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# In situ TEM study of the interface carbon/electrolyte

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## Abstract

The carbon/electrolyte interface was characterized during galvanostatic cycling at different current densities by means of impedance spectroscopy, semi-in situ transmission microscopy and Fourier-transform infrared spectroscopy (FT-IR). These techniques, carried-out in an inert atmosphere, showed that the formation rate strongly influences both the chemical nature and thickness of this interface; its growth will be detailed using a rate corresponding to the intercalation of one lithium in 20 h. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Carbon; Passivation; Transmission microscopy; 3-Electrode

## 1. Introduction

Carbons have been used as negative electrodes in Li-ion batteries for more than 10 years. During the first discharge of a C/Li or the first charge of a Li-ion battery, the carbon is covered with a passivating layer (called SEI). Numerous groups have been working on this topic [1–5]. For example, Aurbach et al. studied the electrochemical intercalation of lithium into carbon anodes using various combinations of solvents, salts and additives. Using Fourier-transform infrared spectroscopy (FT-IR), they concluded that the formed passivating layers were essentially made of  $(\text{ROCO}_2\text{Li})_2$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{Li}_2\text{O}$ ,  $\text{LiOH}$ ,  $\text{LiF}$ ,  $\text{ROLi}$ , ... depending on the electrolyte composition. Later, Geniès [6] considered the formation of polycarbonate resins and poly(ethylene oxide). Others groups [7–9] used transmission electron microscopy (TEM), FT-IR and electrochemical impedance spectroscopy (EIS) to study the evolution of the film upon the first cycle. Despite these papers, characteristics of the passivating layer are not yet clearly defined. The main reason is that most studies were carried out in air, while it is well known that some chemical components of the SEI are unstable in this atmosphere.

In order to alleviate this difficulty, we performed TEM observations during the first cycle, by means of a home-designed sample holder that enables sample investigation without any exposure to air, coupled with both AC-impedance and FT-IR measurements. From these three techniques we

followed, upon its formation, the evolution of SEI chemical/physical parameters, such as resistance, thickness, composition and thermal stability as a function of the current density used. We succeeded in visualizing the dual (organic and inorganic) natures of the passivating layer as well as their evolution upon cycling.

## 2. Experimental

The experiments were carried out using Swagelok<sup>TM</sup> cells, with metal lithium as negative electrode and carbon Super P powder (SP, MMM Carbon, Belgium) as positive electrode. The choice of this carbon was motivated by the particle size (between 500 and 1000 Å), which is easily observed by TEM. The electrolyte used was  $\text{LiPF}_6$  (1 M) in EC:DMC (1:1, w/w).

All observations were made in the charged state (e.g. delithiated). The study consists in lithiating the carbon to 0.02 V, and then charging it to 3 V (versus  $\text{Li}^+/\text{Li}$ ). TEM observations were performed with a Philips CM12 under a high tension of 100 kV. The samples were prepared in the glove box and transferred to the microscope in a hermetic sample-holder that prevents sample exposure to air. The FT-IR observations were made on a Nicolet 510. The pellets, made using a few milligrams of carbon powder in 200 mg of KBr in the glove box, were loaded into an IR hermetic heat-chamber, and then transferred to the spectrometer for observation under argon flow at temperatures ranging from 20 to 400°C. The AC impedance measurements were carried out using Autolab PGSTAT 20 impedance analyzer. Impedance

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spectra were potentiostatically measured by applying a 5 mV AC-voltage over the frequency ranging from 1 mHz to 50 mHz.

### 3. Results

The carbon formation cycle was performed at 20°C, using different current densities, and the resulting samples separately investigated by EIS, TEM and FT-IR measurements.

#### 3.1. Electrochemical impedance spectroscopy

To determine the current density influence on the carbon/electrolyte interface, EIS experiments were performed in a 3-electrode cell at 20°C, upon the first cycle only at a rate of one lithium in 20 h ( $j_1 = 0.312 \mu\text{A}\cdot\text{cm}^{-2}$ ) and of one lithium in 5 h ( $j_2 = 1.248 \mu\text{A}\cdot\text{cm}^{-2}$ ) with a data acquisition every hour and a half, respectively.

##### 3.1.1. $j_1 = 0.312 \mu\text{A}\cdot\text{cm}^{-2}$

The impedance diagram is composed of two depressed semi-circles in the high-mid frequency range and two others in the low frequency range. A comparison between the Nyquist plots before and after one cycle enables to deduce that the second semi-circle is most likely representative of the passivating layer. Each diagram was fitted with an equivalent circuit, and the  $R_2$  and  $C_2$  values corresponding to the chemical/physical characteristics of the SEI were extracted from the modeling (Fig. 1). During the discharge, the  $R_2$  value increases to  $x = 0.5$  then decreases to  $x = 0.85$ , and increases again to  $x_{\text{max}}$ . We also noted that, at the beginning of discharge, the relaxation frequency ( $f$ ) of this loop rapidly decreases to  $x = 0.4$  and slowly after  $x = 0.85$ . Interestingly, during oxidation the  $R_2$  value continuously decreases while the relaxation frequency remains constant.

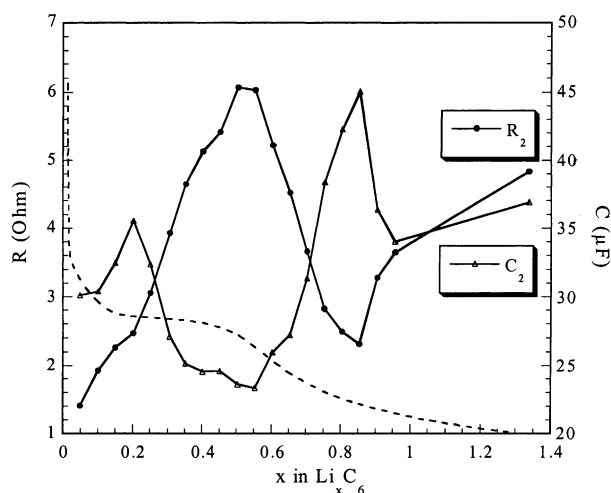


Fig. 1. Evolution of  $R_2$  and  $C_2$  upon the first discharge at a current density  $j_1 = 0.312 \mu\text{A}\cdot\text{cm}^{-2}$  (dotted line is the discharge curve).

##### 3.1.2. $j_2 = 1.248 \mu\text{A}\cdot\text{cm}^{-2}$

At this rate, Nyquist plots are nearly similar except for one instead of two semi-circles in the low frequency range. As previously, we assume that the second high-mid frequency semi-circle is due to the passivating layer. After modelisation, we obtained the  $R_2$  and  $C_2$  values, which evolved upon charge and discharge in the same way as previously described for the  $j_1$  rate. Nevertheless,  $f$  more rapidly reaches its minimum value (1100 Hz) than previously but, as before, remains constant afterwards.

#### 3.2. Fourier-transform infrared spectroscopy

We followed the formation of the passivating layer with  $j_1$  by discharging the carbonaceous powder at different depths ( $x = 0.1, 0.3, 0.5, 0.7, 0.9$  and fully discharge) and charging up to 3 V (versus  $\text{Li}^+/\text{Li}$ ). For  $j_2 = 1.248 \mu\text{A}\cdot\text{cm}^{-2}$ ,  $j_3 = 3.12 \mu\text{A}\cdot\text{cm}^{-2}$  and  $j_4 = 12.48 \mu\text{A}\cdot\text{cm}^{-2}$ , observations were made after one cycle. The IR spectra mainly consist of two sets of bands characteristic of  $\text{Li}_2\text{CO}_3$  and lithium alkylcarbonates from  $x = 0.9$ , consistent with the disappearance of the latter as the sample temperature is raised to 150°C. For the current densities  $j_2$  and  $j_3$ , we essentially observed the presence of  $\text{Li}_2\text{CO}_3$  but no lithium alkylcarbonates, and for  $j_4$ ,  $\text{Li}_2\text{CO}_3$  was still detected with the most important compounds being polycarbonate resins (consistent with other findings [5]), which disappeared as the sample temperature reached 200°C.

#### 3.3. Transmission electronic microscopy

The evolution of the passivation film thickness at  $j_1$  current density is shown on Fig. 2. This film (essentially constituted of  $\text{Li}_2\text{CO}_3$  as deduced by IR measurement) grows up to  $x = 0.5$  to reach 1.9 nm (Fig. 3), and remains constant up to  $x = 0.9$ , the lithium content beyond which

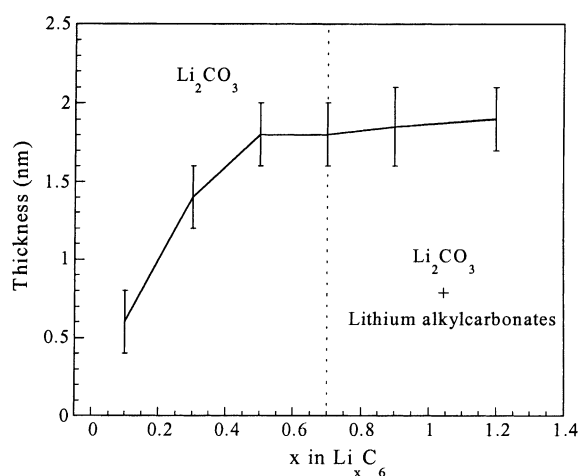


Fig. 2. Thickness evolution of  $\text{Li}_2\text{CO}_3$  upon the first cycle at a current density  $j_1 = 0.312 \mu\text{A}\cdot\text{cm}^{-2}$  and most important SEI compounds.

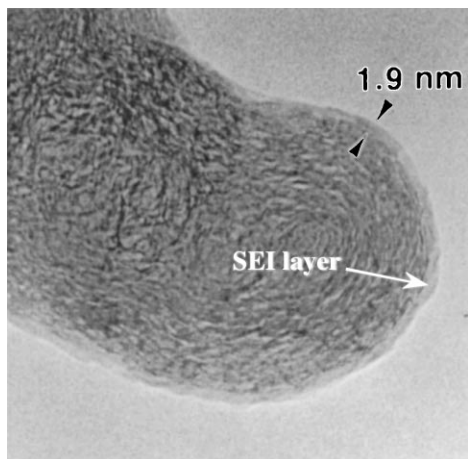


Fig. 3. TEM micrograph of carbon SP after one cycle at a current density  $j_1 = 0.312 \mu\text{A}\cdot\text{cm}^{-2}$ .

lithium alkylcarbonates appear. Because these organic compounds react under the beam (temperature near  $150^\circ\text{C}$ ), it was difficult to measure their thickness prior to their evaporation. Occasionally it could be estimated at about 2 nm. The thickness of this SEI layer (without lithium alkylcarbonates) seems to be independent of the current density, at least at  $20^\circ\text{C}$ , but evolves as the temperatures change, as we will report elsewhere.

#### 4. Discussion

As the electrochemical reduction of carbon by Li proceeds at a rate of  $j_1$ , three different domains of the discharge curve can be distinguished. At the beginning of discharge and deduced from FT-IR there is formation of  $\text{Li}_2\text{CO}_3$  that results in a SEI layer, whose thickness increases up to  $x = 0.5$ , and whose nature does not change between  $x = 0.5$  and  $0.85$ . At the end of discharge, lithium alkylcarbonates are formed leading to a thickness increase in the SEI layer as observed by TEM measurements. Interestingly, we note that such organic species are not found when high current densities are used. These observations are totally consistent with the AC-impedance results as explained below. The resistance and capacitance expression for a SEI layer are  $R = \rho e/S$  and  $C = \varepsilon S/e$  (where  $e$ : thickness,  $S$ : surface, with both  $\rho$  and  $\varepsilon$  being resistivity and permittivity of the SEI), respectively. From combination of both, we can deduce the relaxation frequency expression:  $f = 1/(2\pi RC) = 1/(2\pi\rho\varepsilon)$ , which permits to indirectly follow chemical/physical variations of the SEI layer. On the basis of these relations one could expect that an increase in resistivity would result in a frequency decrease, and similarly, a thickness increase would result in a resistance increase.

Thus, it is quite consistent that the growth of an insulating layer ( $\text{Li}_2\text{CO}_3$  or lithium alkylcarbonates) induces a decrease in the frequency and a resistance increase in the

first and third part of the C/Li cells discharge, as experimentally observed. In the middle part, both SEI nature and thickness remain constant, which implies that  $f$  should be constant. But we note that the resistance decreases. A possible explanation for this observation is the formation of ionic conducting paths through the passivating layer that will lead to a surface increase, and hence, a resistance decrease.

At higher current density ( $j_2$ ), the processes are the same, except for the absence of lithium alkylcarbonates at the end of discharge that could explain why the  $R_2$  value levels off rather than increases as previously observed for  $j_1$ . Finally the unaltered value of the  $f$  constant at the end of discharge is also consistent with the fact that the SEI layer is solely composed of  $\text{Li}_2\text{CO}_3$ .

Now turning to the oxidation process (i.e. charge), for both current densities ( $j_1$  and  $j_2$ ) the relaxation frequency remains constant implying no evolution of the SEI. As before, we believe that the creation of conducting paths through the SEI layer (e.g. modifying the surface) can explain the observed resistance decrease.

A final point worth stressing is that the SEI components are influenced by the current density. Indeed, polycarbonate resins become the most important compound at the highest rates instead of  $\text{Li}_2\text{CO}_3$  at lower rates with, for the lowest, the formation of lithium alkylcarbonates at the end of discharge.

#### 5. Conclusion

Using EIS, semi-in situ FT-IR and TEM measurements performed in a controlled atmosphere, we reported the room temperature formation rate influence upon the chemical nature of the SEI layer forming at the carbonaceous electrode. For a low current density, we showed the different steps in the passivating layer formation with apparition of  $\text{Li}_2\text{CO}_3$  from the beginning and apparition of lithium alkylcarbonates at the end of discharge. The importance of the formation cycles on the capacity retention of the carbonaceous electrode material is presently determinant.

#### References

- [1] Y.-G. Ryu, S.-I. Pyun, J. Electroanal. Chem. 433 (1997) 97.
- [2] D. Aurbach, B. Markovsky, A. Shechter, Y. Ein-Eli, H. Cohen, J. Electrochem. Soc. 143 (1996) 3809.
- [3] S. Mori, H. Asahina, H. Suzuki, A. Yonei, K. Yokoto, J. Power Sources 68 (1997) 59.
- [4] C.R. Yang, Y.Y. Wang, C.C. Wan, J. Power Sources 72 (1998) 66.
- [5] R. Yazami, S. Genies, Denki Kagaku 66 (1998) 1293.
- [6] S. Genies, R. Yazami, J. Garden, J.C. Frison, Synth. Met. 93 (1998) 77.
- [7] A. Najji, J. Ghanbaja, P. Willmann, D. Billaud, J. Power Sources 81/82 (1999) 207.
- [8] M.D. Levi, D. Aurbach, J. Phys. Chem. B 101 (1997) 4630.
- [9] A. Funabiki, M. Inaba, Z. Ogumi, S.-I. Yuasa, J. Otsuji, A. Tasaka, J. Electrochem. Soc. 145 (1998) 172.