



Original Research Article

The influence of carbon nanotubes characteristics in their performance as positive electrodes in vanadium redox flow batteries



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ARTICLE INFO

Article history:

Received 14 August 2014

Revised 4 November 2014

Accepted 16 December 2014

Keywords:

Vanadium redox flow battery

Carbon nanotube

Crystallinity

Chemical composition

Electrochemical activity

Kinetic reversibility

ABSTRACT

Three types of multi-walled carbon nanotubes are investigated as electrodes in the positive half-cell of a vanadium redox flow battery (VRFB). Pure (MWCNTs), nitrogen-doped (CN_xMWNTs) and oxygen functionalized (MWCNT-Cs) carbon nanotubes exhibit significant structural differences at the nanoscale, as well as different chemical and physical properties. The influence of such different characteristics on the electrochemical behavior towards the VO²⁺/VO₂⁺ redox reactions is investigated by cyclic voltammetry, electrochemical impedance spectroscopy and charge/discharge experiments. MWCNT-Cs exhibit the best performance despite not having the largest specific surface area, neither the greatest amount of oxygen nor nitrogen functional groups on their surface. Therefore, their enhanced performance in terms of electrochemical activity and kinetic reversibility towards the vanadium reactions and energy efficiency of the corresponding static battery, are attributed to the highest sp² carbon content, which brings the highest electrical conductivity. These results represent a significant advance in the fundamental understanding and design of effective electrode materials that will lead to more efficient batteries.

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Introduction

Over the past decades, new sources of renewable energy (e.g. solar- and wind-based sources) have rapidly grown in order to cover the rising energy demand, thus leaving aside those technologies based on fossil fuels. Despite the numerous advantages of these clean energy sources, their intermittent nature in terms of power generation/power demand raises also a need for energy storage. Therefore, there is a great interest in the scientific community for the development of efficient energy storage systems that could contribute to the implementation of these renewable power generation approaches in large-scale and remote applications [1].

Vanadium redox flow batteries (VRFBs) have emerged as promising large-scale electrochemical energy storage devices offering attractive features, such as long life (>10,000 cycles), flexible design, high energy efficiency (70–80%) and low maintenance cost

[2]. One of the main characteristics of VRFBs is that they store energy through the chemical changes of electroactive species dissolved in two separate solutions, and not in the electrodes like in conventional batteries [3]. Therefore, VRFBs offer the possibility of acting separately on their energy capacity and output power, thus facilitating their scaling-up processes. Moreover, the use of the same metal in both half-cells ([VO₂⁺]/[VO²⁺]) in the positive electrolyte and V³⁺/V²⁺ in the negative one), reduces the problem of cross-contamination, which constitutes the main cause of self-discharge in other redox flow batteries as bromine/polysulfide or iron/chromium [4].

Although the energy is converted and stored in the electrolytes, the electrodes also have an important role in the battery performance as supports for the reactions involved during the charge/discharge of the device. Consequently, the selection of adequate electrode materials, with the highest possible combination of electrical conductivity, surface area and mechanical strength, along with a good stability in the electrolyte and electrochemical activity [5], is of paramount importance in order to maximize the efficiency of the VRFB. A great deal of effort has been directed to enhance the

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poor electrochemical properties of commonly used graphite felts, carbon cloths and carbon fibers [6–8]. However, the tedious procedures required to improve their electrochemical activity and kinetic reversibility [9,10], restrict their use as active electrode materials.

Carbon nanotubes (CNTs), due to their remarkable physical and chemical properties [11,12] and their potential large scale production, have been increasingly investigated for applications related to electrochemical devices such as batteries, supercapacitors and fuel cells [13–17]. In the last years, CNTs have been also tested as electrode reaction catalysts in VRFBs. Many of these studies report the influence of the different types of oxygen functional groups (C–OH, C–COOH) on the electrochemical performance of carbon nanotubes, trying to elucidate their role in the $\text{VO}^{2+}/\text{VO}_2^+$ redox reactions [18]. More recently, an improvement of the electrochemical activity of graphite felts and mesoporous carbons in VRFBs was observed when they were modified with nitrogen-doped multi-walled CNTs [19].

In the present study, three types of multi-walled carbon nanotubes with similar morphology but rather different nano and microstructure and chemical composition have been synthesized: pure (MWCNTs), oxygen functionalized (MWCNT-Cs) and nitrogen-doped (CN_xMWNTs) carbon nanotubes. The influence of such different characteristics of the materials on their electrochemical response towards the $\text{VO}^{2+}/\text{VO}_2^+$ redox reactions is investigated by cyclic voltammetry, electrochemical impedance spectroscopy and charge/discharge tests. In the search of effective positive electrode materials for VRFBs, which will contribute to develop more efficient batteries, the understanding of the role played by the structure and chemical composition of the carbon nanotubes in the vanadium redox reactions is also studied.

Experimental

Synthesis of the carbon nanotubes

The synthesis of the three different types of MWCNTs was carried out by aerosol assisted chemical vapor deposition (AA-CVD). Three different solutions containing a liquid carbon source and 2.5 wt% of ferrocene as a catalyst (FeCp_2 , 98%, Sigma–Aldrich) were atomized and pyrolyzed at temperatures ranging from 800 to 850 °C in an Argon atmosphere for 30 min. Toluene (C_7H_8 , ACS grade, BDH®) was used as the carbon source in order to obtain both MWCNTs and MWCNT-Cs. Moreover, for the synthesis of MWCNT-Cs, a low concentration (1 wt%) of EtOH (200 proof, Koptec) was added to the precursor solution [20]. The nitrogen-doped sample (CN_xMWNT) was synthesized using benzylamine ($\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$, 99%, Sigma–Aldrich) as the C and N precursor [21].

Morphological, structural, chemical and physical characterization

The morphology of the samples was studied by scanning electron microscopy (SEM), using an FEI Nova NanoSEM 630 operated at 5 kV) and by transmission electron microscopy (TEM, using a JEOL2010 and a JEOL 2010F operated at 200 kV). Raman spectra were acquired using a Jobin–Yvon T64000 spectrometer operating in the subtractive triple configuration and a Renishaw inVia confocal microscope-based Raman spectrometer. The samples were analyzed in the backscattering $z(xy)z$ geometry using a 514.5 nm laser excitation wavelength. The apparent BET surface areas were determined by applying the BET equation to the nitrogen adsorption isotherms obtained at 77 K on a Micromeritics ASAP® 2420 instrument. The electrical conductivity of the carbon nanotubes (without any binder) was measured (at 20 MPa) using a modification of the four-probe method of Van der Pauw [22]. The atomic

oxygen and nitrogen contents on the surface were determined by XPS analysis in a VG–Microtech Multilab 3000 device. The type of bonding and the functional groups present in the samples (mainly, the oxygen functional groups) were estimated using X-ray photoelectron spectroscopy (XPS). Curve fittings of the spectra were obtained using a Gaussian–Lorentzian peak shape, after performing a Shirley background correction. For the high resolution C1s line scan, the binding energy profiles were deconvoluted as follows: undamaged structures or sp^2 -hybridized carbon (284.5 eV), damaged structures or sp^3 -hybridized carbons (285.5 eV), C–O groups (286.5 eV), C=O functional groups (287.7 eV) and COO groups at 288.7 eV). In addition, the energy profiles corresponding to Csp^3 and C–O possibly incorporate nitrogen-carbon bonds.

Electrochemical measurements

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) experiments were performed in a Teflon home-made three-electrode cell at room temperature (Fig. S1, Supporting Information). The cell consisted of samples of MWCNTs, MWCNT-Cs or CN_xMWNTs as the working electrode, Ag/AgCl/3.5 M KCl as the reference electrode and a graphite rod as the counter electrode. All the working electrodes were disk-shaped with the same exposed area (0.5 cm^2) and the same mass (30 mg), consisting of 75 wt% of the active material and 25 wt% of polyvinylidene fluoride (binder). The electrodes were dried in a vacuum oven at 110 °C overnight before each experiment. All the potentials reported in this study were referenced to Ag/AgCl/3.5 M KCl (i.e., 0.205 V vs. NHE). The electrolyte consisted of a solution of 0.5 M VOSO_4 (Sigma Aldrich) in 1.0 M H_2SO_4 (VWR International). The electrochemical measurements were performed on a BioLogic VMP Multichannel Potentiostat.

In the CV experiments the potential sweeps always started from the open circuit potential (OCP), with a positive initial scan direction. The scan rate, v_{scan} , was varied from 1 to 5 mV s^{-1} . Repetitive voltammograms (25–100 scans) were recorded at each v_{scan} in order to evaluate the long term stability of the electrode materials and study the kinetics of the vanadium redox processes. It is important to remark that prior to all these CV experiments, ZIR measurements (Ohmic drop determination technique) were done, to ensure the proper set up of the three electrode cell and, subsequently, the suitable comparison of the three active electrode materials. EIS measurements were performed at a polarization potential of 0.8 V (vs. Ag/AgCl/3.5 M KCl) and an amplitude of 10 mV over a frequency range from 100 kHz to 500 mHz.

Single cell test

Three lab-scale static vanadium redox batteries (VRBs) were assembled, the only differing component being the positive electrode (see Fig. S2, Supporting Information). Disk-shaped electrodes of MWCNTs (in VRB-P), MWCNT-Cs (in VRB-C) and CN_xMWNTs (in VRB-N) were placed in the positive half-cell. Pieces of thermally treated graphite felt (TTGF), a standard electrode material in these types of batteries, acted as the negative electrode for all VRBs. For the charge/discharge experiments, the active area of each electrode was fixed to 1 cm^2 . The two compartments of each cell were separated by a commercial membrane (Nafion® NRE-212) and graphite disks were used as current collectors. The starting electrolytes for the positive and negative half-cells consisted of solutions containing 0.5 M $\text{VOSO}_4/1.0$ M H_2SO_4 and 0.5 M VCl_3 (Aldrich)/1.0 M H_2SO_4 (each electrolyte volume being approximately 1 mL), respectively. Charge/discharge experiments were carried out in the three VRBs, applying constant current densities of 40 and 50 mA cm^{-2} . The upper and lower limits of the charge/discharge voltages were fixed at 1.7 and 0.7 V, respectively.

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