

In situ detection of lithium metal plating on graphite via reference electrodes and optical test-cells

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The progress in electromobility depends on numerous improvements of lithium-ion-batteries. Special emphasis is put on shorter charging times and on recuperation of braking energy.

However, large charging currents may cause lithium plating which describes the deposition of metallic lithium at the anode surface. It takes place at conditions of high currents and/or low temperatures because of several kinetic limitations. The main reason is the slow solid-state diffusion of lithium inside the active material. If the anode surface potential falls below 0 V versus Li/Li⁺, the formation of metallic lithium becomes thermodynamically allowed (see Fig. 1).

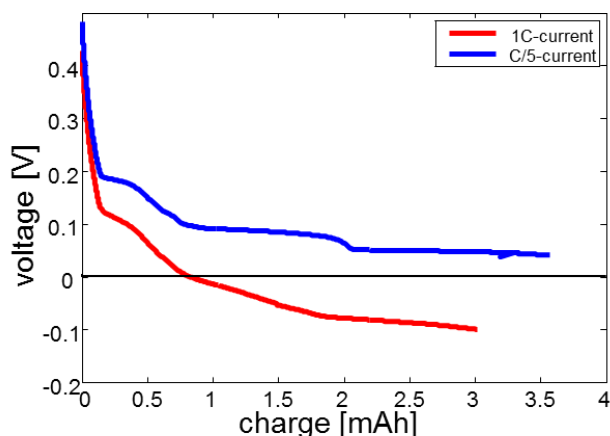


Figure 1: Cell voltage of a lithium-graphite-test-cell during lithium intercalation at different C-rates (T=25°C). The overpotential at 1C is sufficiently high to lower the cell voltage below 0 V versus Li/Li⁺.

Due to side reactions of the metallic lithium, plating can cause an irreversible capacity fade^[1]. Furthermore, it causes safety risks, as dendritically grown lithium can lead to an internal short circuit^[2]. Therefore, it is of great importance to identify and prevent lithium plating.

The aim of this study is to increase the understanding of this phenomenon and furthermore to enable the detection of plating. For that purpose, experimental graphite half-cells were investigated in parallel with optical inspection and electrochemical measurements.

Electrochemical measurements were performed by measuring the potential of the graphite anode via a reference electrode during current pulses and the subsequent period of potential relaxation. Fig. 2 shows typical relaxations curves for charging currents varying between 1 C and 10 C. The pulse length was adapted in order to keep the total charge constant at 1/6 of the cell capacity. A plateau evolves in the potential relaxation

curves as soon as plating takes place. Furthermore, we investigated the influence of temperature (between 0°C and 25°C) on the tendency for Li plating. It was found that plating is more pronounced at lower temperatures.

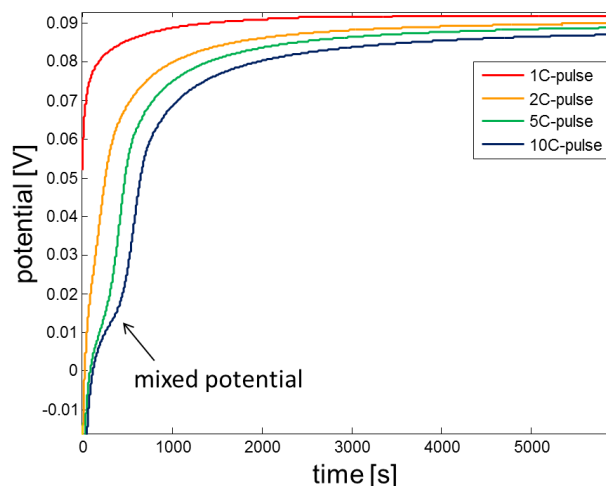


Figure 2: Relaxation of the graphite potential vs. Li/Li⁺-reference electrode following the different pulse rates (T=25°C). Every pulse transferred the same amount of charge (1/6 of cell capacity). A mixed potential occurs as soon as plating takes place. It can be recognized by the resulting “plateau”.

Furthermore, a test-cell was designed for the observation of lithium metal plating in situ by using a confocal microscope. This set up allowed us to study the kinetics of lithium metal plating and dissolution at the surface of individual graphite particles.

By combination of optical and electrochemical in-situ investigation methods, the occurrence of lithium plating could be directly correlated with the formation of a plateau in the potential relaxation curves after a charging pulse. This plateau was interpreted as mixed potential resulting from the interplay of lithium intercalation and dissolution of deposited metallic lithium on the anode surface.

- [1] J. Fan and S. Tan, "Studies on Charging Lithium-Ion Cells at Low Temperatures", *Journal of The Electrochemical Society* **153** (6), p. A1081-A1092 (2006).
- [2] L. Gireaud, S. Grugeon, S. Laruelle, B. Yrieix and J.-M. Tarascon, "Lithium metal stripping/plating mechanisms studies: A metallurgical approach", *Electrochemistry Communications* **8**, pp. 1639-1649 (2006).