

Filming mechanism of lithium–carbon anodes in organic and inorganic electrolytes

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Abstract

To study the filming mechanism of graphite-based LiC_n electrodes, electrochemical reduction of graphite materials was carried out in 1 M LiClO_4 /ethylene carbonate (EC)–1,2-dimethoxyethane (DME) (1:1 by volume). Due to film forming a peak at potentials around 0.8 V versus Li/Li^+ was observed during the first reduction. The reversibility of this peak was examined by cyclic voltammetry; in addition, the crystal expansion/contraction was checked by means of dilatometry. The results indicate that ternary solvated graphite-intercalation compounds (GICs) were formed at those potentials leading to drastic expansion of the graphite matrix (> 150%). These $\text{Li}(\text{EC})_{y,1}(\text{DME})_{z,2}\text{C}_n$ -GICs decompose and build up a protective layer on the graphite that prevents further solvent co-intercalation. The beneficial effect of EC-containing electrolytes on the stability of lithium–carbon anodes seems to be related to inorganic films formed via secondary chemical decomposition of electrochemically formed EC-GICs. The key-role of inorganic films is also demonstrated by the fact that inorganic additives, such as carbon dioxide, suppress the formation of solvated GICs. Furthermore, it can be seen that lithium–carbon negatives can even be operated in inorganic electrolytes such as SO_2 and SOCl_2 .

Keywords: Carbon filming; Dilatometry; Inorganic electrolyte additives; Inorganic protective films; Lithium–carbon anodes; Lithium–graphite intercalation compounds; Solvated graphite-intercalation compounds

1. Introduction

Long-term operation of lithium, lithium alloy and lithium–carbon negatives in liquid organic, polymer organic and liquid inorganic electrolytes requires ‘filming’ of the electrode by electronically insulating permselective solid electrolyte membranes being permeable to Li^+ cations but impermeable to any electrolyte component which is not chemically stable versus the negative electrode.

Reductive decomposition of electrolytes in contact with lithium–carbon negatives is not simply a surface reaction but a complex three-dimensional problem. This is caused by solvated graphite-intercalation compounds (GICs)– $\text{Li}(\text{solv})_y\text{C}_n$ [1] which are thermodynamically favoured over the binary compounds LiC_n , as long as the content of lithium is relatively low (critical C/Li ratio typically ‘ n ’ \geq ~18) and hence, coulombic interaction between the small Li^+ cations and the balancing

negative charge smeared over large C_n^- anions is weak and moreover, space to accommodate solvent molecules is still available. Graphitic carbons fully charged with lithium, i.e., ‘ n ’ in LiC_n is about 6, do not solvate in standard organic ‘battery’ solvents.

The well-established way to avoid excessive formation of ternary compounds $\text{Li}(\text{solv})_y\text{C}_n$ is to choose poorly graphitic matrix carbons, characterized by: (i) fairly amorphous areas embedding and crosslinking more crystalline ones and/or by (ii) twisted and wrinkled packages of carbon layers resisting, or at least hindering very much, the drastic swelling related with solvation (typically ~200%).

As rate capabilities and maximum lithium acceptance of electrodes made from poorly crystalline carbons are worse than those of electrodes made from small particle-size crystalline graphites, there is a search for electrolytes (e.g., based on ethylene carbonate (EC) [2]) or electrolyte additives (e.g., crown ethers [3]) preventing or retarding the formation of ternary graphite compounds $\text{Li}(\text{solv})_y\text{C}_n$. Indeed, a highly effective filming of the

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prismatic faces of graphite crystals, with membranes permeable only to Li^+ cations, should render possible the operation of lithium-graphite electrodes in almost any kind of Li^+ electrolyte.

2. Experimental

The formation of films on various carbon samples was examined by means of cyclic voltammetry. Carbon was used as a cathode in a Pyrex glass cell (large excess

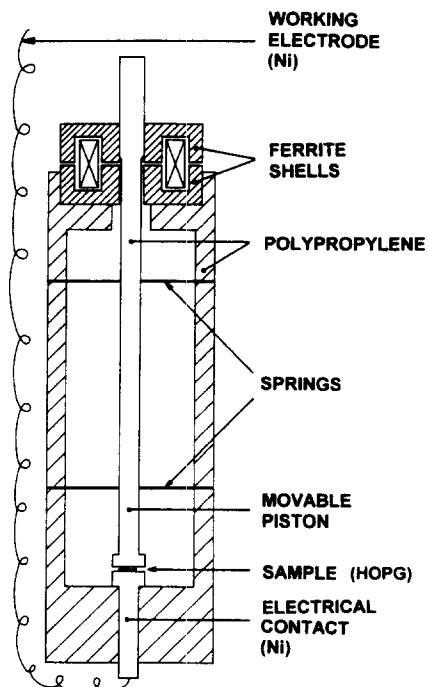


Fig. 1. Setup of the dilatometer.

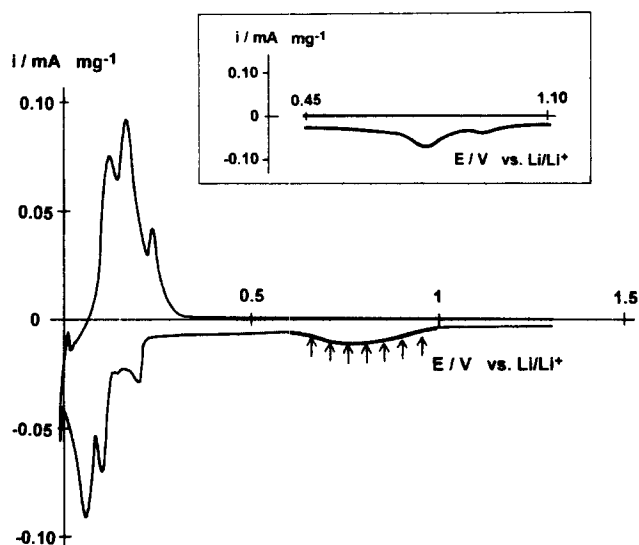


Fig. 2. First voltammetric cycle of artificial graphite (Alfa 00641) in EC-DME(50:50)/1 M LiClO_4 at low sweep rate, $\nu = 0.01 \text{ mV s}^{-1}$; insert: $\nu = 0.05 \text{ mV s}^{-1}$.

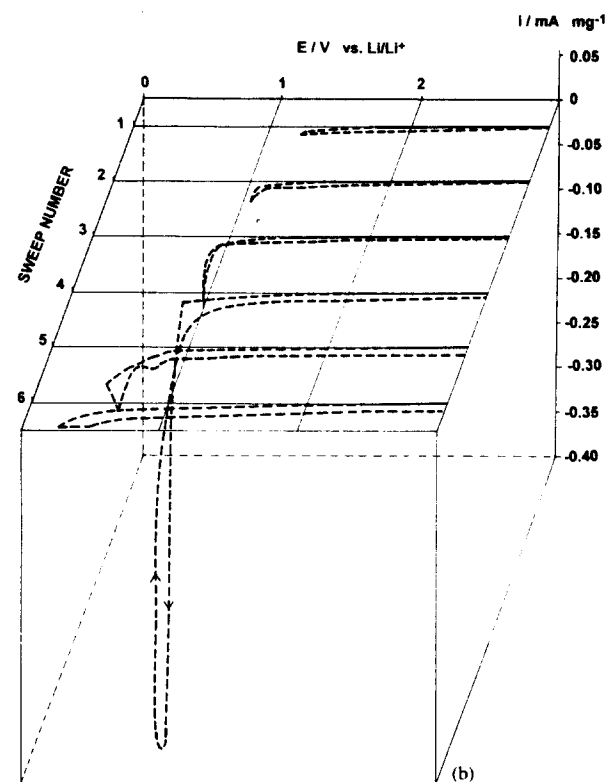
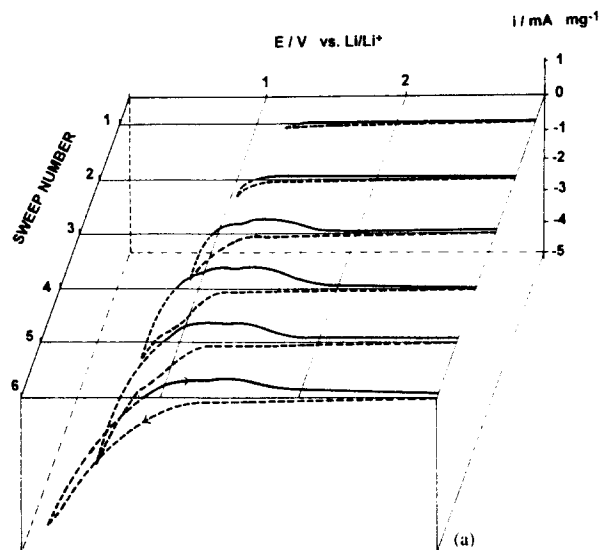


Fig. 3. Series of consecutive voltammograms, each series taken with only one graphite electrode (Alfa 00641) in EC-DME(50:50)/1 M LiClO_4 : (a) $\nu = 10 \text{ mV s}^{-1}$, and (b) $\nu = 0.1 \text{ mV s}^{-1}$. Note that at 0.1 mV s^{-1} there is a strong irreversible reduction ('filming') in sweep no. 4, the onset of this reduction is indicated in sweep no. 3, it is almost finished in sweep no. 5.

of electrolyte) with bulk lithium counter anodes. The artificial graphite cathode mix consisted of 97 wt.% artificial graphite (Alfa 00641) and 3 wt.% polytetrafluoroethylene (PTFE) binder. Highly oriented pyrolytic graphite (HOPG, Union Carbide) and mesophase pitch fibre P 100 (FMI Composites, Union Carbide) were used as-received. Solvents, electrolytes and electrodes

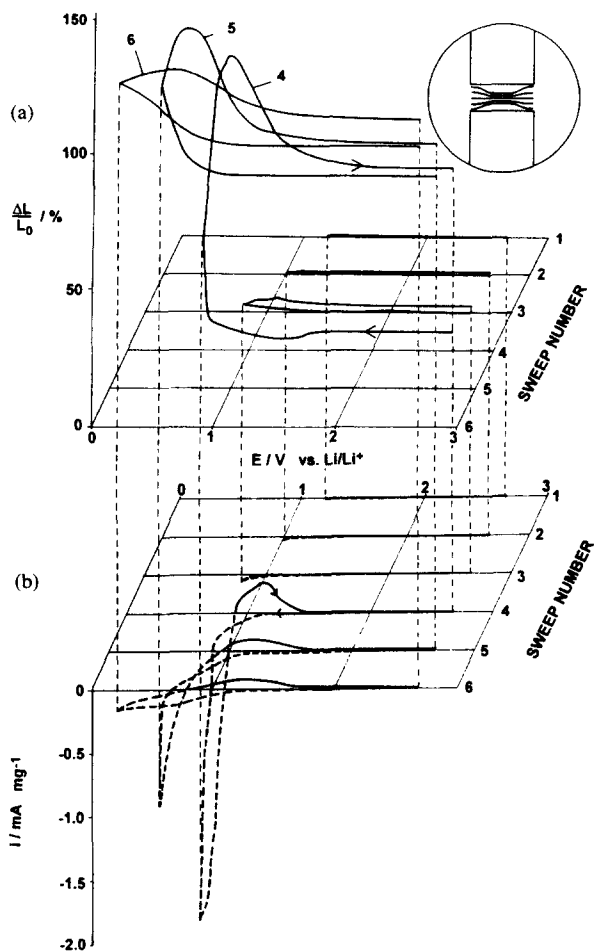


Fig. 4. Series of consecutive voltammograms and expansion recordings of the graphite sample (highly oriented pyrolytic graphite (HOPG)) in EC–DME(50:50)/1 M LiClO₄, $\nu=10$ mV s⁻¹: (a) expansion recordings, and (b) voltammograms. Note that in sweep no. 4 the partly reversible intercalation (of solvated Li⁺ cations) is paralleled by a very strong (~150%) expansion and followed by a partial contraction during de-intercalation; the 150% expansion does not refer to the bulk but only to the edge region of the graphite sample, see insert in Fig. 4(a).

were purified, dried and prepared using standard methods. All procedures for handling the cells and electrodes were performed in an argon-filled glove box.

The crystal expansion/contraction of HOPG was observed by means of dilatometry (Fig. 1). The recording of the crystal thickness is based on the resonance shift of an oscillator whose inductivity consists of a ferrite coil with a variable shift. The HOPG sample is placed between two parallel pistons. The upper piston transmits the crystal expansion to the upper ferrite shell. The oscillator frequency converted in voltage is plotted. A detailed description of the dilatometer is given in Ref. [4].

3. Results and discussion

An apparently irreversible peak is observed at about 1.0 to about 0.5 V versus Li/Li⁺ during the first reduction

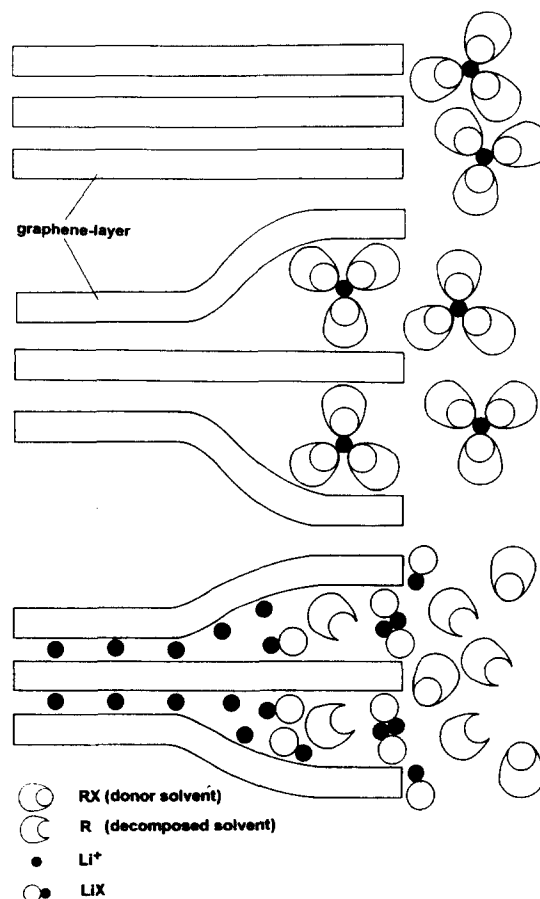


Fig. 5. Schematic illustration of the film forming mechanism via decomposition of Li(solvent)_n. Note that decomposition of GICs–Li(solvent)_n re-provides electronic sites for a further insertion of cations. As the space requirements for the accommodation of unsolvated Li⁺ ions are quite low, even ‘galleries’, which are completely filled up with electrolyte decomposition products, should still be able to take part, to some extent, in the reversible electrode reaction.

of an artificial graphite sample in EC–DME (Fig. 2). Similar peaks have been reported in the literature and the common interpretation is ‘irreversible solvent decomposition’ leading to ‘irreversible capacity’.

It has been recognized for more than twenty years [5] that reductive decomposition of propylene carbonate (PC) at graphite electrodes is in fact a secondary (chemical) reaction of PC-solvated GICs. The same is valid for EC-solvated GICs. This can be shown easily by the sweep rate dependence of voltammograms, indicating reversible intercalation/de-intercalation at higher sweep rates (related with considerable swelling of the graphite matrix, reversible potentials around +1 V versus Li/Li⁺) but mostly irreversible reduction at lower sweep rates. As the viscosity of pure EC electrolytes is too high for battery applications, mixtures of EC with low viscosity solvents such as 1,2-dimethoxyethane (DME) or diethyl carbonate (DEC) are widely used as electrolytes for graphite-based LiC_n electrodes. Figs. 3 and 4, show series of voltammograms

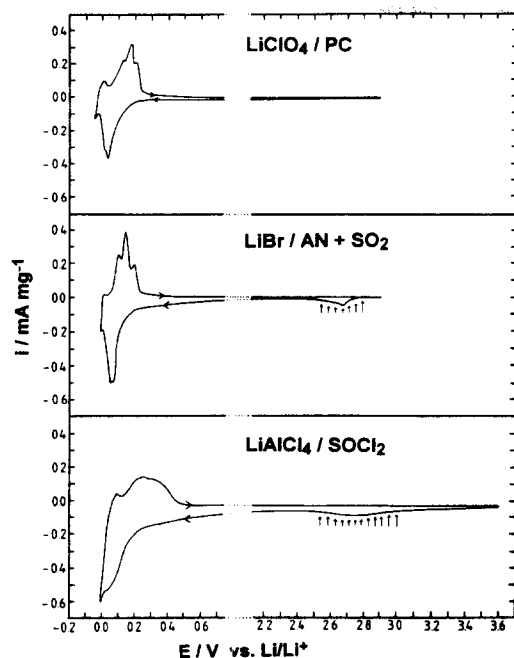


Fig. 6. Voltammograms of carbon fibre electrode (FMI, Composites-Union Carbide mesophase pitch fibre P 100), $\nu=0.05 \text{ mV s}^{-1}$: (a) PC/0.5 M LiClO_4 ; (b) SO_2 -AN/1 M LiBr, and (c) SOCl_2 /1.8 M LiAlCl_4 .

and the corresponding expansion recordings of graphite electrodes in (50:50 volume) EC-DME/ LiClO_4 .

The results presented in Figs. 3 and 4 prove clearly that (i) the reduction reaction starting at the threshold potential of about +1 V versus Li/Li^+ is the intercalation of solvated Li^+ cations and must not be interpreted in terms of formation of higher stage binary compounds LiC_n , and also that (ii) the lifetime of the ternary GICs- $\text{Li}(\text{EC})_{y1}(\text{DME})_{y2}\text{C}_n$ is rather short. Film formation obviously occurs via secondary (chemical) reduction of solvated GICs, although on the timescale of low sweep rate voltammograms (see Fig. 3(b)) this process might be mistaken as an ordinary irreversible (electrochemical) reduction of the electrolyte.

The poor recovery of charge observed during the de-intercalation of solvated GICs (Fig. 2(b)) is paralleled by a poor reversibility of the graphite lattice expansion (Fig. 2(a)). As the mobility of solvated ions in GICs is usually quite high, it may be concluded that after the intercalation/de-intercalation cycle immobile electrolyte decomposition products remain between the

graphene layers (see Fig. 5), i.e., that the permselective film is in fact penetrating into the bulk.

The exceptional stability of lithium-carbon negatives in electrolytes containing EC (which is more sensitive to reduction than PC [6]) may be related with its 'almost inorganic' character, resulting in a relatively small fraction of 'soft' organic decomposition products. Considering the diameter of the Li^+ cation, it is hard to design a solid electrolyte membrane with organic molecules. The beneficial effect of various inorganic electrolyte additives (e.g., CO_2 , N_2O , S_x^{2-} [7]) on the filming process is supporting this view. Voltammetric studies of Li^+ intercalation into graphitic carbons indicated clearly that the peaks due to intercalation of solvated Li^+ cations and subsequent solvent decomposition (see, Fig. 1, 1.0–0.5 V versus Li/Li^+) are suppressed considerably by inorganic additives, such as CO_2 .

The highly effective protection of lithium-carbon negatives by inorganic solid electrolyte membranes is also demonstrated by the fact that these electrodes, after filming, can even be operated in SO_2 - and SOCl_2 -based electrolytes (compare the almost identical voltammograms shown in Fig. 6(a)–(c)). Due to their stability against oxidation, inorganic electrolyte systems may be of advantage in '4 V' systems. Moreover, SO_2 is one of the rare examples of a lithium-compatible solvent that could be 'repaired' after cathodic decomposition by an anodic electrochemical/chemical recombination cycle [8]. Promising results have been observed in SO_2 -AN (acetonitrile) electrolytes with carbon electrodes that had been 'pre-filmed' in a PC electrolyte containing S_x^{2-} anions as the additive.

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