

# Construction and destruction of passivating layer on $\text{Li}_x\text{C}_6$ in organic electrolytes: an impedance study

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## Abstract

The microstructure and thermal stability of the passivating layer formed on  $\text{Li}_x\text{C}_6$  during electrochemical intercalation reaction is investigated by using electrochemical impedance spectroscopy. A porous structure is inferred from the destruction of the passivating film built in 1 M  $\text{LiClO}_4$  ethylene carbonate after transferring to 1 M  $\text{LiClO}_4$ /propylene carbonate. The film is shown to be thermally stable, while the electrode suffers from self-discharge. The formation process involves three reactions: gas evolution, film formation and intercalation. In ethylene carbonate-based electrolytes, the resistance of the surface layer is higher in absence of ester co-solvents. The relative importance of the three reactions is used to explain the results.

*Keywords:* Organic electrolytes; Lithium; Carbon; Passivating layer

## 1. Introduction

Carbon materials are now generally accepted as excellent alternatives for lithium metal as anodes for lithium batteries. A primary objective of research is to solve the safety problem due to lithium dendrite growth during cycling [1–3]. Moreover, the low coulombic efficiency observed for the first electrochemical intercalation of lithium ions in carbon materials retards the commercialization of these ‘rocking-chair’ batteries [4]. The electrolytes are reduced on the electrode surface to form a passivating layer that is electron insulating and ionic conducting [5,6]. Thus, the formation and properties of the surface layer play a vital role in aspects of battery performance such as capacity, cycle life and storage capability. It follows that the composition of the electrolytes that yield the protective layer must also have a major influence on battery characteristics.

Lithiated graphite has been studied extensively as a possible alternative material to lithium. This is due to its high theoretical capacity (372 mA/g) and voltage relative to lithium, i.e., high cell voltage and power density [7]. Moreover, the material is cheap and requires no further major processing prior to use. On the other hand, it is rather sensitive to electrolyte composition. For example, graphite was reported to exfoliate upon electrochemical intercalation of lithium in propylene carbonate (PC). Nevertheless, it readily

forms  $\text{LiC}_6$  in electrolytes based on ethylene carbonate (EC) [2,8].

In the work reported here, graphite is examined by impedance spectroscopy to explore the microstructure and thermal stability of the passivating layer. The effect of solvents on the formation of the film are also discussed.

## 2. Experimental

Graphite electrode (usually 6 to 8 mg and  $\sim 1 \text{ cm}^2$ ) were prepared by mixing natural graphite powder (Shanghai,  $< 30 \mu\text{m}$ ) with poly(tetrafluoroethylene) as a binder, followed by pressing on to a nickel screen. After vacuum drying at  $100^\circ\text{C}$  for 6 h, the electrodes were placed in glass cells (with a large excess of electrolyte) under argon atmosphere. Lithium metal was used as both the counter and the reference electrodes. PC (Shanghai),  $\gamma$ -butyrolactone ( $\gamma$ -BL, Shandong), diethylene carbonate (DEC, Aldrich) and EC (Aldrich) were dehydrated with a 4 Å molecular sieve and distilled under reduced pressure. 1,2-dimethoxyethane (DME, Shanghai) and 2-methyltetrahydrofuran (2-MeTHF, Aldrich) were dehydrated and distilled.  $\text{LiClO}_4$  (Shanghai) was vacuum dehydrated at  $150^\circ\text{C}$  for 24 h.

The characteristics of the electrochemical process were investigated by a.c. impedance spectroscopy over a frequency range of 0.01 to 100 000 Hz by means of a Solartron 1250 frequency response analyser and a Solartron 1286 electro-

chemical interface coupled to a HP85 computer. The response over the whole frequency range will be presented, if not otherwise indicated.

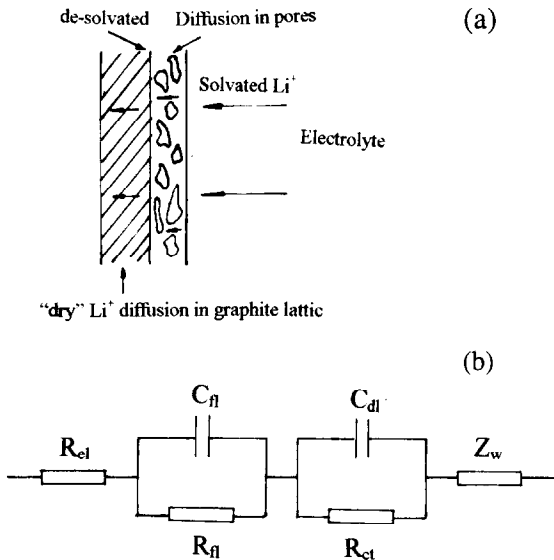


Fig. 1. (a) Illustration of  $\text{Li}_x\text{C}_6/\text{electrolyte}$  interface; (b) electrical equivalent circuit.

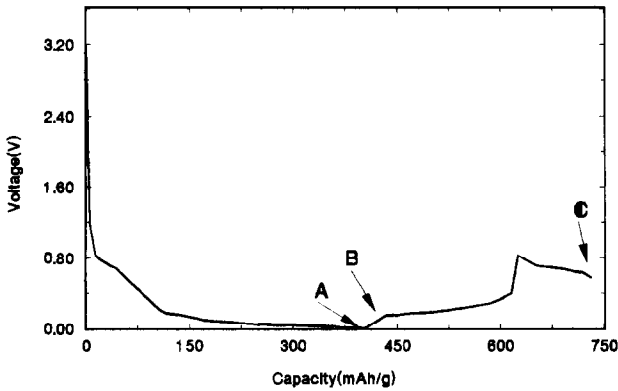


Fig. 2. Discharge and charge curves of graphite electrode (8 mg);  $i = 0.1 \text{ mA cm}^2$ . (A) on transfer to 1 M  $\text{LiClO}_4$  after short-circuited for 48 h in  $\text{LiClO}_4/\text{EC}$ . (B) beginning of charging. (C) electrode exfoliation.

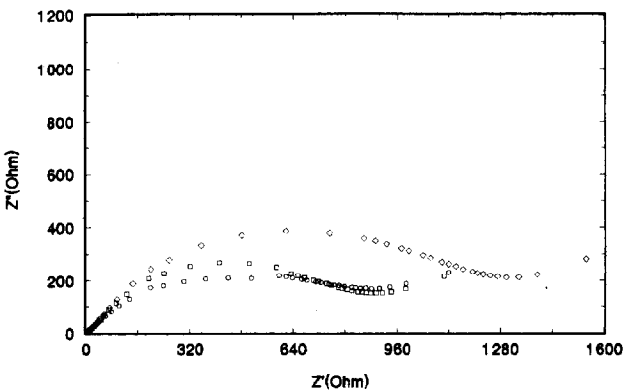


Fig. 3. Impedance spectroscopy of  $\text{LiC}_6$  (built in 1 M  $\text{LiClO}_4/\text{EC}$ ) in 1 M  $\text{LiClO}_4/\text{PC}$ : (O) 12 h; (□) 20 h, and (◇) 34 h.

### 3. Results and discussion

#### 3.1. Physicochemical process and electrical equivalent circuit

It has been extensively shown that discharging of graphite to a negative potential around 0.8 V (versus lithium) causes the formation of insulating surface layers on the electrode [4]. These layers consist of organolithium compounds and inorganic salts e.g.,  $\text{LiCl}$ ,  $\text{Li}_2\text{CO}_3$ , etc. The electrochemical process after the formation of the surface layers is illustrated schematically in Fig. 1 (a). Assuming that the solid-state ion diffusion is considerably slower than that in both the electrolyte solution and the porous surface layer (as will be discussed below), the kinetics of the reaction are governed by the charge-transfer process and by the diffusion of lithium ions in the graphite lattice. A plausible equivalent circuit is proposed in Fig. 1 (b), where  $R_{el}$ ,  $R_{fil}$ ,  $C_{fil}$ ,  $C_{dl}$ ,  $R_{ct}$  and  $Z_w$  represent the resistance of the electrolyte and contacts, the resistance of the film, the capacity of the film, the double-layer capacity, the charge-transfer resistance and the resistance for the diffusion process, respectively. For a rough electrode such as graphite (power electrode), however, the frequency dispersion is analogous to a non-uniform transmission line [9]. A more general constant phase angle element (CPE),  $Z_{cpe}$ , is introduced. This has the form:

$$Z_{cpe} = \sigma \omega^{-m} [\cos(m\pi/2) - j \sin(m\pi/2)] \quad (1)$$

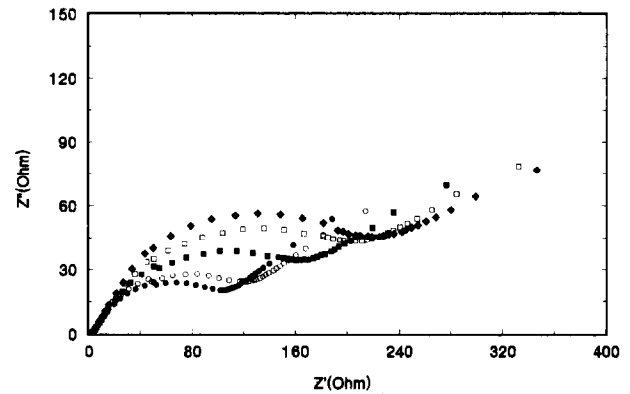


Fig. 4. Impedance spectroscopy of  $\text{LiC}_6$  in 1 M  $\text{LiClO}_4/\text{EC}$  at 303.2 K after being kept at different temperatures for 8 h: (●) 303.2 K; (○) 309.1 K; (■) 318.4 K; (□) 324.6 K, and (◆) 336.3 K.

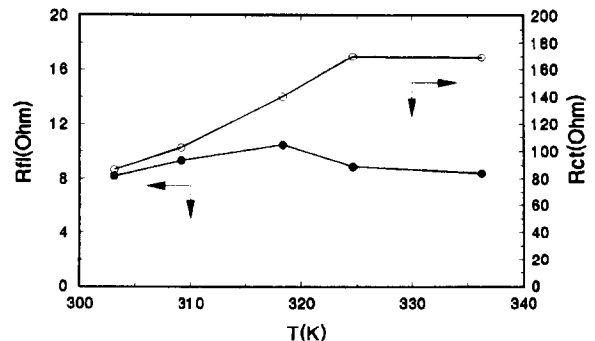


Fig. 5. Effect of thermal history on  $R_{fil}$  and  $R_{ct}$ . Fitting results of Fig. 4.

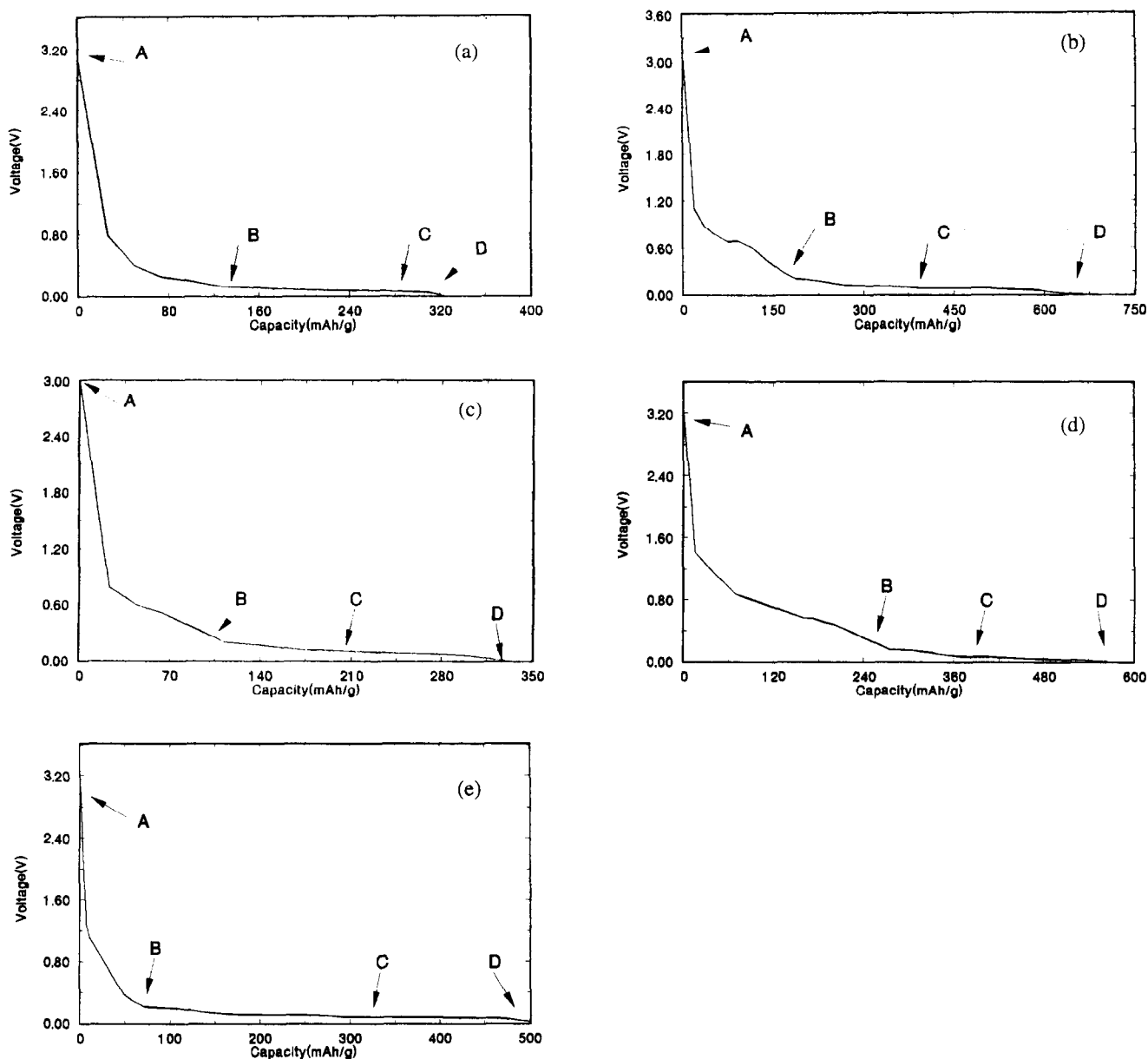


Fig. 6. First discharge of graphite in 1 M LiClO<sub>4</sub> with different electrolytes. (a) 6.9 mg electrode in EC +  $\gamma$ -BL (1:1); (b) 6.6 mg electrode in EC + 2-MeTHF (1:1); (c) 7.8 mg electrode in EC + DEC; (d) 6.3 mg electrode in EC + DME (1:1), and (e) 6.3 mg electrode in EC.  $i = 0.05 \text{ mA cm}^{-2}$ . A, B, C, D are points where impedance data were obtained.

where  $\sigma$  is termed the CPE factor, and  $m$  the CPE exponent. For  $n = 0, 0.5, 1$ , the impedance of the CPE element is identical to a resistance, a Warburg factor and a capacitance, respectively. When using the non-linear-least-squares fitting programme developed by Boukamp [10],  $C_{dl}$  and  $Z_w$  are replaced by  $Z_{cpe}$ ; both the former two parameters are affected by the roughness of the surface.

### 3.2. Porous structure

Thevenin and Muller [11] presented two models — SPI (solid polymer layer) and CSL (composite stratified layer) — to describe the lithium/organic electrolyte interface. In the SPL model, it is assumed that a film of solid compounds

is dispersed in a polymer electrolyte while the CSL model, a double sub-layered structure is formed. These two models suggest compact surface films. In another study [12], both porous and compact structures were considered in a treatment of the Li/Li<sub>3</sub>N system. The porous structure fitted the experimental data better. Nevertheless, a method to identify the microstructure of the passivating layer is still lacking. A simple method is developed in the work presented here.

The graphite electrode was first discharged to 0 V in 1 M LiClO<sub>4</sub>/EC, followed by short circuit for 48 h to ensure the formation of a complete film. It was then transferred to 1 M LiClO<sub>4</sub> in PC. Impedance spectroscopy and discharge curves were recorded (Figs. 2 and 3).

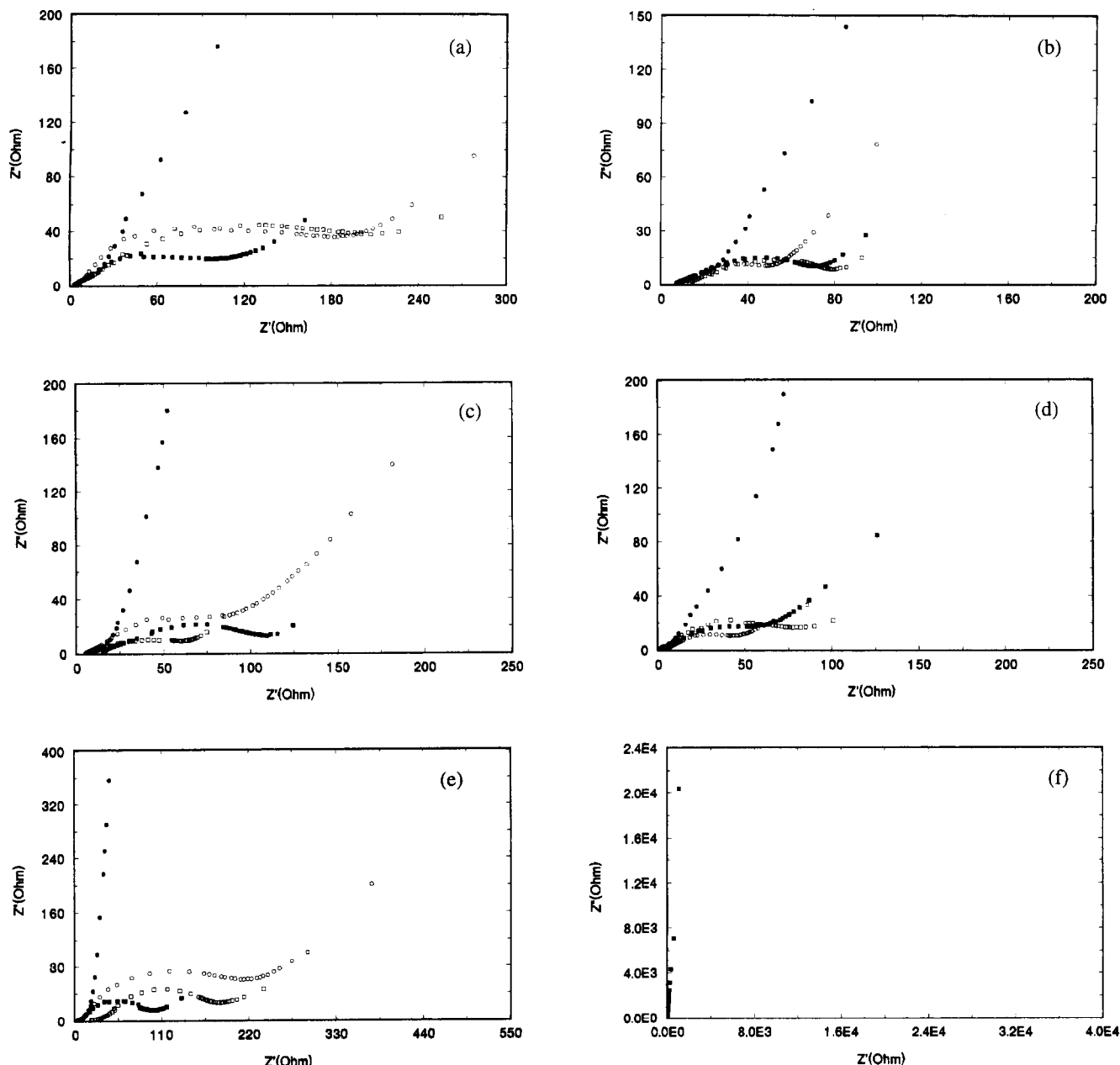


Fig. 7. Impedance spectroscopy of lithiated graphite in different electrolytes as indicated in Fig. 6: (●) A; (○) B; (■) C, and (□) D. Low limit frequencies of A's are: (a) 2.512 Hz; (b) 1.585 Hz; (c) 0.97 Hz; (d) 0.83 Hz; (e) 0.67 Hz, and (f) fresh graphite.

$\text{LiC}_6$  can be charged in PC, but attempts to discharge the electrode failed, even when the voltage limit was set as low as 0.8 V. Large amounts of gas were evolved. This was taken to be propylene [4]. Exfoliating phenomena of the type witnessed on discharging a fresh graphite electrode in PC again took place. If the film is dense and no dissolution is assumed, the electrode should exhibit good cycling behaviour. Thus, the passivating layer should be porous.

After  $\text{LiC}_6$  was transferred to PC, impedance spectroscopy was recorded at different times (Fig. 3). The results showed that the resistance of the film was 65  $\Omega$  (12 h), 202  $\Omega$  (22 h) and 286  $\Omega$  (34 h), respectively. Dissolution should result in a decrease in the film resistance. The increase in the film resistance was ascribed to PC penetrating into the pores of

the surface layer, which may induce a modification of the microstructure. PC-solvated lithium ions were thus transported to the surface of the electrode and co-intercalation of the electrolyte was inevitable which, finally, gave rise to exfoliation of graphite.

### 3.3. Thermal stability

In order to determine the stability of  $\text{Li}_x\text{C}_6$  at different temperatures, the lithiated graphite was first short circuited for 48 h. It was then held for 8 h at different temperatures, followed by equilibration at 30 °C. The a.c. impedance spectrum was then measured (Fig. 4). The results are given in Fig. 5.

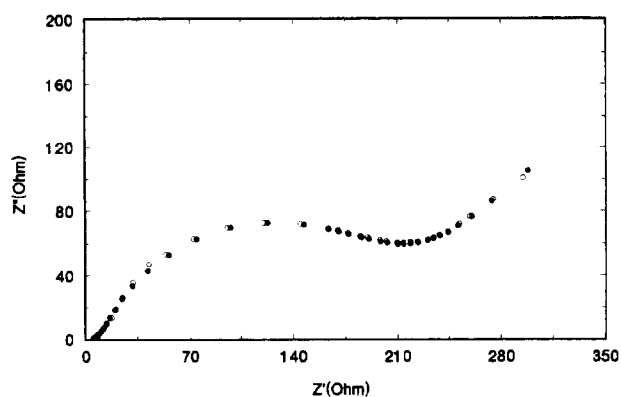


Fig. 8. Typical impedance spectroscopy with fitted results: (○) experimental, and (●) fitted results.

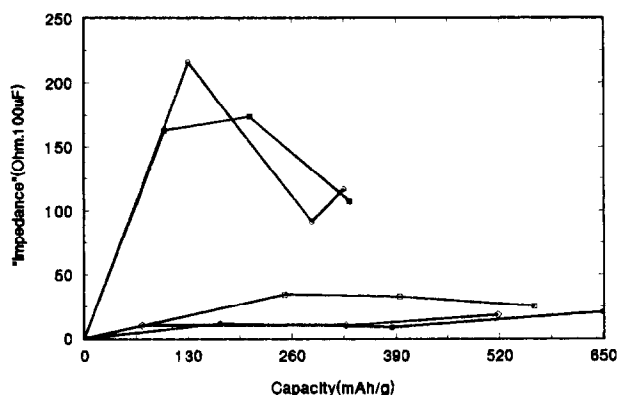


Fig. 9.  $R_n C_{fr}$  of lithiated graphite in different electrolytes. Legends and  $C_{fr}$  used: (○) 750  $\mu\text{F}$ ; (●) 700  $\mu\text{F}$ ; (■) 1200  $\mu\text{F}$ ; (□) 1200  $\mu\text{F}$ , and (◇) 710  $\mu\text{F}$ . (○)–(◇) correspond with (a)–(e) in Fig. 6.

The resistance of the film remained constant at the temperatures examined. This suggests that the film has good elastic properties. While no obvious change in the golden colour of the electrode nor in the voltage was observed (0.093 V versus lithium), the  $R_{ct}$  increased with temperature, as shown in Fig. 5. For intercalation electrodes,  $R_{ct}$  usually changed with intercalation depth [12], for example, with  $x$  in  $\text{Li}_x\text{C}_6$ . The self-discharge of the electrode is responsible for the increase of  $R_{ct}$  and this may be accelerated by increasing the temperature. It can be inferred that if a practical lithium battery is kept at elevated temperature, a loss in energy is likely but the rechargeable capacity of the anode will not be affected.

### 3.4. Film formation in different electrolytes

Electrolytes have a significant effect on the behaviour of graphite in lithium batteries. An appropriate lithium-ion solvating energy is essential. At the interface, solvated lithium ions lose their surrounding solvent molecules, and then undergo a charge-transfer process. When the host material is graphite, an excessive solvating energy will lead to co-intercalation which, in turn, forms ternary graphite intercalation compounds and finally leads to exfoliation of graphite.

The discharge and impedance behaviour of graphite in five EC-based electrolytes were examined. The results are shown in Figs. 6 and 7. A typical response with fitted results is given in Fig. 8.

In order to make the comparison between different electrodes more reasonable, the fitted resistance of the film should be assigned a common standard. For simplicity, the resistance is assumed to have the following form:

$$R = \rho L / S \quad (2)$$

where  $L$  is the film thickness,  $S$  the film area, and  $\rho$  the resistivity, which is assumed to be constant for different films. The electrode surface area should be electrochemically active. The capacitance of the fresh graphite electrode was measured and is directly proportional to the surface area. Fig. 7(f) shows the typical impedance spectroscopy of fresh graphite. At low frequencies ( $< 0.1$  Hz), a limiting capacitance ( $C_{fr}$ ) can be obtained.  $R_n C_{fr}$  was then taken as the 'impedance form' to compare different electrodes (Fig. 9).

Three reactions, namely, passivating layer growth, gas evolution and lithiated graphite formation, contribute to the overall apparent capacity. The latter is sometimes much higher than the theoretical one. The change in resistance reflects the contribution of the growth of the surface layer. In electrolytes with EC, EC +  $\gamma$ -BL, or EC + DEC, initial film formation consumed most of the charge passed, and the film grows to the extent that it is electron insulating. Nevertheless, the parallel gas evolution enlarged the overall surface area of the film and the resistance began to fall. Due to the better stability at low potential, the film was expected to be thinner when only EC was present. An equilibrium was finally reached. In electrolytes with EC + DME or EC + 2-MeTHF, however, these esters were easier to reduce and initial gas evolution dominated the whole reaction. The passivating film slowly developed and alleviated the above process. The resistance was maintained at a low level.

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