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# Influence of temperature and upper cut-off voltage on the formation of lithium-ion cells

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## HIGHLIGHTS

- The influence of temperature on the formation of Li-ion cells was investigated.
- Increasing temperature decreases formation loss due to enhanced Li-diffusion in NMC.
- Increasing formation temperature worsens cell performance of graphite anode.
- The influences of both anode and cathode on a full cell were examined.
- The components of the solid electrolyte interphase on the anode were determined.

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## ABSTRACT

The influences of temperature on the formation losses and subsequent electrical performance of $Li_x(Ni_{1/3}Co_{1/3}Mn_{1/3})_yO_2$ (NCM)/graphite lithium-ion cells were investigated. It was shown that the total capacity loss during formation of a full cell at 25 °C consists of losses on the positive and negative electrode to about one half each. The losses of the negative electrode (ca. 10%) are due to solid electrolyte interphase (SEI) formation on graphite but are masked by the losses of the positive side (ca. 20%) which are mainly caused by a kinetic inhibition of NCM and are theoretically reversible when the cell is discharged to very low potentials. The total loss of a full cell fits with the loss of the positive electrode. With increased temperature the ratio of losses on positive and negative electrode decreases as the diffusion coefficient of lithium in NCM increases. In total, an elevated formation temperature leads to increased irreversible losses on both electrodes and significantly lower cell performance of graphite. The upper cut-off voltage has an influence on the positive electrode formation losses in a reversible manner. The constituents of the SEI identified via the combination of XPS and FTIR are mainly $RCH_2OCO_2Li$, RCOOLi and LiF for the outer SEI and mainly $Li_2CO_3$, $Li_2O$ and LiF for the inner SEI.

## 1. Introduction

Lithium-ion batteries have been used since the early 1990s as power sources for portable devices like cell phones, laptop computers or digital cameras. Due to their high energy and power densities, reliability, long cycle life and safety, they also became attractive for hybrid electric vehicles, full electric vehicles and stationary energy storage.

Many commercially available lithium-ion batteries consist of a graphite negative electrode and a lithium metal oxide positive electrode, e.g. $Li_{1+x}(Ni_{1/3}Co_{1/3}Mn_{1/3})_{1-x}O_2$ (NCM).

It is generally known that the initial charge of a graphite negative electrode leads to irreversible loss of lithium (irreversible capacity). This is due to the formation of the so-called solid electrolyte interphase (SEI), a passivating layer on the surface of graphite, which is formed via the reaction of electrolyte components with lithium particularly during the initial charge before intercalation [1–3]. The SEI protects the electrolyte from further decomposition and the negative electrode from co-intercalation of solvent molecules into graphite and thus its exfoliation. The performance, aging

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and safety of a lithium-ion cell are strongly affected by the properties of the SEI, therefore it is indispensable to assure a sufficient SEI formation [4–7]. For this reason the first charge and if required also further charge–discharge cycles, in total called the formation, must undergo a defined process with well selected parameters. Influences of temperature [8–12], current [13–15], voltage profile [16–18] and the used materials (type of graphite and electrolyte composition) [19,20] on the composition and morphology and therefore functional properties of the SEI have been investigated. With the use of ethylene carbonate (EC)-based electrolytes, typical species found in the SEI are lithium alkyl carbonates ($ROCO_2Li$), lithium alkoxides (ROLi), lithium alkyl carboxylates (RCOOLi), lithium carbonate ($Li_2CO_3$), lithium oxide ($Li_2O$), lithium hydroxide (LiOH) and lithium fluoride (LiF) [21–24].

Also NCM positive electrodes show poor first-cycle efficiency. There are reports on formation losses due to surface film formation [25] or other parasitic electrochemical reactions as a function of particle surface area [26]. In contrast Kang et al. showed that the assumed physical loss of lithium in conventional voltage range is only a kinetic behavior and can be fully recovered below 1.5 V by applying a deep discharge [27,28].

However, in most commercial lithium-ion cells both graphite negative electrode and metal oxide positive electrode are present and it is not trivial to assign the initial losses and further aging effects to the different electrodes. In this work, the charging conditions and materials (graphite and NCM) of a commercial pouch cell were applied to three-electrode half cells containing either graphite or NCM as the working electrode to figure out the roles of the two electrodes in matters of formation losses and aging impact in full cells. For this procedure the formation was executed at different temperatures to understand its effect on the SEI formation and subsequent cell performance. Also the influence of the upper cut-off voltage on the formation was investigated.

The characterization of the SEI was performed with X-ray photoelectron spectroscopy (XPS), attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) and Raman spectroscopy.

## 2. Experimental

Lithium-ion pouch cells (“full cells”) from Li-Tec Battery (HEA50, 50 Ah) consisting of a graphite negative electrode, $Li_x(Ni_{1/3}Co_{1/3}Mn_{1/3})_yO_2$ (NCM) positive electrode, polymer separator and an ethylene carbonate based organic electrolyte with lithium hexafluorophosphate as conducting salt were used in this study. The “half cells” (electrochemical measurements of electrodes vs. metallic lithium) were assembled using three-electrode test cells (EL-Cell, type ECC-Ref) with the electrode (graphite or NCM) to be investigated as working electrode, lithium metal (Alfa Aesar, purity 99.9%) as counter and reference electrodes, a glass microfiber mat (Whatman, type GF/D) soaked with electrolyte as separator. For some experiments the test cells were configured with both graphite and NCM electrodes as well. Before transferred into the argon-filled glovebox ($H_2O$ and $O_2 < 1$ ppm) for half-cell assembly the active materials and separators were dried under vacuum at 130 °C for at least 12 h and subsequently hermetically sealed. The electrochemical tests with pouch cells were carried out using a multiple cell tester (Digatron, MCT Series). The test cells were investigated by the use of potentiostats (Gamry, type Reference 600). For temperature control, temperature chambers (Vötsch, different types) were used.

The formation was performed for all cells in a similar way. The C-rate is based on the capacity of the positive electrode (limiting electrode) of the pouch cell after formation, and was downscaled using the area of the electrode for the test cells. The terms charge and discharge always refer to a full cell. Charging of a graphite half-cell is therefore the intercalation of lithium into graphite. Charging NCM means the extraction of lithium out of the NCM host lattice. First the cells were charged with a current of C/10 (1C is the current needed to charge a cell within 1 h to its nominal capacity) for 10 h, and then discharged to 3.0 V (full cell), 3.0 V vs. $Li^+/Li$ (NCM) or 1.5 V vs. $Li^+/Li$ (graphite), respectively. The time-limited charge has been chosen to achieve a comparable capacity in all cells since the exact potentials vs. $Li^+/Li$ of the electrodes in the full cell are not known. In the case of discharging a time-limited process would be useless in respect to the differences in formation losses considered here. In the subsequent cycles potential limits were used for both charge and discharge processes to observe the capacity fade due to the increase of the internal resistivity. For the pouch cells limits of 4.2 and 3.0 V and a current of 3C were chosen. NCM was cycled between 3.0 and 4.2 V vs. $Li^+/Li$ and graphite between 0.04 and 1.5 V vs. $Li^+/Li$, both with a current of C/2, respectively. The different currents were chosen according to the different internal resistivities.

For analysis of the SEI the pouch cells (50% state-of-charge) were opened in a glovebox and appropriate negative electrode samples were cut out. The samples were washed with diethyl carbonate (DEC) for various times and vacuum-dried in the antechamber for 1 h before hermetically sealed for transport or directly measured in the glovebox.

The ATR-FTIR analysis was carried out in the glovebox using a Tensor 27 system (Bruker) together with a DuraSamplIR II (Smiths Detection) containing a three-reflection DuraDisk. A resolution of 4 $cm^{-1}$ and a scan number of 16 were used.

XPS measurements were conducted with a PHI 5600 CI (Physical Electronics) spectrometer with a pass energy of 29 eV and an analysis area of 800 μm in diameter. Monochromatic Al-$K_\alpha$ excitation (350 W) and a low-energy electron neutralizer were used. To avoid air contact of the samples, the system was equipped with a transfer chamber. Sputter depths profiling was done using $Ar^+$ ions (3.5 keV, scan size $3 \times 3$ mm) with conditions leading to a 0.4 nm $min^{-1}$ sputter rate, determined for a $SiO_2$ reference.

For the Raman spectroscopy the electrodes were placed in airtight spectroscopic cells equipped with glass optical windows. The measurements were carried out using a LabRAM HR (Horiba Jobin Yvon) with a 633 nm HeNe laser (about 11 mW), an 100× objective, a motorized *xy*-stage and an analysis area of $3 \times 4$ μm (wobble scan technique, 15 s integration time).

## 3. Results and discussion

### 3.1. Formation

Fig. 1a shows the formation curves at 25 °C for a commercial pouch cell, an NCM half-cell and a graphite half-cell. The differences in capacity between charging and discharging curves are the formation losses. Obviously, the losses of both NCM and the full cell exceed those of graphite. In Fig. 1b these losses are displayed for different formation temperatures, respectively. The losses of the full cell and that of the NCM half-cell are about the same at one formation temperature (25–45 °C). The small deviations can be related to the chosen lower cut-off voltages of 3.0 V for both potentials NCM vs. $Li^+/Li$ and NCM vs. graphite (Fig. 1a). The significant higher losses at 15 °C for the NCM half-cell compared to the full cell could be due to the inner resistivity which plays a more dominant role at low temperatures for the half-cell geometry. Apparently, the formation losses of graphite electrodes increase with temperature while those of NCM decrease. The temperature dependency of the irreversible charge losses of the commercial cell