



Lithium plating in lithium-ion batteries at sub-ambient temperatures investigated by in situ neutron diffraction



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HIGHLIGHTS

- Li plating in commercial Li-ion cell at $-20\text{ }^{\circ}\text{C}$ studied by in situ neutron diffraction.
- A lower degree of graphite lithiation is found as a result of lithium plating.
- Lithium diffusion into graphite takes place during a 20 h rest period.
- Immediate discharge: no changes in lithiated graphite since Li is oxidized.
- Li plating amounts to 19% of nominal cell capacity.

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ABSTRACT

Lithium plating in commercial $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2/\text{graphite}$ cells at sub-ambient temperatures is studied by neutron diffraction at Stress-Spec, MLZ. Li plating uses part of the active lithium in the cell and competes with the intercalation of lithium into graphite. As a result, the degree of graphite lithiation during and after charge is lower. Comparison of graphite lithiation after a $C/5$ charging cycle fast enough to expect a considerable amount of Li plating with a much slower $C/30$ reference cycle reveals a lower degree of graphite lithiation in the first case; neutron diffraction shows less LiC_6 and more LiC_{12} is present. If the cell is subjected to a 20 h rest period after charge, a gradual transformation of remaining LiC_{12} to LiC_6 can be observed, indicating Li diffusion into the graphite. During the rest period after the $C/5$ charging cycle, the degree of graphite lithiation can be estimated to increase by 17%, indicating at least 17% of the active lithium is plated. Data collected during discharge immediately after $C/5$ charging give further evidence of the presence and amount of metallic lithium: in this case 19% of discharge capacity originates from the oxidation of metallic lithium. Also, lithium oxidation can be directly related to the high voltage plateau observed during discharge in case of lithium plating.

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1. Introduction

Today, graphite is used as anode material in most Li-ion batteries [1]. However, because the potential of lithium intercalation into graphite is within 100 mV [2] of the potential of Li/Li^+ , the deposition of metallic Li on the graphite anode, so-called Li plating, can occur during fast charging. Whether or not Li plating occurs, depends not only on charging speed, but also on factors like electrode

balancing, the electrolyte used in the cell and the temperature during charge [3–8]. For example, several studies by Smart et al. show Li plating can be drastically enhanced at sub-ambient temperatures [2,3,5].

The consequences of Li plating can be severe safety problems, because metallic Li tends to be deposited in the form of dendrites [8–10]. In the worst case scenario, such a dendrite may pierce the separator and short-circuit the cell. On the other hand, Li plating can also lead to loss of active lithium and capacity fading. Plated lithium may react with the electrolyte (adding to SEI growth) or become disconnected from the graphite forming a reservoir of inactive metallic lithium [7,8].

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For all these reasons, it is necessary to avoid Li plating, and to be able to avoid Li plating it is necessary to study it more closely and find out exactly when and why it occurs. Unfortunately, studying Li plating ex situ is difficult, since the deposition of metallic lithium is partly reversible. Also, it is difficult and potentially dangerous to open a cell in the charged state because of possible short-circuiting. In the discharged state, on the other hand, only irreversible Li plating can be expected to be present. Studying Li plating in situ is also difficult, because the method has to be sensitive to lithium without being hampered by the cell casing. Apart from a number of electrochemical studies, where a high voltage plateau observed during discharge was used as indication for the presence of lithium plating [2,3,5,11], to our knowledge there is only one other study by Harris et al. where Li plating was observed in situ in an optical half-cell [12].

Neutron diffraction offers a promising alternative to derive information about the processes within a lithium-ion battery. In contrast to x-ray diffraction, it has the advantage of being sensitive to lighter elements (like lithium, oxygen and nitrogen) and the high penetration depth of thermal neutrons makes it possible to investigate Li-ion cells in a non-destructive way. There are two approaches to neutron diffraction on lithium-ion batteries: One is to build special in situ cells, optimized for the diffraction experiment (special geometry, deuterated electrolyte, etc.) [13,14]. The other approach is to use commercial cells, with the benefit that electrochemical performance and balancing of the electrodes are optimized by the manufacturer. A number of studies address the structural changes that take place in anode and cathode materials during charging and discharging of commercial LiCoO₂/graphite [15–18] or LiFePO₄/graphite [19] cells. Also the influence of cell fatigue on structure and phase composition [17], aging at different temperatures [20] as well as inhomogeneous degradation of large format pouch cells [21] has been studied. While it is usually necessary to charge a lithium-ion battery very slowly (or repeatedly [22]) to collect reasonable neutron diffraction patterns, diffraction data on the strong (002) reflection of graphite and similarly prominent reflections of the intercalation compounds may be collected with a good signal to noise ratio in rather short time intervals of ~5 min, if high neutron flux can be provided. This makes it possible to follow the lithiation and delithiation of graphite in a cell under real-life conditions, as shown in two recent publications on the overcharge of a lithium-ion battery [23] and the current dependency of Li_{1-x}C₆ phases within the anode during discharge [24].

In this study Li plating in commercial NMC/graphite cells was studied by neutron diffraction. To enhance Li plating, the measurements were performed at a temperature of -20 °C. The degree of Li intercalation into graphite was monitored during slow (no/little plating expected) and fast (plating expected) charging cycles, subsequent rest periods and discharge. Our observations allow us not only to show the presence of Li plating, but also to estimate its amount and study associated kinetic phenomena.

2. Experimental

For the experiment a commercial 18650-type NMC (LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂)/graphite round cell (Molicel IHR18650A by E-ONE MOLI ENERGY CORP.) was used. To our knowledge, the cell electrolyte contains dimethyl carbonate, ethylene carbonate, LiPF₆ and propylene carbonate. In a number of cycling experiments prior to the neutron measurements, both room and low temperature behavior were studied. The battery is rated to deliver 1950 mAh nominal capacity. All C-rates in this paper are given relative to this rated capacity.

The cell was cycled using a BioLogic VSP potentiostat. The experimental procedure is shown in Fig. 1: prior to the neutron

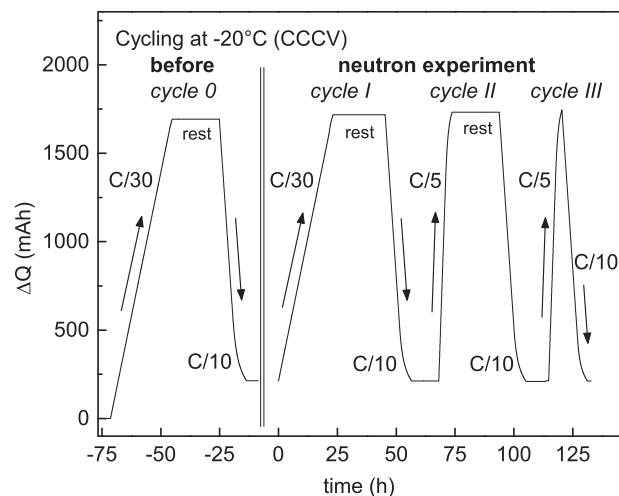


Fig. 1. ΔQ vs. time for cell cycling prior to (cycle 0) and during neutron experiment (cycle I–III) at -20 °C.

experiment, the cell was cycled once (C/30) at -20 °C in a freezer and then transferred to a pre-cooled cryostat (cycle 0). When the cell had reached again a temperature of -20 °C, the battery was first charged with a very slow charging rate (C/30) to 4.2 V, followed by a constant voltage phase with a cutoff current of C/50 (cycle I). Unfortunately, a voltage peak, possibly due to contact problems occurred, the CV phase was triggered too soon and the current rose to a maximum of C/15.35 and was above C/30 for 39 min. The C/30 charge was followed by a rest period of 20 h. After discharge (CCCV, C/10, 3.0 V, cutoff: C/100), the battery was charged quickly to induce Li plating (cycle II: CCCV, C/5, 4.2 V, cutoff: C/50), followed by another 20 h rest period and discharge (again CCCV, C/10, 3.0 V, cutoff: C/100). Additionally, a third charging cycle (CCCV, C/5, 4.2 V, cutoff: C/50), immediately followed by another C/10 discharge without a rest period, was carried out (cycle III).

In situ neutron diffraction data were collected at the instrument Stress-Spec (Heinz Maier-Leibnitz Zentrum [25]). The wavelength was set to $\lambda = 2.1226(1)$ Å; determined using the NIST SRM 640d Si standard powder. The scattering gauge volume was set by a 5×20 mm² entrance slit and a 5 mm radial collimator in front of the detector (Fig. 2). Since our preliminary experiments showed that metallic lithium is difficult to detect directly in a battery due to reflection overlap and its comparatively small amount, we focused instead on the strong reflections of the lithium graphite phases, where even small changes in Li content lead to considerably changes. Diffraction data of the strong (002) reflection of graphite and the similarly prominent reflections of the intercalation compounds LiC₁₂ and LiC₆ in the scattering angle range of 30–40° 2 θ were collected in 5 min intervals throughout the experiment to monitor the changes within the graphite anode of the battery. The integral intensity of reflections was extracted by fitting pseudo Voigt profiles to the data. In case of overlapping reflections, the FWHM (full width at half maximum) was constrained; e.g. one value was refined for all reflections.

3. Results and discussion

3.1. Charging at low temperature

During charge, Li-ions intercalate into the anode of the battery and a stepwise lithiation of the graphite anode via a number of Li_{1-x}C₆ phases with lower lithium content, LiC₁₂ and finally LiC₆ takes place. Fig. 3 shows diffraction data collected in situ during the

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