

On the origin of gases evolved during electrolyte decomposition at silicon anodes in Lithium-Ion batteries

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There is increasing interest in non - carbon anode materials with improved lithium - storage capacity and, in particular, in tin - and silicon - based anode materials. Unfortunately, the capacity retention and cycling efficiency of these materials is still not quite satisfying. Customized electrolyte systems, usually containing fluorinated components apparently improve their performance.

The film - forming reactions taking place at graphite differ from those on lithium storage metals. Not only the reduction mechanisms and SEI compositions, but also the requirements on the SEI properties concerning flexibility and density of the layer are depending on the type of used active material. The reaction mechanism of electrolyte decomposition on the electrode surface comprises essential information for further improvement of electrode/electrolyte systems.

A powerful method for examination of ongoing reactions at the electrode/electrolyte interface is the in situ electrochemical mass spectrometry (EMS). EMS [2], [3] offers the opportunity to measure volatile compounds which evolve during the charge/discharge of active materials.

A Swagelok - based headspace cell for in-situ EMS experiments (Fig. 1) provides an easy way for realizing an airproof battery system that can be attached to the mass spectrometer with or without the use of a carrier gas e.g., argon. Furthermore this system offers a high electrode surface, needed for gas generation and the possibility of three - electrode assembly.

Our contribution will focus on the investigation of evolved gases during the charge of materials suitable for application as lithium alloy anodes. Especially investigations on silicon will be shown. The comparison with experiments done on graphitic materials will show differences regarding reduction reactions and filming mechanisms at the surface of the electrodes. These comparisons can bring up new information helping to develop improved electrolyte systems adapted to the investigated materials.

Using the cell assembly shown in Fig. 1, electrochemical investigations (e.g. Fig. 2) are done and gas evolution during these experiments is in-situ detected by MS (Fig. 3).

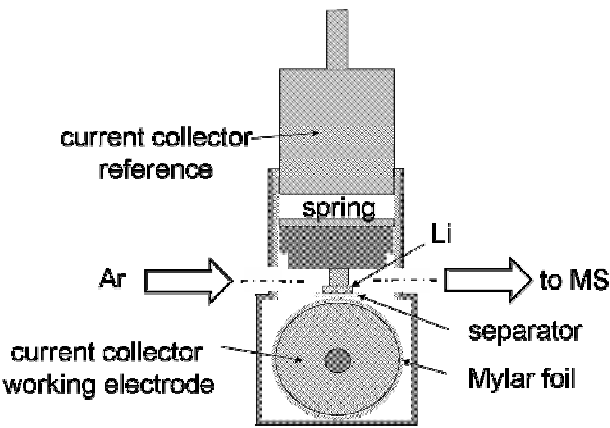


Fig. 1: Swagelok headspace EMS cell.

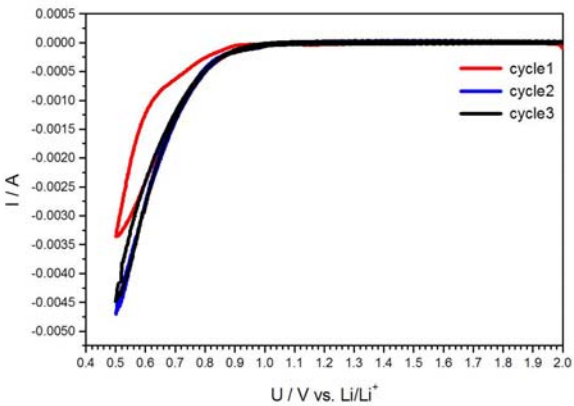


Fig. 2: Cyclic voltammogram of natural graphite electrode. Scanrate 0.4 mV/s, 2 - 0.5 V vs. Li/Li⁺, 3 cycles, 1 M LiPF₆ in PC

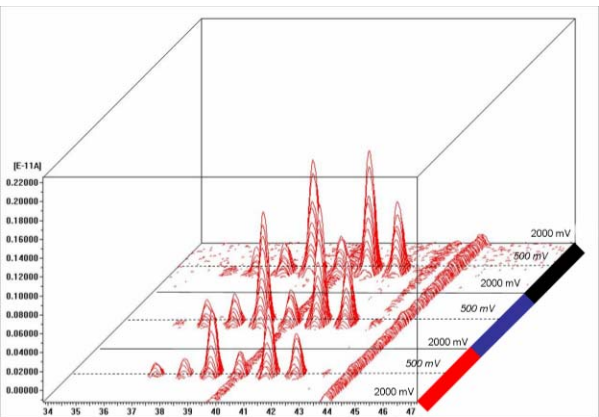


Fig. 3: Corresponding MS spectrum to measurement shown in Fig.2

References

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