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# Electrodeposited manganese dioxide nanostructures on electro-etched carbon fibers: High performance materials for supercapacitor applications

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ABSTRACT

In this article we introduce a facile, low cost and additive/template free method to fabricate high-rate electrochemical capacitors. Manganese oxide nanostructures were electrodeposited on electro-etched carbon fiber substrate by applying a constant anodic current. Nanostructured $MnO_2$ on electro-etched carbon fiber was characterized by scanning electron microscopy, X-ray diffraction and energy dispersive X-ray analysis. The electrochemical behavior of $MnO_2$ electro-etched carbon fiber electrode was investigated by electrochemical techniques including cyclic voltammetry, galvanostatic charge/discharge, and electrochemical impedance spectroscopy. A maximum specific capacitance of 728.5 F $g^{-1}$ was achieved at a scan rate of 5 mV $s^{-1}$ for $MnO_2$ electro-etched carbon fiber electrode. Also, this electrode showed exceptional cycle stability, suggesting that it can be considered as a good candidate for supercapacitor electrodes.



## 1. Introduction

Electrochemical capacitors, also known as supercapacitors, are of the most promising energy strong devices that bridge the gap between batteries and conventional capacitors [1]. Delivering high energy and power densities make supercapacitors versatile devices with potential applications as power sources in a wide variety of applications. Carboneous materials, transition-metal oxides and conducting polymers are the most employed materials for electrochemical supercapacitors [2–8].

Among different transition metal oxides studied so far; hydrous forms of ruthenium oxide are the most promising material for supercapacitor applications. They provide relatively high specific capacitance with remarkable cycleability [9,10]. However, the practical application and commercialization of $RuO_2$ has slowed down because of its high cost and toxicity [11]. Thus, research has been focused on developing low-cost transition metal oxides including $MnO_2$, $Co_3O_4$, NiO, $Fe_3O_4$, $VO_x$, and $TiO_2$[3,12–17]. Amongst them, manganese oxide has attracted intense attention since it is an inexpensive and environmentally friendly material [18–24]. Manganese dioxide is one of the most stable manganese oxides with excellent physical and chemical properties under ambient conditions. A high capacitance (1370 F $g^{-1}$) is expected for $MnO_2$-based supercapacitor electrodes [25]. Such a high capacitance can be obtained by increasing the surface area and the material utilization. Direct deposition of manganese oxide on a carbon host, such as active carbon, graphite, carbon nanotubes and mesoporous carbon have been investigated to enhance the material utilization [26–32].

Electrochemical deposition is an exceptional technique developed to fabricate $MnO_2$ nanostructures, because of its opportunity to control the thickness and the structure of the deposited materials by changing several factors including electrolyte, electrodeposition current or voltage, and temperature [6,13].

Carbon fiber (CF) substrate offers advantages include high conductivity, chemical stability and three dimensional structures, which made it as an excellent substrate for supercapacitor electrode [2]. In this report, we report the fabrication of $MnO_2$ nanostructures on electro-etched carbon fiber surface ($MnO_2$-ECF). It is noteworthy that the use of electro-etched carbon fibers is proposed because of the porous three-dimensional structure with large amount of interior channels, which improves the diffusibility of electrolyte ions [2].

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## 2. Experimental

The CF paper was purchased from Toray Carbon Fibers Inc. (America), with the average diameter of 8 μm for each carbon fiber. All chemicals were of analytical grade and were purchased from Sigma–Aldrich Company. CF substrate was electrochemically etched (ECF) by applying a constant potential of 2 V (using Autolab potentiostat–galvanostat 101, Eco Chemie, BV, Netherlands) for 10 min in a 1 M of $H_2SO_4$ electrolyte solution [2].

Prior to anodic deposition, the electro-etched carbon fiber paper was washed with acetone, and then rinsed with deionized water. Manganese oxide nanostructures were deposited on ECF substrate by applying an anodic current of 0.5 mA $cm^{-2}$ in a solution of 0.1 M manganese acetate and 0.1 M sodium sulfate for 30 s at room temperature. After electrodeposition, the $MnO_2$-ECF electrode was rinsed several times by deionized water and annealed at 300 °C for 1 h in air.

Electrochemical measurements were carried out in a three electrode cell comprised of an Ag/AgCl reference electrode, platinum wire counter electrode and $MnO_2$-ECF working electrode, in a 1 M solution of $Na_2SO_4$. The surface morphology of the electrodeposited manganese oxide was studied by field emission scanning electron microscope (FESEM, Carl Zeiss ΣIGMA) equipped with EDX analyzer. The crystal structure of $MnO_2$-coated electrode was examined by a Bruker Advance D8 spectrometer with a Cu target (Cu-Kα line). Diffraction data were collected over $2\theta$, ranging from 10° to 90°.

Galvanostatic charge/discharge (CD), cyclic voltammetry (CV), and cycle-life stability experiments were performed in a potential range of 0–1 V vs. Ag/AgCl at room temperature. Also, the electrochemical characteristics of $MnO_2$-ECF electrodes were further studied by ac-impedance measurements (EIS). AC-impedance measurements were performed under open-circuit condition by a Zahner/Zennium potentiostat–galvanostat (Zahner, Germany). AC perturbation amplitude of 10 mV was imposed on the open-circuit potential in the frequency range of 100 kHz to 0.01 Hz.

## 3. Results and discussion

### *3.1. Surface characterization of $MnO_2$-ECF*

Firstly, ECF substrate was obtained by electro-etching in $H_2SO_4$. Scanning electron microscopy images (SEM), before and after electro-etching, revealed a densely packed and randomly oriented structure for CF and ECF substrates (Figure S-1 and S-2, supporting information). As seen in Figure S-1 and S-2, this randomly oriented structure provides three-dimensional porous structures. The porous structure of CF is expected to enhance the accessibility of electrolyte ions to this structure [2]. Figure S-2 shows that after electro-etching, new channels are formed on the fiber surface, which results in a considerable increase in substrate surface area. Fig. 1a and b presents SEM images of electrodeposited $MnO_2$ nanostructures on ECF surface (different magnification). The average thickness of electrodeposited $MnO_2$ nanostructures was estimated to be 20 nm. Additionally, a low magnification SEM image of $MnO_2$-ECF is provided as supporting information to show the even distribution of $MnO_2$ nanostructures on the carbon fibers (Figure S-3). It can be seen that $MnO_2$ nanostructures created 3D

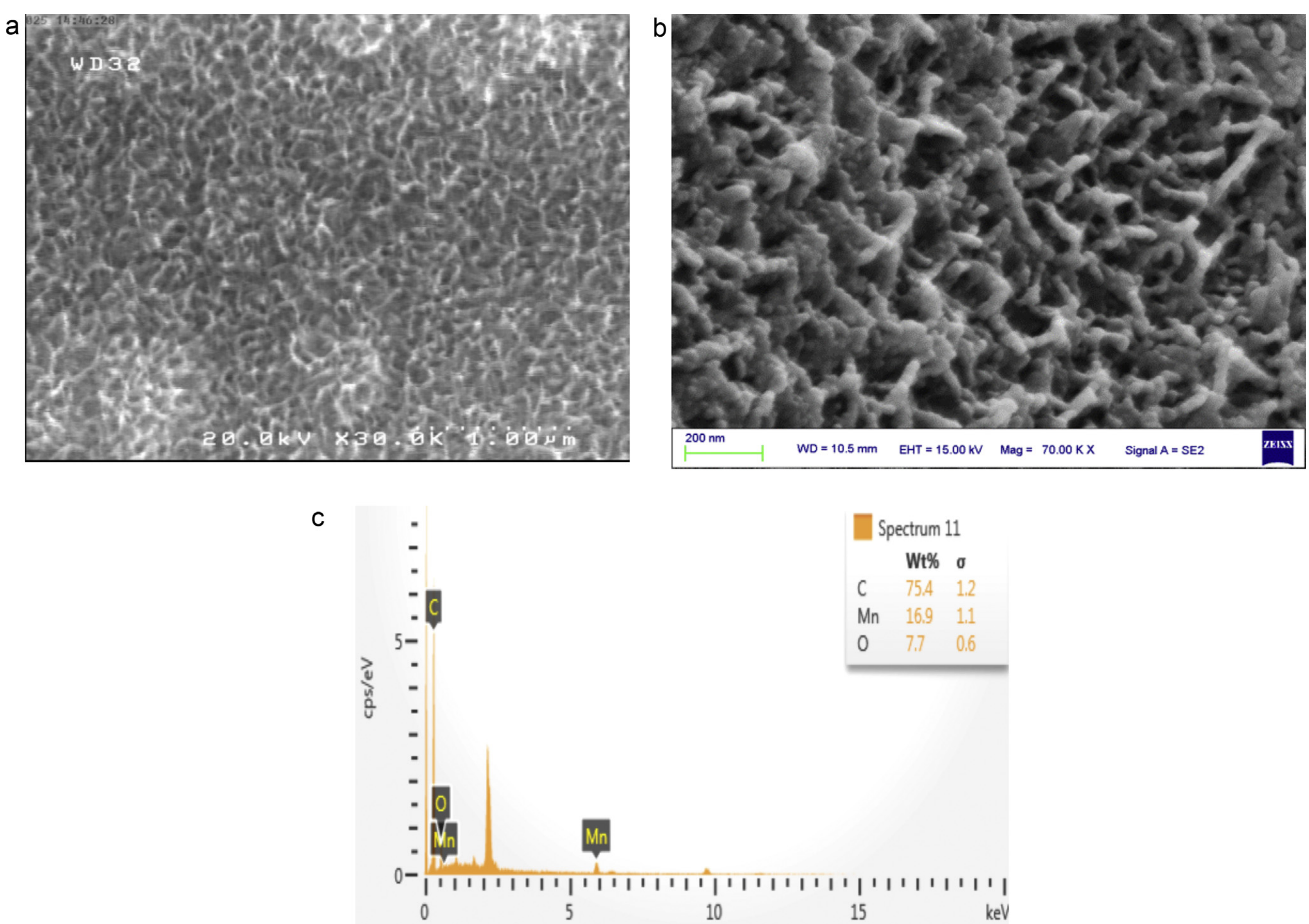


**Fig. 1.** SEM images of (a) and (b) $MnO_2$-ECF at two different magnification, and (c) EDX analysis of $MnO_2$-ECF.