

Enhanced Electrochemical Performance of Ni-Rich Layered Cathode Materials by using LiPF₆ as a Cathode Additive

Sheng S. Zhang,*^[a] Xiulin Fan,^[b] and Chunsheng Wang^[b]

Residual Li compounds are inevitably present in the form of Li_2O , LiOH, and Li_2CO_3 on the surface of layered cathode materials, which not only causes slurry gelation in the cathode-coating process but also degrades liquid electrolyte in the batteries. Owing to their strong alkaline nature, the residual Li compounds can react with acidic LiPF₆ to form Li_3PO_4 and LiF, two of the main components of robust solid electrolyte interphases. By demonstrating $LiNi_{0.80}Co_{0.10}Mn_{0.10}O_2$ (NCM811) as an example in this work, we simply dissolved a small amount of

1. Introduction

Ni-rich lithium nickel cobalt manganese oxides (NCM) are one class of the most promising cathode materials for high energy density Li-ion batteries because of their high capacity and low cost.^[1] The high energy density of these materials are achieved by charging the cathode to high potentials (4.2 V or higher vs. Li/Li⁺). Unfortunately, charging to high potentials not only triggers oxygen evolution of the NCM materials but also causes oxidative decomposition of the electrolyte solvents. Oxygen evolution at high potentials has been identified to be a major source for many known problems with the layered cathode materials, such as irreversible phase transition from hexagonal through cubic to rock salt structure,^[2] mechanical fracture of the secondary particle structure,^[3] and electrolyte degradation as a result of parasitic reactions between the released oxygen and electrolyte solvents, which are accompanied by impedance increase and volumetric swelling of the battery.^[4] To overcome these problems, a number of strategies have been studied to enhance the structural and chemical stability, including cationic doping for stabilizing NCM lattice structure,^[5] surface coating for protecting NCM particles from reacting with the electrolyte components,^[6] synthesizing concentration-gradient^[7] or coreshell^[8] materials with high Ni content core, and using electrolyte^[9] or cathode^[10a, b] additives for chemically trapping the released oxygen.

Another issue with the layered cathode materials is the presence of Li residual compounds on the particle surface, and

[a] Dr. S. S. Zhang Electrochemistry Branch, FCDD-RLS-DC U.S. Army Research Laboratory Adelphi, MD 20783-1138, USA E-mail: shengshui.zhang.civ@mail.mil shengshui@gmail.com
[b] Dr. X. Fan, Prof. C. Wang Department of Chemical and Biomolecular Engineering University of Maryland College Park, MD 20742, USA LiPF₆ into the cathode-coating slurry, finding that as the amount of LiPF₆ is controlled in the 0.5–1.0 wt% range versus the mass of NCM811, the LiPF₆ additive not only improves the cycling stability but also enhances rate capability of the Li/NCM811 cells. The former is because the strongly alkaline residual Li compounds react with acidic LiPF₆ to form stable Li₃PO₄ and LiF. The latter is attributed to a reduction in the surface layer resistance on the cathode, as suggested by the results of surface chemistry and impedance analyses.

the amount of Li residual compounds is increased with increasing of the Ni content.^[11] The Li residual compounds are mainly originated from the excess LiOH that was added in the synthesis process to suppress cationic mixing and compensate for the loss of Li⁺ ions at the synthesis temperature.^[12] Affected by the moisture and CO₂ concentration in storage environment, the Li residual compounds are present in the form of a Li₂O, LiOH, and Li₂CO₃ mixture.^[6c,13] With strong alkalinity, the Li residual compounds have been identified to be the source for many parasitic reactions of the electrolyte components. It was reported that the Li residual compounds not only cause slurry gelation in the coating process of NCM cathodes,^[14] but also trigger volumetric swelling of the Li-ion batteries.^[1c,6b, 15] The former is because the Li residual compounds react with poly (vinylidene fluoride) (PVDF) binder, generating water and > C=C < double bonds,^[16] wherein water is a non-solvent of PVDF polymer and >C=C < double bonds are capable of polymerizing to crosslink PVDF polymeric chains. The latter is partially attributed to gaseous CO2, which is formed either through catalytic decomposition of the carbonate solvents catalyzed by the alkaline Li residual compounds^[17] or through reactions between acidic LiPF₆ salt and alkaline Li₂CO₃ residue.^[6b] Therefore, removing the Li residual compounds from the cathode particle surface is of particular importance for achieving desirable performance of the layered cathode materials. In this regard, a simple washing process in water, followed by a heating treatment, was shown to be very effective in removing the Li residual compounds, which consequently enhanced the cycling stability and rate capability of the layered cathode materials.^[15,18] Alternatively, it was reported that the Li residual compounds could be converted to weak alkaline Li₃PO₄ by treating the layered cathode particles with limited amount of acidic $H_3PO_4^{[19]}$ or $(NH_4)_2HPO_4^{[6a,20]}$ in an alcohol solution. Although the resulting Li₃PO₄ was found not to coat on the particle surface, the conversion was shown to dramatically reduce the rate of electrolyte degradation.^[20]



It was found that in most cases, surface $\mbox{coating}^{[6b,g,21]}$ and removal of Li residual compounds^[6a,19-20] not only improve the cycling stability but also enhance the rate capability of layered cathode materials. Without exceptions, however, all these treatments require additional precipitating (or washing) and heating processes, leading to an increase in the cost of battery manufacture. In order to simplify the treatment process, in this work we simply dissolved small amount of LiPF₆ into the normal cathode-coating slurry, finding that after the slurry milling and cathode drying (heating) processes, the strongly alkaline Li residual compounds can be completely reacted to form much stable Li₃PO₄ and LiF. By selecting LiNi_{0.80}Co_{0.10}Mn_{0.10}O₂ (NCM811) as an example, we demonstrated that the addition of controlled amount of LiPF₆ in the slurry-making process not only improved cycling stability but also enhanced rate capability of the Li/NCM811 cells. In this paper, the mechanism for removal of the Li residual compounds by LiPF₆ and the effect of LiPF₆ additive on the cycling performance of Li/ NCM811 cells will be discussed.

2. Results and Discussion

Li residual compounds on the layered cathode materials are present in forms of Li₂O, LiOH and Li₂CO₃, all of which have strong alkalinity. Based on the acidic nature of LiPF₆ and the fact that LiPF₆ is highly soluble in NMP, the Li residual compounds can be readily removed in the cathode slurry-coating process by the following "solution-solid" two-phase reactions:

$$\text{LiPF}_6 + 4\text{Li}_2\text{O} \rightarrow \text{Li}_3\text{PO}_4 + 6\text{LiF}$$
(1)

 $LiPF_6 + 8LiOH \rightarrow Li_3PO_4 + 6LiF + 4H_2O$ (2)

$$LiPF_6 + 4Li_2CO_3 \rightarrow Li_3PO_4 + 6LiF + 4CO_2$$
(3)

The above reactions can occur not only in the slurry-milling process but also in the cathode-drying (heating) process. The formed H_2O and CO_2 are removed together with NMP solvent in the drying process, whereas the Li_3PO_4 and LiF can be either remained alone or constituted into a protective surface layer. It is known that both Li_3PO_4 and LiF are favorable components for the robust solid electrolyte interphases.

X-ray powder diffraction (XRD) patterns of the pristine and 1.0% LiPF₆-added NCM811 powders are shown in Figure 1, from which no difference can be noticed. This means that the LiPF₆ addition neither changes the crystalline structure of NCM811 nor introduces significant amount of impurities. Like the Li residual compounds, the amounts of Li₃PO₄ and LiF formed in the LiPF₆ addition are too small to be detected by the XRD technique. Figure 2 compares scanning electron microscopy (SEM) images of the pristine and 1.0% LiPF₆-added NCM811 powders in different magnifications. In general, the NCM materials are present in the form of spherical agglomerates as the secondary structure, which are assembled by numerous primary particles with average sizes less than 500 nm. In both samples, the spherical agglomerates of NCM811 were partially

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Figure 1. XRD patterns of NCM811 powder. a) Pristine and b) 1.0 $\% \ \text{LiPF}_{6^-}$ added.



Figure 2. SEM images of NCM811 powder at different magnifications. a, b) Pristine and c, d) 1.0% LiPF₆-added.

broken by the milling process (Figure 2a and Figure 2c), and there are small amount of tiny particles on the surface of granular particles (Figure 2b and Figure 2d). More careful comparison of Figure 2b and Figure 2d reveals that the surface of the LiPF₆-added NCM811 is much rougher than that of the pristine NCM811 as a result of the reactions between NCM811 and LiPF₆.

Figure 3 exhibits energy-dispersive X-ray spectroscopy (EDS) maps of each element in a selected zone of the 1.0% LiPF₆-added NCM811 sample. In particular, the F element is mainly centralized in the NCM particle (Figure 3-F), whereas the P element is distributed not only in the NCM particle but also in the surrounding matrix of the NCM particles (Figure 3-P). This difference reveals that LiF is superior to Li_3PO_4 in adhering to the surface of NCM particles, and that the resultant Li_3PO_4 -LiF mixture is LiF-rich, being a favorite feature of the robust solid electrolyte interphases.^[22]





Figure 3. EDS elemental maps of 1.0% LiPF₆-added NCM811.



Figure 4. Effect of charging cutoff voltage on the cycling stability of Li/ NCM811 cells with pristine NCM811.

Electrochemical properties of the pristine NCM811 are first evaluated by changing the charging cutoff voltage. As indicated in Figure 4, cycling stability of the Li/NCM811 cells is greatly affected by the charging cutoff voltage. When the charging voltage was cut off at 4.1 V, the cell can be cycled stably. However, the cycling stability progressively decreases as the cutoff voltage is raised to 4.2 V or higher. Being in consistence with the previous report,^[23] the observed decrease in the cycling stability with increasing the charging cutoff voltage can be attributed to the oxygen evolution of NCM811 material at high potentials, which consequently results in irreversible phase transition of the NCM811 material and chemical oxidation of the electrolyte solvents.

Effect of LiPF₆ addition on NCM cathode materials was evaluated in terms of the cycling stability (or called capacity retention) and rate capability of Li/NCM811 cells. Figure 5a and Figure 5b compare voltage profiles of the initial two cycles of Li/NCM811 cells with the pristine and LiPF₆-added NCM811, respectively. In the initial two cycles, the cell was charged to 4.5 V in order to form a NiO cubic protective layer on the surface of NCM particles.^[24] It is observed from Figure 5a and

Figure 5b that there are no much differences in the specific capacity and coulombic efficiency except for the charging voltage, showing that the cells with LiPF₆-added NCM811 have slightly larger polarization (see inset in Figure 5a and Figure 5b). This is probably because the formed Li₃PO₄-LiF mixture adds an additional Li⁺ ion conduction barrier between the NCM particles and liquid electrolyte.

Figure 5c and Figure 5d show the effect of LiPF₆ addition on the cycling performance of Li/NCM811 cells. When being cycled between 3.0 V and 4.3 V (Figure 5c), the 0.5 % LiPF₆-added cathode showed higher capacity and better capacity retention while other two with 1.0% and 2.0% LiPF₆ addition, respectively, remained nearly same capacity and capacity retention as compared with the pristine NCM811. When being cycled between 3.0 V and 4.5 V (Figure 5d), all four cathodes started with similar capacity $(175 \sim 177 \text{ mAh g}^{-1} \text{ in the third cycle at C/}$ 3). However, the LiPF₆-added cathodes showed different degree improvements in the capacity retention. In particular, at the 125th cycle the 1.0% LiPF₆-added cathode retained a 147 mAh g^{-1} capacity (equaling to 83% of the third cycle capacity) vs. 122 mAhg⁻¹ (69% of the third cycle capacity) of the pristine cathode. The above improvement in the cycling stability can be attributed to the reduced reactivity of the surface by the conversion from the highly reactive Li residual compounds to much stable Li₃PO₄ and LiF although the conversion is not expected to suppress oxygen evolution and resulting phase transition of the NCM811 material. More significant improvement of the capacity retention in 3.0~4.5 V range (Figure 5d) than in 3.0~4.3 V range (Figure 5c) suggests that the LiPF₆-addition is beneficial to reducing the surface reactions.

More significant improvement by the LiPF₆ addition can be observed from the rate capability (Figure 6). It can be seen in Figure 6a that the pristine and LiPF₆-added cathodes delivered similar capacities when being cycled at the rates lower than 3 C. When the rate was increased to 5 C or higher, however, the 0.5% and 1.0% LiPF₆-added cathodes showed much higher capacities, while the 2.0% LiPF₆-added cathode exhibited slightly inferior capacity as compared with the pristine NCM811. For example, at 10 C, the retained capacity was determined to be 36, 71, 81, and 33 mAhg⁻¹, respectively, for the pristine, 0.5%, 1.0%, and 2.0% LiPF₆-added cathodes. In particular, discharging voltage profiles of the cell with 1.0% LiPF₆-added NCM811 at various rates are illustrated in Figure 6b, showing that the discharging voltage gradually declines with an increase in the discharging rate as a result of the increased ohmic polarization.

In order to understand the improvement of LiPF₆ addition on the rate capability, AC-impedances of the Li/NCM811 cells at the charged state (4.3 V) and discharged state (2.8 V), respectively, were analyzed and the results are shown in Figure 7. Typically, the impedance of Li metal cells is composed of bulk resistance (R_b), surface layer resistance (R_{sl}), and charge-transfer resistance (R_{ct}), of which the R_b and R_{ct} are generally reflected by two semicircles in the impedance spectrum.^[25] While changing vastly with the cell's state-of-charge, the R_{ct} at the discharged state is indefinitely large so that its relative semi-



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Figure 5. Cycling performance of Li/NCM811 cells with pristine and LiPF₆-added NCM811, respectively. a) Voltage profile of the first cycle, b) voltage profile of the second cycle, c) cycling performance in 3.0–4.3 V, and d) cycling performance in 3.0–4.5 V.

circle cannot be formed (Figure 7b). Without exception, all LiPF₆-added cells have much smaller R_s, which largely contributed to their smaller overall impedance as compared with the pristine cell. However, the 2.0% LiPF₆-added cell has exceptionally large R_{ct} so that its overall impedance is higher than that of the pristine cell. The above results explain not only the enhanced rate capability by the 0.5% and 1.0% LiPF₆-added cathodes but also the inferior rate capability of the 2.0% LiPF₆-added cathode, as indicated in Figure 6a.

3. Conclusions

Li residual compounds are inevitably present on the particle surface of layered cathode materials, which triggers parasitic reactions with the electrolyte components and consequently results in performance degradation of the batteries. Based on their strong alkaline nature, the Li residual compounds can be easily removed by reacting with acidic LiPF₆ in the cathode slurry-coating process. More importantly, both Li₃PO₄ and LiF formed by the reactions of Li residual compounds and LiPF₆ are known to be favorable components for the robust solid electrolyte interphases. Selecting NCM811 as an example, we demonstrate that by dissolving small amount of LiPF₆ into the cathode-coating slurry (alternatively, LiPF₆ can be added in the form of liquid electrolyte), Li residual compounds can be reacted to produce much stable Li_3PO_4 and LiF. It is shown that the LiPF₆ addition not only improves cycling stability but also enhances rate capability of the Li/NCM811 cells. The results of this work indicate that our proposed LiPF₆ addition would be a simple and practically feasible means for improving the electrochemical performance of layered cathode materials.

Experimental Section

NCM811 powder was purchased from MTI Corporation (Richmond, CA) and baked at 150°C in a vacuum oven for 2 h before use. Electrolyte used was a solution of 1.0 mol kg⁻¹ LiPF₆ dissolved in a 3:6:1 (wt.) blend of ethylene carbonate, ethyl methyl carbonate, and fluoroethylene carbonate. The LiPF₆-added sample for structural characterizations was prepared by violently milling an NCM811-LiPF₆-N-methyl pyrrolidinone (NMP) suspension (containing 1.0 wt.% LiPF₆ vs. the mass of NCM811) with a stainless steel ball (5 mm in diameter) for 75 min. on a 5100 Mixer Mill® (SPEX CertiPrep), followed by filtering and drying the solid at 120°C under vacuum for 10 h. For comparison, the pristine NCM811 sample was prepared by the same procedure without adding LiPF₆. Structural characterizations of the pristine and LiPF₆-added samples were performed on a D8 ADVANCE X-ray diffractometer (Bruker, USA) and a SU-70 scanning electron microscope (Hitachi, Japan), respectively.

Using NMP as the solvent, the cathode with a composition by weight of 80% NCM811, 10% Super-P carbon, and 10% PVDF was





Figure 6. Rate capability of Li/NCM811 cells. a) Discharging capacity at different rates and b) discharging voltage profiles of the cell with 1.0% LiPF₆-added NCM811.

coated onto an aluminum foil. For the addition of LiPF₆, calculated amount of LiPF₆ was dissolved into the cathode slurry (alternatively, LiPF₆ could be added in the form of liquid electrolyte) without changing any other coating procedures. Resulting cathode was punched into circular disks with a 1.27 cm² area using a puncher with a $\frac{1}{2}$ inch diameter, and dried at 120 °C under vacuum for 10 h. On average, the loading of NCM811 was $8.2 \sim 8.5 \text{ mg cm}^{-2}$. Using Celgard 2350 membrane as the separator, Li/NCM811 coin cells were assembled and cycled on a Maccor Series 4000 tester. For consistency, a fixed 40 µL liquid electrolyte was filled in all cells, and before testing the cells were formed at C/10 between 3.0 V and 4.5 V for two cycles. The cell was cycled at C/3 by charging at C/3 to the pre-defined cutoff voltage, followed by holding the cell at the cutoff voltage until the current declined to C/10. To test the rate capability, the cell was charged at C/2 to 4.3 V and held at 4.3 V until the current declined to C/10, and discharged at various rates to 2.8 V. The 1 C-rate was referenced to a current of $200 \text{ mAg}^{-1} \text{ NCM811}.$

AC-impedance of the Li/NCM811 cells was measured at 20 °C using a Solartron SI 1287 Electrochemical Interface combined with a Solartron SI 1260 Impedance/Gain-Phase Analyzer. Stable testing point was obtained by charging the cell at C/10 to 4.3 V for the charged state and discharging the cell at C/10 to 2.8 V for the discharged state, followed by resting at open-circuit voltage (OCV) for 1 h. The impedance was measured at OCV with a 10 mV perturbation in the frequency range from 100,000 Hz to 0.01 Hz.

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Figure 7. Impedance spectra of Li/NCM811 cells at the charged state (a) and discharged state (b). Within each figure, a) pristine NCM811, b) 0.5% LiPF₆-added NCM811, c) 1.0% LiPF₆-added NCM811, and d) 2.0% LiPF₆-added NCM811.

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Conflict of Interest

The authors declare no conflict of interest.

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