Room temperature, liquid-phase Al₂O₃ surface coating approach for Ni-rich layered oxide cathode material†

Sven Neudeck,‡a Florian Strauss,a Grecia Garcia,a Hannes Wolf,b Jürgen Janek,b ac Pascal Hartmann*aab and Torsten Brezesinski id

A room temperature, atomic-layer-deposition-like coating strategy for NCM811 (80% Ni) is reported. Trimethylaluminum is shown to readily react with adsorbed moisture, leading both to Al₂O₃ surface layer formation on NCM811 and to trace H₂O removal in a single treatment step. Even more importantly, the cycling performance of pouch cells at 45 °C is greatly improved.

Layered lithium transition-metal oxides containing Co, Ni and Mn or Al such as Li₁₅[Ni₁₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋xFigure 1). However, the coating layer, which apparently consists of small-size Al-containing species.

1 Battery and Electrochemistry Laboratory, Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany. E-mail: torsten.brezesinski@kit.edu
2 BASF SE, Carl-Bosch-Str. 38, 67056 Ludwigshafen, Germany. E-mail: pascal.hartmann@basf.com
3 Institute of Physical Chemistry & Center for Materials Research, Justus-Liebig-University Gießen, Heinrich-Buff-Ring 17, 35392 Gießen, Germany
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‡ These authors contributed equally.
thickness and degree of coverage. Furthermore, liquid-phase TMA treatment appeared to result in a different coating morphology than ALD. Nonetheless, this is not very surprising given that a self-limiting growth mechanism cannot be expected.

In analogy to ALD, we assume that the main species formed on the top surface of NCM811 is Al$_2$O$_3$. The presence of proton bearing species of the general formula Al$_2$O$_3$H$_x$ cannot be ruled out though. For reasons of simplicity, we refer to Al$_2$O$_3$ in the following.

The Al$_2$O$_3$-coated and uncoated (bare) NCM811 CAMs were electrochemically tested at 45 °C and at a rate of 1C in the voltage range between 2.8 and 4.2 V using single-layer pouch cells with a graphite anode. The areal loading was about 10 mg NCM811 cm$^{-2}$. Details about the electrode preparation, cell assembly and cycling conditions—including cell formation—can be found in the ESI.† Of note, the coating layer has very little effect on the cyclability (specific capacity, Coulombic efficiency, mean charge/discharge voltage) during the very first cycle (Fig. S1, ESI†). Fig. 2 shows the results from long-term cycling experiments after cell formation. Initial discharge capacities of 182–186 mA h g$^{-1}$NCM811 were achieved for both the Al$_2$O$_3$-coated and bare NCM811 cells. All cells revealed an almost linear capacity decrease with increasing cycle number, and they were stopped after reaching 80% of their rated capacity. The latter is commonly defined as end-of-life. The bare NCM811 could be cycled for about 500 cycles, compared to 1100 cycles for the Al$_2$O$_3$-coated NCM811 (Fig. 2a). This result demonstrates that TMA treatment brings about considerable improvements in cycling stability. A similar trend can be deduced from the evolution of the mean discharge voltage with cycling (Fig. 2b). For the bare NCM811, the discharge voltage was relatively stable at slightly below 3.7 V during the first 100 cycles. However, with further cycling, it dropped quite significantly to about 3.5 V at the 500th cycle. In contrast, even after 1100 cycles, the mean discharge voltage was well above 3.5 V in the case of Al$_2$O$_3$-coated NCM811. This is also reflected in the rate performance, especially for C-rates >1C (Fig. S2, ESI†). During the initial rate capability test after 10 cycles, only slight differences in specific discharge capacity ($\leq$5 mA h g$^{-1}$NCM811) were found between the Al$_2$O$_3$-coated and bare NCM811 CAM. However, already in the second test after 310 cycles there was a notable difference of up to 21 mA h g$^{-1}$NCM811 at 3C rate. Likewise, cells using the Al$_2$O$_3$-coated NCM811 showed Coulombic efficiencies >99.95%, compared to 99.93 on average for the bare NCM811, thus indicating less side reactions after coating with Al$_2$O$_3$ (Fig. 2c).

As expected, almost identical charge/discharge curves in the initial cycles were obtained on cells using the Al$_2$O$_3$-coated and bare NCM811, with the voltage profile being characteristic of Ni-rich NCM CAMs (Fig. 3a and Fig. S1, ESI†). However, there were distinct differences in terms of capacity and overvoltage after 500 cycles (Fig. 3b). The usable specific discharge capacity of the Al$_2$O$_3$-coated and bare NCM811 cells was found to be 169 and 150 mA h g$^{-1}$NCM811, respectively. The corresponding differential capacity plots indicated minor impedance build-up during cycling operation (<100 mV overvoltage with respect to the high-voltage features) when using the Al$_2$O$_3$-coated NCM811 (Fig. S3, ESI†). By contrast, the bare NCM811 CAM showed around two times higher overvoltage after the same number of cycles. In addition, some of the characteristic redox peaks vanished or merged with others.

In order to confirm that the decline in cell performance was mainly due to CAM degradation, electrochemical impedance...
With literature.14,15 Particle fracture (mechanical degradation), different battery technologies has been intensively studied in oxide CAMs.16,17 Few, are currently considered the main issues of Ni-rich layered transition-metal dissolution (surface reactions), to name a few, are currently considered the main issues of Ni-rich layered oxide CAMs.16,17

Although Al2O3 surface coating of electrode material for different battery technologies has been intensively studied in the past,3,7–11 we present here an innovative liquid-phase approach, leading to > 100% improvement in cycling stability (i.e., end-of-life) for a technologically relevant CAM. This is due to not only the presence of a protective shell, but also the decrease in H2O content. Note that trace H2O is detrimental to the cell cyclability (long-term performance etc.).18,19 We also emphasize that no post-heating/annealing is required, which is both costly and time-consuming, especially in industrial fields. In addition, this excludes interdiffusion of Al species (Al3+) into the CAM, resulting in doped samples or different chemically altered interfaces, as reported for LiCoO2 and high-Ni NCMS.7,20

In summary, the aim of the current study was not to explore any new coating chemistry, but rather to simplify an established procedure. This was achieved by solvent-based synthesis at room temperature using highly reactive TMA as the precursor. Taken together, our approach combines two processing steps—usually considered indispensable before implementation of Ni-rich layered oxide CAMs in LIBs—namely drying and coating, at once. Thus, we believe that this simple and easily scalable process is of high interest to the battery community and may even pave the way toward development of a more general concept of surface coating.

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Conflicts of interest
There are no conflicts to declare.

Notes and references