

Understanding the Graphite Failure Mechanism in Lithium-ion Batteries: a Multiple Technique Approach

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During the last years the efforts to investigate new, improved electrode materials for secondary lithium-ion batteries have been increased significantly. At present the anode material of first choice is graphite because of its highly reversible specific charge of 372 mAh/g. The nature of the electrolyte much influences the stability of the graphite upon cycling. Propylene carbonate (PC) often leads to the exfoliation of the particles, whereas ethylene carbonate (EC) permits reversible lithium intercalation by the formation of a stable passivating layer (SEI). But also the crystallinity and morphology of the surface as well as the nature of the surface group chemistry of polycrystalline graphite influence the stability of a graphite electrode. They influence the SEI formation process on the graphite surface in the first electrochemical reduction, which may completely change the stability of graphite in various electrolytes, even EC-based ones [1]. These properties can be influenced, e.g., by thermal treatment of the graphite [1]. We present here a comparative study in order to determine the stability of two different graphite samples: a non treated one (BET specific surface area: 4.9 m²/g, rhombohedral fraction: 39%), which is further denoted graphite A, and a heat-treated one (BET: 2.6 m²/g, rhombohedral fraction: 0%), which is further denoted graphite B (heat-treated for two weeks at ca. 2500°C under inert gas). We employed different techniques as *in situ* synchrotron x-ray diffraction, post-mortem scanning electron microscopy (SEM), and x-ray diffraction, along with classical electrochemical cycling.

Fig. 1 shows the different electrochemical response of the respective graphites in an EC:DMC – 1M LiPF₆ electrolyte. In the case of graphite A, the potential of the electrode rapidly decreases to below 250 mV vs. Li/Li⁺ (beginning of lithium intercalation) and the charge consumption in the potential range of 1.5 V – 0.5 V vs. Li/Li⁺ (corresponding to the reduction of the electrolyte) is low. This indicates the formation of a protective SEI film on the graphite surface. In the case of the heat-treated graphite B, the current flowing at around 0.5 V vs. Li/Li⁺ is strongly increased. This indicates that, the electrolyte is continuously reduced and no passivating layer is formed on the graphite surface. No lithium, hence, can be reversibly intercalated. The different intercalation behavior should be reflected in a difference in the x-ray patterns of the respective materials during the electrochemical cycling. We undertook therefore a synchrotron *in situ* x-ray diffraction study of both graphites, cycled in EC:DMC – 1M LiPF₆. Indeed, as can be seen in Fig. 2, in the case of graphite A the (002)-peak shifts to the left which indicates the insertion of lithium into the host structure of the graphite under expansion of the lattice. For graphite B, however, the position of the (002)-peak remains unchanged. This proves that the consumed charge did not result in the intercalation of

lithium into graphite, but was consumed due to the reduction of the electrolyte. An SEM study of both materials proves that, in the case of graphite A the morphology of the graphite particles remains intact, whereas the particles of graphite B are inflated and the structure is damaged by exfoliation. As a reason for this the morphology and structural chemistry of the particles must be taken into consideration: upon heat-treatment the number of surface defects diminishes which reduces the reactivity of the electrolyte with the surface. The co-intercalation of the solvent molecules into the graphite along with lithium can, hence, compete with reductive formation of the surface SEI film, and exfoliation occurs upon the reduction of the co-intercalated solvents [1].

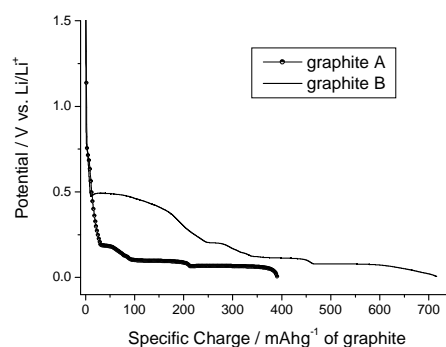
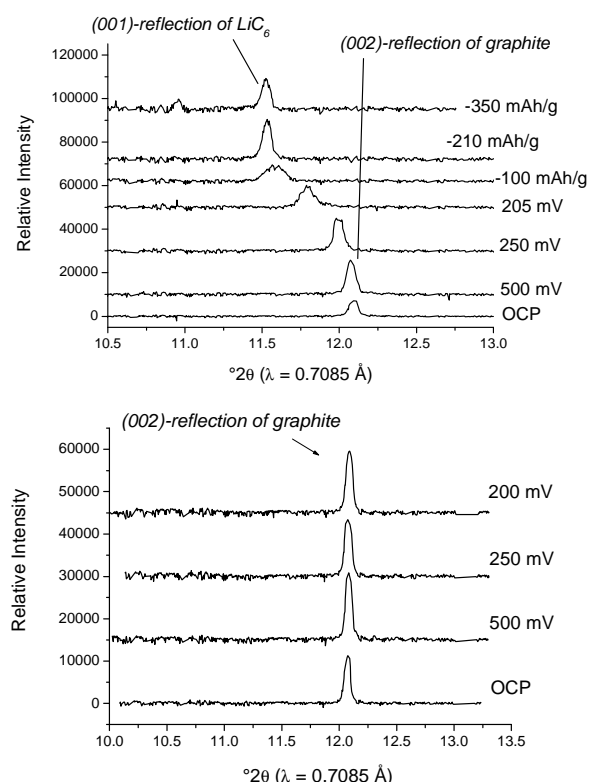


Fig. 1:



First reduction of the graphites A and B.

Fig.2: In situ synchrotron x-ray diffraction patterns of graphite A (top) and graphite B (bottom).

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Reference

- [1] M. E. Spahr, T. Palladino, H. Wilhelm, A. Würsig, D. Goers, H. Buqa, M. Holzapfel, P. Novák, *J. Electrochem. Soc.*, in press (2004).