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Short communication

Nanocrystalline $FeWO_4$ as a pseudocapacitive electrode material for high volumetric energy density supercapacitors operated in an aqueous electrolyte

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ABSTRACT

Iron tungstate ($FeWO_4$) has been synthesized using two low-temperature synthetic routes and investigated as a new pseudocapacitive electrode material for supercapacitors operating in a neutral aqueous electrolyte. Its electrochemical properties are clearly related to the specific surface area and seem to originate from Fe^{3+}/Fe^{2+} fast surface reactions. For $FeWO_4$ obtained by polyol-mediated synthesis, a high volumetric capacitance of 210 $F\cdot cm^{-3}$ (i.e. more than two times higher than that of activated carbon) was measured at 20 $mV\cdot s^{-1}$ with less than 5% fade over 10,000 cycles. Furthermore, unlike most of the previously investigated iron based electrodes, a unique pseudocapacitive behavior is observed, thus emphasizing the role of the crystallographic structure on the electrochemical signature.

1. Introduction

Further research on new supercapacitor electrode materials with improved storage properties (both specific and volumetric energy and power) is necessary to meet the requirements for high-performance energy storage devices while considering a reasonable manufacturing cost and low environmental impact [1–3]. Activated carbons used in today's commercial supercapacitors exhibit high specific capacitances up to 100 $F\cdot g^{-1}$, but their low density makes it difficult to reach the volumetric performance that is required for most of the terrestrial applications [2]. It is thus relevant to seek for capacitive high density oxides, which can potentially outclass industrial activated carbons in terms of volumetric properties, even when displaying a much lower specific capacity.

As such, iron tungstate $FeWO_4$, also called ferberite, exhibits a bulk density of about 7.5 $g\cdot cm^{-3}$ [4]. It crystallizes in the wolframite structure type, is built on alternating layers of distorted $[FeO_6]$ and $[WO_6]$ octahedra and is well known for its magnetic, photocatalytic and photoluminescence properties [5,6]. It has recently been considered as electrode material for lithium-ion batteries [7,8] but its electrochemical properties in supercapacitors have not yet been reported. In this study, $FeWO_4$ was synthesized as high specific area crystalline nanoparticles *via* two low-temperature methods (polyol-mediated and hydrothermal syntheses). Resulting powders were characterized and electrochemically tested as supercapacitor electrode materials in an aqueous neutral electrolyte. The material exhibited very promising pseudocapacitive properties that were assigned to Fe^{2+}/Fe^{3+} surface redox reactions and therefore, closely related to the developed specific area.

2. Experimental

2.1. Hydrothermal synthesis

Ferberite was hydrothermally synthesized according to Yu et al. [9]. In a typical procedure, 5 mmol of $Na_2WO_4\cdot 2H_2O$ (99% purity) and 5 mmol of $(NH_4)_2Fe(SO_4)_2\cdot 6H_2O$ (99% purity) were dissolved under magnetic stirring in 15 mL distilled water in two different beakers. Then the aqueous solution of $(NH_4)_2Fe(SO_4)_2$ was slowly added to the sodium tungstate solution, instantly forming a suspension of amorphous nanoparticles. The pH was adjusted to 6 by adding diluted nitric acid to get the smallest possible particles [10]. The mixture was maintained at 180 °C for 12 h in a Teflon-lined stainless steel autoclave before being allowed to naturally cool down to room temperature. The resulting product was centrifugated (10 min, 10 000 rpm) and washed several times with distilled water and ethanol before being dried under primary vacuum at 35 °C.

2.2. Polyol-mediated route

To prepare iron tungstate *via* polyol-mediated route (P-$FeWO_4$) [11], 25 mL of diethylene glycol was heated at 70–80 °C and adjusted

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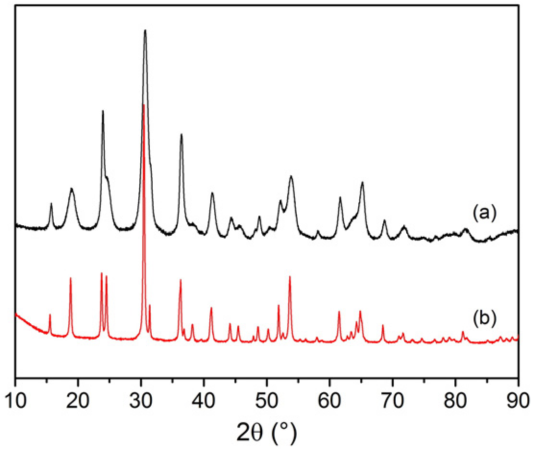

Fig. 1. XRD patterns of $FeWO_4$ obtained *via* (a) polyol-mediated synthesis and (b) hydrothermal synthesis. Patterns were collected at room-temperature using Cu-Kα radiation.

at pH 5 by adding hydrochloric acid. 5 mmol of iron (II) acetate was dissolved in the resulting acidic solution under vigorous stirring before adding an aqueous equimolar solution of sodium tungstate dihydrate (2.5 mL). The mixture was heated up to 220 °C within 15 min and kept at this temperature for 1 h. After being naturally cooled down to room temperature, the resulting nanoparticles were centrifugated (15 min, 10 000 rpm) and resuspended in ethanol and glacial acetic acid thrice to eliminate the remaining salts and other side products. An additional rinsing with distilled water was necessary to remove the last traces of sodium tungstate. The resulting powder was dried under primary vacuum at 35 °C for 5 h. $ZnWO_4$ (iso-structural to $FeWO_4$ and also known as sanmartinite) was synthesized *via* the polyol-method as for P-$FeWO_4$, using zinc acetate as precursor.

2.3. Electrode elaboration

For ferberite obtained by both polyol (P-$FeWO_4$) and hydrothermal (H-$FeWO_4$) syntheses, the electrode preparation was that described by Brousse et al. [12]. $FeWO_4$, carbon black (superior graphite, >99%) and polytetrafluoroethylene (weight ratios: 60/30/10) were respectively used as active material, conductive additive and binder to prepare composite thick films. Carbon black was used to compensate for the moderate electronic conductivity of iron tungstate.

Disk-shaped electrodes (12 mm diameter) were cut out from the film and then pressed at 900 MPa onto stainless steel grids used as current collectors. The mass loading of the electrodes ranged from 5 to 10 $mg \cdot cm^{-2}$ which is a standard loading for evaluating the properties of an electrode for supercapacitors [13].

2.4. Characterizations of the materials and electrodes

The structure, morphology and chemical composition of the prepared nanoparticles were characterized by X-ray diffraction (XRD, PANalytical X'Pert Pro with an X'Celerator detector and Cu Kα radiation), transmission electron microscopy (TEM, Hitachi H9000-NAR) and energy-dispersive X-ray analysis (EDX, Oxford Instrument). Brunauer–Emmett–Teller (BET) surface area measurements were performed with a Quantachrome Nova 4200e operated with nitrogen gas.

Electrochemical performance were measured by cyclic voltammetry (CV) with a VMP3 galvanostat–potentiostat from Biologic run under EC-Lab software. In this study, the experiments were conducted in a 3 electrode cell assembly, using Ag/AgCl (3 M NaCl) as the reference electrode and a platinum grid as the counter electrode. $FeWO_4$ composite electrodes were tested between −0.6 and 0 V vs. Ag/AgCl in 5 M $LiNO_3$ at room temperature. Capacities of the electrodes were calculated by integrating the reductive part of the CVs. The voltammetric charge related

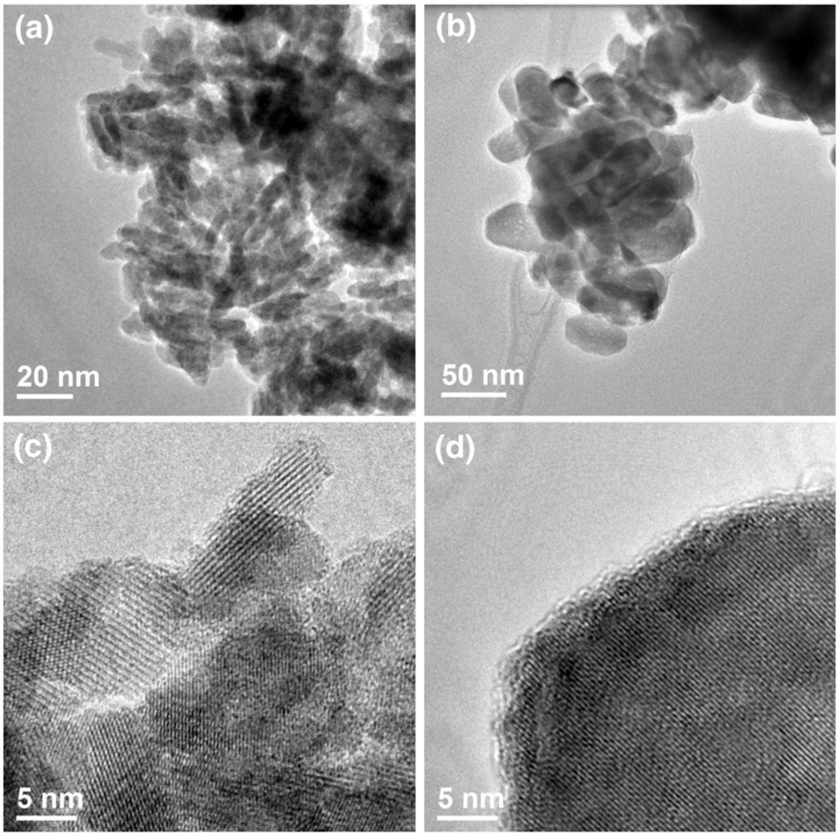

Fig. 2. TEM images of P-$FeWO_4$ (a, b) and H-$FeWO_4$ (c,d).