Effects of Particle Size on Voltage Fade for Li-Rich Mn-Based Layered Oxides

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ABSTRACT: Voltage fade significantly hinders the practical use of Li-rich Mn-based layered oxides (LLOs) as cathode materials for next-generation high-energy-density Li-ion batteries. Therefore, an in-depth understanding of the factors influencing the LLO voltage fade during cycling is fundamentally important for tailoring the structure and thus improving the electrochemical performance of the corresponding electrodes. Herein, we compare the electrochemical performances of LLOs with different particle size and conduct in situ high-pressure response measurements to determine the effects of particle size on voltage fade, demonstrating that small particles can undergo a reversible layer-to-spinel phase transition that results in improved voltage stability during cycling. The above finding provides a novel paradigm for the development of high-capacity LLO electrodes and thus contributes to the establishment of a more energy-efficient and green society.

INTRODUCTION

The high reversible specific capacity, low cost, environmental friendliness, and facile processing of Li-rich layered oxides (LLOs), which exhibit a layered structure similar to that of other conventional layered transition metal oxides, make them promising cathode materials for next-generation high-energy-density batteries.1−4 Despite the ongoing debate on whether LLOs form intermixed nanodomains of separate LiMO2 (M = Ni, Co) and Li2MnO3 phases or are homogeneous solid solutions featuring a Li2MnO3 superlattice, the abnormally high capacities of LLOs are thought to be related to the activation of the LiMn3 ordering component5−25 involving redox reactions of transition metal cations and the oxygen anions.26−30 The reversible formation of O2− peroxo-like species is expected to be accompanied by a massive migration of transition metal cations to Li-depleted layers, inducing a layered-to-spinel phase transition and hence resulting in voltage fade.31−34 To overcome this problem, many studies have been performed to understand the process of Li insertion/desertion and optimize the electrochemical behavior of electrode materials.35−39 Voltage fade can be mitigated in a number of ways, including the use of new electrolytes and binders,40−42 coatings,43−45 doping,46−50 and optimized synthesis conditions.51−54 However, the mechanism of voltage fade suppression is still not fully clear because of the variability of the utilized compositions, morphologies, and electrochemical parameters. Thus, the intrinsic relationship between material structure and voltage fade-governing properties must still be deeply understood from different angles.

Li-ion insertion/desertion during prolonged charge/discharge results in the formation of local stress points in the corresponding intercalation compounds,55 and the concentration of such stress may result in strain.36 For example, the shear stress associated with layered Li intercalation compounds results in plane gliding and induces the migration of transition metal ions during cycling.37,38 Material cracking is observed when the stress exceeds the yield strength, resulting in significant electrode performance deterioration.39 However, to the best of our knowledge, previous studies investigating the mechanical behavior of electrode materials mostly focused on purely physical calculations,40 whereas only few reports dealt with the mechanical behavior of as-prepared cathode materials to understand voltage fade in LLOs.

The high-pressure stability and bulk compressibility of a given material are directly related to its response to stress during charge/discharge.14 Herein, the mechanical properties of electrode materials were analyzed using a high-pressure method that allowed the modulation of the Li-ion-extraction/insertion-induced stress to avoid the interference of other factors and more precisely characterize the intrinsic performance of these materials. Previous works revealed that Co- and Mn-based Li-rich materials suffer from more serious voltage fade and capacity decline than other Li-rich materials.41 During Li-ion intercalation/deintercalation, coarser-grained electrode materials are expected to be exposed to a larger stress than finer-grained ones because a larger amount of Li is removed in the former case. Herein, we prepared coarse- and fine-grained Li1.2Co0.4Mn0.4O2 as a model Li-rich layered oxide and characterized sample structure evolution by high-pressure in situ X-ray diffraction (XRD), exploring the effect of particle size on voltage fade during cycling. Therefore, the insights into the
voltage fade mechanism described herein are expected to serve as a guide for high-capacity cathode material optimization.

## RESULTS AND DISCUSSION

Figure 1 shows the representative scanning electron microscopy (SEM) images of B- and S-LLO, demonstrating that both materials contained nonagglomerated particles with uniform size (~500 and 100 nm, respectively), good dispersion, and smooth surface.

Figure 2 shows that the XRD patterns of B-LLO and S-LLO were almost identical, exhibiting well-defined peaks indicative of a highly crystalline nature and thus suggesting that the corresponding lattice parameters were also similar. The main diffraction peaks were assigned to a NaFeO$_2$-type layered structure of an R$3m$ space group, whereas the minor peaks at 20 = 20°–25° were attributed to the LiMn$_{6}$ ordering reflection. The (003)/(104) intensity ratio was approximately equal to 1.2, and (006)/(102) and (018)/(110) adjacent peak separations could be clearly observed, which indicated that both samples featured well-developed layered structures. Rietveld refinements performed in the R$3m$ space group without including the superlattice peak region (20 = 20°–25°) showed that the obtained lattice parameters of B-LLO and S-LLO ($a = 2.8261$ Å and $c = 14.1453$ Å; $a = 2.8263$ Å and $c = 14.1458$ Å, respectively) were almost identical within the range of allowable error. This finding indicated that the overall compositions of both samples were very close, as confirmed by the results of inductively coupled plasma mass spectrometry analysis, which allowed the composition of these samples to be identified as Li$_{1.2}$Co$_{0.4}$Mn$_{0.4}$O$_{2}$.

The surface compositions and structure of B-LLO and S-LLO were elucidated by X-ray photoelectron spectroscopy (XPS) (Figure 3) analysis, which demonstrated that the two samples featured identical spectra comprising a Mn$^{4+}$ 2p$_{3/2}$ peak at ~642 eV and a Co$^{3+}$ 2p$_{3/2}$ peak at ~780 eV. Because XPS is a surface-sensitive analysis technique, the above finding implied that B-LLO and S-LLO exhibited identical surface states.

Subsequently, the electrochemical performances of the above materials were investigated in a voltage range of 2.0–4.8 V at a current density of 300 mA g$^{-1}$ (Figure 4). Figure 4a,d shows cycle number-dependent specific discharge capacities for each sample, revealing that B-LLO and S-LLO could deliver reversible capacities of 190 and 210 mAh g$^{-1}$, respectively, i.e., the fine-grained sample outperformed the coarse-grained one. Figure 4b,e shows the cell voltage as a function of specific capacity after normalization. After 50 cycles, the average discharge potential dropped from 3.28 to 3.14 V in the case of B-LLO, corresponding to a 0.14 V voltage fade and being in agreement with a previous report, whereas a much smaller voltage fade of only 0.08 V was observed for S-LLO. Figure 4c,f shows differential capacity as a function of cell voltage for cycles 10–50, revealing that for B-LLO, the discharge peak area decreased between 3.45 and 4.35 V but increased in the low-voltage region of 2.45–3.05 V. Thus, the relative contribution of low-voltage capacity to the total capacity and the voltage fade increased with increasing number of cycles, which was previously ascribed to the conversion to a spinel-like phase.

In contrast, the voltage fade was much smaller for S-LLO, which indicated that the use of fine-grained materials could enhance the stability of the layered Li-rich oxide phase and achieve a more stable average discharge voltage.

Figure 5 shows the XRD patterns of B-LLO and S-LLO subjected to 100 cycles. The * peak is assigned to the attribution of binder PTFE. Significant peak broadening was observed for B-LLO, which was ascribed to an increased structural strain, whereas the disappearance of the (006) peak and the merging of adjacent (018) and (110) peaks suggested that the sample underwent a conversion to a spinel-like phase.

This conversion was expected to result in voltage fade and capacity decline, in agreement with the results of electrochemical testing. In contrast, no significant differences were observed between the XRD patterns of S-LLO recorded before and after 100 cycles, which demonstrated the superior...
structural stability of the latter sample upon cycling but was not consistent with the results of Dahn et al.\textsuperscript{44} In the present work, the particle size refers to the size of a primary particle and the primary particle shows a good dispersion.

To gain a deeper insight into the mechanism of particle size influence on the evolution of structure and voltage fade during cycling, we evaluated the high-pressure stability of Li-$[\text{Li}_{0.2}\text{Co}_{0.4}\text{Mn}_{0.4}]\text{O}_2$ because the high-pressure stability and compression response of host materials are directly related to the response of solids to stress. Moreover, because the magnitude of voltage fade is closely related to the degree of delithiation\textsuperscript{14} and increases with the increasing amount of Li accessed upon charging, two lithiation states were characterized, namely, fully and half-lithiated ones.

Figure 6 shows the integrated in situ synchrotron XRD patterns of fully lithiated B-LLO recorded at different pressures. The pattern obtained at ambient pressure corresponded to a highly crystalline material with a NaFeO$_2$-type layered structure of the $R3\overline{m}$ space group. As the pressure was increased from 2.47 to 35.7 GPa, the (003) peak of fully lithiated B-LLO monotonically shifted to higher diffraction angles, concomitantly losing the intensity and becoming broader (Figure 6a). Interestingly, the above peak retained its symmetry throughout the process. At pressures above 37.39 GPa, all of the diffraction peaks disappeared, indicating the occurrence of a pressure-induced disorder. After decompression to ambient pressure, the sample remained amorphous (Figure 6b), which was indicative of a totally irreversible structure destruction.

Figure 7 shows the XRD pattern evolution of the half-lithiated B-LLO, demonstrating that the (003) reflection also exhibited a shift to higher angles, broadening, and intensity loss with increasing pressure. However, in this case, the above peak was markedly asymmetric. Upon further compression to 47.73 GPa followed by the release to 11.81 GPa and then to ambient pressure, the above peak recovered its original lattice position but remained asymmetric, in stark contrast to the behavior of the fully lithiated sample, which turned amorphous. This asymmetric peak was fitted by TOPSWARE, which revealed the

Figure 3. XPS patterns of (a) Mn 2p and (b) Co 2p for S-LLO and B-LLO.

Figure 4. Cycling behavior of (a) S-LLO and (d) B-LLO during 50 cycles performed in the voltage range of 2.0–4.8 V at a current density of 300 mA g$^{-1}$. (b, e) Voltage profiles of the 1st, 10th, 20th, 30th, 40th, and 50th cycles for S-LLO and B-LLO, respectively. (c, f) $dQ/dV-V$ patterns for S-LLO and B-LLO, respectively.
emergence of a shoulder peak to the right of the main (003) peak (Figure 8). The appearance of this new peak agreed well with a previous report, wherein it was attributed the layered-to-spinel phase conversion responsible for voltage fading.

Figure 9a shows that the structural evolution of the fully lithiated S-LLO with increasing pressure was similar to that observed for the fully lithiated B-LLO, but much slower, e.g., the former sample remained crystalline at \( \sim 30 \) GPa. Similar behavior was also observed for the half-lithiated S-LLO (Figure 10a), which indicated that S-LLO was more stable than B-LLO. Importantly, for the fully lithiated S-LLO, no new peaks were observed to the right of the (003) peak at \( 0 \sim 30 \) GPa, and the above peak maintained its symmetry when pressure was released, which indicated that the high-pressure structure of the fully lithiated S-LLO could be reversibly transformed into the initial structure (Figure 9b). At pressures of 10 and 20 GPa, which were applied to mimic the stress during shallow charging, no new peaks were observed. For the half-lithiated S-LLO, a new peak to the right of the (003) peak emerged when pressure was increased to 47.73 GPa. After decompression, this new peak disappeared, and the (003) peak regained its symmetry (Figure 10b), i.e., for half-lithiated S-LLO, the high-pressure structure could be reversibly converted to the initial structure. Therefore, the results of in situ high-pressure XRD analysis demonstrated that the fine-grained sample had a greater ability to bear stress than the coarse-grained one at the same lithiation state, and the migration of transition metal ions occurred reversibly in the grains of the former sample.

## CONCLUSIONS

Herein, we observed unusual mechanical responses of Li-rich layered oxides \( \text{(Li}_{1.2}\text{Co}_{0.4}\text{Mn}_{0.4}\text{O}_{2}) \) in different lithiation states. Specifically, S-LLO maintained its layered structure upon compression to 40.32 GPa, whereas B-LLO underwent a stress-induced conversion to a spinel-like phase. After the subsequent pressure release, S-LLO recovered its initial structure, whereas an irreversible structure destruction was observed for B-LLO, suggesting that the layered-to-spinel phase transition was dependent on particle size. Thus, these findings are expected to benefit the optimization of high-capacity cathode materials and show that the use of fine-grained LLOs facilitates the accommodation of electrode stress and improves the long-term stability of electrodes for Li-ion battery operation.

## EXPERIMENTAL SECTION

**Synthesis of \( \text{Li}_{1.2}\text{Co}_{0.4}\text{Mn}_{0.4}\text{O}_{2} \).** To prepare the coarse-grained (large-particle-size) sample, stoichiometric amounts of citric acid (\( \text{C}_{6}\text{H}_{8}\text{O}_{7} \cdot \text{H}_{2}\text{O} \)), Li\( \text{CH}_{3}\text{COO} \cdot 2\text{H}_{2}\text{O} \), Co-(\( \text{CH}_{3}\text{COO} \)\(_2 \cdot 4\text{H}_{2}\text{O} \), and Mn\( (\text{CH}_{3}\text{COO})_2 \cdot 4\text{H}_{2}\text{O} \) were dissolved in distilled water, and the solution pH was adjusted to 7 by aqueous ammonia. The obtained solution was concentrated on a rotary evaporator at 80 °C to obtain a homogeneous colloidal precursor, which was subsequently dried in a vacuum oven at 150 °C and annealed at 900 °C to afford a product labeled as B-LLO.

The fine-grained (small-particle-size) sample (S-LLO) was prepared similarly to B-LLO using citric acid and glycol as both complexing and esterification reagents.

**Characterization.** Conventional XRD analysis (Bruker D8 X, Germany) was performed using a Cu K\( \alpha \) radiation at 40 keV and 40 mA. Sample morphologies were characterized by cold-field-emission scanning electron microscopy (SEM; Hitachi, S-4800, Japan) and transmission electron microscopy (FEI, TECNAI F20). X-ray photoelectron spectroscopy (XPS; Axis...
Figure 7. (a) In situ high-pressure XRD patterns of half-discharged B-LLO and (b) expansion of region A showing the (003) peak.

Figure 8. (a) Fit of the (003) peak observed after decompression to ambient pressure and (b) graph showing fitting residues.

Figure 9. (a) In situ high-pressure XRD patterns of fully discharged S-LLO and (b) expansion of region A showing the (003) peak.
Ultra, Kratos Analytical Ltd., England) measurements were conducted at the Analytical Instrumentation Center of Peking University. All of the spectra were calibrated using the C 1s photoemission peak at 284.8 eV. In situ high-pressure synchrotron radiation powder XRD measurements were performed at the Beijing Synchrotron Radiation Facility (beamline 4W2). High pressure was applied at room temperature in a diamond anvil cell using Ar gas as a pressure-transmitting medium.

**Electrochemical Testing.** Electrochemical properties were evaluated employing a charge/discharge tester (Neware, China). Coin cells were assembled in an Ar-filled glovebox using glass microfiber separators (Whatman, U.K.) and Li metal anodes. High-pressure in situ XRD measurements were carried out after one cycle of performance testing at a rate of 2C and for fully or half-discharged states (Li content was determined from specific capacity). The cathode was fabricated by mixing B-/S-LLO, poly(vinylidene difluoride) binder, and Super-P conductive carbon black (80:10:10, w/w/w) in N-methyl-2-pyrrolidone and coating the obtained slurry onto Al foil. The cathode was purchased from the Beijing Institute of Chemical Reagents (composition not disclosed).

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