High Voltage Operation of Ni-Rich NMC Cathodes Enabled by Stable Electrode/Electrolyte Interphases

Wengao Zhao, Jianming Zheng,* Lianfeng Zou, Haiping Jia, Bin Liu, Hui Wang, Mark H. Engelhard, Chongmin Wang, Wu Xu, Yong Yang,* and Ji-Guang Zhang*

The lithium (Li) metal battery (LMB) is one of the most promising candidates for next-generation energy storage systems. However, it is still a significant challenge to operate LMBs with high voltage cathodes under high rate conditions. In this work, an LMB using a nickel-rich layered cathode of LiNi0.76Mn0.14Co0.10O2 (NMC76) and an optimized electrolyte [0.6 M lithium bis(trifluoromethanesulfonyl)imide + 0.4 M lithium bis(oxalato)borate + 0.05 M LiPF6 dissolved in ethylene carbonate and ethyl methyl carbonate (4:6 by weight)] demonstrates excellent stability at a high charge cutoff voltage of 4.5 V. Remarkably, these Li||NMC76 cells can deliver a high discharge capacity of >220 mAh g−1 (846 Wh kg−1) and retain more than 80% capacity after 1000 cycles at high charge/discharge current rates of 2C/2C (1C = 200 mA g−1). This excellent electrochemical performance can be attributed to the greatly enhanced structural/interfacial stability of both the Ni-rich NMC76 cathode material and the Li metal anode using the optimized electrolyte.

1. Introduction

With the growing demand for high-energy-density batteries for electric vehicles and large-scale energy storage systems, lithium (Li) metal has been regarded as an ideal negative electrode for energy storage systems because it has an extremely high theoretical specific capacity (3860 mAh g−1), and the lowest negative electrochemical potential (~3.040 V vs the standard hydrogen electrode).[1] Rechargeable Li metal batteries (LMBs), regarded as one of the most promising candidates for next-generation high-energy-density energy storage systems, have been widely investigated since the 1970s.[2] In fact, the Li metal anode (LMA) is indispensable in the research and development of Li–sulfur, Li–air, and solid-state Li batteries.[3,4] Recently, significant progress has been made on high efficiency operation of LMAs, including the modification of electrolyte chemistry,[4,5] selective Li deposition,[4b] application of polymer or solid-state electrolytes,[7] and novel configurations of LMA protection.[4c,8]

Recently, a high concentration electrolyte [4 M lithium bis(fluorosulfonyl)imide (LiFSI) in 1,2-dimethoxyethane (DME)] has been reported to enable high rate cycling of Li||Cu cell with a high Coulombic efficiency (CE) of up to 99.1% without dendrite growth.[6a] This was attributed to the preferential decomposition of LiFSI salt that forms a LiF-rich solid electrolyte interphase (SEI) layer, which is beneficial to stabilize the Li metal anode/electrolyte interface, uniform growth of Li films, and suppress the further corrosion of Li metal. In contrast, DME solvent will be decomposed first in a low concentration LiFSI/DME electrolyte and forms a less stable SEI layer dominated by polymeric components. However, ether-based electrolytes are less suitable with the high voltage (>4 V) cathode required for high-energy-density batteries due to their low oxidation potentials. In this regard, carbonate-based electrolytes are a better choice for high-voltage, high-energy-density LMBs. Our recent work on carbonated-based electrolytes revealed that a dual-salt electrolyte of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and lithium bis(oxalato)borate (LiBOB) in a carbonate solvent mixture with 0.05 M LiPF6 additive can greatly improve the stability of Li metal and suppress Li dendrite formation even at high current densities.[9] However, the energy density of this LMB system is still relatively low owing to the use of LiNi0.4Mn0.4Co0.2O2 (NMC442), which exhibits a limited discharge capacity of ~160 mAh h−1 at C/10 when charged to 4.3 V, corresponding to a limited energy density of ~610 Wh kg−1. In order to achieve a higher energy density in LMBs, the most effective strategy is to develop cathode...
materials of high discharge capacity and high operating voltage, so as to maximally match with a high capacity LMA. Therefore, a stable cathode with higher energy density is still needed to further improve the energy density of LMBs.

In this work, we report for the first time that LMBs based on an LMA and a Ni-rich layered cathode, LiNi0.76Mn0.14Co0.10O2 (NMC76) is able to deliver a much higher energy density of 846 W h kg\(^{-1}\) at 0.1C (1C = 200 mA g\(^{-1}\)) along with an excellent cycling performance in the voltage range of 2.7-4.5 V using an electrolyte consisting of 0.6 m LiTFSI + 0.4 m LiBOB + 0.05 m LiPF\(_6\) dissolved in a solution of ethylene carbonate and ethyl methyl carbonate (EC:EMC, 4:6 by weight), called E-optimized for simplicity. With this electrolyte, Li\|NMC76 cells can retain more than 80% of their capacity after 1000 cycles at 2C rate for both charge and discharge, which is much better than that obtained using the conventional electrolyte of 1 m LiPF\(_6\)/EC–EMC (called E-baseline) (20.8% retention after 300 cycles). To the best of our knowledge, the high energy density and excellent cycling performance demonstrated in this work are among the best ever reported for LMBs.

Electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and scanning transmission electron microscopy (STEM) were adopted to explore the structural/interfacial degradation of the LMA and Ni-rich NMC76 cathode to gain deep insight into the fundamental mechanism for the enhanced performance.

2. Results and Discussion

In order to investigate the effects of the electrolytes on the electrochemical performance of Li\|NMC76 cells, the charge/discharge behaviors of E-optimized and E-baseline were investigated in detail. The SEM images and X-ray diffraction pattern indicate that the synthesized NMC76 demonstrates the uniform size (10 µm) and good layered structure in Figures S1 and S2 (Supporting Information). The electrochemical performances of Li\|NMC76 cells using the two different electrolytes are presented in Figure 1. Three initial formation cycles at 0.1C (1C = 200 mA g\(^{-1}\)) were conducted on the cells prior to the subsequent cycling under higher charge/discharge current densities (0.33C). Comparisons of initial charge/discharge voltage profiles and CE during cycling are shown in Figure S3 (Supporting Information). The cell based on E-optimized exhibits a higher capacity (Figure 1A) and a higher CE (Figure S1, Supporting Information) than that using E-baseline during the formation (0.1C) and following cycles (0.33C), indicating the fast electrode redox reaction kinetics in E-optimized. The Ni-rich NMC76 is able to deliver a high discharge capacity of 220 mA h g\(^{-1}\) in E-optimized, corresponding to an energy density (integrating the area under the voltage-capacity profile shown in Figure 1) of 846 W h kg\(^{-1}\), which is higher than the 213 mA h g\(^{-1}\) (corresponding to an energy density of 769 W h kg\(^{-1}\)) that is obtained in E-baseline. Figure 1B indicates that the cell using E-optimized exhibits a capacity retention of 90.12% at the 200th cycle, which is much higher than the 85.05% obtained for the E-baseline cell. Figure 1C,D shows the charge/discharge profile evolutions for Li\|NMC76 during long-term cycling. The cell using E-baseline shows obvious capacity fade and continuous increase of cell overpotential during cycling, suggesting the formation of more resistive SEI and cathode electrolyte interphase (CEI) layer on the LMA and the cathode, respectively. In comparison, the cell using E-optimized exhibits much less increase in cell overpotential (Figure 1D), indicating that the electrode/electrolyte interphase layer formed in E-optimized is much more conductive for Li\(^+\) ion transport than that formed in E-baseline.\(^4\) The evolution of midpoint voltages of Li\|NMC76 cells using different electrolytes is compared in Figure 1E.

Figure 1. Electrochemical behavior of Li\|NMC76 cells using two different carbonate-based electrolytes at C/3 current rate after three formation cycles at 0.1C rate. Comparison of A) cycling performance and B) capacity retention in the two electrolytes; voltage profiles of LMBs using C) E-baseline and D) E-optimized; comparison of E) midpoint voltage evolution and F) energy density between E-baseline- and E-optimized-based LMBs.
Apparently, the midpoint voltage in the LMB using E-optimized is very stable for 200 cycles. Due to the smaller voltage fade and the better protection for Li metal and/or the cathode, the Li||NMC76 cell using E-optimized exhibits a much better retention in energy density (752 W h kg\(^{-1}\) at 200th cycle) than that using E-baseline (626 W h kg\(^{-1}\) at 200th cycle) (Figure 1F).

The cycling performance of the Li||NMC76 cells using these two electrolytes is also investigated at an elevated temperature of 60 °C at 0.5C rate, and the results are illustrated in Figure S4 (Supporting Information). The Li||NMC76 cell using E-baseline exhibits a drastic drop of discharge capacity after about 40 cycles, accompanied by a sudden drop in CE. In addition to the poor stability of E-baseline toward Li metal as reported previously,[9] the aggressive side reaction between Ni-rich NMC76 material (especially the highly reactive Ni\(^{4+}\)) and E-baseline at the high temperature is another critical reason for the accelerated capacity decay. In contrast, the Li||NMC76 cell using E-optimized shows limited capacity degradation and very stable CE during cycling. Overall, the Li||NMC76 cells using E-optimized exhibit significantly superior electrochemical performance in terms of discharge capacity, capacity retention, voltage stability, and high-temperature performance in comparison with E-baseline cells at 0.33C rate.

In order to further confirm the improved compatibility of the Ni-rich NMC76 cathode with the optimized dual-salt electrolyte, the long-term cycling stability of Li||NMC76 cells was also tested at high charge/discharge current rates of 1C/1C, 2C/2C, and 5C/5C as shown in Figure 2A–C. It is clearly seen that LMBs using E-baseline undergo an abrupt capacity drop after 150 cycles, 80 cycles, and 15 cycles at 1C, 2C, and 5C, respectively. Although the degradation of Ni-rich NMC76 may also contribute to the capacity fade during cycling, the accelerated capacity fading at high charge current densities could be primarily ascribed to the quick corrosion of the LMA and the consequential increase in the overall cell resistance.[9] In comparison, the Li||NMC76 cells using E-optimized show greatly enhanced cycling stability.

![Figure 2](image.png)

**Figure 2.** Comparison of the cycling performance of Li||NMC76 cells using two electrolytes under high charging/discharging current rates of A) 1C/1C, B) 2C/2C, and C) 5C/5C. D) Rate performance at the same charge rate of 0.2C and gradually increased discharge rate from 0.1C to 10C, and then switched back to 0.1C. E) Long-term cycling performance and CE of Li||NMC76 cell using E-optimized over 1000 cycles at 2C/2C charging/discharging current rate.
even at a high current rate of 5C (1000 mA g\(^{-1}\)) for both charge and discharge. These cells still deliver high reversible capacities of 180.4, 159.3, and 129.2 mA h g\(^{-1}\) at 1C, 2C, and 5C after 300 cycles, corresponding to capacity retentions of 93.32%, 91.79%, and 91.37%, respectively, as shown in Figure 2A–C. To further understand the rate capability of the LMBs using these two electrolytes, the charging/discharging performance at other C rates was also evaluated. The Li||NMC76 cell using E-optimized exhibits discharging capability superior to that using E-baseline even at 10C rate, as shown in Figure 2D. The reversible capacity remains stable after high current rate cycling and can recover to the original capacity when the current density returns to 0.1C, substantiating the excellent structural integrity of NMC76 in E-optimized for rapid Li\(^+\) ion extraction/insertion. The long-term stability of Li||NMC76 cells using E-optimized was further investigated at both high charge and discharge currents of 2C/2C within the voltage window of 2.7–4.5 V. Surprisingly, the Li||NMC76 cell using E-optimized can retain 80.61% capacity over 1000 cycles and exhibits a stable CE of more than 99.5% (Figure 2E). To the best of our knowledge, this cycling performance is the best ever reported for LMBs based on a high energy density Ni-rich NMC cathode at a high current rate and a high charge cutoff voltage. As shown in Table S1 (Supporting Information), the capacity retention of NMC76 and E-optimized is much higher than other reported results.\(^{[9]}\) We also investigated the cycling performance of NMC622 and NMC811 using E-optimized and the results are pretty stable as well. The Li||NMC622 cell delivers the capacity retention of 86.9% after 500 cycles under 2C/2C charge/discharge rates, while the Li||NMC811 cell exhibits the capacity retention of 83.5% after 500 cycles at the same test condition (Figure S5, Supporting Information). Therefore, the Li||NMC batteries combining the high energy density Ni-rich NMC cathode, and the highly stable electrolyte E-optimized will be a promising energy storage system.

In order to gain insight into the degradation mechanism of the Li||NMC76 cells using the Ni-rich NMC cathode and different electrolytes, the morphologies of LMA used in these cells were characterized using SEM, as shown in Figure 3. As a reference, the surface and cross-sectional SEM images of a fresh Li metal disk with a thickness of 450 µm before being crimped into a coin cell are shown in Figure S6 (Supporting Information). After 200 cycles, remarkable differences are observed on the cycled LMA surface. The Li metal harvested from the cell using E-baseline shows significant cracking on the surface film (Figure 3A) and severe corrosion of the bulk Li anode (Figure 3C). The large crack and thick corrosion layer (250 µm) in the LMA can be attributed to the loose SEI layer on the Li metal surface, which leads to continuous corrosion of the LMA by the baseline electrolyte (1 M LiPF\(_6\)/EC–EMC) during cycling.\(^{[6]}\) The porous SEI layer formed on the Li metal surface leads to more “dead”/isolated Li metal formed on the surface of the Li anode after cycling (see Figure 3B). As a consequence, the overall cell impedance (Figure 3G–I) increases quickly due to the consumption of electrolyte and the accumulation of poorly conducting by-products, which hinders the fast transport of Li\(^+\) ions and leads to capacity fading of Li||NMC76 cells.

In contrast, the Li metal retrieved from Li||NMC76 cells using E-optimized retains much more of the original morphology of the LMA. The majority of the bulk LMA is still intact, exhibiting no obvious cracks on the surface (Figure 3D) and a corrosion depth of only about 60 µm, as shown in the cross-sectional SEM image (Figure 3F). Remarkably, the surface of the LMA is composed of fibrous Li and some thin SEI-layer “skirt” left after Li metal stripping (Figure 3E). As reported in our previous work,\(^{[9]}\) formation of fibrous type Li deposits, which look more dendritic, is dictated by the presence of LiBOB salt. It is the fibrous Li deposits that allow the fast Li striping/deposition process, enabling the fast charging/discharging of Li||NMC cells. Despite the fibrous morphology, the SEI layer produced in the E-optimized is more dense (Figure 3D) and highly conductive, which shows limited effect on the electrode polarization (Figures 1D and 3H,I), and thereby could prevent the accumulation of isolated/“dead” Li during each deposition/stripping cycle. Moreover, the poly-carbonates formed in the SEI layer are flexible, can efficiently cover the Li metal surface, reduce the side reactions, hold the surface layer tightly, and adhere to the bulk Li anode, thus preventing the detachment of the SEI layer from the bulk Li metal. Therefore, the utilization of Li metal initiates at the surface and slowly propagates inward (Figure 3F).\(^{[9]}\) To further confirm the enhanced Li metal stability in E-optimized, the Li metal from a cell cycled 1000 times at 2C current rate was also harvested and observed by SEM (Figure S7, Supporting Information). There is only a thin corrosion layer (50 µm) on the cycled Li anode, as shown in the cross-sectional SEM image (Figure S5C, Supporting Information) after 1000 cycles. Figure S7A (Supporting Information) indicates that most of the bulk LMA is still maintained well with only a few slight cracks in the SEI layer. It is interesting that the cycled LMA surface is covered by a compact SEI layer formed by interconnected Li nodules (Figure S7B, Supporting Information). This dense surface-film structure could effectively prevent further corrosion of the LMA in the subsequent cycles.

The results shown in Figure 3 and Figure S7 (Supporting Information) could well explain why Li||NMC76 cells using E-optimized demonstrate better cycling capability and more stable midpoint voltage, which is because a robust and conductive SEI layer can greatly enhance the charge transfer reactions. The improved performance is also consistent with the variation of charge transfer resistance (\(R_{ct}\)) shown in Figure 3G–I. More detailed comparisons of EIS spectra of the full progression from pristine to 200th cycle between E-baseline and E-optimized are shown in Figure S8 (Supporting Information). The Li||NMC76 cell using E-baseline exhibits a relatively small surface film resistance (\(R_{sf}\)) value of \(\sim 10\ \Omega\) but exhibits considerable increase of charger transfer resistance (\(R_{ct}\)) during cycling (increasing from \(\sim 25\ \Omega\) at the 10th cycle to 700 \(\Omega\) at the 200th cycle). The quick increase of the \(R_{ct}\) in the EIS spectra of the Li||NMC76 cell using E-baseline may be ascribed to the accumulation of less conductive surface film formed on the electrode/electrolyte interface. In contrast, the cell using E-optimized exhibits a large impedance of \(R_{ct}\) at the initial cycle (Figure 3G) as the result of the dense surface film generated from the decomposition of E-optimized, especially the LiBOB salts. With the increasing of cycling numbers, the surface layer becomes more ionic conductive, which is more beneficial for the Li\(^+\) ions diffuse through the SEI/CEI layer, so the \(R_{ct}\) in Figure 3H,I becomes smaller compared with Figure 3G.
the drastic increase of $R_{ct}$ for the cell using E-baseline, the cell using E-optimized demonstrates only a slightly increased $R_{ct}$ due to the formation of conductive and stable SEI and CEI layers at the electrode/electrolyte interfaces. Therefore, using E-optimized in an LMB can enable longer cycling and enhanced rate capability. In order to further confirm the degradation mechanism of the Li||Ni-rich NMC cell, three-electrode cells were employed to monitor the EIS evolutions during cycling process. An additional electrode of lithiated Li$_4$Ti$_5$O$_{12}$ (LTO) was placed between Li and Ni-rich NMC cathode as the reference electrode, to monitor the anode, cathode, and full cell impedance evolution of the Li||Ni-rich NMC cell using E-optimized and E-baseline. Figure S9 (Supporting Information) indicates that the degradation of Li||LTO||Ni-rich NMC cell using E-optimized mainly comes from the anode, but the degradation mainly comes from the cathode while using E-baseline, which further confirms the generation of a highly benign CEI layer on the interface of electrolyte/NMC using E-optimized.

The E-optimized has been proved to effectively protect the LMA from deep corrosion, which is in good agreement with the results reported earlier by this group. However, this is not sufficient to tell whether the E-optimized can form a high quality CEI layer to improve the stability of a Ni-rich NMC cathode such as NMC76 investigated in this work. Therefore, XPS was carried out to investigate the chemical components of the CEI layer generated on the cycled Ni-rich NMC cathode. As presented in Figure 4A–C, the XPS results reveal that the CEI layer formed in E-baseline includes the components of C=O, C–O, C–F$_2$, a large quantity of C–C, and LiF as well as decomposition products of LiPF$_6$. In C 1s XPS (Figure 4A), the other strong peaks of C=C (284.8 eV), C–O (286.5 eV), ROCO$_2$Li (287.7 eV), and ROCO$_2$Li (289.9 eV) could be ascribed to the decomposition products of baseline electrolyte, while CH (285.5 eV) and CF$_2$ ($\approx$291 eV) are due to the presence of polyvinylidene fluoride binder in the cathode. In Figure 4B, the O 1s data show much C–O (533.7 eV) and some indication...
of C=O (532.5 eV) formation, which is consistent with the C 1s data. This indicates that much solvent is decomposed, leading to the formation of C–O and C≡O compounds. In the F 1s XPS (Figure 4C), the cycled cathode in E-baseline shows a strong LiF signal (685 eV), indicating serious corrosion by the trace amount of hydrofluoric acid (HF) in LiPF₆ electrolyte. The Li₅PO₄F₂ signal also confirms the decomposition of LiPF₆. The presence of highly resistive LiF on the cathode surface can lead to sluggish Li⁺ transport kinetics and consequent capacity fading. [11] In addition, the HF could be considered a predator for attacking the surface of the layered cathode,[12] which may aggravate Li⁺/Ni²⁺ cation mixing as well as the formation of disordered rock-salt phase (NiO-like) because of insufficient coordinating oxygen due to the corrosion reactions. However, in the surface layer on cathode cycled with E-optimized (Figure 4D–G), lower contents of C≡C (Figure 4D), C≡O (Figure 4E), and LiF components (Figure 4F) were formed on the cycled NMC76 cathode. Instead, more carbonates (≈289.9–290.4 eV) and polycarbonates (≈292.4 eV) [poly(CO₃)] are identified in the CEI layer wrapping the surface of the NMC cathode. The reported work suggests that the appropriate LiPF₆ additive helps induce the formation of polycarbonate species.[13] One possibility is that the trace amount of strong Lewis acids PF₅ and POF₃ derived from the additive level of LiPF₆ induces the polymerization of EC solvents.[9] The CEI layer enriched with polycarbonate constituents could effectively mitigate the attack by the electrolyte, and may still allow prompt transport of Li⁺ ions during repeated Li ion deintercalation/intercalation processes. Polycarbonate can be considered as the solid polymer electrolyte (SPE) in the CEI layer. This is strongly correlated with previous studies on SPEs where the following theory is commonly accepted: the local segmental motion of the polymers can contribute significantly to the lithium ion transport, depicted by lithium ions hopping within cages formed by the polymer chains.[14] Moreover, as an electronic-insulating but ionic-conductive compound, the appropriate content of Li₂CO₃ in CEI layer can obviously improve the interface stability by enhancing the kinetics of Li⁺ and electron transport at the electrode/electrolyte interface as well as the high-temperature tolerability of the cell system, which are consistent with the EIS data in Figure 3G–I and high temperature stability in Figure S4 (Supporting Information).[15] In addition, the large amounts of B≡O (292.2, 192.2 eV) and Li–B≡O (193.4 eV) species are detected, as shown in Figure 4E,G, indicating that a B-containing CEI layer formed on the surface of the cathode, which helps inhibit electrolyte decomposition and transition metal dissolution.[16] For this reason, the robust CEI formed in E-optimized could significantly reduce the loss of oxygen coordinates, suppressing the formation of disordered NiO-like rock-salt phase on the NMC surface. Therefore, E-optimized is also beneficial for maintaining the integrity of the cathode structure, by preventing electrolyte attack and avoiding the unwanted phase transformation, which allows sustainable operation of LMBs using high-energy-density, Ni-rich NMC76 even at a high charge cutoff voltage.

To further explore the structural changes in the NMC76 cathode material, the cathodes were harvested from Li||NMC76 cells, and cross-sectional TEM specimens were prepared using a focused ion beam (FIB) lift-out technique (Figure S10, Supporting Information). STEM high-angle annular dark field (HAADF) imaging reveals that the surface structure of the NMC76 particles was modified after 200 cycles. Energy dispersive spectroscopy (EDS) maps are shown in Figures S11 and S12 (Supporting Information). Unlike those from the NMC76 cathode cycled in E-baseline, a sulfur-containing condensed layer was formed on the surface of the NMC76 cathode cycled in E-optimized, indicating the polymerization of LiTFSI to stabilize the cathode structure. Before cycling, pristine NMC76 particles exhibit a Li⁺/Ni²⁺ cation mixing layer less than 1 nm thick, which is commonly observed in Ni-rich NMC cathodes.
because of the similar radii of Li\(^{+}\) (0.76 Å) and Ni\(^{2+}\) (0.69 Å) (Figure 5A,B).\(^{[17]}\) After 200 cycles in E-baseline, a severely disordered layer and rock-salt phase (NiO) were observed on the surface of NMC particles (Figure 5C,D), indicating the poor surface structural stability of Ni-rich NMC when cycled in the baseline LiPF\(_6\)-based electrolyte. The visual STEM observation coincides well with the XPS results regarding the formation of a significant quantity of rock-salt phase in the baseline electrolyte. This again could be attributed to corrosion by the acidic species in the LiPF\(_6\)-based electrolyte, which greatly reduce the oxygen coordinated with the transition metal ions, especially at the particle surfaces. In this case, the migration of transition metal ions from the transition metal layers to the neighboring Li layers via the adjoining tetrahedral sites becomes energetically favorable. Formation of the cation mixing phase is definitely detrimental to the long-term cycling performance of Li||NMC76 cells because it blocks the smooth mobility of Li\(^{+}\) ions in Li layers. In addition, formation of the reconstructed surface layer featuring rock-salt phase is also the reason for the voltage/energy decay in the Ni-rich NMC cathode reaction. The Li\(^{+}\)/Ni\(^{2+}\) disorder and prevents the formation of the disordered NiO-like rock-salt phase. The reduced formation of rock-salt phase could also well explain the better stabilized voltage profiles of Ni-rich NMC76 in E-optimized. On the basis of the above discussions, we can safely conclude that E-optimized not only can improve the stability of Li metal associated with the formation of a robust and conductive SEI layer, but also can maintain the structural stability of the Ni-rich NMC cathode due to a dense CEI formed on the cathode surface. XRD pattern also confirms the structure stability of the cycled electrode (Figure S13, Supporting Information). After 200 cycles under C/3 current rate, both the cycled electrodes in E-optimize and E-baseline do not exhibit obvious phase transformation peaks in XRD patterns. The electrode cycled in E-optimized shows lower cation mixing (I(003)/I(104) = 1.06) compared with electrode cycled in E-baseline (I = 0.89), indicating the better structure stability of cycled electrode in E-optimized, which is consistent with the electrochemical performance (Figure 1) and STEM result (Figure 5). The result further confirms that the robust CEI layer can better protect the cathode from the attack by acidic species, especially HF, thus suppressing the phase transformation.
3. Conclusions

In this work, we demonstrate that a Ni-rich NMC cathode, NMC76, is highly stable at a high charge voltage of 4.5 V when used with an optimized electrolyte \((0.6 \, \text{m LiTFSI} + 0.4 \, \text{m LiBOB} + 0.05 \, \text{m LiPF}_6 \text{ dissolved in EC:EMC (4:6 by weight)})\). An LMB ([Li][NMC76]) using this electrolyte is able to deliver a discharge capacity of \(>220 \, \text{mAh g}^{-1} \) (846 W h kg\(^{-1}\)) along with excellent capacity retention of more than 90% after 300 cycles at 1C/1C, 2C/2C, and 5C/5C current rates, which significantly outperforms cells using conventional LiPF\(_6\)-based electrolyte. More importantly, [Li][NMC76] cells using E-optimized retain more than 80% of their capacity after 1000 cycles at a high rate of 2C charge/2C discharge, which is the best cycling performance ever reported for an LMB using Ni-rich NMC. The remarkably enhanced cycling performance can be ascribed to two aspects: (1) the enhanced CEI layer can protect the Ni-rich NMC cathode from electrolyte corrosion and suppress the structural transformation from layered to disordered rock-salt (NiO) phase; (2) the robust and conductive SEI layer generated on the Li surface prevents deep corrosion of Li metal and improves the stability of the LMA. The key findings of this work provide a new avenue for developing highly stable LMBs with high energy density, high charge cutoff voltage (4.5 V), and high power capability required for the next generation energy storage systems.

4. Experimental Section

Materials: The NMC76 cathode material was prepared by calcining precursor of \(\text{Ni}_{0.76}\text{Mn}_{0.14}\text{Co}_{0.10} \text{(OH)}_2\) and a stoichiometric amount of \(\text{LiOH} \cdot \text{H}_2\text{O}\) at 500 °C for 10 h, followed by further calcination at 750 °C in \(\text{O}_2\) atmosphere for 20 h. The Li anode used in the present study was Li chips (99.9%) with 15.6 mm diameter and 0.45 mm thick form MTI Corporation. The E-baseline electrolyte was composed of 1 m LiPF\(_6\) in EC:EMC (4:6 by weight). E-optimized electrolyte consisted of 0.6 m LiTFSI + 0.4 m LiBOB + 0.05 m LiPF\(_6\) dissolved in EC:EMC (4:6 by weight) solution. All electrolyte components were ordered from BASF Battery Materials.

Electrochemical Measurements: The electrochemical properties of the electrodes were evaluated using CR2032-type coin cells with Al-clad positive cases from MTI. The LiNi\(_{0.8}\text{Mn}_{0.14}\text{Co}_{0.10}\) electrodes with an areal mass loading of \(\approx 4 \, \text{mg cm}^{-2}\) were punched into 1.27 cm\(^2\) disks. Coin cells were assembled in an argon (Ar) filled glove box (MBraun), each having an NMC76-based composite cathode, a Li chip as anode, a piece of Celgard 2500 separator, and the as-prepared electrolyte (100 μL). Electrochemical tests were conducted galvanostatically at various current rates in the voltage range of 2.7–4.5 V on Land-CT2001A battery cyclers in temperature chambers controlled at 30 or 60 °C (for elevated temperature tests). A current density rate of 1C (i.e., charge or discharge in 1 h) was set to 200 mA g\(^{-1}\). The corresponding current density values for the 0.1C, 0.2C, 0.3C, 0.5C, 1C, 2C, 5C, and 10C rates were therefore 20, 40, 66, 100, 200, 400, 1000, and 2000 mA g\(^{-1}\), respectively. Formation cycles were initially conducted for three cycles at 0.1C for both charge and discharge, followed by further cycling at various higher C rates. To explore the mechanism of the cycling failure, the cycled cells were disassembled to harvest the NMC76 cathodes and the Li anodes. The EIS analysis was performed on a Solartron 1255B frequency response analyzer controlled by ZPlot software with a 30 mV perturbation at 4.3 V in the frequency range of 10\(^{-3}\)–10\(^{-2}\) Hz.

Characterization: Cycled Ni-rich NMC cathodes and Li anodes were harvested from the disassembled cells for characterization by SEM, EDS, XRD, and XPS analyses. Before the measurements, the electrodes were immersed in dimethyl carbonate (DMC) for 24 h and then rinsed with fresh DMC three times before drying under vacuum. To avoid side reactions or electrode contamination with ambient oxygen and moisture, Li metal samples were transported from the glove box to the SEM and XPS instruments in a hermetically sealed container protected by Ar gas. SEM images and the corresponding EDS analysis of the Li electrodes for both the surface and the cross-sections were obtained on an FEI Helios FIB-SEM operated at 5.0 kV. The XPS testing was carried out using a Physical Electronics Quantera scanning X-ray microprobe, which was outfitted with a monochromatic Al X-ray source (1486.7 eV) for excitation. The sample was transferred to the transmission electron microscope under Ar atmosphere, and the turbo pump of the microscope was precooled to full speed. Microstructures were investigated with a probe-aberration-corrected FEI Titan STEM operated at 300 kV. The STEM-HAADF detector collects all the incoherently scattered electrons.

Supporting Information

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

Acknowledgements

This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies, Advanced Battery Materials Research (BMR) program of the U.S. Department of Energy (DOE) under contract no. DE-AC02-05CH11231, subcontract no. 18769. W.Z. would like to acknowledge the financial support from the China Scholarship Council (CSC) and Y.Y. acknowledges the Natural Science Foundation of China (Nos. 21233004, 21621091). The microscopic observations and spectroscopic analysis were conducted in the William R. Wiley Environmental Molecular Sciences Laboratory (EMSL), a national scientific user facility sponsored by the DOE’s Office of Biological and Environmental Research and located at the Pacific Northwest National Laboratory (PNNL). PNNL is operated by Battelle for the DOE under Contract DE-AC05-76RL01830.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

cathodes, dual electrolyte, high voltage, interphases, Ni-rich NMC

Received: January 26, 2018
Revised: February 25, 2018
Published online: March 30, 2018
