Oxygen Activity in Li-Rich Disordered Rock-Salt Oxide and the Influence of LiNbO3 Surface Modification on the Electrochemical Performance

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ABSTRACT: Li rich disordered rock salt oxides such as Li1.2Ni1/3Ti1/3Mo2/15O2 are receiving increasing attention as high capacity cathodes due to their potential as high energy materials with variable elemental composition. However, the first cycle oxygen release lowers the cycling performance due to cation densification and structural reconstruction on the surface region. This work explores the influence of lithium excess on the charge compensation mechanism and the effect of surface modification with LiNbO3 on the cycling performance. Moving from a stoichiometric LiNi0.5Ti0.5O2 composition toward Li rich Li1.2Ni1/3Ti1/3Mo2/15O2, oxygen redox is accompanied by oxygen release. Thereby, cationic charge compensation is governed by the Ni2+/3+ and Mo3+/6+ redox reaction. Contrary to the bulk oxidation state of Mo6+ in the charged state, a mixed Mo valence on the surface is found by XPS. Furthermore, it is observed that smaller particle sizes result in higher specific capacities. Tailoring the surface properties of Li1.2Ni1/3Ti1/3Mo2/15O2 with a solid electrolyte layer of LiNbO3 altered the voltage profile, resulting in a higher average discharge voltage as compared to the unmodified material. The results hint at the interdiffusion of cations from the metal oxide surface coating into the electrode material, leading to bulk composition changes (doping) and a segregated Nb rich surface. The main finding of this work is the enhanced cycling stability and lower impedance of the surface modified compound. We argue that surface densification is mitigated by the Nb doping/surface modification.

INTRODUCTION

The development of lithium ion batteries (LIBs) with high energy density is one of the primary objectives in the energy storage field. The cathode material is considered as the bottleneck for improving the energy density. Conventional layered oxides like LiCoO2 and LiNi1/3Mn1/3Co1/3O2 exhibit stable specific capacities between 145 and 165 mAh g⁻¹. These compounds offer specific capacities exceeding 200 mAh g⁻¹, which results from the fact that charge can be stored on both the transition metal (Tm) cation and the oxygen anion. All of these materials have ordered structures. Li rich disordered rock salt oxides (DRS) with α LiFeO2 type structure lately have attracted considerable attention. Even though lithium migration is hindered in cation disordered rock salt oxides, they can in principle function well as high capacity cathode materials. For a threshold ratio lithium:transition metal (Li:Tm) ≥ 1.09, the lithium sites can percolate sufficiently within the structure and form favorable diffusion pathways. Recently, Yabuuchi et al. demonstrated that for Li rich cation disordered Li3NbO4–MO (M = Fe, Ni, Mn), a significant portion of the charge comes from reversible oxygen redox and is not mainly due to oxygen release. Oxygen redox can be beneficial, as it contributes to the capacity in the high voltage range. However,
too much oxidation seems to be detrimental, as oxygen loss can be triggered. This leads to a near surface cation densification, which can severely impede the Li diffusion.\textsuperscript{14} The generation of highly reactive oxygen radicals (in the form of O$_2^−$/O$^−$ or O$_2^{2−}$ in the bulk of the material) or even oxygen vacancies (after oxygen loss) on the particle surface during the electrochemical process is presumed to result in the formation of a resistive surface layer due to electrolyte decomposition and structural transformation.\textsuperscript{15−17} Thus, strategies to stabilize the particle surface to alleviate or even overcome these problems are needed to improve the performance of Li rich disordered rock salt oxides.

\textbf{Li$_{1.2}$Ni$_{1/3}$Ti$_{1/3}$Mo$_{2/15}$O$_2$} is a promising cathode material that exhibits high specific capacities but suffers from oxygen release.\textsuperscript{10,18} Here, we propose a surface modification strategy using LiNbO$_3$ in order to reduce the surface degradation and improve the electrochemical performance.\textsuperscript{19,20}

\section*{RESULT AND DISCUSSION}

\textbf{Synthesis and Characterization.} We chose to investigate a solid solution between the stoichiometric cation disordered Fm$	ext{3m}$ LiNiTiO$_4$ (LiNi$_{0.5}$Ti$_{0.5}$O$_2$) and the lithium enriched cation ordered P1 Li$_2$MoO$_4$ (Li$_{1.6}$Mo$_{0.4}$O$_2$), targeting lithium rich cation disordered Li−Ni−Ti−Mo oxide. For a clear representation of the lithium to transition metal ratio, we use the notation LiMO$_2$. LiNi$_{0.5}$Ti$_{0.5}$O$_2$ is adopting an \textit{α}LiFeO$_2$ type crystal structure, where Li and the transition metals share the same octahedral site and are randomly distributed without any long range order. This type of compounds is referred to as cation disordered rock salt oxides.\textsuperscript{21} Depending on the degree of the random occupation (from partial to full occupancy), the extent of cation disorder varies. For the cation ordered triclinic P1 Li$_2$MoO$_4$, Mo$^{6+}$ ions occupy the octahedral sites in a cubic close packed (ccp) anion lattice with Li$^+$ occupying the remaining octahedral sites. The structure is built up of [Mo$_6$O$_{19}$] clusters, consisting of edge sharing MoO$_6$ octahedra.\textsuperscript{22,23} The hypothetical binary mixture between “Li$_4$MoO$_5$−Li$_2$NiTiO$_3$” forms a single phase solid solution with Li$_{1.2}$Ni$_{1/3}$Ti$_{1/3}$Mo$_{2/15}$O$_2$ stoichiometry and crystallizes in the \textit{α}LiFeO$_2$ type structure, as illustrated in Figure 1a.
Li$_{1.2}$Ni$_{1/3}$Ti$_{1/3}$Mo$_{2/15}$O$_2$ has been synthesized and subsequently coated with 5 wt % LiNbO$_3$ on the pristine powder (see experimental details below). No evidence of the presence of a LiNbO$_3$ phase was found in the diffraction data of the LiNbO$_3$ coated Li$_{1.2}$Ni$_{1/3}$Ti$_{1/3}$Mo$_{2/15}$O$_2$. It has been shown that the metal oxide coating can react with the bulk material under high temperature treatment.24,25 This leads to niobium substitution in this specific case. In the following, LiNi$_{0.5}$Ti$_{0.5}$O$_2$ is referred to as LNT 0, Li$_{1.2}$Ni$_{1/3}$Ti$_{1/3}$Mo$_{2/15}$O$_2$ as LNTM 20, and LiNbO$_3$ coated Li$_{1.2}$Ni$_{1/3}$Ti$_{1/3}$Mo$_{2/15}$O$_2$ as Nb LNTM 20. The number at the end of the abbreviation indicates the lithium excess. Rietveld refinement analysis of LNT 0, LNTM 20, and Nb LNTM 20 is shown in Figure S1a–c of the Supporting Information (SI). The refined lattice parameter for a single phase fit in Fm$ar{3}$m space group is $a = 4.141830(21)$ Å for LNT 0, $a = 4.146881(33)$ Å for LNTM 20, and $a = 4.146980(24)$ Å for Nb LNTM 20. Nb LNTM 20 shows a slightly larger a lattice parameter, which is consistent with the larger cation radius of Nb$^{5+}$ compared to Ni$^{2+}$ and Ti$^{4+}$. The chemical composition of the compounds has been determined by inductively coupled plasma optical emission spectroscopy (ICP OES) and is given in Table S1 (SI). Transmission electron microscopy (TEM) images are shown in Figure S2 (SI), depicting small spherical crystallites around 100 nm in diameter for LNT 0 and LNTM 20. For more insight into the coating, dark field scanning transmission
electron microscopy energy dispersive X ray spectroscopy (STEM EDX) mapping of Nb LNTM 20 was carried out. The corresponding maps of O, Ni, Ti, Mo, and Nb are shown in Figure 1b,c. The Nb signal was found throughout the particle, with an increasing intensity from the center toward the edge. This indicates some Nb segregation to the outer surface. The combined X ray diffraction (XRD) and STEM EDX data suggest partial incorporation of Nb into the Li−Ni−Ti−Mo bulk lattice. A line scan along a crystallite grain confirms a Nb rich outer surface layer of varying thickness (up to 12 nm). We estimate that ∼47% of the Nb is substituted into the phase, leading to a nominal stoichiometry of Li$_{x}$Ni$_{0.328}$Ti$_{0.328}$Mo$_{0.131}$Nb$_{0.016}$O$_{2}$. X ray photoelectron spectroscopy (XPS) results in Figure S3 (SI) indicate that Nb is in the +5 oxidation state. 

**Electrochemical Properties.** The electrochemical properties were analyzed by galvanostatic charge−discharge measurements. Figure 2a shows the charge−discharge profiles for LNT 0, LNTM 20, and Nb LNTM 20 half cells. The samples were cycled in the voltage range of 4.5−1.5 V vs Li+/Li using a constant specific current of 20 mA g$^{-1}$. The specific discharge capacity increased significantly from 100 to 220 mAh g$^{-1}$ upon changing from stoichiometric LNT 0 to Li rich LNTM 20. This increase in accessible capacity agrees with expectations based on percolation theory.$^{10,11,26}$ The latter predicts that the 0 TM site can percolate and form extended lithium networks throughout the edge. This indicates some Nb segregation to the outer particle, with an increasing intensity from the center toward the surface (Figure S5, SI), indicating a particle size dependence of the accessible capacity. This points to diffusion limitations.$^{1,2}$ The first cycle oxygen release for LNTM 20 is believed to cause cation densification and structural reconstruction of the surface phase, thereby impeding Li conductivity and leading to impedance buildup. The observed plateau around 2.2 V has been related to surface densification after oxygen loss.$^{18,29}$ For Nb LNTM 20, this plateau is greatly reduced. Thus, surface modification seems to be beneficial in protecting the reactive surface and impeding surface densification.$^{30}$ For a relatively narrow voltage window of 4.1−2.0 V, oxygen evolution or oxygen participation can be suppressed, and better cycling stability is achieved. This will be discussed in the following sections. Cycling LNTM 20 in a smaller voltage window leads to more symmetric profiles with lower voltage hysteresis, as shown in Figure S6 (SI). Nb LNTM 20 was subjected to milling in organic solvent and sintering as additional processing steps, which may affect its electrochemistry. In order to elucidate the influence of such additional steps on the electrochemistry, LNTM 20 was processed in the same way, without the addition of lithium and niobium precursors. The resulting charge−discharge profile is presented in Figure S7a and the rate capability test shown in Figure S7b of the SI. The processed LNTM 20 showed a slightly lower specific capacity and a larger hysteresis, possibly due to lithium leaching during the solvent treatment.

As mentioned above, we hypothesize that the surface phase evolution is induced by the appearance of the low voltage plateau around 2.2 V. For the modified compound, the first discharge does not reveal any visible low voltage plateau, which only appears with higher cycle numbers, as shown in Figure 2f. On the contrary, the unmodified sample shows already in the first discharge a visible low voltage plateau from which we inferred that the surface phase evolution is mitigated for Nb LNTM 20. Electrochemical impedance spectra were measured to gain a better understanding of the improved cycling performance. Figure 3 shows the ac impedance spectra (Nyquist plots) of pristine LNTM 20 and of surface modified Nb LNTM 20, measured after 2 and 40 cycles for the discharged state. The equivalent circuit$^{31}$ is shown in the inset, and the fitting results are listed in Table S2 (SI). The spectra exhibit two semicircles at high and low frequencies and a Warburg tail at very low frequencies. The first, potential independent semicircle is attributed to the surface processes, e.g., the resistance of Li$^+$ migration through electrode surface films (surface film resistance $R_F$). The second, potential dependent semicircle reflects the charge transfer (interfacial) resistance $R_{ct}$. The Warburg tail is ascribed to the diffusion of Li ions into the electrode material (Warburg element). Both materials (pristine and Nb coated) show a similar starting behavior and display...
growth in impedance with electrochemical cycling. The charge transfer resistances $R_2$ of the pristine and surface modified cathode after the 2nd and 40th cycles have been compared. $R_2$ is 20 and 67 $\Omega$ for the pristine cathode, and 8 and 23 $\Omega$ for the surface modified compound, respectively. During prolonged cycling, the charge transfer resistance significantly increases for the pristine cathode (by 44 vs 16 $\Omega$ for the surface modified cathode). The increase in charge transfer resistance is tentatively attributed to structural changes on the surface. These results demonstrate that the surface modified compound shows a relatively low impedance after oxygen loss as compared to pristine material. However, the increase in impedance with cycling is significant, in accordance with the continuing capacity fading seen for Nb LNTM 20.

The electrode kinetics depend on both the ion transport and electronic conductivity and can limit the overall performance. The total conductivity of LNT 0 and LNTM 20 was studied by ac impedance spectroscopy at various temperatures, as shown in Figures S8 and S9 of the SI. The activation energy ($E_a$) was calculated via the Arrhenius equation, from the slope of $\ln \sigma$ vs $T^{-1}$, where $\sigma$ is the conductivity and $T$ represents the absolute temperature. LNTM 20 shows a higher room temperature conductivity of $\sim 3.0 \times 10^{-6}$ S cm$^{-1}$ compared to LNT 0 ($\sim 7.1 \times 10^{-8}$ S cm$^{-1}$). The donation of d electrons from Mo to the conduction band can explain the increase in conductivity for LNTM 20. The activation energy ($E_a$) for LNT 0 (319 $\pm$ 19 meV) is higher than for LNTM 20 (249 $\pm$ 16 meV). Overall, the conductivity is sufficiently high so that no electronic limitations are to be expected. Important to mention is that, with the state of charge and the number of cycles, the conductivity can vary by several orders of magnitude.

For lithium rich materials, both oxygen redox and lattice oxygen loss upon cycling are well known phenomena. In order to find out whether oxygen release takes place in the case of overlithiated LNTM 20, in situ differential electrochemical mass spectrometry (DEMS) measurements were conducted and the results compared to LNT 0, which served as reference material. To this end, half cells were charged at C/10 to 4.5 V (1C = 210 mA g$^{-1}$ for LNTM 20 and 100 mA g$^{-1}$ for LNT 0) while monitoring gas evolution. As depicted in Figures 4 and S10 (SI), the LNTM 20 and LNT 0 half cells showed first cycle charge capacities of 157 and 88 mAh g$^{-1}$. The specific capacities were lower for the thicker electrodes used in the DEMS measurements. CO$_2$ evolution was observed, starting around 3.9 V for LNTM 20 and 4.1 V for LNT 0. The quantities detected for LNTM 20 were below 2 ppm up to 4.1 V (50 mAh g$^{-1}$), thus making a precise determination of the onset potential difficult. As expected, significant oxygen release was only observed for the overlithiated material, starting at 4.4 V. This is indicative of lattice changes during cycling operation, eventually leading to an oxygen deficient (surface) structure.
Chemical reactions of released oxygen with the electrolyte are not the only source of CO₂ evolution, as both materials show similar behavior. Electrochemical electrolyte oxidation and decomposition of residual carbonate species from the synthesis, for instance, may also account for the CO₂ evolution.

**Structural Changes upon Cycling.** In situ XRD measurements were carried out to investigate the structural changes of LNTM 20 during two consecutive cycles between 4.5 and 1.5 V at C/30. The voltage profile and the changes in the a lattice parameter from single phase XRD refinement are shown in Figure 5, with an enlarged section displaying the pattern around the 002 reflection. During the first charge, three regimes can be seen. The first charge regime until 4 V reveals a sloped voltage profile, where the a lattice parameter is continuously decreasing, thus reflecting lattice contraction. This finding can be associated with a Ni²⁺/³⁺ oxidation process \([\text{Ni}^{2+} (\approx 0.69 \text{ Å}) \text{ and Ni}^{3+} (\approx 0.56 \text{ Å})]\). The second regime is along the 4.3 V plateau, where the lattice parameter changes only slightly, and the third regime occurs toward the end of the charge, where the lattice parameter is continuously decreasing. This result can be attributed to oxygen oxidation and then release. In the midregime, the lattice parameter is only changing in the beginning and at the end of charge. We argue that oxygen \(\text{(O}^{2-}\) oxidation is associated with a shrinkage of the oxygen framework because of the smaller size of the oxygen anion or due to the formation of peroxo like species with shorter oxygen-oxygen bonds.\(^{40}\) During the first discharge, the lattice parameter continuously increases (lattice expansion) until 2.2 V. Further discharge affects the lattice only slightly. During the second cycle upon discharge, a more pronounced plateau is observed for voltages <2.2 V, with only slight changes in the a lattice parameter.

**Redox Mechanism.** Further information on the redox mechanism of LNTM 20 and LNT 0 was obtained from X ray absorption near edge structure (XANES) measurements. Figure S11a (SI) shows the Ni K edge spectra of pristine LNT 0 after charging to 4.5 V and then discharging to 1.5 V. Comparison of LNT 0 with a NiO reference compound reveals that the edge energy is similar, indicating that the Ni oxidation state is +2. Figure 6a shows similar results for LNTM 20.

**Figure 5.** (left) In situ XRD pattern of LNTM 20 for two consecutive cycles in the range of 4.5−1.5 V at C/30. (right) Corresponding voltage profile and changes in the a lattice parameter from Rietveld refinement analysis. The red curves are the voltage profile and the red dots the measurement points, where the XRD patterns were collected.

**Figure 6.** (a) XANES Ni K edge spectrum for LNTM 20 and (b) Mo K edge spectrum for LNTM 20. (c) FT EXAFS of Ni.

During charging, the Ni K edge shifted significantly to higher energies, thereby reflecting an increase in oxidation state. On the basis of Faraday’s law, the theoretical capacities for different redox processes have been calculated and are listed in Table 1. The oxidation state of Ti was determined by XPS to be +4, as shown in Figure S12 (SI). Ti⁴⁺ was fully oxidized and therefore assumed to be electrochemically inactive.\(^{41,42}\) Note that neither XANES nor XPS can rule out the formation of small amounts of Ti⁵⁺, in the atom percent range. The

<table>
<thead>
<tr>
<th>compound</th>
<th>(\text{Ni}^{2+}/^{3+})</th>
<th>(\text{Ni}^{2+}/^{4+})</th>
<th>(\text{Mo}^{4+})</th>
<th>(\text{Mo}^{5+})</th>
<th>(\text{Li}) specific capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{LiNi}<em>{0.5}\text{Ti}</em>{0.5}\text{O}_{2}) (LNT-0)</td>
<td>144</td>
<td>287</td>
<td></td>
<td></td>
<td>287</td>
</tr>
<tr>
<td>(\text{Li}<em>{0.8}\text{Ni}</em>{0.2}\text{Ti}<em>{0.8}\text{Mo}</em>{0.2}\text{Li}<em>{2}\text{O}</em>{2}) (LNTM-20)</td>
<td>101</td>
<td>202</td>
<td>40</td>
<td>80</td>
<td>364</td>
</tr>
</tbody>
</table>

Table 1. Theoretical Specific Capacity for Different Valence Changes and the Specific Lithium Capacity of LNT 0 and LNTM 20
measured specific capacity for each state of charge can be used to estimate the average valence change.

For LNT 0, the specific capacities for charging to 4.5 V and subsequently discharging to 1.5 V were 145 and 106 mAh g⁻¹, respectively. This corresponds to 0.5 Li extraction and 0.37 Li intercalation per formula unit (fu), which can be attributed to the Ni²⁺/Ni³⁺ redox couple. Interestingly, LNTM 20 delivered 262 mAh g⁻¹ during charge, corresponding to 0.86 Li per fu, which is beyond the theoretical capacity for the Ni²⁺/⁴⁺ redox couple with 202 mAh g⁻¹. This suggests that more redox active species are involved in the reaction, although electrolyte/electrode side reactions can also be expected. As confirmed by DEMS, O₂ evolution takes place during charge, and therefore, oxidation of O²⁻ must be considered as an additional mechanism for charge compensation. For the consecutive discharge to 1.5 V, LNTM 20 exhibited a specific discharge capacity of 212 mAh g⁻¹, corresponding to 0.73 Li per fu. Simultaneously, the Ni K edge shifts back to lower energies, pointing to nickel reduction. In Figure S11b (SI), the comparison between the Ni K edge of LNT 0 and LNTM 20 in the charged state shows similar edge energies, suggesting that Ni is in the oxidation state +3 in both cases. In conclusion, oxidation to Ni⁴⁺ can be excluded for LNTM 20, limiting the nickel redox contribution to Ni²⁺/³⁺. Interestingly to note is that the pre edge peak intensity of Mo increased significantly after the first charge and remained at a higher value after the discharge, which is shown in Figure 6b. This finding indicates an increased distortion of the MoO₆ octahedra compared to the pristine state. The intensities for these transitions are very sensitive to the coordination environment and the symmetry of the metal center. For centrosymmetric symmetry, the pre edge peak is weak, as it is limited by a weak electric quadrupole intensity mechanism. This pre edge structure is typically observed for α MoO₃ with Mo in the oxidation state +6. The increase in pre edge peak, with the shift of the white line to higher energies, suggests oxidation of Mo upon charging. On the basis of the results of a linear combination approach comprising both structural and surface/interface process are the associated oxygen release, leading to surface degradation, side reactions with the electrolyte, cation diffusion, and overall performance degradation. In particular, higher resistances lead to lower rate capability. DEMS measurements provided clear evidence that O₂ is released for Li rich LNTM 20, but not for stoichiometric LNT 0.

In order to alleviate the above mentioned drawbacks, approaches comprising both structural and surface/interface modifications have been intensively studied. Recently, Lee et al. demonstrated that substitution of oxygen by fluorine could mitigate oxygen loss and improve the cycling stability of the Li rich Li°°°°°−Ti°°°−Mo−(O/F) system. The fluorine substitution is an effective way to enable an introduction of lithium excess in low valent systems without the use of heavy high valent charge compensators, which can lower the specific capacity. Practically, this approach aims to increase the cationic redox capacity. Fluorine doping has been reported to mitigate oxygen loss, improve capacity retention, and increase the average voltage in some examples. However, stronger interactions between lithium and fluorine and lithium migration into tetrahedral sites for a high states of charge impose constraints to the accessible capacity. Another interesting approach shown by Shin et al. could experimentally demonstrate that oxygen loss can be mitigated by low level doping of heavy elements such as Ta, resulting in surface modification. The improvement has been rationalized by the enhanced oxygen retention of Ta and the tendency of heavy elements to segregate at the surface due to their larger ionic radii. Our approach targets the surface modification and physical protection through a ceramic coating in order to mitigate the
surface phase evolution, which leads to performance degradation.

Here, we propose an approach comprising a surface treatment with LiNbO$_3$ in order to improve the electrochemical performance of the material. Unmodified Li$_{1.2}$Ni$_{0.333}$Ti$_{0.333}$Mo$_{0.133}$O$_2$ showed a high specific capacity but displayed a significant polarization for high degrees of delithiation (~4.3 V). The LiNbO$_3$ modified Li$_{1.2}$Ni$_{0.333}$Ti$_{0.333}$Mo$_{0.133}$O$_2$ on the other hand, showed less polarization, with a higher average discharge voltage and a significantly higher capacity contribution in the high voltage regime. We argue that the change of the voltage profile can be attributed to the formation of a Li−Ni−Ti−Mo−Nb solid solution due to partial interdiffusion of cations from the surface coating into the active material during sintering. This observation is reflected in the lower impedance growth of Nb LNTM 20 during cycling. We suggest that the lower charge transfer resistance and impedance increase for the surface modified compound can be attributed to the mitigated surface densification. For further optimization, a uniform coating is required. In addition, the influence of sintering temperature on the interdiffusion mentioned above needs to be better understood. Alternatively, Li$_2$TiO$_3$ is a possible candidate compound that could be used for the surface modification, since Ta doping in a disordered rock salt has been shown to affect the surface chemistry due to segregation of the heavy element dopant on the surface, thereby mitigating oxygen loss.\textsuperscript{50}

In summary, we have demonstrated that high delithiation of Li$_{1.2}$Ni$_{0.333}$Ti$_{0.333}$Mo$_{0.133}$O$_2$ triggers oxygen release, resulting in substantial performance decay. The changes in oxidation state, bond distance, and coordination environment for different states of charge are illustrated. XANES spectroscopy revealed that Ni is oxidized from +2 to +3. At the same time, Mo changes its oxidation state from the pristine state with +4.7 to around +6 in the charged state; it is reduced to +3.2 in the consecutive discharge cycle.

Furthermore, an irreversible structural distortion of the Mo environment was observed upon cycling. XPS revealed that in the charged state, Mo has a mixed oxidation state on the surface, with predominantly +6 and +4. Thus, in the fully charged state, we estimate that 109 mAh g$^{-1}$ (around 0.36 Li per formula unit) are charge compensated by oxygen anion oxidation, triggering O$_2$ evolution, accompanied by partial reduction of Mo to +4 near the surface.

Moreover, a strong particle size dependence of the accessible discharge capacity indicates the necessity of using small size material for achieving high specific capacities. To the best of our knowledge, this is the first time a surface modification using the solid state electrolyte LiNbO$_3$ has been tested for cation disordered rock salt oxides. The voltage hysteresis was significantly reduced for Nb LNTM 20 relative to pristine LNTM 20, electrochemical impedance spectra were measured at 25 °C after the 2nd and 40th cycles. Electrochemical impedance spectroscopy (EIS) was performed using a three electrode PAT Cell (EL CELL) with a Li ring as the reference electrode and Li metal (18 mm) as the counter electrode. The working electrode size was 18 mm, and aluminum served as the current collector. The experiments were conducted using a Bio Logic electrochemical workstation with an applied sinusoidal excitation voltage of 10 mV in the frequency range between 200 kHz and 0.1 Hz.

Diffusional Electrochemical Mass Spectrometry. In situ gas analysis was performed by use of diffusional electrochemical mass spectrometry (DEMS). The setup has been described elsewhere.\textsuperscript{37,55} Custom cells with gas inlets and outlets were assembled in an argon filled glovebox. The cathodes used (40 mm diameter with a 4 mm hole for proper gas extraction) had areal loadings of about 1 mg/cm$^2$ and 1.6 mg/cm$^2$ for pristine and modified Nb LNTM 20, respectively. For coating, we prepared a solution between solid lithium ethoxide and ethylene glycol as solvent. Electrode slurries were made of 90 wt % composite and 10 wt % polyvinylidene difluoride (PVDF) binder with N methyl 2 pyrrolidone (NMP) as the solvent. The composite consists of active material and Super C65 carbon black in a weight ratio of 80:20. The mixture was coated on an aluminum foil using the doctor blade technique and dried at 120 °C for 2 h under vacuum. Each working electrode (12 mm diameter) contained about 3 mg of active material. LiPF$_6$ from BASF (ethylene carbonate/dimethyl carbonate, 1:1 weight ratio with 1 M LiPF$_6$) was used as the electrolyte. Galvanostatic charge−discharge experiments were conducted at 25 °C in a climate chamber using an Arbin electrochemical workstation.

Impedance Spectroscopy. For a better understanding of the cycling performance of surface modified Nb LNTM 20 relative to pristine LNTM 20, electrochemical impedance spectra were measured at 25 °C after the 2nd and 40th cycles. Electrochemical impedance spectroscopy (EIS) was performed using a three electrode PAT Cell (EL CELL) with a Li ring as the reference electrode and Li metal (18 mm) as the counter electrode. The working electrode size was 18 mm, and aluminum served as the current collector. The experiments were conducted using a Bio Logic electrochemical workstation with an applied sinusoidal excitation voltage of 10 mV in the frequency range between 200 kHz and 0.1 Hz.

### EXPERIMENTAL SECTION

#### Synthesis.

The procedure to synthesize LiNi$_{0.5}$Ti$_{0.5}$O$_2$ and Li$_{1.2}$Ni$_{0.333}$Ti$_{0.333}$Mo$_{0.133}$O$_2$ was adopted from Lee et al.\textsuperscript{59} Li$_2$MoO$_4$ was synthesized using modified conditions. Li$_2$CO$_3$ (Alfa Aesar, >99%), NiCO$_3$ (Alfa Aesar, >99%), TiO$_2$ nanopowder (~50 nm particle size, Alfa Aesar, 99.7%), and MoO$_3$ (Alfa Aesar, 99%) were employed as the precursors. Other than for LiNi$_{0.5}$Ti$_{0.5}$O$_2$, stoichiometric amounts of precursors were used. For Li$_{1.2}$Ni$_{0.333}$Ti$_{0.333}$Mo$_{0.133}$O$_2$ and Li$_2$MoO$_4$, 5% excess of Li was used. The precursors were ball milled for 24 h with 200 rpm using a Fritsch P6 planetary ball mill with a 80 mL silicon nitride vial and silicon nitride balls, with a ball to powder weight ratio of 20:1. The mixture of the precursors was pelleted and then sintered at 750 °C for 2 h in air, followed by furnace cooling to 200 °C and immediate transfer inside an argon filled glovebox. Li$_2$MoO$_4$ was sintered at 900 °C for 2 h. After sintering, the pellets were manually ground into a fine powder.

For coating, we prepared a solution between solid lithium ethoxide (Sigma Aldrich, >99%) and liquid niobium isopropoxide solution (Alfa Aesar, 99%, 10 wt % niobium isopropoxide in 50:50 (v/v) 2 propanol/hexane) with a molar stoichiometry of 1.05:1.0 of Li to Nb. Li$_{1.2}$Ni$_{0.333}$Ti$_{0.333}$Mo$_{0.133}$O$_2$ was ball milled with the prepared coating solution using a Fritsch P9 with a 15 mL vial volume for 12 h at 200 rpm (ball to powder ratio of 15:1). Subsequently, the mixture was dried overnight in an oven in an argon filled glovebox and then pelleted and sintered at 400 °C for 2 h in air, followed by furnace cooling to 200 °C and immediate transfer into an argon filled glovebox. After the sintering, the pellets were manually ground into a fine powder.

#### Electrochemical Measurements.

Electrochemical tests were carried out in a Swagelok type cell using Li foil as the counter electrode. Electrode slurries were made of 90 wt % composite and 10 wt % polyvinylidene difluoride (PVDF) binder with N methyl 2 pyrrolidone (NMP) as the solvent. The composite consists of active material and Super C65 carbon black in a weight ratio of 80:20. The mixture was coated on an aluminum foil using the doctor blade technique and dried at 120 °C for 2 h under vacuum. Each working electrode (12 mm diameter) contained about 3 mg of active material. LiPF$_6$ from BASF (ethylene carbonate/dimethyl carbonate, 1:1 weight ratio with 1 M LiPF$_6$) was used as the electrolyte. Galvanostatic charge−discharge experiments were conducted at 25 °C in a climate chamber using an Arbin electrochemical workstation.

#### Impedance Spectroscopy.

For a better understanding of the cycling performance of surface modified Nb LNTM 20 relative to pristine LNTM 20, electrochemical impedance spectra were measured at 25 °C after the 2nd and 40th cycles. Electrochemical impedance spectroscopy (EIS) was performed using a three electrode PAT Cell (EL CELL) with a Li ring as the reference electrode and Li metal (18 mm) as the counter electrode. The working electrode size was 18 mm, and aluminum served as the current collector. The experiments were conducted using a Bio Logic electrochemical workstation with an applied sinusoidal excitation voltage of 10 mV in the frequency range between 200 kHz and 0.1 Hz.

#### Diffusional Electrochemical Mass Spectrometry.

In situ gas analysis was performed by use of diffusional electrochemical mass spectrometry (DEMS). The setup has been described elsewhere.\textsuperscript{37,55}
time. The impedance data were fitted and analyzed using the ZMAN 2 software.

**X-ray Absorption Spectroscopy.** The P65 XAS beamline (PETRA III, Hamburg) provides a relatively large beam (0.5 x 1 mm²) and a moderate photon flux density. The 11 period mini undulator delivers a monochromatic photon flux of about 10¹⁴ ph/s. Two plane mirrors with variable angle of incidence and three different surface coatings were installed in front of the water cooled double crystal monochromator. Si(111) and Si(311) crystals were used for the energy ranges of 4–22 and 7–44 keV, respectively. The P65 beamline is also equipped with a 7 pixel HPGe energy dispersive detector and Si PIPS diode. X-ray absorption spectroscopy measurements were performed in both transmission and fluorescence modes. For ex situ measurements, the step scan mode with a duration of about 10–11 min for each spectrum was used. The spectra were processed using the Demeter software package based on IFEFFIT and FEFF.²²

**X-ray Diffraction.** In situ X-ray diffraction (XRD) patterns were collected using modified coin cells on a parallel beam laboratory diffractometer with a microfocus rotating anode (Mo Kα radiation) in transmission geometry and a Pilatus 300 K W area detector. The coin cells comprise an LNTM 20 based cathode, a Li metal anode, and a Whatman glass fiber separator. The electrolyte was 1 M LiPF₆ in ethylene carbonate:dimethyl carbonate 1:1 (v:v) from BASF. Galvanostatic charge–discharge cycling was performed with an Ivium potentiostat between 1.5 and 4.5 V at 10 mA g⁻¹. Diffraction patterns were collected every 300 s. Two consecutive patterns were added up to eliminate cosmic spikes on the detector. The diffraction images were integrated using the pyFAI software and analyzed with the Rietveld method using TOPAS V6.

**X-ray Photoelectron Spectroscopy.** The elemental composition of the surface region was analyzed by X-ray photoelectron spectroscopy (XPS) using a Physical Electronics PHI 5800 ESCA system. The measurements were carried out with monochromatic Al Kα radiation (250 W, 13 kV) at a detection angle of 45° and with pass energies of 93.9 and 29.35 eV for survey and detail measurements, respectively. An electron flood gun was used for sample neutralization. The main C 1s peak was set to 284.8 eV for binding energy calibration. Some samples were subject to Ar⁺ sputtering (sputter rate of 1 nm min⁻¹, 1 mA, 5 kV) to remove the topmost surface layer.

**Transmission electron microscopy.** Transmission electron microscopy (TEM) investigations were performed on a Tecnai F20ST transmission electron microscope operated at 200 kV. Samples for the TEM study were prepared using an FEI STRATA dual beam focused ion beam (FIB)/scanning electron microscope. The FIB lift out samples were milled using a Ga ion beam at 30 kV.

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