ARTICLE IN PRESS

Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

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

High areal capacitance of FeOOH-carbon nanotube negative electrodes for asymmetric supercapacitors

Ri Chen[a,b], Ishwar K. Puri[a,b], Igor Zhitomirsky[b,*]

[a] *Department of Mechanical Engineering, McMaster University, 1280 Main Street West, Hamilton, Ontario, Canada L8S 4L7*
[b] *Department of Materials Science and Engineering, McMaster University, 1280 Main Street West, Hamilton, Ontario, Canada L8S 4L7*

ARTICLE INFO

Keywords:
Powder
Particle
Supercapacitor
Negative electrode
Adsorption
Iron
Extraction
Capacitance

ABSTRACT

The relatively low capacitance of negative electrodes, as compared to the capacitance of advanced positive electrodes, poses a serious problem, since this limits the development of asymmetric supercapacitor (SC) devices with a large voltage window and enhanced power-energy characteristics. We fabricate negative SC electrodes with a high capacitance that match the capacitance of advanced positive electrodes at similar active mass loadings, as high as 37 mg cm^{-2}. Cyclic voltammetry, impedance spectroscopy, galvanostatic charge-discharge data and the power-energy characteristics of the asymmetric SC device exhibit good electrochemical performance for a voltage window of 1.6 V. Our approach involves the development and application of particle extraction through liquid-liquid interface (PELLI) methods, new extraction mechanisms and efficient extractors to synthesize α-FeOOH and β-FeOOH electrode materials. The use of PELLI allows agglomerate-free processing of powders, which facilitates their efficient mixing with multiwalled carbon nanotubes (MWCNT) and allows improved electrolyte access to the particle surface. Experiments to determine the properties of FeOOH-MWCNT composites provided insight into the influence of the electrode material and the structure of extractor molecules on the composite properties. The highest capacitance of 5.86 F cm^{-2} for negative electrodes and low impedance were achieved using α-FeOOH-MWCNT composites and a 16-phosphonohexadecanoic acid (PHDA) extractor. This extractor allows adsorption on particles, not only at the liquid-liquid interface, but also in the bulk aqueous phase and can potentially be used as a capping agent for particle synthesis and as an extractor in the PELLI method.

1. Introduction

The development of efficient electrode materials that work in a negative potential range is a serious challenge for the fabrication of asymmetric aqueous supercapacitors (SC). The capacitances of negative electrodes are typically lower than those of positive electrodes at similar active mass loadings. Therefore, the important task is to match the capacitive performance of cathodes and anodes and enhance device performance over an enlarged voltage window.

There is substantial interest in investigating FeOOH and composite materials for negative electrodes. Recent studies have focused on crystalline α-FeOOH [1–3], β-FeOOH [4–6] and γ-FeOOH [7,8] phases, as well as amorphous FeOOH [9,10] materials. The capacitive behavior of individual electrodes and cells has been studied in different electrolytes, such as KOH [1,9,11], NaOH [9,12], LiOH [13], Li_2SO_4 [14], Na_2SO_4 [2], Na_2SO_3 [9] and others [15,16]. Investigations have emphasized advantages [2] of a mild Na_2SO_4 electrolyte for the fabrication of individual electrodes and asymmetric devices. Particular attention was focused on the synthesis and application of particles with nanorod shapes [1,4,17], which allow improved capacitive performance. Various conductive additives, such as carbon black [1,18], polypyrrole [19], carbon nanotubes [20] and graphene [15,20–22] have facilitated the fabrication of electrodes with high capacitance and reduced impedance. Improved capacitive performance can also be achieved using doped FeOOH [17].

It is important to note that FeOOH electrodes were tested in positive [11,23–25] and negative voltage windows [26]. The highest capacitances in negative voltage windows were achieved using KOH and Na_2SO_4 electrolytes. A capacitance of 463.18 F g^{-1} was reported [1] in a KOH electrolyte with a relatively narrow voltage window from − 0.6 to − 1.0 V versus a saturated calomel electrode (SCE). The charge-discharge characteristics in the KOH electrolyte deviated significantly from ideal capacitive behavior [1,6]. Improved capacitive behavior was also observed for FeOOH-graphene composites [22]. A capacitance of 160 F g^{-1} was reported for FeOOH electrodes in Na_2SO_4 electrolyte [2]. These investigations of electrodes with low active mass loadings

---

[*] Corresponding author.
E-mail address: zhitom@mcmaster.ca (I. Zhitomirsky).

https://doi.org/10.1016/j.ceramint.2018.07.002
Received 10 June 2018; Received in revised form 29 June 2018; Accepted 1 July 2018
0272-8842/

Please cite this article as: Chen, R., Ceramics International (2018), https://doi.org/10.1016/j.ceramint.2018.07.002

indicated that FeOOH is a promising material for negative electrodes.

An important challenge is to achieve good performance of electrodes with high active mass loadings [27]. The mass normalized capacitance (C_m) of various electrode materials [27] decreased drastically with increasing active mass due to poor electrolyte access to the active material and low electronic conductivity of the electrodes. The critical requirement for practical applications [27] is good active material performance at mass loadings above 10–20 mg cm^{-2}. An important characteristic of electrodes with high active mass loadings is the areal capacitance (C_S). The increase in active material loading [28] allowed the fabrication of negative FeOOH electrodes with $C_S = 6.5$ F cm^{-2} in KOH electrolyte. The highest C_S of 3.3 F cm^{-2} in a Na_2SO_4 electrolyte in the negative potential range was obtained using Ti doped FOOH composites containing quantum dots and bacterial cellulose [21].

Despite the impressive progress in the development of FeOOH and its composite materials, further advances in synthesis and electrode fabrication can result in better utilization of FeOOH properties in the SC devices. The use of water insoluble binders facilitates the fabrication of electrodes for stable operation in aqueous electrolytes. During a typical electrode fabrication procedure, the binder must be well dissolved in an organic solvent in order to facilitate mixing with FeOOH and to minimize the binder content in the electrode. FeOOH particles, synthesized in an aqueous phase are usually dried and then re-dispersed in an organic solvent, containing a water insoluble binder. However, particle drying results in the formation of hard agglomerates, which is driven by the reduction of total particle surface energy and surface condensation reactions. Particle agglomeration is detrimental for their mixing with conductive additives and for electrolyte access to the particle surface.

The goal of this investigation was the fabrication of efficient FeOOH-multiwalled carbon nanotube (MWCNT) negative electrodes with high active mass loadings for application in advanced asymmetric SC devices. Agglomerate-free processing of FeOOH particles was achieved by particle extraction through the liquid-liquid interface (PELLI) technique. In this approach, the FeOOH particles synthesized in an aqueous phase were directly transferred to an organic solvent. Therefore, the drying procedure and related agglomeration were avoided. We developed and tested efficient extractors for FeOOH, which contained phosphonic or/and carboxylic anchoring groups. Two extraction methods have been developed, which involve particle modification at the liquid-liquid interface or in an aqueous phase. We compared the electrochemical performance of α-FeOOH-MWCNT and β-FeOOH-MWCNT electrodes at high active mass loading. The test results presented below indicated that C_S as high as 5.86 F cm^{-2} can be achieved at a low impedance in a wide negative voltage window using α-FeOOH-MWCNT electrodes and Na_2SO_4 electrolyte. The capacitance of α-FeOOH-MWCNT negative electrodes matched the capacitance of advanced MnO_2-MWCNT positive electrodes at the same active mass loading of 37 mg cm^{-2}. As a result, the asymmetric SC device showed improved capacitive performance.

2. Experimental procedures

$FeCl_3{\cdot}6H_2O$, NaOH, Na_2SO_4, 16-phosphonohexadecanoic acid (PHDA), hexadecylphosphonic acid (HDPA), palmitic acid (PA), poly (vinyl butyral-*co*-vinyl alcohol-*co*-vinyl acetate) (PVB, M_w = 50,000–80,000), 1-butanol (Aldrich), MWCNT (4 nm ID, 13 nm OD, 1–2 µm length, Bayer, Germany), and Ni foams (95% porosity, Vale Canada) were used.

Chemical precipitation of FeOOH was performed from aqueous $FeCl_3$ solutions, which were adjusted to pH = 7 using NaOH. The synthesis of α-FeOOH was performed at room temperature, whereas reaction at 70 °C resulted in the formation of β-FeOOH. In the PELLI-1 method, the solutions of PHDA, HDPA and PA in 1-butanol were added to the aqueous phases containing precipitated particles. The stirring of the mixtures resulted in particle transfer to the 1-butanol phase. In the PELLI-2 method, a solution of PHDA in NaOH was added to the $FeCl_3$ solution. The precipitation was performed at pH = 7. The addition of 1-butanol resulted in the FeOOH extraction to the 1-butanol phase. The mass ratio of FeOOH: extractor was 3:1 in both methods.

To fabricate supercapacitor electrodes, suspensions of the extracted FeOOH in 1-butanol were separated from the aqueous phase and then MWCNT were added. After ultrasonication of the mixed suspensions, a solution of PVB binder in ethanol was added. The mass ratio of FeOOH:MWCNT:PVB was 80:20:3. The suspensions thus obtained were used to fabricate FeOOH-MWCNT supercapacitor electrodes by impregnating the Ni foam current collectors. The active mass loading of the electrodes was 37 mg cm^{-2}. The MnO_2-MWCNT electrodes of similar mass were prepared using PELLI by the method described by us previously [29].

Electron microscopy investigations were performed using a JEOL JSM-7000F scanning electron microscope (SEM). X-ray diffraction (XRD) studies were performed using a powder diffractometer (Nicolet I2, monochromatized CuK_α radiation). FTIR studies were performed on Bruker Vertex 70 spectrometer. Thermogravimetric analysis (TGA) was performed using a NETZSCH STA-409 thermoanalyser in air at a heating rate of 5 °C min^{-1}.

Cyclic voltammetry and impedance spectroscopy investigations were performed using a potentiostat (PARSTAT 2273, Princeton Applied Research, USA). The capacitive behavior of the electrodes was studied in three-electrode cells using 0.5 M Na_2SO_4 aqueous solution. The area of the working electrode was 1 cm^2. The counter electrode was a platinum gauze and the reference electrode was a standard calomel electrode (SCE). Cyclic voltammetry (CV) studies were performed at scan rates of 2–100 mV s^{-1}. FeOOH–MWCNT negative electrodes were combined with MnO_2-MWCNT positive electrodes for the fabrication of asymmetric cells, which offer the advantage of an enlarged voltage window in aqueous solutions. The electrodes were separated by a porous polyethylene membrane with an average pore size of 0.4 µm.

The capacitances $C_S = Q/\Delta VS$ and $C_m = Q/\Delta Vm$ were calculated using half the integrated area of the CV curve to obtain the charge Q, and subsequently dividing the charge Q by the width of the potential window ΔV and electrode area S or active mass m of an electrode or device. The alternating current measurements of complex impedance $Z^* = Z' - iZ''$ were performed in the frequency range of 10 mHz to 100 kHz with a signal amplitude of 5 mV. The complex differential capacitance $C_S^* = C_S' - iC_S''$ was calculated from the impedance data as $C_S' = Z''/\omega|Z|^2S$ and $C_S'' = Z'/\omega|Z|^2S$, where $\omega = 2\pi f$ (f-frequency). The charge–discharge behavior of the cells was investigated using battery analyzers BST8-MA and BST8-3 (MTI corporation, USA) at current densities of 3–50 mA cm^{-2}.

3. Results and discussion

X-ray diffraction studies of the powders, precipitated at room temperature and at 70 °C, showed the X-ray diffraction peaks of α-FeOOH (Fig. 1a) and β-FeOOH (Fig. 1b), respectively. Thermogravimetric analysis revealed mass loss of 22% and 16% related to the dehydration of α-FeOOH and β-FeOOH, respectively (Fig. 2). The dehydration reaction resulted in the release of water and formation of Fe_2O_3. Both materials showed higher mass loss, compared to the theoretical mass loss of 10%. The additional mass loss resulted from the adsorbed water. The higher mass loss of α-FeOOH compared to that of β-FeOOH was attributed to larger amount of adsorbed water. The difference can be attributed to different structures and synthesis conditions of the α-FeOOH and β-FeOOH phases.

SEM studies (Fig. 3) of the dried powders showed significant agglomeration of α-FeOOH and β-FeOOH particles. The typical size of the agglomerates was about 2–6 µm. The formation of such agglomerates must be avoided in order to improve FeOOH mixing with MWCNT and facilitate electrolyte access to the FeOOH surface. Therefore, PELLI strategies have been developed to transfer the particles precipitated in an aqueous phase directly to an organic phase and avoid particle