Outstanding electrochemical performance of a graphene-modified graphite felt for vanadium redox flow battery application

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Abstract

The development of more efficient electrode materials is essential to obtain vanadium redox flow batteries (VRFBs) with enhanced energy densities and to make these electrochemical energy storage devices more competitive. A graphene-modified graphite felt synthesized from a raw graphite felt and a graphene oxide water suspension by means of electrophoretic deposition (EPD) is investigated as a suitable electrode material in the positive side of a VRFB cell by means of cyclic voltammetry, impedance spectroscopy and charge/discharge experiments. The remarkably enhanced performance of the resultant hybrid material, in terms of electrochemical activity and kinetic reversibility towards the $\text{VO}^{2+}/\text{VO}_2^+$, and mainly the markedly high energy efficiency of the VRFB cell (c.a. 95.8 % at 25 mA cm^{-2}) can be ascribed to the exceptional morphological and chemical characteristics of this tailored material. The 3D architecture consisting of fibers interconnected by graphene-like sheets positively contributes to the proper development of the vanadium redox reactions and so represents a significant advance in the design of effective electrode materials.

Keywords: graphite felt, electrophoretic deposition, graphene, redox flow battery, energy efficiency

1. Introduction

Renewable energy sources (e.g. solar and wind-based) are being developed and implemented around the world in order to avoid the environmental drawbacks of the widely used fossil fuels. However, their intermittent nature makes it necessary to develop large-scale energy storage devices, able to leveling their output over time [1].

Vanadium redox flow batteries (VRFBs) have received considerable attention as promising energy storage systems because they offer desirable characteristics for storing electrical energy: a long cycle life, a flexible design, high safety, no cross-contamination and independence of energy and power densities [2]. Nonetheless, for VRFBs to be competitive with other energy storage devices their size and cost need to be reduced and they must display higher energy efficiency values. Energy efficiency mainly depends on the structural, physical and chemical properties of the electrodes integrating the devices as they act as supports for the vanadium redox reactions involved in the charge and discharge processes. Hence, improving the electrochemical performance of the electrodes of the VRFB is a suitable strategy to enhance battery performance [3].

Among the carbon materials commonly used as electrodes in VRFBs, graphite felts (GFs) stand out due to their chemical stability in acidic media, their high electrical conductivity and their three-dimensional structure [4-9]. However, to date, their poor electrochemical performance has limited their use as active electrodes and several treatments have been investigated in order to enhance their electrocatalytic activity and kinetic reversibility. Most of them, such as thermal/chemical treatments [10, 11], electrochemical activation [12], plasma or microwave treatments [13] and nitrogen doping [14-17], are focused on the development of oxygenated and/or nitrogenated functional groups which act as reactive sites towards the vanadium redox reactions. Moreover, modification of GFs using metallic nanoparticles such as Ir [18], Bi [19], or Pt [20] has been shown to be an effective way to improve their electrochemical performance as it enhances their electrical conductivity. However, most of these procedures are high energy/time consuming and require the use of environmentally unfriendly and expensive chemical reagents but, more importantly, they appear to be unsuitable for synthesizing large- area electrodes.

In this context the electrophoretic deposition (EPD) of graphene materials on conductive substrates has emerged in recent years as an economic and versatile processing technique for obtaining materials suitable for various electronic, catalytic, biomedical and energy storage applications [21]. These graphene materials have attracted a great deal of attention because of

their unique properties i.e., a high electrical conductivity, a high surface-to-volume ratio, their good mechanical stability and widely applicable electrochemical activity [22]. Moreover EPD technology is an interesting deposition method for obtaining films from suspensions, containing well-dispersed charged particles, with high deposition rates, simple operation, easy scalability and avoiding the use of binders [23]. Thus, the combination of graphene materials and the EPD procedure with graphite felt as conductive substrate opens up a new possibility for synthesizing innovative electrode materials with advanced properties. Even though similar hybrid materials have been previously tested as electrodes for several applications such as capacitive deionization [24], supercapacitors [25] and microbial fuel cells [26], their suitability as electrodes in VRFBs has not been widely investigated.

In the present study a graphene-modified graphite felt was synthesized using a graphene oxide water suspension by means of EPD technology. Its performance towards the vanadium redox reactions in the positive side of a VRFB cell was investigated by means of cyclic voltammetry, electrochemical impedance spectroscopy and charge/discharge experiments in a lab-scale flow device.

2. Experimental Section

2.1 Synthesis of the graphene-modified graphite felt

A rayon-based graphite felt, *GF*, (RVG-2000, Société Carbon-Lorraine) was modified with a graphene oxide (GO) water suspension by means of electrophoretic deposition (EPD). Two pieces of the as received *GF* (8 x 4 cm) were immersed in Milli-Q water to ensure their wettability. They were then placed, opposite each other leaving a gap of 1cm, in a home-made cell (Figure S1, Supporting Information) containing a GO water suspension of 6 mg mL⁻¹ obtained following a procedure detailed elsewhere [27]. Next, a voltage of 10 V was applied (BioLogic VMP Multichannel Potentiostat/Galvanostat) for 3 h between the two pieces of *GF*, which act as positive and negative electrodes, respectively. As the graphene oxide sheets are negatively charged, the electric field created by applying the above mentioned voltage made them moved towards the positive electrode of the EPD cell. Finally, the as obtained

samples were washed with distilled water in order to remove the excess of GO not deposited on the *GF*, and dried in a vacuum oven at 110 °C overnight before each experiment. The resultant graphene-modified graphite felt was labeled as *GF-G*.

Two additional graphite felt samples were synthesized for comparative purposes. One was a thermally treated graphite felt (*TTGF*), commonly used as electrode in VRFBs [5], obtained by directly treating the *GF* at 450 °C during 3 h under an air flow in a tubular furnace. The other felt sample was obtained using a similar procedure to that employed to obtain *GF-G*, with the difference that the GO water suspension was replaced by a 1.0 M H₂SO₄ solution and the voltage of polarization was lowered (3V, 3h). The resultant sample was labeled *GF-H₂SO₄*. As the electrical conductivity of this acidic electrolyte was considerably higher than that of the GO water suspension, the application of a lower voltage made it possible to reach anodic currents comparable to those achieved when preparing the *GF-G* (Figure S2, Supporting Information).

2.2 Morphological and chemical characterization

The morphology of the different graphite felts was studied by SEM (using a FEI model Quanta FEG 650 instrument operating at 5 KV) and HRTEM (using a JEOL JEM- 2100F transmission electron microscope, equipped with a field-emission-gun, FEG, operating at 200 kV). This last microscope was also fitted with an energy dispersive X-ray analyser (EDX) to allow the detection and quantification of the oxygen present in selected regions (deposited material). The total oxygen content of the whole samples was determined directly in a LECO-TF-900 furnace coupled to a LECO-CHNS-932 microanalyzer. The atomic oxygen content on the surface was determined by XPS analysis in a VG-Microtech Multilab 3000 spectrometer (SPECS, Germany) equipped with a hemispherical electron analyser and a MgK α ($h\nu = 1253.6$ eV) X-ray source. The type of bonding and the functional groups present in the

samples (mainly, the oxygen functional groups) were estimated by curve fitting the C1s spectra using a Gaussian–Lorentzian peak shape, after performing a Shirley background correction. The binding energy profiles were deconvoluted as follows: undamaged structures or sp^2 -hybridized carbon (284.4-284.6 eV), damaged structures or sp^3 -hybridized carbons (285.5-285.8 eV), C–O groups (286.4-286.6 eV), C=O functional groups (287.6-288.0 eV) and COO groups (288.7-289.0 eV).

2.3 Electrochemical performance

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) experiments were performed in a Teflon home-made three-electrode cell at room temperature (Figure S3, Supporting Information). The cell consisted of samples either of *GF*, *TTGF*, *GF-H₂SO₄* or *GF-G* 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 ($\approx 1 \text{ cm}^2$) and the same thickness (6 mm). All the potentials reported in this study were referenced to Ag/AgCl/3.5 M KCl (i.e., 0.205 V vs. NHE). The starting electrolyte consisted of a solution of 0.05 M VOSO₄ (Sigma Aldrich) in 1.0 M H₂SO₄ (VWR International). The electrochemical measurements were performed on a BioLogic VMP Multichannel Potentiostat.

The potential sweeps in the CV experiments always started from the open circuit potential (OCP), with a positive or negative initial scan direction. The scan rate, v_{scan} , was varied from 1 to 20 mVs⁻¹. Electrochemical impedance spectroscopy (EIS) measurements were performed at polarization potentials of 0.9 V and -0.5 V (vs Ag/AgCl/3.5 M KCl) and at an amplitude of 10 mV over a frequency range from 100 KHz to 100 mHz.

2.4 Single cell tests

The VRFB performances of the different graphite felt electrodes were measured using an in-house designed flow cell system. The system consists of a single cell composed of two compartments, two peristaltic pumps (ColeParmer, Masterflex), and two external glass reservoirs.

The single-cell used (Figure S4, Supporting Information) was made by sandwiching a Nafion® 117 (6 cm × 6 cm) membrane between two pieces of graphite felt electrodes, the only differing component being the positive electrode (*GF* in *VRFB-1*, *TTGF* in *VRFB-2*, *GF-H₂SO₄* in *VRFB-3* and *GF-G* in *VRFB-4*). *GF-H₂SO₄* was used as negative electrode in all cases, as it exhibited the best electrochemical performance towards the $V^{3+/2+}$ redox reactions (see Figure S5 Supporting Information).

Each electrode in its corresponding half-cell was placed inside a groove on the outer face of the graphite bipolar plates which were etched with serpentine flow fields. The area of the electrode in contact with electrolyte solution was 4 cm² (30% of compression). The inner faces of the bipolar plate were sputtered with a layer of copper as current collector. A Viton gasket was used to prevent the leakage of the electrolyte. Metallic aluminium end-plates were used to close the cell. The stack was connected to the external electrolyte reservoirs by tygon tubing, through which the electrolyte was made to flow by a double headed peristaltic pump from the reservoirs to the stack.

The positive and negative starting electrolytes were solutions of 20 mL of 1.0 M VOSO₄ (Alfa Aesar, 98%) in 3.0 M H₂SO₄ (Aldrich, 98%). The electrolyte flow rate to each half-cell was 18 cm³ min⁻¹ and the negative reservoir was continuously purged by nitrogen to minimize oxidation of the active species. The flow cell was charged to 1.8 V and then

discharged to 0.8 V, at 25 mA cm⁻². The charge/discharge tests were carried out using a Parstat 2273 potentiostat/galvanostat (Princeton Applied Research).

3. Results and discussion

3.1 Morphological and chemical characterization of the materials

The morphologies of the graphite felt samples are shown in Figure 1. The pristine graphite felt, *GF*, exhibits a 3D architecture (Figure 1a) consisting of cross-linked fibers with several impurities on their surfaces, probably related to the sizing of the felt [28]. After the thermal treatment in air (*TTGF*, Figure 1b), the impurities vanished and the surface of the fibers became smoother. After the felt was subjected to anodic polarization in the EPD cell containing sulphuric acid (*GF-H₂SO₄*, Figure 1c), the surface of the fibers became rougher, with some visible defects that could act as active sites for the electroactive vanadium species to react [29].

The graphite felt modified by EPD using the GO suspension (*GF-G*) shows graphene-like sheets placed on the surface of the fibers either in a wrinkled configuration (Figure 1d) or anchored between them (Figure 1e), the latter structures being the most abundant throughout the material. These sheets consist of partially reduced GO (rGO), as there is a marked decrease in oxygen from 13 at. % in the initial GO to 3.84 at % (as determined by EDX, Figure S6 Supporting Information) which is in agreement with the anodic reduction of the starting GO sheets previously reported [30]. While the graphene sheets on the surface of the fibers may increase the surface area of the felt, those interconnecting different fibers may contribute to the formation of a conducting network [31]. Figure 1f shows a HRTEM image of an interface region between a fiber of the felt and a fragment of the electrophoretically deposited graphene-like sheets, which is clearly anchored to the surface of the fiber [32]. Moreover, the inset in Figure 1f (a detailed view of the circled area) shows that the graphene material is formed by several randomly arranged graphene layers.

Figure 1. SEM images of (a) *GF* (b) *TTGF* (c) *GF-H₂SO₄* and (d, e) *GF-G*. (f) HRTEM image of an interface region of *GF-G*.

In addition to the morphological differences between the different graphite felts, the samples also have different chemical composition (Table 1). As might be expected, the modified felts have a higher total oxygen content (as determined by elemental analysis) than the raw felt, as the different treatments enrich the surface chemistry. The oxygen content increases slightly from 0.19 wt. % for *GF* to 0.59 and 0.36 wt. % for *TTGF* and *GF-H₂SO₄*, respectively, while the graphene-modified felt (*GF-G*) has a significantly higher oxygen content (8.32 wt. %). Furthermore, significant differences in the surface chemistry were also revealed by XPS (Figure 2). Even though *TTGF* has higher oxygen content than *GF-H₂SO₄*, the amount of oxygenated functional groups on the surface of the fibers of the felt is significantly greater in the latter (Table 1, Figure 2c). This can be ascribed to the fact that, while the thermal treatment leads to the oxidation of the inner structure of the fibers, the anodic polarization affects mostly their surface (giving rise mainly to C=O and COOH functional groups). The higher content of oxygenated functional groups in *GF-G* (mainly C-O and C=O (Figure 2d), is a result of the incorporation of the graphene material (rGO) throughout the 3D structure of the felt.

Table 1. Chemical composition of the graphite felts

SAMPLE	Elem. Anal.	XPS	
	O (wt %)	C (at %)	O (at %)
<i>GF</i>	0.19	95.94	4.06
<i>TTGF</i>	0.59	93.68	6.32
<i>GF-H₂SO₄</i>	0.36	79.52	20.48
<i>GF-G</i>	8.32	78.22	21.78

On the view of these results, *GF-G* is a hybrid material (see SEM images in Figure 1), with oxygenated functional groups distributed throughout its three-dimensional network, a configuration that might improve not only the wettability of the whole *GF-G* but also enhance its active area towards the vanadium species [33].

Figure 2. Curve fitting of C1s XPS spectra of (a) *GF*, (b) *TTGF*, (c) *GF-H₂SO₄* and (d) *GF-G*.

3.2 Electrochemical performance

Due to the marked differences in the morphology and chemical composition of the graphite felts under study, different electrochemical performances as positive electrodes in the VRFB cell can be expected. Cyclic voltammetry (CV) experiments were carried out to determine how their different characteristics influence the response of the four felts towards the $\text{VO}^{2+}/\text{VO}_2^+$ redox reactions.

As can be seen in Figure 3, the anodic/cathodic peaks related to the $\text{VO}^{2+}/\text{VO}_2^+$ oxidation/reduction reactions were developed on the four materials. Although this might suggest that all of them are suitable to act as electrodes in the positive side of the VRFB cell, the significant differences in the main electrochemical data derived from the CVs (Table 2) reflect different electrochemical performances. With respect to the VO^{2+} oxidation, the anodic peak current densities (j_{pa}) measured on the four felts were similar (between 12 and 13.5 mAcm^{-2}). However, the overpotential of activation of the reaction (η_a) and, consequently, the potential of the corresponding anodic peaks, differed significantly from one material to another, being considerably lower on the *GF-G* electrode (0.86 vs 0.98, 0.94 and 0.88 V for *GF*, *TTGF* and *GF-H₂SO₄*, respectively). On the other hand, both the cathodic peak current

densities (j_{pc}) and the overpotential of the VO_2^+ reduction also showed different values, these being significantly better on the $\text{GF-H}_2\text{SO}_4$ and GF-G electrodes than in the commonly used TTGF electrode. The reversibility of the $\text{VO}^{2+}/\text{VO}_2^+$ processes was evaluated on the basis of the peak potential separation values (ΔE_p) and the ratio of peak currents (I_{pa}/I_{pc}), 59 mV and 1.0 being the values corresponding to a reversible one-electron process [34]. In our study, it can be seen that both values improved from the raw GF and the TTGF to the felts modified in the EPD cell (Table 2). In particular, reversibility, which directly affects the kinetic of the vanadium redox processes, was slightly better on the GF-G electrode where the ΔE_p value of 94 mV and the I_{pa}/I_{pc} ratio of 1.2 approximately are characteristic of quasi-reversible processes.

Figure 3. CVs recorded (starting from the OCP and with a positive scan direction) in a 0.05 M $\text{VO}_2\text{SO}_4/1.0$ M H_2SO_4 solution at a scan rate of 1 mV s^{-1} on the different graphite felt electrodes.

Table 2. Electrochemical data obtained from the CVs recorded on the different graphite felt electrodes.

SAMPLE	v_{scan} (mVs ⁻¹)	j_{pa} (mAcm ⁻²)	j_{pc} (mAcm ⁻²)	ΔE_p (mV)	I_{pa}/I_{pc}
<i>GF</i>	1	12	5.5	317	2.2
	5	42.2	18.5	636	2.3
	10	65.7	33.5	802	2.0
	20	99.3	57.2	997	1.7
<i>TTGF</i>	1	13.5	8.9	198	1.5
	5	48.8	30.2	420	1.6
	10	79	48.4	56.8	1.6
	20	124.8	78	785	1.6
<i>GF-H₂SO₄</i>	1	12.6	12.6	104	1.0
	5	34.2	40.0	299	0.8
	10	54.1	63.2	442	0.9
	20	89.4	96.5	650	0.9
<i>GF-G</i>	1	12.6	10.3	94	1.2
	5	33.9	35.5	241	0.9
	10	51.1	55.6	364	0.9
	20	75.7	81.3	541	0.9

The outstanding electrochemical performance of the *GF-G* electrode can be attributed to its exceptional properties described above. The electrophoretic deposition of graphene materials, by means of a water GO suspension, on the raw *GF* is a process that not only modifies the surface of the felt and its whole 3D structure, through the formation of rGO sheets on the surface of the fibers and anchored between them (see SEM images in Figure 1), but also its chemical composition by introducing C-O and C=O groups. Both types of graphene-like structures form a conductive network which facilitates the transport of electrons, thereby improving the charge transfer kinetics which is one of the steps involved in the mechanism of the vanadium reactions [35]. On the other hand the oxygenated functional groups in this hybrid material (mainly C-O groups as they are present in a higher amount) not only improved the wettability of the 3D electrode but also enhanced the number of active sites able to form -C-O-V bonds which facilitate the oxygen transfer process (another fundamental step in the mechanism widely proposed for the VO²⁺ / VO₂⁺ redox processes [7, 36, 37]). Thus it is the improved reaction rate and active surface area that explained the better electrochemical

performance of the *GF-G* electrode towards the development of the vanadium reactions. Another important factor is the increase in the capacitive current measured on this electrode before and after the redox potentials of the $\text{VO}^{2+} / \text{VO}_2^+$ processes and also in the supporting electrolyte (see Figure S7, Supporting Information), possibly due to the larger surface area of the hybrid material, which could have a positive effect on the energy efficiency of the VRFB cell with *GF-G* as positive electrode.

To obtain additional information about the $\text{VO}^{2+} / \text{VO}_2^+$ redox processes on the *GF-G* electrode, CVs at increasing scan rates (v_{scan} , between 1-20 mV s^{-1}) were recorded (Figure 4 (a)). The linear relationship between the anodic and cathodic peak currents and the square root of the scan rates tested (Figure 4 (b)) confirmed that both the VO^{2+} oxidation and the VO_2^+ reduction were mainly controlled by the diffusion of the electroactive species from/to the electrode/electrolyte interface [38].

Figure 4. (a) CVs recorded on the *GF-G* electrode at increasing v_{scan} in a 0.05 M VOSO_4 /1.0 M H_2SO_4 solution. (b) Anodic and cathodic currents measured on *GF-G* vs the square root of v_{scan} .

In addition to diffusion transport and assuming the reaction mechanism described above, the electron transfer between the electroactive vanadium species and the active sites present on the surface of the felts are also key factors influencing the electrochemical performance of the electrodes. To gain further insight into this matter (especially in relation to VO^{2+} oxidation),

EIS measurements were performed on the *GF-G* electrode and also on the other three felts under study for comparative purposes (Figure 5).

Figure 5. Nyquist plots recorded on the different graphite felt electrodes in a 0.05 M VOSO₄/1.0 M H₂SO₄ solution at 0.9 V (vs. Ag/AgCl/3.5 M KCl).

The semicircle developed in the high frequency range of the Nyquist plots represents the electron transfer step, its radius being proportional to the charge transfer resistance (R_{CT}) between the VO²⁺ and the active sites on the surface of the electrode [39]. As can be seen, there are marked differences between the *GF* and *TTGF* electrodes and those materials obtained from the EPD cell. The mentioned charge transfer resistance is much lower on both electrodes, *GF-H₂SO₄* and *GF-G*, indicating a faster electron transfer rate and thus corroborating their better electrochemical performance towards the VO²⁺ oxidation (see also Figure S8, Supporting Information).

3.3. VRFB cell evaluation

Charge/discharge experiments were conducted to investigate the suitability of the different graphite felts as electrodes in the positive side of the VRFB cell. As mentioned above, the four devices assembled only differed in their positive electrode (see Section “Single cell

tests'') so that any difference in their performances can be ascribed to the characteristics of the positive electrode selected [40].

Figure 6. Charge/discharge profiles of the four VRFB cells operating at 25 mA cm^{-2} .

Figure 6 shows the charge-discharge profiles of the four cells, recorded at a current density of 25 mA cm^{-2} . As can be seen there are significant differences in the overpotential values corresponding to their charge and discharge branches and, consequently, in their specific discharge capacities (DC , Table 4)). Thus, the VRFB cells with positive electrodes obtained using the EPD cell (*VRFB-3* with $GF-H_2SO_4$ and *VRFB-4* with $GF-G$) displayed lower overpotentials than those with GF or $TTGF$ (*VRFB-1* and *VRFB-2*, respectively) confirming their better electrochemical performances [41]. Furthermore, the overpotentials for *VRFB-4* in the corresponding charge and discharge processes are still lower than those of *VRFB-3*, suggesting an increase in the electrochemical reversibility of the VO^{2+}/VO_2^+ redox processes on the $GF-G$ electrode, a factor that positively contributes to the voltage (η_v) and coulombic (η_c) efficiency values of this battery (Table 3). Moreover the decrease in the overpotential values can be ascribed to the larger specific discharge capacity of the *VRFB-4* (up to 14.1

AhL⁻¹) indicating that the electrolyte in this battery is being better utilized [38]. As a result, *VRFB-4* showed energy efficiency (η_E) values of up to 95.8 % which resulted significantly higher than those calculated for other VRFB cells reported in the literature under comparable experimental conditions, (25 mA cm⁻²) where η_E between 80-90 % were achieved [32].

Table 3. Efficiencies and specific discharge capacities of the VRFB cells with the different graphite felts as positive electrodes.

CELL TEST	η_C (%)	η_V (%)	η_E (%)	DC (AhL ⁻¹)
<i>GF-H₂SO₄ / GF (VRFB-1)</i>	91.1	91.5	83.3	8.7
<i>GF-H₂SO₄ / TTGF (VRFB-2)</i>	98.6	90.6	89.3	10.2
<i>GF-H₂SO₄ / GF-H₂SO₄ (VRFB-3)</i>	99.5	91.1	90.5	13.0
<i>GF-H₂SO₄ / GF-G (VRFB-4)</i>	99.5	96.3	95.8	14.1

In addition the long term stability of *VRFB-4* applying consecutive charge/discharge cycles at 25 mA cm⁻² was evaluated (Figure 7). The high energy efficiency of the redox flow battery cell with *GF-G* as positive electrode remained almost unchanged, which can be considered as the first proof of the stability of the graphite felt modified with graphene material. These results, in agreement with those obtained in the CV and EIS experiments (see section 3.2) corroborate the outstanding electrochemical behavior of *GF-G* towards the vanadium redox processes. It is also worth pointing out that these results are even better than previously reported values obtained with carbon or graphite felts modified by various treatments or decorated with graphene materials [42, 43].

Figure 7. Evolution of the energy efficiency of VRFB-4 with cycling, at 25 mA cm^{-2} .

Conclusions

A graphene-modified graphite felt synthesized using a GO water suspension and EPD technology exhibited an excellent performance towards the $\text{VO}^{2+}/\text{VO}_2^+$ redox reactions in terms of electrochemical activity and kinetic reversibility. Furthermore, the use of this material as positive electrode in a laboratory scale flow device in a series of charge/discharge experiments led to an energy efficiency of 95.8 % which is markedly higher than values previously reported under the same experimental conditions. The hybrid material obtained exhibited a 3D cross-linked structure with a suitable amount of well distributed oxygenated active sites (C-O functional groups) thus increasing the wettability of the electrode and its active area towards the vanadium redox reactions. Moreover, connecting the felt fibers with the graphene-like material ensured a better charge transfer. These two factors are known to favour the widely accepted mechanism of the vanadium reactions. Thus, the modification of the felt with graphene material represents a significant step forward in the design of more effective electrode materials for developing VRFBs with enhanced performances.

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Figure Captions

Figure 1. SEM images of (a) *GF* (b) *TTGF* (c) *GF-H₂SO₄* and (d, e) *GF-G*. (f) HRTEM image of an interface region of *GF-G*.

Figure 2. Curve fitting of C1s XPS spectra of (a) *GF*, (b) *TTGF*, (c) *GF-H₂SO₄* and (d) *GF-G*.

Figure 3. CVs recorded (starting from the OCP and with a positive scan direction) in a 0.05 M VOSO₄/1.0 M H₂SO₄ solution at a scan rate of 1 mV s⁻¹ on the different graphite felt electrodes.

Figure 4. (a) CVs recorded on the *GF-G* electrode at increasing v_{scan} in a 0.05 M VOSO₄/1.0 M H₂SO₄ solution. (b) Anodic and cathodic currents measured on *GF-G* vs the square root of v_{scan} .

Figure 5. Nyquist plots recorded on the different graphite felt electrodes in a 0.05 M VOSO₄/1.0 M H₂SO₄ solution at 0.9 V (vs. Ag/AgCl/3.5 M KCl).

Figure 6. Charge/discharge profiles of the four VRFB cells operating at 25 mA cm⁻².

Figure 7. Evolution of the energy efficiency of VRFB-4 with cycling, at 25 mA cm⁻².

TABLE CAPTIONS

Table 1. Chemical composition of the graphite felts

Table 2. Electrochemical data obtained from the CVs recorded on the different graphite felt electrodes.

Table 3. Efficiencies and specific discharge capacities of the VRFB cells with the different graphite felts as positive electrodes.