Synthesis of flexible electrodes based on electrospun carbon nanofibers with Mn_3O_4 nanoparticles for vanadium redox flow battery application

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HIGHLIGHTS

- Mn_3O_4/CNF electrode is investigated for vanadium redox flow battery application.
- The high reversibility is ascribed to the several type of redox couples on the spinel structure.
- Cell electrochemical parameters confirm the high reversibility for Mn_3O_4/CNF electrodes.

ARTICLE INFO

ABSTRACT

Flexible carbon nanofiber (CNF)-based electrodes and CNF with a 20% of manganese oxide incorporated (Mn_3O_4/CNF) are prepared by using the electrospinning method for vanadium redox flow battery (VRFB) application. A blend consisting of manganese acetate ($Mn(OAc)_2$) and polyacrilonitrile (PAN) is electrospun and successively subjected to different thermal treatments in which the growth of Mn_3O_4 particles and CNFs occurred together guaranteeing an appropriate electron conductivity for electrodes thus synthesized. Cyclic voltammetry (CV) measurements show an interesting electrocatalytic activity toward the $[VO]^{2+}/[VO_2]^+$ as well as the V^{2+}/V^{3+} redox reactions for the Mn_3O_4/CNF electrospun sample. Charge-discharge tests, carried out at 80 mA cm^{-2}, show a state of charge (SOC) and a depth of discharge (DoD) of 81% and 73%, respectively, for the cells assembled with Mn_3O_4/CNF electrodes. These data are indicative of a high vanadium active species utilization thanks to the better electrocatalytic activity at high current densities. Furthermore, the cell with Mn_3O_4/CNF shows EE values of about 81% (88% of VE and 92% of CE) vs. 70% (75% of VE and 93% of CE) with respect to a commercial carbon felt (CF) electrode used for comparison. These results are attributable to the higher oxygen species content as well as the improved electron conductivity due to the synergetic effect of the more graphitic carbon and to the structural defects within the Mn_3O_4 spinel structure.

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1. Introduction

Redox flow batteries (RFBs) represent one of the most promising electrochemical storage technology for large-scale energy applications [1–6] thanks to their scalability, high energy efficiency, long cycle life and the possibility to decouple storage capacity and power [7–10]. While the power rating is correlated to the electrode size and stack cell numbers, the energy storage (or capacity) is correlated to the volume and concentration of the electrolyte. The main issue of RFBs is the cross-over contamination between the electrolytes of the anodic and cathodic compartments. Unlike other redox couples, vanadium redox flow battery (VRFB) employs the same electrolytes in different oxidation states in the

anode and cathode compartments, limiting the cross-over contamination phenomenon. Despite this, the poor electrocatalytic activity of the common utilized carbon-based electrode is a limit for the improvement of the battery energy performance. The increase of kinetic performance parameters allows to improve the current density value during charge/discharge curves and, consequently, to reduce costs in terms of stack materials and components, strictly related to the power density value [9]. In order to enhance the reversibility at the electrode-electrolyte interface, several studies are addressed toward the investigation of modified carbon-based electrodes by chemical or thermal treatments [11–24]. Moreover, thanks to the high stability in acidic environment as well as the good conductivity, great interest is addressed to the introduction of noble metal oxides within the graphite fibers [21–26]. However, due to their high cost and poor mechanical stability, non-precious metal oxides are investigated as valid alternative to improve

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battery electrochemical parameters within a VRFB. Recently, Wu et al. reported interesting results by using PbO_2-modified graphite felt as electrode prepared by pulse electro-deposition method [27], while Li et al. showed the enhancement of the Nb_2O_5-based nanorods electrocatalytic activity prepared by the hydrothermal method [28]. A study on the electrocatalytic activity of modified carbon felt with Mn_3O_4 [29] showed suitable properties for VRFB application. Because of the poor conductivity of the above mentioned non-precious metal oxides, carbon-based materials are usually used as supports for the catalysts deposition. Issues related to the metal oxides adhesion on the support could occur during flowing electrolyte within the cells. Wei et al. obtained promising electrochemical data by using electrospun Bi/CNF as asymmetric electrode towards V^{2+}/V^{3+} redox reaction to prepare embedded electrocatalysts in the carbon nanofibers [30]. Recently the electrospinning method is employed to prepare carbon based nanofibers, forming a freestanding conductive network that is used directly as the negative electrode in VRFBs [31]. In this work, our purpose is to synthesize mechanically flexible electrospun carbon nanofibers electrodes incorporating Mn_3O_4 nanoparticles (denoted as Mn_3O_4/CNF) able to be used both as valid electrocatalyst for anode and cathode redox reactions and directly as useful electrode, without a further carbon-based support (self-supported). In this way, a mechanically flexible electrode can be easily handled and assembled in cell without any damage during the compression phase. Moreover, a good electron conductivity is guaranteed by the carbon nanofibers formation that occur together with the non-noble metal oxide nanoparticles growing. The benefit of using manganese oxide is that it is a valid cost-effective material thanks to the considerable electrocatalytic behaviour as well as the easy availability. The electrospinning method is able to synthesize flexible electrodes characterized by metal oxide-filled CNF at high surface area with an appropriate thickness as well as good mechanical properties, suitable for VRFB. Therefore, a blend consisting of manganese acetate ($Mn(OAc)_2$) with polyacrilonitrile (PAN) (denoted as $Mn(OAc)_2$/PAN) is prepared to be used in the electrospinning process. Two consecutive thermal treatments, at 270 °C in air and at 900 °C in inert gas, are carried out to synthesize flexible electrospun carbon nanofiber electrodes in which manganese oxide nanoparticles are incorporated. In a similar way, pristine carbon nanofibers are prepared to compare the experimental data. Electrochemical performance is evaluated both in a three electrode half cell and in a 5 cm^2 single cell. In particular, the high energy efficiency value recorded at interesting current density demonstrates the promising Mn_3O_4/CNF utilization as a valid cost-effective electrode for a MEA scale-up for a VRFB battery configuration. To our best knowledge, no electrochemical investigations are addressed towards flexible electrospun Mn_3O_4/CNF electrodes for this specific application.

2. Materials and methods

2.1. Physico-chemical characterizations

Thermogravimetric analysis (TGA, 409C NETZSCH-Gerätebau GmbH Thermal Analyse) was carried out on the electrospun electrodes from room temperature up to 800 °C at a heating rate of 5 °C/min in air atmosphere in order to determine the amount of Mn_3O_4 in the composite carbon nanofibers. The specific surface area of the investigated electrospun samples was calculated by the Brunauer-Emmett-Teller (BET) equation and nitrogen adsorption-desorption isotherm, measured at −196 °C by using an ASAP 2020 M Micrometrics. The pore size distribution was determined by Barrett-Joyner-Halenda (BJH) method. A Philips XL 30 scanning electron microscope (SEM) was used to investigate

samples morphology surface. The crystalline structure was investigated by X-ray diffraction (XRD) using a Philips X-pert 3710 X-ray diffractometer and Cu Kα radiation, operating at 40 kV and 20 mA. The crystallite size was calculated by the Marquardt algorithm using the full width at half maximum (FWHM) value of the (2 1 1) at 2θ = 36.3° peak profiles of the Mn_3O_4 nanoparticles (Table 1).

2.2. Electrodes preparation

A 20% Mn_3O_4/CNF was in-house prepared by using the electrospinning technique. The precursor solution was prepared by dissolving a well defined amount of metal acetate and PAN in N, N-dimethylformamide (DMF). 0.2 g of $Mn(OAc)_2 \cdot 4H_2O$ (Carlo Erba Reagents, 99%) was mixed with a solution containing 0.8 g of PAN (Sigma Aldrich, M_w = 150,000) dissolved in 10 ml of DMF (Sigma Aldrich, 99,8%); these precursors amount allowed to obtain a clear solution with appropriate characteristics, suitable for the electrospinning technique. A higher amount of $Mn(OAc)_2 \cdot 4H_2O$ leads to colloidal mixtures creation therefore to beads formation and non-uniform electrospun systems. A constant magnetic stirring at room temperature for 24 h occurred. The obtained solution was loaded into a 20 mL glass syringe, equipped with a 21G stainless steel needle. A strong electric field (17 kV) was applied to the solution jet (a rate of 1.4 mL h^{-1}) in order to collect the fibers on a grounded graphitic target, placed at a distance of 12 cm from the needle tip. During the electrospinning operation, the temperature of 21 °C and the relative humidity <40% were maintained constant. As comparison, carbon nanofibers were prepared by using the same technique, at the same working conditions. Therefore, electrospun pristine CNF electrode was synthesized from a solution containing 10 wt.% PAN in DMF. The collected PAN and Mn(OAc)$_2$/PAN nanofibers were first stabilized in air at 270 °C for 30 min and then carbonized at 900 °C for 1 h in a helium (He) flow (80 mL/min^{-1}) with a heating rate of 5 °C min^{-1}. Two kind of flexible electrospun electrodes, pristine CNF and Mn_3O_4/CNF, were synthesized. After the thermal treatment, both samples were subjected to a reduction of the thickness passing from 650 μm to about 500 μm.

2.3. Electrochemical tests

2.3.1. Cyclic voltammetry and electrochemical impedance spectroscopy

A three electrode half-cell was utilized for electrochemical characterization of all samples. A solution of 0.2 mol l^{-1} VOSO$_4$ (97% wt. VOSO$_4 \cdot H_2O$ Sigma-Aldrich) in 4 mol l$^{-1} \cdot H_2SO_4$ was used for the purpose. Potential values were measured against a saturated calomel (Hg$_2$/Hg$_2$Cl$_2$) reference electrode whereas Pt was used as counter electrode. The active area was 1 cm^2 for all the samples. The reported potential values were normalized with respect to the standard hydrogen electrode (SHE). An AUTOLAB FRA equipped Galvanostat/Potentiostat (Metrohm) was used for the electrochemical tests. Ac-impedance spectra were carried out at potential values of practical interest for application in vanadium flow batteries e.g. 1.1 V and 1.25 V vs. SHE depending on the specific reversibility of the oxidation process recorded for each

Table 1
Full width at half maximum (FWHM) and interlayer distance (d-spacing) of the (0 0 2) carbon peak.

Samples	FWHM (°)	d-spacing (Å)
CNF	7.14	3.51
Mn_3O_4/CNF	1.23	3.37