Reactivity of the Passivation Film on Lithiated Graphite : A DSC Study

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Thermal storage of lithiated graphite electrodes in EC:DMC:DEC (2:2:1) – 1M $LiPF_6$ electrolyte has been performed. The temperatures were varied between 40°C and 90°C and storage durations between 8h and 3 weeks. The lithiated electrodes were in the following examined by DSC and microcalorimetry and the results compared for two separators : Celgard 2402 and a microporous PVdF membrane.

The cycling experiments (galvanostatic cycling at C/10 rate) show that the capacity loss is a function of both temperature and time of storage. A logarithmic law could be fitted to the results, which shows that the capacity loss is an activated process, depending on the transformations occurring in the passivation film (Fig. 1).

DSC measurements show the presence of two peaks, the first of which is attributed to the transformation of the passivation film (1). Reaction of the intercalated lithium with the liquid electrolyte, which corresponds for the second peak, takes place only at higher temperatures ; it is controlled by Li^+-ion diffusion. It was revealed that washing the electrode before the DSC measurement does not deintercalate lithium (as reported in (2)) but that $LiPF_6$, our electrolyte salt, shows an important role on the DSC response (Fig. 2). The mechanism we propose (3) to account for this effect is the nucleophilic attack alkylate and alkylcarbonate species on the PF_5 that is formed in traces by the decomposition of PF_6^- during the storage at elevated temperature (Fig. 3)

An effect of the storage on the intensity and onset temperature of the first peak is evidenced, which reflects the modification of the passivation film on storage (Fig. 4).

The microporous PVdF membrane as separator has been shown to provide comparable results on electrochemical cycling and storage at elevated temperatures as the polyolefinic Celgard separators. Good performance were obtained with this new microporous separator.

References :

1. A.M. Andersson et al. *Electrochim. Acta* **47** (2001), 1885 and *J. Power Sources* **81-82** (1999), 8.
2. Du Pasquier et al., *J. Electrochem. Soc.* **145** (1998), 472.
3. M. Holzapfel et al., submitted to *J. Electrochem. Soc.*

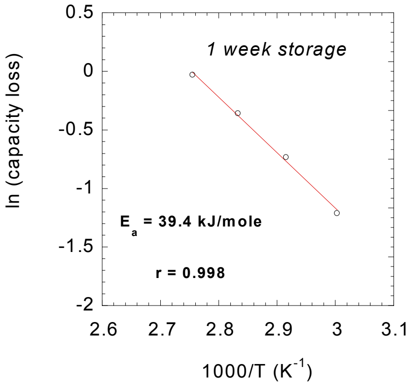

Figure 1 : Logarithmic behaviour of the capacity loss. Example for a 1 week of storage at different temperatures (Separator : PVdF)

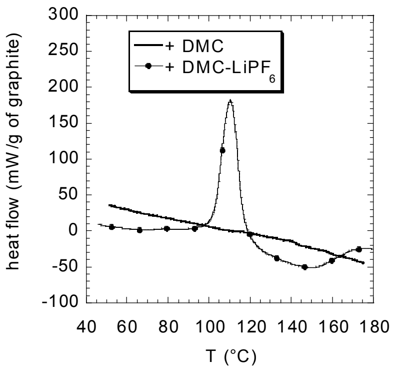

Figure 2 : Influence of $LiPF_6$: A delithiated sample (x = 0) has been cycled in DMC – 1M $LiPF_6$, washed with DMC and analysed either with DMC or with DMC – 1M $LiPF_6$.

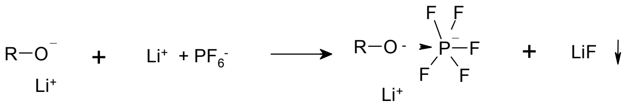

Figure 3 : Proposed reaction scheme for the transformation of the ppassivation film with $LiPF_6$.

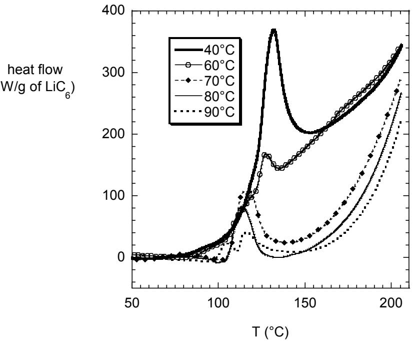

Figure 4 : Elevated temperature storage of lithiated graphite, investigated by DSC analysis. The samples were precycled in EC:DMC:DEC (2:2:1) - 1M $LiPF_6$, stored one week at different temperatures and analysed with EC:DMC:DEC (2:2:1) - 1M $LiPF_6$.