Kinetics of metallic lithium deposition, a side reaction in Li-intercalation batteries

P.E. de Jongh
Philips Research Eindhoven (WA11)
Professor Holstlaan 4
5656 AA Eindhoven, The Netherlands
Petra.de.Jongh@Philips.com

Lithium intercalation batteries are well suited for portable applications, such as cellular phones, shavers and labtop computers. They have a very high energy density, both volumetrically and gravimetrically. Important issues for these applications are battery lifetime and safety. Hence it is important to study not only the default battery reactions, but also the unwanted side reactions. For instance a clear relation is found between cycle life of a Li-ion battery and the maximum voltage reached during charging. Two important side reactions during overcharging are electrolyte solution decomposition, and the deposition of metallic lithium on the graphite electrode. This paper focusses on the latter.

The kinetics of metallic lithium deposition on graphite were studied using a commercial li-ion graphite electrode and standard li-ion electrolyte solutions such as 1 M $LiPF_6$ in EC/DEC. The electrode was cycled several times under external pressure before start of the measurements. Electrochemical methods such as impedance spectroscopy were combined with morphology studies using SEM. Figure 1 shows an example of metallic lithium deposits on graphite.

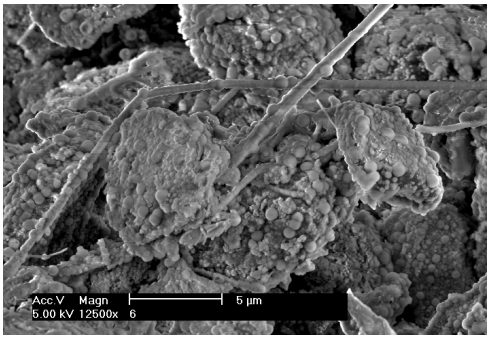

Figure 1: Example of lithium deposits on graphite

The morphology of the deposits was strongly dependent on the deposition current. Lithium is deposited not only on the graphite particles, but also on the carbon fibers (which are present to provide extra electronic conductivity to the battery electrode). The reversibility of the lithium deposition was examined as a function of deposition rate and time.

The kinetic studies were complicated by the simultaneous (de)intercalation of lithium in the graphite. Another complicating factor was that even at open circuit, metallic lithium is not stable in the electrolyte solutions used. Therefore the passivation of metallic lithium was investigated on solid metallic lithium electrodes. With impedance measurements, a continuous increase in charge transfer resistance was found. This is illustrated in Figure 2.

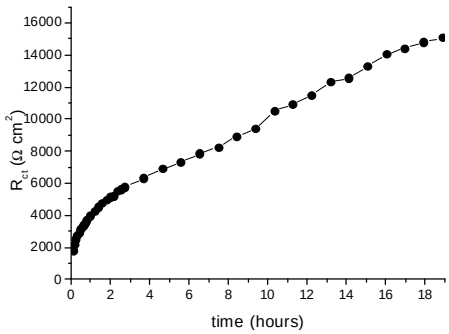

Figure 2: Charge transfer resistance measured on metallic lithium in 1 M $LiPF_6$ EC/DEC as a function of time.

Although the passivation rate clearly decreases during the first hours, even after a day still no complete passivation is reached. As expected, continuously depositing extra lithium (or dissolving part of the lithium) had a strong influence on this passivation behaviour.

Finally the results on graphite and lithium metal samples will be combined and the implications for the battery performance after overcharging will be discussed.