

DILATOMETRIC STUDY OF LITHIUM INTERCALATION INTO GRAPHITE

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During the last years, we have developed an electrochemical dilatometer, which is capable of monitoring the height change of electrodes during charging with a sub-micrometre resolution [1]. Recently, the long term drift stability of this instrument has been improved considerably, so that dimensional changes in the range of a few micrometres can now be followed over time periods of several days, under the rigorous exclusion of ambient air. The drift stability has opened the opportunity to measure experimentally demanding systems such as the lithium intercalation into graphite. Thus, in the context of lithium ion batteries, electrochemical dilatometry may now be considered as a complementary tool to other well established *in situ* techniques like AFM, X-ray diffraction, and Raman spectroscopy. Here we present exemplarily the height change observed for a powder-type graphite electrode upon first cycle Li intercalation.

Experimental

Details of the set-up have been presented elsewhere [1]. In short, the dilatometer contains, hermetically sealed against ambient atmosphere, the graphite working electrode under investigation (10 mm dia., 100 μm thick), a lithium metal counter electrode, and a glass frit (3.5 mm thick) in between. A piece of Li positioned on the edge of the working electrode serves as the reference electrode. During the experiment, any charging induced height changes of the graphite electrode are transmitted through a thin titanium foil to a displacement transducer that is placed on top of the foil. A PVDF bound electrode, containing 90 % of graphite flakes (SFG44, Timcal) served as the working electrode. After filling the cell with LiPF_6 based electrolyte (LP30, Merck), the graphite electrode was cycled following the standard constant current (C/20 rate)/constant voltage protocol.

Results and Discussion

The potential profile and the simultaneous dilatation track recorded during first charging are shown in Figure 1. Generally, the observed potential slopes may be attributed to the stoichiometry domains of pure intercalation phases (stages), while the potential plateaus are related to the coexistence of two phases (i.e., the transformation of one phase into another) [2]. Consequently, electrode swelling should primarily occur during the potential plateaus, and the associated height change can be calculated from the stoichiometry and the lattice parameters of the pure stages. For the case of Li intercalation, X-ray studies indicate that Li intercalation commences with the formation of a diluted stage 1 [2]. This first potential slope (labeled 1d in

Figure 1) is followed by a plateau which is attributed to the transformation of this diluted stage 1 into a stage 4 compound (1d+4). During further lithiation, the pure stages 3 (with $x = 0.22$), 2 ($x = 0.5$) and 1 ($x = 1.0$) are subsequently formed. Under the present conditions, and in variance with the behaviour of pyrolytic graphite [2], no formation of a diluted stage 2 compound (with $x = 0.33$) can be seen.

Notably, the observed maximum expansion of 4.2 % is significantly lower than the 10.4 % widening of the interlayer spacing in the stage 1 compound LiC_6 [2]. This difference may be due to the almost random orientation of the graphite flakes in the powder electrode. In detail, the dilatation record shows three subsequent regions of constant slope which may be attributed to the initial formation of stage 1d, the transformation from stage 4 to 3, and that from stage 2 to 1, respectively. Interestingly, the transformation from stage 3 to 2 does not result in any expansion, a finding that is yet not understood.

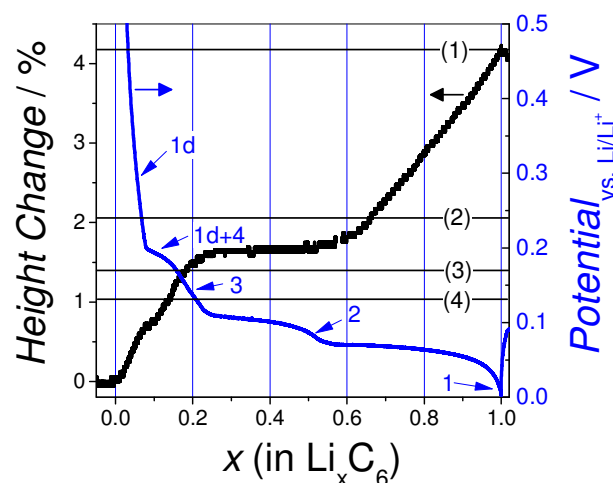


Fig. 1: Potential profile and simultaneous dilatation record of the graphite electrode during electrochemical lithiation. Arrows indicate stage formation along the potential curve [2]. Horizontal lines show the height change predicted for the pure phases (stage numbers in parentheses). These values are derived from X-ray results [2] and normalized to the actually measured expansion for the stage 1 compound LiC_6 .

Conclusions

Electrochemical dilatometry is shown to be a valuable tool for the characterization of the lithium intercalation into technically relevant graphite electrodes. In future work, we will extend the investigations to other types of graphite and compare the macroscopic dilatation behaviour with the results obtained by complementary methods.

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References

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