



Improved performance of electrodes based on carbonized olive stones/S composites by impregnating with mesoporous TiO₂ for advanced Li–S batteries



Noelia Moreno ^a, Álvaro Caballero ^a, Julián Morales ^{a,*}, Enrique Rodríguez-Castellón ^b

^a Dpto. Química Inorgánica, Instituto Universitario de Investigación en Química Fina y Nanoquímica Campus de Rabanales, Universidad de Córdoba, Spain

^b Dpto. Química Inorgánica, Facultad de Ciencias, Campus de Teatinos, Universidad de Málaga, Spain

HIGHLIGHTS

- Activated carbon from olive stones with mesoporous TiO₂–S as cathode is reported.
- Comparing same cell without TiO₂ a performance improvement of 60% is obtained.
- Higher specific capacity values were delivered at current densities 1 C, 2 C and 4 C.
- Post-mortem characterizations confirm TiO₂ sorbent properties vs Li polysulfides.

ARTICLE INFO

Article history:

Received 13 October 2015

Received in revised form

16 February 2016

Accepted 19 February 2016

Available online 1 March 2016

Keywords:

Olive stone

Activated carbons

Titanium dioxide

Lithium/sulphur batteries

ABSTRACT

Carbons obtained from biomass have attracted a lot of attention for use as electrodes for Li-ion batteries. Less attention has been paid to their use in Li–S batteries in spite of the higher energy densities. Here, we optimized the electrochemical properties of an activated carbon (OSAC) obtained from olive stones with the help of mesoporous TiO₂. The OSAC@TiO₂/S hybrid composite exhibited improved electrochemical performance compared with the OSAC/S composite. The presence of TiO₂ increased the delivered capacity of the cell by more than 60%, and the rate capability was notably improved. The cell could operate at current densities of 3350 mA g⁻¹ (2 C), releasing an average capacity of 500 mAh g⁻¹ with a coulombic efficiency close to 100%. This improvement in the electrochemical performance is attributed to the sorbent properties of TiO₂ towards Li polysulfides and its facility to insert Li, which enhances the electronic and ionic conductivity of the hybrid composite.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

New emerging technologies, such as hybrid electric vehicles (HEVs), electric vehicles (EVs) and smart grids, require the development of alternative power sources that are able to efficiently store and deliver energy beyond the capacity of lithium ion batteries. Lithium-sulphur batteries could satisfy the future demand by offering a higher energy density and lower cost [1]. Sulphur is considered the most promising cathode candidate due its high theoretical specific capacity, i.e. 1675 mAh g⁻¹, and gravimetric and volumetric energy density of about 2600 Wh kg⁻¹ and 2800 Wh L⁻¹, respectively, versus lithium anodes. Moreover, this

element is abundant and environmentally benign [2,3].

However, these promising characteristics are not sufficient for commercial development since lithium-sulphur batteries have inherent problems, such as the insulator nature of sulphur, the low active material utilization, volume changes upon conversion into Li₂S and self-discharge, which restrict their practical applications [4–6]. One of the main problems is the solubility of polysulfides generated in the cathode that could react with the lithium anode, producing the “shuttle effect”, which is detrimental to the cycling stability of the cell [7–9]. The use of carbons with different textures and morphologies, such as mesoporous [10–17] and microporous [18–24] carbons, graphenes [25,26] and carbon fibres [27,28], among others, has been proposed to alleviate this effect based on their ability to physically trap the polysulfide ions in the cavities and to simultaneously increase the electrode electronic conductivity. The use of electrolyte additives, such as P₂S₅ [29], LiNO₃ [30]

* Corresponding author.

E-mail address: iq1mopaj@uco.es (J. Morales).

and Li_2S_8 [31,32], can also help to diminish the polysulfide shuttle effect, and at the same time can passivate the lithium metal surface.

Another strategy is the use of metal oxides as polysulfide species adsorbents, such as Al_2O_3 [33] La_2O_3 [34] and SiO_2 [35], among others. Special attention has been focused on TiO_2 owing to its high sorption (absorption and adsorption) ability towards sulphur and polysulfides [36–44]. The pioneering work of Evers et al. [40] demonstrated the suitability of this oxide as an additive of sulphur-carbon composites to improve the long-term cycling performance of Li–S cells. Later, different reports demonstrated that TiO_2 itself mixed with S yielded a good electrochemical performance, and were the first examples of sulphur cathodes using carbon-free hosts [40–44].

Here, we report a hybrid structure formed by S impregnated with TiO_2 nanoparticles and a microporous carbon obtained from agricultural residues, specifically olive stone activated carbon (OSAC), as a positive electrode for Li–S batteries. Carbons obtained from biomasses are an attractive option to be used as electrodes in Li batteries for several reasons [45], namely (i) an alternative method of waste management; (ii) low cost of raw materials; and (iii) good electrochemical performance compared with Li metal. In fact, this OSAC has been used as an electrode in full Li-ion [46] and Li–S [24] batteries with promising prospects. The presence of TiO_2 enhances the electrochemical performance of the electrode owing to its capacity to trap polysulfides, thus limiting polysulfide dissolution in the electrolyte.

2. Experimental section

2.1. Synthesis of olive stone activated carbon@ TiO_2 (OSAC@ TiO_2) and sulphur composites

The olive stone activated carbon was obtained at the bioenergy plant of S.C.O. El Tejar, Córdoba (Spain) and was used as received; details of its synthesis are described elsewhere [24]. The OSAC@ TiO_2 composite was prepared as follows. First, OSAC (0.5 g) was added to ethanol (400 mL) and tetra-isopropyl orthotitanate (4.35 mL, Sigma Aldrich), and the mixture was ultrasonicated for 2 h. Then, 10 mL of distilled water was added dropwise into the above solution with continuous stirring for 2 h and subjected to ultrasonication again for 1 h to obtain a homogeneous black dispersion. Finally, the product was filtered and washed with deionized water followed with ethanol. The solid was dried at 100 °C for 12 h and then heated to 500 °C for 5 h with a heating rate of 5 °C min^{-1} in a tubular furnace under a nitrogen atmosphere.

To synthesize OSAC@ TiO_2 –S and OSAC–S composites, sulphur was *in situ* deposited from an aqueous solution. Firstly, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (3.90 g, Sigma Aldrich) was dissolved in distilled water (200 mL) containing 1% Triton X-100 (6 mL, Sigma Aldrich). The solution was heated to 70 °C in an oil bath. OSAC@ TiO_2 /water suspension (500 mg/300 mL) that had been sonicated for 1 h was added with magnetic stirring. Then, HCl (12 M, 20 mL) was slowly added. The system was kept for 15 min under vigorous magnetic stirring, cooled down to room temperature and stirred for 24 h. Finally, the product was filtered and washed several times with water, ethanol and acetone. The solid obtained was dried at 80 °C overnight. The same procedure was followed for the preparation of OSAC–S composite. The sulphur content in both composites was 47% w/w, which was determined by thermo-gravimetric analysis.

2.2. Materials characterization

The structural properties of carbon, carbon hybrid and composites were examined by X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman spectroscopy and X-ray

photoelectron spectroscopy (XPS). The XRD patterns were recorded with a Siemens D5000 X-ray diffractometer. Particle size distribution was obtained by laser diffraction with a Mastersizer 3000 (Malvern). The SEM images were obtained with a Helios Nanolab 650 electron microscope, and the Raman analysis was performed on a WITTEC UHTS 300 spectrometer using 532-nm laser irradiation. XPS spectra were obtained on a Physical Electronics PHI 5700 spectrometer using non-monochromatic Mg K α radiation (300 W, 15 kV, 1253.6 eV) and a multi-channel detector. Spectra for the samples were recorded in the constant pass energy mode at 29.35 eV, using a 720- μm diameter analysis area. Binding energy (BE) values were referred to the C 1s peak at 284.8 eV. The CA PHI ACCESS ESCA-V6.0F software package was used for data acquisition and processing. A Shirley-type background was subtracted from all signals. Recorded spectra were always fitted using Gauss-Lorentz curves to more accurately determine the binding energy of the different element core levels. The error in the BE was estimated to be ca. ± 0.1 eV. The cycled electrodes were dried inside the glove box under vacuum, collected in an Eppendorf vessel and sealed for transfer to the XPS instrument.

The sulphur content was determined by thermo-gravimetric analysis using a Mettler Toledo-TGA/DSC at a heating rate of 5 °C min^{-1} from 25 °C to 600 °C under a nitrogen atmosphere and the TiO_2 content in the hybrid composite at the same heating rate from 25 °C to 800 °C under oxygen atmosphere. The textural properties were measured with a Micromeritics ASAP 2020 and using nitrogen as adsorbent.

2.3. Electrode preparation and electrochemical tests

Electrochemical experiments were performed on a CR2032 coin cell assembled inside an Ar-filled glove box (M-Braun 150 model) under 1 ppm water and oxygen conditions, using Li metal foil as a counter and reference electrode. To prepare the electrode, the composites were mixed with Super P carbon black and polyvinylidene fluoride (PVDF) binder in a mass ratio of 80:10:10 in N-methylpyrrolidone (NMP) solution. The slurry was coated onto an aluminium foil current collector using the doctor blade technique and dried for 12 h at 50 °C. Here, 13-mm disks with a 2-mg loading of sulphur were cut and dried in a vacuum oven at 50 °C for 1 h before assembling the cell. The electrolyte was LiTFSI (1 M, Sigma Aldrich) and LiNO_3 (0.4 M, Sigma Aldrich) in 1:1 v/v 1,3-dioxolane (DOL, Sigma Aldrich) and 1,2-dimethoxyethane (DME, Sigma Aldrich) soaked in a Celgard polyethylene membrane as a separator. The cyclic voltammograms (CV) were recorded with an Arbin BT2143 at 0.1 mV s^{-1} between 3.5 V and 1 V. The cycling tests were performed in the potential window 1.8–2.8 V using the same potentiostat-galvanostat.

3. Results and discussion

3.1. Structural and textural properties of carbon and composites

The XRD pattern of OSAC, OSAC@ TiO_2 , OSAC–S and OSAC@ TiO_2 –S are shown in Fig. 1a. The OSAC sample exhibited two peaks at 24.5° and 43.4° 2 θ , which were assigned to (002) and (100) crystallographic planes of graphite, respectively. The high broad peaks and their low intensity were typical of a highly disordered carbon. The OSAC@ TiO_2 hybrid showed broad and low-intensity peaks, which were indicative of the anatase structure (JCPDS, n° 21–1272), and were further confirmed by the Raman spectrum. The pattern suggests a small crystallite size, which is consistent with the result from the SEM images and the textural properties obtained. Well-defined peaks of orthorhombic sulphur were observed in both composites, and the anatase structure was also identified in

Download English Version:

<https://daneshyari.com/en/article/1286243>

Download Persian Version:

<https://daneshyari.com/article/1286243>

[Daneshyari.com](https://daneshyari.com)