Enhancing the electrochemical performance of Li-rich layered oxide \( \text{Li}_{1.13}\text{Ni}_{0.3}\text{Mn}_{0.57}\text{O}_2 \) via \( \text{WO}_3 \) doping and accompanying spontaneous surface phase formation

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HIGHLIGHTS

- \( \text{WO}_3 \) doping improves the \( \text{Li}_{1.13}\text{Ni}_{0.3}\text{Mn}_{0.57}\text{O}_2 \) performance via forming a surface phase.
- The surface phase forms spontaneously via a facile mixing and annealing route.
- The surface phase has distinct structure, composition, and valence state.
- The discharge capacity is increased by \( \sim 13\% \) at \( \text{C}/20 \) and by \( \sim 200\% \) at \( 40\text{C} \).
- The spontaneously-formed surface phase also improves the cycling stability.

ABSTRACT

\( \text{WO}_3 \) doping and accompanying spontaneous formation of a surface phase can substantially improve the discharge capacity, rate capability, and cycling stability of Co-free Li-rich layered oxide \( \text{Li}_{1.13}\text{Ni}_{0.3}\text{Mn}_{0.57}\text{O}_2 \) cathode material. X-ray photoelectron spectroscopy, in conjunction with ion sputtering, shows that W segregates to the particle surfaces, decreases the surface Ni/Mn ratio, and changes the surface valence state. High-resolution transmission electron microscopy further suggests that W segregation increases surface structural disorder. The spontaneous and simultaneous changes in the surface structure, composition, and valence state represent the formation of a surface phase (complexion) as the preferred surface thermodynamic state. Consequently, the averaged discharge capacity is increased by \( \sim 13\% \) from 251 to 284 mAh g\(^{-1}\) at a low rate of \( \text{C}/20 \) and by \( \sim 200\% \) from 30 to 90 mAh g\(^{-1}\) at a high rate of \( 40\text{C} \), in comparison with an undoped specimen processed under identical conditions. Moreover, after 100 cycles at a charge/discharge rate of 1C, the \( \text{WO}_3 \) doped specimen retained a discharge capacity of 188 mAh g\(^{-1}\), being 27\% higher than that of the undoped specimen. In a broader context, this work exemplifies an opportunity of utilizing spontaneously-formed surface phases as a scalable and cost-effective method to improve materials properties.

1. Introduction

Li- and Mn-rich layered oxides \( x\text{Li}(\text{Li}_{1/3}\text{Mn}_{2/3})\text{O}_2(1-x)\text{LiMO}_2 \) (that can alternatively be expressed as \( x\text{Li}_2\text{MnO}_3(1-x)\text{LiMO}_2 \) \( 0 < x < 1 \); \( M = \text{Mn}, \text{Ni}, \text{Co} \)) are promising candidates of next-generation cathode materials for lithium ion batteries due to their high specific capacity of \( > 280 \text{ mAh g}^{-1} \); with an average discharge voltage of \( \sim 3.6 \text{ V} \), this capacity corresponds to an energy density of \( > 1000 \text{ Wh kg}^{-1} \) [1–3]. The Li-rich layered oxides are also low cost and environmentally friendly due to the reducing of Co content in their composition. However, the practical applications of these layered oxides are still hindered by the irreversible capacity loss in the first cycle, the subsequent poor cycling stability, the low rate capability, and the voltage fading [4–6].

It is interesting to note that the above-mentioned challenging electrochemical properties can be highly affected by the surface properties of the Li-rich layered oxides. The significant irreversible capacity loss in the first cycle is believed to be resulted from formation of oxygen vacancies [7,8] and/or the occupation of lithium sites by transition metal ions on the surfaces (when the cathode is charged over 4.4 V) [9], which subsequently triggers an irreversible surface phase-like transition from the layered structure to a spinel-like structure [1,9–11]. Moreover, the rate capability can also be explained by the above-mentioned surface structure/chemistry changes as the lithium diffusion path could be partially blocked by the occupancy of lithium layer sites by transition...
metal cations [5,6,9,12-17]. Hence, surface modifications could be an effective way to improve electrochemical performance of Li-rich layered cathode materials. Here, we explore the possibility of utilizing WO3 segregation induced formation of a surface phase (also known as “complexion” [18,19]) with structure and chemistry that are markedly different from those inside a bulk phase as a spontaneous surface modification method to improve the properties.

Recently, Sathiya et al. reported that Ru(4d) substitution of M(3d) in Li2M03 in the bulk phase can significantly relieve the first-cycle irreversible capacity loss, voltage fade and cycling decay [20–22]. A density functional theory calculation suggested that a strong covalent character of the M-O bond would likely promote reversible high capacity of Li-rich layered oxides, which can be achieved by substituting M(3d) with M(4d, 5d) metal cations [23] because M(4d, 5d)-O are stronger covalent bonds that enhance the structural stability of Li2M03 and reduce voltage fade during cycling. However, the rate capability of M(4d, 5d) substituted Li-rich layered oxides are generally poor (< 50 mAh g−1 at 5C) and these materials are more expensive due to the use of noble metals. Thus, simultaneous achieving high discharge capacity, stable voltage during cycling, and low cost remains a major challenge.

In this study, we used a small amount of WO3 (a 5d transition metal oxide) to “surface dope” a Li-rich layered oxide. WO3 is selected because it has a low surface free energy and tend to spread spontaneously on the surfaces of other oxides (such as TiO2 and ZrO2) during annealing (i.e., segregate or adsorb at the surface thermodynamically that may also change the surface structure and other chemistry, e.g., the critical surface Ni/Mn ratio in this case); such surface phases can form spontaneously as the thermodynamically-preferred surface states via a facile and cost-effective “mixing and annealing” procedure that is employed widely to make so-called “supported oxide catalysts” or “monolayer catalysts” in the petroleum and chemical industries [24–26]. As a result, these WO3 doped specimens exhibit improved rate capabilities (e.g., retaining a capacity of 90 mAh g−1 at a high discharge rate of 40C that represent a 200% improvement from the undoped specimens) and cycling stability as well as reduced voltage fading, in comparison with an undoped benchmark specimen prepared using the identical ball milling and annealing procedure. The improvements are attributed to an appreciable surface chemistry change, i.e., W segregation along with a reversed surface Ni/Mn ratio in comparison with undoped specimen, as revealed by X-ray photoelectron spectroscopy (XPS) in conjunction with ion sputtering, accompanying with simultaneous surface structural disordering and surface valence change, induced by as low as ~1 vol % WO3 doping.

2. Experimental

The Li-rich prepared by coprecipitation method which is described in our previous publications [4,6]. To prepare 1 vol % WO3 doped Li1.13Ni0.3Mn0.57O2 (where the volume percentage was calculated based on the molar volumes before mixing and the overall chemical composition) to Li2M03 in the bulk phase can significantly relieve the first-cycle irreversible capacity loss, voltage fade and cycling decay (20–22). A density functional theory calculation suggested that a strong covalent character of the M-O bond would likely promote reversible high capacity of Li-rich layered oxides, which can be achieved by substituting M(3d) with M(4d, 5d) metal cations because M(4d, 5d)-O are stronger covalent bonds that enhance the structural stability of Li2M03 and reduce voltage fade during cycling. However, the rate capability of M(4d, 5d) substituted Li-rich layered oxides are generally poor (< 50 mAh g−1 at 5C) and these materials are more expensive due to the use of noble metals. Thus, simultaneous achieving high discharge capacity, stable voltage during cycling, and low cost remains a major challenge.

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X-ray diffraction (XRD) was carried out on a diffractometer using Cu Kα radiation (λ = 1.5418 Å) operating at 40 kV and 40 mA with a step size of 0.02° and a step time of 1 s. XRD data analysis was carried out by Rietveld refinement method using FullProf software. Particle sizes and morphologies were characterized using a FEI XL30 scanning electron microscope (SEM).

The surface composition and depth profile of the WO3 doped Li1.13Ni0.3Mn0.57O2 particles were characterized by XPS. The XPS experiments were carried out by using a Kratos AXIS ULTRA DLD XPS system equipped with an Al Kα monochromated X-ray source and a 165 mm mean radius electron energy hemispherical analyzer. 4 keV Ar ion beam was used for sputtering. The sample current was ~4 μA. Depth profile data were collected after sputtering time of 2 s, 5 s, 10 s, 30 s, and 90 s. The XPS characterization provided the overall surface composition and depth profiles that are averages of many different particles and crystalline facets. All XPS measurements were collected with a 300 mm × 700 mm spot size using a charge neutralizer during acquisition. Survey scans were collected with a 1.0 eV step size, and were followed by high resolution scans with a step size of 0.05 eV for Mn 3p, Ni 2p, and W 4d region. Bonding Energies were calibrated using C 1s peak of 284.6 eV.

Particle surfaces were characterized by high-resolution transmission electron microscopy (HRTEM) using a FEI Titan 80–300 microscope at 300 kV. HRTEM specimens were prepared by dispersing powders ultrasonically in acetone and dropping a small amount of the suspension onto carbon coated copper grids; the specimens were then dried overnight in a desiccator. Minimum exposure was used during HRTEM to reduce electron beam damage.

To prepare cathodes, 80 wt. % active materials, 15 wt. % carbon black (MITI, 5 wt. % PVDF (MITI), 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 area density of dried electrode coating is ~2.5 mg cm−2. Half cells were made with a cathode electrode, a metal Li chip (MITI, 99.9%) as the anode, 1 M LiPF6 in EC/DMC 1:1 vol electrolyte LP 30, BASF), C480 separator (Celgard), and 2032 coin cell cases (SS304, MITI).

Electrochemical cycling tests were carried out on an Arbin 2143 tester. The rate performance of specimens was tested at the discharge rates of C/20, C/10, C/2, 1C, 2C, 5C, 10C, 20C, 40C, 60C, 80C, 100C, and C/10 sequentially (1C equates to 250 mA h g−1; 1 cycle at each discharge rate) with a constant charge rate of C/10 at room temperature. The cycling stability of Li1.13Ni0.3Mn0.57O2 specimens were measured at a constant charge and discharge rate of 1C between 2.0 V and 4.8 V at room temperature. Electrochemical impedance spectroscopy (EIS) was performed using a Solartron 1287A/1255B analyzer measured from 1 MHz to 0.05 Hz at 10 mV. Cells after the testing were charged to 4.8 V at C/10 and kept for 10 h for subsequent impedance measurements. The EIS data were fitted with the ZView software in the frequency range of 10−6 to 10−Hz.

3. Results

No obvious difference of particle morphology between undoped and WO3 doped Li1.13Ni0.3Mn0.57O2 was observed, as shown in Fig. 1. Both specimens have similar agglomerated secondary particles (Fig. 1(a) and (c)). The measured primary particle sizes are 89.8 ± 36.9 nm for the undoped specimen and 88.2 ± 30.5 nm for the WO3 doped specimen, respectively; the representative SEM images are shown in Fig. 1(b) and (d). The difference in the measured particle sizes is within the range of measurement errors and negligible. Moreover, the primary particles of both undoped and doped specimens have similar round morphology without observed faceting. Hence, a fair comparison study of
electrochemical performance between undoped and doped specimens can be conducted without significant effects of the particle size and morphology.

XRD results reveal only Li$_{1.13}$Ni$_{0.3}$Mn$_{0.57}$O$_2$ peaks in both undoped and WO$_3$ doped specimens, as shown in Fig. 2. All peaks are indexed to the $R3m$ space group that corresponds to the LiMO$_2$ structure, except for the superstructure peaks between 20 and 30° which are associated with a honeycomb ordering of Li, Ni, and Mn in the transition metal layers [9]. The XRD patterns were refined by the Rietveld method. The lattice constants of the undoped Li$_{1.13}$Ni$_{0.3}$Mn$_{0.57}$O$_2$ were obtained as: $a = 2.8654(2)$ Å and $c = 14.257(2)$ Å, while the WO$_3$ doped Li$_{1.13}$Ni$_{0.3}$Mn$_{0.57}$O$_2$ has lattice constants of $a = 2.8667(2)$ Å and $c = 14.262(3)$ Å.
c = 14.262(2) Å. The slight increases in the lattice parameters of the WO₃ doped specimen indicates the W is successfully doped into the Li-rich.

A comparison of Fig. 3(a) and Fig. 3(b) shows that the WO₃ doped specimen has a higher initial discharge capacity tested at C/20 and room temperature. On one hand, the first-cycle charge and discharge capacities for the undoped specimen are 363 and 251 mAh g⁻¹, respectively, with a coulombic efficiency of 69%, which are consistent with the typical values reported in prior studies [10,27,28]. On the other hand, the WO₃ doped specimen has charge and discharge capacities of 350 and 284 mAh g⁻¹, respectively, with an improved coulombic efficiency of 81% (representing a 12% increase from that of the undoped specimen). Correspondingly, the reversible discharge capacity is increased by 33 mAh g⁻¹ or 13% with as low as 1 vol % WO₃ doping, in comparison with that of the undoped specimen.

The WO₃ doping improves the rate capability significantly. With WO₃ doping, the discharge capacity is increased from 164 to 198 mAh g⁻¹ (by ~21%) at 5C, and from 30 to 90 mAh g⁻¹ (by ~200%) at 40C on an average as shown in Fig. 3(c). The cells after the rate performance test were characterized by electrochemical impedance spectroscopy (EIS) and the spectra are shown in Fig. 3(d). The EIS results have revealed that the WO₃ doped specimen has smaller total resistance than that of the undoped specimen. After WO₃ doping, the charge transfer resistance decreases from 66.6 Ω to 18.9 Ω, while the surface film resistance in fact increases from 3.5 Ω to 13.3 Ω; thus, the total resistance decreases from 70.1 Ω to 32.2 Ω by 54% with WO₃ doping.

The cycling stability is also enhanced by WO₃ doping, as shown in Fig. 4. The WO₃ doped specimen maintains a discharge capacity of 188 mAh g⁻¹ after 100 cycles at a relatively high charge and discharge rate of 1C, which is about 27% higher than that of the undoped specimen (Fig. 4(a)). This improved cycling stability is comparable with some of the best reported performance in literature [12,27]. Furthermore, the voltage fading is also mitigated significantly by minor WO₃ doping, which is in Fig. 4(b). Consequently, an energy density of ~664.6 Wh kg⁻¹ is achieved after 100 cycles at 1C, which represents a ~30% improvement from the undoped specimen (Fig. 4(c)).

Fig. 3. The rate performance of undoped and doped specimens. Charge/discharge curves of (a) undoped and (b) WO₃ doped Li₁.13Ni₀.3Mn₀.57O₂ at various rates. The black lines represent the initial charge/discharge curves tested at C/20 (1C = 250 mAh g⁻¹) and color lines show subsequent discharge curves at various rates labeled in the graph (with a constant charge rate of C/5). (c) Rate capabilities of undoped (red circles) and WO₃ doped (blue triangles) Li₁.13Ni₀.3Mn₀.57O₂. The fittings were based on the equivalent circuit shown in the inset. All tests were performed at room temperature in a voltage window of 2.0–4.8 V. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
XPS in conjunction with sputtering also shows the surface segregation (enrichment) of W (Fig. 5(c)), while W is also present inside the bulk phase. Furthermore, the surface segregation of W leads to a decrease of Ni/Mn ratio on the surface; interestingly, the surface of the undoped specimen is enriched with Ni, whereas the surface of the WO₃ doped specimen is enriched of Mn.

This work exemplifies an opportunity to use spontaneously-formed surface phases (with simultaneous and spontaneous changes in surface structure/disorder, composition and valence towards the thermodynamically preferred surface state), along with bulk doping, as facile and scalable method to enhance the electrochemical performance of cathode materials.

4. Discussion

Summarizing the results shown in Fig. 5, we know that (1) Ni
segregates at the surfaces in the undoped specimen; (2) W segregates at the surfaces with a surface reduction (W$^{6+}$ inside the bulk phase vs. predominately W$^{5+}$ at the surface), and (3) the surface segregation of W suppresses the surface segregation of Ni to increase (reverse) the relative surface Ni/Mn ratio (w.r.t. that in the bulk phase) in comparison with the undoped surface (Fig. 5(c) noting the absolute surface Mn cation ratio may not increase because of surface enrichment of W). Furthermore, HRTEM images (Fig. 7) show that the surfaces of WO$_3$ doped specimen is more disordered than that of the undoped specimen.

Noting that we carefully monitored the change of surfaces during the HRTEM imaging and we did not observe the any amorphization or other significant damages during the observation so that the disordering was not caused by the beam irradiation under HRTEM.

Such a unique surface configuration in the WO$_3$ doped Li$_{1.13}$Ni$_{0.3}$Mn$_{0.57}$O$_2$ formed spontaneously (during annealing) as the equilibrium surface thermodynamic state with its own thermodynamically-determined chemistry (composition and valence states; Fig. 5) and structure (more disordered; Fig. 7) that are markedly different from those of the underneath bulk phase. Thus, the thermodynamically-determined surface state can be considered as a 2-D surface phase (also called “complexion” to differentiate it from a thin surface layer/coating of a bulk phase [19,34,35]), akin to those nanoscale surface amorphous films (SAFs) [18,36–38] and other surface complexions [39] previously observed to form in a few other battery materials that improved the rate capabilities [18,36,38–40] and cycling stabilities [18]. In contrast to the prior cases of phosphate-based, nanometer-thick SAFs that are discrete in HRTEM, the 2-D surface phase observed in the WO$_3$ doped Li$_{1.13}$Ni$_{0.3}$Mn$_{0.57}$O$_2$ appears to have more gradually-varying profiles of composition and structures (Figs. 3 and 4). Nonetheless, this surface phase observed in the WO$_3$ doped Li$_{1.13}$Ni$_{0.3}$Mn$_{0.57}$O$_2$ in this study can also contribute to improved rate capability and cycling stability as well as reduced charge transfer and voltage fading (similar to other types of surface phases [18,36,38–40]). Specifically, several possible benefits of this surface phase can be discussed.

In the first charge, the region below ~4.4 V is usually attributed to a reversible Ni$^{2+}$/Ni$^{4+}$ oxidation, corresponding to the lithium extraction from the lithium layer [5]. The plateau above 4.4 V is attributed to a partially reversible anionic O$^{2-}$/O$^{4-}$x and irreversible oxygen loss, corresponding to the lithium extraction from the lithium layer and transition metal layer with oxygen vacancy formation, which will inevitably lead to the migration of transition metal cations from the transition metal layer to the lithium layer [3,12,41]. Consequently, there is always a high irreversible capacity observed in the first cycle of Li-rich. A prior study showed that in the Li$_{1}$Ru$_{1}$Mn$_{1.4}$O$_3$ with Ru partial substitution of Mn, a Ru$^{5+}$/Ru$^{4+}$ redox was accompanied by the O$^{2-}$/
O\(^-\) redox processes [22]. It is also suggested that M(4d, 5d)-O bonds are stronger than those of M(3d)-O and can enhance the M-O covalency and structural stability of Li\(_2\)M\(_3\)O\(_7\) [23]. Likewise, W doping in Li\(_{1.13}\)Ni\(_{0.3}\)Mn\(_{0.57}\)O\(_2\) phase (as well as the spontaneous formation of WO\(_3\) segregation induced surface phase) may also have similar stabilization effects as those of Ru. Specifically, W has a higher formation enthalpy of W-O (~598–632 kJ mol\(^{-1}\)) than that of Mn-O (~402 kJ mol\(^{-1}\)) and Ni-O (391.6 kJ mol\(^{-1}\)), which may strengthen the M-O covalency and reduce oxygen release from breaking M-O bonds (via promoting reversible M-O\(^2+/M-O^2\) redox instead of oxygen loss from lattice structure) [20]. In this work, the first cycle irreversible capacity of Li-rich is significantly reduced from 112 mAh g\(^{-1}\) to 66 mAh g\(^{-1}\) by W doping. At the same time, the reversible discharge capacity of W doped specimen shows 33 mAh g\(^{-1}\) enhancement than the undoped specimen. All these facts suggest that the W doping may suppress the irreversible oxygen loss and facilitate the reversible O\(^2+/O^-\) redox processes, which could help to maintain the structural stability of Li-rich and further improve the cycling performance.

The low oxidation state cation (Ni\(^{2+}\)) migration to the lithium layer blocks the lithium diffusion during electrochemical charge and discharge, which leads to poor rate capability. The existence of oxygen vacancy facilitates this cation migration [7]. In this work, it appears that WO\(_3\) doping and surface segregation decreases the Ni content at the surface. As a consequence, the transition metal migration might be suppressed, results in an improved rate performance of Li-rich [3].

5. Conclusions

As low as 1 vol % WO\(_3\) doping can simultaneously enhance the reversible capacity in the first cycle, the rate capability, and the cycling stability, as well as reduce voltage fading, of the Li\(_{1.13}\)Ni\(_{0.3}\)Mn\(_{0.57}\)O\(_2\) cathode material. XPS (with depth profiling) and HRTEM characterizations showed that W segregates at the particle surfaces, occurring concurrently with a surface reduction of W, a change of surface Ni/Mn ratio, and surface structural disordering. Consequently, a thermodynamically-preferred surface structure forms spontaneously, which can be considered as a surface phase or complexion. The spontaneous formation of this surface phase benefits both cycling stability and rate capability. It is further suggested that the stronger covalent character of the W-O bond could alleviate oxygen loss on the surface and the migration of the transition metal cations.

This work suggests, and subsequently exemplifies, a new strategy of improving the performance of Li-rich layered oxide and potentially other cathode and anode materials via a facile and cost-effective “mixing and annealing” procedure to enable their uses in the next-generation batteries throug the spontaneous formation of thermodynamically-preferred surface phases.

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