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Electrochemical performance investigation of electrospun urchin-like V_2O_3-CNF composite nanostructure for vanadium redox flow battery

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ABSTRACT

Home-made electrospun catalyst based on urchin-like vanadium (III) oxide-carbon nanofiber (V_2O_3-CNF) composite is synthesized from a solution containing vanadium (V) oxytriisopropoxide VO-$(OiPr)_3$ as metal oxide precursor and polyvinylpyrrolidone (PVP) as carbon source for vanadium redox flow battery (VRFB) application. X-ray diffraction (XRD) as well as scanning electron microscopy (SEM) analysis show a typical V_2O_3 rhombohedral structure and an urchin-like V_2O_3-CNF morphology, respectively. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements show a high electrocatalytic activity for the composite electrospun samples both in terms of peak to peak separation ($\Delta E = 0{,}02$ V) and lower charge transfer resistance ($R_{ct} = 0.12$ ohm cm^2) with respect to a pristine CNF. The better reversibility is ascribed to the oxygen functional groups presence that act as catalytic sites reducing kinetic overpotentials. Moreover, thanks to the rhombohedral structure of V_2O_3, as well as to the more graphitic structure of the carbon, a suitable electrical conductivity is guaranteed for reducing ohmic overpotentials.

1. Introduction

Redox flow batteries (RFBs) represent an electrochemical energy storage device having attractive features such as flexible design, long cycle life, uncoupled power output and energy capacity. The main drawbacks are essentially the low energy density due to poor solubility and stability of the electrolytes [1,2] in addition to the poor electrochemical activity of the commercial carbon based electrode used in the most promising technology among the several RFB, such as vanadium redox flow battery (VRFB) [3–5]. Nanostructured materials represent a good alternative to conventional micro or millimetre size materials able to improve the electron transfer properties thanks to high porosity, high surface/volume ratio, enhanced conductivity [6–8] as well as the interesting electrical, optical, mechanical and magnetic properties [9–12]. As alternative to solvothermal, sol-gel and microemulsion preparation methods [13–15], electrospinning is a valid technique thanks to its simplicity, versatility, cost-effectiveness and potential to scale up. By this method is possible to control fibers properties in terms of diameter, porosity and surface morphology allowing to obtain nanomaterials with different size and shape such as nanofibers, nanotubes, nanosheets etc. starting from polymers, inorganic species and composites [16–19]. The diameter of the resulting fiber can be varied from 10 μm to 10 nm depending on the working parameters, including solution viscosity, applied voltage, feed rate and collector type [20]. In recent years, this technique has been used to prepare metal oxides, carbon nanofibers, ceramic nanofibers and metal oxide-carbon composite materials [21–27]. In particular, the metal oxide-carbon composites are suitable as electrodes in electrochemical devices thanks to the combination of electrical conductivity due to carbonaceous materials with the catalytic properties of the metal oxides able to improve the electrochemical performance. Recently, Kim et al. [28] obtained interesting electrocatalytic activity by using polyacrylonitrile (PAN)-based carbon felt modified with Mn_3O_4 as electrode material for vanadium redox flow battery. In literature, polyacrylonitrile (PAN) is largely used in the electrospinning method as carbon nanofiber (CNF) precursor mixed with metal precursor solution. Wang et al. [29] prepared electrospun carbon-cobalt (C/Co) composite nanofiber starting from a solution of PAN and cobalt acetate $Co(CH_3COO)_2$. This C/Co composite showed a high conductivity and interesting performance as anode materials for

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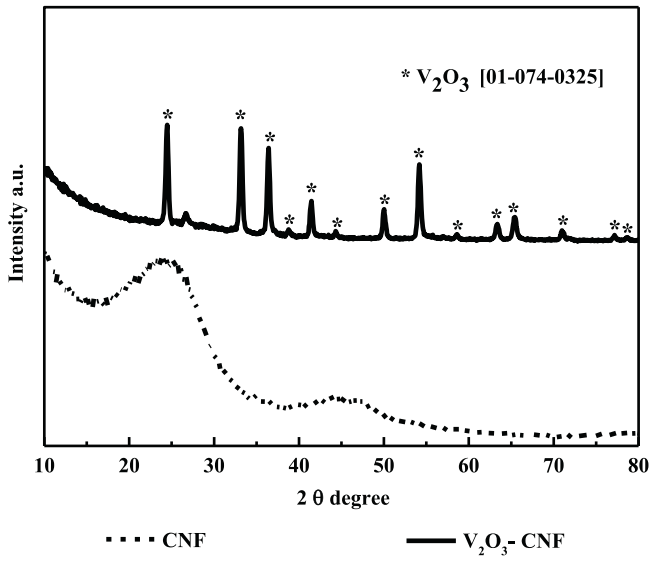

Fig. 1. XRD diffraction patterns comparison among CNF and urchin-like V_2O_3-CNF composite samples.

lithium ion batteries. B.-H. Kim et al. [30] tested as supercapacitor electrodes vanadium pentoxide (V_2O_5)/carbon nanofiber composites (CNFCs) prepared by electrospinning technique using polyacrylonitrile (PAN) as carbon nanofiber precursor. Despite of the large use of PAN as carbon source, more recently, Wang et al. [31] developed a three step process to synthesize electrospun carbon nanofibers with a surface area up to 806 m^2/g by using thermoplastic polyvinylpyrrolidone (PVP) overcoming some limitations of using PAN. They started from an electrospinning precursor solution containing ethanol and PVP, avoiding the use of more pollutant and expensive solution of dimethylformammide (DMF), commonly used to dissolve the PAN powder. Furthermore, due to the toxicity of V_2O_5, the lower valence vanadium oxides are considered more promising [32,33]. In particular, V_2O_3-CNF composites have attracted much attention thanks to their low toxicity, structural properties, high specific capacity, cost effectiveness. Therefore, V_2O_3-carbon composites with several morphologies have been prepared by using different synthesis methods and employed as electrodes materials in supercapacitors, lithium batteries etc. [33–36]. The aim of this work is V_2O_3-CNF composite synthesis by using electrospinning technique for VRFB application. The purpose is the electrocatalytic activity improvement by using home made cost-effective materials characterized by high electrical conductivity, high surface area and a large number of active sites [37–39]. As far as we know, no scientific work are addressed to the study of the electrochemical properties of electrospun V_2O_3-CNF composite for vanadium redox flow battery.

2. Experimental

2.1. Physico-chemical investigation methods

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 (012) peak at $2\theta = 24.32^\circ$ of the V_2O_3 profile. Brunauer-Emmett-Teller (BET) equation and nitrogen adsorption-desorption isotherm, measured at −196 °C (ASAP 2020 M Micrometrics), was used to calculate the specific surface area of the investigated electrospun samples. A Philips XL 30 scanning electron microscope (SEM) was used to investigate samples morphology surface. The surface chemical composition of the catalysts was investigated by X-ray photoelectron spectroscopy (XPS) using a Physical Electronics (PHI) 5800-01 spectrometer. A monochromatic Al Ka X-ray source was used at a power of 350 W.

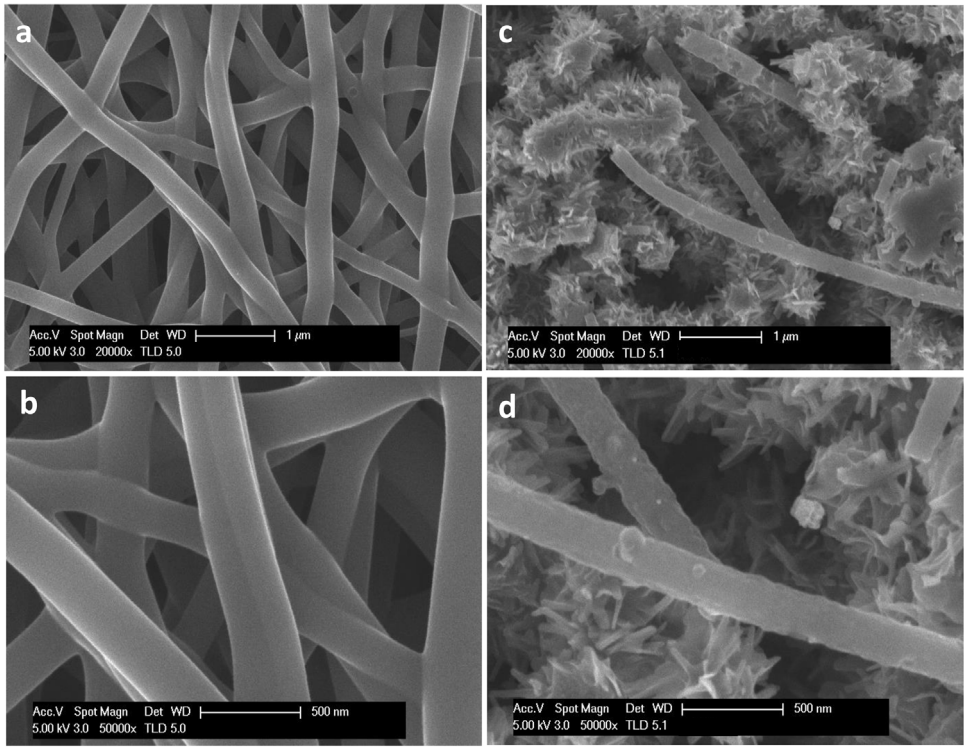

Fig. 2. SEM images of a-b) pristine CNF, c-d) urchin-like V_2O_3-CNF composite samples.