

# Studies of petroleum coke in carbonate-based electrolyte

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## Abstract

The behaviour of petroleum coke (CONOCO) was examined in a PC/EC/DMC (1/1/3 volume) mixture with  $\text{LiCF}_3\text{SO}_3$  as the lithium salt. The influence of the lithium content on the diffusion coefficient of lithium ions has been explored and the reactivity of the intercalated lithium in petroleum coke with small volumes of electrolyte at 45 °C has been investigated. This reactivity was found to be greater with a  $\text{V}_2\text{O}_5$  cathode and a mechanism is proposed to explain this tendency. © 1997 Elsevier Science S.A.

*Keywords.* Petroleum coke; Electrolytes; Propylene carbonate; Dimethyl carbonate

## 1. Introduction

For the last two decades, an increasing interest in lithium batteries has been developed among battery manufacturers. Primary lithium batteries have already been commercialized while the development of secondary lithium batteries encountered difficulties due to problems associated with the use of lithium metal as the negative electrode [1]. Many studies have been done in order to find a material being able to intercalate reversibly lithium as a substitute for lithium metal. The publication by Nagura (Sony) on a carbon-based battery system has prompted an increased research activity in this area [2]. While many articles describe the reversible intercalation of lithium in several types of carbon in lithium salt solutions of polar aprotic solvents [3–7], only a few authors studied the reaction between the electrolyte and the carbon/lithium anode and the self-discharge mechanism in rocking-chair batteries.

This paper describes the thermodynamic and kinetic characteristics of a petroleum coke anode in a PC/EC/DMC (1/1/3 by volume) mixture with  $\text{LiCF}_3\text{SO}_3$  as the lithium salt. We showed the behaviour of this anode during a long storage period in the electrolyte solution and proposed a self-discharge mechanism in  $\text{V}_2\text{O}_5$ /coke cell. The petroleum coke is an interesting material because of its good stability during the charge/discharge cycles.

## 2. Experimental

### 2.1. Materials

Petroleum coke designed XP grade 3 was obtained from CONOCO and was used as received. This coke is heat-treated to approximately 1100 °C during the manufacturing process. The spacing between carbon planes ( $d_{002}$ ) equals to 3.453 Å and the crystallite size along the *c*-axis ( $L_c$ ) equals to 60 Å. A mixture of the carbon powder, Teflon in aqueous solution from Ausimont, terpineol and ethanol was prepared (5 wt.% of Teflon and 95 wt.% of carbon in the finished electrode.) This mixture was then spread onto a glass sheet in a 250 μm thick membrane. After drying at 100 °C for 12 h (in order to evaporate water and alcohols) electrodes were cut from the membrane.

Coin cells were constructed using the electrodes described above, Celgard 2400 microporous film from Hoechst Celanese was used as the separator to prevent lithium dendrites from generating short-circuits during electrochemical process, Viledon macroporous foil from Freudenberg as the electrolyte reservoir and a lithium foil from Aldrich which acts as the counter and reference electrodes. Coin cells were constructed for the study of the behaviour of the carbon/lithium anode during storage because they were perfectly watertight. Teflon cells with three electrodes were used to determine the lithium diffusion coefficient in the petroleum coke. The electrolyte was a 1 M  $\text{LiCF}_3\text{SO}_3$  solution (3M Corporation) dissolved in a 1/1/3 volume mixture of propylene carbonate (FLUKA), ethylene carbonate (MERCK) and dimethyl carbonate (MERCK). This mixture of solvents was stored over

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molecular sieves, previously activated at 200 °C, in order to lower the water content.  $\text{LiCF}_3\text{SO}_3$  was dried at 100 °C under vacuum for 12 h prior to use. Thus, the water content in the electrolyte was maintained at  $\sim 50$  ppm and 300  $\mu\text{l}$  was used during the coin cell assembly. All potentials are expressed versus  $\text{Li}/\text{Li}^+$ .

## 2.2. Apparatus

A 'Mac Pile' system from Bio-Logic that can operate either in a galvanostatic or potentiostatic mode was used to perform cycling experiments or electrochemical evaluation. A potentiostat, EG&G PAR 273 A, was also used for the electrochemical measurements.

Infrared spectra were recorded on a Bruker IFS 28 Fourier-transform spectrometer with an Zn Se ATR.

## 3. Results and discussion

### 3.1. Thermodynamic and kinetic study

It is well known that carbon can reversibly intercalate the lithium after the formation of passivating layer according to the following equation [3–7]:



Fig. 1 illustrates the cycling behaviour of a petroleum coke in a PC/EC/DMC electrolyte coin cell. Formation of the passivating layer mainly takes place in the three first charge/discharge cycles; the faradic yield of the fifth cycle is close to 100% and we observe only the lithium intercalation and de-intercalation reaction.

GIT technique (galvanostatic intermittent titration) [8] was used in order to determine the diffusion coefficient of the lithium content during the sixth charge. The diffusion of lithium ions into the petroleum coke is obtained when a constant current density is applied for a few seconds (500  $\mu\text{A cm}^{-2}$  during 60 s).  $D_{\text{Li}}$  is calculated from the following relation:

$$D_{\text{Li}} = \frac{4}{\pi} \left( \frac{IV_{\text{M}}}{z_{\text{A}}FS} \right)^2 \left[ \frac{(dE/dx)}{(dE/d\sqrt{t})} \right]^2 \quad (2)$$

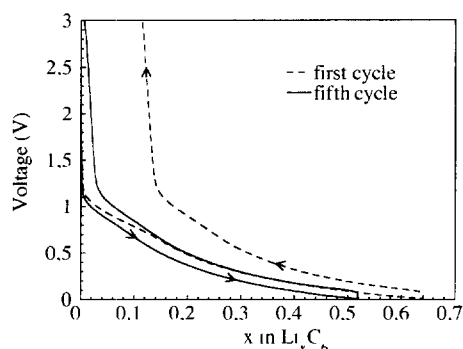


Fig. 1 First and fifth cycles of  $\text{Li}$ -petroleum coke coin cell in a mixture PC/EC/DMC (1 1.3) with 1 M  $\text{LiCF}_3\text{SO}_3$  ( $J = 380 \mu\text{A cm}^{-2}$ ).

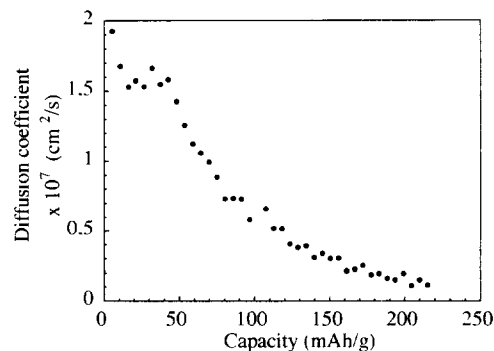


Fig. 2 Variation of the lithium diffusion coefficient as a function of the lithium content

where  $I$  is the applied current.  $V_{\text{M}}$  the molar volume of the electrode ( $V_{\text{M}} = 33 \text{ cm}^3 \text{ mol}^{-1}$ ). The variation of the molar volume during the experiment is negligible (less than 7%).  $Z_{\text{A}}$  is the charge number of the electroactive species,  $S$  the cross-sectional area common to both the electrolyte and the electrode ( $S$  the geometric area of electrode:  $0.785 \text{ cm}^2$ ) and  $x$  the amount of lithium in the carbon matrix.  $dE/d\sqrt{t}$  is directly obtained from the measurement of the voltage as a function of  $\sqrt{t}$  during the constant current pulse.  $dE/dx$  is determined from the slope of the coulometric titration curve which was obtained by plotting the steady-state equilibrium voltage of the electrode against the composition after each galvanostatic titration step.

Fig. 2 shows the lithium diffusion coefficient in petroleum coke as a function of the lithium content in  $\text{Li}_x\text{C}_6$ .  $D_{\text{Li}}$  remains constant for  $x < 0.1$  and then gradually decreases as  $x$  increases from 0.1 to 0.6. This evolution is in contrast with the results given in Ref. [9] reporting a linear decrease of the coefficient diffusion.

This is caused by the presence of two host sites available for the intercalation in petroleum coke [10]. The first ones are microcavities present in the carbon matrix as suggested by Mabuchi et al. [11]. During storage in the cavities, the motions of lithium ions are only limited by the diffusion between carbene layers, and  $D$  is then constant. The second host sites are between the layers of carbons. Motions of lithium ions become slower as their number into the carbon matrix increases, and  $D_{\text{Li}}$  decreases [12].

### 3.2. Study of the carbon/lithium reactivity

In order to accelerate kinetics of the reaction between carbon and lithium and the electrolyte experiments were performed at 45 °C. The carbon electrodes were stored after the sixth charge in a fully reduced state for several weeks in the PC/EC/DMC–1 M  $\text{LiCF}_3\text{SO}_3$  electrolyte. This storage induces a lithium loss [13] which is presented as a function of the time in Fig. 3. The lithium loss increased continuously during the first 2000 h and then stabilized. To conclude, the reactivity of the intercalated lithium in petroleum coke decreases because the passivation layer becomes thicker, or more compact, versus storage time. The reactivity does not

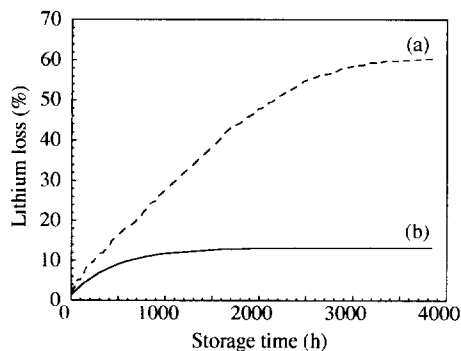


Fig. 3. Evolution of the lithium loss (%) vs. storage time: (a) overall lithium loss, and (b) loss due to dissolution of passivating layer.

depend on the amount of lithium intercalated. Indeed, after a long storage time the carbon electrodes are reduced again, but no lithium loss is observed.

The stability of the passivating layer in the electrolyte was also investigated [13]. Carbon electrodes have previously undergone five charge/discharge cycles. In this condition, the passivating layer is formed and the electrode contained no intercalated lithium. The electrodes were then stored for various times in the electrolyte. After a period of storage, the faradic efficiencies became less than 100%. The difference in faradic efficiencies corresponds to the quantity of lithium needed to re-build the passivating layer. This layer (denoted by P) undergoes an equilibrium of dissolution/precipitation (see Eq. (3)) where  $k_1$  is the precipitation rate constant and  $k_2$  is dissolution rate constant.



Fig. 3(b) gives the percentage of lithium loss as a function of the storage time. The passivating layer dissolves mainly during an initial storage period of the storage ( $< 500$  h). During a storage time greater than 1000 h the electrolyte was saturated involving a constant lithium loss.

Examination of Fig. 3(a) suggests that the lithium loss due to the passivating layer dissolution is still lower than the overall lithium loss. These two losses would be of the same order of magnitude only if the cause of the intercalated lithium consumption consisted only of the dissolution of the passivating layer. In fact, we think that the lithium also reacts directly with the electrolyte in spite of the presence of passivating layer because the latter did not protect perfectly the intercalated lithium. The lithium consumption may be explained by two processes:

1. dissolution of the passivating layer followed by a reaction of the intercalated lithium in order to build again the passivating layer, and
2. reaction of the intercalated lithium with the electrolyte through the passivating layer.

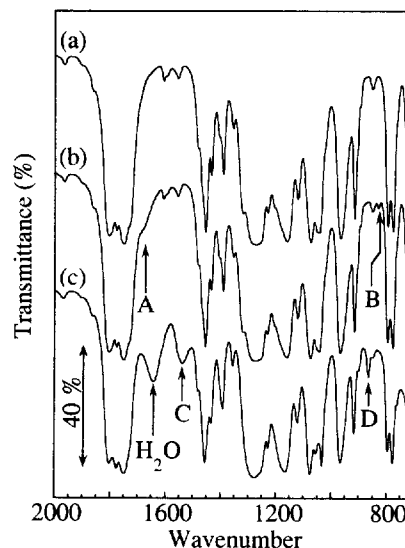


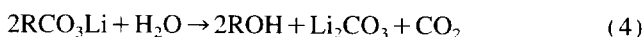
Fig. 4. IR spectra of electrolyte solution (PC/EC/DMC-1 M LiCF<sub>3</sub>SO<sub>3</sub>): (a) stored without carbon-lithium electrode, (b) stored with carbon/lithium electrode, and (c) after water addition

### 3.3. Study of the carbon/lithium storage solution

IR analysis were performed on electrolytes in which carbon-lithium electrodes have been stored in order to detect soluble species resulting from the dissolution of the passivating layer. IR spectra of the solutions stored with and without carbon/lithium electrode are presented in Fig. 4.

After one month of storage at 45 °C, two new bands at 1680 and 829 cm<sup>-1</sup> (respectively A and B) are found. They have been previously attributed to RCO<sub>3</sub>Li species [14]. The formation of these species has been supposed to occur during the reduction of DMC, PC or EC by carbon-lithium and formed the passivating layer [15]. RCO<sub>3</sub>Li species in the electrolyte result, in our opinion, from the dissolution of the passivating layer.

In order to support that the two bands are due to RCO<sub>3</sub>Li, water was added to electrolyte. RCO<sub>3</sub>Li are sensitive to water and formation of Li<sub>2</sub>CO<sub>3</sub> is obtained according to the following equation:



Addition of water leads to a removal of the 1680 and 829 cm<sup>-1</sup> bands and the appearance of two new bands at 1520 and 870 cm<sup>-1</sup> attributed in the literature to Li<sub>2</sub>CO<sub>3</sub>. Thus, the A and B bands are really due to RCO<sub>3</sub>Li species resulting from dissolution of the passivating layer.

### 3.4. Reactivity of carbon/lithium with a V<sub>2</sub>O<sub>5</sub> cathode

Reactivity of carbon-lithium was also investigated when a V<sub>2</sub>O<sub>5</sub> cathode is present. Fig. 5 gives the lithium loss (expressed in %) as a function of the storage time with a cathode (curve a) or without a cathode (curve b) in the electrolyte. Lithium loss is greater when a cathode is present. This is explained by the following equations:

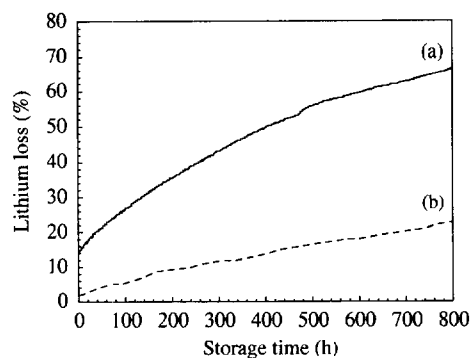
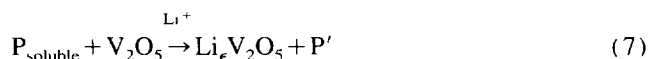


Fig. 5 Evolution of the lithium loss (%) vs storage time: (a) with V<sub>2</sub>O<sub>5</sub> cathode, and (b) without V<sub>2</sub>O<sub>5</sub> cathode.



During its electro-insertion in the carbon, lithium reacts with the electrolyte in order to generate the passivating layer (Eq. (5)). The layer partially dissolves in the electrolyte and the resulting soluble species might be oxidized by the cathode (Eqs. (6) and (7)). Therefore, the saturation degree of electrolyte in soluble species is not respected, leading to an extra dissolution of the passivating layer and a dramatic enhancement of the lithium consumption.

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