



# Highly loaded manganese oxide with high rate capability for capacitive applications

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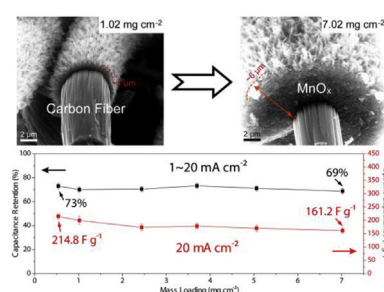
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## HIGHLIGHTS

- Highly loaded  $\text{MnO}_x$  is grown on carbon cloth via an electrodeposition.
- The nanostructure and content of hydrous states of  $\text{MnO}_x$  can be optimized.
- M-0.625 electrode exhibits high areal capacitance of  $1.64 \text{ F cm}^{-2}$ .
- M-0.625 electrode with high mass delivers excellent rate performance.
- The as-assembled device shows a high volumetric energy density of  $2.67 \text{ mW h cm}^{-3}$ .

## GRAPHICAL ABSTRACT



## ARTICLE INFO

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## ABSTRACT

Manganese oxide ( $\text{MnO}_x$ ), as a benchmark pseudocapacitive material, has aroused great interest in electrochemical energy storage community. However, ion transport is seriously hindered in the densely packed bulk materials of highly loaded  $\text{MnO}_x$  electrodes. Here, the structural engineering for the electrodeposited  $\text{MnO}_x$  materials is realized by tuning the concentration of the complexing agents used in the electrodeposition process. The fabricated highly porous nanostructure in the thick oxide layer can minimize the ion diffusion distances to the interior electrode surface, and the optimized content of the hydrous species can facilitate the solid-phase diffusion of the electrolyte ions in the oxide lattice. The deposited  $\text{MnO}_x$  electrode with a high mass loading of  $7.02 \text{ mg cm}^{-2}$  exhibits excellent rate capability due to the dual-tuning effect. An excellent specific capacitance of  $161.2 \text{ F g}^{-1}$  ( $1.13 \text{ F cm}^{-2}$ ) at a high current density of  $20 \text{ mA cm}^{-2}$  can be obtained, which is comparable to the capacitance delivered by the low mass loading electrode at the same current density ( $214.8 \text{ F g}^{-1}$  for  $0.54 \text{ mg cm}^{-2}$  sample), indicating its high material utilization. The performance of the fabricated electrode ranks on the top of the reported  $\text{MnO}_x$  materials with high mass for capacitive applications.

## 1. Introduction

How to accommodate fast charging/discharging rate for pseudocapacitive materials inexpensively and efficiently becomes a great challenge and inspires extensive research [1–5]. The challenges involved are probably best exemplified by manganese dioxide ( $\text{MnO}_2$ ), a benchmark pseudocapacitive material that roused great interest but

failed to exhibit its expected performance. Currently, the gravimetric capacitance of  $\text{MnO}_2$  has been pushed to approach its theoretical value ( $1110 \text{ F g}^{-1}$  in the potential window of 1 V) [6,7]. However, the mass loadings of these electrodes are still low (usually less than  $0.5 \text{ mg cm}^{-2}$ ), which cannot meet the requirement for real applications in energy storage community [7–12].

Integrating  $\text{MnO}_2$  with three-dimensional (3D) conductive scaffold has

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been devoted to enhance the capacitive performance of highly loaded  $\text{MnO}_2$  [13–17]. For example, He et al. used highly conductive 3D graphene network to load  $\text{MnO}_2$  via an electrochemical method. The as-prepared electrode with a large mass loading of  $9.8 \text{ mg cm}^{-2}$  can exhibit a high areal capacitance of  $1.42 \text{ F cm}^{-2}$  at low scan rate of  $2 \text{ mV s}^{-1}$  [15]. Xu et al. deposited nanostructured  $\text{MnO}_2$  on a highly oriented ultralong Ni-nanowire array electrode for capacitive applications. This electrode ( $\text{MnO}_2$  mass loading:  $3.51 \text{ mg cm}^{-2}$ ) can deliver a good gravimetric capacitance of  $214 \text{ F g}^{-1}$  at low scan rate of  $1 \text{ mV s}^{-1}$  [16]. However, these materials cannot deliver high capacitance at fast discharging rate [15,17,18]. It is difficult for the  $\text{MnO}_2$  with elevated mass loading to maintain good rate capability and deliver high specific capacitance at high discharging rate. Though employing 3D conductive current collector can provide fast electron transport pathway, increasing the mass loading would inevitably increase the thickness of the electrode materials, leading to sluggish ion transport. It is reported that the ion diffusion process in the thick oxide materials should include two parts: liquid-phase diffusion (e.g. ion transport from the electrolyte to the electrode interface) and solid-phase diffusion (e.g. ion migration in the oxide lattice) [19]. Therefore, both aspects should be considered to further improve the mass transport kinetics of the highly loaded  $\text{MnO}_2$  materials.

In this work, we demonstrated that the capacitive performance of highly loaded  $\text{MnO}_x$  electro-deposited on conductive carbon cloth can be improved by simultaneously facilitating the liquid-phase diffusion *via* creating highly porous nanostructures, and the solid-phase diffusion *via* optimizing the contents of hydrous states in the thick oxide layer. This improvement was realized by simply tuning the concentration of the complexing agents used in the plating solution. When the mass loading of  $\text{MnO}_x$  increased 13 times from  $0.54$  to  $7.02 \text{ mg cm}^{-2}$ , the rate retentions upon 20 times discharging current increase of these electrodes are almost the same (from 73% to 69%). In addition, the electrode with a high mass loading of  $7.02 \text{ mg cm}^{-2}$  can deliver an excellent gravimetric capacitance of  $161.2 \text{ F g}^{-1}$  at a high current density of  $20 \text{ mA cm}^{-2}$ , which is 75% of the capacitance delivered by the low mass loading electrode ( $0.54 \text{ mg cm}^{-2}$ ) at the same current density. Both experimental observations indicate the excellent rate capability and high utilization rate of the deposited  $\text{MnO}_x$  materials. Furthermore, an asymmetric supercapacitor using the highly loaded  $\text{MnO}_x$  as cathode and polypyrrole/functionalized carbon cloth (PPy/FCC) as anode can exhibit a remarkable volumetric energy density of  $2.67 \text{ mW h cm}^{-3}$  at a power density of  $8.73 \text{ mW cm}^{-3}$ .

## 2. Experimental

### 2.1. Materials

All the reagents were analytical grade and used as received, except the pyrrole (Py) which was reduced pressure distillation (ca.  $80 \text{ kPa}$ ,  $110\text{--}120^\circ\text{C}$ ,  $30 \text{ min}$ ) prior to use. Carbon cloth (CC, thickness:  $0.17 \text{ mm}$ ) and carbon paper (CP) were purchased from Fuel Cell Earth LLC (USA) and SGL group (Germany), respectively.

### 2.2. Electrodeposition of highly loaded manganese oxide materials on carbon cloth

Electrochemical deposition methods have been widely used to fabricate manganese oxides ( $\text{MnO}_x$ ) for energy storage applications [20–23]. In this work, we used a modified approach *via* tuning the concentration of the reagents in the deposition electrolyte to obtain highly loaded manganese oxide electrode materials. Briefly, electrochemical deposition of highly loaded  $\text{MnO}_x$  was conducted by a galvanostatic method at a current density of  $0.2 \text{ mA cm}^{-2}$  in a three-electrode configuration containing  $\text{MnSO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$  and sodium acetate (NaAc) aqueous solution. The CC (working area:  $1 \times 1 \text{ cm}^2$ ), CP and saturated calomel electrode (SCE) were used as working electrode, counter electrode and reference electrode, respectively. The

concentration of manganese source ( $\text{MnSO}_4$ ) used in the deposition process was fixed as  $0.0125 \text{ M}$ . The concentrations of the complexing agents [e.g.  $(\text{NH}_4)_2\text{SO}_4$  and NaAc] were varied as  $0.0125 \text{ M}$   $(\text{NH}_4)_2\text{SO}_4 + 0.025 \text{ M}$  NaAc,  $0.025 \text{ M}$   $(\text{NH}_4)_2\text{SO}_4 + 0.05 \text{ M}$  NaAc,  $0.125 \text{ M}$   $(\text{NH}_4)_2\text{SO}_4 + 0.25 \text{ M}$  NaAc,  $0.625 \text{ M}$   $(\text{NH}_4)_2\text{SO}_4 + 1.25 \text{ M}$  NaAc, and  $1.25 \text{ M}$   $(\text{NH}_4)_2\text{SO}_4 + 2.5 \text{ M}$  NaAc, respectively, keeping the ratio of  $(\text{NH}_4)_2\text{SO}_4/\text{NaAc}$  to be 1:2. The volume of the solution used in the electro-deposition cell was  $\sim 50 \text{ mL}$ . The depositions were conducted for 9 h and as-prepared electrodes were denoted as M-0.0125, M-0.025, M-0.125, M-0.625, and M-1.25, respectively. The deposition duration for M-0.625 was also varied from 1 to 15 h to obtain electrodes with different mass loadings of  $\text{MnO}_x$  (from  $0.54$  to  $7.02 \pm 0.01 \text{ mg cm}^{-2}$ ). After the electrodeposition, the as-prepared  $\text{MnO}_x$  electrodes were rinsed repeatedly with ethanol and deionized water to remove the residual electrolyte and dried in a vacuum oven at  $60^\circ\text{C}$  for 12 h.

### 2.3. Electrochemical polymerization of pyrrole on functionalized carbon cloth

Electrochemical polymerization of Py on functionalized carbon cloth (FCC) was conducted using an electrochemical method reported elsewhere [24]. Briefly, FCC was prepared by a potentiostatic method at  $1.9 \text{ V}$  (vs. SCE) for  $2.5 \text{ h}$  in a three-electrode cell filled with  $1 \text{ M}$   $\text{KNO}_3$  aqueous electrolyte, using CP and SCE as counter and reference electrodes, respectively. After the electrochemical functionalization, the FCC was rinsed with deionized water to remove residuals and dried for use. Subsequently, electrochemical polymerization of Py was conducted on FCC by a potentiostatic technique at  $0.5 \text{ V}$  (vs. SCE) for  $25 \text{ min}$  in an aqueous solution containing  $0.1 \text{ M}$  Py and  $0.05 \text{ M}$   $\beta$ -naphthalene sulfonic acid to afford PPy/FCC electrode.

### 2.4. The assembly of PPy/FCC//M-0.625 asymmetric supercapacitor

Asymmetric supercapacitor (ASC) of PPy/FCC//M-0.625 was assembled using M-0.625 ( $\sim 7 \text{ mg cm}^{-2}$ ) as cathode and PPy/FCC as anode electrodes (working area  $1 \text{ cm} \times 1 \text{ cm}$ ). The two electrodes were separated by a cellulose separator (NKK separator, Nippon Kodoshi Corporation), which was soaked by  $5 \text{ M}$  LiCl aqueous solution for  $10 \text{ min}$ . The active mass loadings of cathode and anode materials were  $7.02 \text{ mg cm}^{-2}$  and  $3.31 \text{ mg cm}^{-2}$ , respectively. The thickness of the ASC device was  $1.033 \text{ mm}$ .

### 2.5. Characterization

The morphologies of the materials were studied by field-emission scanning electron microscopy (FE-SEM, Ultra Plus, Carl Zeiss, Germany) and transmission electron microscopy (TEM,  $200 \text{ keV}$ , FEI, USA). Surface areas of the products were determined by the Brunauer-Emmett-Teller (BET) method using  $\text{N}_2$  adsorption-desorption measurements at  $77 \text{ K}$  (ASAP 2460, Micromeritics, USA). Crystal structure of  $\text{MnO}_2$  was characterized by X-ray diffraction (XRD, X'Pert Pro, PANalytical B.V., Netherlands) using  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.15405 \text{ nm}$ ). X-ray photoelectron spectroscopy analyses were conducted on an XPS spectrometer (ESCALAB 250 Xi, Thermo Scientific Escalab, USA). The average masses of the active materials were measured using a microbalance with a sensitivity of  $0.01 \text{ mg}$  (BT 25 S, Sartorius, Germany).

LiCl electrolyte has been widely used in the fundamental research for supercapacitors [9,25–30]. Therefore, in this work, electrochemical measurements were carried out using a multichannel electrochemical analyzer (VMP 3, Bio-Logic-Science Instruments, France) in  $5 \text{ M}$  LiCl aqueous solution with CP and SCE as counter and reference electrodes, respectively. Electrochemical impedance spectra (EIS) were collected from  $0.05 \text{ Hz}$  to  $40 \text{ kHz}$  at open circle potential. Electrochemical measurements of the model ASC were conducted in a conventional two-electrode configuration.

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