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Communication—Enhancing the Electrochemical Performance of Lithium-Excess Layered Oxide Li$_{1.13}$Ni$_{0.3}$Mn$_{0.57}$O$_2$ via a Facile Nanoscale Surface Modification

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In this work, a facile surface modification with nanoscale equilibrium Li$_3$PO$_4$-based surface amorphous films (SAFs) has been applied to Lithium-excess layered oxide Li$_{1.13}$Ni$_{0.3}$Mn$_{0.57}$O$_2$, which significantly improves the first cycle coulombic efficiency, rate capability, and cycling stability. The nanoscale surface modification can be easily achieved by ball milling and isothermal annealing. The optimized surface modified Li$_{1.13}$Ni$_{0.3}$Mn$_{0.57}$O$_2$ is capable of maintaining a high capacity of 201 mAh g$^{-1}$ after 60 cycles at 55°C testing with a rate of 1 C. This work provides a facile and scalable surface modification method to improve electrochemical performance of cathode materials for lithium-ion batteries.

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The Lithium-excess layered oxides benefit from an extraordinary high reversible capacity (>280 mAh g$^{-1}$) and is one of the most promising cathode materials for plug-in electric vehicle application. However, this high-energy-density material suffers from large irreversible capacity in its first electrochemical cycle when it is charged to high voltages, namely more than 4.6 V. In addition, its rate capability is yet unsatisfactory for high power application. Moreover, the gradual voltage and capacity degradation upon electrochemical cycling, especially at elevated temperature when side reactions related to the interactions with the electrolyte occur more prevalently, represent the most serious technical challenge for this material. In the past few years, significant amount of surface modification works have been carried out to protect the surfaces of the Li-excess. Most of the reported surface modifications are performed under solution-based reactions. For example, Bian et al. used LiOH and NH$_4$H$_2$PO$_4$ to coat Lithium-excess with Li$_3$PO$_4$. However, the solution based surface modification adds an additional layer of complexity for preparation of Lithium-excess, which will definitely raise the cost of production. Although Komishi coated high voltage spinel LiNi$_{0.5}$Mn$_{1.5}$O$_4$ with uniform Li$_3$PO$_4$ via pulsed laser deposition (PLD), this technique requires special equipment, which is difficult to realize for large scale production.

In this work, we modify the surface of Lithium-excess layered oxide Li$_{1.13}$Ni$_{0.3}$Mn$_{0.57}$O$_2$ via simple mixing and calcination to form Li$_3$PO$_4$-enriched and nanometer-thick surface amorphous films (SAFs). Our results indicate that the optimized material shows remarkably improved performance.

Experimental

The synthesis of the Li-excess is described in our previous publications. The procedure for preparing Li$_3$PO$_4$ surface modified Li$_{1.13}$Ni$_{0.3}$Mn$_{0.57}$O$_2$ (LPLNMO) was adapted from work by Huang et al. Li$_3$PO$_4$ was calcinated at 500°C, 600°C, and 700°C (LP500), and 700°C (LP600), and 700°C (LP700), respectively, for 5 h in air. Electrochemical test, XRD, SEM and HRTEM characterization are described with details in our previous work.

Results and Discussion

**Results.—** Figure 1 shows the SEM images of the LNMO and LPLNMOs. All materials show secondary particles with a wide size distribution below 10 μm; the primary particle size distribution ranges from 50 to 200 nm. There were no dramatic changes to the morphology or particle size after Li$_3$PO$_4$ surface modification.

HRTEM is used to identify the Li$_3$PO$_4$ coating (SAFs) on LP600. The TEM images show very good layered bulk crystal structure, and amorphous films on the surface of LP600. More than 20 particles are analyzed to examine the amorphous film. As shown in Figure 1i, particles have the amorphous film evenly coated on the surface, with the thickness of ~2 nm. While the majority of particles exhibit uniform coatings, there are some particles that still show clean surfaces with no indication of surface coatings, as illustrated in Figure 1j.

The XRD of LNMO and LPLNMOs are refined and plotted in Figure 2. The major diffraction peaks of these materials are indexed no indication of surface coatings, as illustrated in Figure 1j.

The Optimized surface modified Li$_{1.13}$Ni$_{0.3}$Mn$_{0.57}$O$_2$ is capable of maintaining a high capacity of 201 mAh g$^{-1}$ after 60 cycles at 55°C testing with a rate of 1 C. This work provides a facile and scalable surface modification method to improve electrochemical performance of cathode materials for lithium-ion batteries.
Both LNMO and LP600 are cycled at 55°C within the voltage window of 2–4.8 V, at 250 mA g\(^{-1}\). Figure 4a compares their first charge/discharge voltage profiles. Both materials show larger charge/discharge capacities than their low current testing values at room temperature, which is due to the higher lithium activity at elevated temperature.\(^{10}\) An obvious elongated slope (~218 mAh g\(^{-1}\)) appears in LNMO, which indicates the reactions between electrode and electrolyte happens below 4.4 V at 55°C. After the Li3PO4 surface modification, the charge capacity decreases from 390 to 332 mAh g\(^{-1}\) while the discharge capacity increases from 246 to 271 mAh g\(^{-1}\), respectively. The corresponding coulombic efficiency escalates from 63.1% to 81.6%.

The charge/discharge capacities of both materials are compared in Figure 4b. Large irreversible capacities exist in each cycle of LNMO, while the LP600 only exhibits irreversible capacity in its first cycle. LP600 delivers 201 mAh g\(^{-1}\) with an enhanced capacity retention of 74.2% after 60 cycles. As a comparison, LNMO only shows 41% capacity of its first cycle.

**Figure 3.** Comparison of electrochemical performances between LNMO and LP-LNMOs: (a)–(d) voltage profiles under different current density; (e) discharge capacity under different current density; and (f) comparison of capacity upon cycling, the voltage range is 2.0–4.8 V at 1 C = 250 mA g\(^{-1}\).
In this work, we applied nanoscale self-regulated Li$_3$PO$_4$-based surface amorphous films to Lithium-excess layered oxide Li$_{1.13}$Ni$_{0.3}$Mn$_{0.57}$O$_2$ via a facile method. The mixture of 2 wt% Li$_3$PO$_4$ and Li$_{1.13}$Ni$_{0.3}$Mn$_{0.57}$O$_2$ annealed at 600°C shows significantly improved coulombic efficiency in first cycle, rate capability, and cycling stability of Li-excess. These improvements are valid even at an elevated temperature. We expect that this scalable method will also work for other high voltage cathode materials for lithium ion batteries.

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Conclusions
The electrochemical performances of LNMO and LP600 at 55°C are compared in Figure 4. Figure 4(a) shows the voltage profile during the first cycle. Figure 4(b) compares the capacity over 60 cycles, and Figures 4(c) and 4(d) show the voltage profiles at different cycles. The voltage range is 2.0–4.8 V at 1 C = 250 mA g$^{-1}$.

General discussions.—LP600 delivers a high coulombic efficiency of 86.4% in its first cycle. Both suppressed irreversible lattice oxygen loss and reduced undesired side reactions with electrolyte lead to lower charge capacity, which is indicated by the shorter charge plateau. As a consequence, LP600 gets a better electrode/electrolyte interphase, which facilitates the lithium transports during discharge and following cycles. The high temperature tests are designed to verify this hypothesis. In Figures 4c–4d, the LNMO demonstrates large discharge voltage slippage, which indicates the rapid growth of cathode electrolyte interphase (CEI) on the surface of LNMO. This undesired CEI traps or slows down the lithium diffusion, thus causing serious capacity and voltage degradation in LNMO. In the case of LP600, the CEI is mitigated by the Li$_3$PO$_4$ coating layer by reducing direct contact between the electrode and electrolyte. In addition, the Li$_3$PO$_4$ coating layer protects the electrode from etching by acidic species in the electrolyte. Moreover, the surface reconstruction of Li-excess may also be alleviated through suppressing the oxygen loss. The Li$_3$PO$_4$ coating improves the voltage stability for Lithium-excess, however, it is suggested that surface modification, bulk substitution, and interphase optimization should work together in order to overcome the voltage fading in Li-excess.

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