1 Ti@ δ -MnO₂ core-shell nanowire arrays as self-supported electrodes of
2 supercapacitors and Li ion batteries

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6 Abstract

7 δ -MnO₂ is a promising electrode material of supercapacitors and Li ion batteries
8 (LIBs) owing to its low cost, layer structure and composite valence of Mn. However,
9 the unfavorable electronic conductivity of δ -MnO₂ restricts its rate capability in both
10 of the two devices. Herein, a vertically standing Ti nanowire array modified with
11 δ -MnO₂ nanoflakes is prepared by a electrodeposition method, and the
12 electrochemical properties of Ti@ δ -MnO₂ nanowire arrays in supercapacitors and
13 LIBs are investigated. The results show that, the arrays have a capacity of 195 F g⁻¹ at
14 1.0 A g⁻¹ and can cycle more than 10000 rounds at 10 A g⁻¹ as electrodes of
15 supercapacitors. On the other hand, the arrays behave good rate capability as LIB
16 cathodes, which can release a capacity of 70 mAh g⁻¹ at 10 C rate charge/discharge.
17 We suggest that, the good electronic conductivity owing to the core-shell structure and
18 the facilitated mass transport supplied by the array architecture are responsible for the
19 enhanced rate performances in the two devices.

20 Keywords: titanium nanowire arrays; delta type manganese dioxide; lithium ion
21 batteries; supercapacitors

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1. Introduction

Manganese dioxide (MnO_2) is one of the most important transition metal oxides because of its unique structures and physicochemical properties, as well as low environmental impact and low cost. MnO_2 has many polymorphs, including α -, β -, γ -, λ -, δ -, ϵ -crystallographic polymorphs. Amongst various MnO_2 polymorphs, δ -type has drawn great attention with respect to its adsorptive [1], catalytic [2], ion-exchange [3], and electrochemical properties [4]. δ - MnO_2 has a two-dimensional layered structure that consists of edge-sharing MnO_6 octahedra with water molecules in the interlayer space [5]. Scheme 1 presents schematically the crystal structure of a δ -type MnO_2 . Here, some of the Mn^{4+} ions are replaced with Mn^{3+} , giving a net negative charge to be balanced electrically by the intercalation of foreign cations, typically hydrated alkaline metals [4]. Owing to its relatively open structure, δ -type MnO_2 is believed to provide favorable pathways for Li^+ intercalation and deintercalation. In other words, reversible injection/extraction of electrons into/from the MnO_2 layers can take place, accompanying the intercalation/deintercalation of Li^+ into/from the interlayer. The unique layer structure leads a reversible capacity of more than 140 mAh g^{-1} in the voltage window of 2.0–4.0 V [6,7], more suitable as cathode material compared with other type MnO_2 . Although the performances of δ - MnO_2 can't catch up conventional cathode materials, its low cost still attracts much attention. On the other hand, δ - MnO_2 is also applicable as electrodes in pseudocapacitors [8,9]. Owing to the easy intercalation/deintercalation of cations in the interlayer in such a structure, all of the material can be regarded as “surface”, offering an increase in the number of

electrochemically active sites per unit volume. However, the poor conductivity ($10^{-6}\sim 10^{-5}$ S cm⁻¹) restrains the performances of δ -MnO₂ at high current densities causing unfavorable rate capability in both LIBs and supercapacitors [10]. Although considerable strategies are explored to improve this drawback in previous literatures, such as self-supported nanoflakes on Ni foam, hierarchical nanostructures and nanosheets on more conductive titania-based nanowires [11–14], alternative methods to prepare δ -MnO₂ material with improved rate capability for LIBs and supercapacitors are still desired.

Herein, we present a δ -MnO₂ nanoflake modified Ti nanowire arrays prepared by an electrochemically assistant method. This hierarchical array structure integrated the advantages of above strategies by electrodepositing nanostructural active material on Ti nanowire arrays. The rate capability of δ -MnO₂ in both LIBs and supercapacitors was all improved due to the outstanding conductivity provided by the Ti nanowire arrays.

2. Experimental

Sample Preparation: The Ti nanowire arrays were fabricated on circular Ti (Ti-Mo, Mo=0.3 wt%) alloy foam plates purchased from Baiji Jinkai Corporation of China using a electroless wet chemical etching method. The etching was carried out in 2.0 wt% HF solution in 700s. The obtained Ti nanowire arrays were rinsed with deionized water fully and dried overnight. δ -MnO₂ nanoflakes were prepared by a potentiostatic electrodeposition in a three-electrode cell with a Ti nanowire arrays covered Ti wafer

(2 cm diameter) as working electrode, a Ag/AgCl (in sat' KCl) reference electrode and a Pt plate (1 cm×1cm) as counter electrode. The deposition was carried out at -0.2 V in 500 s in a 0.2 mM KMnO₄ solution. The as-prepared samples were rinsed with deionized water fully and dried at 50 °C overnight. The weight of the deposited MnO₂ was measured by means of a micro-balance (Mettler Toledo, USA) with an accuracy of 0.01 mg. The masses of Ti substrate and MnO₂ were around one hundred and several mg, respectively.

Instruments for Characterization: Scanning electron microscope (SEM) images and Energy dispersive X-ray spectroscopy (EDS) were obtained on a Hitachi Su-8100. The X-ray diffraction (XRD) patterns were obtained on a PANalytical X'pert PRO X-ray diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). X-ray photoelectron spectra (XPS) were obtained with a K-Alpha electron spectrometer (ThermoFisher Scientific Company) using Al K α (1486.6 eV) radiation. The base pressure was about 1×10^{-8} mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests of the batteries were carried out on a CHI 660 electrochemical workstation.

LIB and Supercapacitor tests: The LIB measurements were carried out in the CR2025 button testing batteries using a two electrode electrochemical cell consisting of a Ti@MnO₂ nanowire array electrode (circle plate, 15 mm in diameter), two sheets of microporous membrane (Celgard 2400) and lithium foil as the counter electrode. The model battery electrolyte was LiPF₆ (1M) in a 50:50 (V/V) mixture of ethylene

carbonate (EC) and dimethyl carbonate (DMC) provided by Tinci Company (Guangzhou China). A BTS-2000 Neware Battery Testing System was employed for galvanostatic charge/discharge tests. A CHI660 electrochemical workstation was used for the cyclic voltammetry (CV) measurements. For supercapacitive measurement, a three electrode cell was used for all electrochemical measurements. A nanowire array electrode (circle plate, 15 mm in diameter) was vertically inserted into the electrolyte and acted as the working electrode, a Pt plane (10 mm×10 mm) acted as the counter electrode, and the SCE acted as the reference electrode to work in the asymmetric electrochemical capacitor system. The electrochemical measurements were performed using a CHI 660D with Na₂SO₄ solution (1.0 M) as the electrolyte.

3. Results and discussion

The Ti foam used in our work is manufactured by rolling the Ti alloy powder to porous plates, which are usually used as catalyst supports or filter for wastewater treatment. Therefore, when as electrodes of LIBs and supercapacitors, there are adequate channels for ion transport in the Ti foams, as seen in Fig. S1a. The higher amplification image in Fig. S1b indicates a smooth surface of the Ti alloy foam. Diffraction peaks of the XRD pattern from pristine Ti alloy foam in Fig. 1 can be ascribed to Ti metal (JCPDS: 65-6231 $a=2.950$, $b=2.950$, $c=4.681$), revealing the primary component is Ti. The Mo peaks are undetected in XRD pattern due to the low content, which can be verified by EDS measurement. The EDS result of the Ti foam corresponding to Fig. S1 demonstrates that Mo content is 0.34 wt%. For the

application in water filtration and catalyst support, the addition of Mo in Ti alloy foam is a common strategy to improve the mechanical strength of the Ti foam. The existence of Mo is significant for forming Ti nanowire arrays, as discussed in following.

Fig. 1

The existence of Mo in the foam is significant for forming Ti nanowire arrays in hydrofluoric acid (HF) corrosion. The Mo grains and Ti metal formed micro-batteries on the foam in HF solution, similar with the preparation of Si nanowire arrays by wet etching [15,16]. Ti metal was dissolved continuously as anode in the micro-batteries, because of a lower standard electrode potential of Ti^{4+}/Ti (-0.86) than Mo^{4+}/Mo (-0.15). The continuous dissolution of Ti metal led Ti nanowire arrays forming. The XRD pattern of the Ti foams after corrosion is shown in Fig. 1, which indicates a typical Ti metal structure primarily. The all-metal construction endows Ti nanowire arrays coated Ti foams high conductivity when as a substrate of electrode. Furthermore, several weak peaks belonging to Mo metal (JCPDS: 65-7442 $a=3.147$, $b=3.147$, $c=3.147$) are detected in the XRD pattern. The residual Mo grains on the sample surface resulted from Ti corrosion causes the Mo diffraction peaks clearer compared with the raw Ti foam (Fig. 1). The variation of XRD patterns also verifies the mechanism of preparing Ti nanowires is a process of heterogeneous corrosion. The SEM images of Ti nanowire arrays are shown in Fig. 2. The images from low to high magnification reveal that, Ti nanowires in a length of $1\text{ }\mu\text{m}$ are freestanding on the Ti foam vertically and the nanowires are widespread on Ti surface with no dead

corner. Otherwise, the corrosion process is carried out in HF solution, which can prevent the final product from being oxidized, resulting in no peaks of oxide in the XRD pattern.

Fig. 2

Fig. 3

Fig. 4

Cathodic electrodeposition with galvanostatic conditions is a facile and effective method to synthesize δ -MnO₂, which has been tried in previous literatures [6,8]. We prepared the δ -MnO₂ flakes modified Ti (Ti@ δ -MnO₂) nanowire arrays by a galvanostatic electrodeposition and treated them with various temperatures. XRD patterns of the samples are shown in Fig. 3. The peaks can be ascribed to Ti and δ -MnO₂ (JCPDF: 23-1239 $a=8.520$, $b=14.760$, $c=17.540$) primarily. Although the crystal form of δ -MnO₂ is stable in the temperature range, the peaks of the sample treated at 300 °C exhibit a obvious decay due to the transformation to α -MnO₂ [7]. Therefore, the heat-treated temperature was settled at 250 °C for obtaining stable δ -MnO₂ flakes. Additionally, the coverage of MnO₂ on Ti nanowires causes the weak peaks of Mo difficult to be detected. SEM images of the as-prepared Ti@ δ -MnO₂ nanowire arrays are shown in Fig. 4, and the SEM images of δ -MnO₂ flakes prepared with same conditions on raw Ti foam are shown in Fig. S2. Apparently, the δ -MnO₂ on different substrates all have flake morphology though different flake-sizes. The nanoflakes deposited on the nanowires from a bottom-up process have no interference to the architecture of Ti nanowire arrays, which

guarantees obtaining vertically freestanding nanowires with abundant inner-space in them. The core-shell structure of Ti@ δ -MnO₂ nanowires has good electronic conductivity and the multilevel array structure of nanowire@nanoflake has good mass transport as used in electrochemical energy storage devices.

Fig. 5

The most attractive application of Ti@ δ -MnO₂ is as supercapacitor electrodes owing to its merits of a coexistence of Mn(III) and Mn(IV), a large electrode electrolyte interface and strong interaction with the current collector, resulting in low contact resistance and optimized conduction pathways. In the present study, to examine the supercapacitive properties, measurements of the Ti@ δ -MnO₂ arrays obtained from 250 °C heat-treatment were investigated in a 1.0 M Na₂SO₄ aqueous solution with a voltage window from -0.1 to 0.9 V vs. SCE. The comparison of CV curves between Ti@ δ -MnO₂ and pristine Ti nanowire arrays is shown in Fig S3. Apparently, the Ti nanowires almost have not capacitance compared with MnO₂ nanoflakes. Fig. 5a shows CV curves of the electrodes with different scanning rates, the curves exhibit a near rectangle surrounded by the cathodic and anodic sweeping lines ascribed to sharp double-layer capacitance and pseudocapacitance of MnO₂. Accordingly, the galvanostatic charge/discharge curves at different current densities in Fig. 5b exhibit a nearly symmetric triangle feature. At a current density of 1.0 A g⁻¹, the electrode presents a specific capacitance of 195 F g⁻¹, which is relatively high value compared with the literatures, as shwon in Table 1 [11–14]. Even at the high current density of 10 A g⁻¹, the capacitance still remains 60 F g⁻¹. More attractive

property of Ti@ δ -MnO₂ arrays is that, the electrode maintains high specific capacitances at high current densities and for a long-term charge–discharge period (Fig. 5c). The rate capability of the array electrodes is much better than the literatures especially at high rate current densities, as shwon in Table 1. The capacitance retention of the electrode after 10000 cycles at a current density of 10 A g⁻¹ is 91%, better than the values in literatures. The capacities in the present work are all calculated on "per gram of MnO₂".

Fig. 6

Apart from the good rate capability as supercapacitor electrodes demonstrated above, δ -MnO₂ is an attractive cathode material for Li⁺ intercalation/deintercalation due to its stable layer structure. We investigate the electrochemical properties of Ti@ δ -MnO₂ arrays as the LIB cathode material in a potential window of 2.0-4.0 V. The CV curve (Fig. 6a) of the cathode shows a coupled peak of 2.7/3.0 V in cathodic/anodic sweeps ascribed to Li⁺ intercalation/deintercalation in MnO₂. Compared with pristine Ti nanowire arrays, the curve of core-shell nanowires exhibits a large area surrounded by the cathodic and anodic base lines. The weak response currents in the CV demonstrate Ti nanowire substrate almost can not charge/discharge in LIB. On the other hand, we suggest the capacitive contribution generated from Li⁺ interacting with MnO₂ is responsible for the large area of CV curve, which can lead good rate capability of core-shell nanowires, as shown in Fig. 6b. Although considerable strategies were explored to improve the rate capability of δ -MnO₂, the capacity of more than 70 mAh g⁻¹ at 10 C is still rarely achieved. However, the

capacity fading is serious in cycle tests, both in the varying rate currents and constant rate current, as shown in Fig. 6c and d. The capacity fading results in a unfavorable recovery after high rate test (Fig. 6c) and a continuous decay in the cycle test with constant current (Fig. 6d). We suggest the instability of Mn(III) in cycle test is responsible for the poor durability of δ -MnO₂. XPS pattern of the raw sample and that after cycle test are shown in Fig. 7. The oxidation state of Mn in the δ -MnO₂ samples with different morphologies are qualitatively analyzed by studying the Mn 2p spectra [17–22]. The Mn 2p spectra of the samples before and after cycle test are deconvoluted into four peaks (Fig. 7). Two peaks around ~641.8 and ~653.3 eV are assigned to Mn 2p_{3/2} and Mn 2p_{1/2} of Mn³⁺ species, respectively, while two peaks around ~643.5 and ~654.6 eV are assigned to those of Mn⁴⁺ species [18–20]. No Mn²⁺ species are detected by XPS. As calculating from the integral area ratios of Mn(III) and Mn(IV) in the deconvoluted peaks, the samples before and after cycle test possess the Mn³⁺/Mn⁴⁺ atomic ratio of 5.0 and 1.2, respectively. Therefore, the Mn(III) is not stable in the LIB operation conditions, which causes the capacity continuous fading in cycle tests. As reported previously, the instability results from dissolution of disproportionation reaction of Mn³⁺ to Mn⁴⁺ and Mn²⁺ followed by dissolution of Mn²⁺ ions is responsible for the poor durability of the manganese oxides as a positive electrode material for lithium ion batteries [23, 24]. It is concluded that Mn dissolution is induced by acids generated either through secondary chemical reactions that occurred at the manganese oxides/electrolyte interface or by water contamination of the cell components either present in the electrolyte/cell components or introduced

during the manufacturing/assembly cell process, thereby accounting for some of the missing capacity[24].

Fig. 7

4. Conclusion

A vertically freestanding core-shell Ti@ δ -MnO₂ nanowire array was prepared by an electrochemical deposition. The core-shell structure endows the Ti@ δ -MnO₂ nanowires good electronic conductivity, and the vertically freestanding architecture supplies the arrays abundant mass transport channels when using them in electrochemical energy storage devices. These merits are beneficial to improve the rate capability of δ -MnO₂ as electrodes of supercapacitors and LIBs. As shown in our results, the performances at high rate current densities of Ti@ δ -MnO₂ nanowire arrays in the two devices are all enhanced compared with the reported in literatures. However, the instability of Mn³⁺ in the LIB operation conditions causes the arrays an unfavorable cycle performance, verified by the XPS measurement.

Acknowledgments

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Scheme 1. Schematic diagram of layered δ -MnO₂.

Fig. 1 XRD patterns of the Ti foam before and after corrosion.

Fig. 2. SEM images of vertically standing Ti nanowire arrays on Ti foam.

Fig. 3. XRD patterns of as-prepared Ti@ δ -MnO₂ nanowire arrays (a) and those heat-treated at different temperatures: (b)150 °C, (c)200 °C, (d)250 °C, (e)300 °C.

Fig. 4. SEM images of δ -MnO₂ on Ti nanowire arrays.

Fig. 5. Electrochemical characteristics of Ti@ δ -MnO₂ nanowire arrays as supercapacitor electrodes: (a) CV curves with various scanning rates; (b) galvanostatic charge/discharge curves at different current densities; (c) cycle performance using a current density of 10 A g⁻¹.

Fig. 6. Electrochemical characteristics of the LIB with Ti@ δ -MnO₂ nanowire arrays as anode: (a) CV curves of the battery with 0.1 mV s⁻¹ in a potential window of 4.0–2.0 V; (b) discharge/charge curves at various rate current densities; (c) cycle performance using varying rate currents; (d) cycle performances and the coulombic efficiency at 1 C rate.

Fig. 7. Mn 2p XPS spectra of the Ti@ δ -MnO₂ nanowires before and after cycle test.

Scheme 1

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Table 1. Electrochemical characteristic comparison of our Ti@ δ -MnO₂ nanowire arrays with the other δ -MnO₂ materials in literatures.

material	electrolyte	capacitance (F g ⁻¹)	cycle performance: current	ref
		/current (A g ⁻¹)	(A g ⁻¹)/cycle/retention	
δ -MnO ₂ nanosheets	1M Na ₂ SO ₄	173/1.0	1.0/2000/94%	[12]
δ -MnO ₂ /AC	1M Na ₂ SO ₄	29.4/1.0	1.0/1000/84%	[13]
δ -MnO ₂ /TiO ₂ NWs	1M Na ₂ SO ₄	120/0.1	1.0/1000/95%	[11]
δ -MnO ₂ /Ni foam	1M Na ₂ SO ₄	325/1.0	30 mV s ⁻¹ /1000/85%	[14]
Ti@ δ -MnO ₂ NWs	1M Na ₂ SO ₄	195/1.0	10.0/2000/97%	ours