Rational design of metal oxide nanocomposite anodes for advanced lithium ion batteries

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HIGHLIGHTS

- A rational design of 3D-staggered metal-oxide nanocomposite structure was prepared.
- Metal oxides are homogeneous distributed in a staggered manner.
- The nanoparticles are rigorously confined at their original sites.
- Integrity structure can be maintained due to little migration during cycling.
- 3D-staggered metal-oxide nanocomposite anodes demonstrate excellent cycle performance.

GRAPHICAL ABSTRACT
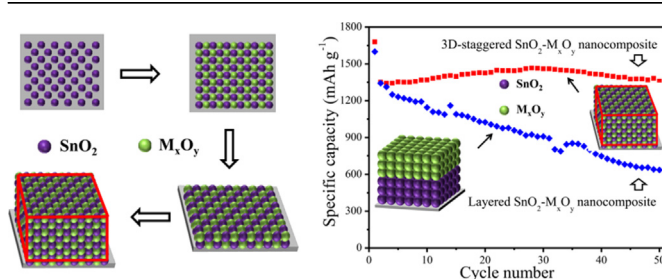
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ABSTRACT

Metal-oxide anodes represent a significant future direction for advanced lithium ion batteries. However, their practical applications are still seriously hampered by electrode disintegration and capacity fading during cycling. Here, we report a rational design of 3D-staggered metal-oxide nanocomposite electrode directly fabricated by pulsed spray evaporation chemical vapor deposition, where various oxide nano-components are in a staggered distribution uniformly along three dimensions and across the whole electrode. Such a special design of nanoarchitecture combines the advantages of nanoscale materials in volume change and Li$^+$/electron conduction as well as uniformly staggered and compact structure in atom migration during lithiation/delithiation, which exhibits high specific capacity, good cycling stability and excellent rate capability. The rational design of metal-oxide nanocomposite electrode opens up new possibilities for high performance lithium ion batteries.

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1. Introduction

Lithium ion batteries (LIBs) are entering into an advanced stage for high energy/power density because of increasing demand in electric vehicles (EVs) and energy storage systems (ESSs) [1—4]. The commercial graphite anode has been becoming outdated due to its low theoretical capacity (372 mAh g^{-1}) [5]. Metal oxides (SnO$_2$, Fe$_2$O$_3$, MnO, Co$_3$O$_4$ and *etc.*), offering much larger theoretical capacity *via* alloying and/or conversion reaction, have been under intensive investigation in the past decades [6—10]. However, the enormous volume change between lithium insertion and extraction, which leads to pulverization of active materials and fast capacity fading of metal oxide electrodes, has extremely hinder their practical applications [11]. An effective strategy through building multi-oxide composites has been adopted to synergistically buffer the volume-variation-induced stress and keep the structure

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integrity for improving the cyclability [12,13]. These components in multi-oxide composites are electrochemical active at different potentials; namely, when one kind of metal oxide is engaged for lithium insertion, other oxides could act as buffering matrix and vice versa [14–16]. Importantly, compared to those largely reported metal-oxide/carbon composites, these multi-oxides electrodes could deliver a higher specific capacity since the composed oxides are all electrochemically active for lithium storage [17–21]. For example, Fan and coauthors reported the improved LIBs performance in the branched α-Fe$_2$O$_3$/SnO$_2$ nano-heterostructures where α-Fe$_2$O$_3$ branches may relieve the stress exerted on inner SnO$_2$ nanowires due to the severe volume change arising from alloying-dealloying processes [12]. Xiong et al. prepared Fe$_2$O$_3$@Co$_3$O$_4$ array with large reversible capacity and excellent cycling life, which is mainly benefited from unique hierarchical nanowire architecture and an elegant synergistic effect of two electrochemically active materials [22]. Additionally, Wu et al. designed ternary core/shell structure of Co$_3$O$_4$/NiO/C nanowire arrays as high performance anode material for LIBs. The enhanced electrochemical properties are mainly ascribed to the core/shell nanowire architecture with potential synergistic contribution such as the improved mechanical stability [10]. Despite that there is some improvements regarding electrochemical performance for these reported metal oxide composites as compared to single metal oxide, the integrity maintenance of the metal-oxide composite electrode is still unsatisfactory by the fact that the morphology of cycled electrode has greatly changed from the pristine one [10,15,16,22–24]. Although metal oxide nanoparticles themselves are able to accommodate the stress induced by the volume change, they are more inclined to aggregate together due to direct contact among the same oxide component and the corresponding enormous atom migration during long term lithiation/delithiation processes [25,26].

In this paper, we report a rational design of 3D-staggered metal oxide nanocomposite structure consisting of densely packed superfine nanoparticles with various oxides being homogeneous distributed in a staggered manner over the whole electrode, as schematically shown in Fig. 1a. The superfine nanoparticles in 3D-staggered metal-oxide nanocomposites can reduce the Li-ion diffusion length and effectively accommodate the stress during cycling. More importantly, since one kind of oxide nanoparticles is uniformly separated by the other kind of nanoparticles, the nanoparticles can be strictly confined across the whole electrode [27]. In view of atom migration, the nanoparticles are rigorously confined at their original sites by the other sort of surrounding particles with little atom migration and aggregation during lithiation/delithiation, which leads to spatially-confined lithiation/delithiation and assures the structure integrity of electrode. To realize the specially designed nano-architectures, a powerful technique—pulsed spray evaporation chemical vapor deposition (PSE-CVD) is applied for the deposition of multi-oxide nanocomposites [28]. Superior to the conventional CVD mounted with bubbler evaporator, PSE-CVD, like the atomic layer deposition (ALD), is equipped with direct pulsed liquid delivery (DPLD) unit [29]. Such improvement provides precise control over the thickness and film composition, and shows high flexibility for designing nanostructure and tuning the particle size of target materials [30]. By using PSE-CVD, Bahlawane et al. successfully fabricated functional metal oxide films with embedded superfine metallic nanoparticles for magnetic and plasmatic applications through tailoring the pulse sequences [28].

Application of PSE-CVD in fabricating electrode materials for LIBs is a novel strategy. As demonstrated in Fig. 1b, three computer-controlled injectors are mounted on the top of the set-up. Precursor solutions are injected as fine sprays into the reactor. By tailoring the pre-set pulse sequence, multi-components can be orderly assembled into well-designed nanoarchitectures (Fig. 1c). As the composites are directly deposited on the surface of the substrate, the active materials which firmly adhere to the current collector can be assembled as working electrode directly without any binder and carbon black (Fig. 1d) [31]. Our research is based on the SnO$_2$-M$_x$O$_y$ (M = Fe, Co and Ni) nanocomposites, particularly focusing on SnO$_2$–Fe$_2$O$_3$ nanocomposites. Compared to pure SnO$_2$, 3D-staggered SnO$_2$–Fe$_2$O$_3$ nanocomposite with uniform distribution of SnO$_2$ and Fe$_2$O$_3$ exhibits high specific capacity, outstanding cycling stability and excellent rate capability. The 3D-staggered SnO$_2$–Fe$_2$O$_3$ nanocomposite delivers an initial specific discharge capacity of 1626.8 mAh g^{-1}, and still maintains 1369.5 mAh g^{-1} after 50 stable cycles. More impressively, as high as 824.2 mAh g^{-1} can be retained even at a large current density of 8 A g^{-1}. Additionally, the 3D-staggered SnO$_2$–Co$_3$O$_4$ and SnO$_2$–NiO composites with the similar structure also show good electrochemical performance. This work may provide a rational strategy in fabricating multi-oxide nanocomposite electrodes for advanced LIBs.

2. Experimental section

2.1. Materials preparation

SnO$_2$-M$_x$O$_y$ nanocomposite and SnO$_2$ films prepared by PSE-CVD. The ethanol solution of SnCl$_4$·5H$_2$O (60 mM) and the other ethanol solution of Fe(acac)$_3$ (10 mM) were used as the liquid feedstock. The two solutions were injected as the fine spray into the reactor using a pulse width of 10 ms and a pulse frequency of 1 Hz (Fig. S1). For the 3D-staggered SnO$_2$–Fe$_2$O$_3$ nanocomposite, the pulse time (duration time for single phase deposition) is 15 min. While for the layered SnO$_2$–Fe$_2$O$_3$ nanocomposite, the pulse time is as long as 60 min. The total deposition time is 2 h for all the samples. Glass slides (for XRD and XPS characterization), copper foils (element mapping) and stainless steels (for electrochemical test and SEM characterization) were used as substrates, which were maintained at 300 °C. N$_2$ (800 sccm) was used as carrier gas. The working pressure in the reactor was stabilized at 380 Pa during deposition process. For the deposition of SnO$_2$–Co$_3$O$_4$ and SnO$_2$–NiO composites, except the precursors of Co$_3$O$_4$ and NiO were Co(NO$_3$)$_2$·6H$_2$O (15 mM of ethanol solution) and Ni(NO$_3$)$_2$·6H$_2$O (15 mM of ethanol solution), other parameters were the same as the preparation of 3D-staggered SnO$_2$–Fe$_2$O$_3$ nanocomposite. For comparison, pure SnO$_2$ films were also prepared under the same parameters as the synthesis of 3D-staggered SnO$_2$–Fe$_2$O$_3$ composites.

2.2. Materials characterization

The identification of the crystalline phase was performed using X-ray diffraction (XRD) on a Rigaku D/Max-2550pc diffractometer equipped with Cu Kα radiation (λ = 1.5406 Å), with a scan range of 20–80°. To study the electronic structure and understand the compositional behavior in the compounds, X-ray photoelectron spectroscopic (XPS) measurement was performed with an ESCALAB 250 X-ray photoelectron spectrometer, using excitation energy of 1486.6 eV (Al Kα). The surface morphology was characterized by scanning electron microscopy (SEM, Hitachi S-4800 and SU-70). TEM was performed with a FEI Tecnai G^2 F20 Microscope operated at 200 kV.

2.3. Electrochemical measurement

The mass of the active layer was calculated by using a micro-balance with an accuracy of 0.002 mg (Sartorius CPA26P, Germany) before and after the deposition directly. The PSE-CVD derived films on stainless steel were used as the electrodes of electrochemical