Microcalorimetry and XRD study of HOPG-LiC_6 reactivity with organic electrolytes

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In previous studies [1], we showed that chemically lithiated highly oriented pyrolytic graphite (HOPG) of the LiC_6 stage-1 composition reacts with organic electrolytes used in lithium batteries. Reaction with electrolytes is fueled by highly active lithium stored between the graphene layers. Some solvents such as PC and DME form ternary compounds such as $Li_{1-x}C_6$ (solvent)$_y$. EC containing electrolytes have higher stability towards other solvent(s) co-intercalation due to higher protective SEI.

In this study, we compared the structure changes and the heat generated after mixing organic liquids with HOPG- LiC_6. We used single-, dual- and triple-solvent solutions based on EC, DMC and DEC in presence or not of $LiPF_6$ Microcalorimetry isotherms were performed between 30ºC and 80ºC.

Figures 1 and 2 show the heat generated with different solvents-solute combinations. In single-solvent experiments, a very strong difference was observed between EC and DMC in one hand and DEC in the other hand. The heat generated at 40ºC with DEC was in the order of 100 and 25 times higher than in EC and DMC respectively. Adding $LiPF_6$ increased the heat generated in EC by a factor of 7 to 4 at 40ºC and 80ºC respectively, and decreased the one with DMC by a factor of 2 to 4, while DEC was less affected. The differences in generated heat were much lower in dual and triple-solvents as the presence of EC and DMC slowed the DEC reactivity.

Figure 3 shows the XRD charts of Li-HOPG before (a), and after reaction with pure EC (b), DMC (c)

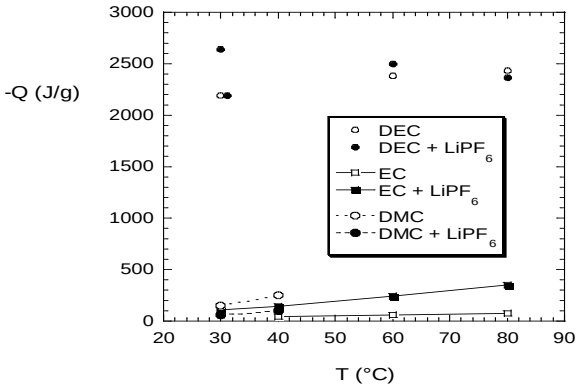

Figure 1: Heat released upon the reaction of lithiated graphite with single solvents.

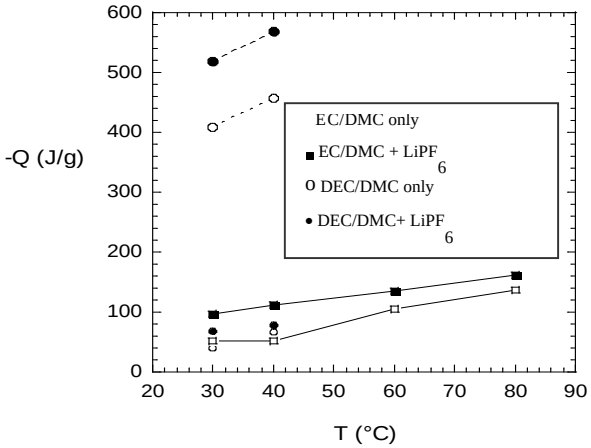

Figure 2: Heat released upon the reaction of lithiated graphite with dual-solvents electrolytes.

and pure DEC (d). The starting material contains about 96.4% stage-1 (LiC_6), 0.5% stage-2 (LiC_{12-18}) and 3.1% graphite. After reaction with EC only stage-1 (97.6%) and stage-2 (2.4%) compounds were found. For DMC, stage-3 and graphite appeared as new phases. The composition was about 35% stage-1, 52.6% stage 2, 12.3% stage 3 and 2.7% graphite. The sample reacted with DEC transformed to pure graphite as result of full delithiation.

Structure differences are related to the protective nature of SEI formed which increases in the order DEC<<DMC<EC.

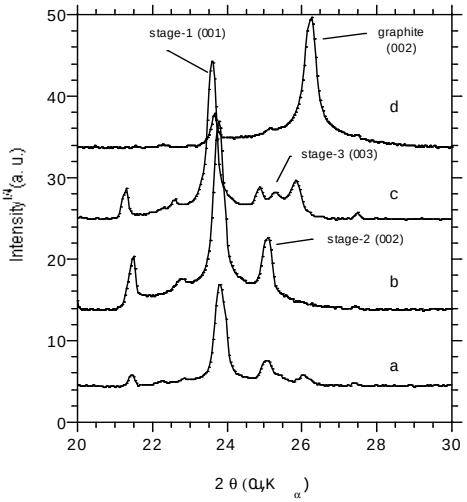

Figure 3 XRD charts of Li-HOPG before (a), and after reaction with pure EC (b), DMC (c) and pure DEC (d).

[1] R. Yazami, S. Genies, Denki Kagaku 66 (1998)129