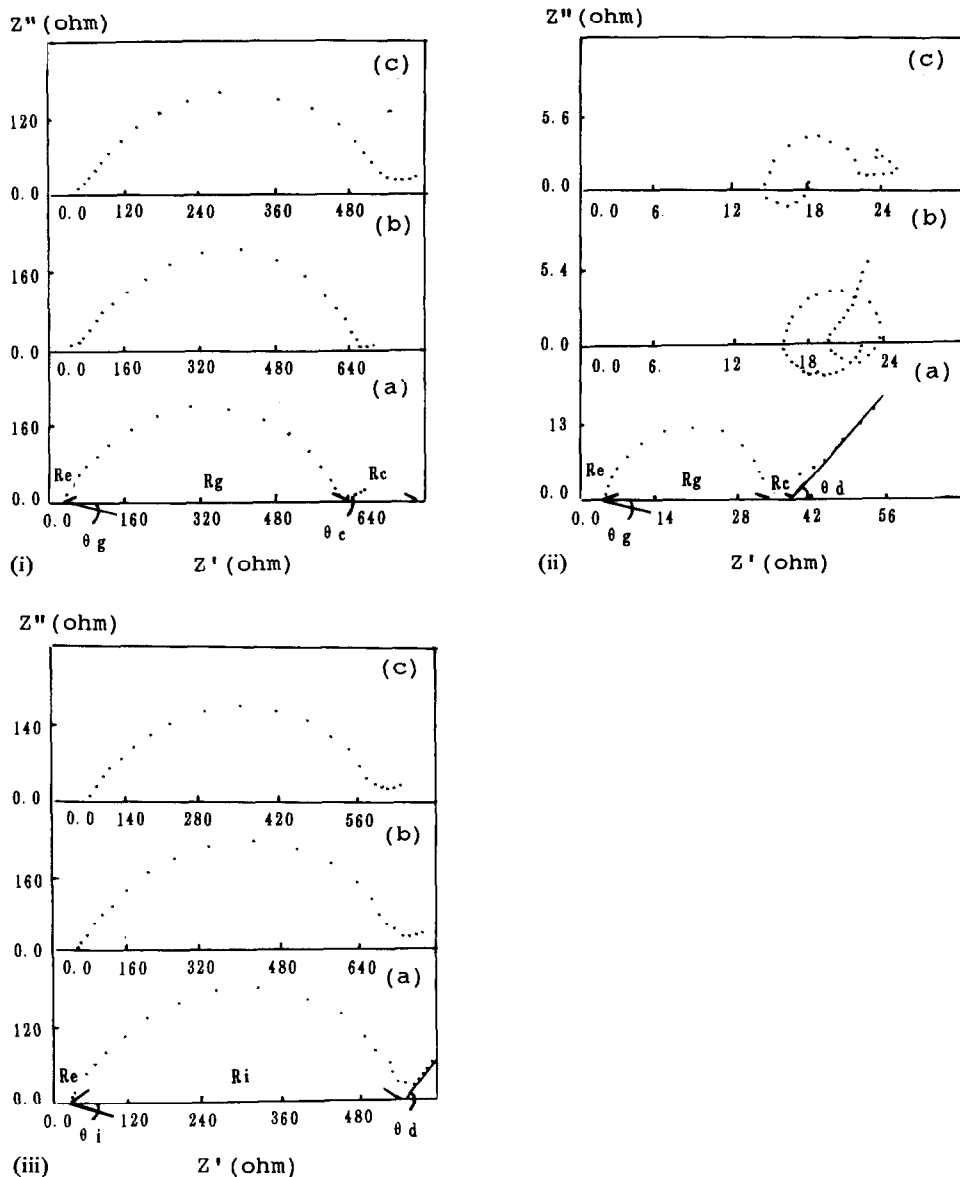
Fig. 1. Impedance spectra measured by a three-electrode battery with lithium as a reference electrode, at 0.1 mA/cm² discharge and 0.05 mA/cm² charge current density (constant capacity 0.5 mA h): (a) after the 3rd charge; (b) after the 3rd discharge, and (c) new (i) for Li/PAN-based electrolyte interface; (ii) for composite cathode/PAN-based electrolyte interface, and (iii) for battery including both interfaces above mentioned.

Figure 4 not only shows the parameters of Li/PANLPE interface and whole battery variety versus the cycle, but also the difference between discharge and charge. The charge resulted in a minor increase in resistance R_e and R_Ω in comparison with
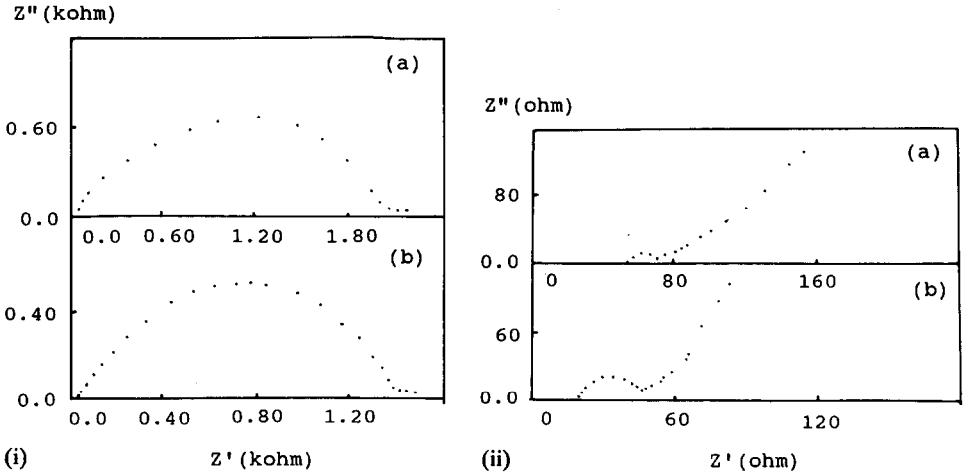
Fig. 2. Impedance spectra measured by a two-electrode cell at the same charge/discharge current density and capacity as the three-electrodes battery; (a) after the 10th cycle for (i), after the 5th cycle for (ii); (b) new (i) for a Li/PAN-based electrolyte interface, and (ii) for a composite cathode/PAN-based electrolyte interface.
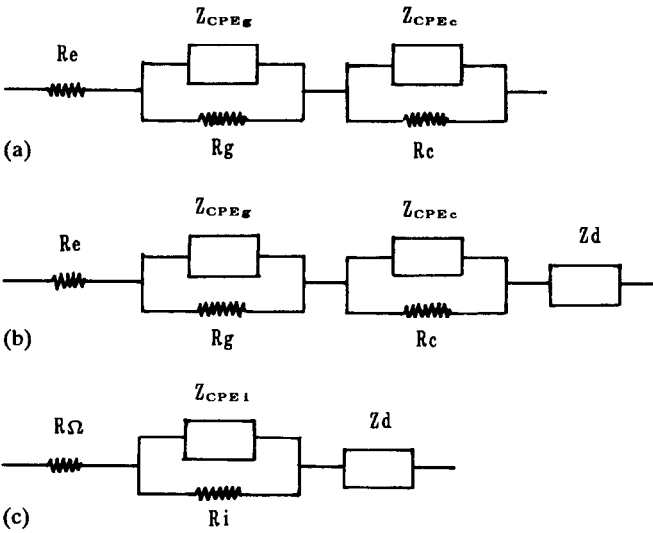

Fig. 3. The equivalent circuit (a) for the anode/electrolyte interface, (b) for the cathode/electrolyte interface, and (c) for the whole battery ($Z_{CPE} = A(j\omega)^{-\alpha}$, $\alpha = 1 - 2\theta/\pi$).

discharge. This means that the charging process will become dominant in controlling the battery behaviour.

The whole battery includes both different interface above, so its IS represents the superposition of them, such as R_Ω is about the sum of R_e from anode and cathode and electrode resistance itself and R_i also coming from both interfaces. Nevertheless, big change happened in both interfaces, the whole battery's discharge curves has not obviously changed with the cycle, except the first time (Fig. 7). Under a constant
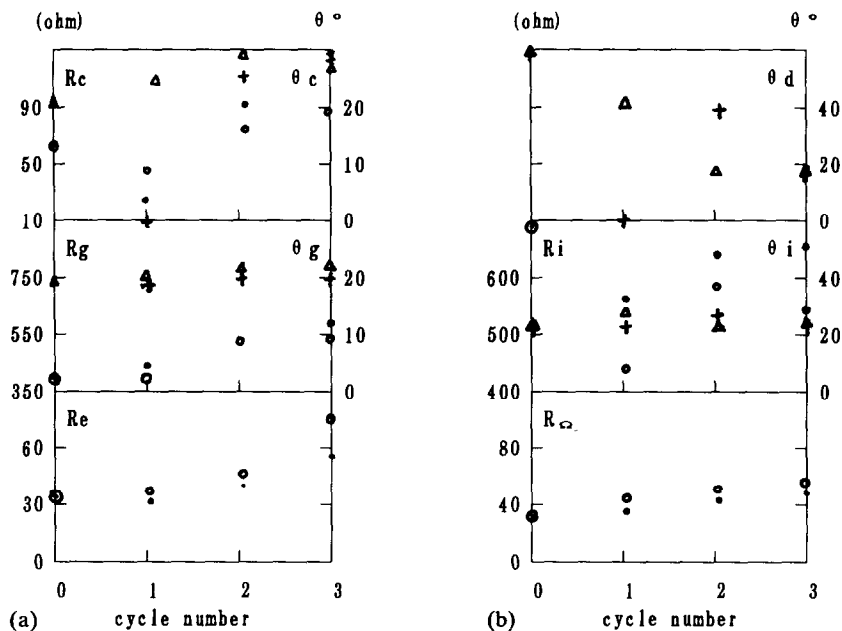
Fig. 4. Parameters vs. cycle number (a) for the Li/electrolyte interface, and (b) for the full cell. (●) discharge and (○) charge both for resistances, and (+) discharge and (△) charge both for angles.
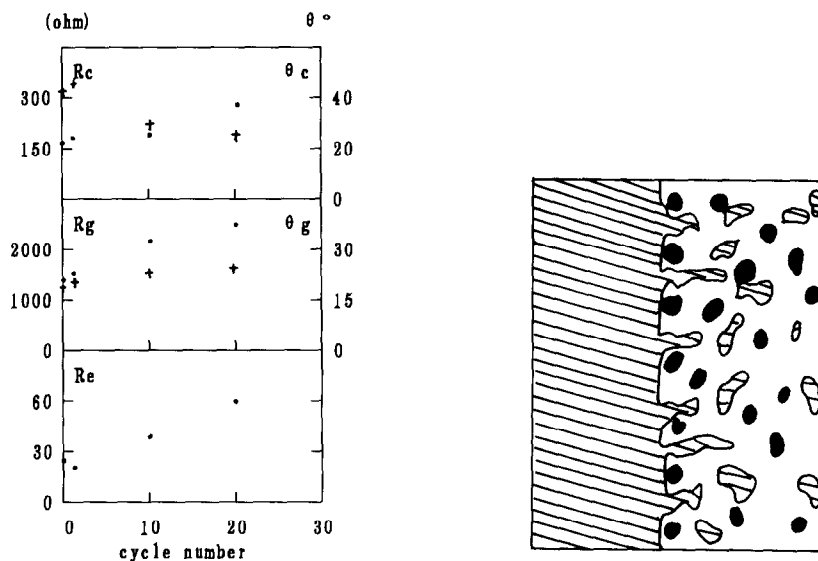

Fig. 5. Parameters vs. cycle number for Li/electrolyte/Li cell (●) resistances and (+) angles.

Fig. 6. Schematic design for composite cathode electrolyte interface: (▨) electrolyte, (□) Li$_{1+x}$V$_3$O$_8$, and (■) carbon black.

TABLE 1

The parameters for composite cathode/electrolyte interface in two-electrode cell

Cycle no.	Resistance (Ω)				Angles (θ)		
	R_e	R_g	R_c	R_d	θ_g	θ_c	θ_d
New	18	30	23	696	24	0	6
After 5th cycle	51	25	71	711	34	29	14

TABLE 2

The parameters for composite cathode/electrolyte interface in three-electrode cell

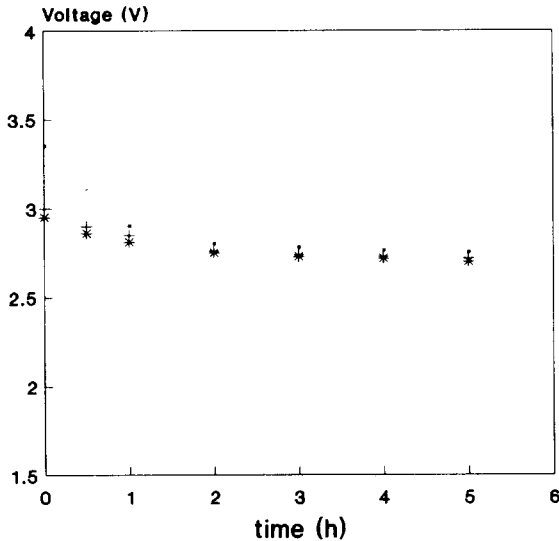| Cycle no.	Resistance (Ω)			Angle (θ)		
	R_e	R_g	R_c	θ_g	θ_c	θ_d
New	4	30	7	10	0	47
After 1st discharge	12	71	10	22	20	0
After 1st charge	14	14	6	6	0	45

Fig. 7. Discharge curve for a three-electrode battery with a lithium reference electrode opening: ($\cdot$) 1st discharge, ($+$) 2nd discharge and ($*$) 3rd discharge.

capacity cycle (the discharge and charge were run at 0.1 mA and 0.05 mA/cm^2, respectively, and the capacity was kept at 0.5 mA h), the voltages of upper and lower limits kept nearly the same until 6th cycle, after that the initial voltage tended to decrease with cycle as shown in Fig. 8. We may predict that the degradation of both interfaces will make that the battery's life declines.
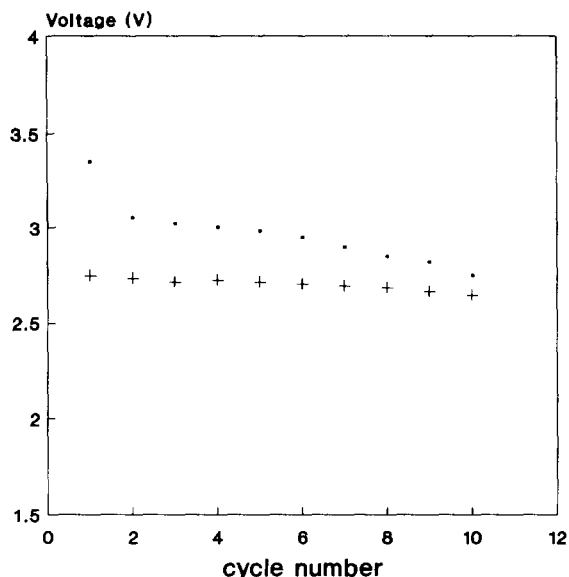
Fig. 8. Voltage vs. cycle number for a three-electrode battery with a lithium reference electrode opening: ($\cdot$) initial voltage and ($+$) final voltage.

In contrast Figs. 1 and 6, we may draw a conclusion that the increase of the interface resistance of the battery comes mainly from the increase of the Li/PANLPE interface resistance.

Conclusion

The fact that R_e, R_g and R_c in the Li/PANLPE interface increase with cycle means the interface layer grows. It may form single-phase passivation layer because the activation energy associated with θ_g and θ_c is nearly constant. This behaviour controls the battery's property, especially under charging. The complicated IS of the composite cathode/PANLPE interface arise from the heterogeneity of the electrode. Nevertheless, the battery may still be used under certain conditions.

List of abbreviations

IS	impedance spectrum
Z_{CPE}	constant-phase-element impedance
CPE	constant-phase-element
Z_d	diffusion impedance
PAN	polyacrylonitrile
PC	propylene carbonate
EC	ethylene carbonate
PANLPE	PAN–LiClO$_4$–BC/EC
V	composite cathode: $Li_{1+x}V_3O_8$+carbon black+PANLPE

R_e	electrolyte resistance
R_g	interface layer resistance
R_c	charge-transfer resistance
R_i	interface resistance
R_Ω	ohmic resistance for the battery
τ_0	single relaxation time
E_0	single relaxation activation energy

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