THE INFLUENCE OF GRAPHITE SURFACE MODIFICATION ON THE EXFOLIATION DURING ELECTROCHEMICAL LITHIUM INSERTION

H. Buqa[a], D. Goers[a], M. E. Spahr[b], P. Novák[a]*

[a]*Paul Scherrer Institute, Laboratory for Electrochemistry, CH-5232 Villigen PSI, Switzerland*
[b]*TIMCAL Group, CH-6743 Bodio, Switzerland*

**Corresponding author: e-mail: hilmi.buqa@psi.ch*
Fax: + 41 56 310 4415

Keywords
anode, graphite, graphite surface, lithium-ion battery, solid electrolyte interphase

Lithium-ion cells have good performance in terms of high voltage, high specific energy, and long cycle life. Graphitic carbons are the first-choice anode materials in lithium-ion cells for the reasons of performance and cost. It is now well known that, in lithium-ion cells the carbon surface is always covered by a protective thin solid film called the Solid Electrolyte Interphase (SEI). The SEI formation mechanism is rather complex and not yet completely understood. Lithium ions are consumed for the formation of this protective film. This decreases the maximum possible charge and energy density of the battery. Thus, losses have to be minimized.

For an optimum anode performance both, a careful selection of the graphite material and surface modification prior to electrochemical operation is obviously advantageous [1,2]. In this contribution, we report on the effects of graphite surface modification on its exfoliation (i.e., on the irreversible lithium consumption) during electrochemical lithium intercalation into graphite electrode.

The surface of graphite particles can be modified by, e.g., heat treatment and/or oxidation. For the better anode performance the heat treatment conditions have to be carefully selected with respect to the electrochemical behaviour of graphite.

In Figure 1, the effects of graphite surface modification on the SEI formation are shown for an example, the oxidation of TIMREX® SLX50 - HT[1] in air at different temperatures for 1 h.

The electrochemical measurements were performed in sealed test cells described elsewhere [3]. 1 *M* $LiPF_6$ in EC (ethylene carbonate) : DMC (dimethyl carbonate) (1:1) was used as the electrolyte. A specific current of 10 mA/g of graphite was used in the galvanostatic charge/discharge experiments.

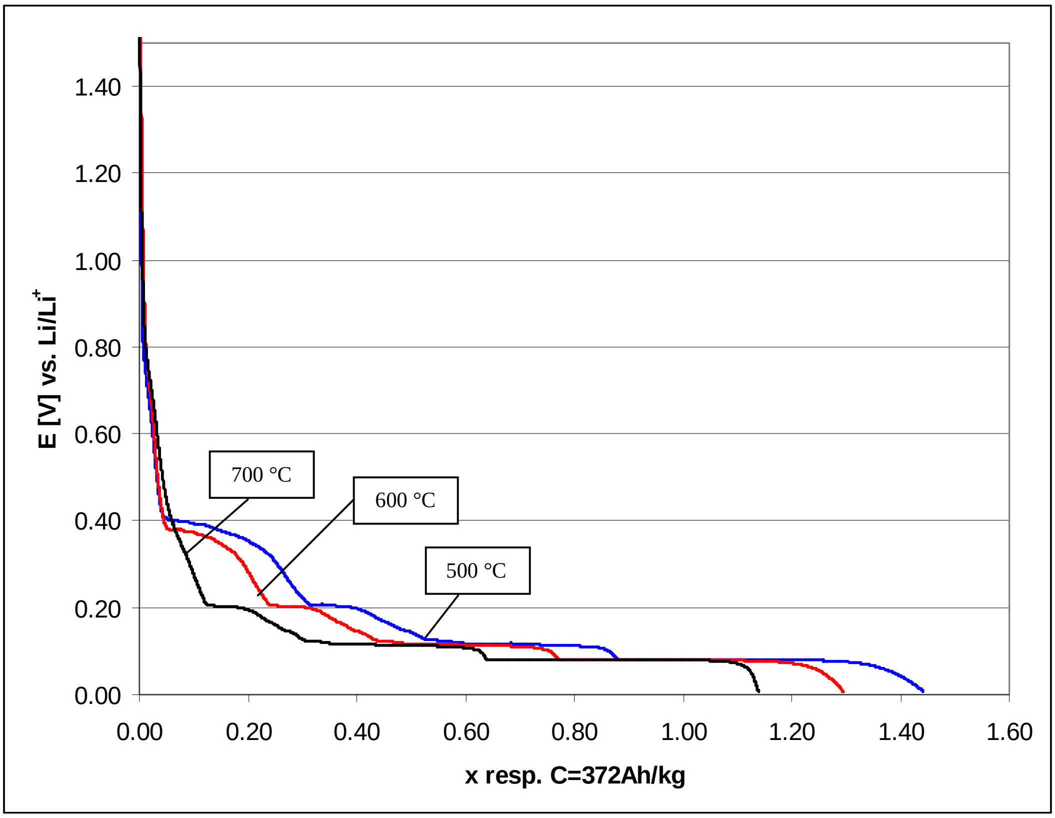
The exfoliation of the graphite structure during electrochemical lithium intercalation, manifested by potential plateaus at ca. 0.4 V vs. Li/Li^+, strongly depends on the oxidation temperature. Treatments at temperatures lower than 700 °C give rise, in 1 M $LiPF_6$ EC : DMC to an exfoliation plateau negative at ca. 0.4 V vs. Li/Li^+. When oxidized at 700°C, the

---

[1] Synthetic graphite TIMREX® SLX50 was modified by heat treating this graphite at 3000 °C under an inert gas atmosphere for 2 weeks. This modified graphite TIMREX® SLX50 - HT has a purely hexagonal structure and is very sensitive to exfoliation.

graphite SLX50 - HT showed no evidence of exfoliation of the graphite structure during first electrochemical Li^+ insertion.

Best electrochemical results in terms of reduced irreversible capacities have been obtained when the graphite was oxidized at 700 °C. Thus, we demonstrated that the treatment oxidation of TIMREX® SLX50 - HT at an optimum temperature leads to significant improvement of its electrochemical performance. From other experiments we know that, the treatment affected both, the surface morphology and surface group chemistry of the graphite. In conclusion, oxidation treatment of graphite can result in different anode performance in terms of graphite exfoliation. The oxidation temperature has an influence on the electrochemical properties, particularly on the formation of the SEI layer.



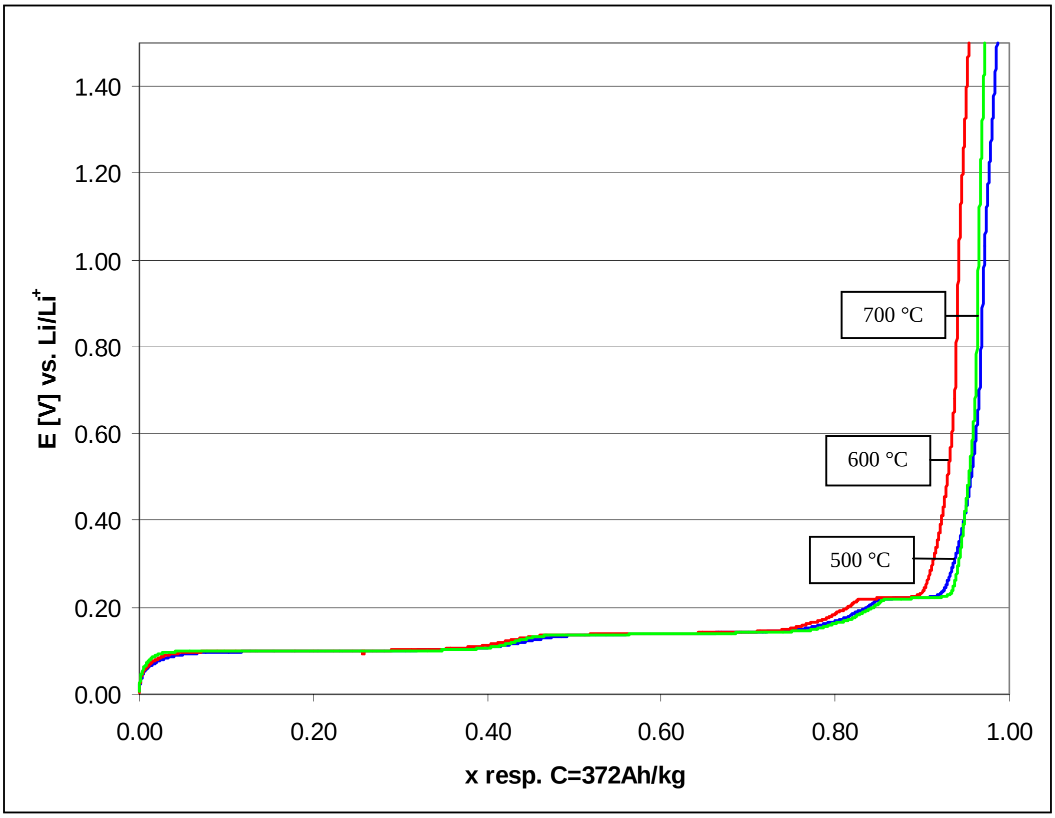


Figure 1. First electrochemical insertion (top) and de-insertion (bottom) of Li^+ *into TIMREX*® *SLX50 - HT oxidized at different temperatures. Electrolyte: 1 M* $LiPF_6$ *in EC:DMC (1:1), current 10 mA/g.*

Acknowledgments

We thank Dr. H. Wilhelm (TIMCAL SA) and Dr. F. Joho (PSI, now with ESEC SA) for numerous helpful discussions and the European Community for financial support of a part of this work.

References

[1] M. E. Spahr, H. Wilhelm, F. Joho, J.-C. Panitz, J. Wambach, P. Novák, N. Dupont-Pavlovsky, J. Electrochem. Soc., in press (2002).

[2] H. Buqa, P. Golob, M. Winter, J. O. Besenhard, J. Power Sources, 97-98 (2001) 122.

[3] F. Joho, B. Rykart, A. Blome, P. Novák, H. Wilhelm, M. E. Spahr, J. Power Sources, 97-98 (2001) 78.