Mechanism Study of Carbon Coating Effects on Conversion-type Anode Materials in Lithium-ion Batteries – Case Study of ZnMn_2O_4 and ZnO-MnO composites

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Abstract

The carbon coating strategy is intensively used in the modification of conversion-type anode materials to improve their cycling stability and rate capability. Thus, it is necessary to elucidate the modification mechanism induced by carbon coating. For this purpose, bare ZnMn_2O_4 , carbon-derivative-coated ZnMn_2O_4 , and carbon-coated ZnO-MnO composite materials have been synthesized and in-depth investigated. Herein, high-temperature synchrotron radiation diffraction is used to monitor the phase transition from ZnMn_2O_4 to ZnO-MnO composite during the carbonization process. The electrochemical performance has been evaluated by cyclic voltammetry, galvanostatic cycling and electrochemical

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impedance spectroscopy. The carbon- and carbon-derivative-coated samples display well-improved cycling stability in terms of suppressed electrode polarization, a moderate increase in resistance, and slight capacity variation. The influence of carbon coating on the intrinsic conversion process is investigated by *ex situ* X-ray absorption spectroscopy, which reveals the evolution of Zn and Mn oxidation states. This result confirms that the strong capacity variation of the bare ZnMn_2O_4 is induced not only by the reversible charge storage in the solid electrolyte interphase but also by the phase evolution of active materials. Carbon coating is an effective method to prevent the additional oxidation of MnO to Mn_3O_4 , which leads to a stabilization of the main conversion reaction.

1. Introduction

Nowadays, lithium-ion batteries (LIBs) are intensively used in portable electronic devices and electric vehicles. Therefore, LIBs with high energy density, high power density, long cycle life, and high safety are definitely needed. Among various anode materials, conversion-type materials (transition-metal oxides, sulfides, etc.) are widely investigated as promising candidates for next-generation LIBs. This is due to the following advantages: 1) higher specific capacities compared to commercial graphite anode (more than one electron are delivered per formula unit (pfu) during redox reactions); 2) abundant resources and low cost; 3) superior safety performance, owing to the higher redox potentials which reduce the possibility of lithium dendrite formation (contrary to graphite anode).¹⁻³ However, some intrinsic drawbacks should be emphasized, including the low electronic conductivity, particle pulverization, severe volume change, and large voltage hysteresis, which result in poor rate capability, short cycling life, and low energy efficiency.⁴ Reducing the particle size to nanoscale and hybridization with carbonaceous materials are two main strategies to attenuate these issues. Nanosizing is beneficial not only to shorten the Li^+ diffusion length for (de)insertion but also to accommodate volume changes, thus improving both rate performance and cycling stability.^{5,6} On the other hand, the hybridization with carbonaceous materials enhances the electronic conductivity and suppresses excessive electrolyte decomposition by avoiding direct contact between active particles and electrolyte.^{7,8} Thus, in recent years, many carbon-composited metal oxides have been explored as high-performance anode materials for LIBs.^{1,3,9}

In order to explain the reason for this improvement, *ex situ* transmission electron microscopy (TEM) and scanning electron microscopy (SEM) are used to demonstrate the integrity of the active particles and electrodes after cycling.^{7,10} Electrochemical impedance spectroscopy (EIS) is also used as a tool to reveal the lower resistance of the carbon composited electrodes.^{3,11,12} However, there are few reports concerning the influence of carbon compositing on the intrinsic redox chemistry, which is directly related to capacity change.¹³ Although high-resolution transmission electron microscopy (HRTEM) can visualize the converted nanoparticles and reveal the phase composition during the 1st cycle,¹⁴ it is difficult to distinguish

the phase composition after long-term cycling due to the small crystallites and the messy morphology.¹⁵ On the other hand, since *ex situ* X-ray absorption spectroscopy (XAS) is a powerful method to elucidate the evolution of oxidation state and local structure of the related transition-metals,¹³ it is a useful tool to follow the evolution of the intrinsic redox chemistry upon cycling.

In general, Mn-containing conversion anode materials exhibit large capacity fluctuations upon cycling.^{12,16–19} In most cases, the capacity decreases slightly in initial cycles, and then increases intensively and followed by a fast fading. It is obvious that these strong capacity variations are not desirable in commercial applications. In the previous reports, this extra increasing capacity is generally attributed to the dynamic reversible decomposition of the solid electrolyte interphase (SEI).^{20–22} In our previous work about ZnMn_2O_4 , this phenomenon is partially attributed to the evolution of redox chemistry, specifically evidenced by the appearance of a new pair of redox peaks ($\text{Mn}^{2+}/\text{Mn}^{3+}$) in cyclic voltammetry (CV) curves.²³ Therefore, taking into account the interesting redox chemistry and its evolution during cycling, ZnMn_2O_4 nanoparticles have been chosen as a typical conversion-type material for understanding the role of carbon compositing. Specifically, carbon-derivative-coated ZnMn_2O_4 and carbon-coated ZnO-MnO were prepared through a simple carbon-thermal reduction method using glucose as carbon source. The phase transitions of ZnMn_2O_4 during carbonization process was analyzed by high-temperature synchrotron radiation diffraction (HT-SRD). Afterwards, the structural and chemical properties of the samples were characterized. The electrochemical performance was tested by galvanostatic cycling with potential limitation (GCPL), CV and EIS. Importantly, *ex situ* XAS (Mn K-edge and Zn K-edge) study was performed on cycled electrodes to investigate the evolution of the transition-metal oxidation state and the local structure. Thus, the present results reveal the mechanisms behind carbon coating improvement in cycling stability and rate capability.

2. Materials and Methods

2.1 Synthesis

Firstly, ZnMn_2O_4 nanoparticles were prepared via a simple co-precipitation method, as depicted in Ref. ²¹. Zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, Alfa-Aesar, 98%), manganese acetate tetrahydrate ($\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, Aldrich, 99%), oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$, Aldrich, 99%), and D-(+)-Glucose anhydrous ($\text{C}_6\text{H}_{12}\text{O}_6$, Alfa Aesar, 99%) were used without further purification. Briefly, zinc acetate (16 mmol) and manganese acetate (32 mmol) were dissolved in deionized water to form solution A. Subsequently, oxalic acid (72 mmol) was dissolved in deionized water to form solution B. Then, solution A was slowly dropped into solution B under vigorous stirring. The as-obtained precipitate was washed several times with deionized water and ethanol, and dried at 80 °C for 12 h as a precursor. After that, the precursor was calcined

at 500 °C for 1 h in air, named ZMO. Further, the ZMO was mixed with glucose with a mass ratio of ZMO: glucose=2:1 in deionized water. After drying at 80 °C for 12 h, the ZMO/glucose precursor was sintered at 300, 400, and 500 °C for 1 h under Ar flow. The obtained compounds were named CZMO-300, CZMO-400, and CZMO-500, respectively.

2.2 General characterization

A field emission scanning electron microscope Merlin (FESEM, Carl Zeiss SMT AG) was used to study the morphology of the samples. The elemental composition was investigated by energy dispersive X-ray spectroscopy (EDS, Bruker, Quantax 400 SDD). X-ray powder diffraction (XRD) was carried out by an STOE Stadi P XRD diffractometer (50 kV, 40 mA) in Debye-Scherrer geometry with Mo-K α_1 radiation ($\lambda = 0.70932$ Å). Rietveld refinement was performed to analyze the diffraction data using the FullProf software package.²⁴ To further investigate the morphology and phase composition, high-angle annular dark field (HAADF), selected area electron diffraction (SAED) and high-resolution TEM imaging (HRTEM) were performed on a Titan 80–300 electron microscope, equipped with a CEOS image aberration corrector. The TEM samples were prepared by dispersing the sample powder into ethanol through ultra-sonication and then drop casting on a copper grid. Thermogravimetric analysis (TGA) was conducted through a thermogravimetric analyzer (STA 449C, Netzsch GmbH) under Ar/O₂ flow (30/10 mL min⁻¹) from 35 °C to 800 °C with a heating rate of 10 °C min⁻¹. Nitrogen adsorption-desorption isotherms were obtained in an ASAP2460 instrument (Micromeritics GmbH) at -195.8 °C. Samples were degassed at 120 °C for 12 h prior to the analysis. Specific surface areas (SSAs) were calculated based on the Brunauer-Emmett-Teller (BET) equation in the 0.05~0.25 relative pressure range. Raman study was performed by a Raman spectrometer (LabRam Evolution HR, HORIBA Jobin Yvon) with 633 nm laser excitation and laser power of 17 mW. Fourier-transform infrared spectroscopy (FTIR) was obtained by using a Bruker Tensor 27 FT-IR spectrometer.

2.3 Electrochemical characterization

The working electrode was prepared by coating a uniform slurry on a 10 μm thick copper foil with a mass loading of ~ 2 mg cm⁻² and a dry thickness of ~ 15 μm . The slurry consisted of active material (60 wt.%), sodium carboxymethyl cellulose (10 wt.%, NaCMC, CRT2000, WaloCel), styrene-butadiene co-polymer latex (10 wt.%, TRD2001, JSR Micro), and carbon black (20 wt.%, Super P Li, Timcal Ltd.). CR2032 type coin cells were assembled for CV and GCPL measurements. The coin cell consisted of a working electrode, a glass fiber separator (Whatman®-GF/D), a Li foil (Alfa Aesar) counter electrode and LP30 electrolyte (Merck, 1 M LiPF₆ in ethylene carbonate/dimethyl carbonate = 1:1 by mass). PAT-cells (EL-CELL®) used in EIS measurement were assembled with PAT-Cores, which consist of a working electrode, a thin glass

fiber separator, a Li foil counter electrode, LP30 electrolyte, and a Li-ring reference electrode. All the cells were assembled in an Ar-filled glovebox (Labstar glove box workstation, MBraun).

CV, GCPL and EIS tests were carried out by a multichannel potentiostat (VMP3, Bio-Logic) at 25 °C in a climate chamber (Binder GmbH). GCPL was measured in the potential range of 0.01~3.0 V vs. Li/Li⁺ at different current densities (0.05, 0.1, 0.2, 0.5, 1.0, 2.0 and 5.0 A g⁻¹). For the *ex situ* XAS measurement, the working electrodes were cycled with specific numbers of cycles at 0.5 A g⁻¹ (40cy, 60cy, 80cy, 100cy) and 0.05 A g⁻¹ (1cy). The as-cycled electrodes were taken out at both lithiated (0.01 V) and delithiated (3.0 V) states and washed with dimethyl carbonate in Ar atmosphere. CV was carried out in the potential range of 0.01~3.0 V vs. Li/Li⁺ at a scan rate of 0.1 mV s⁻¹. EIS measurements were conducted at 0.4 V during lithiation every 6 cycles at a current density of 0.5 A g⁻¹. Prior to each EIS test, the working electrodes held at the setting potential for 3 h to reach the equilibrium. Impedance spectra were recorded over the frequency range from 500 kHz to 10 mHz with an amplitude of 5 mV. The Nyquist plots were fitted using RelaxIS3 software (rdh Instruments GmbH & Co. KG).

2.4 Synchrotron radiation measurements

To study the phase transition of the ZMO during carbonization process, *in situ* high-temperature synchrotron radiation powder diffraction (HT-SRD) was conducted by monochromatic synchrotron diffraction ($\lambda = 0.20737 \text{ \AA}$) at P02.1, PETRA-III, DESY. LaB₆ was used as a standard sample for wavelength calibration. The ZMO/glucose precursor (m:m=2:1) was sealed in a quartz capillary (ϕ 0.5 mm) under Ar and heated with a rate of 20 °C min⁻¹ up to 800 °C. The temperature was stabilized (3~5 min) during data collection. The as-obtained 2D image data were transformed to intensity-2 θ data using the Fit2D software.²⁴

Ex situ XAS measurements were performed at P65, PETRA III, DESY. XAS spectra were recorded in transmission geometry with the conventional step-scan mode at Mn K-edge and Zn K-edge. The double-crystal fixed exit monochromator was equipped with Si (111) crystal. The spectra were processed by using the Demeter software.²⁵ Background subtraction, normalization, energy alignment, and extraction of $\chi(k)$ oscillatory functions were performed with the Athena program of the Demeter package.²⁵ Further analysis with Artemis program includes calculation of theoretical amplitudes and phases by the FEFF6 code²⁶ and the fitting in the R-range from 1.0 to 3.2 Å of the Fourier-transformed data k^2 -weighted $\chi(k)$ applying Δk Hanning window from 3 to 8.0 Å⁻¹ with the width of the window slope $dk = 1 \text{ \AA}^{-1}$. The fitting parameters were the Mn–O and Mn–Mn interatomic distances ($R_{\text{Mn–O}}$ and $R_{\text{Mn–Mn}}$), Debye-Waller factor (σ^2), and zero energy shift (ΔE_0). The passive electron reduction factor S_0^2 was set to be 0.6 according to the analysis of reference data. For each spectrum collected on the delithiated samples, the following models were tested: single phase MnO (ICSD 162039 $Fm\bar{3}m$) for 6 neighbor oxygen and 12 neighbor manganese, or mixed phase of MnO and Mn₃O₄ (ICSD 252953 $I4_1amd$) for 6 (MnO) and 4+2 (Mn₃O₄) neighbor oxygen, as well

as 12 (MnO) and 2+4 (Mn₃O₄) neighbor manganese. The one with best R-factor was chosen to report.

3. Results and discussion

3.1 Phase transition of the ZMO/glucose precursor during the carbonization process

Figure 1 (a) *In situ* HT-SRD patterns of the ZMO/glucose precursor, and (b) the fraction evolution of the crystallized phase during the carbonization process.

Carbonization process should be employed under inert gas atmosphere for carbon coating. However, the ZnMn₂O₄ can be partially reduced to ZnO-MnO composite under high-temperature carbonization. Therefore, *in situ* HT-SRD has been used to monitor the phase transitions. As shown in Figure 1a, the ZnMn₂O₄ phase (#COD 96-901-2843, *I4₁amd*) forms after sintering at 500 °C in air (the 20 °C pattern at the bottom). The ZnMn₂O₄ phase remains stable below 250 °C, and then gradually converts to MnO (#COD 96-101-0394, *Fm $\bar{3}$ m*) and amorphous ZnO (250~400 °C). Above 400 °C, the amorphous ZnO starts to crystallize (ZnO, #COD 96-210-7060, *P6₃mc*). Based on Rietveld refinement calculation (Figure 1b), it is revealed that the phase fraction of crystallized ZnO increases slowly upon heating (400~750 °C), whereas the crystallized MnO forms faster at lower temperatures (300~400 °C). This can be attributed to the different rates of nuclei formation and growth for the ZnO and MnO. After cooling down from 800 °C to 20 °C, the sample is composed of MnO (64.6 wt.%) and ZnO (35.4 wt.%), which well agrees with the theoretical molar ratio Mn:Zn=2:1 (63.55 wt.% MnO and 36.45 wt.% ZnO). Moreover, the unit cells of ZnMn₂O₄ and MnO expand as the temperature increases. In detail, ZnMn₂O₄ expands mainly along the *c* axis. The parameter *c* enlarges linearly from 9.227 Å at 20 °C to 9.306 Å at 350 °C ($\Delta c/c = 0.86\%$), while the parameter *a(b)* shows less changes ($\Delta a/a = 0.28\%$), as shown in Figure S1a&b. In contrast, the unit cell of ZnO shrinks from 400 °C to 500 °C, indicating the crystallization of ZnO (Figure. S1c). Besides, the carbonization of glucose mainly occurs in the temperature range of 200~400 °C, and the weight losses of pure glucose are ~50 wt. % at 300 °C and 80 wt. % at 400 °C.²⁷ Therefore, 300 °C, 400 °C and 500 °C have

been chosen as carbonization temperatures for further study, namely carbon-derivative-coated ZnMn_2O_4 (CZMO-300), and carbon-coated ZnO-MnO (CZMO-400 and CZMO-500).

3.2 Morphology and phase composition

Morphological and microstructural characterization of the samples was performed by SEM. As observed from Figure 2a&b, the ZMO displays clusters of flakes with a size of 2~5 μm composed of interconnected nanoparticles (30~50 nm), while the CZMO-300 looks like large blocks, due to the linking of carbon derivative (Figure 2c). As shown in Figure 2d, metal oxide nanoparticles are surrounded by the carbon derivative. When calcined at 400 °C and 500 °C, the glucose is well carbonized into thin carbon layers. In detail, the CZMO-400 looks like porous blocks consisting of carbon-coated nanoparticles (Figure 2e). The CZMO-500 (Figure 2g) shows a similar morphology like the bare ZMO. Moreover, the CZMO-400 and CZMO-500 are composed of smaller nanoparticles (average size of 15~30 nm) due to the collapse of the original particles during the phase transition from ZnMn_2O_4 to ZnO-MnO composite (Figure 2f&h). The smaller particle sizes benefit to the rate performance of the electrode materials.²⁸ The EDS result confirms that Zn, Mn and O are homogenously distributed in all the as-prepared samples, and the surface of the CZMO samples are fully covered with carbon (Figure S2).

Figure 2 SEM images: (a,b) ZMO, (c,d) CZMO-300, (e,f) CZMO-400, and (g,h) CZMO-500.

Figure 3 (a) XRD (Mo $K_{\alpha 1}$) patterns and (b) TGA curves of the noted samples.

The crystal structure of the as-prepared samples has been characterized by XRD (Mo $K_{\alpha 1}$), as shown in Figure 3a. It is evident that the tetragonal spinel ZnMn_2O_4 is successfully synthesized, as previously confirmed by HT-SRD. The carbon-coated samples (CZMO-400 and CZMO-500) show a clear reduction from ZnMn_2O_4 to ZnO-MnO. Crystallized phase composition of the as-prepared samples has been calculated according to Rietveld refinement (see Figure S3), and it is in good agreement with the HT-SRD results. In detail, the CZMO-300 is composed of 89 wt.% ZnMn_2O_4 and 11 wt.% MnO, whereas the CZMO-400 consists of 91 wt.% MnO and 9 wt.% ZnO, and the CZMO-500 is composed of 81 wt.% MnO and 19 wt.% ZnO. It is noteworthy that amorphous ZnO in these samples can't be detected by XRD. To determine the content of coated carbon or carbon derivative, TGA was performed from 30 °C to 800 °C in Ar/ O_2 flow ($v/v=3/1$). As shown in Figure 3b, the ZMO shows high thermal stability with no obvious weight loss during heating, while the other three samples display a weight main loss at ~300 °C, due to the combustion of the coated carbon or carbon derivative. Except for the CZMO-300, the weight of the CZMO-400 and CZMO-500 increases at an onset temperature of ~284 °C, which can be attributed to the oxidation of MnO. Therefore, the weight change due to both the MnO oxidation and the carbon combustion results in a fluctuation of the residual weight around 370 °C. Finally, the carbon or carbon-derivative contents of the coated layers in CZMO-300, CZMO-400 and CZMO-500 are calculated to be 22.2 wt.%, 15.7 wt.% and 12.3 wt.%, respectively. The EDS result also shows a similar trend for their carbon contents of 25.3 wt.%, 12.5 wt.%, 10.4 wt.%, respectively.

The morphology and phase composition of the CZMO samples are also investigated by transmission electron microscopy. The HAADF images presented in Figure 4a~c show a few nanometers thick carbon layer coating the CZMO-300 particles, a thinner and less homogeneously distributed layer around the CZMO-400 sample and a barely visible coating for the CZMO-500. Moreover, STEM-HAADF imaging shows that CZMO-400 and CZMO-500 nanoparticles to be smaller as compared with the CZMO-300 sample, in agreement with the analysis of SEM imaging. The results of the SAED analysis of the crystal

phase evolution throughout the heat treatment are shown in Figure 4d~f. The diffraction patterns of the CZMO-300 sample can be identified as the ones of the ZnMn_2O_4 spinel structure, whereas the ones of the CZMO-400 and CZMO-500 samples correspond to the MnO and ZnO phases. The corresponding patterns of the ZnMn_2O_4 phase are not present in the CZMO-400 and CZMO-500 diffractions and this can be easily highlighted by following the $d_{(101)} \sim 0.48\text{nm}$ reflection that cannot be observed in the last two samples. High-resolution TEM imaging (Figure 4g~i) shows a similar evolution of the crystal phases as the electron diffraction. The crystal lattice fringes exhibited by the CZMO-300 nanoparticles can be indexed as the $d_{(101)} \sim 0.48\text{nm}$, $d_{(112)} \sim 0.31\text{nm}$ and $d_{(113)} \sim 0.245\text{nm}$ spacing of the ZnMn_2O_4 spinel phase. These reflections disappear for the CZMO-400 and CZMO-500 samples. Moreover, the HRTEM image of the CZMO-500 sample shows the presence of a homogenous carbon layer around some nanoparticles.

Figure 4 STEM - HAADF, SAED and HRTEM images of the CZMO-300 (a, d&g), CZMO-400 (b, e&h), and CZMO-500 (c, f&i). The insets in g, h and i represent the fast Fourier transform (FFT) of the corresponding HRTEM images.

Figure 5 (a) Raman spectra and (b) FTIR spectra of the as-prepared samples.

Furthermore, N_2 adsorption-desorption isotherms and the corresponding pore size distributions are shown in [Figure S4](#). The ZMO and the CZMO-400 display SSAs of $44.1 \text{ m}^2 \text{ g}^{-1}$ and $30.8 \text{ m}^2 \text{ g}^{-1}$, respectively. The pore sizes of the two samples are mainly distributed in 2~20 nm. This is because that the coated carbon layer can block some mesopores (2~10 nm), leading to the lower SSA of the CZMO-400 sample.²⁹ To further analyze the coated carbon or carbon-derivative in the CZMO samples, Raman and FTIR studies were conducted ([Figure 5](#)). In low Raman shift range ($100\sim 800 \text{ cm}^{-1}$), the modes of the ZMO and CZMO-300 are similar, confirming the formation of tetragonal spinel ZnMn_2O_4 ,^{23,30} whereas the modes of the CZMO-400 and CZMO-500 become broader and shift to lower Raman shift, indicating the phase transition from ZnMn_2O_4 to MnO .³¹ The two broad modes at $1000\sim 1800 \text{ cm}^{-1}$, corresponding to defective and graphitic carbon (D band and G band), appear in the spectra of the CZMO-400 and CZMO-500, confirming that the carbon-coated layer is fully formed above 400°C and that the coated layer in the CZMO-300 is a carbon-derivative. In [Figure S5](#), the fitting of the D band and G band are performed by using four vibration modes (G $\sim 1580 \text{ cm}^{-1}$, D1 $\sim 1350 \text{ cm}^{-1}$, D3 $\sim 1500 \text{ cm}^{-1}$, and D4 $\sim 1200 \text{ cm}^{-1}$).³² The I_{D1}/I_G intensity (peak area) ratios of the CZMO-400 and CZMO-500 are calculated to be 2.44 and 1.57, respectively. This indicates a higher degree of graphitization of the coated carbon in the CZMO-500. In [Figure 5b](#), the FTIR spectra show that the bands of glucose disappear after the heat treatment. In the spectra of the CZMO-300, the bands located at $\sim 1580 \text{ cm}^{-1}$, $\sim 1408 \text{ cm}^{-1}$, and $\sim 1084 \text{ cm}^{-1}$ correspond to the functional groups of C=C, O-H, and C-O, respectively.³³ Above 400°C , these peaks related to the organic functional groups almost disappear, demonstrating the formation of the graphitic carbon.

3.3 Electrochemical measurements

The electrochemical performance was evaluated by CV, GCPL and EIS. [Figure 6](#) displays the CV curves measured at a scan rate of 0.1 mV s^{-1} . Due to the initial conversion process, the 1st cathodic curve is different from the subsequent cycles. The ZMO shows cathodic peaks at $\sim 1.28 \text{ V}$ (Mn^{3+} to Mn^{2+}) and at $\sim 0.26 \text{ V}$

(Mn^{2+} to Mn^0 and Zn^{2+} to Zn^0),¹⁹ as displayed in Figure 6a. The weak peak at ~0.9 V can be attributed to the initial formation of the SEI.^{22,34} Metallic Zn can immediately alloy with Li to form LiZn_4 once Zn^{2+} is reduced to Zn^0 . The alloy reaction further proceeds to finally form LiZn and Li_2O .^{35,36} Additionally, an extra Li storage process occurs at the interface of metal nanograins and Li_2O in the low potential region. This process is due to the space charge storage mechanism caused by nanosize effect.^{37,38} In contrast, the CZMO samples display higher electrode polarization in the 1st cathodic curve. The peaks shift towards lower potential, and current tails are also observed in the low potential region (Figure 6d, g and j). This can be ascribed to the carbon layer, which covers the active sites of the active materials.^{39,40}

In subsequent cycles, two anodic peaks at ~1.2 V (Mn^0 to Mn^{2+}) and ~1.5 V (Zn^0 to Zn^{2+}) and one cathodic peak at ~0.5 V (Mn^{2+} to Mn^0 and Zn^{2+} to Zn^0) can be observed, indicating the occurrence of conversion reactions.¹⁹ In Figure 6b&c, the cathodic peak of the ZMO shifts to lower potential and the intensities of redox peaks decrease upon cycling. This indicates that the electrode polarization continuously increases, which is accompanied by a decrease in capacity. In contrast, the CZMO samples display much higher cycling stability. The CZMO-300 displays a tiny decrease in peak current after ~120 cycles, without an increase of electrode polarization (see Figure 6e&f). As for the CZMO-400 and CZMO-500, a tiny increase in the peak intensities during 30th~70th cycles can be noted (see Figure 6h&k). A weak increase of electrode polarization occurs after ~120 cycles (see Figure 6i&l).

As observed in our previous work,²³ ZMO shows an increasing additional capacitive charge storage after ~30 cycles (see Figure 6b&c). This corresponds to extra reversible charge storage in the SEI.^{21,22,34,41} The new pair of redox peaks observed during 60~100 cycles can be assigned to the $\text{Mn}^{3+}/\text{Mn}^{2+}$ redox reaction. A similar, but much weaker phenomenon, can also be observed in the CZMO samples. These results evidence that carbon coating not only prevents an excessive electrode polarization but also improves the reversibility of charge storage processes.

Figure 7a displays the long-term cycling performance at a current density of 0.5 A g⁻¹, and selected potential profiles are shown in Figure S6. The ZMO shows a high capacity during the initial cycles (~800 mAh g⁻¹), followed by dramatic variations, as previously reported.²³ Specifically, the capacity increases intensively up to ~1100 mAh g⁻¹ at the 80th cycle, and then suddenly decreases, to ~400 mAh g⁻¹ at the 150th cycle. In contrast, the CZMO samples deliver much more stable capacities. Within the initial 100 cycles, the capacity gradually increases from 500 to 700 mAh g⁻¹. After that, the capacity remains stable for the next hundreds of cycles. Regarding the coulombic efficiency, it can be noted that the ZMO displays the highest value of 66.2% at the 1st cycle, whereas the coulombic efficiencies of the CZMO-300, CZMO-400 and CZMO-500 are 47.3%, 52.3% and 51.9%, respectively. These results indicate that the carbon- and carbon-derivative-coated layers induce higher irreversible capacity during the 1st lithiation. In the

subsequent cycles, the ZMO and the CZMO-300 possess lower coulombic efficiencies than that of the CZMO-400 and CZMO-500. The coulombic efficiencies of the ZMO and CZMO-300 gradually increase to 99.2 % after ~40 and ~50 cycles, respectively. The highest coulombic efficiency is obtained after ~10 and ~20 cycles for the CZMO-400 and CZMO-500, respectively (see the inset image in Figure 7a). This result indicates that a stable SEI can be faster formed on the carbon layer, whereas the bare ZMO needs more cycles to stabilize the interface.

Figure 6 CV curves of the samples: (a~c) ZMO, (d~f) CZMO-300, (g~i) CZMO-400, (j~l) CZMO-500 scanned at 0.1mV s^{-1} .

A rate capability test was performed to evaluate the electrochemical performance of the samples at different current densities (Figure 7b). At lower current densities, the ZMO shows the highest capacity with $\sim 994 \text{ mAh g}^{-1}$ at 0.05 A g^{-1} and $\sim 620 \text{ mAh g}^{-1}$ at 1 A g^{-1} , while the CZMO-300 and CZMO-400 deliver similar capacities of $\sim 771 \text{ mAh g}^{-1}$ at 0.05 A g^{-1} and 538 mAh g^{-1} at 1 A g^{-1} . In contrast, the CZMO-500 shows a poor rate capability, delivering only 233 mAh g^{-1} at 1 A g^{-1} . At higher current densities, the CZMO-400 shows the highest capacity with 428 mAh g^{-1} at 2 A g^{-1} and 225 mAh g^{-1} at 5 A g^{-1} . Moreover, when the current density returns to 0.05 A g^{-1} , the ZMO electrode shows a failure in cycling stability. The corresponding capacity retention is shown in Figure S7. Among these samples, the CZMO-400 displays the best rate capability. This can be attributed to the coated carbon layer with proper coated amount and degree of graphitization. In the CZMO-300, the coated layer is not graphitized, inducing a limited electronic conductivity, whereas, in the CZMO-500, the carbon content is too low to connect all the metal oxide particles.

As discussed in the CV study, the capacity of the conversion electrodes can be separated into different potential ranges based on the specific charge storage processes. Figure 7d&g show the capacity related to the main conversion processes ($\text{Mn}^0/\text{Mn}^{2+}$ and $\text{Zn}^0/\text{Zn}^{2+}$). The ZMO exhibits a capacity which is $150\sim 200 \text{ mAh g}^{-1}$ higher than the CZMO samples during the initial 80 cycles. This indicates the higher conversion capacity in the ZMO sample. In contrast, the CZMO samples show much higher capacity retention within 200 cycles. The evolution of the $\text{Mn}^{3+}/\text{Mn}^{2+}$ conversion and the SEI charge storage can be observed in Figure 7c&h. The ZMO shows a higher reduction capacity during the initial 10 cycles, indicating that the $\text{Mn}^{3+}/\text{Mn}^{2+}$ conversion reaction is partially reversible and that the Mn^{3+} converts to Mn^{2+} gradually at the delithiated state. During the $60^{\text{th}}\sim 80^{\text{th}}$ cycles the capacity of ZMO rapidly increases, and then fast fades in the subsequent cycles. On the other hand, the capacity of the CZMO samples increase gradually, due to the slow increase in the $\text{Mn}^{3+}/\text{Mn}^{2+}$ redox reaction and charge storage in SEI. Figure 7f shows the capacity originated from the de-alloy reaction and the extra space charge.^{37,38} The capacity evolution related to the alloy/de-alloy process is similar to the one related to the main conversion process. Besides the capacity of alloy mechanism and extra space charge, the capacity displayed in Figure 7e also contains the extra capacity due to the SEI. The capacity of the ZMO rapidly increases and decreases at the $60^{\text{th}}\sim 100^{\text{th}}$ cycles, in contrast to the modest capacity growth of the CZMO samples. Among the samples, the CZMO-300 shows the highest SEI extra capacity. It can be attributed to its higher amount of surface functional groups, $-\text{OH}$, which is detected by FTIR (Figure 5b). Yan-Yan Hu, *et al.* have reported that the surface $-\text{OH}$ groups of electrode materials can involve the formation of LiOH in SEI, which can contribute to extra capacity.²²

Figure 7 GCPL lithiation (solid spots) and delithiation (circles) capacities (a) with 0.5 A g⁻¹ for long-term cycling and (b) with varied current densities; the inset in (a) shows the coulombic efficiency in the initial 50 cycles; and (c-h) capacity vs. cycle number separated into different potential ranges: (c) 3.0~0.8 V, (d) 0.8~0.3 V, and (e) 0.3~0.01 V during lithiation, and (f) 0.01~1.00, (g) 1.0~1.9 V and (h) 1.9~3.0 V during delithiation.

To further understand the different electrochemical behavior of the ZMO and CZMO-400, EIS measurements were conducted every 6 cycles at 0.4 V during the lithiation process at the current density of 0.5 A g⁻¹ (see Figure 8a&c). Figure 8b shows the capacity variation of the ZMO upon cycling. The maximum capacity of the ZMO is achieved at the ~48th cycle, while the CZMO-400 shows a monotonous increase of the specific capacity. This is also in agreement with the above GCPL results. The Nyquist plots consist of two semicircles and an inclined line. In the high-frequency region (100~20 kHz), the intercept between the first semicircle and the real axis is related to the resistance of the cell system (R_s), including

the cell parts, electrolyte, separator, and working electrode contact. In the mid-frequency range (400~3 Hz), the first semicircle corresponds to the parallel connection of the resistance of SEI (R_{SEI}) and the corresponding capacitance (CPE1). The second semicircle at lower frequencies (2~0.06 Hz) is attributed to the parallel connection of the charge transfer resistance (R_{ct}) and the corresponding capacitance (CPE2). The inclined line appearing at even lower frequencies indicates the diffusion process, which is represented by a constant phase element (CPE3).^{15,42} The equivalent circuit is shown in Figure 8d and the fitted Nyquist plots are depicted in Figure 8a&c.

The evolution of the fitted resistances is shown in Figure 8d. The R_s variation reflects the change of the electrode contact resistance. The R_s of the ZMO obviously increases from the 50th cycle (~1 Ω) to the 120th cycle (~3 Ω), whereas the CZMO-400 has a stable R_s (~1.5 Ω). This result demonstrates that the coated carbon layer can delay the pulverization process, and help to keep the integrity of the electrode, thus avoiding the loose of contact between the active particles. The R_{SEI} of the ZMO displays a dramatic decrease from 3.5 to 1.5 Ω after the initial SEI formation. By contrast, the much higher R_{SEI} (~7 Ω) of the CZMO-400 indicates that the SEI formed on the carbon-coated surface is less conductive. Furthermore, the evolution of R_{SEI} is different for the two samples. The R_{SEI} of the ZMO slowly increases before that the electrodes reach their highest capacities: the increase of additional capacity occurs in parallel with the increase of R_{SEI} . This confirms that the growth of conductive SEI can accommodate more and more Li^+ ions. Afterwards, the R_{SEI} of the ZMO rapidly increases, while, in parallel, a fast capacity fading occurs. It can be speculated that the SEI becomes less conductive after repeated charge/discharge cycles and seriously impedes the Li^+ migration. In comparison, the R_{SEI} of the CZMO-400 decreases gradually and keeps a low value after ~80 cycles. It indicates that the less conductive SEI formed on the coated carbon is activated as the cycling proceeding. The initial R_{ct} of the ZMO and CZMO-400 are 3 Ω and 39 Ω , respectively. The higher R_{ct} of the CZMO-400 can explain the high electrode polarization observed during the 1st lithiation process in the CVs (Figure 6d, g and j). However, after the 1st cycle, the R_{ct} becomes very low (~1 Ω for the ZMO and ~2 Ω for the CZMO-400). Thereafter, the R_{ct} of the ZMO obviously increases after ~50 cycles, corresponding to the phase transformation and segregation upon cycling. In contrast, the stable R_{ct} of the CZMO-400 confirms the role of the coated carbon on the suppression of phase changes.

3.4 *Ex situ* XAS measurements

XANES and extended X-ray absorption fine structure (EXAFS) are powerful methods to characterize the valence and local structure of related elements.⁴³ To further reveal the effect of the coated carbon on the redox chemistry evolution, *ex situ* XAS was performed on ZMO and CZMO-400 electrodes. The *ex situ* samples analyzed are listed in the following: the electrodes (de)lithiated with a current of 0.05 A g⁻¹ after the 1st cycle, and the electrodes (de)lithiated with a current of 0.5 A g⁻¹ after the 40th cycle, the 60th cycle,

the 80th cycle and the 100th cycle. This allows to understand the redox processes during the 1st cycle and to relate the evolution of the redox pairs to the capacity variations of the ZMO (Figure S8&S9). As shown in Figure S10, delithiated electrodes with different cycle numbers (1st, 60th, and 100th) show similar XANES spectra at Zn K-edge and Zn local structure, presenting the Zn²⁺ oxidation state and hexagonal ZnO structure (space group $P6_3mc$). It indicates that the conversion reaction of the Zn/ZnO is still reversible after 100 cycles for both the ZMO and CZMO-400.

Figure 8 EIS test during GCPL cycling: (a&c) Nyquist plots recorded at 0.4 V during lithiation (point: raw data, line: fitted data) for (a) the ZMO and (c) the CZMO-400; (b) capacities during lithiation (solid spots) and delithiation (circles) at 0.5 A g⁻¹, and (d) R_s , R_{SEI} , and R_{ct} obtained by fitting the Nyquist plots.

Furthermore, a detailed analysis of the Mn K-edge XANES spectra is shown in Figure 9. Compared with the spectra of standard Mn₂O₃ and MnO, the pristine ZMO sample displays a valence near to Mn³⁺, while the pristine CZMO-400 sample displays a lower Mn oxidation state (between Mn³⁺ and Mn²⁺), which is due to the reduction of ZnMn₂O₄ during carbonization (Figure 9a&d). The spectra of delithiated samples

show slight differences in the edge energy in comparison with the standard MnO spectrum. This implies the presence of other species, like Mn^{3+} and Mn^0 . On the other hand, the edge energy of the lithiated samples locates between the MnO and Mn, demonstrating the reduction of manganese oxides to metallic Mn (Figure 9b&e). Moreover, an isosbestic point at 6544 eV can be observed in the spectra of the lithiated samples, implying a phase transition process upon cycling. This confirms that MnO and Mn, whose spectra intersect at the isosbestic point, are involved in this process.⁴⁴

Since both the lithiated and delithiated samples are composed of different valences, linear combination fitting was performed on XANES data. The spectra of standard Mn_2O_3 , MnO and Mn are used as references for linear combination fitting to evaluate the fractions of different Mn components, Mn^{3+} , Mn^{2+} and Mn^0 .^{45,46} Firstly, the delithiated samples are discussed. The ZMO electrode after the 1st cycle (Figure 9c) contains a certain amount of Mn^{3+} , which agrees with the plateau near 3 V (Mn^{2+} to Mn^{3+}) observed in the galvanostatic profile (Figure S8). This indicates that Mn can be partially oxidized to Mn^{3+} when applying a low current density (0.05 A g⁻¹ in this case). At the same time, a small amount of Mn^0 is also observed, suggesting some irreversibility during the oxidation reaction. After the 40th cycle, the amount of Mn^{3+} decreases while the amount of Mn^0 increases. This demonstrates a decrease of reversibility for the oxidation reaction, and it can be well correlated to the capacity fading observed during the initial cycles. Interestingly, at the 60th and 80th cycle, the amount of Mn^{3+} increases and Mn^0 decreases, evidencing an enhanced oxidation reaction, which can be the main reason for the obvious capacity increase. This is attributed to the shorter Li diffusion distances and faster reaction kinetics induced by the conductive SEI growing into the active particles through the cracks formed during cycling. At the 100th cycle, repeated conversion process and excessive SEI formation induce particle pulverization, resulting in a decreased reaction activity and leading to the subsequent capacity loss. This is evidenced by a decreased amount of Mn^{3+} and an increased amount of Mn^0 . In contrast, the fitting results of the CZMO-400 electrodes show a stable amount of Mn^{3+} , and a decreased amount of Mn^0 during long-term cycling (Figure 9f), indicating a limited oxidation reaction to Mn^{3+} and improved reaction reversibility of the $\text{Mn}^0/\text{Mn}^{2+}$ oxidation. These phenomena imply a suppressed phase composition evolution process, which can be attributed to the fact that the coated layer inhibits excessive SEI growth and suppresses particle pulverization.

On the lithiated ZMO electrodes (Figure 9e), the fraction of Mn^0 decreases to the lowest value at the 40th cycle, then increases to high values from the 60th to the 80th cycle, and finally decreases again at the 100th cycle. This also agrees with the trend as described above, displaying a well-improved reaction activity from the 60th to the 80th cycle and capacity fading at the 100th cycle. In comparison, in the lithiated CZMO-400 electrodes (Figure 9f), the fraction of Mn^0 is much higher than that in the ZMO, and it even reaches 100 %

at the 100th cycle, demonstrating an improved reduction conversion and enhanced efficiency induced by carbon coating.

Figure 9 *Ex situ* XANES spectra for Mn K-edge: (a) delithiated ZMO, (b) lithiated ZMO, (d) delithiated CZMO-400 and (e) lithiated CZMO-400 and the LCF results based on the relative derivative normalized energy spectra in XANES region: (c) ZMO and (f) CZMO-400.

Figure 10 Fitting of the Fourier transformed EXAFS spectra for selected *ex situ* electrodes: (a-c) delithiated ZMO at the 1st cycle (a), the 40th cycle (b) and the 80th cycle (c); (d) lithiated ZMO at the 1st cycle; (e-g) delithiated CZMO-400 at the 1st cycle (e), the 40th cycle (f) and the 80th cycle (g); (h) lithiated CZMO-400 at the 1st cycle.

The Mn local structure obtained from Fourier transform of EXAFS spectra is shown in Figure S11. The fitting results of the electrodes after 1 cycle, 40 cycles and 80 cycles at delithiated state are shown in Figure 10 and Table 1. The results indicate that both, the ZMO and CZMO-400, are composed of MnO and Mn₃O₄ mixture after the 1st cycle, and composed of only MnO after the 40th cycle. Thereafter, the ZMO changes to a mixed composition of MnO and Mn₃O₄ after the 80th cycle, whereas the CZMO-400 still exhibits the MnO composition. This is in agreement with the oxidation state analysis based on the XANES spectra. Moreover, the long-range orderliness of the crystal structure is weakened during cycling. As for the lithiated samples (Figure S11c&d and Figure 10d&h), the single broad peak is attributed to the overlapped Mn-Mn interaction (~2.6 Å) of Mn metal (ICSD 163411 *P4₁3₂*) and Mn-O interaction (~2.1 Å) of MnO (ICSD 162039 *Fm $\bar{3}$ m*). The long-range orderliness is not constructed after the conversion process.

Table 1 The fitted parameters based on the EXAFS spectra for the delithiated electrodes.

Parameters	Coordination numbers	The delithiated ZMO electrodes			The delithiated CZMO-400 electrodes		
		1 st cycle	40 th cycle	80 th cycle	1 st cycle	40 th cycle	80 th cycle
ΔE_0	--	-7.93	-4.26	-2.78	-1.06	-5.39	-5.39
$R_{\text{Mn-O1}}$ (MnO)	6	1.99	2.04	2.03	2.06	2.03	2.04
$R_{\text{Mn-O2}}$ (Mn ₃ O ₄)	4	1.74	--	1.98	2.08	--	--
$R_{\text{Mn-O3}}$ (Mn ₃ O ₄)	2	2.06	--	2.43	2.43	--	--
$R_{\text{Mn-Mn1}}$ (MnO)	12	3.01	3.26	3.06	3.39	3.23	3.22
$R_{\text{Mn-Mn2}}$ (Mn ₃ O ₄)	2	2.99	--	3.07	2.98	--	--
$R_{\text{Mn-Mn3}}$ (Mn ₃ O ₄)	4	3.23	--	3.31	3.21	--	--
σ^2_{O1} (MnO)	--	0.0115	0.0128	0.0384	0.0405	0.0122	0.0138
σ^2_{O2} (Mn ₃ O ₄)	--	0.0288	--	0.0147	0.0040	--	--
σ^2_{Mn1} (MnO)	--	0.0387	0.0317	0.0383	0.0320	0.0312	0.0292
σ^2_{Mn2} (Mn ₃ O ₄)	--	0.0033	--	0.0118	0.0079	--	--
R-factor	--	0.0055	0.0146	0.0015	0.0033	0.0188	0.0254

4. Conclusions

In summary, carbon-derivative-coated ZnMn₂O₄ and carbon-coated ZnO-MnO composites were synthesized by a simple carbon-thermal reduction method. The HT-SRD shows that the ZnMn₂O₄ is converted to ZnO-MnO composite at 250~400 °C, and the crystallized MnO and ZnO are formed above 350 °C and 600 °C, respectively. As anodes for LIBs, the carbon- or carbon-derivative-coated samples

show slow conversion kinetics than the bare ZnMn_2O_4 during the 1st lithiation. This is ascribed to the fact that the coated layer covers the active sites on metal oxide particles. However, the carbon or carbon-derivative coating efficiently improves the cycling stability and rate capability compared to the obvious capacity variations of the bare ZnMn_2O_4 . In addition, the long-term CV and EIS tests reveal that the effective carbon coating is not only protecting the active material from excessive pulverization, but it also efficiently inhibits the excessive growth of SEI and particle insulation. *Ex situ* XAS result illustrates the evolution of the metal oxides during repeated conversion reaction. It confirms that the increase in $\text{Mn} \rightarrow \text{Mn}_3\text{O}_4$ conversion reaction occurs after ~60 cycles on the bare ZnMn_2O_4 , and explains the increase in capacity. The carbon coating can suppress the phase evolution from MnO to Mn_3O_4 , leading to a stabilized conversion reaction. Hence, these results can provide a deep insight to understand the effect of the carbon coating on conversion-type, especially Mn-containing, electrode materials.

Associated Content

The following file is available free of charge.

Supporting Information (PDF file)

Crystal lattice parameters variations of the ZnMn_2O_4 , MnO and ZnO upon temperature increasing when the ZMO/glucose precursor was heated in Ar; EDS mapping and crystalized phase composition of the as-prepared samples; N_2 adsorption-desorption isotherms and related pore size distributions of the ZMO and CZMO-400 samples; Raman spectra of the CZMO-400 and CZMO-500; GCPL potential profiles with current density of 0.5 A g^{-1} ; retention rates of the GCPL delithiation capacities at different current densities; GCPL potential profiles of the ZMO and CZMO-400 with 0.05 and 0.5 A g^{-1} current densities; specific capacities upon GCPL cycling of the ZMO and CZMO-400 at a current density of 0.5 A g^{-1} , labelled with the points for *ex situ* XAS measurement; *ex situ* XANES spectra at Zn K-edge and Zn local structure of the delithiated ZMO and CZMO-400 electrodes; Mn local structure obtained from Fourier transform of EXAFS spectra of the ZMO and CZMO-400 electrodes at delithiated and lithiated states.

Author Contribution

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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