Preparation of N-doped porous carbon coated MnO nanospheres through solvent-free in-situ growth of ZIF-8 on $ZnMn_2O_4$ for high-performance lithium-ion battery anodes

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ABSTRACT

We present a novel and facile strategy to prepare porous N-doped carbon coated MnO (MnO@NC-Z) nanospheres through solvent-free in-situ growth of ZIF-8 on $ZnMn_2O_4$ followed by carbonization. The obtained MnO@NC-Z nanospheres are composed of numerous MnO nanoparticles that are uniformly coated by an ultrathin (~5 nm) and nitrogen-rich (~3.7 wt%) carbon layer derived from the in-situ grown ZIF-8 layer, which could not only restrict the volume expansion of MnO during the charge-discharge process but also substantially improve the electrical conductivity. Meanwhile, the synthesized MnO@NC-Z also possesses a high porosity and large specific surface area due to the porous structure of the ZIF-8 precursor and the evaporation of nano-sized Zn reduced from the ZIF-8 during the carbonization process, which could facilitate the fast transport of Li ions. As the anode in lithium-ion batteries (LIBs), the prepared MnO@NC-Z nanospheres deliver excellent performance with a high reversible capacity of $1261\ mA\,h\,g^{-1}$ at $0.2\ A\,g^{-1}$, brilliant rate performance of $305\ mA\,h\,g^{-1}$ at a high rate of $5\ A\,g^{-1}$, and excellent cycling stability for 1000 cycles at $1\ A\,g^{-1}$ with a 96.5% capacity retention. Importantly, this solvent-free strategy of in-situ growth of ZIF-8 can also be extended to synthesize various metal oxides@carbon composites (e.g., FeO_x@NC and CoO_x@NC) for different applications such as energy storage and conversion.

1. Introduction

Lithium ion batteries (LIBs) with high power densities and long cycling life are regarded as promising, green, and versatile energy storing devices to satisfy the ever-increasing performance demands for electronic equipment [1–4]. As a commercial anode material, graphite cannot meet the desired high-power/-energy density and stability for the next-generation LIBs because of its low theoretical capacity ($372\ mA\,h\,g^{-1}$) and unsatisfactory rate capability [5]. Recent work has demonstrated that transition metal oxides with high capacities and low costs could be served as suitable and promising substitutes for graphite in LIBs [6–8].

Among various transition metal oxides, MnO has received enormous attention owing to its low voltage hysteresis (<0.8 V), environmental friendliness, low cost, high theoretical capacity ($756\ mA\,h\,g^{-1}$), and low operation potential (1.032 V vs Li/Li^+) [9–11]. However, like other transition metal oxides, some intrinsic drawbacks of MnO have dramatically hindered its further development [12,13]. The terrible electrical conductivity of MnO makes it suffer from an unsatisfactory capacity and terrible rate capability. Besides, the drastic volumetric change of MnO during the lithiation/delithiation process leads to pulverization of the MnO anodes and gradual aggregation of the active materials, causing severe capacity fading [6,12]. Up to now, much effort has been dedicated to solving these drawbacks of MnO. One effective strategy is to synthesize nanoscaled MnO with proper morphologies

that can largely shorten the diffusion lengths of Li ions, improving the capacity and rate capability of the MnO anodes [14,15]. Another common method is to coat MnO with conductive carbon to improve the electrical conductivity and to hinder the volume expansion of MnO during the Li-ion insertion/extraction process, consequently improving its electrochemical performance (e.g., capacity, rate capability, and cycling stability) [16–18].

To date, various strategies have been developed to synthesize carbon coated MnO (MnO@C) composites. Liu group synthesized a MnO@C composite through sintering a mixture of the pre-prepared Mn_2O_3 microspheres and pyrrole [19]. Cao and co-workers synthesized MnO@C through a hydrothermal reaction of $Mn(OAc)_2 \cdot 4H_2O$ and ascorbic acid (as a carbon source) followed by carbonization [20]. Zhang et al. utilized polydopamine (PDA) as a carbon precursor to coat Mn_3O_4 nanocrystals and then obtained MnO@C composites through carbonization [21]. However, these methods usually produced the MnO@C composites with incomplete carbon coatings due to the weak binding forces between MnO and C. Therefore, the development of strategies to fabricate metal oxide@C composites with a strong interaction between the carbon and metal oxides is still necessary. As a kind of metal-organic frameworks (MOFs), zeolitic imidazolate framework-8 (ZIF-8), which is formed by the coordination of Zn^{2+} and 2-methylimidazole, has attracted extensive attention on gas separation [22], catalysis [23], and drug delivery [24] due to its tunable porosity, large specific surface area, and stable structure [25–27]. In addition, ZIF-8 can also serve as a sacrificial template to synthesize porous carbon or ZnO/C composites for LIBs [28–30]. Since 2-methylimidazole is a nitrogen-containing ligand, the ZIF-8 derived carbon is N-doped porous carbon. Many studies have shown that the N-doped carbon possesses an improved electrical conductivity compared to the pristine carbon [31–34]. Bu group used an ex-situ strategy to synthesize α-MnO_2/ZIF-8 and then obtained yolk-shell MnO@$ZnMn_2O_4$/N-C nanorods through carbonization. This obtained samples exhibited a stable capacity of 371 mA h g^{-1} at 1000 mA g^{-1} after 200 cycles [35].

Based on the above consideration, coating MnO with a N-doped carbon layer through the in-situ growth of ZIF-8 on the oxide surface might be an effective strategy to address the drawbacks of MnO. Meanwhile, the reported synthetic methods for ZIF-8 are mostly solution-based, which are usually associated with low yields and complicated processes. Our group recently reported a facile synthesis of a ZnO@NC composite through a solid-phase reaction of ZnO nanorods and 2-methylimidazole [36]. The results demonstrated that the zinc from the surface of ZnO nanorods indeed can react with 2-methylimidazole to form a ZnO@ZIF-8 core-shell structure. Inspired by this strategy, it is possible that other MO_x@NC (e.g., M = Mn, Fe, Co, and Ni) composites could also be obtained through the solvent-free in-situ growth of a ZIF-8 layer on the surface of a properly chosen mixed metal oxide containing Zn, e.g., $ZnMn_xO_y$, $ZnFe_xO_y$, $ZnCo_xO_y$, and $ZnNi_xO_y$.

In this work, a bimetallic oxide, $ZnMn_2O_4$ (as both the precursor of MnO and the source of Zn^{2+}) was reacted with 2-methylimidazole to in-situ synthesize ZIF-8 on the surface of the metal oxide via a facile solvent-free method, leaving MnO_x inside the ZIF-8 coating. After carbonization, the MnO nanospheres coated by N-doped porous carbon derived from ZIF-8 (MnO@NC-Z) were obtained. Compared to the conventional coating methods with a weak interaction between the carbon and metal oxides, this in-situ growth strategy is an effective and facile way to completely and uniformly coat MnO with a carbon layer. Moreover, this solvent-free method simplifies the synthetic process and improves the yield rate of ZIF-8. During the carbonization process, manganese oxides are easily reduced to MnO. Meanwhile, the decomposition of the ZIF-8 frameworks and the volatilization of the Zn develop

nanoporous channels in the formed N-doped carbon layer, which could facilitate the transport of Li ions and shorten the conduction paths of electrons. As the anode in LIBs, the MnO@NC-Z shows great electrochemical performance with a high reversible capacity of 1261 mA h g^{-1} at 0.2 A g^{-1} and excellent cycling stability with capacity retention of 96.5% after 1000 cycles at 1 A g^{-1}. The in-situ strategy in this work can also be extended to the synthesis of other nitrogen-rich porous carbon coated metal oxides (e.g., FeO_x and CoO_x) for energy devices.

2. Experimental section

2.1. Materials

Zinc acetate hydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$), manganese acetate tetrahydrate ($Mn(CH_3COO)_2 \cdot 4H_2O$), cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), ammonium bicarbonate (NH_4HCO_3), ethylene glycol ($C_2H_6O_2$), and 2-methylimidazole ($C_4H_6N_2$) were all purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents were analytical grade and used as received without further purification.

2.2. Material synthesis

Initially, $ZnMn_2O_4$ was synthesized by a facile hydrothermal method. In detail, $Mn(CH_3COO)_2 \cdot 4H_2O$ (4 mmol), $Zn(CH_3COO)_2 \cdot 2H_2O$ (2 mmol), and NH_4HCO_3 (60 mmol) were dissolved in 70 mL of ethylene glycol under vigorous stirring for 10 min. Then, the well mixed solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave and heated at 200 °C for 12 h, followed by slowly cooling down at room temperature. The formed brown powder was collected through centrifugation and then thoroughly washed with ethanol and distilled water for several times before being dried at 70 °C for 6 h to obtain $ZnMn_2O_4$. Subsequently, the obtained $ZnMn_2O_4$ power (180 mg) and 2-methylimidazole (400 mg) were mixed and grinded for 20 min and then transferred into a porcelain boat. The mixture was heated at 180 °C for 8 h and then at 800 °C for 2 h under an Ar/H$_2$ (10%, v/v) atmosphere to obtain the MnO@NC-Z composite. For comparison, a carbon coated MnO composite synthesized using glucose as the carbon source (MnO@C-G) and pure MnO were also prepared. Briefly, the initial reactant MnO_x was prepared by using the same method for the synthesis of $ZnMn_2O_4$ without adding $Zn(CH_3COO)_2 \cdot 2H_2O$. The MnO_x (200 mg) was transferred into 60 mL of 1 M glucose and the mixture was stirred for 24 h at room temperature to obtain the MnO_x@glucose composite. The MnO_x@glucose composite and pure MnO_x were sintered at 800 °C for 2 h under an Ar/H$_2$ (10%, v/v) atmosphere to obtain the MnO@C-G composite and pure MnO, respectively.

In addition, in order to prove the applicability of this solvent-free method, FeO_x@NC and CoO_x@NC composite were also prepared following the same procedures by using $ZnFe_2O_4$ (180 mg) and $ZnCo_2O_4$ (180 mg) as the oxide precursors, respectively.

2.3. Characterizations

X-ray diffraction (XRD, Bruker AXS D8, 40 kV, 250 mA, Cu Kα radiation, λ = 1.5418 Å) was performed to analyze the structure of the samples in the 2θ range of 5–80°. The Raman spectra were obtained with a LabRAM Aramis spectrometer (HORIBA Jobin Yvon) operating in the spectrum range of 800–2000 cm^{-1} with an excitation wavelength, λ, of 633 nm. The thermogravimetric analysis (TGA) was conducted on a NETZSCH STA 449C differential scanning calorimeter from 30 to 700 °C at a ramping rate of 5 °C min^{-1} in air. The XPS measurements were carried out on an ESCALAB 250Xi