Journal of Alloys and Compounds 649 (2015) 579–584

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Facile synthesis of MnO_2/rGO/Ni composite foam with excellent pseudocapacitive behavior for supercapacitors

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ARTICLE INFO

Article history:
Received 3 June 2015
Received in revised form
22 July 2015
Accepted 23 July 2015
Available online 29 July 2015

Keywords:
Porous MnO_2/rGO
Ni foam
Composite
Directly grown
Supercapacitor

ABSTRACT

In this study, the MnO_2/reduced graphene oxide/Ni (MnO_2/rGO/Ni) composite foam as a binder-free supercapacitor electrode was prepared by a facile method. The rGO film has been firstly coated on the skeletons of Ni foam current collectors by chemical deposition method and that have been used as substrates for preparation of a novel three dimensional rGO/Ni composite foam-supported porous MnO_2 film by the hydrothermal method. The structure of MnO_2/rGO/Ni composite foam was characterized by Raman spectra, IR spectra and Scanning electron microscopy. It indicated that the high-quality rGO film have been coated on skeletons of Ni foam current collectors and the MnO_2 film had a 3D network microstructure, consisting of interlaced nanosheets. Furthermore, the binder-free MnO_2/rGO/Ni composite foam electrode has been characterized by the cyclic voltammetry, galvanostatic charge/discharge and electrochemical impedance spectra. It exhibited excellent pseudocapacitive behavior with specific capacitance of 479.0 F/g. The capacitance could retain about 83.5% after 1000 charge–discharge cycles. This simple synthetic approach provides a convenient route for the large scale preparation of 3D porous MnO_2/rGO/Ni composite foam for lots of applications in future.

1. Introduction

The MnO_2 materials have been used for supercapacitor electrodes due to its high theoretical capacitance (1380.0 F/g) and low cost, environment-friendly and high stability in alkaline electrolyte [1,2]. However, there is still a great number of challenges remained in the application of high-capacity MnO_2 electrodes. For example, one of the major drawbacks for MnO_2 as supercapacitor active materials is the poor electrical conductivity (~10^{-5} to 10^{-6} S/cm) [3], which greatly limits its practical applications. Fortunately, it may be improved by introducing high electrical conductivity carbon in the electrode [1–7]. As one of the nanostructured carbons, rGO has been receiving a great deal of attention in recent years due to its excellent electronic, capacitive and mechanical properties, superior chemical stability and high specific surface area, which is commonly used as electrode materials for supercapacitors and Li-ion batteries [8–13]. On the other hand, the surface of rGO was modified (anchored) with inorganic particles, which was commonly believed to improve the electrical conductivity, reduce the equivalent series resistance and charge-transfer resistance of MnO_2 [14,15]. So, the development of MnO_2/rGO nanocomposite materials could draw on each other's merits and raise the level together for the both electrode materials. Currently, many strategies have been developed for the synthesis of MnO_2/rGO nanocomposites, such as hydrothermal route [16], solution phase approach [17,18], solid–state reaction approach [19], chemical precipitation approach [20,21], and microwave heating approach [22]. However, products generated by the most methods were often in powder composite type. Therefore, further electrode preparation is still necessary for realizing their application in supercapacitors, which leads to additional cost and time. Furthermore, the MnO_2/rGO powder were coated on the current collector (such as platinum, gold or titanium) with the assistance of binder (such as PVDF, PTFE) [23]. The high contact resistance between MnO_2/rGO powder and current collector and the nonconductive binder would greatly

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http://dx.doi.org/10.1016/j.jallcom.2015.07.212

decrease the rate capability and poor cycle stability of supercapacitors. Recently, many methods by directly growing composites on the conductive Ni substrates have been developed, for example, Xia and co-workers prepared a Ni foam-supported rGO/porous NiO hybrid film by the combination of electrophoretic deposition and chemical-bath deposition [24]. Wang and co-workers successfully electrodeposited $Ni(OH)_2$ nanoflakes on graphene that have been produced by radio frequency plasma-enhanced chemical vapor deposition (PECVD) on Ni foam [25]. However, the electrodeposition and PECVD route is difficult to large scale preparation of composites grown on the conductive Ni foam substrates, which restrict its practical application. Moreover, to the best of our knowledge, there is still few works reporting on preparation of MnO_2/rGO composite grown on conductive Ni foam substrates.

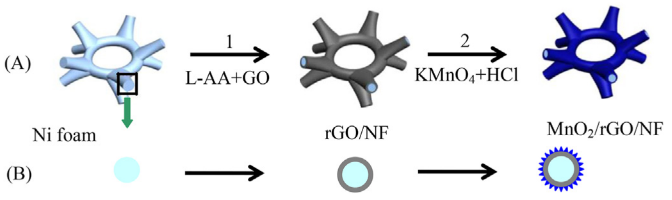
In this study, we report a green, simple, low-cost approach for the synthesis of 3D porous MnO_2/rGO/Ni composite foam electrodes. In the composite, rGO film was directly coated on skeleton of the Ni foam without assistant of any surfactant, which serve as a conductive network and, meanwhile, provide abundant ion transport channels. The nanostructured porous MnO_2 sheets were further anchored on the skeleton of the rGO/Ni composite foam. This novel structure ensured the fast transportation of electrons and electrolyte ions within the whole electrode structure. So the MnO_2/rGO/Ni composite foam exhibited high specific capacitance and good capacitive retention.

2. Experimental

2.1. *Preparation of porous MnO_2/rGO/Ni composite foam (MnO_2/rGO/NF)*

The porous MnO_2/rGO/Ni composite foam was prepared by a facile method as shown in Scheme 1. Firstly, the rGO/Ni composite foam (rGO/NF) was prepared as shown in following. The commercial Ni foam was purged with acetone, diluted hydrochloric acid and deionized water in turn and then dried for use. Graphite oxide was prepared from natural flake graphite by the Hummers method [26]. The graphite oxide was further dispersed in aqueous solution under ultrasonication for 1.5 h to form brown graphene oxide (GO) aqueous solution. And then, the Ni foam with a diameter of 3 cm was transferred into a beaker filled with 10 ml GO aqueous solution (1.0 mg/ml) and 0.02 g ascorbic acid (L-AA). The beaker was heated at 95 °C for 6.0 h and allowed to cool down. The rGO/Ni composite foam was got out from beaker, and then was heated-drying at 50 °C for 6 h.

Secondly, 4.7 mg $KMnO_4$ and 6 ml HCl solution (0.15 M) were dissolved in 15 ml water. Subsequently, a clean rGO/Ni composite foam with a diameter of 3 cm was added into the above solution. The mixture was transferred into a Teflon cup in a stainless steel-lined autoclave. The autoclave was maintained at 150 °C for 6 h and then cooled down to room temperature. The final MnO_2/rGO/Ni composite foam was washed with distilled water and ethanol for several times to remove any salts, and then dried in a vacuum oven at 50 °C for 6 h. In a comparison, the MnO_2/Ni composite foam (MnO_2/NF) was also prepared at the same condition, in which the Ni foam was used to be substr. To measure the mass of MnO_2 and rGO on composite foam, the composite foams were put into HCl solution (6 M) at 80 °C for 6 h to completely remove the Ni. The composition of the composite foams was concluded in Table 1.



Scheme 1. (A) Schematic illustration of the fabrication procedures of the MnO_2/rGO/Ni composite foam electrode by the facile method. (B) Cross-section view of a Ni foam and composite foam branch during each fabrication step.

2.2. *Characterization*

X-ray diffraction (XRD) was recorded on a Rigaku Dmax-r C X-ray diffractometer using Cu Kα radiation ($\lambda = 1.540$ Å) operated at 40 kV and 100 mA.

Raman spectrum was collected on a Jobin-Yvon Lab Ram HR800 Raman spectroscope equipped with a 514.5 nm laser source.

IR spectrum was collected on a Bruker TENSOR27 IR spectroscope equipped.

The morphology and structure of composite foam was observed by Scanning electron microscopy (SEM) (Su-1500 and Su-8010, HITACHI Japan) equipped with an energy dispersive X-ray spectrometer (EDS).

2.3. *Electrochemical characterization*

All electrochemical measurements were carried out in a conventional three-electrode system using an electrochemical workstation (CHI660D, Chenhua Instruments, China) with KOH solution (6 M) as the electrolyte. The porous composite foams were directly tested as the electrode, while saturated calomel electrode (SCE) as the reference and a platinum plate as the counter electrode. The electrochemical performances of the prepared electrodes were characterized by cyclic voltammetry, electrochemical impedance spectroscopy measurements (EIS) and galvanostatic charge–discharge tests. The specific capacitance was obtained from the discharge process according to the following equation, Cs (F/g) $= I\Delta t/\Delta E{*}m$, where I is the current loaded (A), Δt is the discharge time (s), ΔE is the potential change during the discharge process, and m is the mass of active material (g).

3. Results and discussions

Fig. 1A shows the Raman spectrum of MnO_2/rGO/Ni composite foam. It clearly shows two peaks of 1351.5 cm^{-1} and 1575.5 cm^{-1} assigned to D and G band of rGO, and the I_D/I_G intensity ratios is about 1.1, implying the existence of rGO in the composite foam [8]. In addition to this, the Raman peak at 565.5 cm^{-1} can be attributed to the symmetric stretching vibration (Mn–O) of MnO_2 [20,21], indicating the existence of MnO_2 in the composite foam, too. Furthermore, there presents a new Raman peak at 1100 cm^{-1}, which may be attributed to the interaction between rGO and MnO_2. All Raman peaks assigned to rGO and MnO_2 in MnO_2/rGO/Ni composite foam are blue shift compared to that of rGO/Ni and MnO_2/Ni composite foam. These results indicate the formation of MnO_2/rGO/Ni composite foam, in which the MnO_2 is anchored on rGO by the chemical interaction. The formation of MnO_2/rGO/Ni composite foam was further confirmed by the IR spectra as shown in Fig. 1B. The peak at ca. 546 cm^{-1} is assigned to the Mn–O bond of MnO_2 [16]. It clearly shows that the absorption peak assigned to the Mn–O bond of MnO_2 in MnO_2/rGO/Ni composite foam is blue shift compared to that of MnO_2/Ni composite foam. The absorption peaks of 1635 cm^{-1} and 1053 cm^{-1} assigned to C–C and C–O–C bond of rGO almost disappear compared to that of rGO/Ni composite foam. So the IR spectra further reveal that MnO_2 anchoring on the rGO have been successfully synthesized.

Fig. 2A shows the XRD pattern of MnO_2/rGO/Ni composite foam.