Elucidating and Mitigating the Degradation of Cationic—Anionic Redox Processes in Li$_{1.2}$Mn$_{0.4}$Ti$_{0.4}$O$_2$ Cation-Disordered Cathode Materials

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Supporting Information

ABSTRACT: Cation-disordered rock-salt oxides with the O$^{2-}$/O$_2^{--}$ redox reaction, such as Li$_{1.2}$Mn$_{0.4}$Ti$_{0.4}$O$_2$ (LMTO), are critical Li-rich cathode materials for designing high-energy-density batteries. Understanding the cationic—anionic redox accompanying the structural evolution process is really imperative to further improve the performance. In this work, the cationic—anionic redox and capacity degradation mechanism of carbon-coated LMTO during (dis)charge processes are elucidated by combining in situ X-ray diffraction, X-ray absorption near-edge spectroscopy, differential electrochemical mass spectrometry, transmission electron microscopy, and electrochemical analyses. It is concluded that the redox reaction of Mn$^{3+}$/Mn$^{4+}$ is quite stable, while the severe degradation is mainly caused by the O$^{2-}$/O$_2^{--}$ redox process. Moreover, we clearly clarify how the cationic—anionic interplay governs sluggish kinetics, large polarization, and capacity fading in LMTO, and reveal for the first time that a certain amount of carbon coating is capable of suppressing the irreversible lattice oxygen loss and results in an encouraging cycling performance. In summary, we elucidate the degradation of cationic—anionic redox processes in cation-disordered cathode materials and propose strategies for adjusting the electronic/ionic conductivity of the electrodes to modulate the oxygen redox reactions, setting a new direction for the design of better cation-disordered oxides.

KEYWORDS: cation-disordered cathode materials, lithium ion battery, anionic redox, carbon coating, capacity degradation

1. INTRODUCTION

Rapid development of portable electronic devices and electric vehicles has driven the evolution of lithium-ion batteries (LIBs) with higher performances.1,2 The energy density of LIBs is mainly restricted by the cathode materials. The classical layered oxide cathode materials Li$_{2}$MeO$_2$ (Me = Co, Ni, Mn, etc.) have been extensively investigated and widely used in commercial LIBs.3−6 Nevertheless, their capacities are limited by the number of reversible (de)intercalation lithium ions during (dis)charge and cannot meet the growing demand for energy density. Thus, it is crucial to explore new types of cathode materials with a much higher energy density. Over the past decade, cation-ordered Li-rich materials have attracted much interest, as they can deliver capacities higher than 250 mAh g$^{-1}$ on account of both cationic and anionic redox.7−10 In these compounds, Li sites and pathways are separated from the transition-metal (TM) framework, forming typical layered Li−TM channels for Li diffusion, thus providing excellent Li migration and capacity. A well-ordered structure between the Li and TM framework has been generally considered to be important for obtaining a cathode material with high capacity and good cycling stability.11 Recently, Li-rich cation-disordered rock-salt materials, for example Li$_{1.2}$Nb$_{0.3}$Mn$_{0.4}$O$_2$,12 Li$_{1.2}$Ti$_{1.4}$Mn$_{0.4}$O$_2$,13,14 Li$_{1.2}$Ni$_{1/3}$Ti$_{1/3}$Mo$_{2/3}$O$_2$,15 and Li$_{1.2}$Ta$_{0.3}$Mn$_{0.4}$O$_2$16 have received much attention, as they are capable of delivering reversible capacities higher than 300 mAh g$^{-1}$. In typical cation-disordered rock-salt oxides, Li$^+$, redox-inactive TM cations (Nb$^{5+}$, Ti$^{4+}$, Mo$^{6+}$, etc.), and redox-active TM cations (Mn$^{3+}$, Ni$^{2+}$, V$^{3+}$, etc.) form various novel cathodes for LIBs. A channel with no face-sharing TM ion (0-
TM channels) becomes more extensive in these cation-disordered oxides, enabling a higher fraction of Li diffusion through the 3D network avoiding the interruption of Li–TM channels. The 0-TM channels are considerably less sensitive to the reduction of the local O–O distance than the Li–TM channels owing to the cation disorder.17–21 Therefore, these materials are capable of delivering a higher capacity by employing O2-/O2 redox.18–23 The Li-rich and cation-disorder structures generate the linear Li–O–Li configurations, in which the relatively higher energy of these labile O 2p states make them easier to be oxidized upon delithiation.13,25 Thus, the anionic O can donate electrons during the charging process, providing extra capacity beyond the TM redox.14,25 The materials would form cation-densified phases after delithiation, presenting poor Li-transport kinetics as their lowered Li content puts them below the threshold of 0-TM percolation. Additionally, the delithiation reaction involving the O 2− would lead to oxygen loss from the lattice, leading to a gradual performance degradation.

Recently, Yabuuchi et al. investigated the origin of stabilization and destabilization in solid-state redox reactions of oxide ions in Li1.2Mn0.4Ti0.4O2 (LMTO) for the first time, delivering a reversible capacity of 300 mAh g−1 (5 mAh g−1 at 50 °C).18 At the same time, Ceder et al. presented a strategy of combining high-valency cations and the partial substitution of fluorine for oxygen in a disordered rock-salt structure to incorporate the reversible Mn3+/Mn4+ double-redox couple.15,27,28 Significant success has been achieved for the Li-rich cation-disordered cathode, but issues such as a large polarization and poor cycling performance need to be addressed.1,26 The causes of these problems are not thoroughly understood and only rare effective solutions are proposed. Specially, the structural evolution and specific cationic–anionic redox degradation processes in the cation-disordered cathode materials and effects on electrochemistry are not fully recognized. A deep and systematic understanding of the cationic–anionic redox accompanying the structural evolution process is still lacking.

Herein, we focus on understanding how the TM and O redox reaction processes influence the observed electrochemical performance. LMTO and carbon-coated LMTO with a high capacity and low cost (Co and Ni free) were synthesized. The structural evolution and corresponding cationic–anionic redox reactions are discussed by employing electrochemical analyses, in situ X-ray diffraction (XRD), X-ray absorption near-edge spectroscopy (XANES), differential electrochemical mass spectrometry (DEMS), and transmission electron microscopy (TEM) technologies. Consequently, we correlate the polarization and degradation mechanism with these detailed electrochemical profiles to reveal the interplay between the cationic–anionic redox and electrochemical kinetics/thermodynamics of the materials. What’s more, we observe that the cycling performance of LMTO@C can be significantly improved by a certain amount of carbon coating due to the suppressing oxygen loss during cycling, which provides an effective pathway to improve the performance of the materials by kinetic methods.

2. EXPERIMENTAL SECTION

2.1. Material Synthesis. Li1.2Mn0.4Ti0.4O2 (LMTO) was synthesized by a solid-state method. Stoichiometric amounts of Li2CO3 (Alfa Aesar, ACS, 99%), MnO2 (Alfa Aesar, 99%), and TiO2 (Alfa Aesar, 99.9%) were ball-milled thoroughly with acetone for 10 h and then dried in an oven for 12 h. The obtained mixture was pressed into a pellet and then sintered at 950 °C for 16 h under an Ar atmosphere, followed by furnace cooling to room temperature. The pellet was then ground into fine powder. As-prepared LMTO samples were mixed with acetylene black (AB) (samples: AB = 90:10, 80:20, 70:30, and 60:40 wt %) using a planetary ball mill for 24 h at 500 rpm in a zirconia container, which is marked as LMTO@C (LMTO/10, 20, 30, and 40 wt %). Additionally, Li1.2Mn0.4Ti0.4O2 was also ball-milled under the same conditions without carbon and marked as LMTO-B.

2.2. Electrochemical Tests. All samples were mixed with acetylene black and poly (vinylidene fluoride) at a weight ratio of 8:1:1 using a planetary ball mill at 300 rpm in a zirconia container to obtain a slurry, which was cast on an Al current collector and then dried at 120 °C in a vacuum oven as the cathode. A metallic lithium disk was used as the anode. The electrolyte was 1 M LiPF6 dissolved in ethylene carbonate and dimethyl carbonate solution (1:1 volume ratio). A polyolefin microporous membrane was used as a separator. Two-electrode 2025-type coin cells were assembled in an Ar-filled glovebox. The specific capacities are calculated according to the LMTO, and the mass of C is excluded. The cells were cycled in the voltage range of 1.5–4.8 V at a rate of 30 mA g−1 at either room temperature or 50 °C. The exchange current density and electrochemical impedance measurements were carried out using a potentiostat equipped with a frequency response analyzer.

2.3. Characterizations. XRD pattern for as-prepared materials and ex situ samples were collected by a Rigaku Ultima IV powder X-ray diffractometer using Cu Kr radiation (λ = 1.5406 Å) operated at 40 kV and 30 mA from 2θ = 10 to 90° at a scan rate of 2° min−1. Rietveld refinement of the XRD pattern was performed using a GSAS software with the EXPGUI interface. In situ synchrotron XRD was conducted at beamline BL14B1 at the Shanghai Synchrotron Radiation Facility (Shanghai, China) with an X-ray wavelength of 0.6887 Å. A coin cell with holes at both the top and the bottom that were sealed with a Kapton tape was used for in situ XRD measurements, which was continuously charged and discharged while collecting the data. The collection time for each XRD scan was 5 min.

The exact compositions of Li, Mn, and Ti were determined by Optima 2000DV inductively coupled plasma emission spectrometry (ICP-OES, PerkinElmer).

Morphological features of the samples were observed using a scanning electron microscope (SEM, ZEISS Sigma, Germany) with an energy-dispersive X-ray spectroscopy (EDS) detector used for EDS elemental mapping, operating at 15 kV, and conducted on a scanning transmission electron microscope (TEM, FEI, Netherlands), operating at 200 kV.

X-ray photoelectron spectroscopy (XPS) measurements were carried out with a Quantum 2000 ESCA spectrometer (Physical Electronics) with a monochromatic Al Kα radiation (hν = 1486.6 eV), operating at 23.2 W and in a vacuum of <10−8 Torr. The cells were dismantled in a glovebox under an argon atmosphere. The dismantled electrodes were then transferred into the XPS vacuum.

A custom-built differential electrochemical mass spectrometer (DEMS) and the cell geometry used are described in previous publications.26 The electrochemical cells used with the DEMS device were assembled in an Ar-filled glovebox. The composition of the cathode film was the same as that discussed previously and the loading density was ≈5 mg cm−2. The assembled cells were charged under a static head of positive Ar gas pressure (approximately 1.2 bar) after being appropriately attached to the DEMS. Throughout the charging process, Ar gas pulses periodically swept accumulated gases to a mass spectrometer chamber. The absolute sensitivity of the mass spectrometer has been calibrated for O2 and CO2, and therefore, the partial pressures of these gases can be determined. The amount of gas evolved during the charge/discharge processes is then quantified based on the volume of gas swept to the mass spectrometer per pulse.

The ex situ X-ray absorption near-edge structure (XANES) data at the Mn and Ti K edges were obtained with beamline BL14W1 of the Shanghai Synchrotron Radiation Facility. The intensities of the
incident and transmitted X-rays were measured using ion-chamber detectors at room temperature in the transmission mode. The spectra were obtained with a silicon(111) double-crystal monochromator. The data were collected over a range of energies, from 200 eV below to 500 eV above the Mn (6539 eV) and Ti (4979 eV) K edges, respectively. The composite electrodes were rinsed with dimethyl carbonate and sealed in a water-resistant polymer film in an Ar-filled glovebox. The incident photon energy was calibrated using standard Mn and Ti metal foils. Processing of the XANES data was performed using the Athena software.31

3. RESULTS AND DISCUSSION

3.1. Morphology and Crystal Structure. XRD patterns of LMTO (Figure 1a), LMTO-B, and LMTO@C (10 wt %, as shown in Figure 1b, which are all indexed to the cation-disordered rock-salt phase (space group Fm3m), indicating that pure-phase materials are prepared. The exact compositions of the compounds were determined by using ICP-OES and are shown in Table S1, demonstrating that the chemical compositions of the prepared materials are in good agreement with the theoretical values. Their morphologies and particle sizes are exhibited in Figures 1c,f and S1a, which show that the primary particles sizes of LMTO are decreased from around 10 μm to 2 μm, and the surface of the LMTO becomes rough after ball-milling. Additionally, the LMTO@C material displays a uniform distribution of around 10 nm of carbon layer on the surface of LMTO particles, as shown in the EDS elemental-mapping results (Figures 1e,h, S2a–c). Furthermore, the refined lattice parameters of LMTO and LMTO@C are 4.152(5) Å and 4.140(5) Å, respectively (Figure S2d,e), which implies that the ball-milling process does not change its crystal structure (Figure S1b and Table S2). The broadening of XRD peaks after ball-milling is caused by the reduction of particle sizes. The Raman spectra of LMTO@C in Figure S3a confirm the presence of the carbon-coating layer with obvious D and G bands located at 1350 and 1600 cm⁻¹, respectively.

3.2. Electrochemical Performance. Electrochemical impedance spectra (EIS) of LMTO, LMTO-B, and LMTO@C powders were tested by a symmetric cell with a conductive glass (Figure S3b), and the results are exhibited in Figure 2a. A significant arc decrease from thousands to 38 Ω was observed in the LMTO@C powder compared with the LMTO material. The arc impedance is attributed to the grain boundary impedance of the materials. Thus, the decrease of impedance in LMTO@C can be attributed to the carbon layer on the surface, which should improve the electronic conductivity of LMTO. The exchange current density (I₀) of the electrode materials was tested (Figures 2c and S3c). The I₀ values of the LMTO@C powder and in the electrolyte are much larger than those of LMTO. The results indicate that the carbon-coating layer significantly enhances the electronic conductivity of electrode materials, which will greatly improve their electrochemical performance. On the contrary, the electronic conductivity of the LMTO-B material decreases and the impedance increases, and thus, the electrochemical properties of the material become poor.

In Figure 2c, the electrochemical performances of LMTO, LMTO-B, and LMTO@C are compared at room temperature. In the first cycle, LMTO and LMTO-B exhibit discharge capacities of 158 and 125 mAh g⁻¹, respectively. In addition, the voltage profiles of the two materials exhibit a large hysteresis between charge and discharge. These results imply that the electrochemical performance of LMTO cannot be improved merely by ball-milling, and it becomes even worse. As a comparison, LMTO@C delivers a much higher discharge capacity of 242 mAh g⁻¹ and shows a significantly reduced polarization. In particular, both charge voltage curves and differential capacity-versus-voltage (dQ/dV) curves indicate that the 4.5 V plateau associated with the anionic redox becomes more evident after carbon coating (Figure 2d), which leads to a higher charge capacity. LMTO@C achieves a reversible discharge capacity of more than 300 mAh g⁻¹ at 50 °C (Figure S4a).11 From the corresponding dQ/dV curves in Figure 2d, two strong redox peaks were significantly strengthened. These phenomena are attributed to the improvement in electronic conductivity and relatively fast kinetics for LMTO@C. Figure 2e,f shows the discharge profiles of LMTO and LMTO@C under different current densities between 1.5 and 4.8 V. LMTO@C shows the best rate capability. As the current density increases from 10 to 20, 40, 100, 200, and 400 mA g⁻¹, the capacity of LMTO@C decreases from 293 to 246, 201, 174, and 132 mAh g⁻¹, respectively, which are all higher than that of LMTO. The differences are more obvious at higher current densities; for example, at 400 mA g⁻¹, the capacity of LMTO@C is 132 mAh g⁻¹, which is 169% higher than that of LMTO (49 mAh g⁻¹).

It is notable that the first and second charge/discharge profiles of LMTO@C (Figure S4b,c) are asymmetric, indicating that different redox processes take place during (dis)charge processes. This difference indicates that the electrochemical process is kinetically limited by the redox processes in LMTO@C. To understand the cationic and anionic reaction processes and their kinetic limitations, galvanostatic intermittent titration tests (GITT) were conducted on LMTO and LMTO@C. The voltage relaxation in LMTO@C is considerably less than that in LMTO (Figure S5a,b), indicating that
the mass transfer is more favorable in LMTO@C. Figure S5b shows the severe polarization of LMTO@C above 4.3 V, indicating that the polarization mainly appears at high-voltage areas. The voltage profiles of the first and second cycles for LMTO@C with various cutoff voltages from 3.8 to 4.8 V are presented in Figure 3a,b. For the first cycle, when the cutoff voltage is less than 4.3 V (Figure 3a), the discharge capacity is higher than the charge capacity. Above 4.5 V, the discharge...
capacity is relatively small and a high irreversible capacity (91 mAh g$^{-1}$) occurs. Moreover, the capacity of LMTO@C exceeds its theoretical capacity of the Mn$^{3+}$/Mn$^{4+}$ reaction. This indicates that not only Mn$^{3+}$/Mn$^{4+}$ but also other redox couples are active in LMTO@C, which is considered to be the O$^{2-}$/O$_2$$^{-}$ redox. Such an extensive O$^{2-}$/O$_2$$^{-}$ redox leads to severe oxygen loss near the surface of the cathode particles and generates TM migration, which in turn results in a large polarization. As for the second cycle (Figure 3b), the slope of Mn at 4.3 V is mostly maintained while the plateau of O oxidation at 4.5 V is significantly reduced during the charging process. This implies that the severe oxygen loss mainly occurs in the first cycle. The corresponding dQ/dV curves in Figure 3c,d show similar trends. The broad reduction peak is associated with both Mn$^{4+}$ and O$^{2-}$ reduction, which suggests that Mn and O reductions are coupled. The capacity retention under different cutoff voltages in Figure 3e reveals that anionic redox reactions at high-voltage regions during charging greatly affect the cycling performance of LTMO@C. When the cutoff voltage is lower than 4.5 V, the capacity retention is almost 100% for 50 cycles, while the capacity decays rapidly with higher cutoff voltages of 4.5 and 4.8 V. The capacity retentions are 56 and 43% at 4.5 and 4.8 V, respectively. The results present that more anionic reactions involved would lead to a poorer cycling performance. In the 50th cycle of LTMO@C between 1.5 and 4.8 V, the voltage profile becomes sloppy in the entire voltage window (Figure S4d), showing a continuous decrease of the discharge voltage. During cycling, the TM reduction voltage of LMTO@C also decreases (Figure S4e), and the same for LTMO and LMTO-B (Figure S5c,d). These results indicate that the polarization and capacity decay are mainly caused by anionic redox (Figure S4f).1,27

3.3. Cationic–Anionic Redox of the Materials by XPS, DEMS, and XANES. XPS, DEMS, and XANES measurements are employed to clearly investigate the cationic and anionic redox reactions during (dis)charge processes. Figure 4a shows the O 1s XPS spectra of the LTMO and LMTO@C electrodes charged to 4.8 V in the first cycle. The strong peak at 529.5 eV is assigned to the lattice oxygen (O$^{2-}$), whereas the weaker peaks at 530.5 eV are attributed to the oxidized lattice oxygen (O$^{n-}$, n < 2). The shoulder peaks appearing at 532.5 eV are due to the organic oxygenated species produced by the decomposition of carbonate solvents. Furthermore, these XPS spectra also reveal that more O$^{2-}$ and O$^{n-}$ and less surface deposits are observed in LMTO@C than in LMTO, thus presenting more anionic reactions involved in LMTO@C. In addition, O$^{n-}$ radical-triggered electrolyte decomposition can also be observed in the F 1s spectra (Figure 4b). The relative intensity of the F 1s peak at 685 eV in LMTO@C is significantly reduced compared with that of LMTO, which is in line with LiF in cathode–electrolyte interface (CEI) films. These data suggest that the carbon-coating layer not only promotes the O$^{2-}$/O$_2$$^{-}$ process, but also suppresses the electrolyte decomposition on the surface of the cathode.

Figure 4c presents the DEMS results of LMTO@C. In the first charging process, 0.003 μmol mg$^{-1}$ of O$_2$ gas was detected between 4.2 and 4.8 V. Combined with XPS, it can be inferred that O$_2$ originates from lattice O$^{2-}$ oxidation, thereby showing lattice oxygen loss in the form of O$_2$ for LMTO@C. Besides, a noticeable amount of CO$_2$ gas (0.188 μmol mg$^{-1}$) is detected between 4.0 and 4.8 V. Previous works have found that at least 70% of the CO$_2$ gas evolved during cycling can be accounted for from surface carbonate decomposition (e.g., Li$_2$CO$_3$) with a low charge potential (3.8–4.0 V). The remaining small amount of CO$_2$ gas at a high voltage presumably originates from the lattice oxygen on the surface or from some oxygen species evolved from the materials reacting with the electrolyte on the surface of the cathode. Some CO$_2$ can be observed in the discharge process, as is a small amount of CO$_2$ in the pipeline. Combined with the experimental results of GITT, the
indicating Mn4+ reduction to Mn2+. In fact, Mn2+ produced between 4.3 and 4.8 V at 30 mA g−1 (∆V = 0.6887 Å). The Re1 region includes a slight Ti4+ reduction, which correspond to the discharge process above 4.4 V. This indicates that Mn oxidation mainly occurs below 4.4 V during the first charging process. Therefore, the charging process above 4.4 V can be classified as oxygen oxidation. In the discharge process, the absorption edge gradually returns to a lower-energy position compared with that of Mn2O3 (Mn3+). In the early stage of Li extraction (4.4 V), a clear energy shift (∼4 eV) of the absorption edge is found (Mn4+), with a minor change by further Li extraction (4.4−4.8 V). This indicates that Mn oxidation mainly occurs below 4.4 V during the first charging process. Therefore, the charging process above 4.4 V can be classified as oxygen oxidation. In the discharge process, the absorption edge gradually returns to a lower-energy position compared with that of Mn2O3, indicating Mn3+ reduction to Mn4+. In fact, Mn4+ produced by the Mn3+ disproportionation reaction and H+ derived from the electrolyte lead to an obvious TM dissolution upon cycling. The lithium metal anode of LMTO@C half-cell after the first charge/discharge process is depicted in Figure 4f. The detailed (dis)charge processes of LMTO@C mainly include three parts: Ox1 (oxidation of Mn), Ox2 (oxidation of O), and Re1 (reduction of Mn and O). The Ox1 region represents Mn oxidation between 3.0 and 4.3 V corresponding to the slope in the charging curve. The Ox2 region is the O oxidation process between 4.3 and 4.8 V corresponding to the long plateau indicating a relatively sluggish reaction process. The oxidation of O involves two processes, which are oxidation to O2− (n < 2) (reversible) and O2 (irreversible). The Re1 region includes the reduction of Mn3+ and O2− between 4.8 and 1.5 V and a slight Ti4+ reduction, which correspond to the discharge plateau. The overall charge compensation mechanism of the cationic–anionic redox can be thus understood.

3.4. Structural Evolution of the Material by Synchrotron X-ray Diffraction and TEM. In situ XRD was utilized for the analysis of the crystal structure change of LMTO@C in Figure 5. The asymmetric structural evolution behavior indicates that the Li+ insertion–extraction processes for LMTO@C are not completely reversible when cycled at the cutoff voltage of 4.8 V. The in situ XRD patterns of the initial cycle are divided into four regions according to their evolution behaviors (Figure 5a). In region I, the continuous shifting of the (200) and (220) peaks to a higher angle reveals a solid-solution reaction of Phase I. The parameter a decreases from 4.145 Å as the Li+ are extracted (Figure 5b). As the cell is further charged to the slope between 3.8 and 4.3 V, a new phase (Phase II) forms in region II, which was caused by a non-uniform reaction owing to different reaction depths of the LMTO@C particles. The lattice parameter decreases in these two regions (below 4.3 V) as a result of Mn oxidation (Mn3+(0.72 Å) to Mn4+(0.53 Å)). Then, Phase II becomes the only phase in the sample because the reaction is complete, and all peak shifts are negligible from 4.3 V to the end of charge at 4.8 V (region III), indicating that there is no phase transformation and cell parameters remain almost unchanged at the plateau.2,15 This is supported by the DEMS and XANES results that oxygen oxidation dominates in this voltage range. The whole charging process leads to a volume shrinkage of around 9.6%. When the discharge process starts, the (200) peak shifts to a lower angle continuously. In region IV, an additional peak appears at the lower-angle side, forming a new phase. This is also caused by a non-uniform reaction. The whole discharge process leads to a volume expansion of around 5% with Mn4+/Mn3+ reduction and Mn3+-induced Jahn–Teller distortion. The in situ results clearly show that the lattice parameters of the material are not completely recovered after cycling. These results give a structural explanation to the greater polarization and poor cycling performance where cationic and anionic redox are located.

TEM and high-resolution TEM (HRTEM) images are obtained to further investigate the structural evolution of LMTO@C upon the first and 50th discharges.24,35 The HRTEM images of LMTO@C after the first cycle (Figure 6a,b) show obvious lattice fringes, representing the (200) planes (d = 0.32 nm). The (200), (220), and (311) reflections were observed and measured to be 0.207, 0.147, and 0.105 nm in the corresponding SAED patterns (Figure 6c), respectively. Compared with the XRD testing results of LMTO@C, the
change of the d value of the plane can be seen, which implies that cell parameters become larger after the first cycle compared with the pristine state. This is also consistent with in situ XRD results. The phase transition of the 50th cycle is detected and shown in Figures 6d–f and S7c. It is observed that crystal planes are severely distorted and the diffraction peak shifts to a low angle and is almost absent, which indicate a continuous structural change during cycling.

From the detailed analyses and discussions of LMTO and LMTO@C, we have demonstrated that (i) a carbon coating can significantly improve the capacity and rate capability of LMTO by enhancing its electronic conductivity. (ii) The voltage profiles and dQ/dV curves for LMTO@C show cationic–anionic redox during (dis)charge processes. Specifically, the middle dQ/dV peak at around 3.8 V shows Mn activity, and the O oxidation is above 4.3 V. Although the oxygen reaction provides a large capacity, it brings severe polarization and it is not good for the cycling performance. (iii) Cationic and anionic redox processes are revealed by XPS, DEMS, and XANES measurements. The cationic redox reaction of the Mn$^{3+}$/Mn$^{4+}$ is highly stable, while the severe degradation is mainly caused by the anionic O$^{2-}$/O$^{4-}$ redox process. The release of O$_2$ and the formation of CEI is the source of the irreversible capacity in first cycle of LMTO. (iv) Irreversible surface and bulk structural changes are observed. The side reactions on the surface and the dissolution of the TM, together with oxidation of lattice oxygen, were demonstrated by in situ synchrotron XRD, SEM, TEM, and HRTEM. These problems will be harmful to the coulombic efficiency and cycling performance.

3.5. Strategies for the Improvement of the Cycle Performance. Given the side reactions taking place on the interface and the surface oxygen loss, it is easy to consider coating the material with more carbon. Therefore, we have made 20, 30, and 40 wt % coatings on the basis of a 10 wt % carbon coating in the previous section. The Raman spectra in Figure S8a indicates that the bond between Mn/Ti and O of the 20 and 30 wt % carbon coatings almost disappears, as some of the Mn−O bonds are covered due to the carbon layer. Figure 7a demonstrates the voltage profiles of LMTO@C with different carbon contents for the first cycle at 30 mA g$^{-1}$, delivering discharge capacities of 242 mAh g$^{-1}$ (10 wt %), 263 mAh g$^{-1}$ (20 wt %), 279 mAh g$^{-1}$ (30 wt %), and 266 mAh g$^{-1}$ (40 wt %), respectively.
(40 wt %), respectively. The LMTO@C of 30 wt % exhibits the best electrochemical performance. Although the carbon layer provides good electronic conductivity between the particles, it is expected that the electrochemical performance of LMTO@C reaches its limit at certain coating amounts. Figure S8b shows that 10 wt % of the carbon coating greatly increases the electronic conductivity, but a higher amount of carbon does not show a significant improvement. On the contrary, when the carbon content increases, the interface impedance also increases (Figure S8c). From the previous discussion of cationic–anionic redox and the dQ/dV curves with different carbon ratios in Figures 7b and S8b,c, an obvious manganese activation reaction (oxidation peaks at 3.5 V rises) and less anionic redox reaction is observed in LMTO@C (30 wt %) (oxidation peaks at 4.5 V are weakened). It is worth mentioning that DEMS results (Figure 6d) show that the coating layer substantially mitigates oxygen loss: the O2 gas evolution decreases from 0.003 μmol mg−1 for LMTO@C (10 wt %) to 0.002 μmol mg−1 for LMTO@C (30 wt %) (reduced by 33%). Meanwhile, the amount of CO2 gas has been greatly reduced to 0.154 from 0.188 μmol mg−1 (reduced by 18%). These findings indicate that the surface oxygen redox reaction from LMTO@C (30 wt %) is suppressed by carbon coating. A schematic diagram of the gas production process is illustrated in Figure 7c, indicating that LMTO@C (30 wt %) produces less O2 and CO2 than LMTO@C (10 wt %). In addition, the reduction in the amount of CO2 indicates that the carbon layer can significantly reduce side effects at the interface. The cycling performances of all materials are compared in Figure 7c. It shows that LMTO@C (30 wt %) exhibits a promising capacity retention. At the 50th cycle, LMTO@C (30 wt %) maintains a high capacity of 197 mAh g−1, which is almost two times that of LMTO@C (10 wt %). These results show the strategy of coating more carbon, which maximizes the Mn4+/Mn²⁺ redox capacity and minimizes the surface oxygen redox reaction. Therefore, surface modification, as one effective strategy, can ameliorate the oxygen loss of the electrode. In addition, it can also retard the side surface reactions and stabilize the surface/interface structure upon cycling. Of course, we also believe that some elemental doping strategies can regulate the oxygen loss at the interface. The authors declare no competing financial interest.

4. CONCLUSIONS
In this work, the cation-disordered Li1.2Mn0.4Ti0.4O2 materials coated with carbon were successfully synthesized, which can deliver a high capacity of up to 250 mAh g−1. The carbon coating accelerates electron conduction and enhance the kinetics of redox reactions, and thereby improves the capacity and rate capability of LMTO. The detailed charge/discharge processes of cation-disordered oxide materials are further analyzed, which mainly include Ox1 (Mn²⁺/Mn⁴⁺ to Mn⁴⁺), Ox2 (O²⁻/O⁰⁺), and Rei (Mn⁴⁺ to Mn³⁺/Mn²⁺ and O⁻⁰ to O²⁻) reactions. We find that cationic redox is kinetically fast and anionic redox is sluggish. The anionic redox process leads to oxygen loss, a severe polarization and an irreversible structural change, which will result in a low initial coulombic efficiency, poor rate capability, and poor cycling performance. Finally, a certain amount of carbon coating (30 wt %) can partially suppress irreversible oxygen loss from the lattice, achieving a better cycling performance. We believe that surface modification could mitigate the irreversible oxygen reaction and maintain the high energy density of LMTO at the same time.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.9b16011.

SEM image and Rietveld refinement of XRD patterns for LMTO-B; BF TEM image of LMTO@C; EDS elemental maps and Rietveld refinement of XRD patterns for LMTO and LMTO@C; Raman spectra of LMTO, LMTO-B, and LMTO@C; photo of symmetric cells with conductive glass; exchange current densities of LMTO, LMTO-B, and LMTO@C in the electrolyte; voltage profiles of LMTO@C at 50 °C under 30 mA g⁻¹ and dQ/dV curves for the first and second cycles of LMTO@C at room temperature under 30 mA g⁻¹; the voltage profiles and dQ/dV curves of LMTO, LMTO@C, and LMTO-B between 1.5 and 4.8 V under 30 mA g⁻¹ at room temperature; capacity retention of LMTO and LMTO@C; voltage profiles of LMTO, LMTO@C, and LMTO-B from a galvanostatic intermittent titration test; mapping and EDS images of lithium metal anode for LMTO@C after five cycles; ex situ X-ray diffraction patterns for LMTO@C at the first and 50th cycles; Raman spectra of LMTO@C with different carbon contents; exchange current densities of different ratios of LMTO@C in electrolytes; EIS spectra of LMTO@C (10 wt %) and LMTO@C (30 wt %); voltage profiles and dQ/dV curves for the second cycle of LMTO@C (10 wt %) and LMTO@C (30 wt %) at 30 mA g⁻¹.

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Notes
The authors declare no competing financial interest.

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