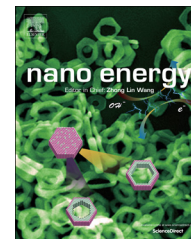




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RAPID COMMUNICATION

# Transition metal oxides for high performance sodium ion battery anodes



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## Abstract

Sodium-ion batteries (SIBs) are attracting considerable attention with expectation of replacing lithium-ion batteries (LIBs) in large-scale energy storage systems (ESSs). To explore high performance anode materials for SIBs is highly desired subject to the current anode research mainly limited to carbonaceous materials. In this study, a series of transition metal oxides (TMOs) is successfully demonstrated as anodes for SIBs for the first time. The sodium uptake/extract is confirmed in the way of reversible conversion reaction. The pseudocapacitance-type behavior is also observed in the contribution of sodium capacity. For  $\text{Fe}_2\text{O}_3$  anode, a reversible capacity of  $386 \text{ mAh g}^{-1}$  at  $100 \text{ mA g}^{-1}$  is achieved over 200 cycles; as high as  $233 \text{ mAh g}^{-1}$  is sustained even cycling at a large current-density of  $5 \text{ A g}^{-1}$ .

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## Introduction

Renewable clean energy technologies are important to address global concerns regarding depletion of fossil-based

resources, global warming and environmental pollution. However, the widespread implementation of the renewable energy is seriously hampered by the intermittent nature of geographic and climatic environment. Energy storage plays a crucial role in succeeding for renewable energy integration [1–5]. Among the various available energy storage technologies, lithium-ion batteries (LIBs), being used as power sources of portable electronics for decades,

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are currently considered as the dominant candidate to power the next generation of electric vehicles and stationary applications. Unfortunately, the large-scale commercial manufacturing of LIBs faces severe challenges from the increasing cost of lithium and the limited size of reserves (0.006 wt% abundance on earth) [6,7]. On the other hand, there is no doubt that the sodium resources are inexhaustible and unlimited everywhere around the world (4th most abundant element, 2.64 wt% on earth). Similar to LIBs, sodium-ion batteries (SIBs) could provide an alternative chemistry and might thus become economically more competitive especially in large-scale energy storage systems (ESSs) [8-11]. Most SIB research were focused on exploration of stable and low-cost cathode materials, including Prussian blue,  $\text{NaFePO}_4$  and  $\text{NaNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  [12-14]. There are continuous efforts on exploring the anode material, most of which, limited in nongraphitic carbonaceous materials. Hard carbon is the top ranked nongraphitic carbonaceous materials for sodium storage due to the large interlayer distance and the disorder structure [8]. Stevens and Dahn reported an initial reversible capacity of hard carbon as high as  $300 \text{ mAh g}^{-1}$  [15]. However, some disadvantages are revealed for non-graphitic carbonaceous materials such as the large irreversible capacity and poor capacity retention [14-17]. Some approaches on Na-alloying metals such as Sn and Sb based materials were also confirmed with sodium storage capability [18-23]. The SnSb/C nanocomposites exhibited  $435 \text{ mAh g}^{-1}$  at  $100 \text{ mA g}^{-1}$  after 50 cycles; also, a capacity of  $274 \text{ mAh g}^{-1}$  was sustained when applying a large current density of  $1000 \text{ mA g}^{-1}$  [19]. Monconduit et al. reported a good cycling performance of bulk Sb ( $600 \text{ mAh g}^{-1}$  at C/2 after 100 cycles) subject to the amorphous intermediate phase  $\text{Na}_x\text{Sb}$  acting as a buffer to relieve strain [20].

The conversion-type materials (e.g. transition metal oxides, TMO), with superior lithium storage properties, are also proposed to act as anodes for SIBs. The concept was first demonstrated with the spinel  $\text{NiCo}_2\text{O}_4$  which delivered  $\sim 200 \text{ mAh g}^{-1}$  of reversible capacity after an initial discharge of  $618 \text{ mAh g}^{-1}$  [24]. Balaya et al. investigated the sodium storage of  $\text{Fe}_3\text{O}_4$  anode, which exhibited an initial discharge of  $643 \text{ mAh g}^{-1}$  but accompanied with nearly 50% irreversible capacity and very poor capacity retention [25]. Recently,  $\alpha\text{-MoO}_3$  was demonstrated with highly electrochemical activity for sodium storage, delivering high first cycle sodiation and desodiation capacities of 771 and  $410 \text{ mAh g}^{-1}$  respectively. Moreover, the  $\alpha\text{-MoO}_3$  anodes showed favorable rate performance  $100 \text{ mAh g}^{-1}$  at a current density of  $1.117 \text{ A g}^{-1}$  and long durability over 500 cycles [26]. Edström et al. examined nanostructured  $\text{Fe}_2\text{O}_3$  for both lithium and sodium storage. A specific sodium capacity of  $250 \text{ mAh g}^{-1}$  at  $130 \text{ mA g}^{-1}$  was attained after 60 cycles [27]. However, there are also contradictory reports that transition metal oxides such as FeO, CoO and NiO showed almost no electrochemical activity with Na-ion [18,28,29]. In all, there is limited investigation on using TMOs SIB anode and the mechanism remains poorly understood.

In this paper, we develop a series of TMOs including  $\text{Fe}_2\text{O}_3$ , NiO,  $\text{Co}_3\text{O}_4$  and  $\text{Mn}_3\text{O}_4$  thin films as anodes of SIBs. The results show high electrochemical activities of all these TMOs in SIBs. Especially for  $\text{Fe}_2\text{O}_3$ , as high as  $386 \text{ mAh g}^{-1}$  capacity at  $100 \text{ mA g}^{-1}$  could be sustained after 200

cycles. More surprisingly, a reversible capacity of  $233 \text{ mAh g}^{-1}$  is achieved even at an ultra-large current density of  $5000 \text{ mA g}^{-1}$ , which is one of the best rate performances among all SIB anodes ever reported. Further investigation clearly indicates that both the traditional conversion reactions and the pseudocapacitance-type behavior contribute the distinguished sodium storage performance. This work demonstrates that TMO based materials may act as a suitable candidate forward to develop high performance anodes of SIBs.

## Experimental section

### Preparation of transition metal oxide film

With a precursor solution of 0.005 M ferric nitrate in ethanol and ethylene glycol (4:1 in volume), porous  $\text{Fe}_2\text{O}_3$  thin films were prepared by electrostatic spray deposition (ESD) technique for 3 h on a stainless steel substrate heated at  $180^\circ\text{C}$  (feeding rate:  $2 \text{ mL h}^{-1}$ ). The distance and the applied voltage between the nozzle and substrate were 4 cm and 15 kV, respectively. The mass of the deposited material was measured using a microbalance with an accuracy of 0.002 mg (Sartorius CPA26P, Germany) before and after deposition. The deposition conditions of NiO,  $\text{Co}_3\text{O}_4$  and  $\text{Mn}_3\text{O}_4$  thin films are listed in Table S1, the other unlisted conditions remained same as  $\text{Fe}_2\text{O}_3$ .

### Characterization

The crystal structure of the film was characterized with a Rigaku D/max 2550PC X-ray diffractometer (XRD). The morphology of the film was observed using scanning electron microscopy (SEM; Hitachi S-4800, Tokyo, Japan). The crystal structure details were further characterized by transmission electron microscopy (TEM; CM-200 microscope, PHILIPS, Amsterdam, the Netherlands). X-ray photoelectron spectroscopic (XPS) measurements were performed with an ESCALAB 250 X-ray photoelectron spectrometer, using excitation energy of 1486.6 eV (Al K $\alpha$ ).

### Electrochemical measurements

The electrochemical behavior was examined in CR2025 coin-type cells using the as-deposited films on stainless steel substrate as the working electrode and sodium foil as the counter and reference electrode, respectively. Cell assembling was carried out in an argon filled glovebox, in which the oxygen concentration and moisture level were maintained less than 1 ppm. Celgard 2300 microporous polypropylene was used as a separator. The electrolyte was 1 M  $\text{NaPF}_6$  in a mixture solvent of ethylene carbonate (EC), diethyl carbonate (DEC) and propylene carbonate (PC) (4:4:2 by volume). The cells were charged and discharged galvanostatically on a Neware BTS battery cyler at 0.005-3.0 V (vs.  $\text{Na}/\text{Na}^+$ ). Cyclic voltammetry (CV) tests were conducted on a CHI660C electrochemistry workstation between 0.005 and 3.0 V (vs.  $\text{Na}/\text{Na}^+$ ) at  $0.1 \text{ mV s}^{-1}$ . All the electrochemical measurements were carried out at room temperature.

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