

Electrochemical behaviour of coated lithium–carbon electrodes

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Abstract

On lithium–carbon intercalation electrodes a thin protective layer on the electrode surface is formed during the first charge/discharge cycle. This film formation is investigated by means of impedance spectroscopy and cyclic voltammetry. Uncoated LiC_n electrodes show a continuous increase of the low frequency semicircles during the first charge/discharge cycle. The protective films can be simulated by a polymer precoating. But any coating of the electrode should influence the behaviour due to modification of the film and/or modification of the surface in general. The influence of different coatings like poly-2-vinylpyridine, poly(ethylene oxide) and TiO_2 on the electrochemical behaviour of lithium–carbon electrodes is demonstrated in propylene carbonate electrolyte. Impedance studies during charge and discharge show that the low frequency semicircles decrease due to a modification of the resistances and the capacities. Cyclic voltammograms are also clearly influenced by the coatings and demonstrate differences in the electrode kinetics and the film formation from decomposition products of the electrolyte.

Keywords: Electrodes; Lithium; Carbon; Protective layers

1. Introduction

Lithiated carbon is a most suitable substance often considered for the negative electrode in rechargeable lithium batteries [1]. Though this material shows an excellent cycling behaviour the decreasing capacity during storage, due to self-discharge reactions, is a serious drawback. The protective layer formed at the surface from reduction products of the organic electrolyte during cycling [2] does not work as efficiently as the films formed on metallic lithium electrodes [3–5]. Much effort has been devoted to improve the self-discharge behaviour by adding additives like CO_2 , N_2O or polysulfide to the electrolyte to modify the protective layer formed [6,7]. Another way to solve the problem is the pre-treatment of the electrode by coating. This layer should only be conductive for Li^+ ions, and not for electrons or solvent molecules, to prevent electrode corrosion due to solvent co-intercalation and direct interaction between the solvent and electrode or the stored lithium. Precoating the carbon electrodes should simulate as well as modify the original protective layer. In this paper we report on the electrochemical behaviour of precoated carbon electrodes in comparison with untreated ones in a propylene carbonate electrolyte.

2. Experimental

The electrolyte was purified by standard procedures. The typical water content of the 0.5 M propylene carbonate (PC)/ LiClO_4 electrolyte was 50 ppm. Carbon fibres (P 100, Amoco Union Carbide and GY 70, Celanese) were dip-coated with solutions of poly-2-vinylpyridine (P2VP), poly(ethylene oxide) (PEO) or isopropyltitanate (IPT) in organic solvents. The P2VP was reduced in a previous reaction with dilithium anthracene in tetrahydrofuran (THF), forming a networked structure insoluble in organic solvents. IPT was hydrolysed on the fibre at 393 K in H_2O -saturated atmosphere, giving a thin TiO_2 layer. These compounds were chosen because of their Li^+ conductivity and their impermeability to electrons and solvent molecules. Impedance spectra were recorded in the controlled current mode (about $50 \mu\text{A}/\text{mg C}$) applying a Solartron FRA 1250/1255 connected to an ECI 1286. For carrying out cyclic voltammetric experiments an ECI 1286 or a Bank LT 75 potentiostat was used. Capacity losses due to storage were determined under standard conditions: charge/discharge at about $50 \mu\text{A}/\text{mg C}$, cutoff voltage at 0.0 V and +2.0 V. All potentials were measured versus Li/Li^+ .

3. Results and discussion

The interpretation of impedance spectra was based on a simple equivalent circuit shown in Fig. 1. The corresponding impedance diagram is characterized by three semicircles which may be depressed because of time constant dispersion [4-6]. The symbols R_{el} , R_f , R_{ct} , R_d , C_{dl} , C_f , C_{dl} and C_{if} correspond to the electrolyte resistance, the solid-state resistance of the film, the charge-transfer resistance, the diffusion resistance in the pores of the film, a geometric capacity, the double-layer capacity and an interfacial capacity, respectively. The third semicircle was not observed in these experiments due to the galvanostatic experiment conditions.

3.1. Untreated carbon electrodes

The cyclic voltammogram in Fig. 2 shows the intercalation of lithium into the carbon material during the first cycle with a very slow voltage scan rate of 0.005 mV/s. Single peaks due to staging at charging and discharging can be observed and assigned to the third, second and first stage, respectively.

Whereas at very low sweep rate the intercalation into the carbon fibre can be studied in detail, processes on the carbon surface can be investigated at higher sweep rates. The first cycle of the cyclic voltammograms of the untreated LiC_n electrode at a voltage scan rate of 15 mV/s and 100 mV/s in Fig. 3(a) and (b) shows an irreversible reduction during the intercalation which is not observed at the slow scan rate. At 15 mV/s, it appears at 0.6 V versus Li/Li^+ and at 100 mV/s it

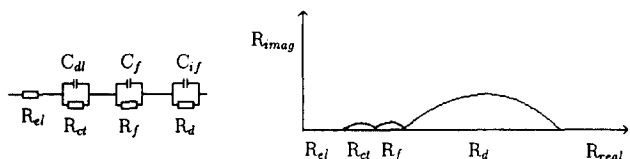


Fig. 1. Equivalent circuit for the interpretation of the observed impedance spectra.

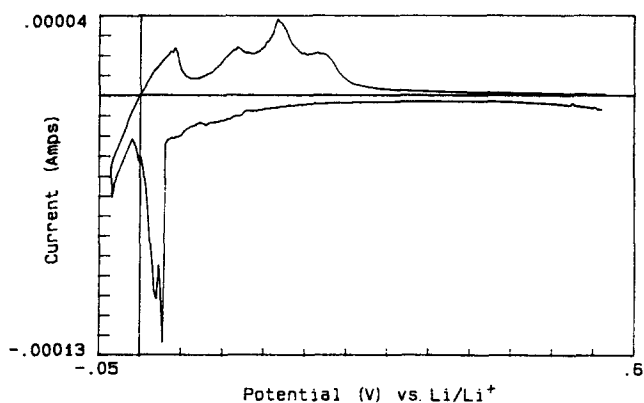


Fig. 2. Cyclic voltammogram of untreated LiC_n in the first charge/discharge cycle with 0.005 mV/s.

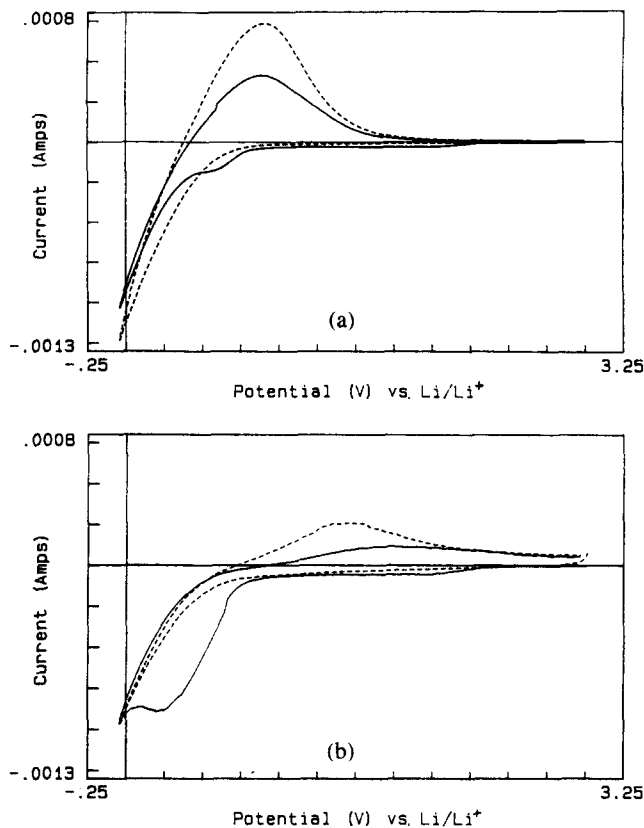


Fig. 3. Cyclic voltammogram of untreated LiC_n in the (—) first and (---) second charge/discharge cycle with (a) 15 mV/s and (b) 100 mV/s.

shifted to 0.3 V with a higher current. The capacity of this peak is independent of the scan rate in both voltammograms of about 2.0 mC/mg C. It is due to the film formation from electrolyte decomposition products in the first cycle and does not appear in the second cycle.

The impedance diagram of the untreated electrodes during the first charge and discharge process shown in Fig. 4(a) and (b) demonstrates an increase in the overall impedance.

Whereas the high frequency semicircle remains nearly constant during the cycle the low frequency semicircles increase continuously during charge and discharge according to a film formation from electrolyte decomposition products on the fibres (Fig. 5).

In the second charge/discharge cycle no further increase in the overall resistance is observed. The shape of the impedance diagrams depends on the amount of intercalated lithium.

3.2. Precoated carbon electrodes

Whereas the PEO layer is soluble in the $PC/LiClO_4$ electrolyte, the TiO_2 layer and the networked P2VP layer remain on the surface for at least hundreds of

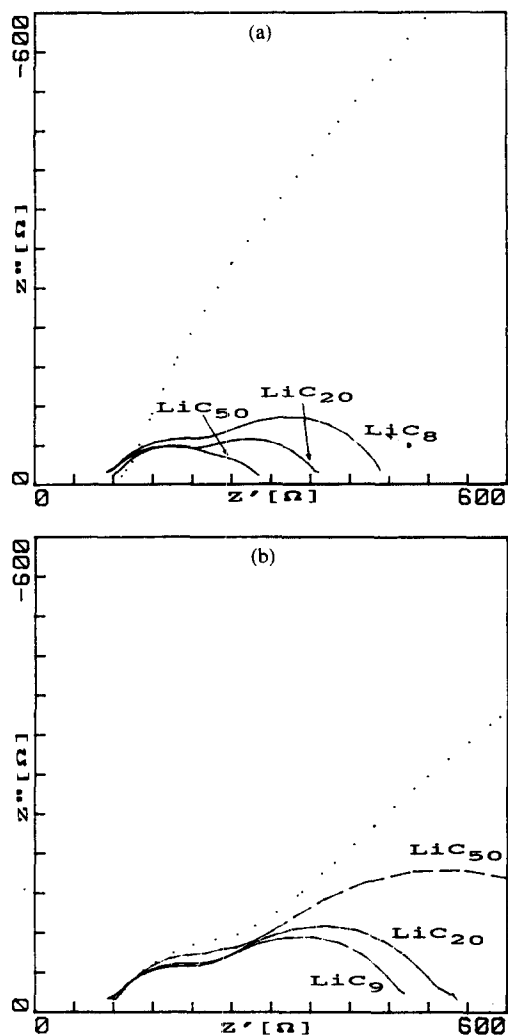


Fig. 4. Impedance diagram of untreated LiC_n (P 100) (a) first charge, and (b) discharge cycle.

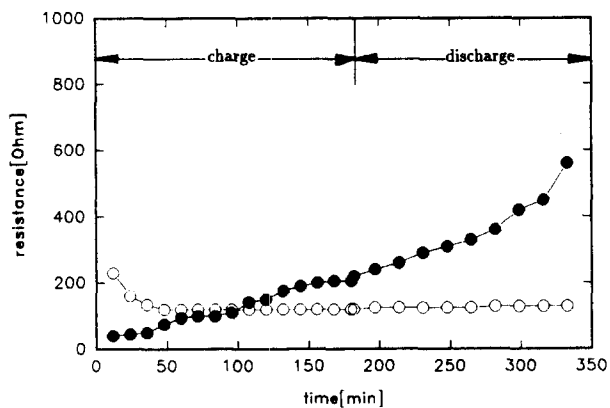


Fig. 5. Dependence of (○) high-frequency semicircle and (●) low-frequency semicircle in the impedance diagram of the untreated LiC_n in the first charge/discharge cycle.

hours. The solubility of the PEO depends on the thickness of the layer and the molecular masses of the polymer molecules and cannot be clearly reproduced. The properties of the protection layers formed during

the first cycle were strongly influenced by the presence of the coating materials.

The first cycle of the voltammograms of a P2VP(atc)-coated LiC_n electrode in Fig. 6 indicate an irreversible reaction on the electrode/polymer interface at 0.5 V versus Li/Li^+ which does not occur on the untreated carbon electrodes in this manner. There is no clear interpretation for this reduction process until now. Besides the organic electrolyte, the polymer-bonded pyridine as well as anthracene can accept electrons forming radical anions which can react in different ways.

The second cycle (Fig. 6(b)) demonstrates a nearly complete reversibility of the intercalation reaction and a slightly different shape of the curve in comparison with the untreated electrode.

The cyclic voltammogram of a TiO_2 -coated electrode in Fig. 7 shows a similar effect at higher voltages in the first cycle. This can also be observed with galvanostatic intercalation (voltage-time) where a plateau at 1 V occurs in the first cycle. The second cycle indicates that at this scan rate the intercalation only occurs into the TiO_2 and not into the carbon material because the typical carbon peaks between 1 and 0 V

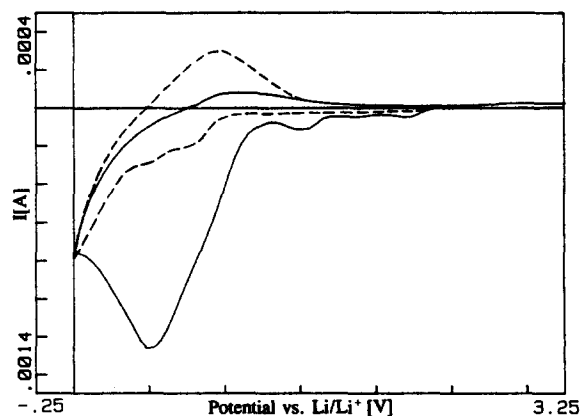


Fig. 6. Cyclic voltammogram of P2VP(atc)-coated LiC_n in the (—) first and (---) second charge/discharge cycle.

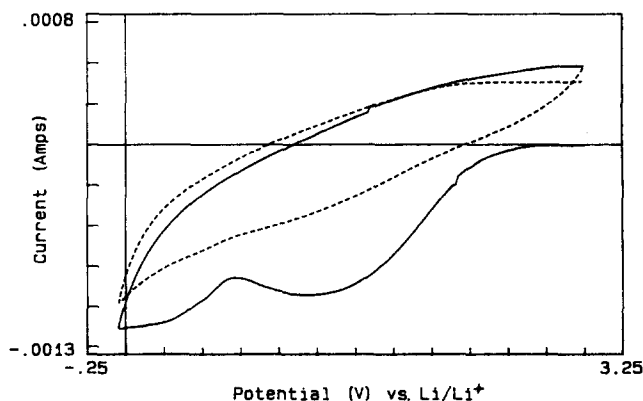


Fig. 7. Cyclic voltammogram of TiO_2 -coated LiC_n in the (—) first and (---) second charge/discharge cycle.

are missing. Voltammograms with slower scan rates show two different completely reversible reactions due to intercalation into TiO_2 between 1 and 2 V and into carbon between 0 and 1 V, respectively. The cyclic voltammogram of PEO-coated carbon fibres shows no differences in comparison with the untreated one.

The impedance studies of the P2VP-coated electrodes during the charge and discharge process are given in Fig. 8(a) and (b). The impedance diagram shows a semicircle which is broadened in the high-frequency region suggesting untreated fibres after film formation. This means that the native film, built up from polymer and inorganic reduction products of the organic electrolyte, can be simulated by a polymer pre-coating of the fibres.

The ranges of the semicircles of P2PV-coated LiC_n are relatively independent of the state-of-charge. Especially the low frequency semicircle is decreased in comparison with the fully grown film on the untreated

fibres. This low frequency semicircle should be related to the film resistance. That means that the higher polymer content of the simulated protective film decreases the film resistance. In a second charge/discharge cycle the overall resistance was decreased. This can be caused by dissolution of the polymer film or by an alteration of the surface film due to electrolyte reduction. This effect was observed with the P2VP layer as well as with the PEO layer. The impedance spectra of the other coating layers are similar to those shown in Fig. 8.

Whereas electrode impedances and shape of cyclic voltammograms are clearly influenced by pre-coating the layers, the capacity losses were only slightly reduced in the case of pre-coated electrodes.

4. Conclusions

The surface layer on carbon fibres being in contact with the organic electrolyte is mainly formed during the first charge/discharge cycle. This protective layer can be simulated by pre-coating the carbon fibre with a polymer layer. The differences between the used polymeric and the inorganic coatings are the more electrolyte-like behaviour of the P2VP and the more electrode-like behaviour of the TiO_2 coating, respectively, according to the use of those compounds considered earlier [8,9].

Acknowledgement

This work was supported by 'Deutsche Forschungsgemeinschaft'.

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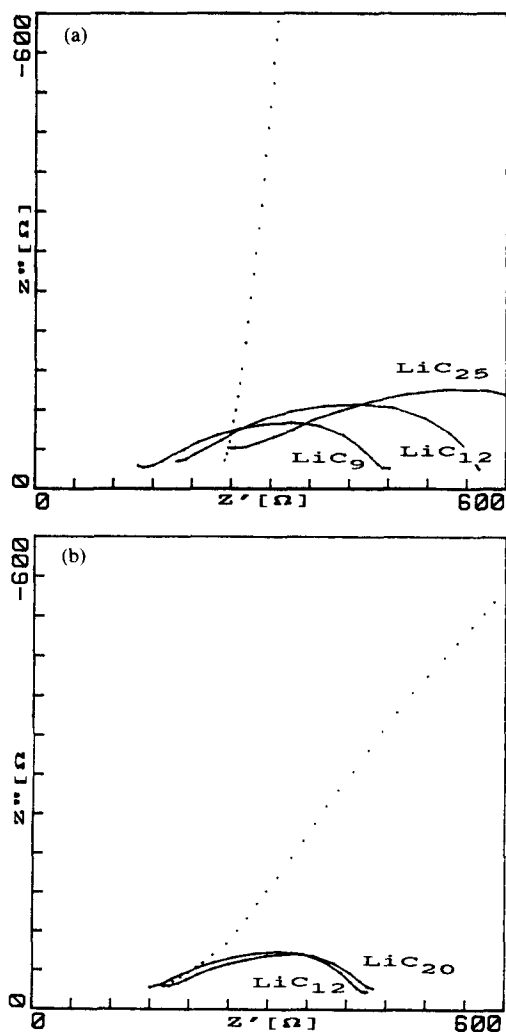


Fig. 8. Impedance diagram of P2VP(atc)-coated LiC_n (P 100): (a) first charge, and (b) discharge cycle.