



## Graphite oxide-based graphene materials as positive electrodes in vanadium redox flow batteries



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### H I G H L I G H T S

- Graphene materials as positive electrodes in vanadium redox flow batteries.
- Increased electrical conductivity after restoration of the 2D graphitic structure.
- Enhanced electrochemical activity and kinetic reversibility to  $\text{VO}^{2+}/\text{VO}_2^+$  reactions.
- Encouraging coulombic, voltage and energy efficiency values in a VRB.

### A R T I C L E I N F O

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### A B S T R A C T

Two graphene materials, TRGO-1 and TRGO-2, prepared by the thermal exfoliation/reduction at 1000 °C of two graphite oxides with different characteristics, are investigated as positive electrodes in a vanadium redox flow battery (VRFB). A detailed study of their electrochemical response toward the  $[\text{VO}_2^+]/[\text{VO}^{2+}]$  redox system is carried out through cyclic voltammetry, electrochemical impedance spectroscopy and charge/discharge experiments. As a consequence of the differences in the structure of the parent graphite oxides, TRGO-1 and TRGO-2 exhibit different structural and physicochemical properties resulting in significantly different electrochemical performances toward the vanadium redox reactions. TRGO-1 exhibits a markedly enhanced electrochemical activity (higher peak current densities and lower overpotentials) and a better kinetic reversibility toward the oxidation/reduction vanadium processes than TRGO-2. Furthermore, charge/discharge tests performed on two VRB single cells, the only differing component being the positive electrode, present higher coulombic, voltage and energy efficiency values in that battery containing the TRGO-1 electrode. The better results achieved with this sample are attributed to the higher degree of restoration of the 2D graphitic structure, and to the consequently higher electrical conductivity which increases the heterogeneous electron transfer rate. Moreover, residual hydroxyl groups present may act as active reaction sites and contribute to enhance its electrochemical response.

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### 1. Introduction

New sources of renewable energy have been developed in recent years in an attempt to achieve sustainable energy production. Although they offer clean energy, their intermittent nature in terms of power generation/power demand makes it necessary to storage the energy. There is therefore great interest amongst the scientific community to develop electrochemical energy storage systems [1].

Vanadium redox flow batteries (VRFBs) have attracted increasing interest as large-scale energy storage devices because they offer attractive features such as a long life, a flexible design, a high energy efficiency and a low maintenance cost [2]. Unlike other batteries, where the energy is stored in the electrodes, VRFBs store this energy through the redox reactions of the electroactive species contained in two separate solutions [3]. Thus, ensuring the inertness of the electrodes, they offer the possibility of acting separately on the energy capacity and output power, facilitating their scale-up. Moreover, the use of the same metal in both half-cells ( $[\text{VO}_2^+]/[\text{VO}^{2+}]$  in the positive electrolyte and  $\text{V}^{3+}/\text{V}^{2+}$  in the negative one), eliminates the problem of cross-contamination, the main cause of self-discharge in other redox flow batteries [4].

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Although the electrodes are not direct storage elements, they have a key role to play in VRFBs by providing sites for the electrochemical reactions necessary for the proper operation of the battery. Consequently, the selection of suitable electrode materials, with a high electrical conductivity, a high surface area, high mechanical strength, a good electrolyte stability and electrochemical activity [5], is of fundamental importance for obtaining a battery with an excellent performance. The poor kinetics and reversibility of commonly used graphite felts [6], carbon cloths [7] and carbon fibers [8] restrict their use as active electrodes. This drawback, together with the tedious procedures required to improve their electrochemical performance [9,10], makes it necessary to search for new electrode materials.

Graphenes have emerged as promising active electrode materials in electrochemical devices, due to their unique properties i.e., a high electrical conductivity, a high surface-to-volume ratio, mechanical stability and widely applicable electrochemical activity [11]. Furthermore, the possibility to prepare bulk quantities of graphene materials through readily scalable chemical methods, like the graphite oxide route, has increased the interest of scientists in their possible use as electrodes in energy-efficient storage/generation systems such as supercapacitors [12], lithium-ion batteries [13] or fuel cells [14].

The thermal exfoliation/reduction of graphite oxide (GO) has been widely investigated for the preparation of graphene [15,16] due to its simplicity, sustainability and scalability. Moreover, this method offers the possibility of controlling the quality of the materials produced by taking into account the characteristics of parent graphite [17], the oxidation method used in the preparation of the graphite oxide [18] and the conditions employed for the thermal reduction of the graphite oxide to graphene [19]. The resulting materials can thus be tailored to exhibit different structures and functionalities and by implication different electrochemical properties [20].

In a previous paper [21] the authors investigated the suitability of graphene materials, prepared by the direct thermal exfoliation/reduction of a synthetic graphite-based GO at different temperatures, as positive electrodes in a VRFB and observed an excellent behavior in that obtained at 1000 °C. Furthermore, the authors have recently demonstrated the better performance of the materials prepared by the direct thermal exfoliation/reduction of graphite oxide (produced in a single step) compared to those obtained by the thermal reduction of graphene oxide (after exfoliation of the graphite oxide, in a two-step process).

In the present study, we prepared two graphene materials, by the thermal exfoliation/reduction at 1000 °C of graphite oxides with different characteristics and investigated the influence of their different structural and physicochemical properties on the electrochemical performance of the electrodes. A detailed study of their response toward the  $[\text{VO}_2^{2+}]/[\text{VO}_2^+]$  redox system was carried out through cyclic voltammetry, electrochemical impedance spectroscopy and charge/discharge experiments. As the electrochemical kinetic limitation of VRFBs is in the positive side [22], an understanding of how the different structural and physicochemical properties of the graphene materials influence their electrochemical performance is key to the development of more active positive electrodes and, consequently, more efficient batteries.

## 2. Experimental

### 2.1. Synthesis of graphene materials

Two graphite oxides, GO-1 and GO-2, were obtained by the oxidative treatment of two synthetic graphites with different characteristics [23] using a modified Hummers method [24]. This

method makes use of Hummers reagents combined with additional amounts of  $\text{NaNO}_3$  and  $\text{KMnO}_4$ . Concentrated  $\text{H}_2\text{SO}_4$  (360 mL) was added to a mixture of the corresponding synthetic graphite (7.5 g) and  $\text{NaNO}_3$  (7.5 g), and the resulting mixture was cooled down to 0 °C using an ice bath.  $\text{KMnO}_4$  (45 g) was added slowly in small doses to keep the reaction temperature below 20 °C. The as-prepared solutions were heated to 35 °C and stirred for 3 h. At this point 3% of  $\text{H}_2\text{O}_2$  (1.5 L) was slowly added, resulting in a pronounced exothermal effect up to 98 °C. The reaction mixtures were stirred for 30 min and then centrifuged (3700 rpm for 30 min), the supernatants being decanted away. The remaining solid materials were washed with 600 mL of water and centrifuged again, this process being repeated until the pH was neutral. Both GO-1 and GO-2 were then thermally treated in a tubular furnace up to 1000 °C ( $5\text{ °C min}^{-1}$ ) for 1 h, under a  $\text{N}_2$  flow of  $100\text{ mL min}^{-1}$  to obtain the two graphene materials (TRGO-1 and TRGO-2, respectively).

### 2.2. Structural, chemical and physical characterization

The morphology of the samples was studied by SEM (using an FEI model Quanta FEG 650 instrument operating at 5 kV) and TEM (on a JEOL 2000 EX-II). Raman spectra were recorded, from 750 to  $3500\text{ cm}^{-1}$ , on a Renishaw 2000 Confocal Raman Microprobe (Renishaw Instruments, England) using a 514.5-nm argon ion laser. 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 samples was measured (at 20 MPa) using a modification of the four-probe method of Van der Pauw [25]. The atomic oxygen content on the surface was determined by XPS analysis in a VG-Microtech Multilab 3000 spectrometer (SPCS, Germany) equipped with a hemispherical electron analyzer and an  $\text{MgK}\alpha$  ( $h\nu = 1253.6\text{ eV}$ ) X-ray source. The type of bonding and the functional groups present in the samples were estimated from the XPS C1s spectra. Therefore, curve fitting of the C1s spectra was performed using a Gaussian–Lorentzian peak shape after performing a Shirley background correction [26]. The resulting spectra show the binding energy of the  $\text{Csp}^2$  hybridization at 284.5 eV. The chemical shifts of +1.0 and +2.1 eV were assigned to the  $\text{Csp}^3$  hybridization and COH functional groups, respectively [27].

### 2.3. Electrochemical measurements

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) experiments were performed in a Swagelok® type three-electrode cell at room temperature. The cell consisted of samples of TRGO-1 or TRGO-2, as the working electrode,  $\text{Hg}/\text{Hg}_2\text{SO}_4$  as the reference electrode and a platinum gauze acting as the counter electrode. Both working electrodes were disk-shaped with the same geometric area ( $0.5\text{ cm}^2$ ) and the same mass (25 mg), consisting of 70 wt% of active material and 30 wt% of polyvinylidene fluoride (as binder). The electrodes were dried in a vacuum oven at 110 °C overnight before each experiment. All the potentials in this study are quoted with reference to  $\text{Hg}/\text{Hg}_2\text{SO}_4$  (i.e., 0.65 V vs. NHE). The positive electrolyte consisted of a solution of 0.5 M  $\text{VOSO}_4$  (Sigma Aldrich) in 1.0 M  $\text{H}_2\text{SO}_4$  (VWR International). 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), the initial scan direction being positive. The scan rate,  $v_{\text{scan}}$ , was varied from 1 to  $50\text{ mV s}^{-1}$ . Repetitive voltammograms (25 scans) were recorded at each  $v_{\text{scan}}$  to evaluate the long-term stability of the electrode materials and to study the kinetics of the vanadium redox processes.

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