

# Effect of polysulfide-containing electrolyte on the film formation of the negative electrode

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## Abstract

The improvement of cycling behaviour and self discharge of lithium–carbon intercalation electrodes as well as metallic lithium electrodes in polysulfide-containing propylene carbonate-based electrolyte is demonstrated. Cyclic voltammetry of  $\text{LiC}_n$  electrodes indicates a more complex reductive behaviour only during the first charge/discharge cycle than in an additive-free electrolyte. The products of the polysulfide reduction seem to improve the properties and the quality of the film that is also produced in the absence of  $\text{S}_x^{2-}$  and promotes its formation on Li or  $\text{LiC}_n$ , respectively. The improvement may be related to thinner polymer–electrolyte interface layers (PEI layers) and/or a larger amount of insulated inorganic compounds in the PEI layers. © 1997 Elsevier Science S.A.

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## 1. Introduction

Due to safety problems of the metallic lithium electrodes alternative materials came into the center of interest in lithium batteries. Lithium–carbon intercalation compounds were found to be the most interesting and promising materials for the negative electrode of a lithium battery.

A serious drawback of the  $\text{LiC}_n$  system is the large loss of capacity during storage due to self discharge. The protective layer on the surface consisting of reduction products of the organic electrolyte during cycling [1] does not work as efficiently as the films formed on metallic lithium electrodes. Attempts have been made to cover the surfaces of the carbon electrode with organic or inorganic coatings such as poly-2-vinylpyridine (P2VP) or  $\text{TiO}_2$  before the electrolyte reduction occurs [2].

Another disadvantage of carbon black or graphite is the need for a binder that reduces the energy density of the electrode and influences its electrochemical behaviour. Therefore, turbostratic carbon materials such as graphitized carbon fibres have been tested and were found to be a good intercalation material

There have been considerable research activities in improving the electrolyte systems for rechargeable lithium

batteries by the addition of small amounts of organic or inorganic additives [3–6]. These additives improve the properties of the surface films on the electrodes and work in both, the metallic lithium and the  $\text{LiC}_n$  system. Organic surface active additives like *t*-decaline improve the cycling behaviour of lithium due to a smoother deposition morphology whereas film-forming additives such as  $\text{CO}_2$  and  $\text{N}_2\text{O}$  improve the metallic lithium deposition and the self discharge of lithium–carbon compounds [6,7].

Unfortunately, the nature of the film is still unknown and much effort has been devoted for its elucidation [8,9]. In FT-IR spectra different compounds have been found depending on the electrolyte system. In propylene carbonate solvent alkoxycarbonates  $\text{ROCO}_2\text{Li}$  have been determined on the surface of the film. The insertion of inorganic salts such as  $\text{Li}_2\text{CO}_3$  in the film can just be postulated due to X-ray photoelectron spectroscopy (XPS) studies [9] and the influence of inorganic additives on the electrochemical behaviour is discussed in different models [10,11].

## 2. Experimental

The electrolyte was purified by standard procedures. The typical water content of the 0.5 M propylene carbonate (PC) /  $\text{LiClO}_4$  electrolyte was less than 50 ppm.  $\text{S}_x^{2-}$  was prepared

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in situ by electrochemical reduction of a sulfur electrode (including 20% graphite as a conductive binder) placed in the electrolyte solution. The concentration of  $S_1^{2-}$  in the electrolyte was determined to be  $3 \times 10^{-4}$  mol/l. Less than  $10^{-4}$  mol/l had no clear effect. Higher concentration of the electrolyte did not increase the beneficial effect of the polysulfide. The water content of the PC/LiClO<sub>4</sub>/S<sub>1</sub><sup>2-</sup> electrolyte was less than 60 ppm.

Carbon fibers (P 100, Amoco Union Carbide) were cut with a scalpel and fitted between two nickel plates for electrical contact. Each carbon fibre bundle electrode had a weight of 1 mg inside the electrolyte which was determined with a Teflon distance holder. The electrodes were placed in a Pyrex glass cell with a large excess of electrolyte and with bulk lithium counter electrodes. The nickel electrodes for cycling and deposition of metallic lithium were cleaned and dried in vacuum prior to be put into the Pyrex glass cells. These studies were performed in open configuration without any separator and force on lithium.

Standard cycling conditions were  $I_c = I_d = 1$  mA/cm<sup>2</sup> with  $Q = 2.7$  C/cm<sup>2</sup> on nickel substrates and  $I_c = I_d = 50$   $\mu$ A/mg C on LiC<sub>n</sub> electrodes. Cyclic voltammetry was carried out with an ECI 1286 potentiostat. Impedance spectra were obtained by using a FRA 1255 connectet to an ECI 1286 in the potentiostatic mode. The measured potentials were 3.0 and 2.0 V, and in 0.1 V steps from 1.0 to 0.0 V during intercalation in the frequency range from 65 kHz to 0.1 Hz. During de-intercalation the same potentials and frequencies were used. All impedance spectra were measured near equilibrium after relaxation (current  $\leq 1$   $\mu$ A/mg C) to minimize the current dependencies on the complex resistances. All potentials were measured versus Li/Li<sup>+</sup>.

### 3. Results and discussion

#### 3.1. Lithium-carbon electrodes

Fig. 1 shows the beneficial effect of S<sub>1</sub><sup>2-</sup> on the cycling behaviour of LiC<sub>n</sub> electrodes.

The capacity losses per cycle ( $L_n$ ) over a large number of cycles ( $L_1 + L_2 + \dots + L_n$ ) showed that the additive caused a higher capacity loss during the first intercalation/de-intercalation cycle but during the following cycles the irreversible capacity loss is drastically decreased as compared with the unmodified electrolyte and with the CO<sub>2</sub>-containing electrolyte, respectively.

The self discharge of fully charged lithium carbon electrodes was found to be lower in the S<sub>1</sub><sup>2-</sup>-containing electrolyte in the first cycle. During the second intercalation/de-intercalation cycle a positive effect can be observed, even if the self-discharge behaviour of the electrodes in the unmodified electrolyte is improved due to the formation of a protective layer during the first cycle. The charge recoveries were found to be nearly 10% higher than in PC/LiClO<sub>4</sub>. The intercalation capacity of the electrode was not influenced by the

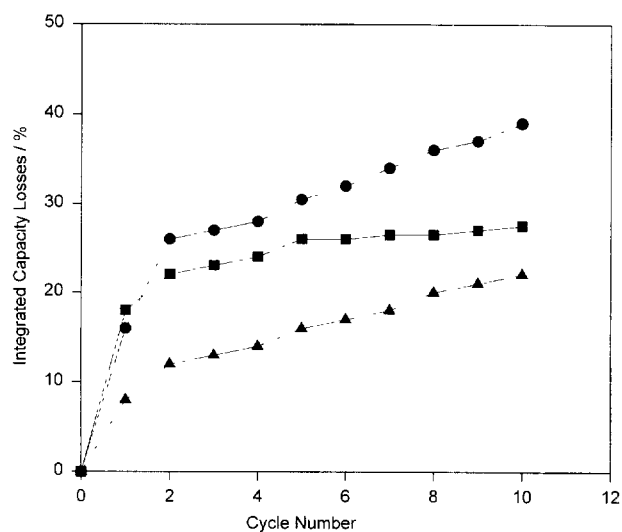


Fig. 1 Integrated capacity losses of LiC<sub>n</sub> electrodes in different propylene carbonate-based electrolytes: (●) PC/LiClO<sub>4</sub>, (■) PC/LiClO<sub>4</sub>/S<sub>1</sub><sup>2-</sup>, and (▲) PC/LiClO<sub>4</sub>/CO<sub>2</sub>.

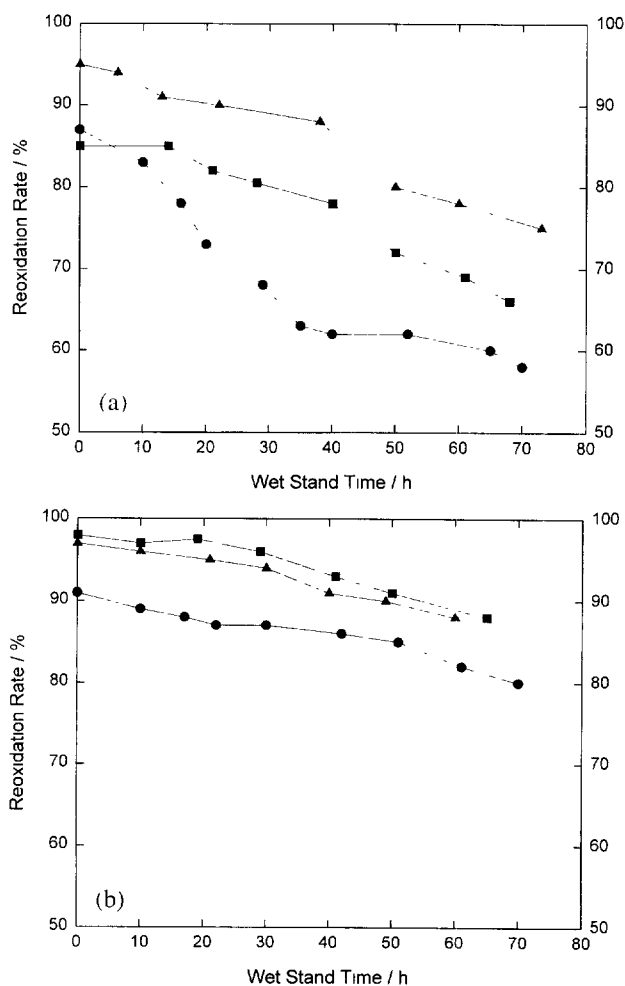


Fig. 2 Self-discharge behaviour of LiC<sub>n</sub> electrodes in different propylene carbonate-based electrolytes during the first two cycles: (a) first cycle, and (b) second cycle: (●) PC/LiClO<sub>4</sub>, (■) PC/LiClO<sub>4</sub>/S<sub>1</sub><sup>2-</sup>, (▲) PC/LiClO<sub>4</sub>/CO<sub>2</sub>.

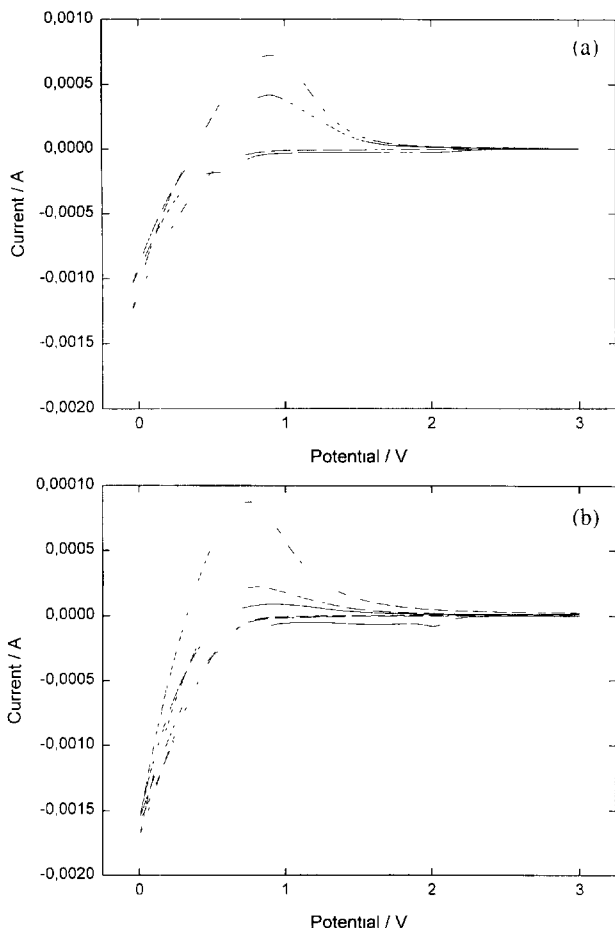


Fig. 3. Cyclic voltammograms of LiC<sub>n</sub> electrodes at 15 mV/s, (a) PC/LiClO<sub>4</sub>, and (b) PC/LiClO<sub>4</sub>/S<sub>i</sub><sup>2-</sup>, (—) first cycle; (---) second cycle, and (- - -) tenth cycle.

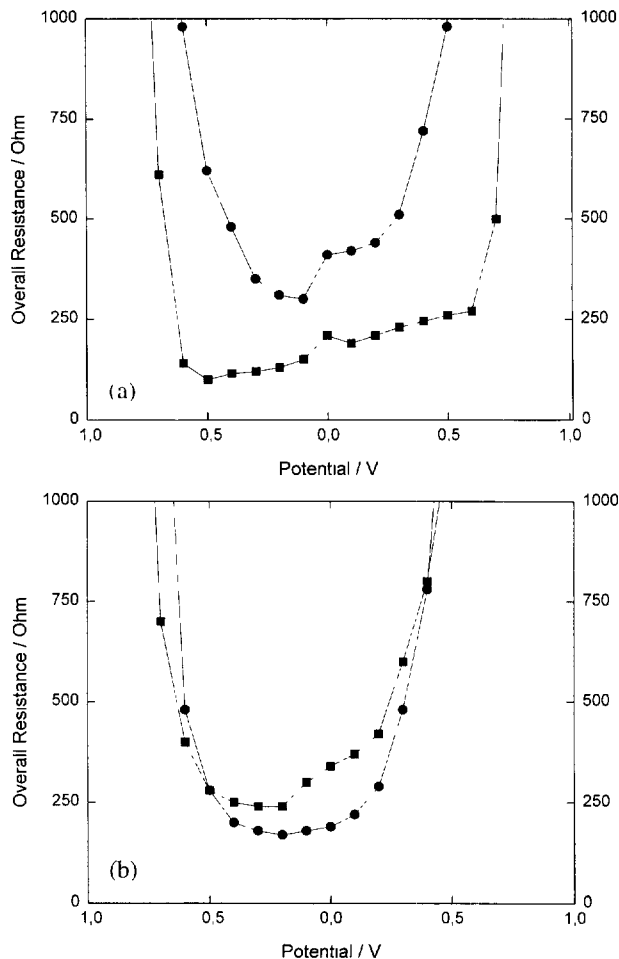


Fig. 4. Overall resistance of LiC<sub>n</sub> electrodes vs. electrode potential during the first two cycles, (a) PC/LiClO<sub>4</sub>, and (b) PC/LiClO<sub>4</sub>/S<sub>i</sub><sup>2-</sup>; (■) first cycle, and (●) second cycle.

additive. In comparison the CO<sub>2</sub>-containing electrolyte showed a lower self discharge in the first cycle and even a slightly higher self discharge in the second cycle than the polysulfide-containing electrolyte, see Fig. 2.

Cyclic voltammetry and impedance spectroscopy help to understand the improved cycling behaviour, see Fig. 3.

In the cyclic voltammogram of the polysulfide-containing electrolyte at least three reductive parts are observed during the first cycle. The intercalation of lithium ( $U \leq 0.5-0.0$  V) as well as the electrolyte reduction (0.6 V) can be observed in unmodified and in S<sub>i</sub><sup>2-</sup>-containing electrolyte. A difference occurs in PC/LiClO<sub>4</sub>/S<sub>i</sub><sup>2-</sup> at a potential of 2 V. Here the reduction of the additive S<sub>i</sub><sup>2-</sup> occurs. Whereas in the unmodified electrolyte during the second cycle an almost reversible intercalation process takes place, the reversibility in the S<sub>i</sub><sup>2-</sup> electrolyte is rather poor but constantly increasing with cycle number.

Fig. 4(a) and (b) shows the overall resistances of LiC<sub>n</sub> electrodes in PC/LiClO<sub>4</sub> and PC/LiClO<sub>4</sub>/S<sub>i</sub><sup>2-</sup> in the first two cycles versus the electrode potentials. The overall resistance consists of the film resistance  $R_b$  and the charge-transfer resistance  $R_{ct}$  as demonstrated in Fig. 5 [12].

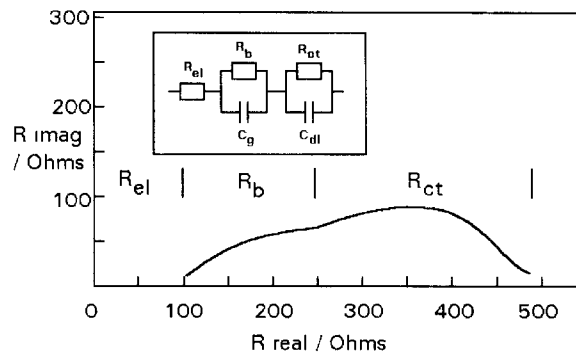


Fig. 5. Example of a measured impedance spectrum and the proposed equivalent circuit.

This overall resistance in the polysulfide-containing electrolyte was found to be higher during the first cycle compared with that in the unmodified electrolyte. During the second cycle the overall resistances at corresponding potentials were lower whereas in the additive-free electrolyte higher overall resistances are noticed. This corresponds to the fact that films in the polysulfide-containing electrolyte are mainly formed during the first cycle. In the absence of the additive further irreversible capacity losses occurs.

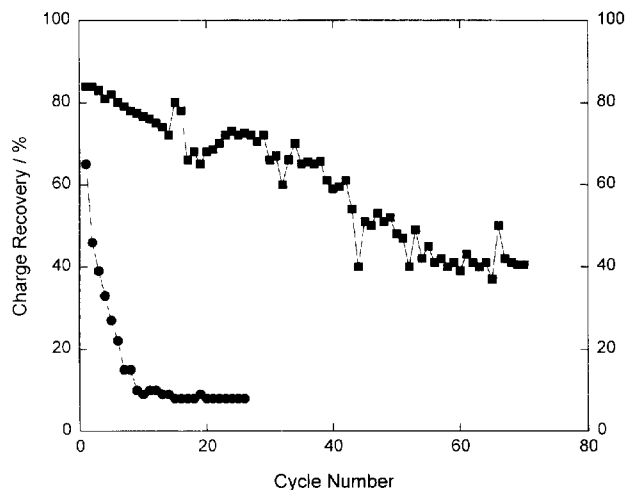


Fig. 6. Cycling of lithium on nickel substrate (●) PC/LiClO<sub>4</sub>, and (■) PC/LiClO<sub>4</sub>/S<sub>i</sub><sup>2-</sup>.

### 3.2. Metallic lithium electrodes

The effect of S<sub>i</sub><sup>2-</sup> on the cycling behaviour of metallic lithium on inert nickel substrate in comparison with the pure PC/LiClO<sub>4</sub> electrolyte is shown in Fig. 6.

Under these conditions lithium cannot be cycled in PC/LiClO<sub>4</sub> because the growth dendrites of the lithium deposition leads to a high loss of active material. This can also be observed macroscopically. Larger particles of the deposition of dendrites tend to loose contact with smaller ones and precipitate on the bottom of the cell. The addition of S<sub>i</sub><sup>2-</sup> to the electrolyte improves the cycling behaviour. A macroscopically less deposition of dendrites and less inactive lithium on the bottom of the cell are seen.

The effect of S<sub>i</sub><sup>2-</sup> on the morphology of the lithium deposition on inert nickel electrodes was studied with scanning electron microscopy (SEM), see Fig. 7.

The lithium deposition from PC/LiClO<sub>4</sub> leads to highly dendritic structures. The cycle efficiency of lithium cannot be high due to the corrosion and the high surface area of the deposited lithium. The growth dendrites leads to isolated lithium that loses electrical contact with the electrode. In contrast, the deposition from PC/LiClO<sub>4</sub>/S<sub>i</sub><sup>2-</sup> shows a more compact surface. The particles are of the same size as of the deposits from the additive-free electrolyte but are fitted together. The surface does not consist of dendrites but is smooth.

## 4. Conclusions

The addition of S<sub>i</sub><sup>2-</sup> to a PC/LiClO<sub>4</sub> electrolyte improves both the lithium–carbon intercalation electrode and metallic lithium electrode. These beneficial effects are related to the formation of protective layers on the electrodes and their improved behaviour, respectively. LiC<sub>n</sub> electrodes show a lower self discharge and a better long-term cycleability due to less corrosion compared with the additive-free electrolyte.

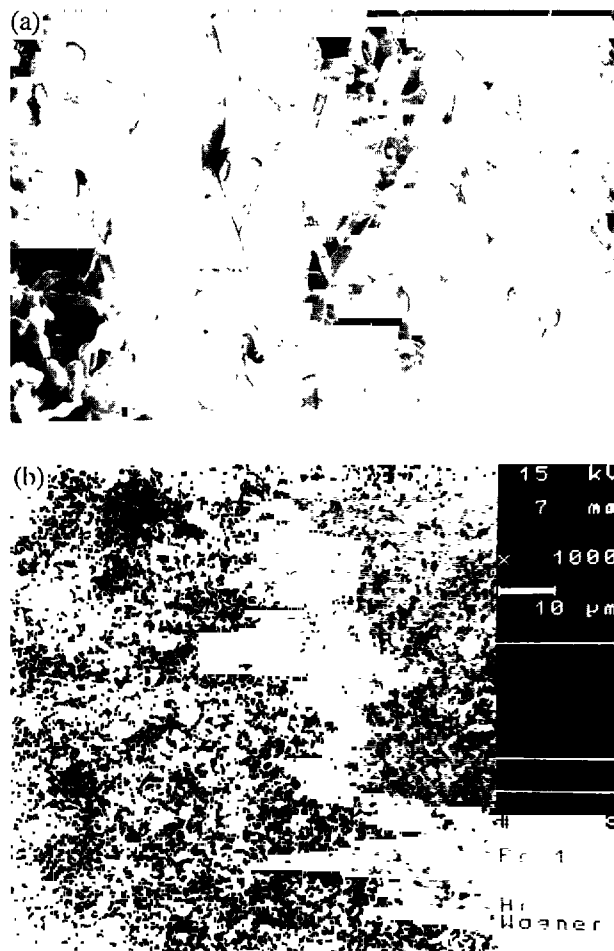


Fig. 7. SEM micrographs of lithium deposited on nickel substrate: (a) PC/LiClO<sub>4</sub>, and (b) PC/LiClO<sub>4</sub>/S<sub>i</sub><sup>2-</sup>.

Lithium metal electrodes show a highly improved cycleability due to a less dendritic but smoother lithium deposition. Unfortunately, the mechanical aspects of the film formation on lithium–carbon electrodes and the smoother lithium deposition on lithium–metal electrodes are not yet clear and further examination of these systems has to be done.

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