

# Surface modification of graphite by coke coating for reduction of initial irreversible capacity in lithium secondary batteries

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Received 25 August 2000; accepted 6 October 2000

## Abstract

Surface modification of graphite to reduce the irreversible capacity loss during the first charging period of graphite anodes is described. For the surface modification, artificial graphite (Lonza KS44) is dispersed in a tetrahydrofuran/acetone solution which contains coal tar pitch. The solvent is then evaporated. The loaded pitch component is converted to coke by a heat treatment at 1000°C in argon atmosphere. The resulting coke-coated graphite has a smaller surface area than that of the pristine one. The reduction of surface area, which is due to the coverage of pores of <10 nm by the coke component, causes a decrease in the irreversible capacity on the first cycle. The extent of electrolyte decomposition, gas evolution and surface film growth is also less with the coke-coated graphite electrode. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Lithium secondary batteries; Graphite anodes; Coke-coated graphites; Irreversible capacity loss; Ac impedance spectroscopy

## 1. Introduction

The major problem encountered in using graphites for negative electrode materials in lithium secondary batteries is the irreversible reactions which occur during the initial charging period of cell operation [1,2]. A surface layer, called the ‘solid electrolyte interface’ (SEI), forms as a result of these irreversible reactions and subsequent deposition of reaction products. The capacity related to this irreversible reaction is unusable because the charge consumed cannot be recovered during the subsequent discharging process. In practical lithium secondary cells, this capacity loss is compensated by the use of excess positive electrode material. This, however, should be minimized if batteries with high specific energies are to be developed.

The irreversible reactions which occur on graphitic materials can be classified into several types; namely: (i) chemical or electrochemical reaction of solvent and/or salt on graphite surface [3–6]; (ii) electrochemical reduction of solvent molecules between graphene layers through a co-intercalation with solvated ions [7]; (iii) irreversible storage of Li<sup>+</sup> ions [8,9]. The last mechanism is not important in highly graphitized materials. Numerous research activities have focused on the suppression of irreversible capacity loss,

either by proper choice of electrolyte components [3–7,9–14] or by pre-conditioning of graphite materials [15–18]. The well-known example in the first approach is the use of ethylene carbonate (EC)-based solvents instead of propylene carbonate (PC) [4]. Several additives have also been proven to be effective for this purpose [11–14]. The rationale for the second approach is to minimize the irreversible reactions by modification of surface structure, composition and exposed area of graphitic materials. It has already been reported that the extent of irreversible reactions is proportional to the specific surface area of graphites and is also affected by the graphite surface structure where the solvent co-intercalation takes place [4,19–21].

It is intuitive that the solvent decomposition mostly takes place on graphite surface defects or edge sites. The coverage of these sites with other materials may, thus, be one of the simple ways to minimize the irreversible reactions. In view of this, a coke-coated graphite was prepared by Isao et al. [15] by first coating graphite with a blend of pitch and resin, and subsequent carbonization. The authors claimed, but without detailed reasoning, that the surface-modified graphite exhibits a smaller irreversible capacity than the pristine one.

The work presented here is an extension of the earlier studies of coke-coated graphites. An artificial graphite which has a reasonably high surface area, thereby exhibiting an appreciable irreversible capacity loss in the first cycle, has

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been selected. The graphite is modified by treatment with coal tar pitch and subsequent carbonization. The effect of coke coating on the surface area and pore-size distribution is examined. Also, the extent of irreversible reactions, gas evolution, and surface film formation is compared for pristine and coke-coated graphite electrodes.

## 2. Experimental

### 2.1. Materials

To prepare the pitch-coated graphite sample, 50 mg of an artificial graphite (Timrex (Lonza) KS-44, 30  $\mu\text{m}$  average particle size) was dispersed in a solution made by dissolving 10 mg of coal tar pitch (110°C softening point) in 20 ml of tetrahydrofuran/acetone solvent (1:1 v/v). After vigorous stirring overnight, the solvent was evaporated and the solid residue was collected. The resulting pitch-coated graphite was oxidatively stabilized in air by heating from room temperature to 240°C, with a heating rate of 5°C min<sup>-1</sup>, followed by ‘soaking’ at 240°C for 3 h. The loaded pitch component was carbonized by heat treatment at 1000°C for 1 h in an argon atmosphere. The BET (Brunauer, Emmett, and Teller) surface area and pore-size distribution was measured by the nitrogen adsorption method.

For the preparation of negative electrodes, the graphite was mixed with polytetrafluoroethylene (PTFE) (10:1 w/w) and dispersed in isopropyl alcohol. The resulting slurry was coated on a copper mesh sheet (1 cm  $\times$  1 cm) which served as the current-collector, and dried at 120°C under vacuum overnight. Each anode contained approximately 9 mg of graphite. The electrolyte was 1.0 M LiClO<sub>4</sub> dissolved in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 v/v).

### 2.2. Instrumentation

The galvanostatic charge/discharge and electrochemical voltage spectroscopy (EVS) measurements were made in a three-electrode cell, in which lithium metal foil was used for both the counter and the reference electrodes. For galvanostatic charge/discharge cycling, a gravimetric current density of 30 mA g<sup>-1</sup> was applied within a voltage range of 0.0–2.0 V (versus Li/Li<sup>+</sup>). For electrochemical voltage spectroscopic (EVS) measurements, an EG&G M362 scanning potentiostat/galvanostat and a programmable voltage source were combined in order to control the applied potential step (=10 mV). The potential step was started from the open-circuit potential of the fresh cell and the sequential step was applied after the current decayed down to the threshold current ( $I_{\text{threshold}} = 0.02$  mA). The ac impedance measurements were made with an IM6e instrument (Zahner elektrik). The frequency range was 0.1 to 10<sup>5</sup> Hz and the ac amplitude was 5 mV. All the electrochemical measurements were performed in a glove-box which was filled with argon.

A mass spectrometer (VG-Mass, Monitorr) equipped with a quadrupole mass analyzer was used for the analysis of the gaseous products which formed during the charging period. To this end, the cell was charged down to 0.0 V and the evolved gas was sampled with a gas-tight syringe. Mass signals were detected at  $m/e = 2$  (H<sub>2</sub>) and 28 (ethylene). Other signals were too small to be counted.

## 3. Results and discussion

Fig. 1(a) shows the first galvanostatic charge/discharge voltage profiles for pristine graphite and coke-coated graphite. Results obtained with a physically mixed coke/graphite electrode are also provided for comparison. As the coke coating caused a weight increase of about 10% after the carbonization, the physically mixed coke/graphite electrode was prepared by adding 10 wt.% of coke to the graphite sample. Here, the coke sample was prepared by heating the coal tar pitch at 1000°C under an argon atmosphere. The result shown in Fig. 1(a) illustrates that the pristine graphite electrode delivers a charging capacity of 580 mA h g<sup>-1</sup> in

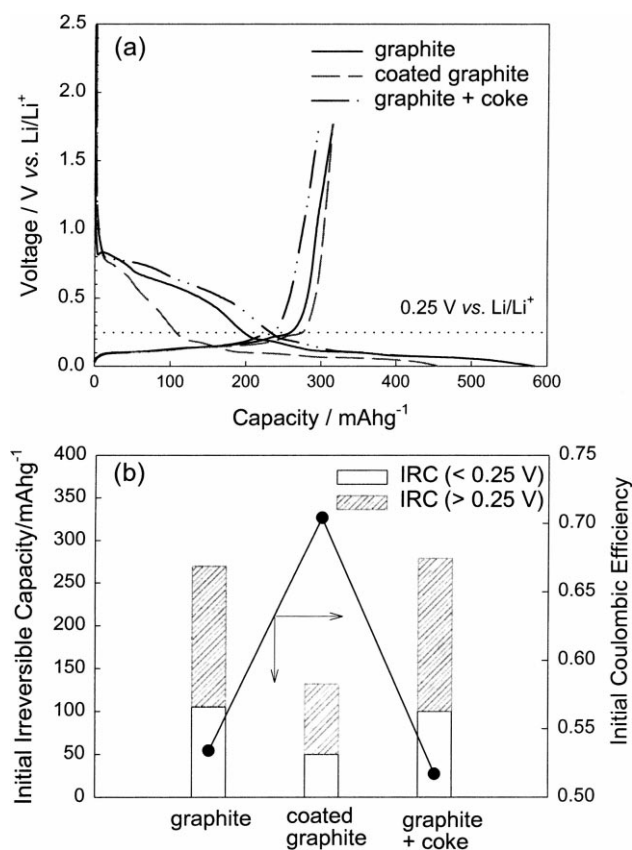


Fig. 1. (a) First galvanostatic charge/discharge profile for pristine graphite, coke-coated graphite, and coke/graphite mixture electrodes. The electrolyte is 1.0 M LiClO<sub>4</sub> in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 v/v). (b) irreversible capacity (IRC) at >0.25 V and <0.25 V, and the initial coulombic efficiency for the three electrodes in (a). A gravimetric current density of 30 mA g<sup>-1</sup> was applied within the voltage range 0.0 to 2.0 V (vs. Li/Li<sup>+</sup>).

the first cycle, but the discharging capacity amounts to only  $310 \text{ mA h g}^{-1}$ . The coulombic efficiency (discharging capacity/charging capacity) is, thus, calculated to be 0.53, which indicates that about half of the electric charges consumed for the charging are not recovered in the discharging period. In Fig. 1(b), the irreversible capacity (IRC) that was calculated from the data shown in Fig. 1(a) is presented after dividing it into two potential regions. In the case of pristine graphite electrode, the irreversible capacity at  $>0.25 \text{ V}$ , where electrolyte decomposition is the major irreversible reaction, is  $270 \text{ mA h g}^{-1}$ . The irreversible capacity at  $<0.25 \text{ V}$  is about  $100 \text{ mA h g}^{-1}$ , which may be ascribed to the charge consumed for irreversible  $\text{Li}^+$  storage or hydrogen generation [19,20]. The coke coating leads to a significant decrease in the irreversible capacity in both potential regions. As a result, the coulombic efficiency is raised from 53 to 70%. There appears, however, to be a negligible decrease in the irreversible capacity with the physically mixed coke/graphite electrode, which suggests that the coke component in the coated graphite plays a somewhat different role to that present in the coke/graphite mixed electrode.

The nature of irreversible charging reactions was examined using EVS. In Fig. 2(a), the charging EVS profiles are presented in the potential range 1.5–0.3 V. The graphite electrode exhibits two major EVS peaks which are related to electrolyte decomposition and SEI formation. Previous

reports [4,21] ascribed the irreversible peak near 0.9 V to the electrolyte decomposition and formation of SEI layer, both of which take place simultaneously at graphite surfaces. The irreversible peak near 0.6 V is caused by side reactions which take place at the edges of graphite grains. The result shown in Fig. 2(a) reveals that the coke coating leads to a significant decrease in both peaks, indicative of a lesser degree of irreversible reactions on this electrode. Furthermore, the EVS profile of coated graphite is rather similar in shape to that of the pristine coke, which illustrates that the outermost surface region of graphite that comes into contact with the electrolyte solution is coated by coke. There is, however, a difference of 0.1 V between the peaks of pristine coke and coke-coated graphite electrode, indicative of a change in the surface property of coke upon being coated on graphite surface. Until now, any tenable explanation cannot be given for this observation. Nonetheless, it is of value to provide the previous findings whereby the microstructure of one carbon in carbon-carbon composites is commonly affected by the other component. For instance, the tendency for graphitization of non-graphitizable carbons increases when they are intimately contacted with graphite [22]. A similar situation likely prevails at the coke/graphite interface in the present sample.

Fig. 2(b) displays the charge/discharge EVS profiles recorded at  $<0.5 \text{ V}$ , where distinct three peaks in both the charging and discharging profiles are observed. These are associated with the stage transformation of Li-graphite intercalation compounds [23,24]. The pristine and coke-coated graphite exhibits a similar EVS profile, which implies that the bulk structure of graphite is not affected by the coke coating. In both electrodes, however, the charging capacity (integrated area of the bottom profiles) is slightly larger than the discharging capacity (integrated area of the upper profiles). This irreversibility has been ascribed either to hydrogen generation or to irreversible storage of  $\text{Li}^+$  ions [19,20]. Further differentiation, however, is not possible from the EVS profiles.

The amounts of hydrogen and ethylene that evolve during the charging period of two electrodes are compared in Fig. 3. The coke-coated graphite produces a lesser amount of hydrogen and ethylene. It would appear, therefore, that both the electrolyte decomposition and hydrogen generation are less severe on the coated graphite electrode. Ethylene is generated from the decomposition of ethylene carbonate [5–7].  $\text{Li}_2\text{CO}_3$  or related products deposit as a film on graphite surface. The hydrogen evolution mechanism is not clarified yet in the literature, but some reports claim that it is caused by a reaction between the surface film and impurity water in electrolyte [16,20].

The BET surface area of coated graphite is compared to those of pristine graphite and coke in Fig. 4(a). It is apparent that the surface coating results in a decrease in surface area. The pore-size distribution of carbon materials is presented in Fig. 4(b). The pristine graphite has pores which range from 1 to 100 nm in radius. Pores of size  $<10 \text{ nm}$  largely disappear

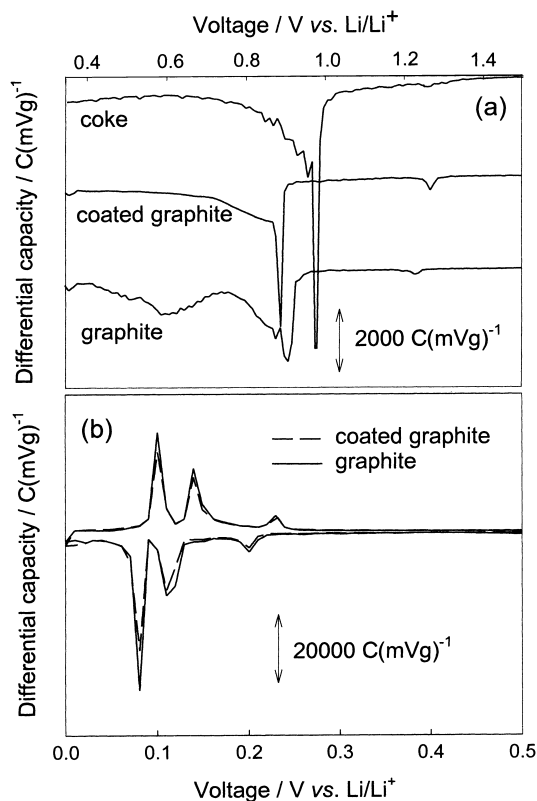


Fig. 2. (a) EVS charging profiles for three electrodes from 1.5 to 0.3 V (vs.  $\text{Li/Li}^+$ ); (b) EVS charge/discharge profiles in potential range 0.5–0.0 V.

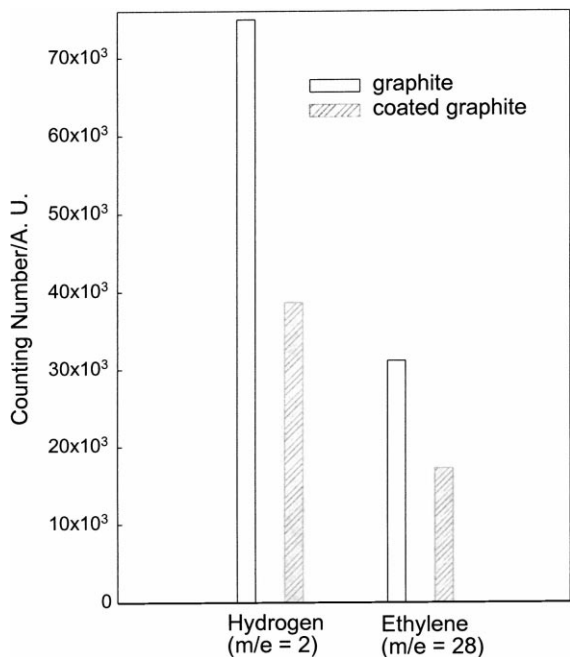


Fig. 3. Comparison of gas evolution on pristine and coated graphite electrodes. Gaseous species were collected during first charging from 2.0 to 0.0 V (vs. Li/Li<sup>+</sup>). Experimental conditions same as for Fig. 1.

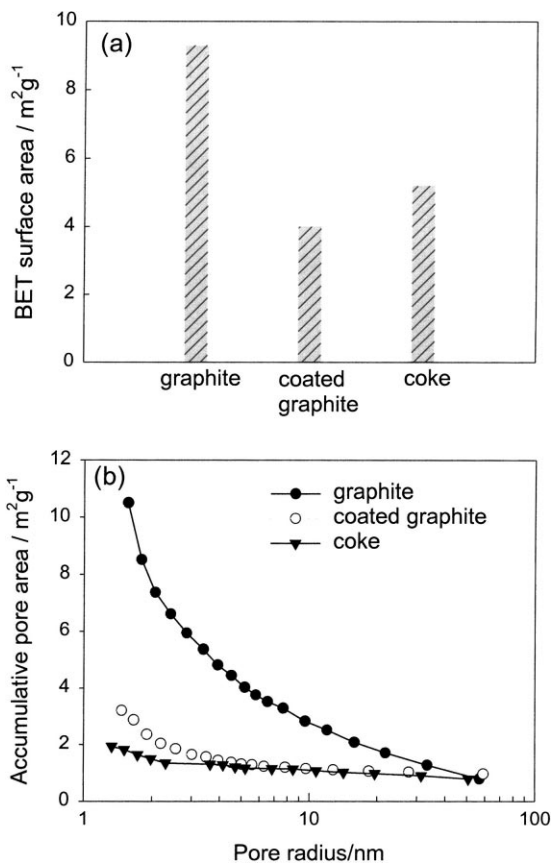


Fig. 4. (a) BET surface area, (b) pore-size distribution of pristine graphite, coke-coated graphite, and pristine coke powders.

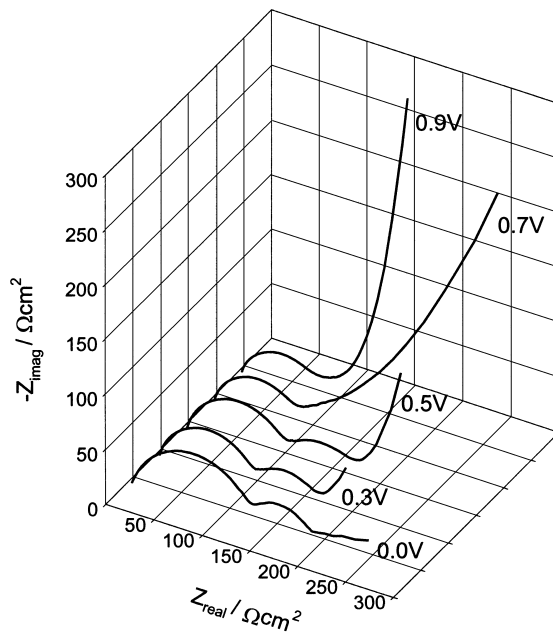


Fig. 5. The ac impedance spectra for pristine graphite electrode (frequency range = 10<sup>-1</sup> to 10<sup>5</sup> Hz).

after the coke coating. It is, thus, likely that the small pores where defects or irregular edge sites are highly populated are coated by the coke component, and this leads to a decrease in the irreversible reactions.

In order to examine the effects of coating on the electrochemical performance of graphite electrode, ac impedance measurements were made by varying the dc potential. The impedance spectra recorded with Lonza KS-44 and the coke-coated graphite electrodes are displayed in Figs. 5 and 6, respectively. When the dc potential is changed from

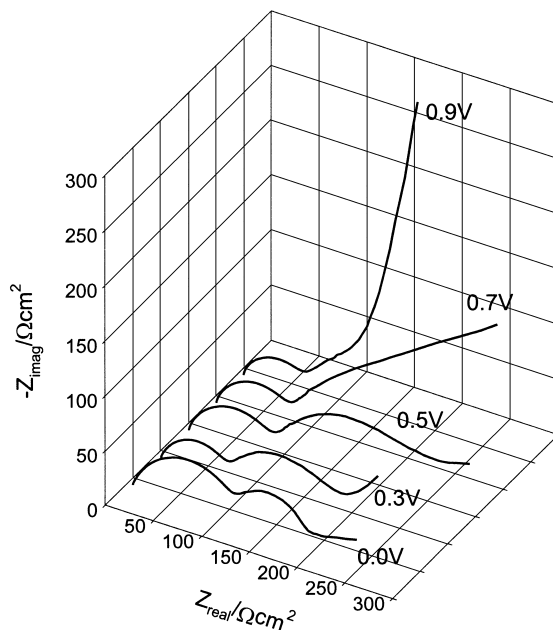


Fig. 6. The ac impedance spectra for coke-coated graphite electrode. Experimental conditions same for Fig. 5.

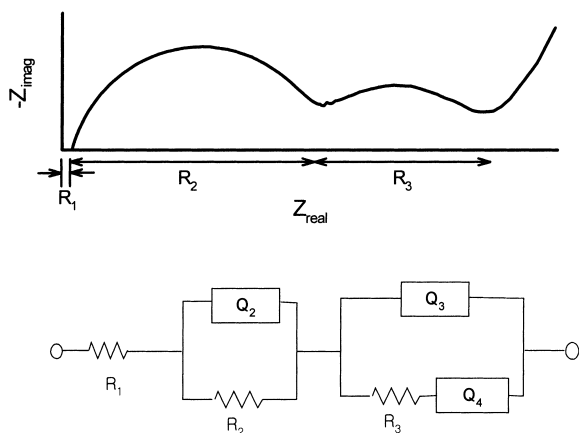


Fig. 7. Typical ac impedance spectrum and equivalent circuit used to fit impedance spectra.

0.9 to 0.0 V, both electrodes give one depressed semi-circle at  $>0.7$  V, and two arcs at  $<0.5$  V. All the spectra can be deconvoluted with the equivalent circuit depicted in Fig. 7. A typical impedance spectrum is also presented. The  $R_1$  component certainly corresponds to the electrolyte resistance. The semi-circle appearing at the higher frequency region ( $R_2Q_2$ ) is assigned to the  $\text{Li}^+$  migration through surface film [25,26], based on the observation that the semicircle starts to develop from 0.9 V and its size steadily grows on decreasing the dc potential (Figs. 5 and 6). That is, as shown in Fig. 2(a), the electrolyte decomposition and concomitant surface film formation starts from about 0.9 V. It, thus, appears that the surface film gradually thickens with a negative potential sweep from 0.9 to 0.0 V, and this is reflected by a steady growth in  $R_2$  (film resistance) in the impedance spectra. The other semi-circle located in the lower frequency region ( $R_3Q_3$ ) is assigned to the charge-transfer process of the intercalation reaction ( $R_3 =$  charge-transfer resistance). This is based on the observation that this component appears from 0.5 to 0.0 V where  $\text{Li}^+$  intercalation takes place [27]. Finally,  $Q_4$  is associated with diffusion process of  $\text{Li}^+$  ions in the electrolyte solution.

The evolution of  $R_2$  and  $R_3$  is plotted as a function of the imposed dc potential in Fig. 8. The  $R_2$  component increases, even if some data are scattered, and the dc potential is moved in a negative direction. This is the result of steady growth of the surface film, as discussed above. Of the two electrodes, however, the coke-coated graphite electrode shows a smaller  $R_2$ , which suggests that both the electrolyte decomposition and surface film formation are less severe in this electrode. The  $R_3$  component starts to develop from about 0.5 V as the charge-transfer reaction prevails from this potential. The steady decrease of  $R_3$  with negative potential sweep illustrates facilitation of the charge transfer reaction when the applied dc potential approaches zero volts. The coated electrode exhibits the higher value of  $R_3$ . This may be explained by the fact that the electrochemically active surface area for  $\text{Li}^+$  intercalation is smaller in the case of the coated graphite electrode as a result of coke coating.

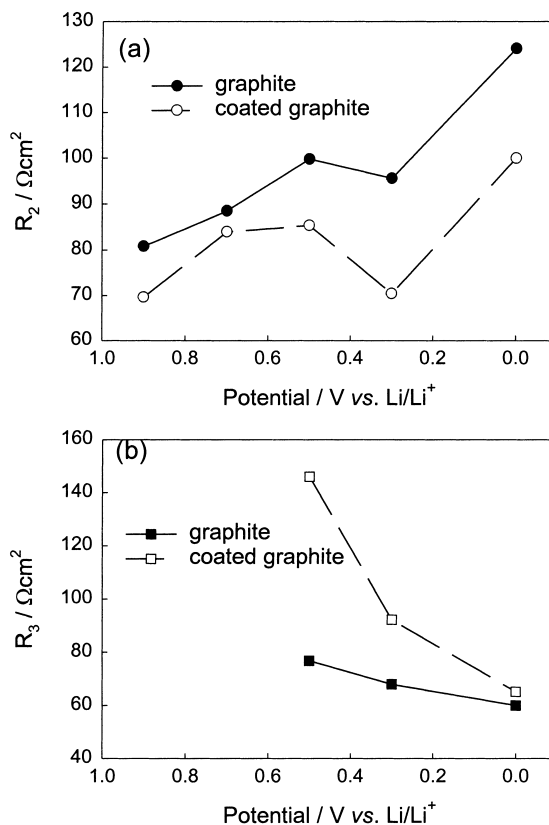


Fig. 8. Comparison of film resistance ( $R_2$ ) and charge-transfer resistance ( $R_3$ ) with variation in dc potential for pristine and coke-coated graphite electrodes.

#### 4. Conclusions

A coke-coated graphite powder is prepared by depositing coal tar pitch on the graphite surface followed by heat treatment. The resulting coke-coated graphite electrode shows a smaller irreversible capacity than that of the pristine graphite in the first cycle. The extent of electrolyte decomposition, gas evolution and surface film growth is also notably reduced with the coke-coated graphite electrode. These favorable features have been attributed to a decrease in the exposed surface area of graphite. It is found that pores of  $<10$  nm, where the active sites for electrolyte decomposition such as defects and edge sites are highly populated, are covered by the coke component.

#### Acknowledgements

This work was supported by the Korea Science and Engineering Foundation (98-2-03-01-01-2).

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