In situ forming an F- and B-rich interphase on cobalt-free LiNiO₂ cathode is firstly demonstrated to improve LiNiO₂ cathode performance with high-capacity, fast-rate capability, and >80% capacity retention at 400 cycles at a high cut-off voltage of 4.4 V (versus Li/Li⁺). This work highlights the interface engineering method by regulating the component of electrolyte to stabilize high-energy LiNiO₂. The cheap high-energy LiNiO₂ cathode provides a promising choice for next-generation Li metal/ion batteries.
Designing In-Situ-Formed Interphases Enables Highly Reversible Cobalt-Free LiNiO₂ Cathode for Li-ion and Li-metal Batteries

Tao Deng, Xiulin Fan, Longsheng Cao, Ji Chen, Singyuk Hou, Xiao Ji, Long Chen, Shuang Li, Xiuquan Zhou, Enyuan Hu, Dong Su, Xiao-Qing Yang, and Chunsheng Wang

SUMMARY
Cathode materials control both the energy density and cost of Li-ion and Li-metal batteries. The cobalt-free LiNiO₂ with relatively low cost and extremely high theoretical energy density (~1,050 Wh kg⁻¹) is one of the most promising cathode materials for high-energy batteries. However, the continuous Ni dissolution, structural disordering, particle cracking, and unstable cathode electrolyte interphase (CEI) hinder its applications. Here, we surmount these challenges by forming a robust fluoride (F)- and boron (B)-rich CEI on LiNiO₂ using a high-fluorinated electrolyte with LiDFOB additive. The LiNiO₂ cathode maintains an unprecedentedly high capacity retention of >80% after 400 deep cycles at a high charge cut-off voltage of 4.4 V (versus Li/Li⁺). In addition, the electrolyte forms an F- and B-rich interphase on the Li metal and graphite anodes, allowing stable cycling of full cells. This work sheds light on designing interfacial chemistry for high-energy cathodes, and its principle is applicable for other alkali metal ion cathodes.

INTRODUCTION
The ever-expanding energy markets from electronic devices and electric vehicles (EVs) to large-scale energy storage systems have stimulated massive investigation of high energy density batteries with long cycle life and low cost. Nowadays, the most-used energy storage system is Li-ion batteries (LIBs) consisting of a LiCoO₂ cathode (~140 mAh g⁻¹) and a graphite anode (372 mAh g⁻¹). The capacity and energy density of current Li-ion batteries are always limited by the transition metal (Ni) dissolution, particle cracking, surface film thickening, and irreversible phase transformations. Among these NMCs, the Co-free layered-type LiNiO₂ (LNO) is able to deliver a highest capacity of ~270 mAh g⁻¹ at a high average voltage (3.8 V versus Li/Li⁺), which renders EVs with 500-mile driving range in a single charge possible and therefore revives great interests.

However, the aggressive LNO exhibits much poorer cycling stability and reversibility especially under high cut-off potential (≥ 4.3 V versus Li/Li⁺), due to transition metal (Ni) dissolution, particle cracking, surface film thickening, and irreversible phase transformations. LNO has a much worse mechanical stability than other NMCs. The continuous Ni dissolution, structural disordering, particle cracking, and unstable cathode-electrolyte interphase (CEI) in cycling hinder its practical applications. In this work, we successfully resolved the above challenges by in situ forming a robust fluoride (F)- and boron (B)-rich CEI on LNO using a high-fluorinated electrolyte with LiDFOB additive. The LNO cathode maintains an ultra-high capacity retention of >80% at 400 cycles at high charge cut-off voltage of 4.4 V (versus Li/Li⁺). The electrolyte also forms an F- and B-rich solid electrolyte interphase on the Li metal/graphite anodes, allowing stable cycling of full cells. This work sheds light on designing interfacial chemistry for high-energy cathodes, and its principle is applicable for other alkali metal ion cathodes.
cathodes during charge and discharge cycles. At delithiation around 4.15 V (versus Li/Li+), Li$_{1-x}$NiO$_2$ experiences a large volume change of ~7% due to phase transition from H2 (rhombohedral phase, 0.55 ≤ x ≤ 0.75) to H3 (0.75 ≤ x ≤ 1.0), inducing significantly high strain and crack formation in LNO particles. Such pulverization of particles not only causes loss of electrical contact between primary particles, but also intensifies the parasitic reactions with the electrolyte. Upon further delithiation at a high potential above 4.3 V, Li$_{1-x}$NiO$_2$ itself became instable. As demonstrated in the LiNiO$_2$-NiO$_2$ phase diagram, the highly delithiated phase (H4 phase) of Li$_{1-x}$NiO$_2$ with Ni$^{4+}$ is thermodynamically metastable. Besides, the Ni$^{2+}$ tends to migrate into the interslab by replacing Li ions in tetrahedral sites at a high oxidation state. The mixing of Li/Ni ions in the slab and interslab, aggravated by surface dissolution, finally transforms the layered structure of LNO into disordered rock-salts structure (NiO phase). Moreover, since the conventional organic carbonate electrolytes have a limited HOMO (highest occupied molecular orbital), the excess radicals from the oxidation of electrolyte at high voltage (>4.3 V) tend to corrode the surface of LNO by continual reduction of Ni$^{4+}$ into Ni$^{2+}$ with O$_2$ release.

Extensive efforts have been devoted to ease these issues of LNO. The most effective methods are elemental substitution or doping (Fe, Ti, Al etc.), surface coating (ZrO$_2$, Al$_2$O$_3$, SiO$_2$ etc.), core-shell structure, gradient strategies, etc. Recently, Yoon et al. reported that introducing an excess Zr (1.4 atom %) in LNO can form a self-passivating Li$_2$ZrO$_3$ layer on LNO, which improved the capacity retention to 86% after 100 cycles. The co-doping of Co and Mg in LNO was proved to improve structural and thermal stability by suppressing the anisotropic lattice distortion, thereby enhancing the cycling life to 500 cycles in pouch-type full cells. Unfortunately, under high cut-off voltages (>4.3 V), none of these approaches could improve the long cycling stability of LNO cathode without sacrificing the energy density.

Previously, we demonstrated that all-fluorinated electrolyte composing of 1.0 M lithium hexafluorophosphate (LiPF$_6$) in a mixture of fluoroethylene carbonate, 3,3,3-fluoroethylmethyl carbonate, and 1,1,2,2-tetrafluoroethyl-2,2,2-trifluoroethyl ether (FEC: FEMC: HFE, 2:6:2 by weight) can form a fluorinated nanolayer interphase on both Li metal anodes and NMC811 cathodes, which significantly enhanced the Coulombic efficiency (CE) of Li plating and stripping to 99.2% and NMC811 to 99.9%. Herein, we reported that the fluorinated electrolyte with 2% LiDFOB additive enables more aggressive LiNiO$_2$ cathode to provide a high capacity of >210 mAh g$^{-1}$ at a charge and discharge rate of 0.5 C and retains more than 80% of the capacity after 400 deep cycles, because the in-situ-formed fluoride (F-) and boron (B)-rich interphase (CEI) on the surface of LNO can withstand a large volume change of high-capacity LNO. In a sharp contrast, only ~65% capacity of LNO is retained after ~200 cycles in 1M LiPF$_6$ ethylene carbonate/dimethyl carbonate (EC/DMC) electrolytes. The F- and B-rich interphase (solid electrolyte interphase [SEI]) on Li metal and graphite anodes also greatly enhanced the cycling stability and CE of Li and graphite anodes. Considering these benefits from the stable CEI and SEI, this work sheds light on rational design of electrolytes to form stable interfacial layer for high-energy batteries.

**RESULTS AND DISCUSSIONS**

**Characterization and Electrochemical Properties of Cobalt-free LiNiO$_2$ Cathode**

The LiNiO$_2$ microspheres (s-LNO) were synthesized by lithiation of the Ni(OH)$_2$ microspheres with LiOH·H$_2$O at high temperature.$^{9,32}$ Figure 1A presents the Rietveld
refinement of the powder X-ray diffraction (XRD) pattern of s-LNO, where the unusual background from 15° to 30° is due to the amorphous scattering of Kapton tape that protects the sample from air and moisture. The XRD pattern of s-LNO can be fitted to a 3R-type layered rhombohedral system (space group: R̅3̅m) with a hexagonal unit cell, and the lattice parameters are \( a = b = 2.8768(5) \, \text{Å} \) and \( c = 14.2025(8) \, \text{Å} \), which agrees well with literature.\(^9\,^12\) The inset diagram of Figure 1A illustrates the 3R-type LNO, where edge-sharing NiO\(_6\) octahedra forms NiO\(_2\) layers stacking in the A-B-C-A-B-C-fashion, and lithium atoms occupy the interstitial octahedral site between NiO\(_2\) layers. Scanning electron microscopy (SEM) images in Figure 1B shows the micro-sized (6–10 μm) spherical s-LNO consisting of primary particles with a size of ~200 nm. The energy-dispersive X-ray spectroscopy (EDS) and

Figure 1. Physical and Electrochemical Characterizations of As-Synthesized Cobalt-free LNO Microspheres

(A) Rietveld refinement of X-ray diffraction data and schematic structure of the layered LNO.
(B) SEM images of as-synthesized LNO microspheres consisting with secondary particles (~200 nm), the inset is the enlarged view of the small particles.
(C) Galvanostatic intermittent titration technique (GITT) profiles of the LNO cathode in F-262A using a pulse current of 1/15 C (12 mA g\(^{-1}\)) for 30 min and intervals of 5 h in a stable cycle after a 10-cycle activation process.
(D) The first three cyclic voltammetry (CV) curves of LNO cathode at a scanning rate of 0.1 mV s\(^{-1}\) in F-262A.
(E) Electrochemical charge/discharge curves of LNO in F-262A with different rates, increasing from 1/15 C to 5 C (1 C = 200 mA g\(^{-1}\)).
(F) Rate capability of LNO in F-262A at different C rates.
(G) Electrochemical charge and discharge curves of LNO cathode in F-262A at 0.5 C.
(H) Cycling comparison of LNO cathode at constant 0.5 C in F-262A and E-baseline electrolytes, DC, discharge capacity; CE, Coulombic efficiency.
high-resolution transmission electron microscopy (HRTEM) results (Figure S1) show the uniform mixing of Ni and O atoms with a ratio of ~0.5, and clear lattice fringes with a d-spacing of 0.47 nm corresponding to the (003) planes of LNO.

The electrochemical performance of LiNiO₂ cathode was evaluated under a high charge cut-off voltage of 4.4 V in three different electrolytes: conventional electrolyte of 1.0 M LiPF₆ EC/DMC (1:1 by volume, denoted as “E-baseline”); the fluorinated electrolyte of 1.0 M LiPF₆ FEC/FEMC/HFE (2:6:2 by weight, denoted as “F-262”); and F-262 with 2 wt % LiDFOB as the additive (“F-262A”). The s-LNO||Li cells in F-262 exhibit an initial discharge capacity of 216 mAh g⁻¹ at 0.5 C (Figure S2A), 1C = 200 mA g⁻¹ as well as high cycling CE of >99.7%. However, the battery with F-262 still shows continuous capacity decay and an increase of cell over potential during cycling. The capacity retention is around ~88% after 125 cycles (Figure S2B), which is significantly higher than previously reported cycle performance of LNO.³⁸ Inspired by the promising results, we further optimized the F-262 electrolyte by adding additional LiDFOB salt to improve the cycling of s-LNO by forming more compact and robust CEI.³³–³⁷

The amount of LiDFOB additives in the fluorinated electrolyte need to be optimized by balancing the low salt solubility and consumption during cycling. A large amount of LiDFOB cannot be dissolved in the electrolyte and limits the capacity of LNO (Figure S3). As an optimization, 2 wt % of LiDFOB is preferable to add in the F-262A to achieve a high performance of LNO. Meanwhile, the LiDFOB additives can further improve the oxidation stability of fluorinated electrolyte, as demonstrated by extreme low oxidation current up to 6.5 V in Figure S4. The Li plating and stripping curves the Li||Cu cell in F-262A electrolyte (Figure S5A) show a small overpotential of 28 mV and the corresponding CE reaches to 99% after 20 cycles (Figure S5B), which is much better than that in the conventional EC-based electrolytes (<90%). Generally, a CE of 99.9% with 30% excess of Li is required to enable 500-cycle life of Li metal batteries (LMBs), so more work aiming to improve the CE of Li metal to >99.9% is required to enable practical LNO-based LMBs.³⁸ The electrochemical behavior of s-LNO in the F-262A electrolyte was systemically investigated and compared with that in E-baseline electrolyte in half-cell configuration.

The quasi-equilibrium potential and overpotential of s-LNO cathode in F-262A electrolyte were investigated in s-LNO||Li coin cells using the galvanostatic intermittent titration technique (GITT). As shown in Figures 1C and S6, s-LNO exhibits a low quasi-equilibrium potential hysteresis of 0.10–0.15 V and ultra-small overpotential of <40 mV during lithiation and delithiation at 1/15 C (13 mA g⁻¹). Since the F-rich CEI has very low electronic conductivity,³⁹ the LNO can avoid the continual growth of CEI caused by electrolyte decomposition. The thin F-rich CEI also reduces the interface resistance. The maximum capacity of s-LNO measured using GITT in Figure 1C is 264 mAh g⁻¹, which is comparable with its theoretical capacity of 275 mAh g⁻¹. Moreover, the first three cyclic voltammetry (CV) curves in Figure 1D are overlapped, suggesting the excellent reversibility for the s-LNO electrode in F-262A even though the complex phase transitions take place between rhombohedral and monoclinic phases during cycling. The CV curves at different sweep rates from 0.1 to 5.0 mV s⁻¹ (Figure S7) suggest that redox reaction of s-LNO is limited by Li-ion diffusion process in s-LNO, which is similar to other types of layered LIBs cathodes.⁴⁰–⁴²

Figures 1E and 1F present the rate performances of s-LNO in F-262A with different rates from 1/15 C to 5 C (1 C = 200 mA g⁻¹). The corresponding discharging capacities of s-LNO at 1/15, 2/15, 1/3, 1, 2, 3, and 5 C are 265, 250, 224, 192, 168, 148, and
112 mAh g$^{-1}$ with high average CE of >99.9%, suggesting the excellent rate capability of s-LNO within F-262A. Compared with the E-baseline electrolyte, the s-LNO electrode in F-262A exhibits significantly enhanced long cycling stability with only a minimal increase of cell overpotential after 200 cycles (Figures 1G and S8). The s-LNO in F-262A retains a high specific capacity of 173 mAh g$^{-1}$ with average CE > 99.9% even after 400 cycles at a current rate of 0.5 C, corresponding to 81% capacity retention (Figure 1H). The CE of LNO electrode with F-262A quickly increases from 85% to >99.9% after several cycles, demonstrating that the CEI formed by oxidation of F-262A can efficiently prevent the electrolyte from further consumption and also protect the LNO from continual Ni dissolution, thereby leading to a high CE in more than 400 cycles. In contrast, the capacity of s-LNO cathode in E-baseline electrolyte drops quickly to less than 150 mAh g$^{-1}$ over 200 cycles and decays quickly to zero after 215 cycles (Figure 1H). The low initial CE of 65% (versus 85% in F-262A) and fluctuation of CE during cycling imply the severely parasitic reactions and transition metal dissolution of s-LNO in the E-baseline electrolyte.$^{7,9}$

The cycling stability of high-loading s-LNO electrode (~12 mg cm$^{-2}$) was also investigated at a low current of 0.1 C. No capacity decay was observed in 20 cycles and high CE of >99.9% was achieved (Figure S9A). However, s-LNO with baseline electrolyte shows a fast capacity decay and low efficiency due to severe side reactions between the electrolyte and s-LNO (Figure S9B). To our best knowledge, the performance of cobalt-free cathode LNO within F-262A electrolyte is the best ever reported for LIBs and LMBs at such high charge cut-off voltage of 4.4 V. The high energy density of LMBs by coupling with s-LNO cathode far exceeds those with any other types of NMC cathodes.

To understand the capacity decay mechanism of s-LNO, the evolution of impedances for s-LNO||Li cells with the F-262A and E-baseline electrolytes at different charge and discharge cycles were measured (Figure S10). The semicircle at a high frequency range in the electrochemical impedance spectroscopy (EIS) are attributed to the interfacial resistances ($R_{\text{int1}} + R_{\text{int2}}$) of the Li anode and LNO cathode, while the second semicircle in the intermediate frequency could be caused by charge transfer resistance ($R_{\text{ct}}$) on the surface of LiNiO$_2$ cathode.$^{16,31}$ As shown in Figures S10A and S10B, the interfacial resistance of ($R_{\text{int1}} + R_{\text{int2}}$) in these two electrolytes decreases from the 0th to 20th cycles due to the breaking of highly resistive passivation layer (Li$_2$CO$_3$) on Li and reforming of ionic conductive CEI and SEI films on electrodes. After 20 cycles, the interfacial resistance ($R_{\text{int1}} + R_{\text{int2}}$) and charge transfer resistance ($R_{\text{ct}}$) of LNO in F-262A electrolytes is almost constant thanks to the protection of stable SEI and CEI films. However, the rapidly increased interfacial resistance ($R_{\text{int1}} + R_{\text{int2}}$) and charge transfer resistance ($R_{\text{ct}}$) of LNO in the E-baseline electrolyte manifests a continuously growing SEI and CEI films.

The Li||LiNiO$_2$ cells after 100 cycles in F-262A and baseline electrolytes were disassembled. The surfaces of Li metal anode and LNO cathode in F-262A are clean and intact (Figure S10C). On the contrary, the Li metal anode after 100 cycles in baseline electrolyte was covered by a thick layer and a lot of black compounds were stuck on the separator (Figure S10D). The inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis demonstrated that the black compounds contain high content of Li and Ni. Therefore, serious side reactions and continual Ni dissolution of LNO occurred in E-baseline electrolyte (Figure S10E). Meanwhile, a much cleaner separator was observed, and only a very small amount of Ni was identified by ICP-OES in F-262A electrolyte. Therefore, F-262A electrolyte can effectively suppress the Ni dissolution by forming robust F-, B-rich CEI on LNO cathode.
The excellent cycling stability of s-LNO in fluorinated electrolyte with 2 wt % of LiDFOB additive inspires us to investigate the electrochemical performance of s-LNO||graphite full cells. Figure S11 shows the electrochemical performances of graphite anode in F-262A electrolyte shows excellent reversibility (Figure S11A) and cycling stability at a current rate of 0.5 C (1 C = 320 mA g$^{-1}$) (Figure S11B). The high reversibility of graphite electrode in F-262A is attributed to the stable SEI with high Li$^+$ conductivity, as evidenced by the constant EIS impedances during cycling (Figure S11C). After 100 cycles, the graphite anode still retains 97% of capacity at 5th cycle, and the CE of graphite reaches >99.99% after 5 activation cycles (Figure S11D). The high cycling stability and rate capability of both s-LNO cathode and graphite anodes in F-262A electrolytes ensure the exceptional electrochemical performance of s-LNO||graphite full cells (Figure 2).

Electrochemical Performance of Li-Ion Full Batteries

The electrochemical performance of LiNiO$_2$||Graphite Full Cell with Capacity Ratio of LNO to Graphite of 1.1:1

(A) Electrochemical charge/discharge curves of LNO in F-262A with different rates, increasing from 1/5 C to 5 C (1 C = 200 mA g$^{-1}$).

(B) The corresponding rate capability of LNO at different C rates.

(C) Electrochemical charge/discharge curves of LNO cathode in F-262A electrolyte at 0.5 C.

(D) Electrochemical charge/discharge curves of LNO cathode in E-baseline electrolyte at 0.5 C.

(E) Nyquist spectra of LNO cathodes before cycling/after 100 cycles with a rate of 0.5 C in F-262A and E-baseline electrolytes.

(F) Cycling comparison of LNO cathode at constant 0.5 C in F-262A and E-baseline electrolyte, DC, discharge capacity; CE, Coulombic efficiency.
Figures 2A and 2B present the rate performances of s-LNO||graphite full cells in F-262A at current rates of 1/5 C, 1/2 C, 1 C, 2 C, and 5 C, which delivers stable discharging capacities of 151, 121, 110, 88, and 78 mAh g$^{-1}$. Besides, significant enhancement in cycle life is also achieved for s-LNO||graphite full cells in F-262A (Figure 2C) compared to that in E-baseline electrolyte (Figure 2D). Since the baseline electrolyte has demonstrated capability to enable excellent reversibility of graphite anode by forming high Li$^+$ conductive SEI, the rapid capacity fading and low CE of full cell with E-baseline are mainly due to the continuous CEI formation on LNO cathode surface which induces the consumption of electrolyte and increase of the cell resistance (Figure 2E). As a result, capacity retention of only 18% is obtained after 100 cycles in E-baseline electrolyte, while ~94 % is achieved in F-262A (Figure 2F). The high CE of >99.9% for the full cell using F-262A in Figure 2F further verified the formation of robust SEI on graphite anode, which prevents the electrolyte consumption and Li-solvent co-intercalation during charging and discharging cycling.

**Stability Mechanism Induced by Cathode Electrolyte Interphase**

The morphologies of cycled LNO electrode were characterized by SEM. The LNO electrode recovered from the cell after 100 cycles in E-baseline shows significant thick and non-uniform CEI layer and byproducts due to severely parasitic surface reactions (Figures S12A and S12B). The enlarged views of s-LNO (Figures S12C and S12D) present large cracks and destroyed secondary structure due to volume expansion and shrinkage during lithiation and delithiation. On the contrary, a uniform CEI layer is formed on the surface of s-LNO after 100 cycles in F-262A, while the primary particles on the outer surface of s-LNO microparticles remain almost intact (Figure 3A). The elemental mapping shows the CEI layer covered on s-LNO is rich of C, O, F, B, C, and P elements (Figures 3B and 3C). The higher content of F element (15.5%) and B element (1.8%) on s-LNO surface (Figure 3B) in F-262A electrolytes than that in E-baseline electrolyte (10.3% for F, 0% for B; Figure S13) indicates that the formation of F-, B-rich interphase on cathode might be the key to hold the s-LNO integrity during lithiation and delithiation cycling.

Another advantage of the F-, B-rich interphase is to protect the cathode materials from being attacked by the byproducts generated due to the oxidation of electrolyte at high voltage, thereby preventing the dissolution of Ni and irreversible phase transition to rock-salts phase. As shown in Figure S14, the ex situ XRD patterns of lithiated s-LNO cathode show the structure change of s-LNO with long cycles in both electrolytes. The structure changes can be monitored by the XRD intensity ratio of (003) to (104) (denoted as I (003/104)). The (003) peak occurs from the diffraction of layered structure of R3 m, whereas the (104) peak appears from both the diffractions of layered and cubic rock-salt structures. The faster decreasing intensity ratio of I (003/104) for s-LNO in E-baseline electrolyte than that in F-262A electrolyte indicates severe phase transition induced by Ni dissolution or Li/Ni mixing during cycling in E-baseline, resulting in the transition of layered LNO to cubic-type of LNO and rock-salt phase due to the displacement of nickel ions into the lithium layer. However, the relatively constant I (003/104) for the s-LNO in F-262A electrolyte illustrates that few disordered rock salt phases are formed after 100 cycles. Thus, by forming the protective F- and B-rich interphase, the s-LNO in F-262A maintains good structural integrity with limited detrimental phase transformation.

The valence variations of Ni in the fully charged s-LNO electrode at different cycles were further studied using X-ray absorption spectroscopy (XAS). Figure 3D shows the ex situ X-ray absorption near edge structure spectra (XANES) of Ni K-edge for
LNO electrodes under full-charged state (4.4 V) at the 1st cycle and 150th cycle in F-262A and E-baseline electrolytes. Both edge position and white line intensity are sensitive indicators for valence state of Ni. The edge position of Ni$^{2+}$, Ni$^{3+}$, and Ni$^{4+}$ in XANES spectra increases from 8350.5 eV, 8352.5 eV, to 8355.5 eV respectively, while the white line intensity decreases in the order of: Ni$^{2+}$ > Ni$^{4+}$ > Ni$^{3+}$ (Figure 3E). As shown by the ex situ XANES in Figure 3D, the edge position of Ni K-edge shifts to higher energy region due to Ni$^{2+}$/Ni$^{4+}$ redox. However, the edge shifting of s-LNO electrode at 1st fully charged state in F-262A is higher than that in E-baseline electrolyte, indicating better utilization of Ni$^{3+}$/Ni$^{4+}$ redox due to the formation of stable and less-resistive CEI. After 150 cycles, while the edge positions are mostly the same for both electrolytes, the white line intensity of s-LNO electrode in E-baseline electrolyte is much higher than that in F-262A. This is presumably due to the accumulation of Ni$^{2+}$ compounds on the surface and presence of Ni$^{4+}$ as the main oxidized form in the bulk. Such combination makes the average Ni valence of s-LNO in E-baseline electrolyte close to that in F-262A case, in which...
there is less Ni\(^{2+}\) on the surface and more Ni\(^{3+}\) in the bulk, explaining the closeness in edge position and the difference in white line intensity in two cases.

The Fourier transformed extended X-ray absorption fine structure (EXAFS) of the Ni XAS (Figure S15A) also shows that the cycled LiNiO\(_2\) in F-262A has weaker first peak intensity than that in baseline electrolytes. Compared with the Ni valence and first ft-EXAFS peak intensity (Figure S15B), the EXAFS result suggests more Ni\(^{3+}\) in the Li-NiO\(_2\) cycled in F-262A, due to the Jahn-Teller distortion of Ni\(^{3+}\). But for the LiNiO\(_2\) cycled in baseline electrolyte, LiNiO\(_2\) has an excess of Ni\(^{3+}\) presumably because of surface degradation. The continual degradation of s-LNO induced by the unstable interphases further leads to irreversible phase transition of layered structure, which has already been confirmed by the ex situ XRD patterns of LNO. Thus, the ex situ XANES result further demonstrates the excellent electrochemical performance of s-LNO in F-262A due to good utilization of Ni\(^{3+}/Ni^{4+}\) redox and limited surface degradation.

Chemistry of Cathode Electrolyte Interphase and Solid Electrolyte Interphase

The compositions on the surface of the cycled s-LNO electrode in F-262A and E-baseline electrolytes were characterized using time of flight secondary ion mass spectrometry (ToF-SIMS) (Figures 4A–4C and S16). Figure 4A shows the edge surface of the crater sputtered by Ga\(^+\) ions. Compared with the cycled s-LNO recovered from E-baseline electrolyte, significantly high F and B signals are found within top surface layer (\(<\sim 50\) nm) in the F-262A electrolyte. However, the content of Li, O components on depth profile are relatively constant (Figures 4B and 4C), indicating a thin and robust F-, B-rich CEI layer is formed on the surface of s-LNO in F-262A, which is consistent with the SEM and corresponding EDS mapping results in Figure 3. More detailed morphology of the CEI thin layer was further characterized by high-resolution transmission electron microscopy (HRTEM). Obviously, the active particle of cycled s-LNO electrode in F-262A is uniformly covered by a thin layer of CEI (Figure 4D).

The magnified HRTEM image reveals that the thin layer has a thickness of \(\sim 3\) nm, and the inner parts of active particle remain intact with good crystallinity as pristine s-LNO. In contrast, the active particle cycled in E-baseline electrolyte presents large amount of non-crystal phases, indicating a severe structural degradation from layer R\(3\) m phase to the non-active rock-salt NiO phase (Figure 4E).\(^8\),\(^9\),\(^12\) Meanwhile, the outer surface of cycled LNO particle in F-262A presents only several layers (\(<\sim 1\) nm) of rock-salt NiO structure due to protection of F-, B-rich CEI layer (Figure 4F), while the LNO particle cycled in E-baseline shows a thick rock-salt structure caused by continues surface degradation (Figure 4G). These results, combined with ex situ XRD patterns of cycled s-LNO, provide clear evidence regarding the protective role of CEI derived from fluorinated solvents with LiDFOB on suppressing unwanted side reactions between the LNO cathode and electrolyte, thereby significantly increasing the electrochemical performance of cells.

CEI chemical compositions of s-LNO electrode after 100 cycles in E-baseline, F-262, and F-262A electrolytes were characterized using X-ray photoelectron spectroscopy (XPS) (Figures 5, S17–S19). Figure S18 compares the CEI elemental compositions of s-LNO in 0 s and 300 s sputtering depth. Different from E-baseline electrolyte, the CEI of s-LNO in F-262 contains a large amount of F content, but less C and O species, which might be due to the limited oxidation of fluorinated solvent. After adding 2 wt % LiDFOB into F-262, the concentration of B species on s-LNO increases to 2.6 atom %, while the C species further decreases from 52.9 to 42.2 atom %. In the meantime,
Figure 4. Characterization of the CEI Layer and Surface Degradation of Cycled LNO Particles

(A) Surface morphology of LNO particle after 100 cycles in F-262A for time of flight secondary ion mass spectrometry (ToF-SIMS) and the crater is sputtered by Ga⁺ ion beam.

(B) The corresponding lithium (Li), oxygen (O), fluorine (F), and boron (B) element distributions in the sputtered active particle.

(C) The depth profiles of ToF-SIMS analysis for F, Li, O, and B elements on the cycled active particles.

(D and E) High-resolution transmission electron microscopy (HRTEM) images of (D) LNO cathode particle after 150 cycles in F-262A electrolyte, covering with a thin CEI layer on surface (~3 nm); (E) LNO cathode particles after 70 cycles in E-baseline electrolyte, below images are enlarged views of particles.

(F and G) STEM images of (F) LNO cathode after 100 cycles in F-262A electrolyte with several layers of rock-salt NiO (~1 nm); (G) LNO cathode particles after 100 cycles in E-baseline with thick rock-salt NiO structure (>20 nm), below images are enlarged views of particles.
the O content increases from 6.3 to 10.2 atom % while the F content increases from 39.7 to 43.9 atom %. After sputtering etching about 300 s, similar results are obtained, and the P content from the LiPF_6 salts for all cases remains almost identical. These results indicate that the LiDFOB-tuned CEI is F- and B-rich, which originates from the participation of DFOB-ligand in the CEI formation upon initial cycling, as shown in the insets of Figures 1G and S8. The reduction of C, O species suggests the F-, B-rich CEI can protect the LNO by reducing continual side reactions with the electrolyte.

The high-resolution XPS spectra in Figure 5 offer deeper insight into the CEI compositions of s-LNO in F-262A. Generally, the CEI layer formed in F-262A consists of C=O, C=O, -(CO_3)_2, Li_2CO_3, and LiF and the decomposition products of LiDFOB. In C1s spectra with different sputtering time (Figure 5A), the ultra-high signals of C-C (284.5 eV, from carbon black or chemisorbed solvent), C-H (285.5 eV, from PVDF binder), and CF_x (~291 eV, from PVDF binder) indicate that the CEI in F-262A is much thinner than in E-baseline. In addition, the contents of C=O (286.5 eV) and C=O (287.7 eV) of CEI cycled in F-262A electrolyte are lower, while the components of Li_2CO_3 (290.4 eV) and -(CO_3)_2 (289.6 eV) are higher than that in E-baseline electrolyte (Figure S19A). The less amount of C=O and C=O suggests a limited solvent decomposition for s-LNO in F-262A electrolyte, while the higher -(CO_3)_2 and Li_2CO_3 are consistent with previous studies that the ODFB-ligand contributes to more lithium oxalates and ROCO_2Li in the CEI formation. In Figure 5B, the O1s data show the reduction of C=O content compared with the baseline electrolyte (Figure S19B), which is consistent with the C1s data. The continually parasitic reactions with the LNO, indicated by the increase of C=O, C=O contents, well explained the sharp increase of surface resistance in E-baseline (Figure S10).

In the F1s spectra of XPS (Figures 5C and S19C), the cycled s-LNO electrode in F-262A shows a significantly strong LiF signal (685 eV), which again confirms that...
the CEI contains a large amount of LiF from the fluorinated electrolyte. In addition, the presence of LiₓPOᵧF₂ signal might be from the absorbed LiPF₆ salts and the decomposition of LiPF₆ in both electrolytes. Although the bulk LiF is highly resistive to Li-ion conduction, the in-situ formed LiF-rich CEI layer did not reduce the ion transport kinetics, due to (1) its small thickness (Figure 4D) and close contacting with LNO, also (2) much lower energy barrier for Li⁺ surface diffusion (0.17 eV). As a result, a LiF-rich CEI is an ideal shield to protect the surface layer of delithiated LNO from the attacking of HF and other free radical groups in electrolytes, thereby reducing the loss of oxygen coordinates and suppressing the irreversible phase transformation of LNO into disordered NiO-like rock salt phase. Moreover, the large amount of Li-B-O (193.4 eV, Figure 5D) and B-O (292.2 eV) after the addition of LiDFOB, can also help inhibit the electrolyte decomposition and transition metal dissolution by regulating the CEI components with more robust oligomers. The line-scan analysis using electron energy loss spectroscopy (EELS) on the cycled LNO particle in F-262A indicates that the outer surface of LNO is rich in F, O, and C compounds (Figure S20). Combining the analysis of XPS, ToF-SIMS, and EELS, it can be concluded that the F- and B-CEI was formed on the cycled LNO in F-262A electrolyte. In all, the fluorinated solvents, together with LiDFOB, can be decomposed at the surface of LiNiO₂ to form a B- and F-rich protective CEI, which is the origin for the improved ionic diffusivity and superior electrochemical stability at high voltages.

Besides the protective F- and B-rich CEI formed on the surface of cathode, the stability of SEI on the anode sides is also essential to achieve good performance of cells by reducing unwanted side reactions and maintaining small interfacial resistance. The cycled Li metal anode maintains a dense and smooth surface with Li mounds of ~4 μm in diameter (Figure S21). The cycled graphite particles are covered by a uniform SEI layer with a thickness of ~4 nm (Figure S22), containing C, F, O, P, and B species (Figures S23–S25). The high content of F- and B-rich species effectively blocked the formation of Li dendrites during cycling. Figure S23 depicts the elemental concentration of the graphite SEI in F-262A and E-baseline electrolytes. Similar to the cathode side, the graphite surface manifests a F- and B-rich SEI after cycled in F-262A, as evidenced by the significantly high signals of LiF (685 eV), Li-B-O (193.4 eV), and B-O (292.2 eV). Although the signals of C-C and C-H (~285 eV) for both electrolytes appear roughly identical, the high content of C-O (286.5 eV) and C=O (532.5 eV) of graphite SEI in E-baseline suggests that the formed SEI is highly related to the reduction of EC solvent. Considering the excellent reversibility and cycling stability of graphite in F-262A (Figure S11), we can safely conclude that the F-, B-rich SEI has the similar effect as the EC-based SEI to achieve stable Li⁺ intercalation and deintercalation within the layered structure of graphite by preventing the Li-solvent co-intercalation.

Compared with the s-LNO cells in E-baseline electrolyte, the significant improvement in the performance of the s-LNO||Li or s-LNO||graphite cells in F-262A electrolyte can be attributed to at least three aspects. First, the formation of a dense, electronically insulated LiF-rich nanolayer stabilized the surface of s-LNO cathode, Li metal, and graphite anode, preventing the continual reactions with electrolytes. Second, the decomposition of LiDFOB in electrolyte further enhanced the robustness of SEI and CEI layers by introducing borates or its derivative products, which are able to complex more Li⁺ because of the donation of the lone electron pairs on oxygen and boron atoms. Third, the addition of LiDFOB improves the overall stability of LiPF₆-based electrolytes by generating lithium tetrafluoroaluminate (LiPF₄C₂O₄) at elevated temperature. The excellent electrochemical
performance of s-LNO by pairing with Li metal anode or graphite anode in F-262A electrolyte demonstrated its potential application in high-energy LIBs or LMBs.

Conclusions

Overall, this work demonstrates that the cobalt-free cathode LiNiO$_2$ can be stably charged and discharged at a high charge cut-off voltage of 4.4 V in F-262A (1.0 M LiPF$_6$ + 2 wt % LiDFOB dissolved in FEC: FEMC: HFE [2:6:2 by weight]) electrolytes. An LiNiO$_2$ cathode in F-262A electrolyte is able to deliver a discharge capacity of 216 mA h g$^{-1}$ ( 820 W h kg$^{-1}$) along with excellent capacity retention of more than 80% after 400 cycles at 0.5 C current rates, which is the best cycling performance ever reported for an LNO cathode. More importantly, the LNO||graphite full cell in F-262A retains ~92.5 % of their capacity after 100 cycles at 0.5 C, which significantly outperforms the performance of LNO||graphite full cells in conventional EC-based electrolyte (18% retention). The remarkably enhanced cycling performance can be ascribed to two aspects: (1) the in-situ-formed F-, B-rich CEI layer protects the LNO cathode from continuous reactions with electrolyte and suppress the structural transformation from layered to disordered rock-salt (NiO) phase; (2) the robust and conductive F-, B-rich SEI layer generated on the Li and graphite anode surfaces prevents deep corrosion of anode and improves the stability of the battery. Although the CE of Li metal is still not sufficient, the key findings of this work provide a new avenue to enable high energy and low cost cathodes for developing high-energy LMBs or LIBs as the next generation energy storage systems.

EXPERIMENTAL PROCEDURES

Full details of all experiments and materials are provided in Supplemental Experimental Procedures.

SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at https://doi.org/10.1016/j.joule.2019.08.004.

ACKNOWLEDGMENTS

This work was supported by the Energy Efficiency and Renewable Energy Office of the U.S. Department of Energy through the Battery500 Consortium Seedling project under contract DE-EE0008202. T.D. acknowledges support from the Engie Chunk Edwards Memorial Fellowship. The authors gratefully acknowledge the support of the Maryland NanoCenter and its AIMLab. The work done at Brookhaven National Laboratory was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Vehicle Technology Office of the U.S. Department of Energy through the Advanced Battery Materials Research (BMR) Program, including Battery500 Consortium under contract DE-SC0012704. This research used beamlines 8-ID of the National Synchrotron Light Source II, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Brookhaven National Laboratory under contract no. DE-SC0012704. Partial electron microscopy work was used from resources of the Center for Functional Nanomaterials, which is a US DOE Office of Science Facility, at Brookhaven National Laboratory under contract number DE-SC0012704.

AUTHOR CONTRIBUTIONS

T.D. designed the experiments, analyzed the data, and wrote the paper. X.F., L.C., J.C., S.H., L.C., S.L., X.Z., E.H., D.S., and X.-Q.Y. conducted the experiments. X.J.
conducted the calculations. C.W. and X.F. conceived and supervised the project. All authors contributed to interpretation of the results.

**DECLARATION OF INTERESTS**

The authors declare no competing interests.

Received: March 4, 2019
Revised: June 12, 2019
Accepted: August 6, 2019
Published: September 4, 2019

**REFERENCES**


22. Mohan, P., and Kalaighan, G.P. (2013). Structure and electrochemical performance of LiFe0.5Ni0.5O2 (0.00 ≤ x ≤ 0.20) cathode materials for rechargeable lithium-ion batteries. J. Electroceram. 31, 210–217.


46. Xu, M., Zhou, L., Hao, L., Xing, L., Li, W., and Lucht, B.L. (2011). Investigation and application of lithium difluoro(oxalato)borate (LiDFOB) as additive to improve the thermal stability of electrolyte for lithium-ion batteries. J. Power Sources 196, 6794–6801.