Ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Cathode in Bis(fluorosulfonyl)imide-Based Ionic Liquid Electrolyte: Importance of the Cathode-Electrolyte Interphase

Hyeon Jeong Lee,[†] Zachary Brown,[†] Ying Zhao,[‡] Jack Fawdon,[†] Weixin Song,[†] Ji
Hoon Lee,[¶] Johannes Ihli,^{†,§} and Mauro Pasta^{*,†}

[†]*Department of Materials, University of Oxford, Oxford OX1 3PH, UK*

[‡]*Department of Aerospace Engineering and Applied Mechanics, Tongji University 100
Zhangwu Road, 200092 Shanghai, China*

[¶]*School of Materials Science and Engineering, Kyungpook National University, 80
Daehak-ro, Buk-gu, Daegu 41566, Republic of Korea*

[§]*Paul Scherrer Institut, 5232 Villigen PSI, Switzerland*

E-mail: mauro.pasta@materials.ox.ac.uk

Abstract

The high voltage (4.7 V vs. Li^+/Li) spinel lithium nickel manganese oxide ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, LNMO) is a promising candidate for the next-generation of lithium ion batteries due to its high energy density, low cost and environmental impact. However, poor cycling performance at high cutoff potentials limits its commercialization. Herein, hollow structured LNMO is synergistically paired with an ionic liquid electrolyte, 1M lithium bis(fluorosulfonyl)imide (LiFSI) in N-propyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide

(Pyr_{1,3}FSI) to achieve stable cycling performance and improved rate capability. The optimized cathode-electrolyte system exhibits extended cycling performance (>85% capacity retention after 300 cycles) and high rate performance (106.2 mAh g⁻¹ at 5C) even at an elevated temperature of 65 °C. X-ray photoelectron spectroscopy and spatially resolved x-ray fluorescence analyses confirm the formation of a robust, LiF-rich cathode electrolyte interphase. This study presents a comprehensive design strategy to improve the electrochemical performance of high-voltage cathode materials.

Introduction

The development of cathode materials that exhibit high energy density, high rate capability, low cost and stable cycling performance is essential to meet the requirements of next-generation lithium-ion batteries (LIBs). LiNi_{0.5}Mn_{1.5}O₄ (LNMO) is one of the potential cathode materials for next-generation LIBs. Its specific capacity of 147 mAh g⁻¹ delivered at an average potential of 4.7 V vs. Li⁺/Li leads to a theoretical energy density of ~650 W h kg⁻¹, which is ~15% lower than the state-of-the-art NMC811 (~760 W h kg⁻¹) but at ~40% lower cost, due to its Co free and low Ni composition.¹⁻³ Moreover, the three-dimensional diffusion pathways in LNMO's spinel crystal structure results in rapid diffusion of Li-ions and high power density.^{4,5}

However, the high working potential of LNMO is a double-edged sword: if on one hand it provides high energy and power density, on the other it means dealing with the instability of carbonate-based organic electrolytes at potentials above 4.5 V vs. Li⁺/Li.⁶⁻⁹ At the high cutoff voltage of 5 V, traditional electrolytes containing organic carbonates and LiPF₆ readily decompose to form various by-products such as oxocarbons (CO and CO₂) and acidic species, which not only hinder the formation of a stable cathode-electrolyte interphase (CEI) layer, but also cause the dissolution of the transition metals, ultimately leading to poor cycling performance.¹⁰⁻¹³

To mitigate the parasitic reaction between the liquid electrolyte and LNMO surface at

high cutoff potential, surface coatings of conductive polymers,^{14–16} oxides,^{17–19} and fluorides^{20–22} have proven an effective strategy to improve cyclability and therefore extensively investigated. However, their synthetic complexity effectively undermines the competitive advantage of LNMO’s lower bill of materials. Advanced binders and solid polymer electrolytes have also been employed to induce a stable CEI layer on the surface of LNMO, but the uneven coverage of binders and low ionic conductivity of solid polymer electrolytes impede the stability and rate capability of LNMO.^{23–27} Electrolyte solutions using bis(fluorosulfonyl)imide (FSI[−]) based ionic liquids show promise thanks to their relatively low viscosity, high chemical and electrochemical stability, and ability to form a robust solid–electrolyte interphase (SEI) that protects the liquid electrolyte from continued decomposition on the surface of the electrode particle.²⁸

In this study, we investigate 1M lithium bis(fluorosulfonyl)imide dissolved in N-propyl-N-methyl-pyrrolidinium bis(fluorosulfonyl)imide (1M LiFSI in Pyr_{1,3}FSI) as the electrolyte to empower reversible cycling of hollow-structured, ordered LNMO. The composition and morphology of the CEI layer are analysed by means of x-ray photoelectron spectroscopy (XPS) and high-resolution transmission electron microscopy (HR-TEM), respectively highlighting the formation of a uniform and thin (<8 nm) CEI layer, with composition rich in inorganic fluorides. The robust CEI prevents the side reaction between cathode and electrolyte at high voltages, which is confirmed by spatially resolved x-ray fluorescence (XRF) analysis. Electrochemical impedance spectroscopy (EIS) confirms the formation of a low-resistance CEI that is virtually unaffected by cycling, leading to enhanced coulombic efficiency and prolonged cycle life at both 30 °C and 65 °C, when compared to a commercial LP30 electrolyte. In addition, we carry out a detailed physicochemical and electrochemical characterisation of the electrolyte to investigate its impact on rate performance. Finally, we hypothesize how a mechanically robust CEI layer coupled with our hollow-structured, spherical secondary particle morphology could function as a capping layer to prevent volume expansion of the particle, thus further improving coulombic efficiency and cycle life. The present study provides a

useful guideline for designing cathode material-electrolyte systems which attains both stable operation at a high cutoff voltage and enhanced rate capability.

Results and discussion

Hollow LNMO (H-LNMO) particles were synthesized by a two steps procedure (co-precipitation followed by solid-state reaction) described in detail in the Materials and Methods Section. Synchrotron x-ray diffraction with Rietveld refinement (Figure 1a, Table S1) confirms the synthesis of phase pure LNMO with the cubic ($P4_332$ space group) crystal structure ($a=8.199$ Å) characteristic of “ordered” LNMO.^{4,29–32}

Figure 1. (a) XRD pattern of H-LNMO. The SEM images of H-LNMO at (b) low and (c) high magnification. (d) The high-angle annular dark-field STEM image of H-LNMO. (e) The SEM image of H-LNMO sample using a focused ion beam (FIB)

Scanning electron microscopy (SEM) images show spherical secondary particles 1–3 μm

(Figure 1b) consisting of platelet-shaped primary particles of about 500 nm, corroborating the average crystallite size of 569 nm predicted by the Reitveld refinement (Figure 1c, Table S1). Scanning transmission electron microscopy (STEM) image reveals the hollow nature of the particles, with a shell thickness of about 300 nm (Figure 1d). The hollow structure was confirmed by scanning electron microscopy (SEM) of a focused ion beam (FIB) cross-sectioned particle (Figure 1e). Hollow particles are formed because of the difference in diffusion rate between oxygen and transition metals (Ni and Mn) at the gas-solid interface during synthesis (Kirkendall effect).^{33,34}

The electrochemical performance of H-LNMO electrodes prepared as described in the Materials and Methods Section was evaluated in a half cell setup, using lithium metal as reference and counter electrode. The electrolyte we selected was 1 M lithium bis(fluorosulfonyl)imide (LiFSI) dissolved in N-propyl-N-methyl-pyrrolidinium bis(fluorosulfonyl)imide (Pyr_{1,3}FSI). We will refer to this electrolyte as the room temperature ionic liquid (RTIL) from this point forward. The performance of the RTIL electrolyte was compared with commercial LP30 (1M LiPF₆ in 1:1 EC DMC). FSI⁻-based ionic liquid (IL) electrolytes have gained popularity in recent years owing to their many favourable properties: namely, low viscosity (η), high ionic conductivity (χ), large electrochemical stability window and the resultant, robust SEI/CEI formed from its decomposition products.^{35,36} As an aliphatic quaternary amide (AQA), Pyr₁₃⁺-based ILs have proven to show high cathodic stability compared to aromatic-based ILs. Specifically, a 1,3-side chain was chosen because of its favourable melting point, and viscosity at RT.³⁷ To balance ionic conductivity, and favourable interfacial kinetics, a 1M concentration was selected. To understand some of the relevant transport properties of our RTIL, viscosity measurements, and symmetric Li/Li cell electrochemical impedance spectroscopy (EIS) measurements were run at 30 °C and 65 °C. Compared to other IL solutions' viscosities, our RTIL compared favourably, exhibiting viscosities of 63.2 mPa·s at 30 °C and 23.2 mPa·s at 65 °C. Measurements using a symmetric Li/Li custom-built cell were run to elucidate information on Li metal-interfacial kinetics and the Li⁺ transference

Figure 2. (a) EIS spectra of Li/Li cells with the RTIL at 30 and 65 °C. (b) GCD profiles of H-LNMO in LP30 (black) and RTIL (blue) at C/10. (c) Cycling performance of H-LNMO in LP 30 (black) and RTIL (blue) at C/5. (d) EIS spectra of H-LNMO samples after 10, and 100 cycles in LP 30 and RTIL. (e) The rate performance of H-LNMO in RTIL at different operating temperatures of 30 (blue) and 65 °C (red). (f) The cyclability of H-LNMO in LP30 (black) and RTIL (red) at the temperature of 65 °C with the rate of 2C.

number (t_{Li^+}). Shorter, medium frequency measurements were first run over 24h to confirm the electrolyte’s stability against lithium metal. After, a very low frequency measurement was run (200 kHz to 20 μ Hz) to measure the whole EIS spectrum, including the finite-length Warburg diffusion (W_d). This allowed an estimated transference number measurement using the formula $t_{\text{Li}^+} = R_{\text{bulk}}/(R_{\text{bulk}}+W_d)$.^{38,39} Using the equivalent circuit illustrated in Figure 2a, the spectra were fitted and the properties analysed. At 30 °C, χ was calculated to be 3.83 mS cm⁻¹, with a t_{Li^+} of 0.076. And at 65 °C, increased to 10.84 mS cm⁻¹ with a t_{Li^+} of 0.078. It is evident that, like all ionic liquid-based electrolytes, t_{Li^+} is the limiting property, leading to large concentration gradients across the electrolyte, which is illustrated by the large W_d resistance. Linear sweep voltammetry (LSV) was performed on LP30 and RTIL to evaluate the electrochemical stability of each electrolyte (Figure S1). The rapid increase of the oxidation current was observed for LP30 at 4.7 V, whereas the RTIL showed a stable electrochemical window up to 5.1 V.

As shown in Figure 2b, both LP30 and RTIL cells exhibited similar discharge capacities of $\sim 132 \text{ mAh g}^{-1}$ at C/10. Three plateaus at 4.8 V, 4.7 V and 4.1 V (vs. Li^+/Li) were observed in galvanostatic charge-discharge (GCD) curve of H-LNMO, which corresponds to the redox voltage plateaus of $\text{Ni}^{4+/3+}$, $\text{Ni}^{3+/2+}$ and $\text{Mn}^{4+/3+}$, respectively.^{30,40} The very small capacity of $\text{Mn}^{4+/3+}$ plateau is indicative of the ordered structure of H-LNMO. Due to the high operating voltage of H-LNMO (4.7 V vs. Li^+/Li), the carbonate-based organic electrolyte is unstable, which results in rapid capacity decay. Both cycling performance and coulombic efficiency of the cell cycled with RTIL electrolyte were improved compared to the cell cycled with LP30 electrolyte (Figure 2c). After 100 cycles, the capacity retention of the cell cycled with RTIL electrolyte was 89.5% of its first cycle capacity, whereas the cell cycled with LP30 electrolyte retained 83.1% of initial capacity at the same C-rate of C/5. First cycle coulombic efficiency (CE) and average CE of the cell cycled with RTIL electrolyte is 80.8%, and 98.4 %, respectively, higher than the cell cycled with LP30 electrolyte (70.5 and 96.2%, respectively). The lower CE observed for cells cycled with LP30 electrolyte suggests

the formation of an unstable cathode electrolyte interphase (CEI).^{41,42}

The stable cycling performance of the H-LNMO electrode with the RTIL electrolyte is consistent with the EIS measurements of symmetric H-LNMO cells (Figure 2d, Table S2). After 10 cycles, the resistance was quite similar between H-LNMO electrodes cycled with the RTIL and LP30 electrolytes (22.23 vs. 21.94 Ω). After 100 cycles, the real component of the impedance of the cell cycled with RTIL electrolyte slightly increased to 31.95 Ω , whereas the cell cycled with LP30 electrolyte exhibited a significant increase to 148.3 Ω . This suggests an unstable CEI is formed on the surface of H-LNMO, continuously reacting with the LP30 electrolyte upon cycling. The rate performance of the H-LNMO electrode was evaluated in the RTIL electrolyte at 30 °C and 65 °C (Figure 2e). At 30 °C, the H-LNMO electrode exhibited the moderate discharge capacities of 92.6 and 54.8 mAh g⁻¹ at high C-rates of 5C and 10C, respectively. Discharge capacities of H-LNMO electrodes were further increased to 106.2 and 94.5 mAh g⁻¹ at the C-rates of 5C and 10C, respectively, when cycling at 65 °C. High temperatures result in higher diffusivities, which can alleviate the problems associated with low t_{Li^+} , namely reducing the extent of the concentration gradient. This could be a primary reason for increased performance of the 65 °C cell. The cycling performance of H-LNMO cells with LP30 and RTIL electrolytes sharply contrasted at the high operating temperature of 65 °C (Figure 2f). After 50 cycles, the H-LNMO cell cycled with LP30 electrolyte almost showed zero capacity, whereas the H-LNMO cell cycled with RTIL electrolyte exhibited 85.3% retention of initial capacity even after 300 cycles. Rapid capacity decaying of H-LNMO cycled with LP30 at high temperatures is related to the thermal stability of LP30. At a high operating temperature, the LiPF₆ salt rapidly decomposes to form the PF₅, which not only forms HF but also activates the ring-opening reaction of the cyclic carbonate, resulting in a continuous side reaction at the surface of LNMO and the decomposition of solvent.^{43–46} The half-cell performance of H-LNMO with RTIL electrolyte is compared to other LNMO cathode-electrolyte pairs in Table S3.^{14,17,47–50}

The high CE and impressive capacity retention of the H-LNMO cell cycled with RTIL

Figure 3. (a) TEM image of pristine H-LNMO , H-LNMO after 1st charge, 1st discharge and after 10 cycles in (b-d) LP30 and (e-g) RTIL at the temperature of 30 °C.

electrolyte are attributed to the formation of a stable CEI on the surface of H-LNMO. Therefore, we extensively assessed the physical and chemical properties of the CEIs formed in both LP30 and RTIL electrolytes. H-LNMO electrodes were harvested after the 1st charge, 1st discharge, and 10 cycles at 30 °C, and imaged *ex situ* with transmission electron microscopy (TEM) (Figure 3). In the pristine state, the H-LNMO showed a clean surface without an observable layer (Figure 3a). After the 1st charge, amorphous CEI layers with a thickness of less than 8 nm were formed on the surface of H-LNMO cycled in both LP30 and RTIL electrolytes (Figure 3b,e). A dramatic change in the uniformity of the CEI layer was observed for H-LNMO cycled in LP30 electrolyte after the first discharge process (Figure 3c,f). The CEI layer of H-LNMO cycled with LP30 electrolyte showed an irregular morphology, whereas a uniform film was observed for H-LNMO cycled with RTIL electrolyte. The robust CEI layer of H-LNMO, when cycled with RTIL, is maintained after 100 cycles, thus preventing the side reaction between electrolyte and H-LNMO, which also supports the low impedance of H-LNMO cycled with RTIL after 100 cycles (Figure S2, Figure 2d). The TEM

observations suggest the CEI layer of H-LNMO cycled with LP30 electrolyte decomposed, thereby exposing pristine cathode material. This pristine surface catalyses further electrolyte decomposition, causing low CE and rapid capacity decay.^{41,51,52}

Figure 4. (a) XPS spectra of pristine H-LNMO at O1s, P2p, N1s, and F1s. Survey spectra of H-LNMO which is cycled in LP30 (b) and RTIL (c). *Ex situ* XPS spectra of H-LNMO in LP30 and RTIL after 1st charge, 1st discharge and 10 cycles at the binding energy regions of O1s (d), 1s (e) and Mn2p (f).

X-ray photoelectron spectroscopy (XPS) measurements were performed to investigate the composition of the CEI formed on the surface of H-LNMO electrodes cycled with LP30 and RTIL electrolytes (Figure 4, Figure S3–S5). The O1s spectrum of the pristine H-LNMO electrode indicates that most of the signal comes from the bond between transition metals (TM) and oxygen in H-LNMO (Figure 4a). A small amount of carbon component peaks was also observed, indicating the formation of carbonate species on the surface of H-LNMO,

likely from the reaction between H-LNMO and CO_2 in the air atmosphere.^{53,54} No peaks were observed in P2p and N1s spectra of the pristine H-LNMO electrode, eliminating the possibility of impurities overlapping with electrolyte-derived CEI products (Figure 4a, Figure S3). Similarly, the F 1s XPS spectrum of the pristine H-LNMO electrode exhibits only C–F bond at 687.98 eV originating from the poly(vinylidene difluoride) (PVDF) binder (Figure 4a).^{55,56}

The survey spectra of H-LNMO electrodes after the 1st charge demonstrate how the CEI formed on the surface of H-LNMO differ in composition for each electrolyte. Phosphorus-containing decomposition products are observed at ~ 135 eV in the survey spectrum of the H-LNMO electrode cycled with LP30 electrolyte (Figure 4b). For the H-LNMO cell cycled with RTIL electrolyte, the peaks of sulfur and nitrogen were formed at ~ 170 eV and ~ 400 eV, respectively (Figure 4c), indicating the electrolyte participates in the formation of the CEI layer. After the 1st charge of the H-LNMO cell with LP30 electrolyte, C–O and C=O are observed as dominating species in the O1s spectrum indicating that the carbonate solvent was decomposed during the charging process, participating in CEI formation (Figure 4d).^{57–59} Further, the C1s spectrum supports the observation of solvent decomposition occurring in LP30 electrolyte, with a significant increase of C–O and C=O observed on the H-LNMO electrode after the 1st charge of the H-LNMO cell with the LP30 electrolyte (Figure S4).

For the H-LNMO cell cycled with RTIL electrolyte, the ratio of carbon-oxygen component did not increase for the H-LNMO electrode compared to that of the pristine H-LNMO electrode (Figure 4d, Figure S5). Instead of carbon-related species, a significant amount of SO_2 moiety (532.9 eV) is present in the O1s spectra, derived from the decomposition of FSI^- anion (Figure 4d).^{52,60} The S2p spectrum of the H-LNMO electrode after the 1st charge also supports the observation of SO_2 at 169.3 and 170.5 eV for $2p_{3/2}$ and $2p_{1/2}$, respectively (Figure S5).^{61,62} The SO_2 moiety is considered to be an effective functional group to improve surface stability of cathodes because it only allows Li^+ migration by partial negative charge of oxygen atoms while inhibiting the electron transfer at the interface between the electrode

and the electrolyte, thus suppressing electrolyte decomposition during cycling.^{63,64} Also, a peak is observed at 400.1 eV in the N1s spectrum of the H-LNMO electrode after the 1st charge of the H-LNMO cell with RTIL electrolyte, further confirming that the FSI⁻ anion contributes to the formation of the CEI layer (Figure S5).^{61,64,65}

The integrated area ratio of the carbon-oxygen bonds and TM–O decreases for the H-LNMO electrode cycled with LP30 electrolyte, consistent with the exposure of pristine H-LNMO surface observed in the *ex situ* TEM results. Therefore, it is speculated that the vulnerable CEI layer was attacked by byproducts during electrolyte decomposition, degrading into a non-uniform CEI layer. On the contrary, the integrated area ratio between S=O and TM–O for the H-LNMO electrode cycled with RTIL electrolyte has relatively minor change, suggesting a stable CEI was formed (Figure 4d). The F1s XPS spectra directly show the variation in composition of the CEI on the surface of the H-LNMO electrode cycled with LP30 and RTIL electrolytes (Figure 4e). Regarding the 1st charge of the H-LNMO cell with LP30 electrolyte, two peaks at 687.98 eV and 686.45 eV are present in the F1s spectrum of the H-LNMO electrode, attributed to the C–F bond and P–F bond derived from polyvinylidene difluoride (PVDF) binder and LiPF₆ decomposed products, respectively.^{59,66,67} The P2p spectrum supports the observation of P–F species, with peaks observed at 136.20 eV and 134.58 eV for P2p_{2/3}, corresponding to Li_xPF_y and Li_xPO_yF_z, respectively (Figure S4b,d, and f).^{68,69}

The Li_xPO_yF_z is a degraded product from LiPF₆ after 1st charge process based on the following reactions:^{70,71}

However, it is difficult to observe the LiF formation on H-LNMO after the 1st charge of H-LNMO cells with LP30 electrolyte. It is speculated that the hydrofluoric acid (HF), the resultant byproduct in the reaction between the electrolyte and trace water, attacks the CEI layer. After 10 cycles, the new peak arises at 684.93 eV, which suggests the sluggish

formation of inorganic LiF. The formation of LiF is important as it is a robust CEI component that can prevent the side reaction between the electrode and electrolyte.^{20,41,72} However, the CEI formed on the surface of H-LNMO in RTIL electrolyte shows stable LiF formation immediately after the 1st charge. Upon cycling, a minor increase in the ratio of LiF and C-F is observed, indicating stable CEI formation on the surface of H-LNMO.

The *ex situ* XPS spectra of Mn2p further suggest the presence of parasitic side reactions between electrolyte and cathode for the H-LNMO cell cycled with LP30 electrolyte (Figure 4f). After the 1st discharge of the H-LNMO cell with LP30 electrolyte, Mn2p peaks of the H-LNMO electrode are slightly shifted to the lower binding energy when compared to peaks in the Mn2p spectrum of the pristine H-LNMO electrode, suggesting the reduction of Mn⁴⁺ by HF, at high cutoff voltage.^{5,12,73} The shift of the Mn2p peaks to lower binding energy is severe after 10 cycles, suggesting that the CEI layer formed in LP30 electrolyte is not an effective protective layer of the surface of H-LNMO. In contrast, the peak position in Mn2p spectra does not appear to shift for the H-LNMO electrode cycled with the RTIL electrolyte compared to the pristine H-LNMO electrode. From the XPS analysis, the vulnerable CEI formed on the surface of H-LNMO in LP30 electrolyte cannot prevent the parasitic reactions between electrolyte and cathode interface, leading to continuous dissolution of transition metal. However, the CEI formed on the surface of H-LNMO in RTIL electrolyte is robust during cycling and effectively mitigates the parasitic reaction between the electrolyte and cathode interface, which leads to high CE and prolonged cycle life.

In order to investigate the stress build-up in the CEI layer and the volume change of the hollow particle upon lithium insertion/deinsertion, a chemo-mechanical model was employed (see Materials and Methods Section).⁷⁴⁻⁷⁶ The particle was considered as a two-layered hollow sphere, with the active material as the inner layer with thickness t and the CEI as the outer layer with thickness t_o .

As shown in Figure 5 and Figure S6, a mechanically robust CEI layer can effectively constrain the volume change of the H-LNMO particle. Although the empty core inevitably

Figure 5. Changes of radial displacement ($u_R/R\epsilon^c$) and volumetric energy density by shell thickness-radius ratio (t/R) at various t_o values.

reduces the energy density (red solid line), its presence helps to increase the particle compliance. A CEI layer with a thickness (t_o) of 0.4% of the particle radius (R) is able to reduce a solid spherical particle expansion by $\sim 0.5\%$, and the reduction increases to $\sim 1\%$ for a hollow sphere with a shell thickness of $0.4R$ (black solid line) (Figure 5). The constraint becomes increasingly significant when the CEI thickness is increased (black dotted and dash-dotted lines). The hoop stress change in the CEI layer by shell thickness-radius ratio also depicts the same tendency. At $t_o/R=0.4\%$ (blue solid line), the hoop stress of the CEI layer decreases by $\sim 0.4\%$ for a hollow sphere with a shell thickness of $0.4R$. (Figure S6a). When the Young's modulus of the CEI layer is halved, the hollow structure still contributes to a reduction of both particle volume change and stress in the CEI layer (Figure S6b). The robust microstructure of H-LNMO is verified with *ex situ* SEM measurement. After 100 cycles, the H-LNMO maintained its original morphology without surface damage originating from transition metal dissolution (Figure S7).¹⁸ This supports that the accumulated internal stress of the particle originating from the volume change is effectively mitigated due to the hollow structure, resulting in long term cyclability.

The extended cycle life of the H-LNMO electrode in RTIL electrolyte was particularly prominent at the elevated temperature at 65°C as shown in Figure 2e. It is speculated that the CEI layer formed on the surface of H-LNMO in RTIL is thermally stable and mitigates

Figure 6. (a) Spatial resolved XRF image of pristine H-LNMO at 9.9 keV and extracted XRF images of H-LNMO at Ni K-edge, Mn K-edge, and combined Ni/Mn K-edge energies. The fitting result of XRF spectrum of pristine H-LNMO and (b) the extracted Ni and Mn signals from the measured XRF spectrum (c). (d) Low magnitude-spatial resolved XRF images of H-LNMO after 50 cycles at 65 °C. The collected XRF image at 9.9 keV and extracted XRF images at Ni K-edge, and Mn K-edge energies. (e) Spatial resolved XRF image of single H-LNMO particle after 50 cycles at 65 °C. The collected XRF image at 9.9 keV and extracted XRF images at Ni K-edge, Mn K-edge, and combined Ni/Mn K-edge energies. (f) The fitting result of XRF spectrum of H-LNMO single particle after 50 cycles at 65 °C and (g) the extracted Ni and Mn signals.

transition metal dissolution even at the high operation temperature.^{43,77,78} Spatially resolved x-ray fluorescence (XRF) analysis was conducted to identify the morphological change and distribution of elements before and after cycling without sample destruction.^{79–81} The spatial resolution of XRF analysis is 50 nm, allowing for effective detection of the transition metal distribution on the particle with high accuracy and reliable qualitative element analysis. At the excitation energy of 9.9 keV, the XRF image of pristine H-LNMO shows its hollow structure (Figure 6a). Various elements (Ni, Mn, Al, Fe, Ar, Si, and etc.) were detected within the H-LNMO sample (Figure 6b and Table S4). Most of these elements originated from the sample grid, ion chamber of beam path, and beamline hardware. However, these background signals are not correlated with the H-LNMO (Figure S8).

According to the XRF fitting result, Ni and Mn are the only elements which are correlated with the pristine H-LNMO, indicating high sensitivity of the spatial resolved XRF measurement. The Ni and Mn are uniformly distributed in the whole particle (Figure 6a), and the atomic ratio between Ni and Mn was identified to 1:3.10. The qualitative ratio Ni/Mn is calculated by the fluorescence signal of the transition metal at its K-edge (Figure 6c).⁸² After 50 cycles in RTIL at 65 °C, the hollow morphology of H-LNMO is still maintained and exhibits the uniform distribution between Ni and Mn around the particle (Figure 6d,e). In addition, a sulfur signal uniformly distributed around the H-LNMO particles can be observed after cycling in RTIL, corroborating the XPS observation of a sulfur-rich CEI (Figure S9 and Table S5). According to fitted values, the atomic ratio between Ni and Mn is identified to 1:3.14 (Figure 6f,g), a minor change compared to the Ni/Mn ratio of pristine H-LNMO. This observation indicates that the stable CEI layer in RTIL effectively mitigates the transition metal dissolution in a combination of harsh conditions of high operation voltage and high operation temperature.

Conclusion

In conclusion, we have demonstrated that stable CEI layer formation in high cutoff voltage significantly improves both cycling performance and CE over a wide temperature range. The FSI⁻ anion-based RTIL electrolyte is effective in forming a sulfonyl-based CEI layer which is stable at high cutoff voltage and high operation temperature. In addition, the facile formation of inorganic LiF in CEI layer also prevents both reduction or dissolution of transition metals from the HF attack at the surface of H-LNMO. The hollow secondary particle morphology coupled with robust CEI layer effectively mitigates both volume change and stress level of LNMO induced by lithium insertion and extraction, thus improving structural stability of LNMO and CEI layer, which results in stable cycling performance of H-LNMO. The current study confirms the importance of comprehensive material/electrolyte design for high operating voltage cell and highlights the advancement of LNMO cathode design, important for next generation battery technology.

Materials and Methods

Synthesis of H-LNMO

H-LNMO was synthesized by a combination of co-precipitation and solid-state synthesis. All reagents were purchased from Sigma-Aldrich and used without further purification. To obtain the Ni_{0.25}Mn_{0.75}CO₃ precursor of H-LNMO, 0.249 g of nickel(II) acetate tetrahydrate (Ni(OCOCH₃)₂·4H₂O) and 0.523 g of manganese(II) sulfate monohydrate (MnSO₄·H₂O) were first dissolved in a mixture of 12.5 ml of deionized (DI) water and 6.25 ml of ethanol. After vigorous stirring, 6.5 ml of 0.5 M ammonium bicarbonate ((NH₄)HCO₃) and 6 ml of 0.5 M sodium carbonate (Na₂CO₃) were added to the solution followed by additional stirring for 6 h at 25 °C. The resulting suspension was transferred to a 100 ml Teflon-lined autoclave reactor, which was sealed and heated at 140 °C for 10 h. After the reaction was completed,

the $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{CO}_3$ precursor was rinsed with distilled water and ethanol several times and dried at 60 °C under vacuum for 10 h. Finally, the obtained $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{CO}_3$ was mixed with a stoichiometric amount of lithium carbonate (Li_2CO_3) and heated for 10 h at 900 °C in air followed by additional heating at 700 °C for 4 h.

Characterization

Crystallographic information was obtained by Reitveld refinement (GSAS-II) of synchrotron X-ray diffraction (XRD) data ($\lambda=0.24117$ Å) collected on the 17BM-B beamline at the Advanced Photon Source. The following parameters were refined: (1) scale factor, (2) lattice parameters, (3) position of atoms, and (4) atomic isotropic displacement parameters (U_{iso}). Field emission-scanning electron microscopy (FE-SEM, Zeiss Merlin) and transmission electron microscopy (TEM, JEOL-2100) were employed to probe the morphology of the H-LNMO particles.

Electrochemical Measurement

H-LNMO electrodes were fabricated by dispersing the active material, super-P (TIMCAL), and poly(vinylidene difluoride) (PVDF, Sigma-Aldrich) in N-methyl-2-pyrrolidinone (NMP, Sigma-Aldrich) with a mass ratio of 8:1:1. To prevent Al corrosion at high potentials, the slurry was cast onto carbon-coated-Al foil (PI-KEM, UK). The mass loading of the active material was 2.0–2.2 mg cm⁻². The room-temperature ionic liquid (RTIL) was prepared by dissolving 3.816 g of lithium bis(fluorosulfonyl)imide (LiFSI, TCI, 98.0%) in 20 ml of N-Propyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide (Pyr_{1,3}FSI, Solvionic). The LiFSI salt was dried at 80 °C under vacuum for 12 h in order to remove traces of H₂O. LP30 (1 M LiPF₆ in EC:DMC(1:1=v:v)) was purchased from Sigma-Aldrich. 2032 coin cells were fabricated in an Ar-filled glovebox in a traditional half-cell configuration with a Li metal foil (Sigma-Aldrich, 99.9%) acting as both counter and reference electrode. The electrochemical tests were carried out by galvanostatic charge-discharge measurements in the potential range

3.5-5.0 V (vs. Li^+/Li) using a battery cycler (VMP3, Biologic, France) at 30 and 65 °C. The C-rate is defined based on $1\text{C}=146\text{ mA g}^{-1}$. Electrochemical impedance spectroscopy(EIS) measurements were performed using a frequency response analyzer (VMP3, Biologic, France) over the frequency range of 0.01 Hz–1 MHz with a voltage amplitude of 10 mV. The EIS characterization was carried out in a custom built cell using a Li/Li setup with 350 μl of electrolyte, soaked in a Whatman microfiber GF/F separator. The interelectrode distance was 550 μm , and an area of 2 cm for each electrode. Using the same analyzer described above, the frequency range used was 200 kHz–20 μHz , with a voltage amplitude of 5 mV. This voltage amplitude was deemed optimal to balance resolution and linearity. A high-precision temperature-controlled viscometer was used (Lovis 2000 M microviscometer using a 1.8 mm diameter capillary and a 1.8 mm diameter steel ball) to measure the viscosity of the RTIL electrolyte at 30 and 65 °C.

***Ex situ* XPS and TEM Analyses**

For the sample preparation, electrodes were soaked in dimethyl carbonate (DMC) for 24 h to remove residual electrolyte and salt and subsequently dried under vacuum for 10 h. For *ex situ* XPS, the electrodes were transferred to the XPS chamber with a vacuum transfer vessels to avoid air exposure. XPS spectra were collected using a Phi XPS VersaProbe III with an Al K_α X-ray source. Data quantification was performed using CasaXPS software. All spectra were charge-referenced to the disordered C1s component at a binding energy of 284.8 eV. For *ex situ* TEM analysis, the dried electrodes were soaked again in NMP and sonicated for 10 sec. To minimize adverse side reaction with the CEI layer, the sample exposure to NMP was strictly minimised to 30 seconds. The supernatant was dropped on the lacey carbon film of a Cu TEM grid. The TEM grids were dried under vacuum at 60 °C for 10 h. The CEI layer change was observed by TEM (JEOL ARM-200F) at an acceleration voltage of 200 kV.

Mechanical Modelling

In the chemo-mechanical model of volume expansion and hoop stress, the compositional variation of Li^+ ion inside the particle is ignored. In this calculation, LiF is modeled as a CEI layer. Both LNMO and LiF are considered as isotropic linear elastic materials. Analytical expressions for the radial displacement and hoop stress are obtained based on following equations:

$$\frac{u_R}{R\epsilon^c} = \frac{1}{1 + \frac{2\bar{t}_o}{1-(1-\bar{t})^3} \left[\frac{E_o}{E} \frac{1-2\nu}{1-\nu_o} + \frac{E_o}{E} \frac{1+\nu}{2(1-\nu_o)} (1-\bar{t})^3 \right]} \quad (1)$$

$$\frac{\sigma_t}{E\epsilon^c} = \frac{1}{\frac{E(1-\nu_o)}{E_o} + \frac{2\bar{t}_o(1-2\nu)}{1-(1-\bar{t})^3} + \frac{\bar{t}_o(1+\nu)(1-\bar{t})^3}{1-(1-\bar{t})^3}} \quad (2)$$

$\bar{t}$ and $\bar{t}_o$ are the inner and outer shell thicknesses normalized against the particle radius (R). E and ν represent Young's modulus and Poisson's ratio of LNMO, respectively. R_o and E_o refer to the elastic properties of the CEI layer. ϵ^c is the chemical strain due to lithium insertion in LNMO. All the values of elastic properties in this study were extracted from the literature.

Spatial Resolved X-ray Fluorescence (XRF) Analysis

Spatial resolved XRF measurement was conducted at the I14 beamline at the Diamond Light Source. The H-LNMO samples were prepared from pristine electrode and electrode cycled 50 times in RTIL at 65 °C by dispersion in ethanol and loading on either an Al TEM grid or a Si_3N_4 window. The samples were covered by epoxy resin to prevent air exposure during the measurement. The whole process of sample preparation was conducted in an Ar-filled glovebox. A monochromatic beam of 9.9 keV was selected as an excitation energy for spatial resolved XRF analysis. The spatial resolution of each pixel was 50 nm. The obtained ROI (Region of Interest) image processing and data quantification were performed by using PyMca software. The Rayleigh scattering peak of XRF spectrum was calibrated to the excitation energy of 9.9 keV. The resultant mass fraction is converted to atomic ratio

based on the atomic weight of Ni and Mn.

Notes

The authors declare no competing interests.

Acknowledgement

The authors would like to acknowledge the the ISCF Faraday Challenge project SOLBAT [grant number FIRG007] and the Henry Royce Institute (through UK Engineering and Physical Science Research Council grant EP/R010145/1) for capital equipment. We acknowledge technical supports with I14 beamline at Diamond Light Source under Proposal MG22264, and 17-BM-B beamline at Advanced Photon Source (APS, Contract No. DE-AC02-06CH11357). H. J. Lee acknowledges support from the National Research Foundation of Korea (NRF-2019R1A6A3A03031343). Y.Z. is supported by Shanghai Sailing Program (Project No. 20YF1452300) and the Fundamental Research Funds for the Central Universities. We are grateful to the David Cockayne Center for Electron Microscopy for the use of their electron microscopes.

Supporting Information Available

The Supporting Information is available free of charge at <https://pubs.acs.org/XXXXXXXXXX>

LSV curves of electrolytes, *ex situ* TEM/SEM images, additional xps spectra of H-LNMO, Hoop stress of CEI layer, and spatial resolved XRF data of H-LNMO

References

- (1) Wentker, M.; Greenwood, M.; Leker, J. A Bottom-Up Approach to Lithium-Ion Battery Cost Modeling with a Focus on Cathode Active Materials. *Energies* **2019**, *12*, 504.

- (2) Li, W.; Cho, Y. G.; Yao, W.; Li, Y.; Cronk, A.; Shimizu, R.; Schroeder, M. A.; Fu, Y.; Zou, F.; Battaglia, V.; Manthiram, A.; Zhang, M.; Meng, Y. S. Enabling high areal capacity for Co-free high voltage spinel materials in next-generation Li-ion batteries. *Journal of Power Sources* **2020**, *473*, 228579.
- (3) Liang, G.; Peterson, V. K.; See, K. W.; Guo, Z.; Pang, W. K. Developing high-voltage spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes for high-energy-density lithium-ion batteries: current achievements and future prospects. *Journal of Materials Chemistry A* **2020**, *8*, 15373–15398.
- (4) Manthiram, A.; Chemelewski, K.; Lee, E. S. A perspective on the high-voltage $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ spinel cathode for lithium-ion batteries. *Energy and Environmental Science* **2014**, *7*, 1339–1350.
- (5) Ma, J.; Hu, P.; Cui, G.; Chen, L. Surface and Interface Issues in Spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$: Insights into a Potential Cathode Material for High Energy Density Lithium Ion Batteries. *Chemistry of Materials* **2016**, *28*, 3578–3606.
- (6) Leung, K. First-principles modeling of the initial stages of organic solvent decomposition on $\text{Li}_x\text{Mn}_2\text{O}_4(100)$ surfaces. *Journal of Physical Chemistry C* **2012**, *116*, 9852–9861.
- (7) Demeaux, J.; Lemordant, D.; Caillon-Caravanier, M.; Galiano, H.; Claude-Montigny, B. New insights into a high potential spinel and alkylcarbonate-based electrolytes. *Electrochimica Acta* **2013**, *89*, 163–172.
- (8) Zou, Z.; Xu, H.; Zhang, H.; Tang, Y.; Cui, G. Electrolyte Therapy for Improving the Performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Cathodes Assembled Lithium-Ion Batteries. *ACS Applied Materials and Interfaces* **2020**, *12*, 21368–21385.
- (9) Jung, R.; Metzger, M.; Maglia, F.; Stinner, C.; Gasteiger, H. A. Chemical versus electrochemical electrolyte oxidation on NMC111, NMC622, NMC811, LNMO, and conductive carbon. *Journal of Physical Chemistry Letters* **2017**, *8*, 4820–4825.

- (10) Han, J. G.; Kim, K.; Lee, Y.; Choi, N. S. Scavenging Materials to Stabilize LiPF₆-Containing Carbonate-Based Electrolytes for Li-Ion Batteries. *Advanced Materials* **2019**, *31*, 1804822.
- (11) Xu, M.; Tsiouvaras, N.; Garsuch, A.; Gasteiger, H. A.; Lucht, B. L. Generation of cathode passivation films via oxidation of lithium bis(oxalato) borate on high voltage spinel (LiNi_{0.5}Mn_{1.5}O₄). *Journal of Physical Chemistry C* **2014**, *118*, 7363–7368.
- (12) Pieczonka, N. P.; Yang, L.; Balogh, M. P.; Powell, B. R.; Chemelewski, K.; Manthiram, A.; Krachkovskiy, S. A.; Goward, G. R.; Liu, M.; Kim, J. H. Impact of lithium bis(oxalate)borate electrolyte additive on the performance of high-voltage spinel/graphite Li-ion batteries. *Journal of Physical Chemistry C* **2013**, *117*, 22603–22612.
- (13) Jarry, A.; Gottis, S.; Yu, Y. S.; Roque-Rosell, J.; Kim, C.; Cabana, J.; Kerr, J.; Kostecki, R. The Formation Mechanism of Fluorescent Metal Complexes at the Li_xNi_{0.5}Mn_{1.5}O_{4-δ}/Carbonate Ester Electrolyte Interface. *Journal of the American Chemical Society* **2015**, *137*, 3533–3539.
- (14) Dong, H.; Zhang, Y.; Zhang, S.; Tang, P.; Xiao, X.; Ma, M.; Zhang, H.; Yin, Y.; Wang, D.; Yang, S. Improved High Temperature Performance of a Spinel LiNi_{0.5}Mn_{1.5}O₄ Cathode for High-Voltage Lithium-Ion Batteries by Surface Modification of a Flexible Conductive Nanolayer. *ACS Omega* **2019**, *4*, 185–194.
- (15) Kwon, Y.; Lee, Y.; Kim, S. O.; Kim, H. S.; Kim, K. J.; Byun, D.; Choi, W. Conducting Polymer Coating on a High-Voltage Cathode Based on Soft Chemistry Approach toward Improving Battery Performance. *ACS Applied Materials and Interfaces* **2018**, *10*, 29457–29466.
- (16) Gao, X. W.; Deng, Y. F.; Wexler, D.; Chen, G. H.; Chou, S. L.; Liu, H. K.; Shi, Z. C.; Wang, J. Z. Improving the electrochemical performance of the LiNi_{0.5}Mn_{1.5}O₄ spinel

- by polypyrrole coating as a cathode material for the lithium-ion battery. *Journal of Materials Chemistry A* **2015**, *3*, 404–411.
- (17) Kim, J. W.; Kim, D. H.; Oh, D. Y.; Lee, H.; Kim, J. H.; Lee, J. H.; Jung, Y. S. Surface chemistry of $\text{LiNi}_0.5\text{Mn}_{1.5}\text{O}_4$ particles coated by Al_2O_3 using atomic layer deposition for lithium-ion batteries. *Journal of Power Sources* **2015**, *274*, 1254–1262.
 - (18) Zhao, R.; Li, L.; Xu, T.; Wang, D.; Pan, D.; He, G.; Zhao, H.; Bai, Y. One-Step Integrated Surface Modification to Build a Stable Interface on High-Voltage Cathode for Lithium-Ion Batteries. *ACS Applied Materials and Interfaces* **2019**, *11*, 16233–16242.
 - (19) Chong, J.; Xun, S.; Song, X.; Liu, G.; Battaglia, V. S. Surface stabilized $\text{LiNi}_0.5\text{Mn}_{1.5}\text{O}_4$ cathode materials with high-rate capability and long cycle life for lithium ion batteries. *Nano Energy* **2013**, *2*, 283–293.
 - (20) Tiurin, O.; Solomatin, N.; Auinat, M.; Ein-Eli, Y. Atomic layer deposition (ALD) of lithium fluoride (LiF) protective film on Li-ion battery $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathode powder material. *Journal of Power Sources* **2020**, *448*, 227373.
 - (21) Chu, C. T.; Mondal, A.; Kosova, N. V.; Lin, J. Y. Improved high-temperature cyclability of AlF_3 modified spinel $\text{LiNi}_0.5\text{Mn}_{1.5}\text{O}_4$ cathode for lithium-ion batteries. *Applied Surface Science* **2020**, *530*, 147169.
 - (22) Li, Y.; Zhang, Q.; Xu, T.; Wang, D.; Pan, D.; Zhao, H.; Bai, Y. LaF_3 nanolayer surface modified spinel $\text{LiNi}_0.5\text{Mn}_{1.5}\text{O}_4$ cathode material for advanced lithium-ion batteries. *Ceramics International* **2018**, *44*, 4058–4066.
 - (23) Ma, Y.; Chen, K.; Ma, J.; Xu, G.; Dong, S.; Chen, B.; Li, J.; Chen, Z.; Zhou, X.; Cui, G. A biomass based free radical scavenger binder endowing a compatible cathode interface for 5 v lithium-ion batteries. *Energy and Environmental Science* **2019**, *12*, 273–280.

- (24) Pieczonka, N. P.; Borgel, V.; Ziv, B.; Leifer, N.; Dargel, V.; Aurbach, D.; Kim, J. H.; Liu, Z.; Huang, X.; Krachkovskiy, S. A.; Goward, G. R.; Halalay, I.; Powell, B. R.; Manthiram, A. Lithium Polyacrylate (LiPAA) as an Advanced Binder and a Passivating Agent for High-Voltage Li-Ion Batteries. *Advanced Energy Materials* **2015**, *5*, 1501008.
- (25) Xu, H.; Zhang, H.; Ma, J.; Xu, G.; Dong, T.; Chen, J.; Cui, G. Overcoming the Challenges of 5 v Spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Cathodes with Solid Polymer Electrolytes. *ACS Energy Letters* **2019**, *4*, 2871–2886.
- (26) Zhang, H.; Zhang, J.; Ma, J.; Xu, G.; Dong, T.; Cui, G. Polymer Electrolytes for High Energy Density Ternary Cathode Material-Based Lithium Batteries. *Electrochemical Energy Reviews* **2019**, *2*, 128–148.
- (27) Dong, T.; Zhang, H.; Ma, Y.; Zhang, J.; Du, X.; Lu, C.; Shangguan, X.; Li, J.; Zhang, M.; Yang, J.; Zhou, X.; Cui, G. A well-designed water-soluble binder enlightening the 5 V-class $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes. *Journal of Materials Chemistry A* **2019**, *7*, 24594–24601.
- (28) Shkrob, I. A.; Marin, T. W.; Zhu, Y.; Abraham, D. P. Why Bis(fluorosulfonyl)imide is a “Magic Anion” for Electrochemistry? *Journal of Physical Chemistry C* **2014**, *118*, 19661–19671.
- (29) Aktekin, B.; Massel, F.; Ahmadi, M.; Valvo, M.; Hahlin, M.; Zipprich, W.; Marzano, F.; Duda, L.; Younesi, R.; Edström, K.; Brandell, D. How Mn/Ni Ordering Controls Electrochemical Performance in High-Voltage Spinel $\text{LiNi}_{0.44}\text{Mn}_{1.56}\text{O}_4$ with Fixed Oxygen Content. *ACS Applied Energy Materials* **2020**, *3*, 6001–6013.
- (30) Yang, J.; Han, X.; Zhang, X.; Cheng, F.; Chen, J. Spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode for rechargeable lithiumion batteries: Nano vs micro, ordered phase (P4332) vs disordered phase (Fd3m). *Nano Research* **2013**, *6*, 679–687.

- (31) Liu, D.; Zhu, W.; Trottier, J.; Gagnon, C.; Barray, F.; Guerfi, A.; Mauger, A.; Groult, H.; Julien, C. M.; Goodenough, J. B.; Zaghbi, K. Spinel materials for high-voltage cathodes in Li-ion batteries. *RSC Advances* **2014**, *4*, 154–167.
- (32) Toby, B. H.; Von Dreele, R. B. GSAS-II: The genesis of a modern open-source all purpose crystallography software package. *Journal of Applied Crystallography* **2013**, *46*, 544–549.
- (33) Yin, Y.; Rioux, R. M.; Erdonmez, C. K.; Hughes, S.; Somorjal, G. A.; Alivisatos, A. P. Formation of Hollow Nanocrystals Through the Nanoscale Kirkendall Effect. *Science* **2004**, *304*, 711–714.
- (34) Li, S.; Geng, S.; Zhao, J.; Cui, X. Synthesis of LiNi_{0.5}Mn_{1.5}O₄ nano/microspheres with adjustable hollow structures for lithium-ion battery. *Ionics* **2018**, *24*, 681–688.
- (35) Best, A. S.; Bhatt, A. I.; Hollenkamp, A. F. Ionic Liquids with the Bis(fluorosulfonyl)imide Anion: Electrochemical Properties and Applications in Battery Technology. *Journal of The Electrochemical Society* **2010**, *157*, A903.
- (36) Kerner, M.; Johansson, P. Pyrrolidinium fsi and TFSI-based polymerized ionic liquids as electrolytes for high-temperature lithium-ion batteries. *Batteries* **2018**, *4*, 10.
- (37) Matsumoto, H.; Sakaebe, H.; Tatsumi, K. Preparation of room temperature ionic liquids based on aliphatic onium cations and asymmetric amide anions and their electrochemical properties as a lithium battery electrolyte. *Journal of Power Sources* **2005**, *146*, 45–50.
- (38) Wohde, F.; Balabajew, M.; Roling, B. Li⁺ Transference Numbers in Liquid Electrolytes Obtained by Very-Low-Frequency Impedance Spectroscopy at Variable Electrode Distances. *Journal of The Electrochemical Society* **2016**, *163*, A714–A721.

- (39) Sälzer, F.; Pateras Pescara, L.; Franke, F.; Müller, C.; Winkler, J.; Schwalm, M.; Roling, B. Assessing the Ion Transport Properties of Highly Concentrated Non-Flammable Electrolytes in a Commercial Li-Ion Battery Cell. *Batteries & Supercaps* **2020**, *3*, 117–125.
- (40) Kim, J. H.; Huq, A.; Chi, M.; Pieczonka, N. P.; Lee, E.; Bridges, C. A.; Tessema, M. M.; Manthiram, A.; Persson, K. A.; Powell, B. R. Integrated nano-domains of disordered and ordered spinel phases in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ for li-ion batteries. *Chemistry of Materials* **2014**, *26*, 4377–4386.
- (41) Liu, W.; Li, J.; Li, W.; Xu, H.; Zhang, C.; Qiu, X. Inhibition of transition metals dissolution in cobalt-free cathode with ultrathin robust interphase in concentrated electrolyte. *Nature Communications* **2020**, *11*, 3629.
- (42) Kasnatscheew, J.; Evertz, M.; Streipert, B.; Wagner, R.; Klöpsch, R.; Vortmann, B.; Hahn, H.; Nowak, S.; Amereller, M.; Gentshev, A. C.; Lamp, P.; Winter, M. The truth about the 1st cycle Coulombic efficiency of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM) cathodes. *Physical Chemistry Chemical Physics* **2016**, *18*, 3956–3965.
- (43) Cao, X.; He, X.; Wang, J.; Liu, H.; Röser, S.; Rad, B. R.; Evertz, M.; Streipert, B.; Li, J.; Wagner, R.; Winter, M.; Cekic-Laskovic, I. High Voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$ Lithium Ion Cells at Elevated Temperatures: Carbonate- versus Ionic Liquid-Based Electrolytes. *ACS Applied Materials and Interfaces* **2016**, *8*, 25971–25978.
- (44) Weber, W.; Wagner, R.; Streipert, B.; Kraft, V.; Winter, M.; Nowak, S. Ion and gas chromatography mass spectrometry investigations of organophosphates in lithium ion battery electrolytes by electrochemical aging at elevated cathode potentials. *Journal of Power Sources* **2016**, *306*, 193–199.
- (45) He, M.; Boulet-Roblin, L.; Borel, P.; Tessier, C.; Novák, P.; Villevieille, C.; Berg, E. J.

- Effects of Solvent, Lithium Salt, and Temperature on Stability of Carbonate-Based Electrolytes for 5.0 V LiNi_{0.5}Mn_{1.5}O₄ Electrodes. *Journal of The Electrochemical Society* **2016**, *163*, A83–A89.
- (46) Tebbe, J. L.; Fuerst, T. F.; Musgrave, C. B. Degradation of Ethylene Carbonate Electrolytes of Lithium Ion Batteries via Ring Opening Activated by LiCoO₂ Cathode Surfaces and Electrolyte Species. *ACS Applied Materials and Interfaces* **2016**, *8*, 26664–26674.
- (47) Pan, J. J.; Chen, B.; Xie, Y.; Ren, N.; Yi, T. F. V₂O₅ modified LiNi_{0.5}Mn_{1.5}O₄ as cathode material for high-performance Li-ion battery. *Materials Letters* **2019**, *253*, 136–139.
- (48) Liang, F.; Yu, J.; Chen, J.; Wang, D.; Lin, C.; Zhu, C.; Wang, M.; Dong, L.; Li, C. A novel boron-based ionic liquid electrolyte for high voltage lithium-ion batteries with outstanding cycling stability. *Electrochimica Acta* **2018**, *283*, 111–120.
- (49) Wu, C. J.; Rath, P. C.; Patra, J.; Bresser, D.; Passerini, S.; Umesh, B.; Dong, Q. F.; Lee, T. C.; Chang, J. K. Composition Modulation of Ionic Liquid Hybrid Electrolyte for 5 v Lithium-Ion Batteries. *ACS Applied Materials and Interfaces* **2019**, *11*, 42049–42056.
- (50) Qi, H.; Ren, Y.; Guo, S.; Wang, Y.; Li, S.; Hu, Y.; Yan, F. High-Voltage Resistant Ionic Liquids for Lithium-Ion Batteries. *ACS Applied Materials and Interfaces* **2020**, *12*, 591–600.
- (51) Intan, N. N.; Klyukin, K.; Alexandrov, V. Ab Initio Modeling of Transition Metal Dissolution from the LiNi_{0.5}Mn_{1.5}O₄ Cathode. *ACS Applied Materials and Interfaces* **2019**, *11*, 20110–20116.
- (52) Alvarado, J.; Schroeder, M. A.; Zhang, M.; Borodin, O.; Gobrogge, E.; Olguin, M.;

- Ding, M. S.; Gobet, M.; Greenbaum, S.; Meng, Y. S.; Xu, K. A carbonate-free, sulfone-based electrolyte for high-voltage Li-ion batteries. *Materials Today* **2018**, *21*, 341–353.
- (53) Kim, J.; Hong, Y.; Ryu, K. S.; Kim, M. G.; Cho, J. Washing effect of a LiNi_{0.83}Co_{0.15}Al_{0.02}O₂ cathode in water. *Electrochemical and Solid-State Letters* **2006**, *9*, A19–A23.
- (54) Zhuang, G. V.; Chen, G.; Shim, J.; Song, X.; Ross, P. N.; Richardson, T. J. Li₂CO₃ in LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ cathodes and its effects on capacity and power. *Journal of Power Sources* **2004**, *134*, 293–297.
- (55) Jiao, S. et al. Stable cycling of high-voltage lithium metal batteries in ether electrolytes. *Nature Energy* **2018**, *3*, 739–746.
- (56) Cherkashinin, G.; Nikolowski, K.; Ehrenberg, H.; Jacke, S.; Dimesso, L.; Jaegermann, W. The stability of the SEI layer, surface composition and the oxidation state of transition metals at the electrolyte-cathode interface impacted by the electrochemical cycling: X-ray photoelectron spectroscopy investigation. *Physical Chemistry Chemical Physics* **2012**, *14*, 12321–12331.
- (57) Qian, Y.; Schultz, C.; Niehoff, P.; Schwieters, T.; Nowak, S.; Schappacher, F. M.; Winter, M. Investigations on the electrochemical decomposition of the electrolyte additive vinylene carbonate in Li metal half cells and lithium ion full cells. *Journal of Power Sources* **2016**, *332*, 60–71.
- (58) Deng, B.; Wang, H.; Ge, W.; Li, X.; Yan, X.; Chen, T.; Qu, M.; Peng, G. Investigating the influence of high temperatures on the cycling stability of a LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ cathode using an innovative electrolyte additive. *Electrochimica Acta* **2017**, *236*, 61–71.
- (59) Zhao, W.; Zou, L.; Zheng, J.; Jia, H.; Song, J.; Engelhard, M. H.; Wang, C.; Xu, W.; Yang, Y.; Zhang, J. G. Simultaneous stabilization of LiNi_{0.76}Mn_{0.14}Co_{0.10}O₂ cath-

- ode and lithium metal anode by lithium bis(oxalato)borate as additive. *ChemSusChem* **2018**, *11*, 2211–2220.
- (60) Piper, D. M.; Evans, T.; Leung, K.; Watkins, T.; Olson, J.; Kim, S. C.; Han, S. S.; Bhat, V.; Oh, K. H.; Buttry, D. A.; Lee, S. H. Stable silicon-ionic liquid interface for next-generation lithium-ion batteries. *Nature Communications* **2015**, *6*, 6230.
- (61) Zhang, X. Q.; Chen, X.; Hou, L. P.; Li, B. Q.; Cheng, X. B.; Huang, J. Q.; Zhang, Q. Regulating Anions in the Solvation Sheath of Lithium Ions for Stable Lithium Metal Batteries. *ACS Energy Letters* **2019**, *4*, 411–416.
- (62) Chang, Z. H.; Wang, J. T.; Wu, Z. H.; Gao, M.; Wu, S. J.; Lu, S. G. The Electrochemical Performance of Silicon Nanoparticles in Concentrated Electrolyte. *ChemSusChem* **2018**, *11*, 1787–1796.
- (63) Wang, R.; Li, X.; Zhang, B.; Wang, Z.; Guo, H. Effect of methylene methanedisulfonate as an additive on the cycling performance of spinel lithium titanate electrode. *Journal of Alloys and Compounds* **2015**, *648*, 512–520.
- (64) Stokes, K.; Kennedy, T.; Kim, G.-T.; Geaney, H.; Storan, D.; Laffir, F.; Appetecchi, G. B.; Passerini, S.; Ryan, K. Influence of Carbonate-Based Additives on the Electrochemical Performance of Si NW Anodes Cycled in an Ionic Liquid Electrolyte. *Nano Letters* **2020**, *20*, 7011–7019.
- (65) Evans, T.; Piper, D. M.; Sun, H.; Porcelli, T.; Kim, S. C.; Han, S. S.; Choi, Y. S.; Tian, C.; Nordlund, D.; Doeff, M. M.; Ban, C.; Cho, S. J.; Oh, K. H.; Lee, S. H. In Situ Engineering of the Electrode–Electrolyte Interface for Stabilized Overlithiated Cathodes. *Advanced Materials* **2017**, *29*, 1604549.
- (66) Lu, Y. C.; Mansour, A. N.; Yabuuchi, N.; Shao-Horn, Y. Probing the origin of enhanced stability of AlPO₄ nanoparticle coated LiCoO₂ during cycling to high voltages: Combined XRD and XPS studies. *Chemistry of Materials* **2009**, *21*, 4408–4424.

- (67) Zhang, J. N.; Li, Q.; Wang, Y.; Zheng, J.; Yu, X.; Li, H. Dynamic evolution of cathode electrolyte interphase (CEI) on high voltage LiCoO₂ cathode and its interaction with Li anode. *Energy Storage Materials* **2018**, *14*, 1–7.
- (68) Lee, H.; Lim, H. S.; Ren, X.; Yu, L.; Engelhard, M. H.; Han, K. S.; Lee, J.; Kim, H. T.; Xiao, J.; Liu, J.; Xu, W.; Zhang, J. G. Detrimental Effects of Chemical Crossover from the Lithium Anode to Cathode in Rechargeable Lithium Metal Batteries. *ACS Energy Letters* **2018**, *3*, 2921–2930.
- (69) Liu, B.; Li, Q.; Engelhard, M. H.; He, Y.; Zhang, X.; Mei, D.; Wang, C.; Zhang, J. G.; Xu, W. Constructing Robust Electrode/Electrolyte Interphases to Enable Wide Temperature Applications of Lithium-Ion Batteries. *ACS Applied Materials and Interfaces* **2019**, *11*, 21496–21505.
- (70) Kawamura, T.; Okada, S.; Yamaki, J. i. Decomposition reaction of LiPF₆-based electrolytes for lithium ion cells. *Journal of Power Sources* **2006**, *156*, 547–554.
- (71) Yu, Y.; Karayaylali, P.; Katayama, Y.; Giordano, L.; Gauthier, M.; Maglia, F.; Jung, R.; Lund, I.; Shao-Horn, Y. Coupled LiPF₆ Decomposition and Carbonate Dehydrogenation Enhanced by Highly Covalent Metal Oxides in High-Energy Li-Ion Batteries. *Journal of Physical Chemistry C* **2018**, *122*, 27368–27382.
- (72) Ding, X.; Li, Y. X.; Chen, F.; He, X. D.; Yasmin, A.; Hu, Q.; Wen, Z. Y.; Chen, C. H. In situ formation of LiF decoration on a Li-rich material for long-cycle life and superb low-temperature performance. *Journal of Materials Chemistry A* **2019**, *7*, 11513–11519.
- (73) Yi, T. F.; Mei, J.; Zhu, Y. R. Key strategies for enhancing the cycling stability and rate capacity of LiNi_{0.5}Mn_{1.5}O₄ as high-voltage cathode materials for high power lithium-ion batteries. *Journal of Power Sources* **2016**, *316*, 85–105.
- (74) Fischer, F. D.; Svoboda, J. Stresses in hollow nanoparticles. *International Journal of Solids and Structures* **2010**, *47*, 2799–2805.

- (75) Shin, H.; Park, J.; Han, S.; Sastry, A. M.; Lu, W. Component-/structure-dependent elasticity of solid electrolyte interphase layer in Li-ion batteries: Experimental and computational studies. *Journal of Power Sources* **2015**, *277*, 169–179.
- (76) Zheng, J.; Xiao, J.; Yu, X.; Kovarik, L.; Gu, M.; Omenya, F.; Chen, X.; Yang, X. Q.; Liu, J.; Graff, G. L.; Whittingham, M. S.; Zhang, J. G. Enhanced Li⁺ ion transport in LiNi_{0.5}Mn_{1.5}O₄ through control of site disorder. *Physical Chemistry Chemical Physics* **2012**, *14*, 13515–13521.
- (77) Wongittharom, N.; Lee, T. C.; Hung, I. M.; Lee, S. W.; Wang, Y. C.; Chang, J. K. Ionic liquid electrolytes for high-voltage rechargeable Li/LiNi_{0.5}Mn_{1.5}O₄ cells. *Journal of Materials Chemistry A* **2014**, *2*, 3613–3620.
- (78) Qiao, Y.; He, Y.; Jiang, K.; Liu, Y.; Li, X.; Jia, M.; Guo, S.; Zhou, H. High-Voltage Li-Ion Full-Cells with Ultralong Term Cycle Life at Elevated Temperature. *Advanced Energy Materials* **2018**, *8*, 1802322.
- (79) Bak, S. M.; Shadike, Z.; Lin, R.; Yu, X.; Yang, X. Q. In situ/operando synchrotron-based X-ray techniques for lithium-ion battery research. *NPG Asia Materials* **2018**, *10*, 563–580.
- (80) Boesenberg, U.; Falk, M.; Ryan, C. G.; Kirkham, R.; Menzel, M.; Janek, J.; Fröba, M.; Falkenberg, G.; Fittschen, U. E. Correlation between chemical and morphological heterogeneities in LiNi_{0.5}Mn_{1.5}O₄ spinel composite electrodes for lithium-ion batteries determined by micro-X-ray fluorescence analysis. *Chemistry of Materials* **2015**, *27*, 2525–2531.
- (81) Robert, R.; Zeng, D.; Lanzirotti, A.; Adamson, P.; Clarke, S. J.; Grey, C. P. Scanning X-ray fluorescence imaging study of lithium insertion into copper based oxysulfides for Li-Ion batteries. *Chemistry of Materials* **2012**, *24*, 2684–2691.

- (82) Beckhoff, B.; Kanngießer, B.; Langhoff, N.; Wedell, R.; Wolff, H. *Handbook of practical X-ray fluorescence analysis*; Springer Science & Business Media, 2007; pp 335–342.

Graphical TOC Entry

The robust cathode-electrolyte interphase acts as a role of capping layer for alleviating volume change of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles and preventing transition metal dissolution, thus leading to outstanding electrochemical performance