Depolarization of Li-rich Mn-based oxide via electrochemically active Prussian blue interface providing superior rate capability

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Abstract

The high-rate cyclability of Li-rich Mn-based oxide (LMO) is highly limited by the electrochemical polarization resulting from the slow kinetic of the Li₂MnO₃ phase. Herein, the Prussian blue (PB) coating layer with specific redox potential is introduced as a functionalized interface to overcome the side effect and the escaping of O on the surface of LMO, especially its poor rate capability. In detail, the PB layer can restrict the large polarization of LMO by sharing overloaded current at a high rate due to the synchronous redox of PB and LMO. Consequently, an enhanced high rate performance with capacity retention of 87.8% over 300 cycles is obtained, which is superior to 50.5% of the pristine electrode. Such strategies on the high-rate cyclability of Li-rich Mn-based oxide compatible with good low-rate performances may attract great attention for pursuing durable performances.

Keywords

Li-rich Mn-based oxide, Prussian blue coating layer, synchronous redox, high-rate cyclability
1 | INTRODUCTION

Researches on the layered Li-rich Mn-based oxide (LMO) have attracted great attention because of its high reversible capacity of over 250 mAh g\(^{-1}\), but long-term work on anionic redox reaction accompanying charge compensation demonstrated that the releasing of oxygen is closely associated with voltage decaying and capacity fading, as well as poor rate performances.\(^1\)\(^-\)\(^3\) To overcome these issues, constructing a robust TM-O bonding and limiting the escaping of O\(_2\) are regarded as feasible alternatives.\(^4\)\(^-\)\(^5\) Particularly, inspired by a large number of efforts on Ni-rich cathode, surface coating and doping are testified feasible to the stabilization of LMO.\(^6\) For instance, a solid electrolyte was introduced to hinder the side reaction on the LMO surface and simultaneously maintain a fast pathway of Li ions;\(^7\) Si atom was applied to reduce the overlap between transition metal 3d band and O 2p band by forming robust covalence of Si-O;\(^8\) and so forth. Although most previous studies based on LMO revealed that both coating and alien doping contributed to either low- or high-rate cyclability, improving rate cyclability at all rates is still challenging.\(^9\)\(^-\)\(^13\)

According to our previous report on LMO, the capacity fading of LMO showed an apparent phase transformation from the layered to a spinel-like structure upon low-rate cycling, while the same trend at a high rate originated from a large polarization.\(^14\) A following in-depth discussion proposed that such distinction between low- and high-rates results from the sluggish kinetics of the Li\(_2\)MnO\(_3\) component, which has been verified by mediating the activation of the Li\(_2\)MnO\(_3\) phase. Therefore, strategies for accelerating the dynamics and improving the stability of the interface may be available for high-performance LMO. A urea-modified LMO accompanied with a g-C\(_3\)N\(_4\) coating layer and surface oxygen vacancy delivered a long life span and stable performances at both low and high rates;\(^15\) a sandwich-like carbon/spinel/layer structured LMO with oxygen vacancies also performed durably at various current densities.\(^16\) Apparently, a functionalized coating layer, as well as improved dynamic, can be a potential way to increase the performance of LMO. Significantly, in addition to the important strategy of elevating the dynamic of active materials, reducing the overloaded electrons/ions of active materials proposed in this study may be a new feasible way to a soothing polarization.

Metal-organic frameworks (MOFs) with controllable pore size have appealed great attention among the fields like gas separation,\(^17\)\(^18\) oxygen evolution reaction,\(^19\) energy storage,\(^20\)\(^21\) and so forth. The MOF-like Prussian blue (PB) was first utilized as the coating layer of LMO to hinder the side reaction between electrode and electrolyte and the escaping of lattice oxygen. Although a good cyclability can be obtained at a low rate, the long-term performance at a high rate was not uncovered.\(^22\) Considering the new finding about the capacity fading of LMO at various rates,\(^14\) PB is believed to be more powerful than a normal protection layer of LMO due to its specific redox potential.\(^23\)\(^24\) In detail, PB might be an ideal coating material for LMO because of its possibility of sieving O\(_2\) and splitting overloaded current. In this study, PB has been successfully wrapped on the surface of LMO via in situ complexation in water solution. The modified electrode displayed excellent stability in contrast to the pristine one, that is, high capacity retention of 91.4% after 100 cycles at 0.2 C and 87.8% over 300 cycles at 1 C for the former, which are far beyond 78% and 50.5% of latter at the same condition.

2 | EXPERIMENTAL SECTION

2.1 | Preparation of the pristine and PB-wrapped LMO

The preparation process of pristine LMO (0.5Li\(_2\)MnO\(_3\)-0.5Li\(_{1/3}\)Ni\(_{1/3}\)Co\(_{1/3}\)Mn\(_{1/3}\))O\(_2\)) was reported before.\(^14\) After that, the PB-modified LMO was fabricated through an in situ complexation method. In detail, 1 mmol of...
LMO (metal sources) was immersed into 2 mL of water mixed with stoichiometric potassium ferricyanide (complexant, 0.01, 0.05, 0.1 mol/L) for a night at room temperature. Then, these mixtures were filtered and washed with deionized water several times. Finally, these products were dried at 60°C in vacuum ambient for 12 h. The obtained samples in various concentrations of potassium ferricyanide solution were marked as PB-I, -II, and -III, respectively. In the control group, LMO was soaked into deionized water without additive, which was marked as PB-0, and the pristine one was PB-Pri.

### 2.2 Materials characterization

The morphologies and microstructures of the pristine and cycled samples were analyzed by scanning electron microscopy (SEM; MERLIN Compact) and transmission electron microscopy (TEM, JEOL JEM-F200 (HR)) equipped with energy dispersive X-ray spectroscopy (TEM-EDS) mapping. The crystal structure of all samples was verified by X-ray diffraction (XRD; SmartLab). The content of the coating layer was calculated based on the data measured by inductively coupled plasma optical emission spectroscopy (ICP-OES; Agilent 5100). Raman spectra and BET surface areas were obtained by Raman spectrometer (Horiba Scientific LabRAM HR Evolution) and Quantachrome micropore analyzer (Autosorb IQ), respectively, to describe the changes on the LMO surface. The evolution of the valence state on the surface of modified samples at various charging/discharging state were investigated using X-ray photoelectron spectroscopy (XPS; ThermoFisher ESCALAB Xi+).

### 2.3 Electrochemical measurements

The active materials were mixed with carbon black and polyvinylidene fluoride (PVDF) with a weight ratio of 8:1:1 in NMP. The obtained slurry was uniformly spread on the surface of Al foil and dried at 120°C for 12 h. Lithium metal was employed as the anode and 1 M LiPF₆ in the mixture of dimethyl carbonate, ethylene carbonate, and ethyl methyl carbonate (1:1:1 vs. volume) was applied as the electrolyte. The coin cell (CR2032) was assembled in an argon-filled glove box. Galvanostatic charge/discharge test was conducted under NEWARE battery tester at the current density of 50/250 mA g⁻¹ (0.2/1.0 C) during 2.0-4.8 V (vs. Li/Li⁺) at room temperature. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests were carried out in a 2-electrode system by a Princeton Applied Research VersaSTAT 4 electrochemical workstation. The amplitude of the a.c. signal was set to 5.0 mV with a frequency range of 10⁻²–10⁻⁵ Hz.

### 3 RESULTS AND DISCUSSION

The formation process of in situ PB coating layer is given in Figure 1A. Typically, [Fe(CN)₆]⁴⁻ is easily linked with the metal atom of LMO due to the strong bonding between the complexant and metal center. Noticeably, the transition metal from LMO is located at the TMO₆ site, and the new bonding between [Fe(CN)₆]⁴⁻ and the metal center will lead to the distortion of TM-O bonding and result in the disrupted surface structure of LMO. The morphologies of all samples are depicted in Figure S1. Their similar microsized secondary particles and smooth surface demonstrate good stability of LMO in water, while the tiny particles on the surface of PB-Pri are recognized as residual Li salt. Furthermore, high-resolution TEM was applied to probe the surface structure of LMO before/after complexation with K₄Fe(CN)₆. The clear lattice fringes from the bulk to the surface of LMO displayed the characteristic layered structure (Figure 1B). In contrast, although a well-layered structure remained in the inner in Figure 1C, an obvious amorphous layer with a thickness of around 3.5 nm can be observed on the out-surface of PB-III. Such structural evolution from layered (I region) to amorphous phase (II region) fits well in with the formation of the PB coating layer as mentioned above. Meanwhile, the selected area EDS mapping in Figure S2 confirms the success of introducing [Fe(CN)₆]⁴⁻ into the surface of LMO via complexation with a transition metal. Moreover, the ICP-OES results in Table S1 confirmed the content of [Fe(CN)₆]⁴⁻ in PB-III, which is calculated as 0.06 mol%. Interestingly, the low content of the PB coating layer may ascribe to the self-limited reaction mechanism. Typically, the complexant can bond with the exposed metal center and create the PB product, while the produced coating layer will retard a further complexation between the complexant and the inner metal atom. As a result, the thin coating layer not only avoids the excessive consumption of active metal in LMO but also helps to maintain a low charge transfer impedance.

Furthermore, the weak E₂ and A₁g peaks at around 477.2 and 600.8 cm⁻¹ in Raman spectra belong to the vibration of M-O bonding (Figure 1D). The slight red shift of the latter in PB-III demonstrated the distortion of TM-O bonding, which is ascribed to the generation of new bonding between complexant and a transition metal. Meanwhile, XRD patterns of all samples are indexed as LMO without any other signals in Figure S3a, but the apparent differences in their surface area and pore
dispersion displayed the characteristic MOF-like porous structure of PB coating layer (Figure S3b and Figure 1E). In detail, a larger specific surface area (6.164 m² g⁻¹) of PB-0 than PB-Pri (4.947 m² g⁻¹) owes to the dissolution of residual Li salt and slight corrosion of LMO, while the lowest specific surface area for PB-III (3.698 m² g⁻¹) can be ascribed to its dense coating layer (Figure S4). Consequently, less microporous and an additional mesoporous at around 8 nm testified to the abundant pore structure in the PB-wrapped materials.

More importantly, the redox reaction of Fe²⁺/³⁺ accounts for the electrochemical activity of PB. Ex situ XPS in Figure 2 was conducted and compared to catch the valence change of Fe and Mn in PB-III. An increasing Fe²⁺
peak can be detected after discharging to 3.2 V, which corresponds to the reduction of Fe in the PB component (−3.7 V). Simultaneously, the ratio of Mn⁴⁺/Mn³⁺ largely decreased from ~70% to ~45% after discharging from 4.0 to 3.2 V. As a result, the synchronous redox reactions of PB and LMO will lead to the dispersion of ions/electrons upon cycling.

Cycling performances of these electrodes are shown in Figure 3A, the improved reversible capacity of modified samples may associate with the exchange of H⁺ and Li⁺ after soaking into water. More importantly, the optimal LMO (PB-III) performed attractive capacity retention as high as 91.4% after 100 cycles at 0.2 C (~78% for PB-Pri), showing a great potential of PB as the coating layer of LMO. Meanwhile, it is noteworthy that a relatively low coulombic efficiency (around 99%) is observed in the initial 30 cycles, which corresponds to the fading trend of all electrodes, including the high-stable PB-III. To clearly understand the evolution of LMO upon cycling, charge/discharge curves and dQ/dV profiles of all compounds are drawn. The initial charge/discharge profiles of all electrodes in Supporting Information: Figure S5a presented slightly enhanced reversibility among the processed LMO. Furthermore, the CV curves of PB-Pri, −0, and −III at the 2nd cycle are shown in Figure 3B. Different from the voltage polarization of PB-0 (2.98/3.98 V), PB-III displayed a similar redox potential (3.15/3.90 V) to PB-Pri (3.12/3.85 V). More importantly, the in situ PB coating layer helps to buffer the undesirable phase change at 3.2 V, which can be ascribed to the robust bonding between [Fe(CN)₆]⁴⁻ and transition metal on the out-surface of LMO. More charge/discharge profiles at various cycles were introduced to track the capacity fading of each electrode in Supporting Information: Figure S3b–f. Among them, the obvious phase transformation from the layered to a spinel-like structure (voltage decay around 3.2 V upon charging) appeared at the initial 20 cycles, matching the capacity loss of all electrodes. After that, the capacity fading mainly results from the releasing of lattice oxygen followed by enlarged electrochemical polarization. Noticeably, apart from the synchronous phase change at the initial several cycles, the reversibility of oxygen was strongly elevated with the support of PB in PB-III. Further work revealed the changes in structural stability and O₂ reversibility of LMO in Supporting Information: Figure S6. The gradually diminished

**Figure 2** High-resolution XPS (A) Fe 2p and (B) Mn 2p spectra of PB-III at various states. Pristine, C4.8V, D4.0 V, D3.2 V, and D2.0 V. PB, Prussian blue; XPS, X-ray photoelectron spectroscopy.
contributions from O and Ni/Co are due to the continued capacity loss after the phase change at the initial 20 cycles.

High rate cyclability was further detected to measure the advantages of the PB coating layer in Figure 3C. As our previous report on the distinction between high and low rate capabilities of LMO,

14 the Li3MnO3 component with slow dynamic strongly limited their performances at a high current density. In this study, LMO immersed into deionized water (PB-0) quickly died instead of superior to PB-Pri, while PB modified electrodes shown better durability after soaking into water solution. Particularly, although a lower capacity remained at the initial several cycles than PB-I and –II, PB-III displayed an outstanding performance with a high capacity retention of 87.8% over 300 cycles, which is far beyond 50.5% of PB-Pri. Simultaneously, the characteristic voltage decay is also inhibited with the assistance of the PB coating layer in Supporting Information: Figure S7a. To figure out the merits of PB to LMO at the high rate, charge/discharge profiles of pristine and modified samples are applied to observe the corresponding polarization in Supporting Information: Figure S7b,c and Figure 3D. The increasing polarization (ΔE) among various electrodes corresponds to the capacity loss upon cycling. More details about the evolution of ΔE among various electrodes are shown in Figure 3F and Supporting Information: Figure S8. PB-0 and PB-Pri exhibited soaring growth of ΔE after 50 and 100 cycles, respectively, while the PB-modified LMO maintained well upon the whole cycling. Typically, the weaker polarization and more obvious plateaus belonging to oxygen and Ni/Co are depicted in Supporting Information: Figure S9 with the increase of PB content. Inspired by the competition between diffusion and reaction of alkali metal dendrite growth, herein promoting dynamic and slowing down current are
acceptable alternatives to overcome the polarization at a high rate. Consequently, the PB coating layer with specific potential shared part of electrons/ions and resulted in a lower current on the wrapped LMO (Figure 3E). In contrast to the modified LMO reported before, the PB-modified LMO displayed outstanding cyclability at both low and high rates (Supporting Information: Table S2).

The functions and evolution of the PB coating layer were further clarified via EIS and CV plots at various cycles. As depicted in Supporting Information: Figure S10a–c, the increasing Rs of PB-0 may relate to its highly sensitive interface after washing with water. In reverse, both pristine and PB-coated LMO maintained a low Rs even after 200 cycles at 1 C. Besides, surface deterioration is widely acknowledged in the research of LMO, which leads to the limited diffusion ability of Li+. Thus, the lower Rs of PB-III than PB-Pri demonstrates superior stability with the support of the PB coating layer. Nonetheless, the electrochemically active PB layer also suffers from structure change upon cycling. Typically, these electrodes displayed similar Li+ diffusion ability in the initial cycle, demonstrating slight changes on the surface of modified LMO (Supporting Information: Figures S10d–f and S11a). After 50 cycles, however, it seems that both PB-0 and PB-III exhibited obvious polarization, as shown in Figure 4A–C, which is fairly opposite to the stable cyclability of PB-III. Interestingly, the dynamics of these cycled electrodes were further calculated in Supporting Information: Figure S11b and Figure 4D. It is found that a good Li+ diffusion ability of PB-III has remained even though a large polarization has happened after 50 cycles. Accordingly, the large polarization in PB-0 may result from its sensitive surface after soaking into the water, while the same trend in PB-III is deduced attributing to the structural evolution of the PB coating layer instead of LMO due to the generally Jahn–Teller effect of PB material. High-resolution TEM images of cycled PB-Pri and PB-III at 1 C after 200 cycles are shown in Figure 5. Both SAED and local crystalline structures revealed an obvious phase change from the layered to spinel phase in PB-Pri, while the layered structure largely remained with the assistance of the PB coating layer in PB-III. In particular, because of the filter effect of the PB coating layer, a step-by-step and homogeneous phase evolution from the surface to the bulk of PB-III is observed after long cycling at a high rate. On the contrary, the randomly

**FIGURE 4** CV curves of cycled (A) PB-Pri, (B) PB-0, and (C) PB-III at 1 C for 50 cycles with the scan rate from 0.1 to 0.5 mV s⁻¹. (D) The corresponding slopes between peak current (Ip) and the square root of scan rate (v¹/²) of PB-Pri, PB-0, and PB-III at the 2nd and 50th cycle. CV, cyclic voltammetry; PB, Prussian blue.
dispersed mixture in PB-Pri easily leads to the failure of electrodes (Figure 5A).

4 | CONCLUSION

PB coating layer with specific redox potential has been successfully wrapped on the surface of LMO via the in situ complexation method. As a result, both side reactions between electrolyte and electrode and O2 releasing in LMO are restricted. More importantly, this electrochemically active layer also facilitates sharing part of the current from LMO upon cycling, thus reducing the electrochemical polarization arising from the slow kinetic of Li2MnO3. Accordingly, high capacity retention of 91.4% after 100 cycles at 0.2 C and 87.8% over 300 cycles at 1 C can be obtained in the PB-III electrode, which is far beyond the performances of pristine materials. This strategy provides a new solution to the slow kinetics of active materials, which might be further enhanced by improving the stability of the coating layer.

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CONFLICTS OF INTEREST

The authors declare no conflicts of interest.

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FIGURE 5  (A) Schematic illustration of the evolution of (i) PB-Pri and (ii) PB-III after long-term cycling at 1 C. TEM images of (B) PB-Pri and (C) PB-III at 1 C after 200 cycles. The insets: SAED patterns and local magnified images. PB, Prussian blue; TEM, transmission electron microscopy; SAED, selected area electron diffraction.


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**SUPPORTING INFORMATION**

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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