EVOLUTION OF UNSATURATED HYDROCARBENE (ETHYLENE, PROPYLENE) AT GRAPHITE AND LITHIUM STORAGE ALLOY ELECTRODES

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Introduction

With alternative lithium storage metal and alloy anodes becoming increasingly popular, it is important to discuss their Solid Electrolyte Interphase (SEI) formation behaviour in liquid organic electrolytes and to emphasise the differences and similarities to graphitic and lithium metal anodes.

Film formation on the surface of graphitic anodes takes place as a charge consuming side reaction in the first few Li⁺ intercalation/de-intercalation cycles, especially during the first reduction of the carbon host material, leading to the so-called "irreversible capacity". Layered graphite gives rise to basically two kinds of surfaces, prismatic (edge) surfaces and basal plane surfaces. It is well known that the prismatic and basal plane surface areas of graphite show a different SEI formation behaviour (1), eg. solvent co-intercalation is a reaction only proceeding at the prismatic surfaces. SEI formation on lithium storage metals shows some similarities to that on lithiated graphites, as film formation also in this case is an electrochemical, electrode potential dependent and charge consuming side reaction, proceeding mainly during the first reduction of the metallic host material. However, solvent co-intercalation reactions do not play a vital role in the electrolyte reduction process of lithium storage metal electrolyte species. Thus it can be expected, that the SEI formation mechanisms and the SEI composition on graphite and lithium storage metals and alloys is different.

Experimental

By means of on-line electrochemical mass spectrometry (EMS) it is possible to detect volatile compounds that evolve at the electrodes of a lithium ion cell (2). It can be obtained with lithium storage alloy anodes that no ethylene was observed as decomposition product on Sn/SnSb electrodes (Fig. 1) while on the other hand, ethylene is evolved at graphite electrodes (KS 6, Lonza) during film formation (Fig. 2) in a similar experiment. In propylene carbonate (PC), excessive propylene formation takes place at graphite electrodes accompanied by solvent co-intercalation that leads to graphite exfoliation and electrode failure (Fig. 3). On the contrary, no propylene formation was observed at Sn/SnSb electrodes (Fig. 4).



Fig. 1 MSCV (mass spectrometric cyclic voltam-mogram) of a Sn/SnSb anode. Mass signal of m/e = 27 represents ethylene. Electrolyte: EC / DMC / 1 M LiClO₄ (75%/25% by vol.), scan rate: 0.4 $mV.s^{-1}$



Fig. 2 MSCV of graphite TIMREX KS 6 anode. Mass signal of m/e = 27 represents ethylene. Electrolyte: EC / DMC / 1 M LiClO₄ (75%/25% by vol.), scan rate: 0.4 mV.s⁻¹



Fig. 3: MSCV of a graphite TIMREX KS 6 anode. Mass signal of m/e = 41 represents propylene. Electrolyte: PC / 1 MLiClO₄, scan rate: 0.4 mV.s⁻¹



Fig. 4: MSCV of a Sn/SnSb anode. Mass signal of m/e = 41 represents propylene. Electrolyte: PC / 1 M LiClO₄, scan rate: 0.4 mV.s⁻¹

Conclusions

Apart from the possible influence of different catalytic activities of metallic electrodes we conclude, that the formation of ethylene or propylene is associated with the formation of solvated graphite-intercalation compounds.

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References

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