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Ultrasonics Sonochemistry

High-intensity ultrasonication as a way to prepare graphene/amorphous iron oxyhydroxide hybrid electrode with high capacity in lithium battery

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ABSTRACT

The preparation of graphene/iron oxyhydroxide hybrid electrode material with very homogeneous distribution and close contact of graphene and amorphous iron oxyhydroxide nanoparticles has been achieved by using high-intensity ultrasonication. Due to the negative charge of the graphene surface, iron ions are attracted toward the surface of dispersed graphene, according to the zeta potential measurements. The anchoring of the FeO(OH) particles to the graphene layers has been revealed by using mainly TEM, XPS and EPR. TEM observations show that the size of the iron oxide particles is about 4 nm. The ultrasonication treatment is the key parameter to achieve small particle size in these graphene/iron oxyhydroxide hybrid materials. The electrochemical behavior of composite graphene/amorphous iron oxyhydroxide prepared by using high-intensity ultrasonication is outstanding in terms of gravimetric capacity and cycling stability, particularly when metallic foam is used as both the substrate and current collector. The XRD-amorphous character of iron oxyhydroxide in the hybrid electrode material and the small particle size contribute to achieve the improved electrochemical performance.

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1. Introduction

Modern society claims for the development of batteries with more power and energy density, longer life, and lower cost and environmental impact. A strategy to achieve these goals is to replace the negative electrode based on graphite by alternative materials.

Microstructured composites of graphite/metal oxide have extensively studied for the negative electrode of lithium ion batteries [1]. Nanostructured composites of graphene/metal oxide [2–4] and other forms of carbon/metal oxide composites [5–7] are also being explored. The hybrid character (carbonaceous material/non-carbonaceous material) of these composite electrode materials can enhance the resulting electrochemical properties. Thus, for example, the graphene phase can act like a carbonaceous network that provides an electronic conduction pathway, prevents the agglomeration of the metal oxide particles and buffers the volume changes. In addition, graphene can exhibit higher gravimetric capacity than graphite to store lithium. In addition, taking into account the low

toxicity and large abundance of iron, one of the most interesting graphene/metal oxide composites is graphene/iron oxide [8–13]. In all papers cited above, the iron oxide phase was microcrystalline or nanocrystalline to X-ray diffraction (XRD). However, the use of iron oxide particles with very small size and amorphous character may improve the electrochemical behavior in comparison with larger and crystalline particles. Thus, the use of infrared irradiation to obtain graphene/amorphous FeO(OH) was recently reported [14].

On the other hand, previous works found that sonochemistry is a very promising method to prepare electrode materials for batteries [15,16], particularly when high dispersion, small size and amorphous character of the particles are advantageous.

Having all this in mind, we decided to explore the use the sonochemical method to prepare graphene/iron oxide electrode materials. In this paper we report a new and easy way to obtain graphene/amorphous iron oxyhydroxide hybrid nanostructure in which the iron phase is XRD-amorphous. In order to prepare this material we report the use of high intensity ultrasonication for first time. The structure and electrochemical properties of hybrid materials are examined by means of powder XRD diffraction, scanning electron microscopy (SEM) and transmission electron microscopy (TEM), particle size distribution, [57]Fe Mössbauer spectroscopy,

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electron paramagnetic resonance (EPR), thermogravimetric analysis (TGA), galvanostatic measurements and impedance spectroscopy. Here we reveal the interactions between the graphene layers and the iron oxyhydroxide nanoparticles using EPR for the first time. These interactions are correlated with very high electrode capacities.

2. Experimental

2.1. Preparation of graphene and graphene/iron oxyhydroxide

Reduced graphene oxide (RGO) was prepared as follows. Firstly, graphene oxide was obtained from graphite and using the Brodie method [17]. Secondly, graphene oxide was exfoliated and reduced at 700 °C under nitrogen atmosphere.

Composite material containing reduced graphene oxide and iron oxyhydroxide (RGO/Fe) was prepared using the ultrasonication method. For this purpose, 2.5 g of $Fe(NO_3)_3 \cdot 9H_2O$ and 33.3 mg of RGO were dispersed in 250 ml of ethanol and ultrasonicated for 1 h under high intensity radiation using a Sonics VCX750 sonicator with Ti-horn. The ultrasound irradiation formed a homogeneous suspension and promoted the anchoring of ultrafine FeO(OH) particles to graphene layers. It is known that ultrasound irradiation can exfoliate stacked graphene layers and favors formation of stable colloidal dispersions under mild conditions [18]. The amount of iron added to the RGO suspension in ethanol (10,370% wt. as referred to the RGO mass) is in large excess as referred to the amount of iron that is effectively incorporated in the resulting RGO/iron oxide composite. In fact, only a small fraction of the added iron ions are trapped by RGO, as discussed below. For comparative purposes, an RGO/Fe composite was prepared by adding a smaller amount of iron (8% wt.) to the dispersion. The samples prepared with smaller and larger iron amount will be henceforth referred to as RGO/Fe1 and RGO/Fe2, respectively. The resultant suspensions were collected by centrifugation, washed with ethanol, recentrifugated, and dried under vacuum at 120 °C overnight. Also for comparative purposes, a sample was prepared following the same method although ultrasonication was not applied.

In addition, graphene-free iron oxyhydroxide was also prepared by following a similar method except for the absence of graphene. For this sample, heating at 80 °C for 2 h was used to partially evaporate the solvent and to precipitate the solid, due to the fact that in absence of external heating precipitation was not observed. After formation of the precipitate, it was separated by ultracentrifugation, washed with ethanol, re-ultracentrifugated, and finally dried under vacuum at 120 °C overnight.

In order to evaluate the interactions between dispersed graphene particles and iron ions, zeta potential was measured using a ZPALS Brookhaven instrument and the Smoluchovski equation was used. The same instrument was used to obtain particle size distribution by the dynamic light scattering method.

2.2. Materials characterization

X-ray diffraction (XRD) experiments were performed in a Siemens D5000 instrument with CuK_α radiation. Mössbauer spectra were recorded at room temperature using a Wissel instrument and calibration was performed by using a foil of α-Fe.

The EPR spectra were recorded as the first derivative of the absorption signal on an ERS-220/Q spectrometer within the temperature range of 90–400 K. The g factors relative to a Mn^{2+}/ZnS standard were determined. The signal intensity was established by double integration of the experimental EPR spectrum. To facilitate the analysis of the EPR spectra of the hybrid materials, EPR standards for bulk FeOOH and α-Fe_2O_3 was used.

Thermogravimetric analysis (TGA) experiments were performed in an air atmosphere, at 5 °C/min of heating rate, using a Shimadzu instrument and alumina pans.

For scanning electron microscopy (SEM) a JSM6300 instrument with electron probe microanalyzer (EPMA) based on an energy dispersive spectrometer (EDS) was used. Transmission Electron Microscopy (TEM) micrographs were alternatively obtained by using a JEM2010 equipped with EPMA, or a JEOL1400 instrument.

2.3. Electrochemical characterization

The active material of the working (positive) electrode was RGO/Fe (80% wt.) mixed with binder (PVDF, 10% wt.) and carbon black (10% wt.). The mixture was deposited on a Cu foil current collector supplied by Goodfellow. Alternatively, nickel (or copper) foam was used instead of copper foil. The electrodes were dried under vacuum at 120 °C prior to the electrochemical tests, which were carried out in cells mounted in an Ar-filled glove box. The counter electrode was a lithium disk. The electrolyte was 1 M $LiPF_6$ in EC:DEC (1:1) solvents mixture. Galvanostatic cycling experiments and impedance spectra were obtained with a VMP (Biologic) instrument.

3. Results and discussion

3.1. Materials characterization

The zeta-potential of RGO particles dispersed in ethanol by ultrasonication was ca. −20 mV (Fig. 1). After adding 8–14% wt. iron ions (from $Fe(NO_3)_3 \cdot 9H_2O$) to the RGO dispersion, the zeta potential was shifted to values in the 10–15 mV range. These results evidence that the negatively charged surface of the RGO nanoparticles attracts the iron(III) ions and then these ions are anchored to the surface of RGO. Thus, this procedure allows an intimate mixture between graphene layers and iron ions. The high-intensity ultrasound irradiation contributes to enhance the dispersion and mixture homogeneity of RGO particles and iron ions.

The presence of crystalline phases and sample composition were studied by using XRD (Fig. 2) and TGA (Fig. 3). Fig. 2A shows the XRD patterns for pristine RGO, RGO/Fe2 (prepared with and without ultrasonication) and RGO/Fe2 recuperated after the TGA experiment (annealing in air atmosphere up to 600 °C). The XRD pattern of RGO (Fig. 2Aa) exhibits a broadened peak centered at ca. 25°/2θ that is assigned to the (0 0 2) Bragg reflection of graphitic
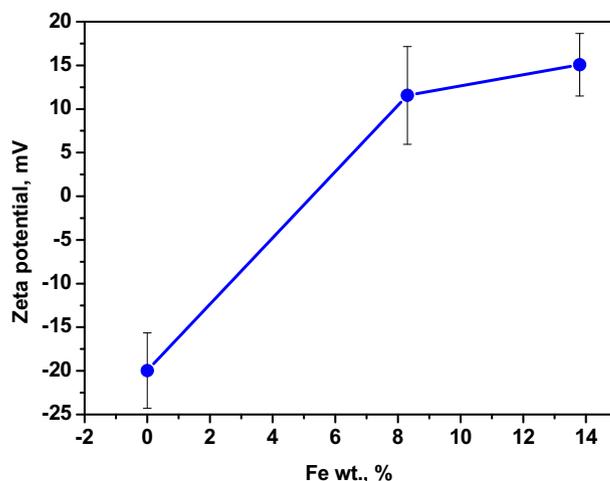
Fig. 1. Zeta potential as a function of relative amount of iron (percentage of iron mass/RGO mass).