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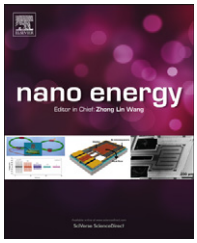

RAPID COMMUNICATION

Carbon nanowalls thin films as nanostructured electrode materials in vanadium redox flow batteries

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Abstract
Three carbon nanowalls (CNWs) thin films, synthesized by Radiofrequency Plasma Enhanced Chemical Vapor Deposition (RF-PECVD) using different processing parameters, are studied as electrode materials in the positive half-cell of a Vanadium Redox Flow Battery (VRFB). These 2D-networks of interconnected graphenes exhibit an excellent electrochemical performance towards the V(IV)/V(V) redox couple in terms of a low overpotential and fast electron transfer kinetics. This can be attributed to certain specific features of CNWs such as the arrangement of the graphene planes perpendicular to the substrate, thus facilitating the electron transfer from the substrate and resulting in a large amount of exposed reactive graphitic edge planes. Repetitive cyclic voltammetry measurements, at various scan rates, together with SEM images evidence the long term stability of these materials. The obtained results represent a significant step forward in the development of highly effective VRFB electrode materials.

Introduction

The need to satisfy the rising energy demand has led to an increase in interest in electrochemical energy storage systems, among which Vanadium Redox Flow Batteries (VRFBs) have acquired increasing importance. Unlike other types of batteries, their operation is entirely related to the chemical changes of the vanadium electroactive species dissolved in two solutions [1]. Thus, these systems exhibit excellent advantages such as a high energy efficiency (~70-90%), a long life, a flexible design, no cross-contamination and a low maintenance cost, so they can be applied for large-scale power generation or in off-grid installations [2].

The electrodes in VRFBs, although not directly involved in the storage of energy, play an important role as support for the electrochemical reactions associated with the

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charge/discharge of the system. For this reason, the selection of a suitable electrode material (high electrical conductivity, mechanical-chemical stability and large surface area with active sites) is one of the keys to obtain a good-performance battery [3]. Metals and different carbon forms such as felts, cloths or fibers appear to be promising materials for this application [4,5]. However, the high cost of the former and the low electrochemical activity of the latter restrict their use as active electrodes. To overcome these drawbacks, thermal, acidic and galvanic treatments, together with the deposition of metallic particles on carbon surfaces, have been investigated, but proved to be tedious and costly procedures [6–9]. Therefore, the development of new more suitable electrode materials is one of the main goals of current research.

In this context, novel nanostructured carbon materials, Carbon Nanowalls (CNWs) thin films, have attracted increasing attention in recent years. They can be described as two-dimensional (2D), several tens of nanometers in width, carbon nanostructures composed of self-aligned graphene nanodomains arranged vertically on a substrate [10]. Their high surface-to-volume ratio, high mechanical and chemical stability, high electrical conductivity and the large amount of graphitic edge planes with a high surface activity have led to these materials being used in several applications such as catalyst supports, hydrogen adsorption and biological sensors [11–13]. Moreover, unlike other CVD-grown materials such as carbon nanotubes, these CNWs can be synthesized without a catalyst, which makes them especially attractive for investigating basic electrochemical phenomena [14]. To our knowledge, despite the increasing interest in CNWs for electrochemical applications as supercapacitors, lithium-ion batteries and fuel cells, the use of these materials as electrodes in VRFBs has still not been reported [15–17].

In the present work, we investigate the suitability and long-term stability of three CNWs thin films, synthesized by Radiofrequency Plasma Enhanced Chemical Vapor Deposition (RF-PECVD) on gold substrates using different processing parameters, as positive electrodes in a VRFB.

Experimental section

Synthesis of CNWs thin films

CWNs thin films were obtained by RF-PECVD. The growth of the films was carried out in two steps using a previously described experimental set-up [18]. As a first step, a gold disk substrate (Ø=12 mm) was subjected to a radiofrequency plasma jet in hydrogen for 5 min in order to remove impurities from the surface. In the second step the as-pretreated substrate, situated 5 cm from the precursor injection position, was exposed to an expanding Ar plasma generated at 300 W and injected with hydrogen and acetylene (H_2/C_2H_2: 25/1) for 30 min while the temperature of the substrate was kept at 700 °C. In the present work three Ar flow rates were selected (700, 1050 and 1600 sccm) while the pressure was established by the pumping system to various values (0.8–1.5 mbar) in order to obtain CNWs films with different characteristics (CNW1, CNW2 and CNW3, respectively).

Characterization of CNWs thin films

The structural and chemical characteristics of the CNWs were studied both on the as-deposited materials and after their use as positive electrodes in a VRFB. SEM studies were carried out in a FEI model Quanta FEG 650 instrument operating at 5 KV. TEM was performed using a JEOL 2000 EX-II. Raman spectroscopy was performed from 800 to 3500 cm^{-1} on a Renishaw 2000 Confocal Raman Microprobe (Renishaw Instruments, England) using a 514.5-nm argon ion laser. A general survey of the chemical composition of the CNWs surface was performed by XPS analysis in a VG-Microtech Multilab 3000 spectrometer (SPECS, Germany) equipped with a hemispherical electron analyzer and a MgKα ($h\upsilon$=1253.6 eV) X-ray source. Curve fitting of the C1s spectra was carried out using a Gaussian-Lorentzian peak shape after applying a Shirley background correction [19].

Electrochemical characterization

Cyclic Voltammetry (CV) experiments were performed in a Swagelok® type three-electrode cell at room temperature (Figure S1, Supplementary Data). Each cell consisted of the corresponding CNWs thin film deposited on a disk-type gold substrate as the working electrode, a Hg/Hg_2SO_4 (sat.) as the reference electrode and a platinum gauze as the counter electrode. All the potentials in this study are quoted with reference to Hg/Hg_2SO_4 (i.e. 0.65 V vs. Normal Hydrogen Electrode, NHE) unless otherwise stated. The positive electrolyte consisted of a solution of 0.5 M $VOSO_4$ (Sigma Aldrich) in 1.0 M H_2SO_4 (VWR International). Electrochemical measurements were performed on a Biologic VMP Multichannel Potentiostat. The potential sweeps (cyclic voltammograms, CVs) always started from the open circuit potential (OCP) and the initial scan direction was positive. The scan rate, v_{scan}, was varied from 1 to 50 mV s^{-1} and repetitive voltammograms were recorded at each v_{scan} to evaluate the long term stability of the electrode materials and to study the kinetics of the vanadium redox processes.

Results and discussion

Structural and chemical characteristics

As-deposited CNWs thin films

SEM images of the three CNWs films under study are shown in Figure 1. In all three cases, the as-deposited carbon material shows a typical 2D wall-like assemblies consisting of interconnected graphene nanostructures [20]. The cross-sectional SEM images of the CNWs thin films (Figure 1e) confirm that most of the carbon nanowalls are oriented perpendicularly to the gold substrate, thereby favouring electrical conduction from the substrate and resulting in a large amount of exposed reactive edge planes [21]. However, depending on the Ar flow rate used during their processing, the shape, size and surface distribution of the CNWs vary significantly from one film to another [22]. Thus, CNW1 is formed by rather small graphene domains, resulting in a film of low thickness (~1 μm), whereas CNW2 and CNW3 are both made up of well shaped nanowalls but being films of different thickness (~4 and ~7 μm, respectively) [23].