

ELECTROCHEMICAL STUDIES ON THE SEI-FORMATION PROCESS IN THE PRESENCE OF VINYLENE ELECTROLYTE ADDITIVES

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The choice of solvents and solvent mixtures as electrolytes for lithium ion batteries is usually a compromise between the physical (electrolyte conductivity, viscosity) and electrochemical properties (SEI film formation behaviour, reduction and oxidation at the respective electrode/electrolyte interfaces).

Propylene carbonate (PC) exposes a large liquid range from $-49\text{ }^{\circ}\text{C}$ to $+240\text{ }^{\circ}\text{C}$. Thus, PC based electrolytes show a low temperature performance desired for use in lithium ion cells. Unfortunately, PC tends to co-intercalate into graphite, resulting in detrimental graphite exfoliation. The use of an electrolyte additive, which during the first charge forms a protective film at a potential before solvated intercalation occurs ($> 0.9\text{ V}$ vs. Li/Li^+) allows to employ PC based electrolytes. Several compounds such as ethylene sulfite [1], vinylene carbonate [2], both analogue to ethylene carbonate have proven to form effective films on graphitic anodes.

A novel class of film forming electrolyte additives are compounds with a vinylene functionality. If these compounds contain electron-withdrawing groups $-X$, their reduction according to a polymerization mechanism (Fig. 1) is facilitated on graphite. One of these novel additive compounds, acrylic acid nitrile (AAN) has proven to suppress solvated intercalation at a low concentration (1% v/v in PC). The performance of AAN in cycling studies depends on the charge procedure in the initial charge step. A better cycling performance can be achieved, if a special charge programme is applied (Fig. 2). This procedure may result in a more favourable SEI formation.

In order to better understand the mode of operation of the vinylene additives, several investigation methods, e.g. cyclic voltammetry, cycling studies, EQCM, in situ FTIR spectroscopy and others were applied. Results on AAN and other additives will be presented.

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References

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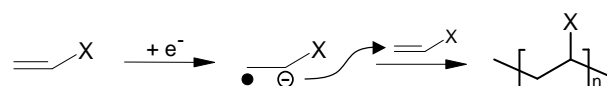


Fig. 1: Cathodic, i.e., by reduction induced polymerization of vinylene monomers [3]

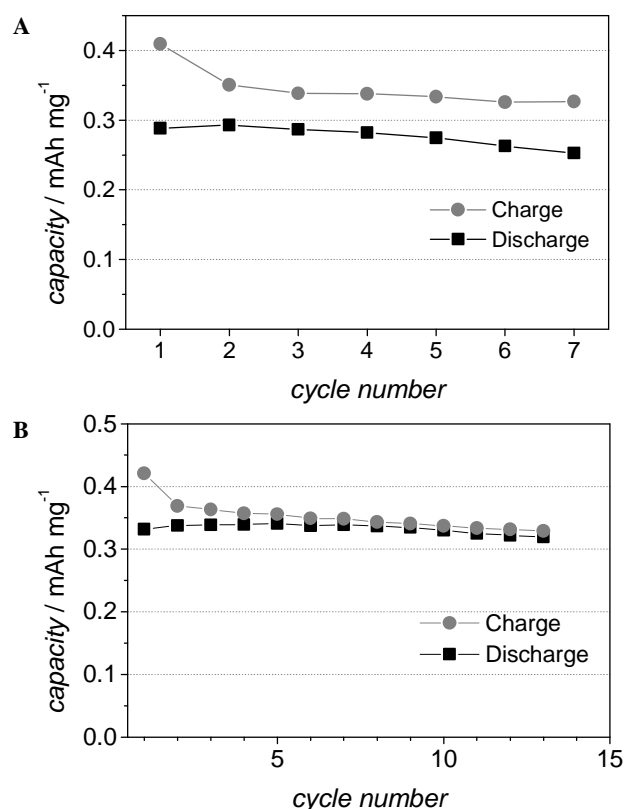


Fig 2: SFG44-graphite in 1M LiClO_4 in PC/AAN (99:1 v:v); constant current cycling at 20 mA g^{-1} (A); potentiodynamic ramp in the 1st charge, followed by constant current cycling at 20 mA g^{-1} (B)