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Solid-state supercapacitor cell based on 3D nanostructured MnO_2/CNT microelectrode array on graphite and H_3PO_4/PVA electrolyte

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ABSTRACT

Rapid development of portable consumer electronics has promoted the need for lightweight, flexible, environmentally friendly, high safety, and highly efficient energy storage technology. Herein, we present the fabrication and characterization of three dimensional (3D) nanostructured supercapacitor microelectrode arrays using manganese dioxide and carbon nanotubes (MnO_2/CNTs) on graphite foil substrate and polyvinyl alcohol (PVA)/phosphoric acid (H_3PO_4) solid polymer electrolyte for integration into a solid-state supercapacitor cell, without any additives or binders. A low-cost, hot filament chemical vapor deposition (HFCVD) process was used to synthesize vertically aligned 3D CNT microelectrode arrays, which act as the current conductors, directly on a flexible, conducting graphite foil current collector. Thin-film MnO_2 deposition on the CNTs was achieved by an electrochemical technique using in-situ reduction of $KMnO_4$, without any supporting electrolyte, which provides excellent bonding between the two for enhanced stability. Electrochemical characterization in aqueous electrolyte (KCl) yielded capacitance of 721 mF or 858 $F\cdot g^{-1}$ at 1 $mV\cdot s^{-1}$ scan rate. After assembling the solid-state supercapacitor cell, we obtained nearly 1.4 F or 830 $F\cdot g^{-1}$ at 1 $mV\cdot s^{-1}$ in a symmetric configuration. Maximum specific power value of 73.9 $kW\cdot kg^{-1}$ and a maximum specific energy of 115.2 $Wh\cdot kg^{-1}$was achieved. The solid-state device exhibits excellent cycling stability with a capacitance loss of only 11% after 3000 cycles. Detailed fabrication and characterization results have been presented.

1. Introduction

In recent decades, there has been greater focus on renewable energy sources as a result of climate change associated with carbon emissions [1]. Alternative sources including wind and solar energy are becoming more popular for residential and commercial deployment. However, their inconsistent nature due to fluctuations in wind speeds or lack of sun light at night necessitates use of efficient energy storage systems for off-peak use [2–3]. Inadequate capacity, limited cycle life, safety considerations and high production costs of lithium ion batteries have proven to be major obstacles in widespread implementation for such applications. Electrochemical supercapacitors (ES), capable of providing thousands of Farads at the electrode-electrolyte interface, offer a promising solution to complement the lithium ion batteries for robust energy storage solutions [4–5].

Supercapacitors can be categorized by their charge storage mechanisms: electrochemical double layer capacitors (EDLCs) and pseudocapacitors. While EDLCs store charge electrostatically at the interface between the electrode and electrolyte, pseudo-capacitors store the energy using reversible faradaic reactions [6]. There are many carbon materials commercially available for supercapacitor production, including carbon nanotubes (CNT), activated carbon, carbon fibers, graphite, and graphite compounds [7–12]. Among pseudocapacitive transition metal oxides such as RuO_2 [13], V_2O_5 [14], NiO_x [15], manganese dioxide (MnO_2) has been regarded as the most appealing electrode material for the next generation of ES due to its availability, affordability, high capacity, mechanical strength, and environment-friendliness [16]. However, several drawbacks limit its application in the development of supercapacitors, including its dense morphology, low ion diffusion constant, and low electronic conductivity [17–18]. To overcome these obstacles, extensive efforts are being made to explore composite structures in which highly conductive materials like metal nanostructures, conducting polymers, carbon black, carbon fibers, or carbon nanotubes (CNTs) are combined with MnO_2 [19–22].

In addition to the active electrode materials in the supercapacitors, electrolytes form another key component critical for optimum performance. Conventionally, liquid organic electrolytes such as tetraethylammonium tetrafluoroborate (TEATFB) in acetonitrile are popular in supercapacitors due to high ionic conductivity, ion mobility and fast charge-discharge kinetics [23]. Despite these advantages, liquid electrolyte leakage and flammability are major concerns, in light of the harm it poses to public safety. Solid-state electrolytes can provide an effective and rugged replacement for liquid-electrolytes, especially for

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applications that require greater thermal stability, longer shelf life, and do not require expensive encapsulation materials to meet safety requirements [24].

Solid polymer electrolytes, which have attracted great attention for many electrochemical devices, have been widely studied for application in supercapacitors. The most extensively utilized polymer electrolytes for supercapacitors, especially flexible and micro-energy storage devices, are acid/polymer blends, which are formed by mixing different strong acids, such as $HClO_4$, H_2SO_4, and H_3PO_4, with polymers [25–29]. Such strong acids are generally selected as proton conductors due to their self-ionization and self-dehydration reactions in natural states. Polymers used in acid/polymer blends include poly(vinylpyrrolidone)(PVP), poly(2-vinylpyridine)(P2VP), PVA, PEO, PAAM, and poly(4-vinylpyridine) (P4VP) [25–29]. Besides improved safety, solid-state polymeric electrolytes enhance overall mechanical strength even under flexural strain due to bending.

In this paper, we report on a solid-state supercapacitor cell using 3D nanostructured CNT/MnO_2 microelectrode array electrodes on highly flexible graphite foil with polyvinyl alcohol-phosphoric acid (PVA-H_3PO_4) gel as the solid electrolyte. Solution casting method was used to fabricate the free standing electrolyte layer which was incorporated into the electrodes using a hydraulic press. Detailed fabrication and electrochemical characterization are presented in this paper.

2. Materials and methods

The graphite foil used in this work was purchased from Mineral Seal Corporation and is non-inhibited grade developed for use in nuclear or semiconductor applications, typically 99.8% pure. Polyvinyl alcohol (PVA) (molecular weight; 89,000–98,000, 99 +% hydrolyzed) and potassium permanganate ($KMnO_4$) were obtained from Sigma Aldrich and phosphoric acid (H_3PO_4) (>85 wt% in water) was purchased from Alfa Aesar.

A perforated brass foil (406 μm thick) with opening of 406 μm diameter and 660 μm pitch was purchased from McMaster-Carr and was used as a shadow mask to create an array layout on the graphite foil substrate. The morphologies and microstructure of MnO_2/CNT electrodes were characterized by Hitachi S4200 and Zeiss Merlin scanning electron microscopes. Raman spectroscopy was also used for material characterization by analyzing vibrational and breathing modes in the as-grown CNTs and MnO_2. This was performed in Thermo Scientific DXR Raman system that uses a 532 nm green laser for excitation with a sampling spot size of the microscope at 100× objective and a 25 μm spectrograph aperture of 0.6 μm in diameter. Raman spectroscopy was performed in the spectral range (1800–200 cm^{-1}). The MnO_2 deposition and electrochemical characterization of the solid-state supercapacitor, including cyclic voltammetry (CV), galvanostatic charge–discharge, and electrochemical impedance spectroscopy (EIS), were performed using a CH Instruments (CHI660C) potentiostat/galvanostat.

The fabrication process to achieve the solid-state supercapacitor cell can be seen in the schematic flow chart in Fig. 1. First, thin layers of titanium (Ti ~45 nm) as a buffer layer followed by cobalt (Co ~7 nm) as the catalyst were deposited on the graphite foil substrates with the metal shadow mask on top using a Cressington 308R DC magnetron sputtering system, as seen in Fig. 1(a). The substrates used had an active area of 3.5 cm × 2 cm and 2 cm × 2 cm tabs for electrical contacts. Prior to the sputtering step, the substrates were rinsed with methanol and then dried with compressed air for 20–30 s.

The 3D array of vertically aligned carbon nanotubes, as seen in the Fig. 1(b) in the schematic, were grown directly on the graphite foil in a hot filament chemical vapor deposition (HFCVD) system. The substrate was annealed at 520 °C for 7 min in hydrogen and ammonia (100 ppm in N_2) ambient at 15 Torr chamber pressure as part of the pre-treatment process. Then, the carbon feed gas, CH_4 was introduced with the tungsten filament at 2000 °C with the substrate maintained at 2.5 cm below the filament; the CNT growth time was determined by the duration of CH_4 flow, which in this case was 15 min. The gas ratio used in this recipe was 3:1:3 (H_2:CH_4:NH_3).

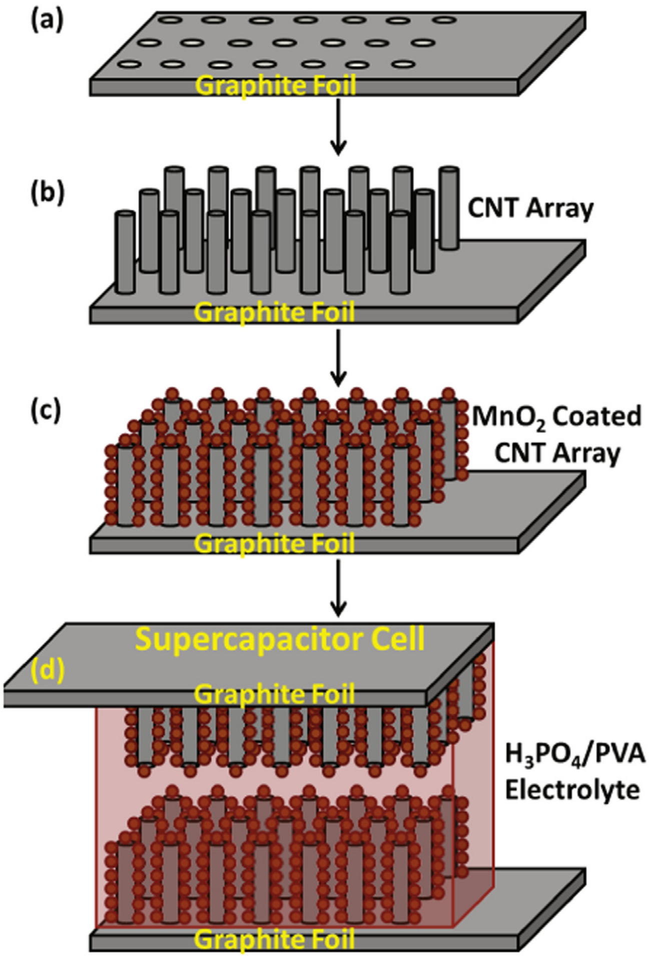

Fig. 1. Schematic representation of the fabrication process of the solid-state supercapacitor assembled in sandwich/symmetric configuration.

Controlled electrochemical deposition of manganese dioxide (MnO_2) on the CNTs was achieved by direct reduction of 10 mM potassium permanganate ($KMnO_4$) solution in de-ionized water (18 MΩ-cm) without any supporting electrolyte. The deposition was carried out in a beaker using cyclic voltammetry (CV) in a standard three electrode configuration with an Ag/AgCl reference electrode and Platinum (Pt) foil as the counter electrode. The CV parameters used for this step consisted of 3 cycles at 0.05 $V \cdot s^{-1}$ in a potential window of −1 V to +1 V and 120 s interval between each cycle. This step yields a 3D supercapacitor electrode as seen in the perspective view in Fig. 1(c). The mass of MnO_2 was determined by weighing the substrate on a microbalance (Denver instruments, APX-100), before and after MnO_2 deposition. Two electrodes were fabricated using this approach with MnO_2 mass of 0.84 mg and 0.81 mg, respectively. Reaction (1), corresponding to MnO_2 deposition, can be expressed as follows:

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^- \quad (1)$$

The H_3PO_4/PVA solid electrolyte works as a separator and allows ionic transport between the electrodes of the supercapacitor cell. An aqueous solution of PVA was first prepared by dissolving 5 g of PVA with 50 ml of de-ionized (DI) water which was heated to 60 °C and mixed using magnetic stirrer for 4 h to completely dissolve the PVA. This was followed by mixing 7.5 g of H_3PO_4 into the aqueous solution based on specific gravity of 1.70. This ratio of 3:2 (H_3PO_4: PVA) was chosen to achieve a balance in terms of flexibility, strength, ionic