Journal of Power Sources 225 (2013) 347–355

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Electrochemical deposition of nanostructured manganese oxide on hierarchically porous graphene–carbon nanotube structure for ultrahigh-performance electrochemical capacitors

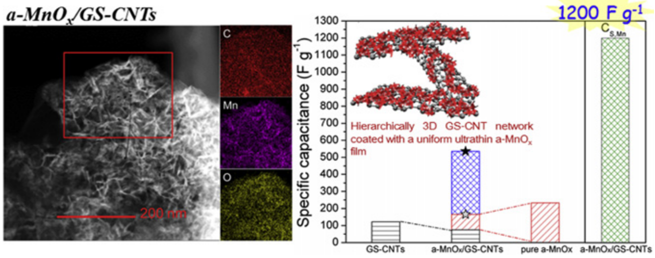
Shin-Ming Li [a,1], Yu-Sheng Wang [a,1], Shin-Yi Yang [a,1], Chia-Hong Liu [a], Kuo-Hsin Chang [a], Hsi-Wen Tien [a], Niann-Tsyr Wen [b], Chen-Chi M. Ma [a,**], Chi-Chang Hu [a,*]

[a] *Department of Chemical Engineering, National Tsing Hua University, Hsin-Chu 30013, Taiwan*
[b] *Chung-Shan institute of Science and Technology, Armaments Bureau, M.N.D., Taoyuan, Taiwan*

HIGHLIGHTS

- ► The *a*-MnO_x/GS–CNT is fabricated by combining the solution-assemble process and anodic deposition.
- ► The use of *a*-MnO_x on the 3D GS–CNT material produces a specific capacitance of MnOx of 1200 F g^{-1}.
- ► The specific energy and specific power of *a*-MnO_x/GS–CNT are as high as 46.2 Wh kg^{-1} and 33.2 kW kg^{-1}.
- ► This work conceptually provides new chances for designing 3D graphene-based architecture.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 17 July 2012
Received in revised form
24 September 2012
Accepted 12 October 2012
Available online 23 October 2012

Keywords:
Manganese oxide
Graphene sheet–carbon nanotube
Hierarchical architecture
Electrodeposition
Electrochemical capacitor

ABSTRACT

A 3D graphene sheet–carbon nanotube (GS–CNT) structure with a good wetting property, high porosity, and large surface area is homogeneously deposited with active amorphous manganese oxide (*a*-MnO_x) by potentiodynamic deposition. The flowery *a*-MnO_x nanostructure with ultra-slender petals (ca. 5–8 nm) on the framework of hierarchically porous GS–CNT matrix not only enables nearly full utilization of *a*-MnO_x but also retains sufficient conductivity and porosity for the high-rate charge–discharge application. The use of *a*-MnO_x on the 3D GS–CNT material produces a specific capacitance of MnO_x of 1200 F g^{-1} which is much-higher than that of a pure *a*-MnO_x electrode ($C_{S,Mn} = 233$ F g^{-1}). The specific energy and specific power of *a*-MnO_x/GS–CNT are respectively as high as 46.2 Wh kg^{-1} and 33.2 kW kg^{-1}, revealing that our work conceptually provides a way to produce porous structures composed of graphene, carbon nanotubes, and various electroactive materials for high-performance energy storage devices.

1. Introduction

With a rapid increase of the global energy consumption coupled with the severe climate change, settling the following two issues is very urgent and indispensable for scientists and engineers worldwide. The first issue is to develop the sustainable, renewable, and alternative energy sources with low emission of global-warming gases. Another crucial issue is the development of advanced

---

* Corresponding author. Tel.: +886 3 573 6027.
** Corresponding author. Tel.: +886 3 5713058; fax: +886 3 571 5408.
E-mail addresses: ccma@che.nthu.edu.tw (C.-C.M. Ma), cchu@che.nthu.edu.tw (C.-C. Hu).

[1] Authors contributed equally to this work.

0378-7753/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jpowsour.2012.10.037

energy-storage systems to efficiently utilize the electricity generated from the intermittently renewable sources, such as solar and wind-power energies. Currently, electrochemical capacitors (ECs) have been considered as one of the most important energy-storage systems [1,2]. ECs, also called supercapacitors or ultracapacitors, have been proposed as an attractive energy-storage device due to their high-impact characteristics, including superior cycle life, high power ability, short charging time, and excellent reliability in comparing with batteries [1,2]. Based on the above advantages, ECs have been combined with batteries or fuel cells to fabricate an advanced power system for various applications, such as portable systems, hybrid electric vehicles, electric vehicles, and large-scale power and energy management [3].

From previous investigations, porous carbon-based materials, conducting polymers, and transition metal oxides are potential candidates for the electrode materials of ECs [3,4]. They generally involve two types of energy storage mechanisms, i.e., capacitance from the electrical double layer charge/discharge and pseudo-capacitance from the superficial redox couples [3,4]. Among these electrode materials, transition metal oxides have drawn a great and extensive research attention due to their large specific capacitance, resulted from fast and reversible redox reactions at the surface of active materials. Nowadays, many efforts on ECs aim at exploring alternative metal oxides to replace RuO_2 in commercial pseudo-capacitors because of high cost and rareness of Ru [4,5]. Among the proposed metal oxides, manganese oxides (MnO_x) have been widely investigated due to the low cost, environmental benignity, and ultrahigh theoretical specific capacitance ($C_{S,Mn} \sim 1370$ F g^{-1}) [6]. Unlike RuO_2, MnO_x was operated in neutral aqueous electrolytes, which provide a further advantage for the commercial application. However, the poor electrical conductivity is the main drawback of MnO_x; as a result, its performance is usually much lower than the theoretical value estimated from its redox reaction [4,7]. Accordingly, many efforts have been paid for promoting the capacitive performances of MnO_x. Due to the high power requirement, the pseudo-capacitive redox reactions generally involve MnO_x in the very thin surface layer and the ideal performances of pure MnO_x were only observed under the extreme case with very low mass loadings, limiting the practical applicability. To date, incorporation of nanostructured MnO_x into a porous conductive substrate is the most promising approach to simultaneously keep smooth pathways of electrons and ions for the pseudo-capacitive redox transitions to promote the utilization of MnO_x [2,8,9]. Thus, a significant enhancement in capacitive performances of many MnO_x/carbon composites (see Table 1) has been demonstrated [8–14]. Based on these examples, the key in developing MnO_x/carbon composites with excellent capacitive performances is to fabricate a conformal coating of ultrathin MnO_x onto a porous, conductive substrate with high specific surface area to optimize the microstructure of hybrid materials and to fully utilize MnO_x.

Table 1
Performances of *a*-MnO_x/carbon hybrid electrodes for ECs.

Method[a]	Description[b]	Electrolyte	$C_{S,T}$ F g^{-1} (scan/discharge rate)	Reference (year)
RD	nr-Mn_3O_4/GS	Na_2SO_4	121 (0.5 A g^{-1})	14 (2012)
ED	GS/nw-MnO_2-textile	Na_2SO_4	315 (2 mV s^{-1})	19 (2011)
RD	ns-MnO_2/GS	Na_2SO_4	188 (0.25 A g^{-1})	12 (2011)
MI	np-MnO_2/GS	Na_2SO_4	303 (10 mV s^{-1})	11 (2011)
MI	np-MnO_2/GS	Na_2SO_4	310 (2 mV s^{-1})	13 (2011)
RD	nr-MnO_2/GO	Na_2SO_4	197.2 (0.2 A g^{-1})	10 (2010)
RD	np-MnO_x/CNT	K_2SO_4	290 (10 mV s^{-1})	9 (2010)
ED	nf-MnO_x/GS–CNT	Na_2SO_4	535 (5 mV s^{-1})	This work

[a] RD = redox deposition, ED = electrodeposition, MI = microwave irradiation.
[b] nw = nanowire, nf = nanoflower, np = nanoparticle, nr = nanorod, ns = nanosheet, GS = graphene nanosheet, GO = graphene oxide, MC = mesoporous carbon, CNT = carbon nanotube.

Recently, graphene sheet (GS) is regarded as a next-generation electrode material for energy storage and conversion systems due to its unique properties, such as ultrahigh theoretical surface area (2630 m^2 g^{-1}), sufficient porosity, superior conductivity, and rich surface chemistry [15,16]. Accordingly, intensive efforts have been paid to use various technologies to synthesize MnO_x/GS composites for the electrode materials of ECs [5,10,12,14]. However, the aggregated issue will ruin the advantage of ultrahigh theoretical surface area of GS due to the fact that the physicochemical properties of aggregated GS are similar to graphite [17,18]. Hence, the actual performances of graphene-based materials are usually lower than the anticipative value estimated from the theoretical surface area. Therefore, how to effectively improve the performances of graphene-based materials is a crucial issue to explore its potential to the energy storage/conversion applications.

In this work, a hierarchically porous structure, consisting of nano-structured *a*-MnO_x, 2D GS and 1D carbon nanotubes (CNTs), is designed to approach the full utilization of electroactive materials (i.e., *a*-MnO_x) meanwhile this idea is also suitable for other electroactive materials. Note that CNTs in the hybrid mainly act as a spacer avoiding the restacking of graphene because the specific surface area of CNTs is low. Consequently, 10 wt% CNTs is a compromise content for obtaining the maximal specific surface area of this series of hybrids [17]. As shown in Fig. 1, a two-step approach is developed to fabricate the 3D *a*-MnO_x/GS–CNT composite with hierarchical porosity. The first step is to insert 1D CNTs into the layers of chemically functionalized GS to construct a mesoporous GS–CNT structure via a simple solution-assemble process [17]. In the second step, *a*-MnO_x is grown as flowery nanostructures with ultra-slender petals (about 5–8 nm) along the framework of a porous GS–CNT matrix via potentiodynamic deposition. This 3D porous network coated with a uniform ultra-thin *a*-MnO_x film is characterized for the supercapacitor application. Clearly, this work develops a simple, efficient and practical approach to fabricate a novel porous manganese oxide/graphene-based composite electrode with outstanding capacitive performances through combining the simple solution-assemble process and the reproducible electrochemical deposition technology. Moreover, the total specific capacitance of *a*-MnO_x/GS–CNTs is higher than those previously reported in the literature on the basis of MnO_x/graphene electrode materials (see Table 1) [10,12–14,19]. Most importantly, this work conceptually provides a way in designing a 3D porous graphene-based matrix for many electroactive materials.

2. Experimental

2.1. Synthesis of graphene oxide (GO)

The preparation of GO completely follows the modified Hummer's method [20]. 0.25 g graphite and 0.125 g $NaNO_3$ were added into a 100-ml flask filled with 12 ml H_2SO_4 (98%) in an ice bath under stirring. Next, 0.75 g $KMnO_4$ was added slowly to the solution, keeping the temperature below 15 °C. Then, the ice bath was removed and the flask was heated to 50 °C, followed by a slow addition of 12 ml deionized (DI) water. The temperature of the solution was increased to 98 °C and the solution was maintained at this temperature for 15 min. Next, 50 ml DI water with 10% H_2O_2 was added to the solution until the cessation of gas evolution. The solution was centrifuged at 11,000 rpm and washed with DI water for several times to remove the impurities. Finally, the solution was dried at 40 °C in a vacuum oven for three days to obtain GO powders.