Lithium Phosphonate Functionalized Polymer Coating for High-Energy Li[Ni\textsubscript{0.8}Co\textsubscript{0.1}Mn\textsubscript{0.1}]O\textsubscript{2} with Superior Performance at Ambient and Elevated Temperatures

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High-energy Ni-rich lithium transition metal oxides such as Li[Ni\textsubscript{0.8}Co\textsubscript{0.1}Mn\textsubscript{0.1}]O\textsubscript{2} (NCM\textsubscript{811}) are appealing positive electrode materials for next-generation lithium batteries. However, the high sensitivity toward moist air during storage and the high reactivity with common organic electrolytes, especially at elevated temperatures, are hindering their commercial use. Herein, an effective strategy is reported to overcome these issues by coating the NCM\textsubscript{811} particles with a lithium phosphonate functionalized poly(aryl ether sulfone). The application of this coating allows for a substantial reduction of lithium-based surface impurities (e.g., LiOH, Li\textsubscript{2}CO\textsubscript{3}) and, generally, the suppression of detrimental side reactions upon both storage and cycling. As a result, the coated NCM\textsubscript{811}-based cathodes reveal superior Coulombic efficiency and cycling stability at ambient and, particularly, at elevated temperatures up to 60 °C (a temperature at which the non-coated NCM\textsubscript{811} electrodes rapidly fail) owing to the formation of a stable cathode electrolyte interphase with enhanced Li\textsuperscript{+} transport kinetics and the well-retained layered crystal structure. These results render the herein presented coating strategy generally applicable for high-performance lithium battery cathodes.

1. Introduction

Ni-rich Li\textsubscript{1−x−y}Ni\textsubscript{x}Co\textsubscript{y}Mn\textsubscript{x}O\textsubscript{2} (NCM\textsubscript{x−y−x} with 1−x−y ≥ 0.6) cathode materials are considered the most practical candidates for high-energy lithium-ion and lithium-metal batteries owing to their high capacities and good rate capability. However, there are several challenges that remain to be overcome for a widespread use in commercial battery cells: 1) the difficulty in synthesizing stoichiometric NCM due to the instability of trivalent nickel during the high-temperature calcination process; 2) the high sensitivity toward moist air and facile formation of surface impurities (e.g., LiOH, Li\textsubscript{2}CO\textsubscript{3}), causing inferior cycling stability; 3) the Li\textsuperscript{+}/Ni\textsuperscript{2+} cation mixing, leading to severe structural changes; and 4) the inferior thermal stability with an increasing nickel content, raising serious safety concerns. In fact, the higher the nickel content, the more pronounced are the abovementioned challenges and the more effective need to be the strategies to overcome these, especially for Ni-rich NCM\textsubscript{1−x−x} with 1−x−y ≥ 0.8. According to Ryu et al., an abrupt anisotropic shrinkage caused by phase transitions toward the end of charge occurs when the Ni content exceeds 0.8. This stress-inducing volume shrinkage and subsequent expansion initiates the propagation of microcracks from the bulk to the surface, leading to progressive capacity decay upon cycling. Moreover, such high nickel contents lead to an increasingly pronounced reactivity with moist air, requiring a consequent storage, handling, and processing under very dry or inert atmosphere – not least as the otherwise formed LiOH, Li\textsubscript{2}CO\textsubscript{3}, and transition metal carbonates (TM\textsubscript{y}CO\textsubscript{3}) cause the gelation of the slurry during the electrode preparation due to the pH increase, exacerbate gas evolution at elevated potentials (along with the oxygen release...
resulting from the layered to spinel and rock-salt structural transition),[9,10] and thus eventually have a detrimental impact on the cycling stability and capacity retention.

To address these challenges, various approaches have been adopted, including advanced material and particle designs such as the realization of core–shell structures[20] and transition metal concentration gradients,[21] the incorporation of functional dopants,[22] and the application of inorganic or organic surface coatings, including metal oxides,[13] metal fluorides,[14] metal phosphates,[15,16] and polymers.[15b,16] The latter approach appears particularly straightforward, as such protective coatings can physically prevent the contact with the ambient atmosphere, while also stabilizing the interface with the electrolyte in the battery cell – especially with regard to the essentially unlimited choice of suitable coating compositions, allowing for well-tailored properties. Nonetheless, the use of inorganic coatings commonly requires additional calcination steps at several hundred degrees Celsius, which leads to significantly higher cost and complicates recycling. In addition, lithium-free coating layers (inorganic or organic) hinder Li⁺ transport across the interface with the electrolyte, particularly when surpassing a certain thickness, which negatively affects the cell performance at elevated current densities.[17]

Herein, we report lithium phosphonate functionalized poly(arylene ether sulfone) (PP10-Li; see Figure 1a) as suitable coating layer for high-energy NCM811 (ONCM811) to overcome the aforementioned challenges. The beneficial interaction with the NCM811 particles allows for a highly homogeneous coating at room temperature, while the lithium phosphonate function facilitates charge transfer and the poly(arylene)-type backbone enhances the thermal stability and thus safety of the cathode material. Advantageously, the application of the PP10-Li coating moreover leads to a substantially reduced amount of detrimental surface impurities such as LiOH and Li₂CO₃ and, instead, an enrichment in LiF at the active material surface. As a result, ONCM811 shows superior rate capability and enhanced cycling stability, especially at elevated temperatures up to 60 °C compared to the non-coated NCM811.

2. Results and Discussion

2.1. Physicochemical Characterization

In a first step, we investigated the morphology of the PP10-Li coating. Figure 1b shows a scanning electron microscopy (SEM) image of the NCM811 active material, containing secondary particles with a diameter of either ≈2 μm or ≈15 μm to increase the electrode packing density and thus the energy density eventually. This particle morphology is well preserved after applying the PP10-Li coating, as depicted in Figure 1c. The only difference at this magnification appears to be the observation of some darker spots, which are assigned to the electronically insulating nature of PP10-Li, uniformly covering the NCM811 particle surface as apparent at higher magnification (Figure 1d). Transmission electron microscopy (TEM) images of NCM811 confirm the secondary particle structure (Figure 1e) and high-resolution TEM analysis of the particles (Figure 1f) reveals clear lattice fringes assigned to the (003) plane of the layered crystal structure, indicating that the material is highly crystalline (see also the fast Fourier transform (FFT) pattern in the inset), which is in good agreement with results obtained by X-ray diffraction (XRD), presented in Figure S1 (Supporting Information). In fact, in both cases – NCM811 and ONCM811 – the same reflections are observed, which can be well assigned to the layered α-NaFeO₂ structure (R–3m) and there is no indication of any phase impurity for neither of the two materials. The TEM analysis of the ONCM811 reveals that the PP10-Li coating layer has a rather homogeneous thickness of 7–12 nm and uniformly covers the particle surface (Figure 1g), which is well in line with the SEM data (Figure 1d). To further confirm the uniformity of the coating, we conducted energy-dispersive X-ray (EDX) spectroscopy mappings of a larger secondary ONCM811 particle (Figure 1h) and an extendedly larger region of pristine ONCM811-based electrodes (Figure S2, Supporting Information); and, indeed, the mappings of the different elements (Figure 1i–p and Figure S2b–i: Supporting Information) – especially sulfur and phosphorus (Figure 1k,l and Figure S2d,e: Supporting Information), which are present only in PP10-Li – reveals a very homogeneous distribution at the particle surface.

In a next step, we performed a comparative investigation of pristine NCM811 and ONCM811 electrodes via X-ray photoelectron spectroscopy (XPS) to study the impact of applying the PP10-Li coating on the surface chemistry. A summary of the findings for the oxygen-containing species is provided in Figure 2a (based on the fitting of the O 1s spectra shown in Figure S3, Supporting Information). The intensity of the M-O contribution (in purple) is noticeably lower in the case of ONCM811 compared to NCM811 as a result of the PP10-Li coating. The presence of the coating is also reflected in the contributions from S = O (in dark purple) and O = POLi (in light purple) as well as the pronounced contribution of -COO⁻ (in orange). The presence of the latter contribution for the NCM811 spectrum, but to a substantially lower extent, is assigned to oxygen species at the surface of the conductive carbon. The minor contribution of R-O(C = O)-O- as additional surface species, observed for both pristine NCM811 and ONCM811 electrodes, originates from the reaction of the electrode material with the atmosphere.[18] Although all the material handling and processing as well as the electrode preparation were conducted in the dry room, the formation of surface contaminations such as LiOH and Li₂CO₃ owing to the reaction with the ambient atmosphere (especially, H₂O and CO₂) could not be fully suppressed. The contribution of LiOH is very low in the case of NCM811 (<0.22 at%) owing to the careful handling in the glove box and dry room, while it is essentially undetectable for ONCM811. Similarly, the contribution of Li₂CO₃ is much more pronounced for NCM811 (4.92 at%) compared to ONCM811 (1.17 at%). The reduced contribution of LiOH and Li₂CO₃ observed for ONCM811 highlights the substantially decreased reactivity with the ambient atmosphere, as a result of the homogeneous PP10-Li coating which effectively prevents the direct exposure to H₂O and CO₂.[19] This finding is of particular relevance with regard to the commercial use of Ni-rich NCM, since the formation of LiOH and Li₂CO₃ does not only cause lower specific capacities, but moreover leads to a higher interfacial resistance, pronounced side reactions with the electrolyte, and gas formation during cycling.[20]
The F 1s core-level spectra recorded for the NCM$_{811}$ and ONCM$_{811}$ electrodes, taken at different sputtering depths, are presented in Figure 2b,c, respectively. Generally, both show two distinct peaks: one with a higher intensity at 688.2 eV, which is assigned to -CF$_2$- and originates from poly(vinylidene difluoride) (PVdF) that has been used as binder (while in the case of ONCM$_{811}$ presumably also including some contribution from the PP10-Li coating),[21] and one with a lower
intensity at 658.5 eV, which is ascribed to the presence of LiF.\[22]\) The appearance of LiF in the pristine electrodes has been reported to be a consequence of the minor dehydrofluorination reaction of PVdF, catalyzed by the alkaline species (such as LiOH and Li$_2$CO$_3$) present in the slurry during the electrode coating process, resulting in the formation of HF that reacts at the NCM surface and eventually forms LiF.\[21a,23]\) Prior to the sputtering, the relative contribution is similar for NCM$_{811}$ and ONCM$_{811}$ (i.e., 0.26 and 0.22 at%, respectively – see also Figure 2d,e). However, the relative contribution increases during the Ar$^+$ sputtering treatment, implying that the LiF formation occurs largely at the NCM surface, which is in line with the earlier reported mechanism. Notably, the relative contribution of LiF after sputtering for 12 min (equivalent to an estimated sputtering depth of 9.6 nm) is higher for ONCM$_{811}$ (3.53 at% vs 2.60 at% for NCM$_{811}$). In combination with the lower concentration of LiOH and Li$_2$CO$_3$ that are (largely) responsible for the formation of LiF\[21a,23]\) this finding indicates that PP10-Li is strongly bound to the NCM$_{811}$ surface and presumably partially reacting. Such enrichment in LiF (in addition to the PP10-Li coating layer) is expected to have a beneficial effect on the Li$^+$ transport kinetics, the suppression of transition metal dissolution, and the stability of the interface with the electrolyte.\[24]\)

2.2. Reactivity with Moist Air

Facile storage and handling of cathode active materials (and materials in general) are critical for the battery industry. Thus, we comparatively studied also the evolution of NCM$_{811}$ and ONCM$_{811}$ upon storage under a controlled ambient atmosphere. For this purpose, we exposed the two materials to a controlled relative humidity of 65% for six days. The comparison of the resulting gain in mass reveals that NCM$_{811}$ is more sensitive to such storage conditions, as it is significantly greater compared to ONCM$_{811}$, i.e., 0.55% versus 0.32% (Figure 3a), further supporting the beneficial impact of the PP10-Li coating as a physical barrier toward the environment. Subsequently, the gain in mass was investigated in more detail, revealing that the reversible water absorption was 0.15% and 0.16% for NCM$_{811}$ and ONCM$_{811}$ respectively, as determined by thermogravimetric vapor sorption analysis (Figure 3b). The slightly higher reversible water absorption of ONCM$_{811}$ might be explained by the hygroscopic nature of the PP10-Li coating, absorbing more water than the NCM$_{811}$ particles – notably without reacting with the ambient moisture, as it is subsequently released again. In fact, the relatively higher reversible water absorption in combination with the relatively lower gain in mass and the lower contribution of common reaction products such as LiOH and
Li₂CO₃ (50% of the overall gained mass, Figure 3c) indicates that the PP10-Li coating suppresses the reactivity with H₂O and CO₂. This is also reflected in the relatively lower increase of the pH value when dispersing the two materials in deionized water (Figure 3d). For NCM₈₁₁, the pH value jumps to 10.73 after about 3 min and subsequently increases slowly to 10.82 after 60 min, which is lower than for ONCM₈₁₁ with 10.64 and 10.81, respectively. This is in agreement with the lower LiOH and Li₂CO₃ content and the mitigated surface reactivity in the case of ONCM₈₁₁, illustrating a facilitated handling and storage of the PP10-Li-coated material.

2.3. Electrochemical Characterization

As any surface coating naturally impacts the de-/lithiation kinetics, we performed a comparative analysis of NCM₈₁₁ and ONCM₈₁₁ electrodes via cyclic voltammetry (Figure S4, Supporting Information). While both cells generally show high reversibility and the characteristic redox couples, related to the three common phase transitions occurring upon de-/lithiation (see the corresponding discussion in the Supporting Information), the determination of the apparent lithium-ion diffusion coefficient reveals slightly higher values for ONCM₈₁₁ (i.e., 201 vs 203 mAh g⁻¹ (0.1C); 195 vs 197 mAh g⁻¹ (0.2C); 186 vs 188 mAh g⁻¹ (0.5C); 178 vs 180 mAh g⁻¹ (1C); 170 vs 172 mAh g⁻¹ (2C); 154 vs 156 mAh g⁻¹ (5C); and 137 vs 137 mAh g⁻¹ (10C)), while the difference is diminishing for higher dis-/charge rates. In fact, the slightly lower capacity at low and medium C rates is assigned to the mass contribution of the PP10-Li coating, which has been included in the calculation of the specific capacity. Accordingly, when normalizing the specific capacity values with regard to the reversible capacity obtained at 0.1C, the values are essentially the same for the low and medium C rates and higher for ONCM₈₁₁ at 10C (Figure 4c), revealing a better rate capability owing to the PP10-Li coating. As a matter of fact, the initial overpotential for the delithiation at elevated dis-/charge rates (2C and higher) is significantly higher for NCM₈₁₁ compared to ONCM₈₁₁ (Figure 4a,b), which underlines the better kinetics in the case of ONCM₈₁₁ and is in agreement with the results of the cyclic voltammetry experiments. To investigate the impact of the PP10-Li coating on the long-term cycling performance, both cells were subsequently subjected to 500 cycles at 1C (Figure 4d). Initially, the capacity for the NCM₈₁₁ cell is slightly higher, as expected from the rate capability test, but it rapidly fades after about 460 cycles, resulting in a capacity retention of only 77.6%. This fading is accompanied by substantial decrease in Coulombic efficiency (CE) down to 99.09%, lowering the average CE to 99.66% upon 500 cycles. Accordingly, the rapid capacity fading toward the end of the
cycling test is attributed to detrimental side reactions at the electrode-electrolyte interface (including newly formed interfaces due to microcracks evolving in the NCM811 particles) and their detrimental impact on the NCM811 active material and its crystal structure.[6,25] Differently, the cycling performance of ONCM811 is very stable for 500 cycles with a capacity retention of 81.1% and no pronounced fading after 500 cycles at 1C. This superior performance is also reflected in the very high average CE of 99.96%, indicating that the application of the PP10-Li coating layer leads to suppressed side reactions with the electrolyte and preserves a stable electrode-electrolyte interface. Subsequently, we studied also the long-term constant current cycling at elevated temperatures of 40 and 60 °C (Figure 5) to stress the beneficial impact of the PP10-Li coating on the stabilization of the interface with the electrolyte, successfully suppressing severe side reactions and active material decay.

Figure 4. Electrochemical characterization at 20°C: a,b) Representative dis-/charge profiles (2nd cycle at each given C rate) of cells comprising (a) NCM811 and (b) ONCM811 as the active material for the positive electrode at varying C rates; c) comparison of the normalized capacity retention at different C rates with regard to the capacity obtained at 0.1C; d) evaluation of the rate capability and cycling stability at 1C after applying varying C rates with an indication of the capacity retention after 500 cycles at 1C; e,f) valuation of the cycling stability at e) 3C and f) 5C after three formation cycles at 0.1C with an indication after how many cycles a capacity retention of 80% is reached.
2.4. Ex Situ Investigation of the (O)NCM811 Surface

To unveil how the application of the PP10-Li coating enhances the electrochemical performance, the electrodes cycled according to the testing protocol shown in Figure 4d were eventually analyzed via SEM/EDX. The SEM images of pristine ONCM811 and NCM811 electrodes are presented in Figure S5 (Supporting Information) and the ex situ SEM data are shown in Figure S6 (Supporting Information). Alike the SEM and TEM data discussed earlier (Figure 1), the surface of the pristine ONCM811 particles appears smoother and the edges of the primary nanograins are less apparent (Figure S5a,b, Supporting Information) compared to the SEM images taken for NCM 811 (Figure S5c,d, Supporting Information) due to the presence of the PP10-Li coating. After cycling (Figure S6, Supporting Information), however, the surface of the NCM811 electrodes appears much smoother than prior to cycling, indicating the formation of a rather thick cathode electrolyte interphase (CEI), while the surface morphology of the ONCM811 electrodes is largely retained. In fact, the ex situ SEM/EDX analysis of the cycled ONCM811 electrodes (Figure S7, Supporting Information), in particular the homogenous elemental distribution of S, for which PP10-Li is the only source (while the other elements are found also for NCM811, Figure S8, Supporting Information), confirms that the coating layer is well preserved, even after such extended cycling for more than 500 cycles.

For a closer look at the particle surface, we performed also ex situ TEM measurements on these cycled electrodes (Figure 6). While it is generally difficult to distinguish between the CEI
layer and the PP10-Li coating due to the amorphous nature of both phases, the amorphous surface layer is clearly thinner in the case of ONCM811 (Figure 6a) compared to NCM811 (Figure 6c) – despite the contribution of the PP10-Li coating in the former case, indicating a pronounced electrolyte decomposition and CEI formation for NCM811. Moreover, when analyzing the crystal structure of the ONCM811 particles in the bulk and the near-surface region (Figure 6b), the resulting FFT patterns confirm that the layered (R-3m) structure is retained.\cite{9c,27}

Differently, for the cycled NCM811 particles (Figure 6d), the FFT patterns reveal the transition from the layered (R-3m) structure to the rock-salt (Fm-3m) structure\cite{28} in the near-surface region (red frame) and a mix of the two crystalline phases in the bulk (orange frame). It is noteworthy that the transition from the layered to the electrochemically inactive rock-salt structure\cite{9c} appears complete for several tens of nanometers from the particle surface toward the particle core, providing an explanation for the pronounced capacity fading in the case of NCM811.

Complementarily, we conducted also an ex situ XPS depth-profiling analysis of the cycled NCM811 and ONCM811 electrodes to gain additional insights into the thickness and composition of the CEI layer (Figure 7). The O 1s and F 1s spectra for NCM811 are depicted in Figure 7a,b and the O 1s and F 1s spectra for ONCM811 are presented in Figure 7c,d (including in both cases the XPS data for the pristine electrodes at the top for comparison). Generally, for both NCM811 and ONCM811,

Figure 7. Ex situ XPS analysis: a) O 1s and b) F 1s spectra of NCM811 cycled electrodes; c) O 1s and d) F 1s spectra of ONCM811 cycled electrodes. In all cases, the spectra shown at the top have been obtained for pristine electrodes and serve as reference. The spectra obtained for cycled electrodes prior to any sputtering are shown in the row below and in the subsequent rows the sputtering time has been stepwise increased (from top to bottom, with an indication of the estimated sputtering depth). The color coding for the fitted contributions is shown below the XPS spectra. It should be noted that the scale for photoelectron yield at the y axis has been kept constant for all O 1s (6400) and F 1s spectra (9000). The O 1s spectra of the pristine NCM811 and ONCM811 electrodes are the same as those presented in Figure S3 (Supporting Information), but shown here once again for the sake of convenience when comparing the XPS spectra before and after cycling.
the spectra recorded prior to any sputtering reveal contributions from organic (e.g., \( \text{RCH}_2\text{OCOOLi} \) and \(-\text{COC}^-\)) and inorganic (e.g., LiOH, \( \text{Li}_2\text{CO}_3 \), LiF, and \( \text{LiPF}_6/\text{LiPO}_2\text{F}_12 \)) electrolyte decomposition products. In line with the XPS data obtained for the pristine electrodes, however, the ONCM811 electrodes show substantially less \( \text{Li}_2\text{CO}_3 \) and essentially no LiOH. Furthermore, the ONCM811 electrodes show generally less decomposition products and a greater intensity for the M-O contribution, indicating that the CEI is thinner overall. Besides, contributions from \(-\text{S} = \text{O} \) and \(-\text{OP} \approx \text{O} \) are observed for cycled ONCM811 electrodes, further corroborating that the PP10-Li layer is preserved on the particle surface. Upon sputtering the M-O contribution increases in both cases, confirming that the CEI layer is increasingly removed. Simultaneously, the relative contribution of the organic electrolyte decomposition products is gradually decreasing, though more pronounced for ONCM811, while the contribution of LiF is increasing in both cases, which is more pronounced for NCM811, however. This observation in combination with the initially higher LiF concentration for the pristine electrodes (charged to 4.3 V) in presence of the electrolyte by differential scanning calorimetry (DSC, Figure 8), generally, the onset temperature for the heat evolution is significantly lower in both cases compared to the base electrolyte only (in grey), revealing the characteristic decomposition profile for DEC, which underlines the greater reactivity of the latter in contact with delithiated NCM. Besides, it is fairly similar for both active materials, while the overall heat evolution is substantially lower for ONCM811 (1139.0 J \( \text{g}^{-1} \)) compared to NCM811 (1321.7 J \( \text{g}^{-1} \)). In fact, the DSC curve recorded for PP10-Li only (in red) does not show any exothermic features up to 300 °C, only a glass transition and an endothermic peak at \( \approx 230 \) and \( \approx 274 \) °C, respectively, further highlighting the beneficial impact of the coating – not only for the electrochemical performance, but moreover regarding safety.

3. Conclusions

The PP10-Li coating addresses the most challenging issues of Ni-rich NCM, i.e., the poor cycling stability and the low thermal stability, by suppressing the undesired surface reactions with moist air (i.e., \( \text{H}_2\text{O} \) and \( \text{CO}_2 \)) upon storage and processing as well as with the electrolyte upon cycling, especially at elevated temperatures. As a result, PP10-Li-coated NCM811 (ONCM811) provides a substantially enhanced electrochemical performance in terms of rate capability, capacity retention, and Coulombic efficiency (99.96% vs 99.66%) owing to the favorable de-/lithiation kinetics as well as the stabilized electrode/electrolyte interface and interphase. Most remarkable is certainly the improvement in capacity retention at 60 °C from 15 cycles (NCM811) to 180 cycles (ONCM811). In combination with the substantially reduced heat evolution, this finding particularly highlights the beneficial impact of the coating also concerning safety. We may anticipate that the use of well-designed lithiated polymer coatings, as reported herein for the first time, is an effective strategy for today’s and tomorrow’s cathode materials.

4. Experimental Section

Chemicals for the Synthesis of PP10-Li: 4,4’-difluorodiphenyl sulfone (DFDPS, \( >\text{98\%} \)) and 4,4’-biphenyl (BP, \( >\text{99\%} \)) were purchased from Alfa Aesar and recrystallized from isopropanol before use. Toluene, potassium carbonate (\( \text{K}_2\text{CO}_3 \), \( >\text{99\%} \)), calcium hydride (\( \text{CaH}_2 \), \( >\text{98\%} \)), methanol, hydrochloric acid (\( \text{HCl} \), 36.5 wt%), and lithium hydroxide monohydrate (\( \text{LiOH} \cdot \text{H}_2\text{O} \), 98%) were purchased from Alfa Aesar and used as received. Dichloromethane (DCM) was purchased from Sigma Aldrich and freshly distilled from \( \text{CaH}_2 \) before use. Hexafluorobenzene (HFB, \( >\text{99\%} \)), anhydrous dimethylacetamide (DMAc), N-methyl-2-pyrrolidone (NMP, \( >\text{99\%} \)), bromine (\( \text{Br}_2 \), 99.99%), anhydrous acetic acid (\( \text{CH}_3\text{COOH} \), 99.8%), palladium acetate (\( \text{Pd(OAc)}_2 \), \( >\text{99.9} \)), triphenylphosphine (TPP, 99%), diethyl phosphite (DEP, \( >\text{98\%} \)), and dicyclohexylmethylene (DCHMA, 97%) were purchased from Sigma Aldrich and used as received unless otherwise noted.

Synthesis of PP10-Li: The complete synthesis of PP10-Li is shown in Figure S9 (Supporting Information) and described in the following in more detail.

Synthesis of HFB End-Capped PES10: HFB end-capped PES10 was synthesized by modifying a one-pot two-reaction procedure reported elsewhere in a typical protocol (Figure S9, Supporting Information), a 100-mL three-neck round-bottom flask, equipped with a mechanical stirrer, a condenser, an argon inlet/outlet, and a Dean-Stark trap, was charged with DFDPS (4.000 g, 15.732 mmol) and BP (3.052 g, 16.388 mmol). DMAc (28 mL) was added to obtain a solid concentration of 25% (wt/v). When all solid components were completely dissolved, \( \text{K}_2\text{CO}_3 \) (6.79 g, 0.0492 mol)
and 14 mL of toluene, serving as azetroping agent, were added. The DMAC to toluene ratio was 2:1 v/v. The reaction bath was heated to 150 °C and kept at this temperature for 4 h to dehydrate the system. Subsequently, the bath temperature was slowly raised to 160 °C to remove the toluene. Afterward, the temperature of the reaction bath was decreased to 120 °C and the polymerization was allowed to proceed for 24 h. In a next step, the reaction temperature was set to 70 °C and 2.44 g (13.11 mmol) of HFB were added, while the argon purge was stopped at this point owing to the low boiling point of HFB. The reaction was allowed to proceed for 12 h. Then, the reaction mixture was precipitated into 2 L of 1 mM HCl aqueous solution with magnetic agitation for 8 h, filtered, and rinsed with distilled water until reaching a neutral pH value. The resulting white powder was dried under vacuum at 80 °C for 24 h to obtain the final product (Mn = 160 600 g mol⁻¹, Mw = 21 500 g mol⁻¹, polydispersity index (Mw/Mn) = 2.0). 1H and 19F nuclear magnetic resonance (NMR) spectra of HFB end-capped PES10 are shown in Figure S10 (Supporting Information).

1H-NMR (CDCl₃): δ (ppm) 7.92 (d), 7.61 (d), 7.54 (d), 7.14 (d), 7.10 (d), 7.06 (d).

19F-NMR (CDCl₃): δ (ppm) −153.78 (d), −159.5 (m), −161.75 (m).

Synthesis of Brominated PES10 (BPES10): The bromination of PES10 (yielding BPES10) was conducted at room temperature using elemental bromine as the brominating agent in the presence of acetic acid (Figure S9, Supporting Information). In a typical protocol, 5.000 g of PES10 (12.10 mmol of the biphenyl unit) was loaded into a 250 mL three-neck round-bottom flask, equipped with a mechanical stirrer, a condenser, an argon inlet, and a funnel. First, 90 mL of DCM, distilled from CaH₂, and 9 mL of acetic acid (10% v/v to DCM) were added. The resulting white powder was dried under vacuum at 80 °C for 24 h to obtain the final product (Mn = 160 600 g mol⁻¹, Mw = 21 500 g mol⁻¹, polydispersity index (Mw/Mn) = 2.0). In a typical protocol, 5.000 g of BPES10 (2.00 g, 7.19 mmol of bromine) was dispersed in a 0.5 mM aqueous solution of LiOH, washed several times with distilled water until completely dissolved, and kept under a constant temperature for 300 min to evaporate all the water. Afterward, the polymer was filtered and rinsed again with methanol until any residual bromine was completely removed. The final product, i.e., BPES10, was dried under vacuum at 80 °C for 24 h. 1H and 19F NMR spectra of BPES10 are shown in Figure S11 (Supporting Information).

1H-NMR (DMSO.d6): δ (ppm) 8.14 (s), 8.03 (d), 7.95 (d), 7.79 (d), 7.49 (d), 7.34 (d), 7.10 (d).

19F-NMR (DMSO.d6): δ (ppm) −137.76 (s), −138.14 (m), −153.23 (s), −153.67 (m), −160.69 (t).

Synthesis of Lithium Phosphonate Functionalized PES10 (PP10-Li): The phosphonate functions were tethered to the brominated BPES10 using a palladium-catalyzed coupling reaction (Figure S9, Supporting Information). In a typical procedure, BPES10 (2.00 g, 7.19 mmol Br₂, 0.182 mol) was added dropwise to the reaction mixture, followed by strong stirring, and the reaction was allowed to proceed at room temperature for 16 h. Subsequently, the reaction mixture was precipitated into 1000 mL of methanol, washed three times with methanol to remove excessive bromine, and kept under continuous agitation for 16 h. Afterward, the polymer was filtered and rinsed again with methanol until any residual bromine was completely removed. The final product, i.e., PP10-Li, was dried under vacuum at 80 °C for 24 h, 7.49 (d), 7.34 (d), 7.10 (d).

Preparation of PP10-Li-Coated NCM811 (ONCM811): First, 0.1 g of PP10-Li were introduced into a 50-mL round-bottom flask. 10.0 mL of NMP were added and the mixture was heated to 120 °C. Subsequently, 4.0 mL of deionized water (DIW) were added dropwise until PP10-Li was completely dissolved. Afterward, the water was removed via azetotropic distillation. For the drying step, 10 mL of toluene were added and the solution was placed in a Dean Stark system. The mixture was heated up to 160 °C and kept at this temperature under reflux overnight. Finally, any residual water and the toluene were removed to yield PP10-Li dissolved in NMP only.

1 g of NCM811 (a pre-commercial material that was generally stored under argon in a glass vial and the glass vial was stored in a dry room with the dew point being always below −60 °C at 20 °C ambient temperature) was added into 2 mL of the PP10-Li in NMP solution (corresponding to 2 w% of PP10-Li with regard to the mass of NCM811). The resulting suspension was stirred slowly and heated up to 80 °C in order to slowly evaporate the NMP, finally yielding the PP10-Li-coated NCM811, herein referred to as ONCM811.

Physicochemical Characterization: 1H and 19F NMR spectroscopy was performed using a Bruker Ascend 400 apparatus. Size-exclusion chromatography (SEC) with a multi angle light scattering detector (MALS) was conducted at room temperature on a Waters 590 GPC equipped with a Waters 410 differential refractometer and a Waters 745 Data Module. A 1 m solution of NaNO₃ in dimethylformamide (DMF) was used as solvent, applying a flow rate of 1 mL min⁻¹. A high-resolution transmission electron microscopy (HRTEM) with ion gun and sputtering rate of 0.8 nm min⁻¹. The spectra were calibrated by means of the C 1s peak of the adventitious carbon, centered at 284.8 eV, and the intensity was normalized. The determination of the water content was carried out via thermogravimetric vapor sorption analysis (Q5000SA, TA Instruments).

The crystal structure of NCM811 and ONCM811 was studied via X-ray diffraction (XRD) – on both powders and electrodes – using a Bruker D8 Advance with Cu-Kα radiation of λ = 0.15406 nm. The morphology of NCM811 and ONCM811 was investigated by scanning electron microscopy (SEM; Zeiss Evo MA 10), equipped with an energy-dispersive X-ray (EDX) spectrometer (Oxford Instruments X-MaxN, 50 mm², 15 kV). The 1 wt% solution of PES10 was filtered using a 0.45 mm Milipore polytetrafluoroethylene filter and three Ultrastraygel columns of 5 × 10², 10⁴, and 10⁶ Å. The calibration was performed using polystyrene standards.

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loading was 2.2 ±0.2 mg cm⁻². All electrode preparation steps were performed in a dry room with the dew point always being below −60 °C at an ambient temperature of 20 °C.

The electrochemical characterization was conducted in CR2032 coin cells (Hohnsen). Metallic lithium (Honjo, battery grade, 500 μm thickness) was used as the counter electrode, 1 m LiPF₆ dissolved in a 1:1 (by weight) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 wt/wt) with 1 wt% of vinylene carbonate (VC), supplied by BASF, was used as the electrolyte, and a single-layer polyethylene membrane (ASAHI KASEI, Hipore SV718) was used as separator. All coin cells were assembled in an argon-filled glove box (with O₂ < 0.1 ppm and H₂O < 0.1 ppm).

**Electrochemical Characterization:** All galvanostatic tests were conducted in a voltage range from 3.0 to 4.3 V using a Maccor battery tester (Maccor 4000). The ambient temperature (i.e., 20, 40, and 60 °C) was controlled by a climatic chamber (Binder). A dis-/charge rate of 1C corresponds to a specific current of 200 mA g⁻¹. Cyclic voltammetry (CV) was performed using a multi-channel potentiostat (VMP Biologic). The electrochemical characterization was conducted at an ambient temperature of 20 °C. For the initial five cyclic sweeps, a lower scan rate of 0.1 mV s⁻¹ was performed using a multi-channel potentiostat (VMP Biologic). The ambient temperature (i.e., 20, 40, and 60 °C) was performed in a dry room with the dew point always being below 40 °C.

**Ex Situ Characterization:** For the ex situ SEM, XPS, and TEM analysis, the cycled cells (540 cycles at varying C rates and 20 °C) were opened in an argon-filled glove box (with O₂ < 0.1 ppm and H₂O < 0.1 ppm). The electrodes were washed several times with dimethyl carbonate (DMC) to remove any residual electrolyte and then dried in a glove box. For the sample transfer to the corresponding instrument, specific sample holders were used which prohibit the contact with the ambient atmosphere. For the ex situ SEM, XPS, and TEM analysis, the same experimental parameters were used as for the pristine samples. The thermal stability of NCM₈₁ and ONCM₇₃ was determined by differential scanning calorimetry (DSC; Discovery TA instruments). The electrodes were initially cycled galvanostatically in half-cells at 0.1C for three cycles, and then charged to 4.3 V with a subsequent constant voltage step with a cut-off current equivalent to 0.01C. The cells were disassembled in a glove box and rinsed with DMC to remove any residual electrolyte. About 7–8 mg of the electrode coating were scratched from the electrodes and hermetically sealed in 30-µm high-pressure gold-plated copper stainless steel vessels, together with some fresh electrolyte. Prior to the heating the samples up to 300 °C a voltage step with a cut-off current equivalent to 0.01C. The cells were disassembled in a glove box and rinsed with DMC to remove any residual electrolyte. About 7–8 mg of the electrode coating were scratched from the electrodes and hermetically sealed in 30-µm high-pressure gold-plated copper stainless steel vessels, together with some fresh electrolyte. Prior to the heating the samples up to 300 °C a voltage step with a cut-off current equivalent to 0.01C. The cells were disassembled in a glove box and rinsed with DMC to remove any residual electrolyte. About 7–8 mg of the electrode coating were scratched from the electrodes and hermetically sealed in 30-µm high-pressure gold-plated copper stainless steel vessels, together with some fresh electrolyte. Prior to the heating the samples up to 300 °C a voltage step with a cut-off current equivalent to 0.01C. The cells were disassembled in a glove box and rinsed with DMC to remove any residual electrolyte. About 7–8 mg of the electrode coating were scratched from the electrodes and hermetically sealed in 30-µm high-pressure gold-plated copper stainless steel vessels, together with some fresh electrolyte. Prior to the heating the samples up to 300 °C a voltage step with a cut-off current equivalent to 0.01C. The cells were disassembled in a glove box and rinsed with DMC to remove any residual electrolyte. About 7–8 mg of the electrode coating were scratched from the electrodes and hermetically sealed in 30-µm high-pressure gold-plated copper stainless steel vessels, together with some fresh electrolyte. Prior to the heating the samples up to 300 °C a voltage step with a cut-off current equivalent to 0.01C. The cells were disassembled in a glove box and rinsed with DMC to remove any residual electrolyte. About 7–8 mg of the electrode coating were scratched from the electrodes and hermetically sealed in 30-µm high-pressure gold-plated copper stainless steel vessels, together with some fresh electrolyte. Prior to the heating the samples up to 300 °C a voltage step with a cut-off current equivalent to 0.01C. The cells were disassembled in a glove box and rinsed with DMC to remove any residual electrolyte. About 7–8 mg of the electrode coating were scratched from the electrodes and hermetically sealed in 30-µm high-pressure gold-plated copper stainless steel vessels, together with some fresh electrolyte. Prior to the heating the samples up to 300 °C a voltage step with a cut-off current equivalent to 0.01C. The cells were disassembled in a glove box and rinsed with DMC to remove any residual electrolyte. About 7–8 mg of the electrode coating were scratched from the electrodes and hermetically sealed in 30-µm high-pressure gold-plated copper stainless steel vessels, together with some fresh electrolyte. Prior to the heating the samples up to 300 °C a voltage step with a cut-off current equivalent to 0.01C. The cells were disassembled in a glove box and rinsed with DMC to remove any residual electrolyte. About 7–8 mg of the electrode coating were scratched from the electrodes and hermetically sealed in 30-µm high-pressure gold-plated copper stainless steel vessels, together with some fresh electrolyte. Prior to the heating the samples up to 300 °C a voltage step with a cut-off current equivalent to 0.01C. The cells were disassembled in a glove box and...