Microelectronic Engineering 157 (2016) 31–34

Contents lists available at ScienceDirect

Microelectronic Engineering

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

Nanoporous all metallic binder free Sn:Pb composite electrode for high performance supercapacitors

M. Zandi [a], M. Amirhoseiny [b,*], A. Mosayyebi [c], M. Khademian [a]

[a] Shahidbeheshti University, Tehran, Iran
[b] Department Of Engineering Science, Buein Zahra Technical University, Buein Zahra, Qazvin, Iran
[c] Tarbiat Modares University, Tehran, Iran

ARTICLE INFO

Article history:
Received 10 March 2015
Received in revised form 25 January 2016
Accepted 9 February 2016
Available online 10 February 2016

Keywords:
Supercapacitor
Nanoporous
Energy storage
Metallic block

ABSTRACT

Exploiting nanoporous binder-free electrode materials is important for the fast development of supercapacitor devices. A simple and effective strategy is demonstrated to fabricate a nanoporous all metallic binder free composite mixing tin (Sn) and lead (Pb) powders together and also, compositing them under pressure and temperature. The anodized metallic composite block have been functionalized and also found a nanoporous structure. A SEM result shows that the nanoflake like arrangement has been synthesized. The XRD results confirm the nanoporous structure of the Sn/Pb foam after etching with 5 M NaOH. The prepared supercapacitor is able to offer large specific capacitance (8.5 F cm^{-3}) and good cycling stability (94% capacitance retention after 100 charge–discharge cycles), with regard to the synergic integration of Sn and Pb metals and the unique nanoporous structure.

1. Introduction

Supercapacitors are such energy storage devices that offer several advantages including high power density, fast charging–discharging processes, and excellent cycling stability [1,2].Depending on the mode of energy storage in supercapacitors, they are classified as in to electrical double layer capacitors (EDLC) and pseudo-capacitors or ultra capacitors [3].Recently, oxide-based nanostructured materials have attracted particular attention due to their perfect properties in a wide range of applications. One of the requirements for these materials is low cost metal oxides as alternative to the hydrous RuO_2 which demonstrated large specific capacitance and also good cyclic stability [4].The key performance parameters of supercapacitors include specific capacitance (normalized by electrode mass, volume, or area), energy density, power density, rate capability (retained capacitance at a high current loading) and cycling stability. To increase the energy density and power density of a supercapacitor, it is desirable to increase the specific capacitance and the operating voltage window as well as reduce the equivalent series resistance [5].The large specific capacitance of electrochemical supercapacitors is a result of two mechanisms that occur at or near the electrode/electrolyte interfaces in the capacitors. The first is double layer capacitance which is a non-faradic process and the second is charge transfer reaction pseudocapacitance, which is a faradic process. These mechanisms can work together or separately, depends on active electrode materials used in the supercapacitors [6].

The general requirements for metal oxides in supercapacitors are: (1) the oxide should be electronically conductive, (2) the metal can exist in two or more oxidation states that coexist over a continuous range with no phase changes involving irreversible modifications of a 3-dimentional structure, and (3) the cations can freely intercalate into the oxide lattice on reduction, allowing facile interconversion of $O^{2-} \leftrightarrow OH^{-}$ [3,7]. Different parameters can be considered to choose materials for the fabrication of supercapacitor electrodes. These materials should be electronically conducting and blocking mobile ions in the electrolyte [8]. The development of nanostructured oxide material scan enhance the capacitive performance due to their high surface area, short electron and ion transport pathways, but the poor intrinsic conductivity of these oxide materials still limits their performance. An emerging new concept is to grow electroactive nanostructures on conductive substrates to be directly used as binder-free electrodes for supercapacitors [9,10].

In this paper, we demonstrated a novel and simple approach to preparing nanoporous all metallic binder free Sn/Pb oxide/hydroxide composite as a cathode for high performance supercapacitors. This low-cost and high-performance active Sn/Pb oxide/hydroxide nanocomposite can offer great promise in developing commercial energy storage devices.

2. Experimental

All chemicals were purchased from Merck and used without any purification. A nanoporous all metallic Sn:Pb composite is fabricated by mixing tin (Sn) and lead (Pb) powders together with a weight ratio

* Corresponding author.
E-mail address: Amirhoseiny_m@yahoo.com (M. Amirhoseiny).

http://dx.doi.org/10.1016/j.mee.2016.02.013
0167-9317/

of 1:1 and also, composited under $1.98 * 10^5$ Pa pressure and 300 °C temperature. Due to the differences in physical and chemical properties of both metals, supercapacitor has been fabricated without the use of a binder and conductive additive. The major issues for metal hydroxides are their poor electrical conductivity, so tuning their morphologies at the nanoscale can improve the electrochemical properties. Therefore, to fabricate a uniform nanoporous structure, the metallic composite block immersed in 5 M NaOH for 45 min. In this electrochemical process, the Sn particles etch by NaOH and produce nanopores in the metal composite. The chemical reaction equation between Sn and NaOH is shown below:

$$Sn + 2NaOH \rightarrow Na_2SnO_2 + H_2. \quad (1)$$

Since a metal hydroxide with poor crystallinity or amorphous phase may result in more transportation channels than that of a highly crystalline one [11], amorphous Sn/Pb hydroxide nanostructures with good electrochemical behaviors were synthesized by anodized metallic composite block in 6 M NaOH with 1 mA cm^{-2} for 5, 10 and 15 min.

The surface morphology of the block was examined by using scanning electron microscopy (SEM), Model KYKY EM-3200. The Fourier transform infrared spectra were recorded using spectrum one: FTIR-spectrometer in the range 2000–4000 cm^{-1} to characterize the functional groups of the composites. X-ray fluorescence (XRF) was employed to analyze the elemental composition of the samples. Voltage measurements are done using an electrochemical analyzer (KimiaStat 126) in aqueous 0.5 M K_2SO_4 electrolyte. The three electrode cell arrangements comprised Ag/AgCl reference electrode, a platinum counter electrode and fabricated Sn/Pb thin film hydroxide as the working electrode.

3. Results and discussion

Fig. 1, shows the SEM image of the Sn–Pb composite after etching with 5 M NaOH for 45 min. A nanoflake like arrangement can be seen in the figure. Porous metals are produced by mixing and compacting metal powders with a space holder which is later removed either during or after sintering, by dissolution or thermal degradation, to leave porosity. The porosity in these components is simply derived from the incomplete space filling of powders poured into and sintered in a die. In addition Sn etched into a nanoflake shape and increased the porosity after etching with 5 M NaOH for 45 min.

The observed nanostructure suggests a possible high surface area for the metal block which can be used as an electrode to contribute greatly the fast and reversible faradaic redox reactions for the pseudocapacitance. The distinctive morphology plays a basic role in supercapacitors. To obtain good capacitive materials, they should have a large surface area and highly ordered dimensions. The larger specific surface area of active materials can accommodate more electrolyte ions for redox process and also providing a suitable nanopore structure is important for the mass transfer of electrolytes [11].

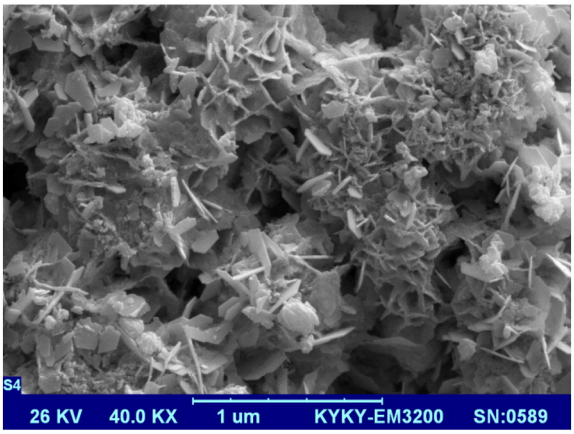

Fig. 1. SEM images of Sn/Pb composites after etching with 5 M NaOH for 45 min.

Fig. 2, shows XRD patterns of the Sn–Pb composite before and after etching with 5 M NaOH. The exhibited patterns were indexed using the Pb, Sn standard data (JCPDS code, Joint Committee for Powder Diffraction Standards, no. 00-004-0 and no. 01-086-2). The mean nanocrystallite size was determined from the FWHM of the XRD peaks using the Scherrer equation [12] as follows:

$$D = \frac{0.89\lambda}{B\cos\theta_B} \quad (2)$$

where B is the full width at half maximum of the diffraction peak, λ is the wavelength of the X-ray, and θ_B is the Bragg diffraction angle in degrees. Table 1, shows the full width at half maximum (FWHM) and calculated crystallite size of the Sn and Pb before and after etching with 5 M NaOH. The FWHM of Sn and Pb increased and the crystallite size decreased after etching the composite. It confirms the nanoporous structure of the Sn–Pb composite after etching with 5 M NaOH.

Fig. 3, shows the FT-IR spectrum of Sn/Pb nanocomposites anodized for 15 min. In the spectrum of nanocomposites, a deep at 2370 cm^{-1} and a broad characteristic deep around 3400 cm^{-1} are present corresponding to –OH stretch mode. The inset shows the FTIR spectrum of Sn/Pb blocks with different anodizing time. As anodizing time increase, the OH species dips are sharper which can be attributed to more Sn/Pb hydroxide factors created in the sample. In the next part we chose the Sn/Pb nanocomposite anodized at 15 min in NaOH with highest hydroxide species to test as a supercapacitor.

XRF measurement was employed to analyze the elemental composition of the samples. The XRF results show that the surface contents of Sn, Pb, and Na on the nanocomposite are determined to be 30, 60 and 3%, respectively. Based on FTIR results, our sample contains some hydrogen and oxygen, which could not be detected with our present XRF equipment. It can be seen that the Sn/Pb ratio has been changed significantly after etching with NaOH which confirms that Sn etched into nanoflake shape and lost 2/3 of its first mass. The element of sodium

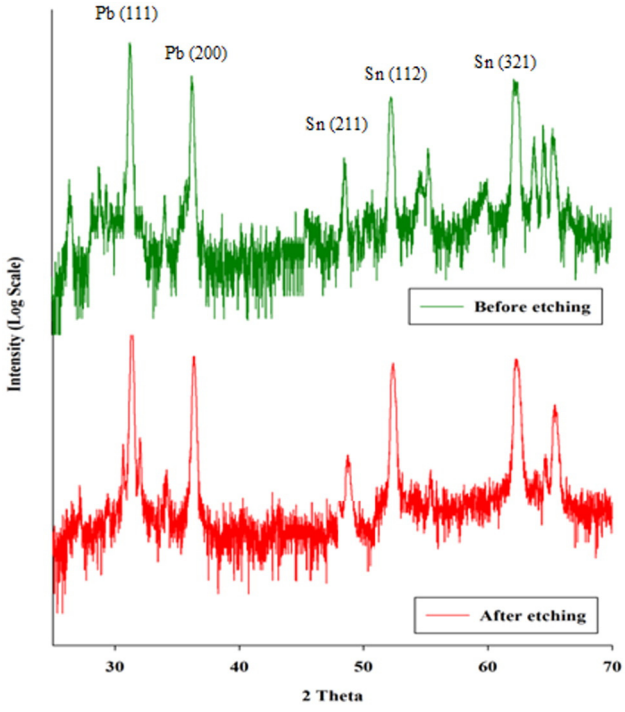

Fig. 2. X-ray diffraction spectra of Sn–Pb composite before and after etching with 5 M NaOH.