



Iron based dual-metal oxides on graphene for lithium-ion batteries anode: Effects of composition and morphology



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ABSTRACT

Dual-transition-metal oxide (DTMO) nanostructures are emerging materials for lithium-ion battery (LIB) anodes with improved structural stability, electronic conductivity and electrochemical performance compared to their single-metal counterpart. Herein, composites of graphene with DTMOs (MFeO, M = Co, Mn, Zn) were controllably prepared by harnessing the synthesis atmospheres and the nanoscale diffusion couple. Their composition and morphology were characterized by TEM, EDS mappings, XRD and XPS. The NH₃ treatment resulted in the formation of hollow DTMO nanoparticles on nitrogen-doped graphene, while H₂ and Ar gave graphene-supported hollow and solid DTMO particles, respectively. Electrochemical tests were applied to compare the performance of these composites as LIB anodes. The superior anode performance DTMO electrodes was demonstrated to the corresponding iron oxide composite. CoFe₂O₄/RGO composites exhibit excellent rate capability and high-rate cycling stability for lithium storage, due to its stable solid structure. However, the hollowing of DTMO particles cannot elevate the capacity and stability, due to the interfacial resistance and structural changes upon cycling.

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1. Introduction

Lithium-ion batteries (LIBs) have become one of the most important energy storage devices in a wide range of applications, including portable electronics, electric vehicles, storage of renewable energy, etc., due to its high energy densities, high working voltage and environmental benignness [1,2]. However, to meet the increasing demand of high density energy storage, there are still challenges to continuously improve the reversible capacity, cycling performance and rate capability of LIBs [3]. Commercialized graphite is currently used as the anode material in LIBs, but it suffers from a low theoretical capacity of 372 mAh g⁻¹. Transition metal oxides (TMOs) have been regarded as a promising alternative to graphite for their high lithium storage. Through the conversion reaction mechanism [4,5], TMO anode materials, including MnO₂, Fe₂O₃, Co₃O₄, NiO, CuO, etc., could deliver reversible capacity higher than 600 mAh g⁻¹ [6–12]. However, the battery performance might

be limited by the low electrical conductivity [13], large volume changes upon cycling [14] and the formation of solid-electrolyte interface (SEI) layer by electrolyte decomposition on the surface of anode materials [10,15].

As one of the approaches proposed to address these issues, combining two metallic cations in a single crystal structure has been developed to improve the structural stability, electronic conductivity and electrochemical performance of its single metal counterpart [16,17]. The internal stress of crystallites could be relieved with the anisotropic volume change of the two elements and thus the capacity stability can be improved [18]. The electronic conductivity of dual-transition-metal oxides (DTMOs) may be enhanced because of the relatively lower activation energy for electron transport between the heterogeneous cations with multiple valence states [19,20]. As a result, the electrochemical properties can be tuned by metal substitution, as the redox potential of the electrode composed of dual-metal oxide is quite different from the single components and their mixture [21]. Recently, Fe-based DTMOs (MFe₂O₄, M = Mn, Co, Ni, Cu, Zn, etc.), working through an eight electrons conversion reaction during the lithiation process, have been investigated as anode materials in LIBs, showing high reversible capacity [22–26]. However, DTMOs still deliver a poor

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cycling performance caused by the volume expansion and contraction so far. Dispersing TMOs on graphene as a matrix with high surface area and good chemical stability can improve the conductivity of the electrode and alleviating the volume change of the supported particles [27,28]. In addition, heteroatom doping of graphene could further increase its electronic conductivity and hence the lithium storage performance of the resulting composite is improved [29].

Besides, controlling the morphology and structure significantly influences the performance of TMOs. Sizing-down TMO particles to nanoscale has been widely proved beneficial to shorten the Li^+ insertion/extraction pathway and thus to increase the reversible capacity and rate capability [30]. However, the larger amount of SEI layer may be formed on the smaller particles because of the relatively high contact area with the electrolyte, resulting in the rapid capacity fading [15]. Furthermore, a rational design of materials structure is desired for the nanosized particles. A variety of designs have been proposed to be effective for improving the electrochemical property, including generating hierarchical meso-/micropores [26], hollow spheres [31] and core/shell structures [28]. These novel geometries display less surface SEI layer compared with plain solid particles [32–35]. Among them, hollow structures would be attractive to give a higher Li^+ permeability to reduce the diffusion length and also a large cavity to cushion the volume variation during the cycling [36]. However, so far, the synthesis and lithium storage study on DTMOs with hollow nanostructures have been rarely reported, due to the difficulties in obtaining the materials with well-defined composition and morphology.

Herein, we present a systematic study on the influential factors and constructing strategies of the Fe-based DTMOs supported on graphenes as LIBs anodes. Three substitutional metals were investigated to optimize the composition of Fe-based DTMOs (MFeO , $\text{M} = \text{Co}, \text{Mn}, \text{Zn}$). Two fundamental issues are addressed, i.e. the effects of hollowing the nanoparticles and N-doping the graphene as supports on the performance of TMOs as LIB anodes. Through the comparative investigations on the DTMO samples with different structures and compositions, the optimized Fe-based DTMO anode materials could be reached.

2. Experimental

2.1. Preparation of graphene oxide

Graphene oxide (GO) was synthesized with a modified Hummers method. 5 g graphite and 3.75 g NaNO_3 were added into 150 mL concentrated H_2SO_4 and the mixture was stirred for 30 min. Then 20 g KMnO_4 was slowly added to the ice-cooled mixture with continuously stirring. After 4 days, the above muddy mixture was diluted with 400 mL DI water in an ice bath. Then the reaction was ended with the addition of 30 mL H_2O_2 solution (30%). The suspension was stirred for 30 min, followed by standing and washing with $\text{H}_2\text{O}/\text{HCl}$ solution (9/1, v/v, 8 L). The mixture was dialyzed for at least one week to remove excess ions. Finally, the resulting suspension was dispersed with DI water and sonicated to form graphene oxide (GO).

2.2. Preparation of $\text{MFe}_x(\text{OH})(y)/\text{GO}$ composites

20 mL aqueous solution of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Fe}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$ (molar ratio of Co^{2+} : Fe^{2+} 1:x) was added dropwise into 300 mL GO/DI suspension (1 mg mL^{-1}) under vigorous stirring. The mixture was dispersed by sonication for 2 h and then stirred overnight, followed by the addition of 0.6 mL $\text{NH}_3 \cdot \text{H}_2\text{O}$. Afterwards, the suspension was refluxed at 90°C for 4 h. It was then centrifuged, rinsed with DI water and lyophilized to obtain $\text{CoFe}_x(\text{OH})(y)/$

GO, where y represents the weight percentage of metal oxide in the final product. Synthesis of $\text{MnFe}_x(\text{OH})(y)/\text{GO}$ and $\text{ZnFe}_x(\text{OH})(y)/\text{GO}$ was similar to that of $\text{CoFe}_x(\text{OH})(y)/\text{GO}$, except for modifying the precursor to $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ or $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$. All these three samples are denoted as $\text{MFe}_x(\text{OH})(y)/\text{GO}$.

2.3. Preparation of $\text{MFe}_x\text{O}(y)$ -graphene composites

To prepare $\text{MFe}_x\text{O}(y)/\text{NG}$, $\text{MFe}_x(\text{OH})(y)/\text{GO}$ samples were thermally treated at 500°C for 2 h under 50% NH_3/Ar , followed by the passivation in 1% O_2/Ar at room temperature (R.T.) for 1 h before being exposed to air. After that, the samples were further heated at 300°C for 2 h in 1% O_2/Ar to obtain $\text{MFe}_x\text{O}(y)/\text{NG-h}$, where h stands for hollow MFe_xO NPs. 50% H_2/Ar or Ar atmosphere were applied instead of NH_3/Ar to give $\text{MFe}_x\text{O}(y)/\text{G-H}_2$ and $\text{MFe}_x\text{O}(y)/\text{G-Ar}$, respectively. The samples were subsequently pyrolyzed with the same oxidation process as above, yielding hollow $\text{MFe}_x\text{O}(y)/\text{G-h}$ and solid $\text{MFe}_x\text{O}(y)/\text{G-s}$, respectively.

$\text{FeO}(y)/\text{NG-h}$, $\text{FeO}(y)/\text{G-h}$ and $\text{FeO}(y)/\text{G-s}$ were prepared through the same procedures as synthesizing $\text{MFe}_x(\text{OH})(y)/\text{GO}$ composites only with $\text{Fe}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$ as salt precursor.

2.4. Electrochemical test

Electrochemical tests were carried out in coin cells (CR2025) which assembled in Ar-filled glovebox. 80 wt% active materials (graphene-metal oxide composites), 10 wt% carbon black (Super P) and 10 wt% polyvinylidene fluoride (PVDF) were mixed well in N-methyl-2-pyrrolidinone (NMP). The obtained slurry was pasted onto Cu foil to form the working electrode, which was dried in vacuum at 100°C and compressed under the pressure at 20 MPa. The coating density of the active materials was about 1.0 mg cm^{-2} . Lithium metal was used as the counter and reference electrode, while Celgard 2325 membrane was used as the separator. The electrolyte was obtained by dissolving 1 mol L^{-1} LiPF_6 in the mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v). The charge/discharge tests were performed using a BTS battery test system at a voltage window of 0.01–3.0 V (vs. Li/Li^+). CV (0.01–3.0 V, 0.2 mV s^{-1}) was performed on a ZAHNER electrochemical workstation. EIS measurements were recorded on the same electrochemical workstation with amplitude of 5 mV in the frequency range of 10 mHz–100 kHz.

2.5. Characterizations

Transmission electron microscopy (TEM) images were obtained using a JEM-2100F (JEOL) microscope operating at 200 kV, while STEM images and EDS mapping of the samples obtained with the accessories attached to the instrument. X-ray diffraction (XRD) patterns were collected with a D8-advance X-ray diffractometer (Bruker) with Cu K α radiation (40 kV, 40 mA) at a scan rate of 1° min^{-1} . X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Axis ultra DLD equipped with an Al K α X-ray source. All XPS spectra were calibrated by setting the graphitic C1s signal to 284.6 eV and were fitted after a Shirley type background subtraction.

3. Results and discussion

3.1. Synthesis and characterizations of DTMO samples

Fig. 1 presents the synthesis strategy of DTMO NPs on NG or RGO. M^{2+} and Fe^{2+} were firstly hydrolyzed with the assistance of ammonia and deposited on GO in the form of hydroxide. Then three kinds of atmosphere, i.e., ammonia, hydrogen and argon, were

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