

Carbon electrode morphology and thermal stability of the passivation layer

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Received 19 June 2000; accepted 31 December 2000

Abstract

Thermal stability of the solid electrolyte interface (SEI)-layers formed on graphite, mesocarbon microbeads and carbon-black anodes is shown to be dependent on the type lithium salt used in the electrolyte. Exothermic breakdown of the passivation layers formed on cycled electrodes using LiCF_3SO_3 or $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ in EC/DMC electrolyte solutions is compared on the basis of DSC, XPS and confocal Raman spectroscopy measurements. Lithium ions in intercalated carbon electrodes are shown not to be involved in the exothermic reactions below 250°C. However, changes are observed in the chemical composition of the SEI-layers using XPS on electrodes stored at 150°C. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: GIC; SEI-layer; Thermal stability; LiCF_3SO_3 ; $\text{LiN}(\text{SO}_2\text{CF}_3)_2$

1. Introduction

Many commercially available lithium ion batteries contain graphite as its anode material. During the first discharge of such a battery, a solid electrolyte interphase (SEI) is formed and acts as a passivation layer on the graphite grain surfaces. This layer is responsible for an irreversible capacity loss (15–30% dependent on the type of graphite), but also serves as protection against co-intercalation of solvent molecules into the graphite, and exfoliation of the graphite surface. A complete understanding of the chemistry and morphology of this layer is, therefore, critical and there have been numerous investigations of these features in recent years [1–4]. However, these studies have been carried out at room temperature, which characterisation of the SEI-layer components at elevated temperatures during cycling and storage will provide new insights into the subtle chemistry of the SEI-layer.

The choice of lithium-salt in the electrolyte has been shown to be of vital importance for the thermal stability of the SEI-layer [5–8]. Thermal breakdown when using LiBF_4 electrolytes starts already at 58°C, while use of LiPF_6 shifts the breakdown temperature to 102°C [7,8]. In this study, we

complement our earlier LiBF_4 and LiPF_6 studies [5,6] by investigating the lithium salts LiSO_3CF_3 (lithium triflate, LiTf) and $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ (lithium imide, LiTFSI) for the purpose of determining their influence on the thermal stability of the SEI-layer. To study the influence of carbon type and structure on thermal behaviour, carbon materials such as synthetic graphite, mesocarbon microbeads (MCMBs) and pure carbon-black (CB) are used.

2. Experimental

A (C||liq.e||Li) cell configuration was used in all experiments. Synthetic graphite KS6 (Timecal A + G, Sins, Switzerland), MesoCarbon MicroBeads (MCMB from Osaka gas) and Schewinigan carbon-black (SB) were investigated. Electrodes were made by mixing 80 wt.% of KS6 or MCMB with 10 wt.% EPDM-binder dissolved in cyclohexane and 10% SB. The SB powder was mixed with 10 wt.% EPDM-binder only. The slurry was spread onto a 18 µm thick copper current collector (Metfoil AB, Sweden). All electrodes were then dried overnight at 120°C in a vacuum furnace contained in an argon-filled glovebox ($\text{O}_2/\text{H}_2\text{O} < 1$ ppm). The cells were assembled using a lithium foil as counter electrode and a mechanical separator soaked with electrolyte and then vacuum-sealed in a polymer laminated aluminium

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foil. The electrolytes used were based on EC/DMC 2:1 with 1 M LiTf or LiTFSI. The salts were pre-dried at 120°C in the vacuum furnace overnight before mixing with solvent. All work was carried out in the glovebox.

The cells were cycled between 0.01 and 1.5 V with a relaxation period of 10 min at the end of each discharge/charge, at a cycling rate of C/5. Electrochemical measurements for XPS (X-ray photon/electron spectroscopy)

characterisation were made by first pre-cycling equivalent cells galvanostatically at room temperature for three cycles. The cycling was interrupted when the cells were at the high cut-off voltage (1.5 V) in a deintercalated state. The cells were then stored at room temperature and 60°C for 7 days under open-circuit conditions. Pre-cycled electrodes were also used for DSC (differential scanning calorimetry) and Raman spectroscopy measurements. They were charged to a

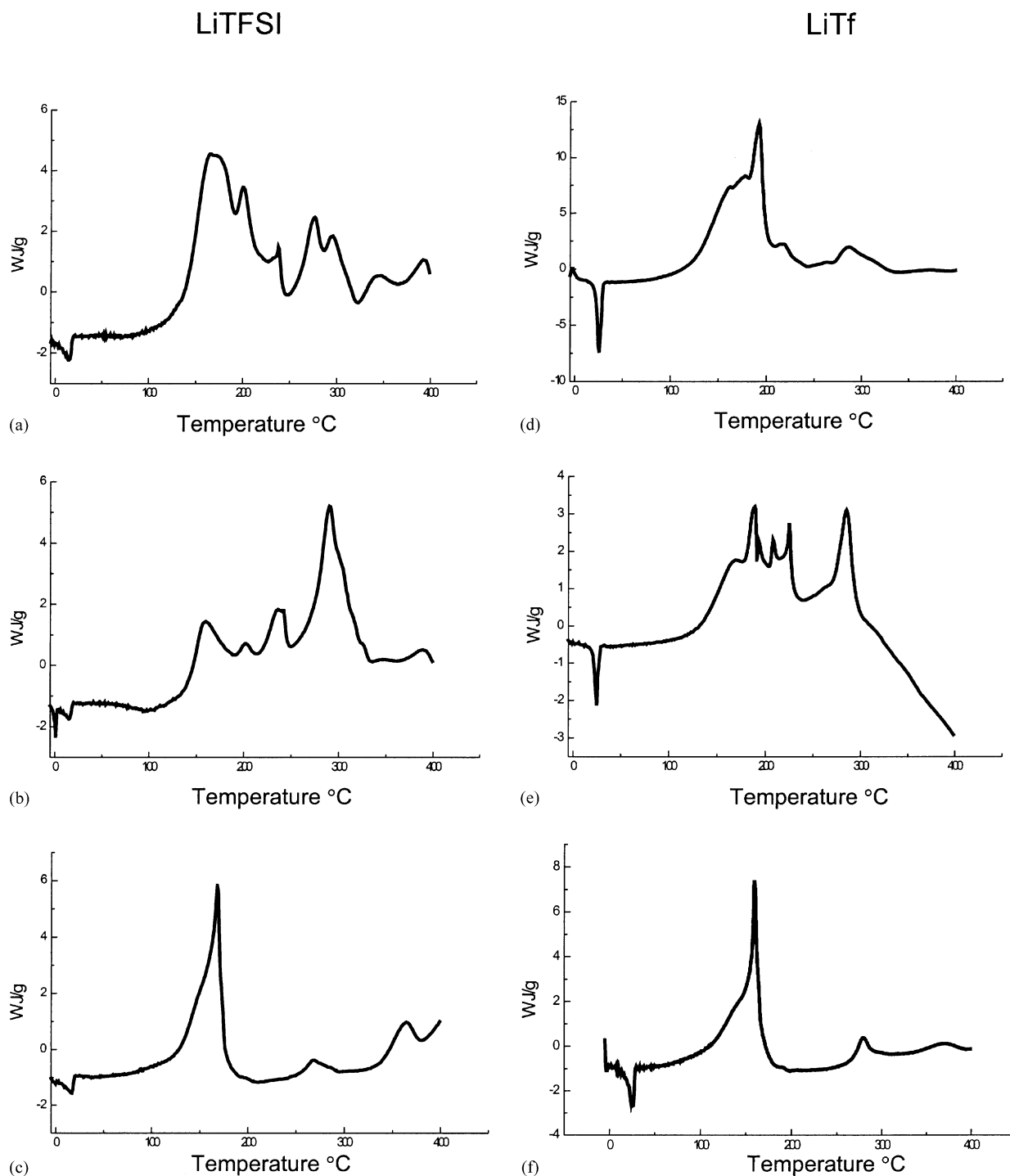


Fig. 1. DSC traces for (a) KS6; (b) MCMB; (c) CB, all fully intercalated using LiTFSI; (d) KS6; (e) MCMB; and (f) CB, all fully intercalated using LiTf.

fully intercalated state, LiC_6 , or to a deintercalated state. The cells were dismantled and prepared for analysis, taking care to avoid exposure to air. The electrodes were not washed to ensure that no material was dissolved into the solvent prior to measurement.

Small pieces of the electrodes were mounted on XPS sample holders and then transported to the analysis chamber in a purpose-built chamber. The XPS measurements were conducted on a PHI 5500 system using an Al $K\alpha$ excitation source.

Small pieces of the electrodes, coated with a thin layer of electrolyte, were punched out and sealed into standard DSC Al crucibles. The Cu-foil current collector was placed against the Al surface to ensure minimum contact between the walls of the crucibles and the LiC_x sample. The reference crucible contained the same amount of Cu-foil without an electrode coating. The measurements were carried out on a Mettler DSC 30 calorimeter, with the heating rate set at $5^\circ\text{C}/\text{min}$ in the temperature range -5 to

400°C . The various components of the cells were studied separately and in all possible combinations: Li(s), graphite, EC, DMC, LiTf, LiTFSI, EPDM, current collector and separator.

Raman spectra were obtained using a Renishaw 200 spectrometer equipped with a 518 nm argon-ion laser and Leica DMLP microscope. Samples were first sealed in a customised cell in the glovebox, then mounted on a Linkham THMS600 heating device on the Raman microscope stage. Measurements were performed in confocal mode using a $50\times$, 8 mm focus objective.

3. Results and discussion

The influence of the lithium salt anion on the exothermic breakdown has been determined from DSC measurements. These exothermic reactions can only be detected for cycled carbon electrodes (Fig. 1a–f) in the temperature region -5 to

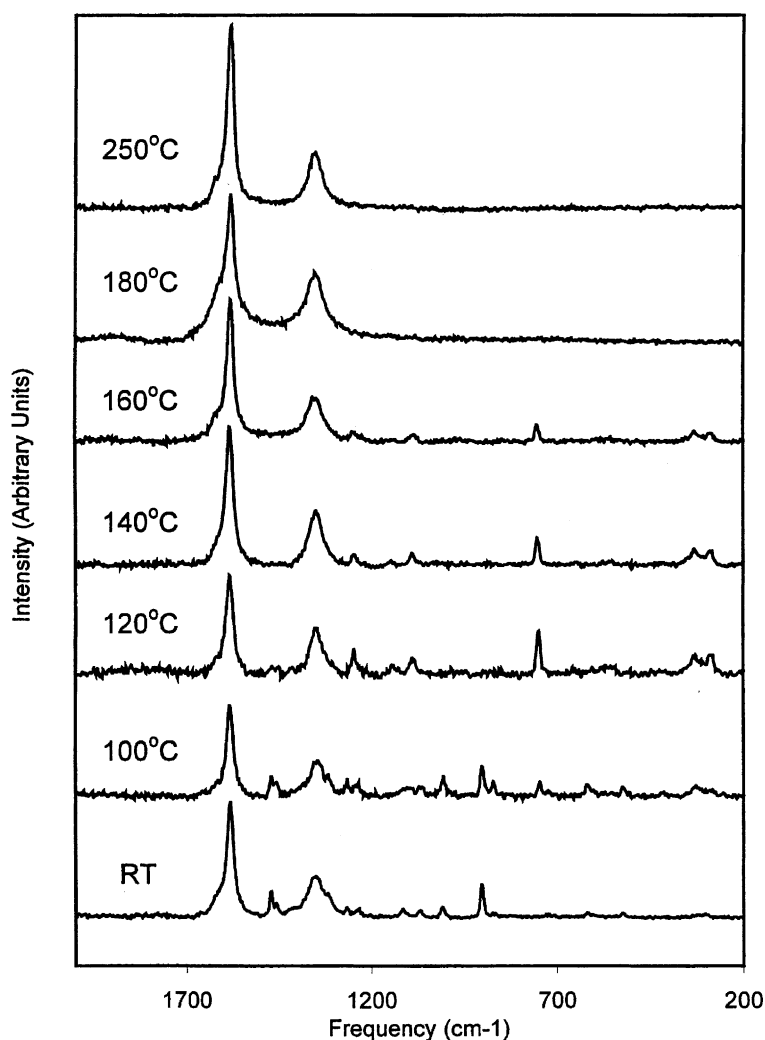


Fig. 2. Raman spectra of the KS6 graphite electrode surface in an intercalated state after cycling with LiTFSI electrolyte. Measurements performed between room temperature and 250°C .

400°C. Uncycled anodes analysed while in contact with these electrolytes undergo no exothermic transition, which may be due solely to SEI reactions or be a consequence of activating the anode surface. The onset temperature for thermal breakdown seems to be more determined by the type of anion than the type of carbon. For all three carbon-types, the onset temperature begins at 104°C using LiTf and at 120°C using LiTFSI. However, the shapes of the exotherms differ (Fig. 1a–f), which may be explained by differences in surface structures, porosity, particle size, etc. of the three different materials.

Raman spectra of graphite materials have been well characterised [9,10]. Intercalation of lithium is known to split the E_{2g} mode at 1580 cm^{-1} . The higher frequency component is attributed to C=C vibrations for atoms close to the intercalated lithium ions. Comparison of Raman spectra for the anodes in uncycled, deintercalated and intercalated states, indicate that some lithium remains in the carbon anodes after deintercalation. There is evidence of surface deposits, in addition to some residual electrolyte, in certain Raman spectra for the LiTFSI system. Changes occur in the spectra of these deposits above 120°C. The bands then diminish and are no longer observed by 180°C (Fig. 2). This coincides with the first exothermic reaction observed in the DSC traces. It is important to note that, in this temperature range, there is no apparent change in the lithiated-carbon bands. This suggests that the *intercalated* lithium is not involved in the first exothermic reaction. In the intercalated graphite samples, the lithium remains in the anodes to temperatures above 250°C.

XPS studies of the outermost 30 Å of the SEI-layers formed at room temperature show many similarities for the LiTf and LiTFSI systems. The C 1s spectra (Fig. 3a and b) show typical R–OCO₂Li peaks, carbon–ether oxygen

(–C–O–) peaks and small graphite peaks. After storage at 60°C in the deintercalated state, the XPS spectra did not change significantly compared to the room temperature measurements; a loss in intensity of the –CO₃ and –C–O– peaks could be discerned, possibly indicating dissolution of the SEI-layer components. The electrodes retained the golden colour of the LiC₆ phase after storage at 150°C in the intercalated state, consistent with the Raman experiments. Both of these techniques indicated the presence of Li₂CO₃ on the electrode surfaces, and that the carbonate solvent rings have opened, with some indication that polymerisation may have occurred. A detailed analysis of the chemical components formed at elevated temperatures is currently underway.

The main conclusions from this work are:

- The thermal stability of “half-cells” prepared using lithium salt–EC/DMC electrolytes is highly dependent on the choice of anion. LiTFSI salt electrolytes form more stable systems than the LiTf salts, and both are more stable than either LiPF₆ or LiBF₄.
- The thermal stability also depends on the type of carbon electrode. The onset temperature for breakdown is the same for each carbon type, but the heat evolved differs in magnitude and temperature range.
- The SEI-layers formed when using LiTf or LiTFSI–EC/DMC electrolytes contain some different components than those formed from the corresponding LiBF₄ and LiPF₆ electrolytes.
- Raman spectroscopic measurements indicate that intercalated lithium remains in the electrode up to at least 200°C and, as such, is not involved in the thermally activated exothermic reaction observed in the range 104–120°C.

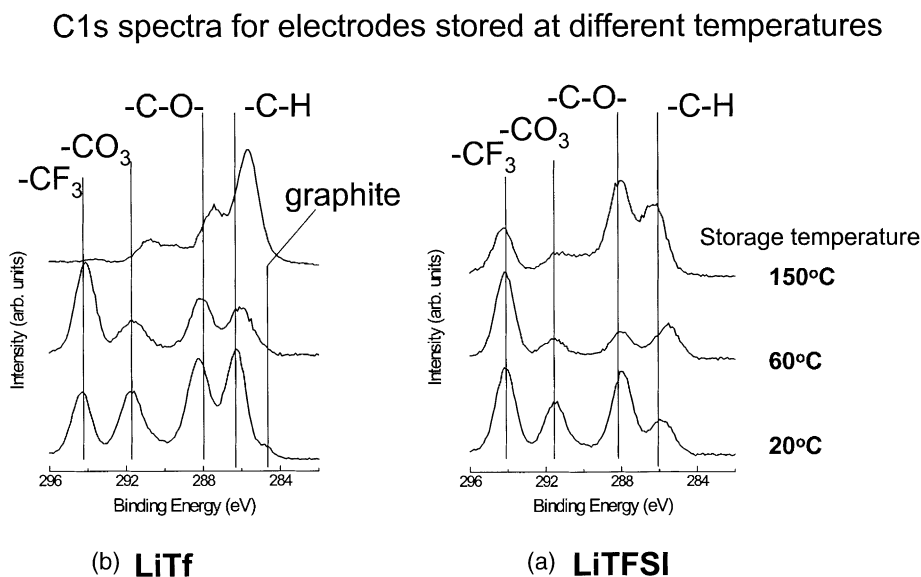


Fig. 3. C 1s XPS spectra for KS6 graphite electrodes at 20°C, stored at 60°C for 1 week and stored as LiC₆ at 150°C for 48 h using (a) LiTFSI-based electrolyte; and (b) LiTf-based electrolyte.

Acknowledgements

This work has been supported by The Swedish Natural Science Research Council (NFR), and The Foundation for Environmental Strategic Research (MISTRA). The authors also wish to extend their thanks to Prof. Josh Thomas, Uppsala University, for his interest in this work.

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