Short communication

A new method for detecting lithium plating by measuring the cell thickness

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HIGHLIGHTS

- A new method for the detection of lithium plating is described.
- The measurement shows a reversible and an irreversible part of lithium plating.
- Fast mapping of the maximum current at different temperatures is possible.

ARTICLE INFO

ABSTRACT

Charging Li-ion cells at low temperatures and/or high currents can cause the lithium ions to deposit on the anode surface rather than intercalating into the graphite lattice. This effect, named lithium plating, may severely affect the performance, reliability and safety of the cell. Because metallic lithium at the anode consumes more space than intercalated into the graphite, the cell volume increases in the case of lithium plating. An experimental setup for precise measuring the thickness of pouch cells with a resolution of 1 μm was built. The cell thickness as a function of its charge under standard cycling conditions was recorded as a reference. In the case of lithium plating an additional increase of the thickness was observed. This can be used as an indicator for the non-destructive detection of lithium plating in pouch cells. Compared with the standard capacity based methods this procedure allows a higher sensitivity and gives results more quickly.

1. Introduction

Due to the wide range of environmental influences Li-ion batteries in automotive applications have to meet high standards. Besides mechanical stability and safety in crash scenarios the wide range of operating temperature poses a great challenge. Particularly acceptable charge rates combined with low temperatures is still a major challenge.

At temperatures below 10 °C charging Li-ion cells with standard graphite based anodes, the currently most common used anode material, is only possible at a fraction of the nominal charge rate. The limiting factor is the intercalation speed of the lithium ions into the anode, which is significantly decreasing at lower temperatures. Exceeding a specific charge current, this leads to the damaging effect of lithium plating, i.e., the deposition of metallic lithium at the anode.

The effect has a negative impact on performance, reliability and safety of the cell. The deposited lithium is not available anymore for the ionic charge transfer which results in a loss of capacity. In addition the metallic lithium reacts with the electrolyte increasing the solid electrolyte interface (SEI), which causes a rise of the internal resistance.

Besides the electrical parameters, the safety aspect of lithium plating has to be considered. The deposition of lithium on the anode is not uniform, but rather in form of dendrites which can grow through the separator. This can lead at least theoretically to soft shorts resulting in higher self discharge or to a short circuit causing a thermal runaway. To guarantee safety, performance and long life an operation condition causing lithium plating has to be avoided by all means.

2. Theory

2.1. Lithium plating

Under normal circumstances Li-ion batteries do not contain metallic lithium at all. Only Li-ions are moving through the

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electrolyte and intercalate into the anode during charge and vice versa into the cathode during discharge. Under certain operating conditions, particularly while charging at low temperature and/or with high currents, lithium ions deposit at the anode surface rather than intercalating into the graphite lattice [1]. This can only occur if the anode potential drops below the potential of 0 V vs. Li/Li$^+$. Depending on the temperature and charge current this can occur any time after starting the charge process or when overcharging the cell [2].

During plating there persists a coexistence between the intercalation of the ions into the lattice and deposition on the surface of the anode. This state remains, until the charge process is stopped or the current in the constant voltage mode is small enough so that the anode potential can recover to a potential above Li/Li$^+$ [3].

A large part of the lithium deposition is reversible [1,2,4,5,15]. Thereby the reduction of plated lithium can take place either through subsequent chemical intercalation into the graphite lattice, which needs sufficient relaxation time, or by dissolving during the following discharge. In the latter case lithium is oxidizing at a potential which is about 100 mV more negative than the deintercalation potential of lithium in graphite [1], resulting in a higher voltage while discharging at low current. This characteristically higher voltage plateau at the discharge voltage graph gives evidence of lithium plating [1]. Since the plateau indicates the reversible part of plating only, a quantitative measurement of the total amount of deposited lithium is not provided.

2.2. Characterization of lithium plating behavior

State of the art methods for detecting lithium plating can be categorized in three types, depending on the effect they rely on:

(i) Detecting a negative anode potential vs. Li/Li$^+$, e.g., with a reference electrode or in half cells.
(ii) Electrical measurement of the cell degradation through plating e.g., loss of capacity, rise of internal resistance.
(iii) Physical/chemical post mortem analysis and proof of metallic lithium.

By now, the only way of detecting lithium plating in progress is method (i), that is measuring the anode potential, either in half cells or through a built-in reference electrode. Both methods need massive modification of a given cell. Moreover, a reference electrode may interfere with the electrode processes and has a negative influence on the measurement [4,14].

For the characterization of unmodified cells in large-scale production measuring the anode potential is not an option. The standard procedure of determining the onset of plating is mapping the maximum charge current at different operating conditions, while periodically checking the performance degradation (ii). The most important parameter here is the degradation of the cell's capacity, since it correlates directly with the loss of active lithium.

Besides the non-invasive electrical tests, a further post mortem analysis (iii) can provide a better picture of the nature of the cell degradation. The wide range of chemical and physical analysis methods will not be addressed here.

2.3. Volume change during cycling

It is well known that active materials vary in volume, depending on the amount of intercalated Li-ions. Graphite anodes, for example, gain about 10% in volume while changing from the unlithiated elementary state to fully lithiated LiC$_6$ [6]. As the common cathode materials have a much smaller dilatation coefficient, e.g., NMC: about 1% [7], the thickness of graphite based batteries is governed by the anode volume change. On the other hand lithium titanate anodes (LTO) for instance are almost unaffected by the amount of intercalated lithium, since its volume change is only 0.1%–0.3% [8].

2.4. Volume change through lithium plating

Lithium can fill the free interstitials when intercalated into the graphite lattice. Hence, the volume of the intercalation compound is smaller than the volume of the two separate materials. While the deintercalation from the cathode has no significant effect on the cell thickness, depositing lithium on the surface instead of intercalating into the anode leads to an additional gain in the overall volume.

The following example estimates the expected extent of volume gain by lithium plating. Side effects like change in porosity, gas evolution, dendritic growth or inhomogeneity within the cell are neglected in the following calculation.

Transferring 1 Ah of charge from the cathode to the anode, the amount of lithium substance is:

$$n_{Li}(1 \text{ Ah}) = \frac{C}{e \cdot N_A} = 37.31 \text{ mmol} \tag{1}$$

n_{Li}: amount of Li substance [mol], N_A: Avogadro constant [1/mol], e: elementary charge [As]; C: transferred charge [As].

Fully charged, every six carbon atoms provide space for one lithium atom. Thus for 1 Ah of charge an amount of $6 \cdot n_{Li} = 223.9 \times 10^{-3}$ mol of carbon is consumed. With the molar volume of carbon in hexagonal structure of 5.31×10^{-6} m^3 mol^{-1} its volume is 1.189 cm^3. According to the literature, carbon based anode materials expand about 10% due to the intercalation of lithium [6]. Thereby charging 1 Ah causes a volume change of:

$$\Delta V_C(1 \text{ Ah}) = \alpha_{LiC_6} \cdot n_{Li}(1 \text{ Ah}) \cdot 6 \cdot V_{m,C} = 0.12 \text{ cm}^3 \tag{2}$$

ΔV_C: Change of the carbon volume due to lithium intercalation [m^3], α_{LiC_6}: coefficient of expansion changing from C to LiC$_6 \approx 10\%$, $V_{m,C}$: molar volume of carbon [m^3 mol^{-1}].

With a molar volume of $V_{m,Li} = 13.02 \times 10^{-6}$ m^3 mol^{-1} the volume of lithium in metallic condition providing 1 Ah of charge is 0.49 cm^3.

If the lithium is depositing rather than intercalating, the resulting expansion equals the volume of the lithium in metallic form minus the volume the anode would gain due to the intercalation, as shown in Equation (2).

The cathode effect is neglected here. The theoretical relation between volume gain and lithium plating is therefore:

$$V_{exp}\left(C_{pl}\right) = \frac{C_{pl}}{e \cdot N_A}\left(V_{m, Li} - \alpha_{LiC_6} \cdot 6 \cdot V_{m,C}\right) \tag{3}$$

$V_{m,Li}$: molar volume of lithium [m^3 mol^{-1}], $V_{m,C}$: molar volume of carbon [m^3 mol^{-1}]; C_{pl}: amount of plated lithium.

According to Equation (3), an amount of 1 Ah of plated lithium causes a gain in volume of V_{exp} (1 Ah)= 0.37 cm^3.

The test cells used in the following experiments contain electrodes with an active area of 188 mm by 122 mm. Plating would thereby lead to a growth in thickness by 16.1 μm per plated Ah, which is independent of the amount of layers inside the cell. Note that due to the overlap, the cathode is sized smaller than the anode. Because of cell inhomogeneity, dendritic deposition and gas evolution, the actual measured value is expected to be larger.

Measuring the volume change as a method for cell characterization has already been described in the literature [6,5,9,10,12,13].