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Enhancing the Ion Transport in $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ by Altering the Particle Wulff Shape via Anisotropic Surface Segregation

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ABSTRACT: Spontaneous and anisotropic surface segregation of W cations in $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ particles can alter the Wulff shape and improve surface stability, thereby significantly improving the electrochemical performance. An Auger electron nanoprobe was employed to identify the anisotropic surface segregation, whereby W cations prefer to segregate to {110} surface facets to decrease its relative surface energy according to Gibbs adsorption theory and subsequently increase its surface area according to Wulff theory. Consequently, the rate performance is improved (e.g., by ~5X at a high rate of 25C) because the {110} facets have more open channels for fast lithium ion diffusion. Furthermore, XPS depth profiling suggested that the surface segregation and partial reduction of W cation inhibit the formation of Mn^{3+} on surfaces to improve cycling stability via enhancing the cathode electrolyte interphase (CEI) stability at high charging voltages. This is the first report of using anisotropic surface segregation to thermodynamically control the particle morphology as well as enhancing CEI stability as a facile, and potentially general, method to significantly improve the electrochemical performance of battery electrodes. Combining neutron diffraction, an Auger electron nanoprobe, X-ray photoelectron spectroscopy, and other characterizations, we depict the underlying mechanisms of improved ionic transport and CEI stability in high-voltage $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ spinel materials.

1. INTRODUCTION

High-voltage $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ spinel is one of the most promising candidates for next-generation cathode materials of lithium ion batteries for electric vehicles and other high-energy density applications due to its high operating voltage ~4.7 V, low cost, and environmental friendliness. Prior studies had investigated the effects of Mn and Ni cation disordering,¹⁻⁵ Mn^{3+} concentration,^{2,6,7} oxygen vacancies,^{1,8,9} impurities^{4,10}, surface coating^{11,12}, cation doping^{5,13-18}, and particle surface crystalline orientation¹⁹⁻²⁷ on improving the electrochemical performance. Several reviews on high-voltage spinel cathodes have been published recently.²⁸⁻³⁵ However, the roles of cation doping on surface segregation and the particle morphology, as well as their subsequent impacts on the electrochemical performance, have not been well established in general.

Several recent studies suggested that the crystalline orientations on the particle surfaces can have significant influences on the electrochemical properties.¹⁹⁻²⁷ In most experiments, different crystalline facets were found to coexist at the surfaces of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ particles:²¹⁻²⁷ {111} and {100} surface facets were most frequently observed. Thermodynamically, {111} and {100} facets tend to coexist due to their similar (low) surface energies, while eliminating {100} facets appears to benefit rate capability and cycling stability.²² Chemelewski *et al.* synthesized

$\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ particles with dominating {111} surface facets by an improved co-precipitation method to kinetically control the particle morphology to eliminate {100} facets, which achieved an improved rate performance comparing to that of particles with coexisting {100} surface facets synthesized by a traditional co-precipitation method.²² Interestingly, it also showed that Fe doping could promote the formation of {111} surface facets of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ particles, though its underlying mechanism remained unclear.

Besides of {111} and {100} surface facets, a smaller fraction of {110} facets was also observed occasionally.²⁴ {110} facets exhibit the most open channels for fast lithium diffusion but appear to have a higher surface energy, which are not thermodynamically favorite to form comparing to {111} and {100}.³⁶ Here, we have demonstrated a novel strategy to increase the fraction of the most favorite {110} facets thermodynamically to improve the rate capabilities via anisotropic surface segregation of WO_3 , along with enhancing the cycling stability via improving the surface stability. Moreover, we have conducted a combination of neutron diffraction, X-ray photoelectron spectroscopy, an Auger electron nanoprobe and other characterizations to verify our hypothesis and reveal the underlying mechanisms at multiple length scales.

1 Furthermore, prior reports already suggested that the
2 surface segregation of dopants can influence the electro-
3 chemical performance of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$.^{5,37,38} Though sur-
4 face segregation appears to be related to the particle mor-
5 phology change,³⁸ the relation between the two phenom-
6 ena has not been investigated (and, in fact, it was often
7 believed that particle morphology was mostly determined
8 by kinetics and the influence surface segregation is unim-
9 portant³⁹). Here, we demonstrated, for the first time to
10 our knowledge, that the anisotropic segregation of W
11 cation preferably on the $\{110\}$ surface facets of
12 $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ can stabilize the most favorite $\{110\}$ facets
13 with the most open channels for fast lithium diffusion, in
14 accord with the well-established Gibbs and Wulff theo-
15 ries. Consequently, the surface segregation and associated
16 particle morphological changes contribute to significant
17 improvements of both rate capabilities and cycling stabili-
18 ties of the high-voltage $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathode.

19 It should be noted that aliovalent doping can also
20 change the Mn^{3+} concentration, which can influence the
21 formation of oxygen vacancies and cation disordering
22 (both inside the bulk phase and at/near the surface). On
23 one hand, the existence of Mn^{3+} cations benefits the rate
24 capability by increasing both of the lithium ion bulk dif-
25 fusion rate and the electronic conductivity and it contrib-
26 utes an extra amount of discharge capacity from
27 $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox at the voltage plateau of ~ 4 V.^{2,6} On the
28 other hand, the presence of Mn^{3+} cations decreases cycl-
29 ing stability by promoting the formation of Mn^{2+} on
30 surface and subsequently dissolution of Mn^{2+} in the elec-
31 trolyte.^{15,39} Notably, a prior study also demonstrated that
32 surface segregation of Fe, Cr and Ga in $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ par-
33 ticles could inhibit the Mn^{2+} dissolution in electrolyte to
34 subsequently improve the cycling stability.⁵ In this study,
35 we further demonstrated, via XPS depth profiling, that the
36 surface segregation and partial reduction of W cation inhibit
37 the formation of Mn^{3+} on surfaces to improve cycling stability,
38 presumably via enhancing the cathode electrolyte interphase
39 (CEI) at high charging voltages.

40 In this study, we added 1 vol. % of WO_3 , which is a well-
41 known “supported oxide catalyst” that would spontane-
42 ously spread (adsorb) on the surfaces of inert oxides (typ-
43 ically Al_2O_3 and TiO_2 nanoparticles) upon annealing due
44 to its low surface energy,⁴⁰⁻⁴² to $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$, which
45 spontaneously adsorbed (segregated) on the particle sur-
46 faces upon a facile and cost-effective “mixing and anneal-
47 ing” process. We further demonstrated that WO_3 dis-
48 solved into the $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ bulk phase and anisotropi-
49 cally adsorbed (a.k.a. segregated) on the surfaces of
50 $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ particles to increase the fraction of the
51 most favorite $\{110\}$ facets.²⁴ The combination effects of
52 bulk doping, surface segregation, and anisotropic-seg-
53regation induced morphological changes improved not
54 only rate capabilities substantially (e.g., an $\sim 500\%$ in-
55 crease in the discharge capacity at 25C) but also the cycl-
56 ing stability (e.g., $>25\%$ increase in the discharge capaci-
57 ty at 55 °C after 200 cycles at 1C).

58 2. EXPERIMENTAL

To prepare 1 vol. % WO_3 doped $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ (a nomi-
nal volumetric percentage calculated using the molar vol-
umes of individual compounds, corresponding to an
overall W/Mn atomic ratio of ~ 0.06), $(\text{NH}_4)_2\text{WO}_4$ (precur-
sor for WO_3) was added to as-received $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$
(Sigma-Aldrich, $>99\%$) and dispersed in 4 ml of acetone.
The mixture was placed in a silicon nitride grinding vial
with two silicon nitride balls. Before sealing the jar, the
corprene gasket was taped by Teflon to prevent it from
acetone corrosion and precursor contamination. High-
energy ball milling was carried out using a SPEX 8000D
mill for a duration of 10 min, followed by a 15-min resting
interval; this milling process was repeated for 3 times. The
mixture was dried isothermally in an oven around 70 °C.
The dried powder was placed in a covered alumina cruci-
ble, isothermally annealed at 800 °C for 4 h in a box fur-
nace with a heating rate of 5 °C/min and subsequently
cooled in the furnace (with power being shut down) after
the isothermal annealing. As a reference, controlled spec-
imens of undoped $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ were prepared with ex-
actly the same ball milling and annealing procedure de-
scribed above, but without the addition of the WO_3 pre-
cursor ($(\text{NH}_4)_2\text{WO}_4$).

Particle sizes and morphologies were characterized us-
ing a FEI XL30 scanning electron microscope (SEM). Spe-
cific surface area was measured on a Micromeritics ASAP-
2000 Gas Adsorption Analyzer.

The surface composition and depth profile of WO_3
doped $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ particles were characterized by both
X-ray photoelectron spectroscopy (XPS) and Auger elec-
tron spectroscopy (AES). XPS was carried out by using a
Kratos AXIS ULTRA DLD XPS system equipped with an
Al $K\alpha$ monochromated X-ray source and a 165 mm mean
radius electron energy hemispherical analyzer with a step
size of 0.1 eV. A 4 keV Ar ion beam was used for sputter-
ing. Binding energies were corrected using C 1s peak 284.6
eV. The sample current was set to be ~ 4 μA . Depth profile
data were collected after sputtering time of 10 s, 30 s, 60 s,
120 s and 240 s. The measured XPS depth profiles repre-
sent averages of many different particles and crystalline
facets. The XPS data were fitted with the XPSPEAK41
software.

AES surface analysis, in conjunction with depth profil-
ing using ion sputtering, was carried out by a PHI 700
scanning Auger nanoprobe with a nanoscale spatial reso-
lution to obtain surface compositions of individual crys-
talline facets. Au foils were used as substrates to eliminate
charging effects. A multiplex mode survey was used to
acquire accurate quantitative results of various elements
on surface. The signals from O, Mn, Ni, and W, respec-
tively, were scanned in ranges of 496.4 – 532.0 eV, 557.8 –
611 eV, 811 – 871 eV and 1692.5 – 1758.8 eV respectively,
and subsequently analyzed in ranges of 502.7 – 526.5 eV,
563.9 – 604.5 eV, 824.1 – 863.0 eV and 1713.0 – 1748.9 eV,
respectively. Each test was carried out with 40 sweeps and
1 eV per step. 10 cycles of measurements were conducted
for obtain high-quality signals, in which process the ac-
quisition area was corrected after each point test to avoid
beam drift and ensure that data was acquired in the same

location. The Mn₂ signal at 536 eV was selected since there is an overlap of the Mn₁ (519 eV) and O (510 eV) signals. Elemental compositions on the facets of (100), (110), and (111) of W doped and undoped LiMn_{1.5}Ni_{0.5}O₄ specimens were investigated. At least two points were taken on each facet. A beam energy of 20 kV was used to get a smaller beam size with a spatial resolution of about 8 – 10 nm. The sputtering source was neutralized Ar of 1 kV beam energy and with a 30° incident angle with the sample. The target emission current was 15 mA. The sputtering area was 1 mm by 1 mm. The sputter time was 30 s (between collecting two data points) with a delay of 3 s. The specimen position was recalibrated after each spot was measured. The AES data were fitted with the MultiPak software.

Neutron diffraction characterization data were collected on the VULCAN beamline at the Spallation Neutron Sources (SNS) in the Oak Ridge National Laboratory (ORNL). An incident beam (5 mm × 12 mm) of 0.7 to 3.5 Å bandwidth, allowing 0.5 - 2.5 Å *d*-space in diffracted patterns in the $\theta \pm 90^\circ$ detector banks, was selected using the double-disk choppers at a 30 Hz speed. The high-resolution mode was employed with $\Delta d / d \approx 0.25\%$. The SNS power was at 1100 KW nominally. Neutron diffraction data were collected for a duration of 3 h^{43,44} at room temperature and were reduced by the VDRIVE software.^{45,46} A full-pattern Rietveld refinement was performed using the GSAS programs with the EXPGUI interface.^{47,48}

To prepare cathodes, 80 wt. % active materials, 15 wt. % carbon black (MTI), 5 wt. % PVDF (MTI), and an appropriate amount of NMP (Alfa Aesar, anhydrous, 99.5 %) were mixed in a glass vial by a vibrating mixer, followed by ultrasonic dispersion. The mixture was coated on an aluminum foil, which was subsequently dried in a vacuum oven at 90 °C for 6 h. Cathode electrodes with a diameter of 10 mm were punched out, pressed at ~187 MPa, and dried in a vacuum oven at 120 °C for 8 h before transferring into an Ar-filled glovebox for battery construction. The density of dried electrode coating was ~3.2 mg cm⁻². Half cells were made with a cathode electrode, a metal Li chip (MTI, 99.9 %) as the anode, 1M LiPF₆ in 1:1 vol. EC/DMC electrolyte (LP 30, BASF), C480 separators (Celgard), and 2032 coin cell cases (SS304, MTI).

Electrochemical cycling tests were carried out on an Arbin 2143 tester. The rate performance of LiMn_{1.5}Ni_{0.5}O₄ specimens was tested at the discharge rates of C/10, C/5, 1C, 5C, 25C, 45C, 65C, and 85C sequentially (with 4 cycles at C/5 to stabilize the battery and 1 cycle for other discharge rates subsequently; 1C equates to 150 mA g⁻¹) with a constant charge rate of C/5 at room temperature. The cycling stability of LiMn_{1.5}Ni_{0.5}O₄ specimens were measured at charge and discharge rate of 1C between 3.2 V and 5.0 V at an elevated temperature of 55 ± 3 °C in a dry oven after first idling at 55 ± 3 °C for 2 h.

The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed using a Solartron 1287A/1255B analyzer. CV was performed between 3.2 V and 5.0 V at a scan rate of 0.1 mV s⁻¹. Electrochemical

impedance spectra were measured from 1 MHz to 0.05 Hz at 10 mV. The EIS data were fitted with the ZView software. The cells after rate capability test were charged to a cut-off voltage of 5.0 V at C/10 and kept for 10 h for the subsequent impedance measurements.

3. RESULTS

3.1. Surface Areas and Particle Morphologies. The measured BET specific surface areas of the undoped and WO₃ doped LiMn_{1.5}Ni_{0.5}O₄ specimens prepared using identical ball milling and annealing conditions were ~1.8 m²/g and ~1.7 m²/g, respectively; the difference was only ~6 % and the undoped LiMn_{1.5}Ni_{0.5}O₄ specimen had a slightly larger specific surface area. The comparable BET specific surface areas ensured fair comparisons so that the enhanced rate capability and cycling stability of the WO₃ doped LiMn_{1.5}Ni_{0.5}O₄ specimen as compared to those of the undoped specimen (that will be discussed subsequently) were not due to different specific surface areas.

The morphologies of the undoped and WO₃ doped LiMn_{1.5}Ni_{0.5}O₄ particles are shown in Figure 1, where some differences are evident. For the undoped LiMn_{1.5}Ni_{0.5}O₄ particles, surface facets of {111}, {110}, {100}, and {311} coexisted, with estimated surface area fractions of ~44%, ~18%, ~20%, and ~18%, respectively, which were calculated from Wulff construction simulation of a particle (Figure 2(a)) that matched the observation by SEM (Figure 1(a)). These observed results are generally consistent with prior density functional theory (DFT) computations.³⁶ For the WO₃ doped LiMn_{1.5}Ni_{0.5}O₄ particles, the surface area fraction of the {111} facets increased slightly from ~44% to ~56 % and the fraction of the {110} facets increased substantially from ~18% to ~43 %, whereas the fraction of the {100} facets decreased drastically from ~20% to <2% and the {311} facets disappeared completely. The surface area fraction of the {110} facets had the largest increase, being more than doubled with WO₃ doping.

The simulation of Wulff shapes was done with the software Wulffmaker running in Wolfram CDF Player.⁴⁹ The simulated Wulff crystals of the undoped and WO₃ doped LiMn_{1.5}Ni_{0.5}O₄ that matched the crystal morphologies observed by SEM (Figure 1) are shown in Figures 2(a) and 2(b), respectively, and corresponding relative surface energies are listed in Table 1. In comparison with that of the {100} facets, the surface energies of both {111} and {110} facets decreased more rapidly with WO₃ adsorption.

3.2. Anisotropic Surface Segregation. Strong surface segregation of W was clearly evident in the XPS depth profile. As shown in Figure 3, the surface atomic ratio of W/Mn was measured by XPS to be 0.23 ± 0.01 based on the fitting results, which decreased rapidly with ion sputtering to ~0.07 after 60 s and leveled off at ~0.03 after sputtering 240 s (while the overall nominal W/Mn ratio is 0.06). The surface Ni/Mn ratio was measured to be 0.23 ± 0.07, which was substantially lower than the nominal bulk Ni/Mn ratio of 1/3. After sputtering 60 s, the measured atomic ratio of W/Mn is 0.33 ± 0.04, approaching to the nominal bulk stoichiometric ratio of 1/3 and stayed roughly a constant. The sputtering rate was calibrated to be

about 30 nm min⁻¹ when a reference SiO₂ material was sputtered at the same experimental condition.⁵⁰

Furthermore, Auger electron spectroscopy (AES) with a nanoprobe of ~10 nm in the beam size was employed to quantitatively analyze the W atomic ratios on various facets to identify anisotropy in surface segregation. The measured depth profiles of W (obtained by ion sputtering) on the facets {110}, {100} and {111} are shown in Figure 4. The atomic ratios of W/Mn on {110}, {100}, and {111} facets, respectively, before sputtering was 0.28, 0.15, and 0.11, respectively. The surface of the {110} facet had the highest W/Mn atomic ratio of 0.28, which was 1.8× of that on the {100} facet and 2.4× of that the {111} facet, respectively. The atomic ratios of W/Mn on all facets decreased with increasing sputtering time and leveled off after sputtering for 90 s. The sputtering rate was calibrated to be ~ 5 nm min⁻¹ for a reference material of Si for using 1 kV Ar. Finally, the atomic ratio of W/Mn on various facets all converged to ~0.05 after sputtering for 240 s, close to the XPS result. The AES depth profiles clearly indicate that W prefers to segregate on {110} facets, in comparison with {100} and {111} facets.

It is worth noting that we used terminology “WO₃ doping” (instead of “WO₃ coating”) here because the materials were prepared by a “mixing and annealing” synthesis route and WO₃ segregated at surfaces spontaneously (driven by thermodynamics) in a chemical/thermodynamically equilibrium with the WO₃ doped bulk material.

3.3. Electrochemical Performances. The rate capability of LiMn_{1.5}Ni_{0.5}O₄ was enhanced significantly by WO₃ doping. Figure 5a showed the comparison of rate capabilities between undoped and doped specimens; it is worth noting that the changes in the discharge capacities in Figure 5a were mainly related to the changes in the testing rates, as different rates (and labeled in Figure 5a) were used in each cycle. The discharge capacities of the doped specimen were substantially higher than those of the undoped specimen at all rates. Specifically, the difference in the discharge capacities between doped and undoped specimens increased with the increasing rate from 1C to 25C. At the rate of 25C, undoped LiMn_{1.5}Ni_{0.5}O₄ only had an average discharge capacity of 16.6 ± 24.3 mAh g⁻¹; in contrast, the WO₃ doped LiMn_{1.5}Ni_{0.5}O₄ maintained an average discharge capacity of 101.3 ± 0.4 mAh g⁻¹, representing an ~500 % increase from the undoped specimen. Furthermore, at rates higher than 25C, the undoped specimen exhibited virtually no discharge capacity (< 1 mAh g⁻¹), but the WO₃ doped specimen still retained discharge capacities of 79.4 ± 5.6 mAh g⁻¹ at 45C, 46.9 ± 16.8 mAh g⁻¹ at 65C, and 13.8 ± 2.4 mAh g⁻¹ at 85C, respectively. Though a relatively low mass loading of 3.2 mg/cm² with 80% active material was used in this study, outstanding rate performance could still be achieved by optimizing the carbon content for a thick electrode.

The measured EIS spectra are shown in Figure 6 and fitted results are displayed in Table 2. Both the surface film and charge transfer resistances decreased from 156.0 and

47.0 Ω of the undoped specimen to 56.3 and 19.5 Ω of the doped specimen, which is consistent with the enhanced rate performance. The decrease of the charge transfer resistance (Figure 6) could be related to the increase of {110} surface facets that may be favorite for the surface charge and ion transfer.

Figure 7 displays the charge and discharge profiles of the doped and undoped specimens in the first cycle at C/10. The discharge capacity of the doped LiMn_{1.5}Ni_{0.5}O₄ is 132.6 mAh g⁻¹, which was higher than 116.9 mAh g⁻¹ of the undoped LiMn_{1.5}Ni_{0.5}O₄. The increase of discharge capacity of ~16 mAh g⁻¹ in the WO₃ doped specimen is mainly resulted from the extended Ni^{2+/4+} plateau (at ~ 4.6 and ~ 4.8 V) and Mn^{3+/4+} plateau (at ~ 4.0 V), indicating increased amounts of Ni^{2+/4+} and Mn^{3+/4+} redox couples.^{3,51} This observation is consistent with measured CV results shown in Figure 8. Specifically, the discharge capacity contributed by Mn^{3+/4+} (3.60 – 4.25 V) and Ni^{2+/4+} (4.25 – 4.8 V) in the doped specimen increased by 6.6 mAh g⁻¹ (from 10.4 to 17.0 mAh g⁻¹) and 10.8 mAh g⁻¹ (from 10.4 to 11.8 mAh g⁻¹), respectively, in comparison to those of the undoped LiMn_{1.5}Ni_{0.5}O₄. In addition, the coulombic efficiency of the first cycle was also improved from 78 % to 86 % with WO₃ doping, leading to a difference of the initial discharge capacity between undoped and doped specimens.

Figure 9 shows that the cycling performance was also enhanced by WO₃ doping. After 200 cycles at an elevated temperature of 55 °C and a relatively high rate of 1C, the discharge capacities were 111.7 mAh g⁻¹ and 88.9 mAh g⁻¹, respectively, for the doped and undoped specimens, respectively, corresponding to the capacity retentions of 87 % and 81 %, respectively. Hence, the significant improvement of the discharge capacity of doped specimen after 200 cycles was mainly attributed to the increase in the initial reversible capacity by WO₃ surface segregation.

Both the rate capability and cycling stability of the undoped specimen obtained in this work are comparable with those previously reported with the same/similar compositions and loading density of the active material.³⁰

3.4. Surface and Bulk Mn³⁺ Concentrations. XPS characterization of the Mn cations of the WO₃ doped specimen as a function of sputtering time (labeled in the graph) are shown in Figure 10(a), where a decrease in the binding energy represents a decrease of the cation valence. Specifically, the Mn 2p binding energy shifted from 641.8 eV at the surface to 640.3 eV in the bulk, suggesting that the average Mn valence at the surface is higher. In other words, the Mn³⁺ concentration on the surface was likely lower than that in the bulk. This result is different from the reported result of the undoped LiMn_{1.5}Ni_{0.5}O₄, where no shift in the Mn 2p binding energy after sputtering implies no change of the Mn valence at the surface.⁵⁰

For W, the distance between the two spin-orbit split doublets, W 4f_{5/2} and W 4f_{7/2}, is 2.15 eV and the area ratio is 4:3, both of which should be constants (as required by quantum mechanics). As shown in Figure 10(b), the W 4f_{7/2} peak was at ~34.7 eV in the XPS spectrum before

sputtering, and shifted by ~ 0.2 eV toward higher energies after sputtering. The lower peak energies suggest the presence of some W^{5+} on the surface, while the shift to a higher binding energy with sputtering time implies more oxidized states of tungsten (presumably W^{6+}) in the bulk phase. The more reduced valence state of W ($W^{6+} \rightarrow W^{5+}$) is likely correlated with more oxidized state Mn ($Mn^{3+} \rightarrow Mn^{4+}$) at the surface, which presumably helps to reduce the dissolution of Mn and improve the cycling stability.

In addition, the $Ni2p_{3/2}$ binding energy was ~ 854.2 eV, which is consistent with that reported in literature,^{50,52} and did not change with the sputtering time, indicating that the Ni valence does not change at the surface.

3.5. Neutron Diffraction. Figure 11 shows the neutron diffraction patterns for the undoped and WO_3 doped $LiMn_{1.5}Ni_{0.5}O_4$ specimens. The Rietveld refinement structure analysis was used to investigate the crystal structure of both samples.⁵³⁻⁵⁶ For long term annealing at 700 °C, $LiMn_{1.5}Ni_{0.5}O_4$ intended to become ordered structure, and the ordered structure is disturbed upon further higher heating.^{57,58} While these samples were annealed at 800 °C and cooled down quickly, both of them retained the fully disordered structure. Both patterns of undoped and doped specimens did not show any superstructure peaks arising from ordered structure ($P4_332$ space group) and both were successfully refined according to the $Fd\bar{3}m$ space group of a disordered structure; the corresponding reliable factors R_{wp} and R_p are 3.76% and 2.89% for the undoped specimen, and they were 3.36% and 2.47% for the doped specimen. The lattice constant was 8.1610 ± 0.0003 Å and 8.1662 ± 0.0002 Å, respectively, for the undoped and doped specimens, respectively. An increase in the lattice constant (0.0052 Å) after WO_3 doping was observed.

A secondary phase indexed with a rock-salt structure ($Fm\bar{3}m$ space group) was found in both patterns.⁵⁸ The impurity content was 0.82 ± 0.07 wt. % for the undoped specimen, and it was 1.83 ± 0.08 wt. % for the doped specimen. The influence of such small amounts of the impurity phase on the electrochemical performance may be negligible. WO_3 doping also decreased the oxygen occupancy from $100.6 \pm 1.8\%$ to $97.7 \pm 1.5\%$, which is consistent with the increased concentration of Mn^{3+} in the bulk phase, as well as the slight increase in the lattice constant.

4. DISCUSSION

4.1. The Change in Particle Morphology and Anisotropic Surface Segregation of W. Both undoped and doped specimens were prepared via the same procedure except for the addition of WO_3 . The resultant particle sizes (Figure 1) and BET surface areas of undoped and doped specimens were roughly identical within the measurement errors. Hence, it is reasonable to assume that WO_3 doping led to the change in particle morphology (Figure 1 and Figures 2(a) and 2(b)).

Furthermore, both XPS and AES have unequivocally demonstrated the surface segregation (adsorption) of W in the doped $LiMn_{1.5}Ni_{0.5}O_4$ particles. The surface energy

can be changed (reduced) with adsorption/segregation of W according to the well-known Gibbs adsorption equation:

$$\frac{d\gamma}{d\mu} = -\Gamma, \quad (1)$$

where γ is the surface energy, and μ and Γ , respectively, are the chemical potential and surface excess (total adsorption amount per unit area) of the adsorbing specie, respectively. Furthermore, AES depth profiles (Figure 4) shows that W prefers to segregate at the $\{110\}$ surface facets (with a greater Γ) that leads to a greater reduction of $\gamma_{\{110\}}$, in comparison with other facets. Consequently, the largest reduction in the relative surface energy in $\gamma_{\{110\}}$ (Table 1) leads to an increase in the fraction of the $\{110\}$ facets according to the well-established Wulff theory (construction) of the equilibrium crystal shape, which are consistent with experimental observations (Figure 1 and Figures 2(a) and 2(b)). Similarly, anisotropic segregation may also destabilize $\{311\}$ facets and change the relative ratios of other facets.

4.2. Mechanisms of the Improved Rate Capability.

The increase fraction of the $\{110\}$ (as well as $\{111\}$) facets may enhance the rate capability because $\{110\}$ (as well as $\{111\}$) facets exhibit more open channels for fast diffusion of Li^+ ions (Figures 2(c) - (e)). Though $LiMn_{1.5}Ni_{0.5}O_4$ is regarded as a 3D lithium diffusion material, the lithium diffusion rates perpendicular to different facets can be different, particularly at high charging and discharging rates. As shown in Figures 2(c) - (e), the $\{110\}$ facets provide the most open path for the lithium diffusion, followed by the $\{111\}$ facets and then the $\{100\}$ facets. Since the anisotropic surface segregation of W significantly increased the fraction of the $\{110\}$ facets (from $\sim 18\%$ to $\sim 43\%$) and moderately increased the fraction of the $\{111\}$ facets (from $\sim 44\%$ to $\sim 56\%$), as shown in Figure 1 and Figures 2(a) and 2(b), it improved the rate performance of the doped specimen (Figure 5).

We note that the bulk doping of W^{6+} can increase the concentration of Mn^{3+} in the bulk phase, which can also improve the rate capability via triggering cation disordering in $LiMn_{1-x}Ni_xO_4$ (being a possible alternative mechanism for the improved rate performance).⁷ However, if the structure is (already) disordered, further increasing the Mn^{3+} content in the disordered structure may not further improve the rate capability.⁷ In the current case, refined structures obtained from neutron diffraction (Figure 11) suggested both undoped and doped specimens are likely fully disordered. Hence, the increase of the Mn^{3+} concentration in the bulk phase of the doped specimen may not play a major role in improving the rate capability in the current case. In other words, the improved rate capability in the current case is mostly likely related to the anisotropic surface segregation of W and the associated particle morphological change of the Wulff shape with increased fractions of the favorite $\{110\}$, as well as $\{111\}$, facets.

In addition to improving the cycling stability (a subject that will be discussed further in the next section), the improved the chemical stability of the W-segregated sur-

faces can also improve the rate capability via suppressing the rapid increase of the surface resistance, as evident directly in EIS results (Figure 6).

4.3. Mechanisms of the Increased Discharge Capacity and Cycling Stability. The neutron diffraction showed evidence of increased oxygen vacancy concentration, as well as an increased lattice constant, with the W doping, implying an increase of the Mn^{3+} concentration in the bulk phase of the WO_3 doped $LiMn_{1.5}Ni_{0.5}O_4$ specimen. It is known that an increased Mn^{3+} content can contribute to an increasing specific capacity at the voltage plateau ~ 4 V (Figure 7).⁹

It is also known that the existence of Mn^{3+} on the surface can trigger disproportionation of Mn^{3+} cations to Mn^{2+} and Mn^{4+} cations, which can promote the dissolution of Mn^{2+} in the electrolyte and subsequently capacity losses; subsequently, the Mn^{3+} concentration on the surface can increase further during electrochemical cycling, which can further promote the dissolution of Mn^{2+} , resulting in poor cycling stability.⁵⁹

However, our cycling stability results (Figure 9) clearly show that the doped specimen (that presumably have a high Mn^{3+} content) had a better cycling stability than the undoped specimen. It is likely related to the W surface segregation (along with the partial reduction of W^{6+} to W^{5+} at the surface; Figure 10(b)), which likely decreases the Mn^{3+} concentration at the surface, thereby enhancing the cycling stability via reducing the disproportionation of Mn^{3+} cations and suppressing the Mn^{2+} dissolution.

It is interesting to note that a most recent report by Kuppan *et al.* suggested “superior kinetics of (100) facets at the vertices of truncated octahedral particles” can promote anisotropic (preferential) delithiation that cause degradation due to strain-induced cracking in larger (micron-sized) particles⁶⁰. In our case, WO_3 segregation increased the fractions of both {110} and {100} planes but reduced the fraction of {100} facets, which could also be beneficial and contributed to the increased cycling stability.

In summary, W^{6+} doping in the bulk phase introduces oxygen vacancies and increases the bulk Mn^{3+} concentration, which can enhance the specific discharge capacity. The surface segregation and partial reduction of W at surface reduce the surface Mn^{3+} concentration, which may increase the cycling stability by suppressing the formation and dissolution of Mn^{2+} at the surfaces (along with the possible beneficial effects of the surface segregation of W).

This beneficial surface configuration (with W segregation and partial reduction, along with suppressed Mn^{3+} concentration at/near the surface) that spontaneously formed during mixing and annealing in the WO_3 doped $LiMn_{1.5}Ni_{0.5}O_4$ specimen (as the thermodynamically equilibrium surface state) is a 2-D surface phase (also called “complexion”⁶¹⁻⁶²) that can be considered as naturally-formed surface protective “coatings,” akin to those nanoscale surface amorphous films⁶³⁻⁶⁶ or nitrated surfaces⁶⁷ observed in prior studies that also improved both the

rate capabilities^{63,64,66,67} and cycling stabilities⁶³ of a range of battery cathode^{63,64,66} and anode⁶⁷ materials.

5. CONCLUSIONS

Minor WO_3 doping, which can be achieved by a facile ball milling and annealing process, can substantially enhance the electrochemical performance of $LiMn_{1.5}Ni_{0.5}O_4$ and, in this study, we depict the underlying mechanisms of improved ionic transport and CEI stability via combining neutron diffraction, an Auger electron nanoprobe, X-ray photoelectron spectroscopy, and other characterizations.

While the W^{6+} doping in the bulk phase leads to extra oxygen vacancies and increase of the bulk Mn^{3+} concentration, the surface segregation and partial reduction of W reduce the surface Mn^{3+} concentration, which improves the cycling stability via reducing the surface disproportionation of Mn^{3+} cations and suppressing the subsequent dissolution of Mn^{2+} cations. Furthermore, anisotropic surface segregation of W changes the relative surface energies of different crystalline facets and subsequently the Wulff shape of the crystalline particles, which improves the rate capability via increasing the areas of {110} and {111} facets with more open channels for fast lithium ion diffusion. For example, the discharge capacity at 25C can be increased by $\sim 500\%$ by 1 vol. % WO_3 doping.

In a broader context, this study has demonstrated the anisotropic surface segregation (or formation of 2-D surface phases⁶³⁻⁶⁷ in general) can be utilized as a facile method to control the particle morphology thermodynamically, as well as modify surface properties (i.e., increase the electrochemical stability and surface transport rates in this particular case), to significantly improve the rate capability, cycling stability, and potentially other properties of battery materials, as well as a broad range of other functional materials for energy-related applications, such as supercapacitors⁶⁸ and photocatalysts^{69,70}.

Table 1. Relative surface energies of the undoped and WO_3 -doped $LiMn_{1.5}Ni_{0.5}O_4$ specimens that matched the experimentally observed Wulff shapes.

	undoped	WO_3 -doped
$\gamma_{\{111\}}/\gamma_{\{100\}}$	0.94	0.69
$\gamma_{\{110\}}/\gamma_{\{100\}}$	1.04	0.76
$\gamma_{\{311\}}/\gamma_{\{100\}}$	1.05	-

Table 2. Fitted surface film and charge transfer resistances from EIS.

Specimen	R_f (Ω)	R_{ct} (Ω)
undoped	156.0 ± 0.7	47.0 ± 1.9
WO_3 doped	56.3 ± 0.3	19.5 ± 1.0

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Author Contributions

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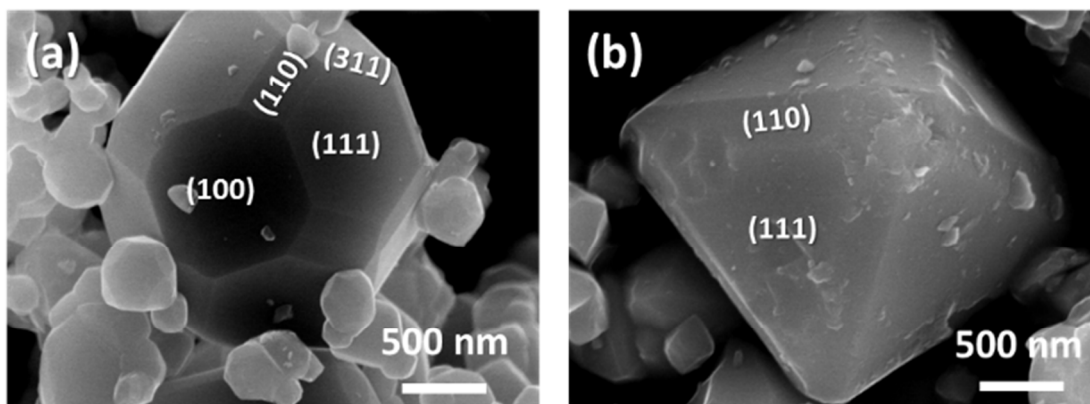


Figure 1. Representative SEM images of the (a) undoped and (b) 1 vol. % WO_3 doped $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ specimens, where were prepared by annealing high-energy ball milled powders at 800 °C for 4 h.

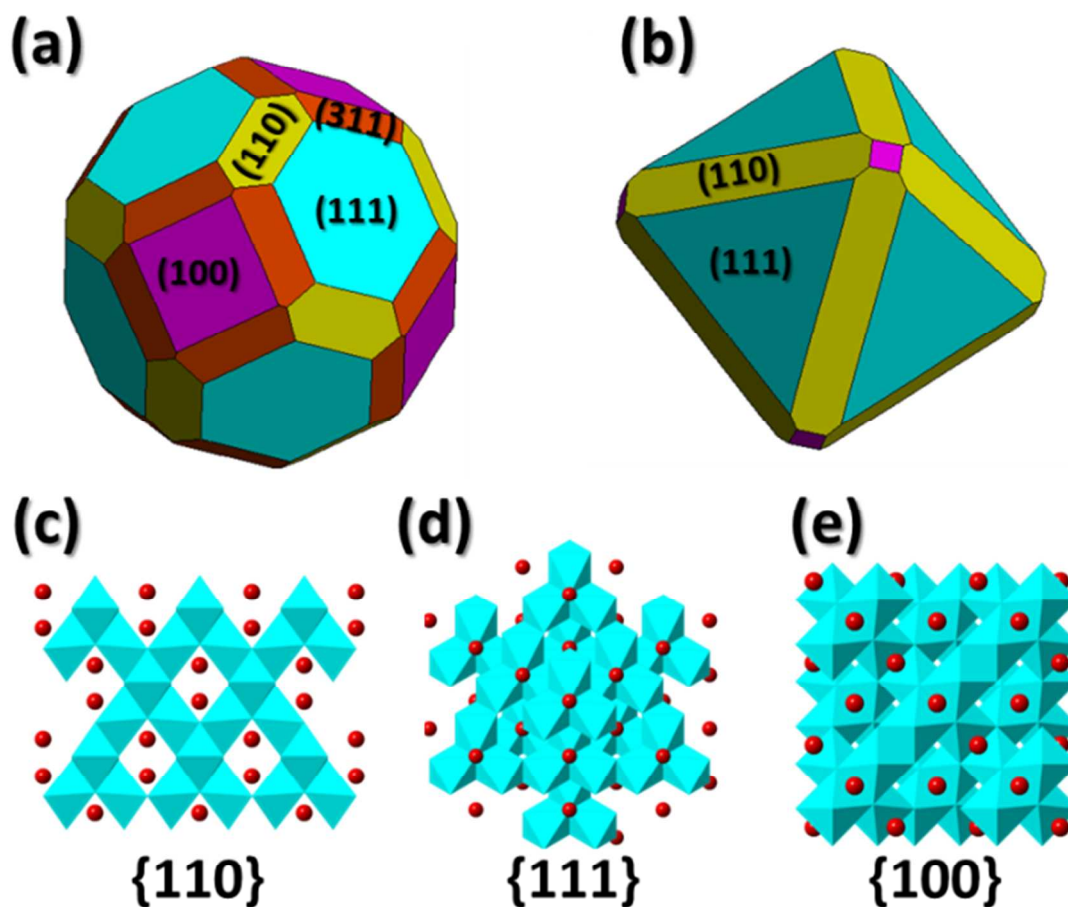


Figure 2. Calculated Wulff shapes of the (a) undoped and (b) WO_3 doped $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ that matched the experimentally observed particle morphologies shown in Figure 1 and schematics of the Li ion diffusion channels on (c) {110}, (d) {111} and (e) {100} facets, respectively. The relative surface energies that produced these Wulff shapes are listed in Table 1.

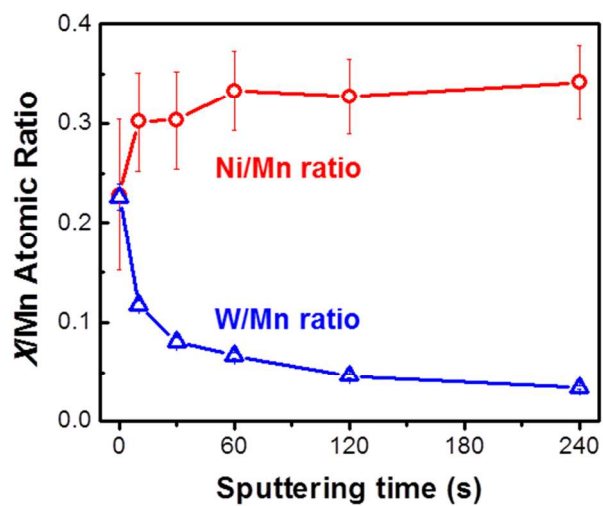


Figure 3. Atomic ratios of W/Mn and Ni/Mn vs. sputtering time curves measured from XPS.

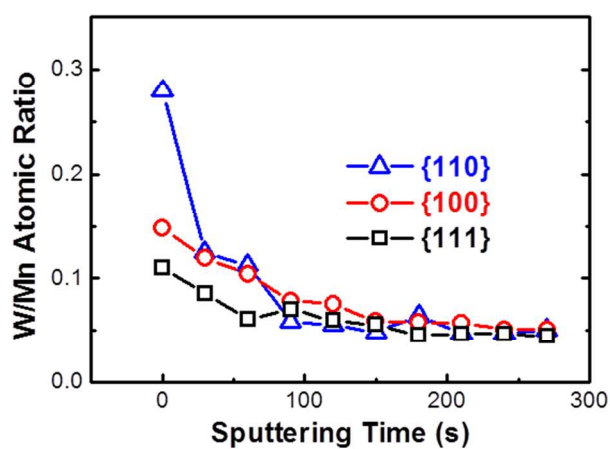


Figure 4. Atomic ratios of W to Mn vs. sputtering time curves measured by AES on three different surface facets of {110}, {100} and {111}. The {110} facet has the highest level of W segregation, which is consistent with the observed largest reduction in the relative surface energy in the WO_3 doped specimen (Table 1).

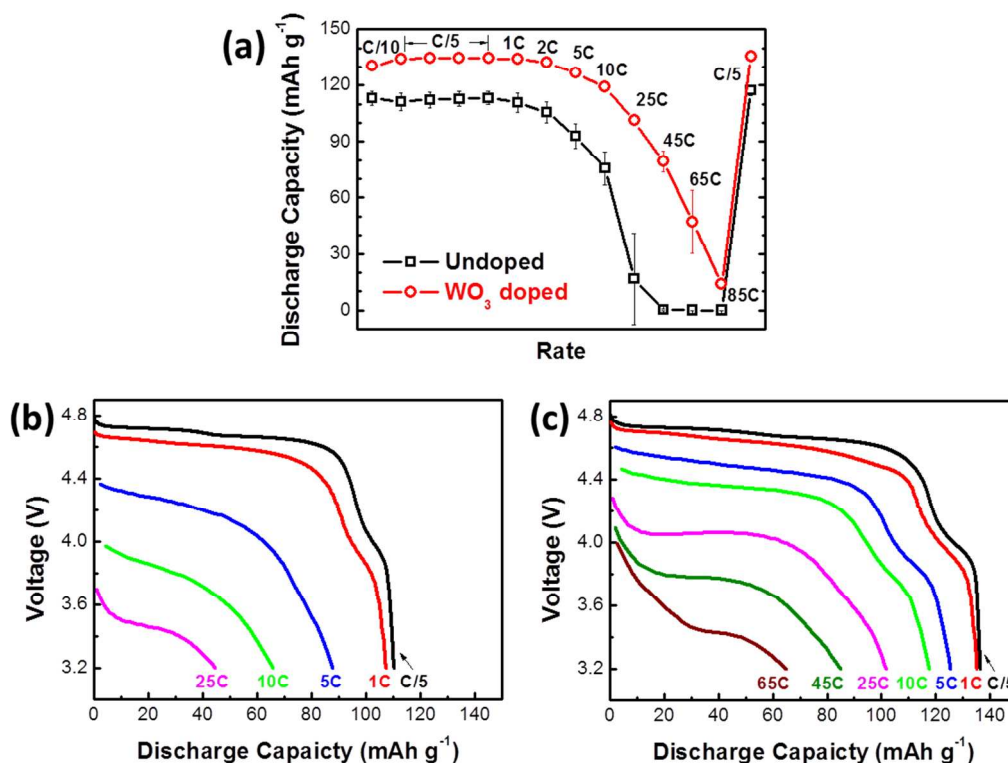


Figure 5. (a) Comparison of rate performance of undoped and WO_3 doped $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ specimens and discharge curves of (b) undoped specimen and (c) WO_3 doped $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ specimens. Three coin cells were made and tested for each specimen. The means are presented in the graph and error bars represent \pm one standard deviations. All cells were first charged and discharged at C/10 for 1 cycle and C/5 for 4 cycles to reach steady states and subsequently charged at C/5 and discharged at various rates (labeled in the graph) at room temperature

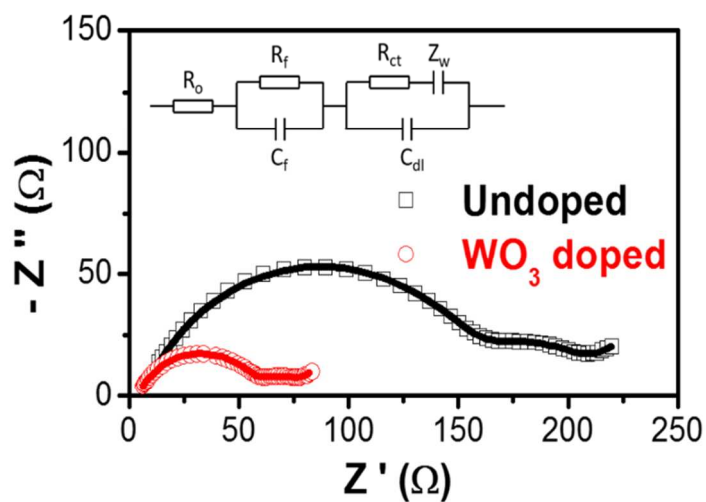


Figure 6. Measured EIS spectra of the undoped and WO_3 doped (red circles) $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ specimens. The inset is an equivalent circuit. The fitted surface film and charge transfer resistances are given in Table 2.

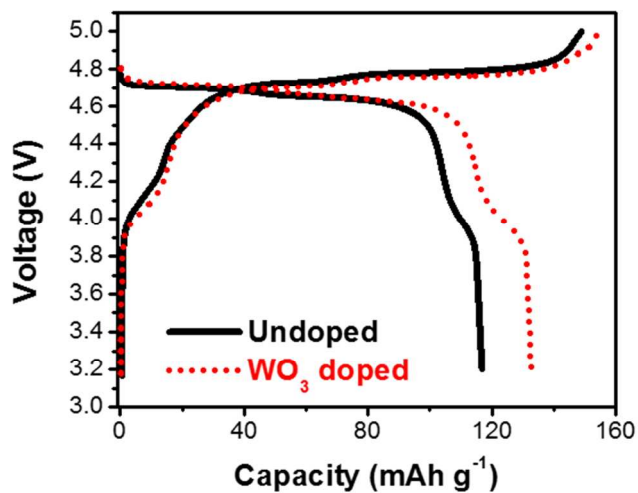


Figure 7. Measured charge/discharge curves for the undoped and WO_3 doped $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ specimens. Both specimens were charged and discharged at a low rate of 0.1C at room temperature.

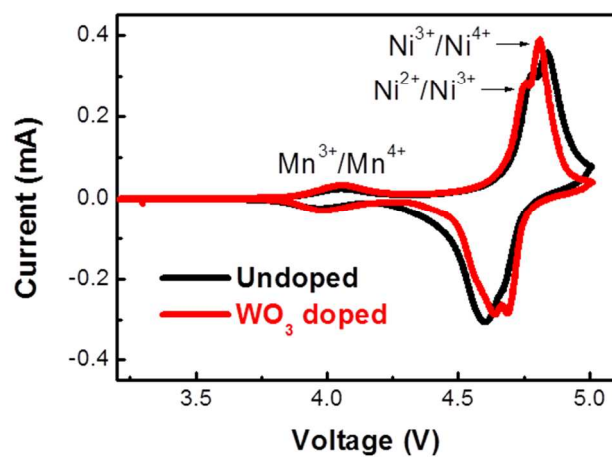


Figure 8. Measured CV curves of the undoped and WO_3 -doped $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ specimens.

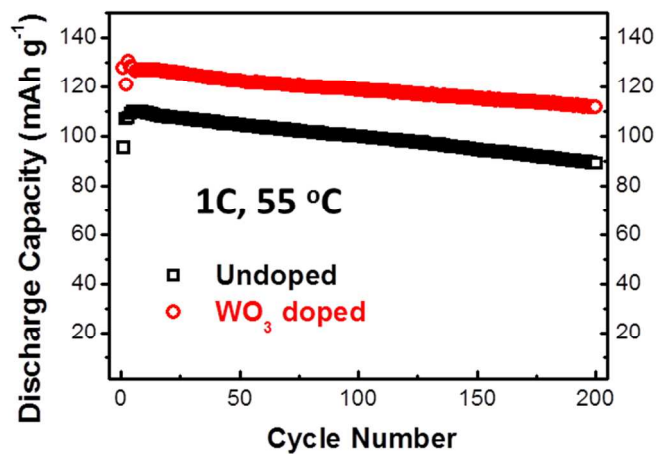


Figure 9. Cycling stability results of the undoped and WO₃-doped LiMn_{1.5}Ni_{0.5}O₄ specimens tested at an elevated temperature of 55 °C with a relatively high charge and discharge rate of 1C as an accelerated test.

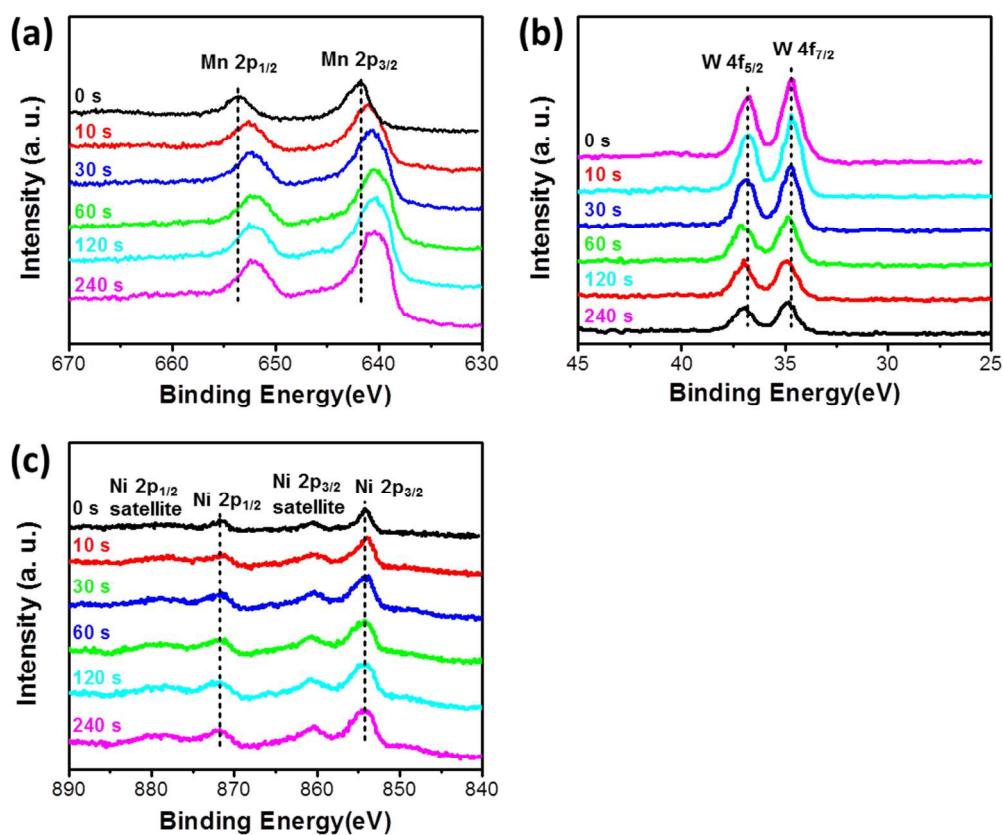
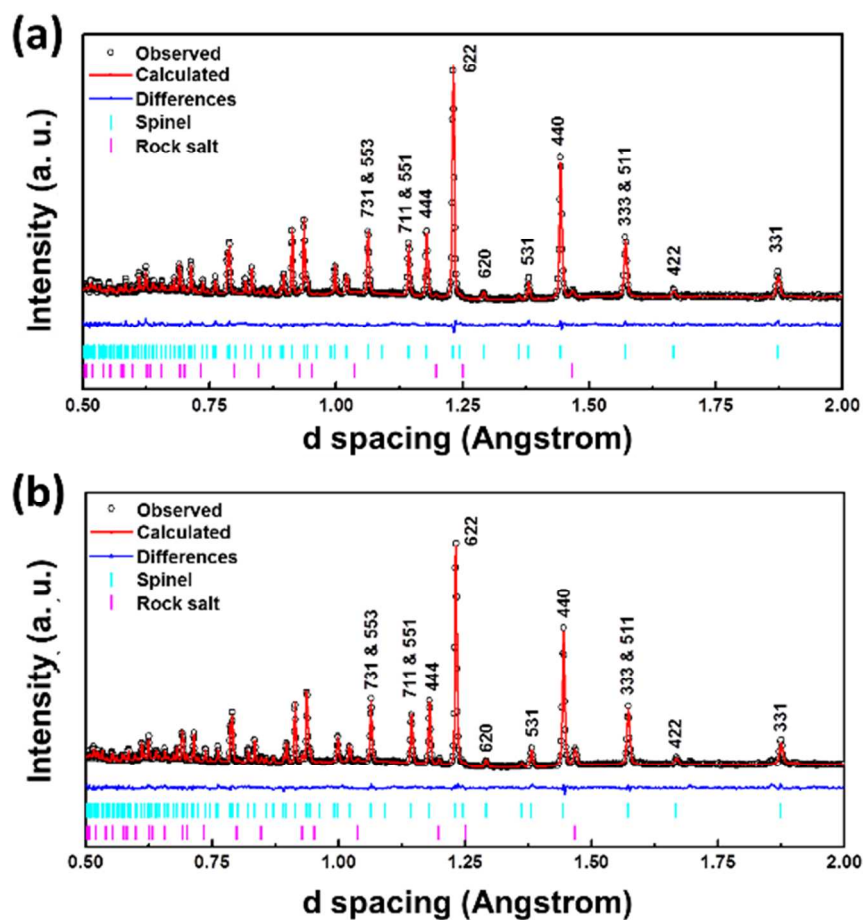


Figure 10. XPS results of (a) Mn, (b) W, and (c) Ni binding energy shifts after sputtering for different times (labeled in the graphs) for the 1 vol. % WO₃ doped LiMn_{1.5}Ni_{0.5}O₄ specimen.



32 **Figure 11.** Neutron powder diffraction patterns of the (a) undoped and (b) 1 vol. % WO_3 doped $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ specimens.

Graphic Abstract for Table of Contents

Spontaneous and anisotropic surface segregation of W^{x+} cations alters the Wulf shape and enhances the ion transport as well as the surface stability.

