At the turn of the 21st century, scientists were working hard to develop a lithium-ion (Li-ion) cathode technology that would change the way people viewed energy storage. A newly developed material had the potential to revolutionize the transportation industry, especially if the material was paired with a high capacity anode material such as silicon (Si). The resulting full cell was proposed to truly enable the electric vehicle, driving down battery costs to less than $200 kWh⁻¹ while supplying double the drive range of state-of-the-art Li-ion technology. The material, formulated as xLi2MnO3 (1−x)LiMO2 or Li[Li1−xMx]O2 (M = Ni, Mn, Co), is known as the lithium–manganese-rich (LMR) oxide. The beauty of the LMR material lies in the activation process undergone at >4.4 V versus Li/Li⁺ during initial charging, resulting in an unprecedentedly high operating voltage and capacities of ~260 mAh g⁻¹.[1–7] Despite the potential for massive technological impact, worldwide research has struggled to enable the LMR material. Early work impressively laid the foundation for widespread efforts targeting this material and its signature drawback: the gradual lowering of cell operating voltage over cycling life as the originally layered crystal structure transforms to a spinel phase, accompanied by oxygen evolution during activation of the Li2MnO3 component and transition metal dissolution.

The pristine LMR oxide structure has been described as either a composite of O3 oxygen stacked layered trigonal LiMO2 (R-3m space group) and monoclinic Li2MnO3 (C2/m space group) phases or as a solid solution.[2,8–11] The degradative structural changes of the LMR material during cycling can generally be understood as (1) an initial activation with concurrent oxygen loss from the originally layered lattice followed by the parallel effects of (2) transition metal (TM) cations filling Li sites upon discharge with simultaneous dissolution of TM ions (most significantly Mn⁷⁺) and (3) reduction of TM cations to lower valence states.[11–13] The result of these structural changes is the loss of Li intercalation sites and the formation of a spinel phase (Fd-3m space group) with a significantly lower operating voltage compared to that of the initial layered material, with the changes becoming more severe with cycling. In an attempt to alleviate oxygen evolution and mitigate phase transformation in the LMR material, a myriad of efforts have focused on surface modification,[12,13] ion substitution or doping,[14–17] and morphological control of particles and grains,[18–20] all with limited success in enhancing long term cell energy retention.

In this work, we focus our efforts on the electrode–electrolyte interactions known to accelerate phase change in the LMR system. Leveraging the understandings of LMR interfacial behavior built by decades of research, we employ a unique electrolyte composition to form a cathode–electrolyte interface (CEI) that allows for the improved long-term capacity and energy retention of the LMR cathode. Our novel CEI is formed in situ through the oxidative decomposition of a room temperature ionic liquid (RTIL) electrolyte doped with a sacrificial fluorinated salt additive. We demonstrate a LMR system capable of 1000 high capacity cycles with minimal energy losses, shedding light on the importance of the LMR CEI and elucidating the complex interplay between the electrolyte and the atomic scale transformations of an unstable crystal lattice.

We start by identifying and addressing the detrimental side reactions known to occur at high voltages between conventional, carbonate-based electrolytes and the LMR surface. While commonly neglected in order to focus attention on bulk material phenomena, these side reactions play a pivotal role in both the short- and long-term performance of the LMR material.
Most notoriously, the formation of H⁺ via the oxidative decom-
position of alkyl carbonate electrolytes leads to exacerbation of
phase change by promoting the disproportionation of TM
valence states within the LMR crystal lattice through the charge
compensation mechanism required for the reaction of 2Mn⁴⁺
to Mn²⁺ and Mn⁶⁺ (a.k.a. Hunter’s redox mechanism).²¹⁻²⁵
In other words, oxidation of Mn in the LMR material occurs
in parallel to partial TM dissolution and phase change due
to interactions with the carbonate electrolyte. It was hypo-
thesized that utilizing an electrolyte that forms more favorable
decomposition products, ideally avoiding parasitic acid attack,
would provide for a higher degree of reversibility in the electro-
chemical cycling of the layered LMR structure. Replacing
the conventional electrolyte with an imide-based RTIL induces
impressive cycling performance, as shown in Figure 1. The
electrochemical performance of LMR half-cells containing the
material, (0.25)Li₂MnO₃(0.75)LiNi₀.₅Co₀.₅Mn₀.₅O₂,
were compared using a conventional, carbonate-based, elec-
tryte, a 50/50 vol. mixture of ethylene carbonate/diethyl carbonate
(EC/DEC) with a 1 M LiPF₆ salt, and a high performance RTIL
electrolyte, N-methyl-N-propylpyrrolidinum/bis(2-fluorosulfonyl)
imidide (PYR₁₃/FSI⁻) with a 1.2 M LiFSI salt. As expected,
the LMR cycled in a carbonate-based electrolyte degrades steadily.
This degradation manifests itself in capacity loss (Figure 1c,
gray profile) and evolution of the discharge voltage trace, with
the high-voltage plateau displaying marked fade within just
100 cycles (Figure 1a). Contrastingly, the LMR half-cell cycled in
PYR₁₃/FSI⁻ (1.2 M LiFSI) electrolyte maintains high capacities
throughout 1000 cycles (75% capacity retention over 980 cycles
at 1C rate, red profile in Figure 1c), with significant capacity
delivered above 3.0 V versus Li/Li⁺ (55% capacity delivered
above 3.0 V on the 500th discharge, Figure 1b). The relatively
high operating voltage of this half-cell suggests more reten-
tion of the layered crystal phase, as the manganese-oxide spi-
nel’s redox chemistry occurs below 3.0 V versus Li/Li⁺ (Mn⁶⁺
reduction at ≈2.8 V).¹⁷ Also of note are the low charge-transfer
resistances found throughout cycling in a FSI-based RTIL, sug-
gesting a thin, robust, and favorable CEI (Figure S1, Supporting
Information). The poor interfacial behavior in a conventional
electrolyte is further exemplified by the destruction of LMR
particles after 1000 cycles, shown in Figure S1 (Supporting
Information), as compared to those cycled in a FSI-based RTIL
which maintain their spherical morphology; this is believed to
be a consequence of H⁺ attack by EC/DEC breakdown products,
lattice breakdown, and vacancy condensation upon delithiation.

In order to confirm and further study the magnitude of
phase change occurring when employing a PYR₁₃/FSI⁻
(1.2 M LiFSI) electrolyte, we turn to X-ray diffraction (XRD)
and Raman spectroscopy (Figure S2, Supporting Information).
The shown XRD and Raman characterization suggests that a FSI-
based RTIL electrolyte is capable of lessening the severity and
pace of LMR phase change during early cycling while providing
marked stabilization, at least at the particle surface, of the LMR
lattice over long-term cycling.

Despite inducing the best long-term performance demon-
strated, to-date, in an LMR half-cell, the PYR₁₃/FSI⁻ (1.2 M
LiFSI) electrolyte alone does not enable truly viable levels of
energy retention. Previous reports suggest that F⁺ doping of the
LMR particle surface⁴,¹³⁻¹⁷ and utilization of fluorinated
electrolyte cosolvents such as fluoroethylene carbonate (FEC)
boost energy retention and rate performance.²⁵⁻²⁸ For example,
F⁺-doping has been shown to reduce the deintercalation bar-
rier of Li⁺ from the LMR lattice by weakening the Li–O bond,
allowing for better high rate performance and more efficient
activation.¹⁶ Most significantly, the presence of F⁻ alters the
material’s electronic environment and prohibits the mobility
of oxygen ions, leading to a decrease in activation of Li₂MnO₃,
which in turn can suppress phase transition as large amounts
of interstitial vacancies serve as a driving force for TM migra-
tion.⁴,⁹,¹⁷,²⁹⁻³² Stronger M–F bonds also mitigate TM migra-
tion.¹⁷ Motivated by Kang and Thackeray’s early work in
forming fluorinated passivation layers on the LMR surface
prior to electrode fabrication,³³,³⁴ we began searching for elec-
trolyte additives capable of forming similar CEIs in situ via
oxidative decomposition at high voltages. While fluorinated
linear carbonates such as FEC were not successful in hindering
voltage fade in our LMR-RTIL system, as shown in Figure S3
(Supporting Information), we found surprising success in
mitigating energy fade and increasing average cycling voltage
throughout the material’s cycle life by adding the well-known
LiPF₆ salt. Adding small concentrations (0.1 M and higher) of
LiPF₆ to the PYR₁₃/FSI⁻ (1.2 M LiFSI) electrolyte drasti-
cally improves (0.25)Li₂MnO₃(0.75)LiNi₀.₅Co₀.₅Mn₀.₅O₂ half-
cell energy retention (Figure 1f, >70% energy retention in
950 cycles at C/2 rate vs <50% energy retention in unmodified
RTIL). To our knowledge, this is the first time that the voltage
profile shape of the LMR material has been maintained for
1000 cycles with >60% discharge capacity provided at voltages
above 3.0 V versus Li/Li⁺ upon the 1000th discharge (Figure Id).
Figure S4 (Supporting Information) provides a direct compar-
ison between the 200th cycle voltage profiles of LMR electrodes
cycled in various electrolytes under ANL’s “Voltage Fade Testing
Protocol” (v1).¹⁵ and Figure S5 (Supporting Information)
provides a direct comparison to state-of-the-art efforts using an
upper cutoff voltage of 4.5 V. Surprisingly, the rate LMR mate-
rials’ shown degradation in energy tracks very closely with the
rate of the material’s capacity degradation, while previous study
shows that lattice instabilities lead to poor energy retention that
remains hidden if observing capacity alone. These results high-
light the energy retention in the m-RTIL. Further evidence of
increased performance in the m-RTIL electrolyte is provided by
the rate study in Figure S6 (Supporting Information). The
degradation in rate performance in a conventional electrolyte is
attributed to the formation of a poor, resistive CEI and the loss
of Li⁺ vacancies and blocking of Li⁺ diffusion channels via the
formation of spinel regions within the LMR composite.³⁶
After demonstrating the ability of our electrolyte composi-
tion to enable long-term energy retention in LMR half-cells, it
is of utmost importance to develop an accurate physical depic-
tion of this interface. Figures S7 and S8 (Supporting Informa-
tion) present the X-ray photoelectron spectroscopy study of
the CEI’s chemical make-up after cycling in each electrolyte. Based
on this interfacial characterization, we conclude that we induce
favorable LMR/m-RTIL interfacial behavior through the in situ
formation of a heavily fluorinated interface, leveraging the elec-
trochemical properties of a high-voltage RTIL-based electrolyte
and the chemical interplay between the LMR lattice and the
decomposition products of a sacrificial salt additive.²⁵⁻²⁸ It
Figure 1. Voltage profile evolution of LMR half-cells cycled in a) EC/DEC (1 M LiPF$_6$), b) PYR$_{13}$FSI (1.2 M LiFSI), and d) PYR$_{13}$FSI (1.2 M LiFSI, 0.1 M LiPF$_6$). Specific capacities of LMR half-cells c) in both PYR$_{13}$FSI (1.2 M LiFSI) and EC/DEC (1 M LiPF$_6$) electrolytes, and specific capacities and specific energies of LMR half-cells cycled in f) PYR$_{13}$FSI (1.2 M LiFSI, 0.1 M LiPF$_6$) electrolyte over 1000 cycles. e) Molecular constituents of the PYR$_{13}$FSI (1.2 M LiFSI).
is proposed that the formation of a fluorine-rich layer on the LMR surface when cycled in m-RTIL contributes to the stabilization of TM ions within the LMR particle, at least at the particle surface. During transformation to the spinel-phase, the average Mn oxidation state shifts toward 3⁺, inducing strain and lattice distortions due to the Jahn–Teller effect (Mn³⁺ is Jahn–Teller active), and this further contributes to lattice instability and layered-to-spinel phase change.[7,10,37] As displayed in Figures S9 and S10 (Supporting Information), which highlight an X-ray absorption spectroscopy (XAS) study of the LMR materials, the electronic structure of manganese has been stabilized by using the m-RTIL electrolyte. Analysis of both total electron yield (TEY) and fluorescence yield (FY) modes reveal significant stabilization at both surface depths (several nm) and deeper particle depths (up to 50 nm), respectively. As the presence of highly electronegative fluorine has been shown to enable more efficient activation,[16] inhibit the mobility and loss of oxygen ions,[4,9,17,29–32] and suppress TM migration through strong M–F interactions,[17] it is likely that the highly fluorinated CEI formed in m-RTIL mitigates phase change, or at least allows for lattice stabilization at the particle surface, and disproportionation/lowering of the Mn oxidation state.

The most effective means of confirming the proposed interfacial mechanism behind the observed LMR energy retention is direct observation via high resolution microscopy. To investigate the physical implications of the CEI formed in situ between the LMR and m-RTIL, high-resolution transmission electron microscopy (HR-TEM) was performed on electrode samples after undergoing 100 cycles in both conventional and m-RTIL electrolytes, as shown in Figure 2. HR-TEM of a pristine (uncycled) LMR particle is shown in Figure S11 (Supporting Information). In both cases, a clearly defined defect layer is evident at the surfaces of the LMR particles. This layer is distinguished by obvious cation reordering, characteristic of...
the surface reconstruction layer (SRL) formed on LMR particles during early cycling in conventional electrolytes.\[9,10,17,28,32,38,39\] The SRLs exhibit reticulate patterns which are suggestive of the topotactic characteristics of the (111) planes of a defect-spinel phase.\[40–42\] This phenomenon (SRL formation) occurs as TM ions with reduced oxygen coordination become destabilized due to a reduced migration energy barrier and migrate into the Li interlayers,\[9,28,39\] suggesting similar activation mechanisms in both conventional and \(m\)-RTIL electrolytes. Differences in SRL thickness formed in these electrolytes are ascribed to reduced activation (extraction of oxygen) in the \(m\)-RTIL electrolyte as well as continuous surface corrosion by acidic species formed in the carbonate electrolyte.\[28,36,43–45\] Figure 2c,d presents HR-TEM images of particle cores after 100 cycles in each electrolyte. Of high importance is the relative disorder found in the LMR particles cycled in a conventional electrolyte; a highly irregular bulk structure is visible, likely caused by continuous attack by electrolyte decomposition byproducts and particle breakage, along with evidence of seemingly amorphous domains. As formation of spinel intergrowths dominates the bulk structure, severe strains and lattice distortion (due to the Jahn–Teller effect induced by the presence of Mn\(^{3+}\) in the spinel crystal) leads to the formation of amorphous-like regions with indistinct fast Fourier transform (FFT).\[17,32,36,40\] After 100 cycles in conventional electrolyte, the spinel/amorphous regions dominate both the bulk and particle edge\[17,32,36,40\] whereas the LMR particles cycled in \(m\)-RTIL show no distortion, likely suggesting higher retention of their layered structure, except at the particle edge. TEM imaging substantiates our previous characterization, finding activation and formation of a SRL during early cycling while showing evidence of long-term stability in the LMR particles.

Combining this work and our recent study of the compatibility between PYR\(_{13}\)FSI electrolytes and the polycaronitride (PAN) coated silicon anode architecture,\[46–48\] we demonstrate the dual-functionality of the \(m\)-RTIL electrolyte in enabling both high performance Si and LMR electrodes by building Si-cPAN/\(m\)-RTIL/LMR lithium-ion batteries (LIBs) capable of reversible, high-energy cycling for an exceptionally long cycling life (see the Experimental Section for details on full-cell fabrication). Figure 3 presents the first-ever academic demonstrations of the long-term, high-energy cycling of Li-ion full cells containing a high performance Si anode and an LMR cathode. Figure 3a presents an Si-cPAN/LMR full-cell, coin-type configuration, containing \(>20\) mg of LMR active material, representing the performance of the Si/\(m\)-RTIL/LMR system with commercially viable mass loadings. This cell displays exceptional energy retention during early cycling 50th, demonstrating that the early-cycling half-cell energy retention behavior depicted in Figure 1 propagates into exceptional full-cell performance. To supplement the demonstration of a nonflammable 5 mAh coin-type Si/LMR full cell, we combine our LMR/\(m\)-RTIL system with the previously developed, ultra-stable nanowire Si anode system (SiNW-cPAN).\[48\] This full cell, shown in Figure 3c, maintains 90.84% capacity over more than 750 cycles at the 1C rate, leveraging both the high rate performance and stability of the SiNW-cPAN anode system and the stability of the LMR/\(m\)-RTIL cathode system, and retains greater than 84% capacity over 1000 cycles at various rates. This cycling performance is well within the Department of Energy Vehicle Technology Office’s (DOE VTO) LIB performance requirements (>80% retention@1000 cycles with 80% DoD).\[49\] Validated by unprecedented cycling data and a thorough combination of materials and system-level characterization, our approach to developing a stable high energy LMR-electrolyte system represents important progress toward a safer, higher-performance secondary LIB.
Experimental Section

Electrode and Electrolyte Preparation: (0.25)Li2MnO3 (0.75) Li0.875Ni0.3Co0.15Mn0.55O2 active material powder was synthesized and supplied by Dr. Sung-Jin Cho from North Carolina A&T State University. (0.25)Li2MnO3 (0.75) Li0.875Ni0.3Co0.15Mn0.55O2 and Si-cPAN electrodes were fabricated according to the procedures described in ref. [46] and [49], respectively. Ionic liquid electrolytes were purchased from Boulden Ionics Corporation (USA) and scanned for halide impurities according to the procedure in ref. [50]. Impurities (F-, Cl-, Br-, SO4-) were quantified using a Dionex ICS-1100 chromatograph, calibrated for sensitivities as low as 1 ppm. Ion chromatography was performed on all ionic liquids as the working electrode and lithium foil as the counter electrode. The separator was a glass microfiber disk (Whatman GF/F) and the shell was a stainless steel CR2032 coin cell (Pred Materials). The electrolyte systems utilized were EC/DEC (1 m LiPF6) and PYR13FSI (1.2 m LiFSI), with additives LiPF6 (Sigma-Aldrich), fluorooctylene carbonate (Sigma-Aldrich), and others. A constant current testing scheme was used to cycle our half-cells. No voltage holds were utilized during cycling (lithiation or delithiation), preventing the currents applied during cycling (lithiated) and charged (delithiated) at room temperature with various cycling currents (where a C/10 rate is equivalent to \( \approx \frac{m}{(2.5 \cdot 4.65 \text{ V})} \)). All half-cells were carried out using an Arbin BT2000 battery test station. All half-cells were cycled and uncycled, using a FIB’s 30 keV Ga dual beam system) equipped with a mobile air-lock chamber was used for TEM sample preparation. TEM analysis was performed with a FEI Tecnai F20 operated at 200 keV. TEM samples were prepared by section electrodes, both cycled and uncycled, using a FIB’s 30 keV Ga+ ion beam.

Full-Cell Fabrication: Full cells were fabricated from preconditioned electrodes selected based on deliverable capacity.\(^{16,17}\) Calculated from the active material mass, Si-cPAN anodes were fabricated and matched with LMR cathodes such that the total anode capacity was \( \approx 130\% \) of that of the cathode capacity. Both electrodes were then preconditioned: the anodes were allowed to run for 10 charge–discharge cycles in a half-cell configuration and were stopped after full lithiation, while the cathodes were allowed to run for 3 charge–discharge cycles in a half-cell configuration and were stopped after full delithiation. The half-cells were then disassembled and the electrodes were used to fabricate 2032 coin-cell (Al-clad cathode cup) type full cells. This method of preconditioning allows for full control of the amount of lithium in the system. A constant current constant voltage testing scheme was used to cycle our full cells. The full cells were discharged and charged at room temperature with various cycling currents between 1.5 and 4.55 V (vs Li/Li\(^+\)), with an activation cycle (first full cycle) carried out between 2.5 and 4.65 V (vs Li/Li\(^+\)) at a C/20 rate. Electrochemical measurements of full cells were all normalized with respect to total mass of electroactive material in both cathode and anode electrodes.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was supported by a grant from the National Science Foundation (NSF, DMR-1268462). This work was also supported by the U.S. Department of Energy, Office of Science under Award No. DE-SC0013852. The work at NREL was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U.S. Department of Energy under Contract No. DE-AC-36-08GO28308 under the Applied Batteries Research (ABR) Program. The synchrotron soft XAS of this research was carried out at the Stanford Synchrotron Radiation Lightsource, a Directorate of SLAC National Accelerator Laboratory and an Office of Science User facility operated for the U.S. Department of Energy Office of Science by Stanford University. Use of the Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515. C.T. and D.N. would like to thank J. S. Lee for his assistance at beamline 8-2 of SSRRL. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the Department of Energy.

Received: August 25, 2016
Revised: December 1, 2016
Published online: