Advanced Nanoparticle Coatings for Stabilizing Layered Ni-Rich Oxide Cathodes in Solid-State Batteries

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Improving the interfacial stability between cathode active material (CAM) and solid electrolyte (SE) is a vital step toward the development of high-performance solid-state batteries (SSBs). One of the challenges plaguing this field is an economical and scalable approach to fabricate high-quality protective coatings on the CAM particles. A new wet-coating strategy based on preformed nanoparticles is presented herein. Nonagglomerated nanoparticles of the coating material ≤5 nm, exemplified for ZrO2 are prepared by solvothermal synthesis, and after surface functionalization, applied to a layered Ni-rich oxide CAM, LiNi0.85Co0.10Mn0.05O2 (NCM85), producing a uniform surface layer with a unique structure. Remarkably, when used in pelletized SSBs with argyrodite Li6PS5Cl as SE, the coated NCM85 is found to exhibit superior lithium-storage properties (qdis = 204 mAh gNCM85⁻¹ at 0.1 C rate and 45 °C) and good rate capability. The key to the observed improvement lies in the homogeneity of coating, suppressing interfacial side reactions while simultaneously limiting gas evolution during operation. Moreover, this strategy is proven to have a similar effect in liquid electrolyte-based Li-ion batteries and can potentially be used for the application of other, even more favorable, nanoparticle coatings.

1. Introduction

The solid-state battery (SSB) is widely regarded as one of the most promising next-generation energy-storage technologies.[1−3] Apart from that, inorganic solid-state batteries (SSBs) are dismissed in SSB systems.[2,4,5] Apart from that, inorganic solid electrolytes (SEs) are required to suppress dendrite formation and facilitating the use of lithium–metal anodes.[1,1,4,6] In addition, SSBs have other advantages, such as a wider operation temperature range or no cross-talk effects due to electrode dissolution.[7,8]

Despite all that, commercialization of SSBs is hindered by their limited cycling performance compared to LIBs.[2,7,9] Especially ensuring compatibility of the cathode active material (CAM) with the SE and stability of their interface have proven difficult, as also the formation of cathode composites with proper ionic/electronic partial conductivities.[10] Thus, an important step toward the development of high-performance SSBs is the fabrication of a robust cathode.[9,11] Until now, different classes of superionic SEs (e.g., thiophosphates, oxides, polymers) have been proposed and studied for use in SSBs.[11,12] Lithium thiophosphate-based SEs stand out due to soft mechanical properties (low elastic modulus), ensuring intimate particle/particle contact even by cold-pressing processes.[2,1,9] More importantly, this class of SEs presents Li-ion conductivities on the order of magnitude as organic liquid electrolytes (e.g., for Li6PS5Cl, $\sigma_{\text{ion}}$ varies from $\approx 3 \text{ mS cm}^{-1}$ at room temperature to 7 mS cm⁻¹ at 45 °C, see related discussion in Figure S1, Supporting Information), allowing for satisfactory rate capability.[2,1,13] Regarding the CAM, layered Ni-rich NCMs (LiNi1−x−yCoMn$_x$O$_2$), such SEs have a mechanically rigid nature and a higher Li transference number ($t_{\text{Li}} \approx 1$ vs $t_{\text{Li}} \approx 0.5$ for liquid electrolytes), both being favorable for suppressing dendrite formation and facilitating the use of lithium–metal anodes.[1,1,4,6] In addition, SSBs have other advantages, such as a wider operation temperature range or no cross-talk effects due to electrode dissolution.[7,8]
as LiNi₀.₅Co₀.₁Mn₀.₄O₂ (NCM811) or LiNi₀.₈₅Co₀.₁₀Mn₀.₀₅O₂ (NCM85105, referred to as NCM85 for brevity), have great academic and industrial significance in advanced LIBs because of their high specific capacity (≥200 mAh g⁻¹) and high mean voltage (≥3.7 V vs Li⁺/Li). For the same reasons, these CAMs are also considered state of the art for SSB applications.⁹⁻¹³,¹⁷ Unfortunately, thionophosphate SEs have a relatively narrow electrochemical stability window (see also cyclic voltammetry (CV) data in Figure S1, Supporting Information) and show poor compatibility with NCM materials, in particular at high states of charge.²,⁹,¹³,¹⁷

This in turn means that the cathode typically suffers from performance degradation during electrochemical cycling because of side reactions occurring at the interfaces, e.g., SE oxidation, leading to poor reversibility and resistance build-up.²,⁹,¹³,¹⁸

Applying a protective coating to the CAM surface is an effective strategy to improve the interfacial stability by avoiding direct physical contact with the SE.³,⁹,¹⁷,¹⁹,²⁰ An ideal coating should not only be thin and uniform, but also feature desirable properties, such as low electronic conductivity and high ionic conductivity. Such a coating would reduce the contact resistance caused by decomposition reactions, thereby enhancing the cycling performance.²,⁹,²⁰ To date, the most common methods are wet-chemical and dry coating, mainly for cost and processing reasons.³,⁹,²¹ However, using these routes, both the thickness and morphology of the coating are difficult to control, leading to inhomogeneities and leaving areas of the surface unprotected.³,⁹,²¹ Although some progress has been made in solving the aforementioned issues via atomic layer deposition, the high cost of precursors, poor scalability, and process complication limit its practical/commercial application.²³⁻²⁴

These challenges prompted the motivation for the present work, namely, developing a scalable coating method for fabricating a uniform, nanoscale layer on the NCM particle surface.⁹,¹⁵,²¹ Specifically, we propose a new coating strategy based on preformed, nonagglomerated nanoparticles (NPs) in solution. Despite previous efforts to investigate and improve NP-derived coatings, the problem of inhomogeneities caused by large particle sizes and/or agglomeration remains to be solved.²⁵⁻²⁷ Herein, the coating material was prepared first as a stable dispersion comprising monodisperse NPs (≤5 nm size) and then applied to the CAM. ZrO₂ NP-modified NCM85 served as a model system to demonstrate the effectiveness of the coating strategy. The as-formed material, referred to as ZrO₂-NCM85 hereafter, was characterized in pelletized (high-loading) SSB cells with Li₄Ti₅O₁₂ (LTO) as SE and anode, respectively. ZrO₂ was selected because it has been reported in the past to be a robust coating material, owing to good chemical and electrochemical stability.²⁰,²¹,²₈⁻²⁹

The results of this study not only highlight the formation of a ZrO₂ monolayer coating with a constant thickness, but also with a unique bilayer structure (Scheme 1). It substantially enhanced the electrochemical performance of bulk-type SSB cells, delivering high reversible capacities and showing good cycling stability and rate capability (up to 1140 mA g⁻¹ NCM85⁻¹). The improvements can be attributed to changes in the CAM/SE interfacial stability, as demonstrated through a combination of operando and ex situ investigations. Data from complementary experiments are also presented (cycling performance of ZrO₂-NCM85 in LIBs and employing a different coating material, HfO₂ NPs, having high (electro-)chemical stability, as reported elsewhere²⁴), further emphasizing the versatility and potential of the new coating approach.

### 2. Results and Discussion

The coating procedure consists of two main steps: i) the preparation of a high-quality ZrO₂ NP dispersion, and ii) its application to achieve a protective layer on the outer surface of the NCM85 particles. More details are provided in the Experimental Section. Note that both the coating content and the annealing temperature were optimized based on a series of control experiments. In summary, for the first step (fabrication of monodisperse ZrO₂ NPs), we used a surfactant-free, nonaqueous solvothermal method (in benzyl alcohol).³⁰⁻³² Importantly, the as-prepared NPs showed high compositional homogeneity and purity, as confirmed by powder X-ray diffraction (XRD, see Figure S2, Supporting Information). The XRD data revealed broad reflections as a result of the nanocrystalline nature of the ZrO₂ particles.³³ The position and relative intensity of all reflections match well with those of the cubic crystal structure of zirconia. However, a turbid suspension was obtained after solvothermal reaction (Figure S3a, Supporting Information), indicative of NP agglomeration (high surface energy).³³⁻³⁴ No apparent improvement was achieved upon redispersing the NPs in nonpolar or polar solvents.³⁰ Obviously, it would be difficult to produce a uniform coating on the NCM85 CAM using such aggregated NPs as the coating material (Figure S4, Supporting Information). Thus, a surface functionalization step was required to properly disperse the ZrO₂ NPs. Specifically, minute quantities of long-chain ligands (oleic acid in this case) were added to the suspension to offer stabilization in nonpolar solvents (chloroform) via steric hindrance.³⁰,³²⁻³³ Ultimately, a highly stable and transparent dispersion of ZrO₂ NPs was obtained, as shown in Figure S3b of the Supporting Information, coupled with a high solid content of up to 70 mg mL⁻¹. Transmission electron microscopy (TEM) imaging showed evenly dispersed NPs with a narrow size distribution of 3⁻⁵ nm (Figure S3c⁻e, Supporting Information). The lattice spacing of 0.18 nm, recorded in high-resolution TEM (HRTEM, see Figure S3d, Supporting Information), is identical with the distance of the (220) lattice planes of cubic ZrO₂. After application of the coating, the ZrO₂-NCM85 CAM was characterized via XRD, X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM) in an attempt to probe

![Scheme 1. Schematic coating morphology. The protective coating has a unique bilayer structure, consisting of ZrO₂ NPs and (mostly) lithium carbonate.](image-url)
the crystal structure and surface chemistry. XRD (Figure 1a) showed that the ZrO$_2$-NCM85 has the expected O3-type layered structure (R-3m space group, see also crystal structure model in the inset of Figure 1a). Refinement of structural models against the diffraction data revealed that the lattice parameters of the coated CAM remain constant within error, see Figure S5 and Table S1 of the Supporting Information, while no appreciable impact on the Ni/Li cation mixing was observed either, 2.9(2)% for bare NCM85 and 3.4(3)% for ZrO$_2$-NCM85. This indicates that the coating process at least does not significantly affect the structural properties of the NCM85 CAM (Figure S6, Supporting Information). The absence of unforeseen reflections further highlights the purity of the material. Reflections from the ZrO$_2$ NPs were not found in the XRD pattern (see Figure 1a; Figure S6, Supporting Information), which is expected due to low overall crystallinity and content. Inductively coupled plasma-optical emission spectroscopy (ICP-OES, see Table S2, Supporting Information) revealed a Zr content of 0.66 wt%, equivalent to 0.92 wt% ZrO$_2$.

The XPS detail spectra of the Zr 3d, C 1s, and Li 1s regions in Figure 1b–d contain compositional information about the coating. Figure 1b shows two Zr 3d signals, Zr 3d$_{3/2}$ at 181.9 eV and Zr 3d$_{5/2}$ at 184.2 eV, confirming the presence of a ZrO$_2$ coating, in agreement with the ICP-OES results. As expected, the Zr 3d signals were absent for the bare NCM85 CAM. The ZrO$_2$-NCM85 had a more pronounced C 1s contribution than the bare NCM85 at 289.6 eV (Figure 1c), which was not the case for the other three peaks (284.8 eV for C=C/C=C, 286.0 eV for C=O, and 288.9 eV for O=O) [37–39]. The binding energy of the increased signal contribution is in the typical range of carbonate species, such as Li$_2$CO$_3$ [37,38] which most likely stem from the ligand and/or solvent decomposition during the final heating step at 400 °C. The presence of Li$_2$CO$_3$ (main surface carbonate) was further corroborated by the fact that the corresponding contribution in the Li 1s core-level region remained virtually unaltered after coating (Figure 1d), while the NCM85 signal intensity strongly decreased [37,38]. These findings suggest that the carbonate fraction is part of the coating in the ZrO$_2$-NCM85 CAM. Additionally, attenuated total reflection-infrared (ATR-IR) spectroscopy confirmed the presence of surface carbonate species (Figure S7, Supporting Information).

Surface characterization of the CAM in the pristine state and after coating was done by SEM (Figure 1e,f; Figure S8, Supporting Information). Low-magnification SEM imaging (Figure S8, Supporting Information) indicated that both the ZrO$_2$-NCM85 and bare NCM85 CAMs possess a uniform (polycrystalline) morphology with an average secondary particle size of 3 μm. This confirms that the NCM85 retains its original structure/morphology upon coating. As can be seen from the high-magnification SEM image in Figure 1e, the top surface of
the bare NCM85 primary particles appeared quite smooth. Similarly, the ZrO₂-NCM85 particles also had a relatively smooth surface (Figure 1f), probably owing to uniform NP deposition.

To gain more insight into the coating microstructure, (scanning) TEM [(S)TEM] and energy-dispersive X-ray spectroscopy (EDS) mapping were conducted on focused-ion beam (FIB)-prepared specimens, as summarized in Figure 2. Note that a carbon layer was deposited onto the ZrO₂-NCM85 CAM to protect the coating from damage during sample preparation and processing. Low-magnification high-angle annular dark-field (HAADF) STEM imaging (Figure 2a) showed that the free surface of the NCM85 secondary particles is uniformly covered by a shell-like structure. Interestingly, the TEM image in Figure 2b reveals a dual coating structure, consisting of an outer darker layer and an inner lighter layer. The outer layer is a monolayer, stemming from the organized assembly of ZrO₂ NPs, see TEM images in Figure 2c,d. The inner layer has a quasi amorphous nature and is represented in a lighter contrast. The monolayer exhibits a thickness of 4–5 nm, which agrees well with the size of the ZrO₂ NPs (Figure S3c–e, Supporting Information). The HRTEM image in Figure 2g shows the lattice fringes of the NPs with a d-spacing of 0.18 nm for the (220) planes. Notably, Figure 2d also shows ZrO₂ lattice fringes within the inner layer (see also Figure S9, Supporting Information). The thickness of the inner layer (Figure 2b,c,e), which seems to be derived from the decomposition of the oleic acid ligands used for functionalization of the NPs, is relatively constant along the coating (~8 nm). By contrast, when using a solution that contained only oleic acid and no ZrO₂ NPs for coating the NCM85 CAM (referred to as C-NCM85, related characterization data presented in Figures S11–S15, Supporting Information), HAADF STEM imaging revealed the presence of irregular deposits on the particle surface.[40] The lack of a continuous carbonaceous layer, as compared to the ZrO₂-NCM85 sample, demonstrates that the NPs play a critical role in the fabrication of a high-quality coating with uniform thickness and good surface coverage. More experiments will be performed in the future to unveil the details of the formation mechanism and the role of the main components.

Finally, the conclusions drawn from (S)TEM imaging were validated by EDS elemental mapping (Figure 2h), verifying that the ZrO₂ NPs primarily distribute on the outer surface (light shell) of the NCM85 secondary particles. Note that the resolution is not high enough to distinguish the carbonaceous coating from the protective carbon layer (see EELS mapping results in Figure S10, Supporting Information, instead).

The electrochemical performance of the uncoated (bare NCM85), coated (ZrO₂-NCM85), and reference (C-NCM85) CAMs was investigated in pelletized SSB cells with a high areal loading [(11.0 ± 0.3) mgNCM85 cm⁻², ≈2.1 mAh cm⁻²]. The cathode composite consisted of the respective CAM, SE (Li₆PS₅Cl), and carbon additive (Super C65). Li₆PS₅Cl SE was also used in the separator layer, and a composite comprising LTO, Li₆PS₅Cl, and Super C65 served as anode. All cells were galvanostatically cycled at 45 °C and at various C-rates in a voltage range of 1.35–2.75 V versus Li₄Ti₅O₁₂/Li⁺, corresponding to ≈2.9–4.3 V versus Li⁺/Li. Figure 3a shows the voltage–capacity profiles of the first 2 cycles at 0.1 C rate. The different electrochemical performance indicators for the initial cycle are displayed in the form of a radar plot in
Figure 3b. In the initial cycle, the bare NCM85 delivered specific charge and discharge capacities of 221 and 175 mAh g\textsubscript{NCM85}\textsuperscript{−1}, respectively, corresponding to a Coulombic efficiency of 79%. For the C-NCM85, the capacities amounted to 217 and 190 mAh g\textsubscript{NCM85}\textsuperscript{−1}, thus indicating a lower irreversible capacity loss (87% Coulombic efficiency). The largest specific capacities of 229 mAh g\textsubscript{NCM85}\textsuperscript{−1} (charge) and 204 mAh g\textsubscript{NCM85}\textsuperscript{−1} (discharge) and the highest Coulombic efficiency of 89% were
obtained with the ZrO₂-NCM85 CAM, which can be attributed to the good surface coverage and uniformity of the protective coating.[23,41] The beneficial effect of the NP coating is further evident from the comparison of the first-cycle discharge curves (Figure S16, Supporting Information), revealing substantial improvements in voltage drop and a higher mean voltage (Figure 3b) for the ZrO₂-NCM85, compared to the C-NCM85 and bare NCM85 CAMs. This result suggests that the coating is capable of suppressing side reactions, thereby reducing the interfacial impedance and polarization, as also apparent from the differential capacity curves and CV profiles in Figures S17 and S18 of the Supporting Information.

In the second cycle, virtually no capacity fading was observed for the ZrO₂-NCM85 and C-NCM85, confirming good reversibility.[39] By contrast, the specific discharge capacity of the bare NCM85 cell decayed to 165 mAh g⁻¹ after 50 cycles, accompanied by an increase in overpotential, indicating that irreversible processes continued to occur after the initial cycle. The long-term performance measurements in Figure 3c included rate capability testing from 0.1 C/0.1 C to 1.0 C/1.0 C (2 cycles at each C-rate), followed by cycling at a constant charge/discharge rate of 0.2 C. The ZrO₂-NCM85 CAM clearly exhibited better rate performance than the other two samples. In particular, the retention at 1.0 C maintained at a high value of ~60% with respect to the first-cycle discharge capacity at 0.1 C (Figure 3b), compared to only 37% and 55% for the bare NCM85 and C-NCM85, respectively. The reversible Li-storage capacity of the ZrO₂-NCM85 CAM in SSBS was also significantly improved, with a higher Coulombic efficiency (up to 99.8%) after 50 cycles. The Nyquist plots of the electrochemical impedance showed a depressed semicircle and a single line in the high- and low-frequency range, respectively. The fitting results (see equivalent circuit model in the inset of Figure 4a) indicate that the cells have a similar bulk resistance (Rbulk) ranging from 21 to 30 Ω, which is typically considered as the SE resistance.[42,43,44] The SE grain boundary resistance (RgB) was found to be 13–26 Ω. The slight variations are believed to originate from local electrode inhomogeneities.[41] The CAM/SE interfacial resistance (Rcam/SE) contributed most to the difference in cell impedance among the three samples. At the 5th cycle, the Rcam/SE followed the order of bare-NCM85 > C-NCM85 > ZrO₂-NCM85. The Rcam/SE increased by a factor of about two after 160 cycles. In contrast to the bare-NCM85 (893 Ω), the Rcam/SE of the ZrO₂-NCM85-based cell (82 Ω) was an order of magnitude lower. These findings are in line with the trends observed from the electrochemical testing and further corroborate the effectiveness of the double-layer coating in suppressing the formation of detrimental SE degradation products.

The decrease in side reactions with application of a protective coating is also evident from top-view SEM images obtained on the cathode composites using the uncoated and coated NCM85 CAMs before and after cycling. The NCM85 and Li₃PS₄Cl particles can be clearly distinguished from one another in the SEM image of the pristine cathode (Figure 4e). After 160 cycles, the cathode with the bare NCM85 revealed significant changes in surface and bulk morphology (Figure 4f). Specifically, the formation of a porous structure between the NCM85 secondary particles (in the previous SE regions) and the appearance of a thick layer on the CAM surface indicated SE decomposition upon cycling. For the C-NCM85, a similar evolution in SE appearance was observed (Figure 4g), albeit to a lesser degree. This kind of degradation was not visible for
the ZrO₂-NCM85-based cathode composite (Figure 4h). The original electrode structure was well maintained after cycling, indirectly stressing that the CAM/SE interface is reasonably robust in terms of stability. These results agree well with those from cross-sectional SEM imaging (Figure S21, Supporting Information). Interestingly, there were no apparent signs of cracking or damage (electrochemical contact loss) near the CAM/SE interface. This suggests that (chemo-)mechanical degradation within the cathode does not play a critical role in the differences in cyclability between the bare and coated NCM85 CAMs in these cells. Additionally, XRD data collected from the cathode composites in the pristine state and after cycling showed that the bulk structure of Li₆PS₅Cl remains stable (see Figure S22 and Table S4, Supporting Information).

Figure 4. Nyquist plots of the electrochemical impedance for SSB cells using the bare NCM85 (black), C-NCM85 (red), and ZrO₂-NCM85 (cyan) after a) 50 and b) 160 cycles at a rate of 0.2 C and 45 °C in the discharged state. The inset in (a) shows the equivalent circuit used to fit the EIS data and describe the resistance contributions from the bulk SE ($R_{\text{Bulk}}$), SE grain boundary ($R_{\text{GB}}$), and CAM/SE interface ($R_{\text{CAM/SE}}$). c,d) Summary of the fitting results. e–h) Top-view SEM images of the cathode (e) in the pristine state and (f–h) after 160 cycles: ZrO₂-NCM85 (e,h), bare NCM85 (f), and C-NCM85 (g).
The differences in the $R_{\text{CAM/SE}}$ and the electrode morphology/microstructure between the cathode composites are largely attributed to the chemistry and thickness of the surface decomposition layer. To examine the chemical nature of the degradation products, ex situ XPS and time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurements were performed after 50 cycles. Figure 5a shows XPS detail spectra of the S 2p and P 2p core-level regions for both the pristine Li$_3$PS$_4$/Cl$_x$ SE and the cycled cathodes. The S 2p spectrum of Li$_3$PS$_4$/Cl$_x$ consisted of four doublets. While the pronounced doublet at 161.7/162.9 eV is characteristic of the PS$_4^{4-}$ units of the argyrodite structure, that at a lower binding energy (160.3/161.4 eV) represents Li$_2$S impurities (or “free” S$^{2-}$ ions).[8,18] The other two minor doublets located at higher binding energies (162.9/164.1 and 163.7/164.9 eV) can be assigned to various compounds, including anionic frameworks that thiophosphate phases can pass through upon oxidative decomposition toward the formation of PS$_x$(e.g., PS$_x^{4-}$, P$_2$S$_{6x}^{-}$) and “S$^0$” species, such as long-chain polysulfides.[8,18] The P 2p spectrum showed two doublets at 132.0/132.8 and 133.0/133.9 eV, representing the PS$_4^{4-}$ units and the aforementioned degradation products and/or lithium phosphate, respectively.[18,45-47] The presence of the latter may be a result of the reaction with trace water/oxygen because of the high reactivity of the Li$_3$PS$_4$/Cl$_x$ SE.[3,13,45] After 50 cycles, the peaks associated with the oxidized sulfur species in the S 2p data increased in intensity for all three cathodes, indicating the decomposition of the thiophosphate SE upon cycling. The coated CAMs showed slightly lower signals compared to the uncoated counterpart (Figure S23, Supporting Information). This confirms that the coatings are capable of partly suppressing the SE degradation. However, the formation of degradation products still seems pronounced and further differentiation between both coated samples is not possible. Note that several degradation zones (in the cathode) overlap in the XPS analysis area and therefore in the signals, as recently reported.[48] The oxidative SE decomposition can, in principle, occur at the CAM/SE and carbon additive/SE interfaces.[48,49] Because the carbon black used in this work was not modified/protected, degradation is believed to occur unhindered at this interface.[49] Consequently, the emerging signals in the S 2p data are expected to be dominated by SE decomposition processes at the carbon additive/SE interface, making a separation of the CAM/SE contribution virtually impossible.

By contrast, changes in the P 2p spectra allow for a better assignment of decomposition signals to the CAM/SE interface due to less interference. In particular, a new doublet at a higher binding energy (P 2p$_{3/2}$ at 134.5 eV) appeared upon cycling because of the formation of oxygenated phosphorus species (phosphates, metaphosphates, etc.).[18,45] Since the CAM is usually the only oxygen source in the cathode, the oxygenated phosphorus species can be directly correlated with the interfacial reaction between CAM and SE.[18] While the C-NCM85 already revealed a slight decrease in such by-products, the ZrO$_2$/NCM85-based cathode showed the lowest intensity of this P 2p doublet contribution and the lowest relative amount of degradation products in general (Figure S23, Supporting Information). This result provides evidence of suppressed side reactions at the CAM/SE interface as the working principle of the protective coatings. However, the effect appears to be much stronger when using the ZrO$_2$/NCM85 CAM, which in turn helps explain the above findings.

To gain a better understanding of the interfacial processes occurring within the electrodes, ToF-SIMS analysis was performed on the different cathode composites (after 50 cycles). ToF-SIMS possesses a high sensitivity and therefore allows probing degradation phenomena and the effect of the CAM coating beyond the XPS detection limit. The results from surface analysis and depth profiling are depicted in Figure 5b,c, showing boxplots for the normalized intensity of the phosphate (PO$_4^{3-}$) and sulfate/sulfite (SO$_4^{2-}$) fragments. The formation of PO$_4^{3-}$/SO$_4^{2-}$ species is a clear sign of degradation at the CAM/SE interface.[45,48,50] In the case of surface analysis (Figure 5b), both the bare NCM85 and C-NCM85 cathodes displayed similar intensities (slightly higher for the C-NCM85) for the PO$_4^{3-}$/PO$_4^{2-}$ and SO$_4^{2-}$/SO$_4^{2-}$ fragments. Only the SO$_4^{2-}$ fragment showed a decrease in intensity for the C-NCM85 cathode, indicating less formation of oxygenated sulfur species. For the ZrO$_2$/NCM85 cathode, reduction in signal intensities for both the PO$_4^{3-}$/PO$_4^{2-}$ and SO$_4^{2-}$/SO$_4^{2-}$ fragments was clearly visible, demonstrating suppression of the oxygen-involved interfacial reactions between CAM and SE. The trend of the phosphate fragments in the surface analysis seems to contradict the XPS results, as the C-NCM85 cathode did not show decreased formation of oxygenated phosphorus species. However, it should be noted that the surface facing the current collector was probed. The analyzed region therefore contains convoluted information about all interfacial reactions (current collector/SE, carbon additive/SE, and CAM/SE) and is likely dominated by the current collector/SE contribution.[48,51] Ultimately, this can lead to measurement uncertainties because of strong mass interferences and variations in total ion intensity (and therefore variations in the normalization approach) among others.

To eliminate the influence of the current collector, depth profiling was done on near-surface regions of the cycled cathodes.[45] Figure 5c shows the results from these experiments. It can be seen that the trends in intensity for the PO$_4^{3-}$ and SO$_4^{2-}$ fragments match with the cycling performance, the impedance, and the trends observed in the P 2p spectra (Figures 3c, 4a, and 5a). The signals suggest decreasing oxygen-involved side reactions in the order of ZrO$_2$/NCM85 > C-NCM85 > bare NCM85.

In contrast to XPS, ToF-SIMS was able to show suppressed formation of oxygenated sulfur species by surface coating because of the higher sensitivity of the analytical method.[18,45,48] In addition, this facilitated the differentiation of both coatings regarding their effect on the interfacial reactions between CAM and SE.

ToF-SIMS measurements were also conducted on crater sidewalls, providing information about the local distribution of fragments with high lateral resolution.[18,45] The secondary ion images for the cathode using the ZrO$_2$/NCM85 are shown in Figure 5d. Each component in the composite could be well resolved by utilizing the respective (specific) fragments. The ZrO$_2^{7+}$ signal indicated that the NP coating maintains a high density (and uniformity) around the NCM85 secondary particles after cycling, thus suggesting that it is capable of addressing consumption issues caused by diffusion and/or...
Figure 5. Characterization of the interfacial degradation after 50 cycles at a rate of 0.2 C and 45 °C. a) XPS detail spectra of the S 2p (left) and P 2p (right) core-level regions. The surface was previously cleaned by sputtering with Ar⁺ ions to reduce detrimental effects of the current collector. Reference spectra for the pristine Li₆PS₅Cl SE are shown at the bottom (see Figure S23, Supporting Information, for comparison of relative amounts of the S 2p/P 2p components). b–d) Results from ToF-SIMS measurements. Boxplots of the normalized intensity of POₓ⁻ and SOₓ⁻ fragments (with 2 ≤ x ≤ 3) from (b) surface analysis (≥14 measurements per sample) and (c) depth profiling (≥3 measurements per sample). Data were normalized to the total ion intensity. (d) Exemplary normalized secondary ion images of negatively charged fragments on an FIB crater sidewall (45°) of the cathode using the ZrO₂-NCM85. The CAM (NiO₂⁻), the coating (ZrO₂⁻), the SE (Cl⁻), and the degradation products [(PO₂⁻ · PO₃⁻), (S⁻ · SO₂⁻ · SO₃⁻), and polysulfides] can be clearly distinguished from one another.
(electro-)chemical reactions.\[18\] Moreover, secondary ion images of fragments that can be attributed to degradation products confirmed that side reactions occur in the bulk of the electrode irrespective of the coating. The signals mainly appeared at the CAM/SE interface and denote both oxidative SE decomposition (long-chain polysulfides ($S_x^-$)) and (electro-)chemical CAM/SE reactions (oxygenated phosphorus and sulfur species ($PO_x^-$ and $SO_x^-')). Similar fragment distributions were observed for composites with the bare NCM85 and C-NCM85 CAMs (Figure S24, Supporting Information). Overall, these results show that protective CAM coatings may indeed suppress unfavorable reactions at the interface with the SE, leading to significantly improved electrochemical performance in bulk-type SSBs.

In situ differential electrochemical mass spectrometry (DEMS) measurements were performed to further evaluate the effectiveness of the coating in suppressing outgassing reactions.\[52\] In recent years, it has been shown that certain coating chemistries are capable of reducing the evolution of gaseous degradation products that are detrimental to the battery operation.\[41,52\] The DEMS results for the different NCM85 CAMs are shown in Figure 6 and Figures S25–S28 (Supporting Information). Four different gases were detected, H$_2$, O$_2$, CO$_2$, and SO$_2$. Because ToF-SIMS analysis showed a decrease in SO$_x^-$ fragments for the ZrO$_2$-NCM85 cell, both the O$_2$ evolution and the SO$_2$ evolution were of great importance here. SSB cells using the bare NCM85 and ZrO$_2$-NCM85 CAMs (see Figure S27, Supporting Information, for C-NCM85) were cycled for 2 cycles and the respective gassing (see Figures S25 and S27, Supporting Information, for H$_2$ and CO$_2$) was observed at increasing onset voltages. In SSBs with Ni-rich NCM CAMs, O$_2$ (potentially reactive singlet oxygen, $^{1}\text{O}_2$) release is typically observed at a state of charge (SOC) $\geq$ 80%. The origin of O$_2$ evolution during cycling stems from the destabilization of the layered lattice at high voltages (e.g., $\approx$4.2 V vs Li$^+$/Li for NCM811).\[53,54\] Unfortunately, not all cells in this study were able to achieve the SOC requirement of $\geq$80%. While the bare NCM85 cell showed a 75% SOC (206 mAh g$\text{NCM85}^{-1}$), the ZrO$_2$-NCM85 cell achieved an SOC of 84% (229 mAh g$\text{NCM85}^{-1}$). Nevertheless, it has been shown that O$_2$ evolution may occur even below 80% because of inhomogeneities throughout the cathode composite.\[55–57\] A case in point, the mass signal ($m/z=32$) of the cell containing the bare NCM85 showed a sharp peak (Figure 6a) upon reaching a voltage of $\approx$4.2 V versus Li$^+$/Li. By contrast, the ZrO$_2$-NCM85 (Figure 6b) did not reveal any distinct peaks corresponding to O$_2$ release. Similarly, O$_2$ evolution was not apparent for the cell using the C-NCM85 (Figure S27, Supporting Information). Recently, Guo et al. reported about oleic acid-induced surface engineering, leading to the formation of a protective spinel type Li$_4$Mn$_5$O$_{12}$ layer on Li-rich layered oxide CAMs. According to the authors, the as-formed heterostructure is capable of stabilizing the surface, thereby suppressing O$_2$ release and preventing related phase transformations and side reactions from occurring.\[58\] Because the coating method employed in this

![Figure 6](https://example.com/figure6.png)

**Figure 6.** In situ DEMS analysis of SSB cells using the a) bare NCM85 and b) ZrO$_2$-NCM85 during the first charge cycle at a rate of 0.05 C and 45 °C. The voltage and corresponding cumulative gas evolution of O$_2$ and normalized ion current for SO$_2$ are plotted versus the SOC.
work comprised the use of oleic acid as a stabilizing agent for the ZrO$_2$ NPs, surface reconstruction may play a role here as well. In fact, EELS mapping of the C-NCM85 indicated Mn enrichment at the particle surface (Figure S29, Supporting Information), but this needs further study. An additional difference between the bare and coated NCM85 CAMs was the lack of SO$_2$ evolution for the latter samples. SO$_2$ release is characteristic of SSBs with thiophosphate SEs, and a mass signal ($m/z = 64$) is normally detected together with the O$_2$ signal. The formation of SO$_2$ has been reported to be a result of the reaction between SE and reactive oxygen released from both the NCM lattice at high SOC and electrochemical decomposition of residual surface carbonates.[56,59] For the bare NCM85, the observed onset of SO$_2$ evolution coincides with the O$_2$ and CO$_2$ signals. On the other hand, no apparent SO$_2$ signal was observed for the ZrO$_2$-NCM85 CAM, and neither for the C-NCM85. This observation indicates that the coating indirectly suppresses the O$_2$ evolution, and in doing so, suppresses interfacial side reactions to some extent, as evidenced by the lack of gaseous degradation products (SO$_3$). Since reported SO$_x^−$ peaks in XPS studies of sulfide-based battery systems are due to the reaction between SE and CAM,[60] the suppressed SO$_x^−$ signals for the ZrO$_2$-NCM85 agree well with the lack of SO$_2$ evolution.

In conclusion, in situ gas analysis of the different SSBs showed a lack of both O$_2$ evolution and SO$_2$ evolution for the coated CAMs at high SOC. Considering the above data from ToF-SIMS and XPS, this result provides profound evidence of decreased oxidation of the argyrodite SE, which is beneficial to the long-term cycling performance and safety of the cells.

To demonstrate that the improvement in cycling performance achieved by applying the NP coating concept to the NCM85 CAM is not limited to an SSB environment, the electrochemical properties of the ZrO$_2$-NCM85 were also probed in liquid electrolyte-based LIB cells using the bare NCM85 as a reference (see Figure S30, Supporting Information, for a comparison of LIB and SSB cells).[61] Specifically, both the ZrO$_2$-NCM85 and bare NCM85 cathodes with high areal loadings of $(11.3 \pm 0.3) \text{ mg}_{\text{NCM85}} \text{ cm}^2$ were cycled at 0.2 C/0.2 C rate and 45 °C in coin cells in a voltage range of 2.9–4.3 V versus Li$^+/\text{Li}$. The initial voltage profiles (Figure 7a) and corresponding differential capacity curves (Figure S31, Supporting Information) revealed that the CAMs show a similar electrochemical behavior ($q_{\text{dis}} = 206/213 \text{ mAh g}_{\text{NCM85}}^{-1}$ and Coulombic efficiencies of 93/94%). However, the ZrO$_2$-NCM85 exhibited a much better stability over 100 cycles, with a capacity retention of 83% (Figure 7b). By contrast, the bare NCM85 cell showed rapid fading to 113 mAh g$_{\text{NCM85}}^{-1}$, corresponding to only 53% retention after 100 cycles.

Finally, different NP chemistries were examined in some detail to highlight the versatility of the coating strategy. As an example, 0.82 wt% HfO$_2$ NPs ($\approx 6$ nm particle size) were applied as surface coating to the NCM85 secondary particles (details in the Experimental Section). SEM imaging and EDS

![Figure 7](attachment:figure7.png)

**Figure 7.** a,b) Cycling performance of ZrO$_2$-NCM85/Li and bare NCM85/Li cells with a liquid carbonate electrolyte at a rate of 0.2 C and 45 °C. c,d) Cycling performance of bare NCM85- and HfO$_2$-NCM85-based SSB cells at a rate of 0.2 C and 45 °C. (a,c) Initial voltage profiles. (b) Capacity retention and (d) specific discharge capacity versus the cycle number.
analysis confirmed the successful coating (Figure S32, Supporting Information). The as-prepared CAM (HfO$_2$-NCM85) was tested in pelletized SSBs under the same conditions as above. The positive effect of the protective coating on the cell performance is evident from the data shown in Figure 7c,d. As can be seen from Figure 7c, the HfO$_2$-NCM85 CAM delivered a larger first-cycle specific discharge capacity (181 vs 168 mAh g$^{-1}$) and showed an improved Coulombic efficiency (88 vs 78%) over the bare NCM85. More importantly, the cell using the HfO$_2$-NCM85 CAM showed superior cyclability (Figure 7d) and was still capable of delivering a specific capacity of 156 mAh g$^{-1}$ after 50 cycles. Overall, these results suggest that the NP strategy offers the potential to develop a variety of coating materials with clear benefits to the electrochemical performance in both SSBs and conventional liquid electrolyte-based LIBs.

3. Conclusions

This work has demonstrated the effectiveness of a new coating strategy based on preformed (nonagglomerated) NPs in solution in improving the cycling performance and stability of a layered Ni-rich CAM in bulk-type SSB cells. A nanoscale coating with a robust structure, consisting of a ZrO$_2$ NP monolayer and a carbonaceous layer, was successfully constructed on the surface of NCM85 secondary particles. Importantly, the as-fabricated coating not only showed a high CAM surface coverage, but also had a uniform morphology with a desirable thickness. Consequently, substantial improvements to the interfacial stability in the cathode composite were achieved, thanks to the suppression of side reactions, as confirmed by EIS, XPS, and ToF-SIMS. In addition, DMS measurements revealed that the coating positively affects the outgassing behavior. Overall, Li$_6$PS$_5$Cl-based SSB cells using the surface-protected NCM85 CAM exhibited superior Li-storage performance at 45 °C.

The data presented herein are promising, and we believe that this relatively simple and likely scalable coating approach will be of great interest to the battery community. Apart from SSBs, the coating strategy also holds promise for liquid electrolyte-based LIBs and can be readily extended to other NP chemistries, showing its versatility and effectiveness. Future experiments, exploring Li-based (ternary) oxide NPs as coating materials and/or applying them to single-crystalline CAMs may foster the development of high-performance electrode materials for various battery applications.$^{[62]}$

4. Experimental Section

Preparation of ZrO$_2$ NP Dispersion: ZrO$_2$ NPs were produced through a microwave-assisted solvothermal approach utilizing a Discover SP microwave (CEM GmbH), as reported previously.$^{[30]}$ All precursor preparation steps were performed in an Ar glovebox. The Zr precursor (zirconium(IV) isopropoxide isopropanol complex, 230 mg) was added to a microwave vial (10 mL inner volume) together with 4.5 mL benzyl alcohol, which was then sealed carefully using a Teflon cap. After 10 min of stirring at room temperature, the as-prepared solution was executed to a two-step microwave procedure: i) stirring at 60 °C for 5 min and ii) heating at 280 °C for 5 h. During the synthesis, the zirconium precursor solution transformed into a mixture consisting of a milky precipitate and an organic supernatant. The precipitate was separated by centrifugation and washed four times with diethyl ether. For XRD investigation, the resulting product was dried at 60 °C overnight. For the preparation of a stable and well-dispersed ZrO$_2$ NP suspension, the white powder was not dried after washing, but chloroform containing oleic acid (30 mg in 10 mL) was added immediately after the decantation. Upon stirring overnight, a transparent dispersion (see photographs in Figure S3, Supporting Information) was formed, having a solid content of ~70 mg mL$^{-1}$.

Preparation of ZrO$_2$-NCM85 and C-NCM85: The NCM85 powder was regenerated first to remove any surface impurities. Specifically, the CAM (15 g) was heated at 750 °C (5 °C min$^{-1}$ heating ramp) for 3 h under O$_2$ flow in an alumina crucible. Then, the NCM85 CAM (2 g) was mixed with a certain volume of the ZrO$_2$ NP dispersion in a beaker before adding chloroform to achieve a volume of 20 mL in total. After sonication for 30 min, the as-prepared suspension was dried at 60 °C under mild stirring, and the remaining powder was vacuum-dried at room temperature overnight. Subsequently, the modified CAM was transferred to a tube furnace and heated at 400 °C (5 °C min$^{-1}$ heating ramp) for 2 h under O$_2$ flow. Finally, the resulting material, ZrO$_2$-NCM85, was collected. For C-NCM85, the same procedure was followed, but without adding ZrO$_2$ NPs in the chloroform-based solution (it just contained the oleic acid).

Preparation of HfO$_2$-NCM85: For the synthesis of HfO$_2$, the work followed an established solvothermal process with some modifications.$^{[63]}$ 200 mg hafnium chloride was dissolved into 20 mL benzyl alcohol under vigorous stirring. After 15 min, a colorless and clear solution was formed for further use. The reaction mixture was added to a Teflon cup (45 mL inner volume) in a steel autoclave. The solvothermal reaction was performed in a furnace at 250 °C for 3 d. The NPs were recovered by precipitation using diethyl ether, followed by washing with both ethanol and diethyl ether. Finally, the HfO$_2$ NPs were redispersed in 5.5 mL chloroform for further modification. Postfunctionalization included adding oleic acid and oleylamine to the suspension under stirring until a transparent dispersion was achieved.$^{[62]}$ Coating of the NCM85 followed the same procedure as for the ZrO$_2$-NCM85 CAM.

Basic Characterization: Powder XRD data were collected using a STOE Stadi-P diffractometer with a Mo anode ($\lambda = 0.70926$ Å) and a DECTRIS MYTHEN 1K strip detector in Debye-Scherrer geometry. The instrumental contribution to the reflection broadening was determined by measuring a NIST 640f Si standard reference material. Rietveld refinement was performed using GSAS.$^{[10]}$ The scale factor, zero shift, and size/strain broadening parameters were allowed to vary. A fixed background was fitted to the data using a Chebyshev polynomial function with 11 terms. In the structural model, the unit cell parameters, oxygen z-coordinate, and atomic displacement parameters (isotropic) for each site were refined. Atoms occupying the same site were constrained to have the same atomic parameters, and site occupancy factors were constrained such that each site remained fully occupied. The site occupancy factor of Ni in the Li layer was refined to verify the off-stoichiometry. SEM imaging was done on a LEO-1530 microscope (Carl Zeiss AG) with a field emission source. TEM was performed both on a Titan 80–300 image-corrected microscope (FEI) and on a Themis Z (ThermoFisher Scientific) double-corrected transmission electron microscope equipped with an EDAX SuperX EDS detector. The acceleration voltage used for both microscopes was 300 kV. EELS data were acquired with an energy resolution of ~1 eV, estimated from the FWHM of the zero-loss peak by a Gatan image filter with K3 camera (Gatan Inc.). Samples for TEM were prepared by the lift-out technique using a Ga FIB on a STRATA dual-beam system (ThermoFisher Scientific). Prior to the ion milling, the ZrO$_2$-NCM85 CAM surface was protected by a carbon layer. Carbon was chosen for coating to exclude possible redeposition of Pt during the final milling steps. By contrast, Pt was chosen as a protective coating for the C-NCM85 CAM. The samples were milled at 30 kV, followed by final polishing at 2 kV to reduce the surface layer damage. Scanning TEM images were collected using an HAADF detector. An ALPHA FT-IR spectrometer (Bruker) was used to collect ATR-IR spectra. The instrument was equipped with a Ge crystal and situated in an Ar glovebox. The ZrO$_2$ content after coating was determined by ICP-OES using both a PerkinElmer Optima 4300 DV and a Thermo Scientific iCAP 7600.
XPS Analysis: XPS measurements were performed using a PHI5000 Versa Probe II system (Physical Electronics). The samples were prepared in an Ar glovebox. Insulating adhesive tape was used to attach the composite cathodes to the sample holder. The samples were transferred to the instrument under inert atmosphere using a transfer vessel from PREVAC. A dual-beam charge neutralization (low-energy electron beam combined with an ion beam) was used during the analysis. Depth profiling (alternating sputter mode) was carried out to minimize the detrimental effect of the current collector and to monitor the surface cleaning process, analogous to previous works. Monochromatic Al-Kα radiation (λ = 1486.6 eV) was used for analysis (200 µm spot diameter). The power of the X-ray source was 50 W with a voltage of 17 kV. For acquiring detailed spectra, the pass energy of the analyser was increased by 25 keV as primary ions. Lower energy electrons were introduced to the surface for charge compensation. The calibration was performed with a raster size of 1024 × 1024 pixels at 1 shot per pixel and frame. The measurement was stopped after a primary ion dose of 10^{12} ions cm^{-2} was reached. Prior to each measurement, a calibration gas with known quantity of H₂, CO₂, and O₂ (ppm) was introduced to the system to correct for the spin-orbit splitting, were used.

ToF-SIMS Analysis: ToF-SIMS measurements were performed on a TOFSIMS 3–100 system (IONTOF). The samples were prepared in an Ar glovebox. Insulating adhesive tape was used to attach the composite cathodes to the sample holder. The samples were transferred to the instrument under inert atmosphere using the transfer system Leica EM VCT500 (Leica Microsystems). All measurements were performed in negative ion mode using Bi⁺ (25 keV) as primary ions. ToF-SIMS data collected from a Li₆PS₅Cl reference were calibrated first to the signal area ratios, FWHM constraints, and reported values for the spin–orbit splitting.

Cell Assembly and Electrochemical Measurements: All SSB and LiFe cells were assembled in an Ar glovebox. For the SSB cells, the cathode composites for testing in SSB cells were prepared as reported elsewhere. The cathode material was mixed with the agglomerate Li₆PS₅Cl (NEI Corp.) and Super C65 carbon black additive (Timcal) in a 69.3:29.7:1 weight ratio to 140 °C under an argon atmosphere using a planetary ball-mill with 1 cm diameter zirconia balls. The preparation of the anode composite was similar, but the weight ratio of carbon-coated LTO (NEI Corp.), Super C65, and Li₆PS₅Cl was set to 30:10:60. The SE-Super C65 composite used in the CV experiment was prepared by manually grinding both materials for 0.5 h using a mortar and pestle. For the LiFe cells, the N-methyl-2-pyrrolidone cathode slurry contained 94 wt% CAM, 3 wt% Super C65, and 3 wt% polyvinylidene fluoride binder. The cathode sheet was prepared by slurry casting onto Al foil, followed by drying at 120 °C in a vacuum and calendaring at 15 N mm⁻¹. Finally, 13 mm diameter (circular) electrodes with an areal loading of ~11.3 mg NCMSS -cm⁻² were punched out.

Supporting Information: Supporting Information is available from the Wiley Online Library or from the author.
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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

all-solid-state battery, interfacial stability, layered Ni-rich oxide cathode, protective coating, side reactions

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