

# Improvement of the electrocatalytic activity of carbon electrodes for redox flow batteries

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Presented in 2023, Instituto de Ciencia y Tecnología del Carbono INCAR-CSIC, Universidad de Oviedo, 33011 Oviedo, Spain.

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## OBJECTIVES AND NOVELTY

The development of energy storage devices with higher energy efficiency is necessary to achieve a sustainable energy system based in renewable energy sources. Vanadium redox flow batteries (VRFB) stand out among the variety of energy solutions for stationary storage, nevertheless, one of the main limiting factors of the performance of these devices are the electrodes, which need to be optimized.

The main objective of this thesis is the modification of carbon fibre felts, typically used as electrodes in VRFB, to improve their electrochemical performance towards the vanadium redox reactions occurring during battery charge and discharge. Carbon-felts are relatively inexpensive, present good electrical conductivity, are resistant to the electrolytic media normally used and are easy to handle. Their architecture also favours the contact with the electrolyte that can flow through the network of fibres. The main drawback of carbon fibre felts is the poor electrocatalytic activity of the raw carbon surfaces together with the development of secondary unwanted reactions, such as hydrogen evolution in negative electrodes or fibre oxidation in positive ones.

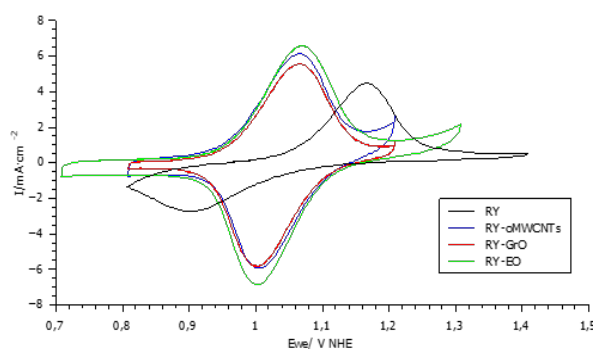
Two different pathways to improve the carbon fibre felt have been proposed in order to obtain novel, efficient and easily scale-up materials. The first method consisted of the incorporation of carbon nanomaterials (graphene materials or multiwalled carbon nanotubes) on the fibre surface by electrophoretic deposition (EPD). The second method proposed was the electrochemical modification of the carbon felt electrodes, which were submitted to electro-oxidation and electro-reduction treatments in different acidic media, seeking to study the influence of the developed oxygen containing functional groups on the electrochemical performance of the electrodes.

Another challenge faced by the scientific community working in this field is the need to define a standardized method for the electrochemical characterization of electrode materials. The limited information regarding the used experimental conditions together with the lack of similitudes on cell geometries and electrode configuration impede the comparison between different results published. In this thesis a reproducible and reliable protocol for the electrochemical characterization of carbon-felt materials has been proposed. The compression

degree of the felt and the electrode configuration setup have been studied, evaluating the influence of both parameters on the resistance and the electrochemical performance of graphitized carbon felts towards vanadium reactions redox.

## RESULTS

The comparison of the electrochemical performance between the electrodes modified with nanotubes or graphene-like materials (*RY- $\alpha$ MWCNTs* and *RY-GrO*, respectively) and an electrode modified under the same experimental conditions but without nanomaterial deposition (*RY-EO*), revealed that the key factor for the improvement of the felt electrocatalytic activity is the underlying oxidation suffered by fibres during the EPD treatment [1]. According to the results obtained, the electro-oxidized felt exhibits the best electrochemical behavior (**Figure 1**), suggesting that the improved performance shown by the electrodes modified with nanocarbons could be mainly ascribed to the structural modifications and surface chemistry enrichment of the raw fibers experienced during the electrophoretic deposition treatment (**Table 1**), in spite of SEM images confirm the nanomaterial deposition on the fibers (**Figure 2**). Although the presence of the carbon nanostructures can also positively contribute to the electrochemical response of the corresponding electrodes, it is difficult to identify their role in such improvement. The excellent performance of the electro-oxidized sample allows us to point out the relevance of electrochemical methods for the modification of carbon fibre. This simple, low-cost and easy pre-conditioning of rayon-based carbon felt is shown as a promising approach to improve the large-scale storage on VRFB.



**Figure 1.** CVs recorded on the different electrodes in 0.05M  $\text{VOSO}_4/1.0\text{M H}_2\text{SO}_4$  at scan rates of  $1 \text{ mVs}^{-1}$ .

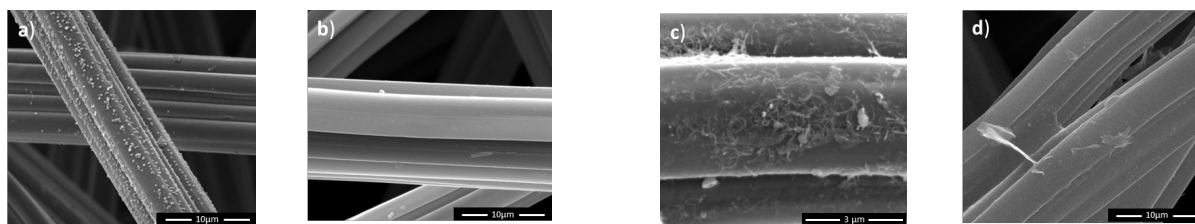


Figure 2. SEM images of RY (a), RY-EO (b), RY-oMWCNTs (c) and RY-GrO (d).

Table 1. Characteristics of the different carbon felts obtained by N<sub>2</sub> adsorption at 77 K (S<sub>BET</sub>), elemental microanalysis (O (at %)) and C1s XPS spectra (Csp<sup>2</sup> (%), Csp<sup>3</sup> (%), COH (%), C=O (%) and COOH (%)).

Samples	S <sub>BET</sub> (m <sup>2</sup> ·g <sup>-1</sup> )	O (at %)	Csp <sup>2</sup> (%)	Csp <sup>3</sup> (%)	C-OH (%)	C=O (%)	COOH (%)
RY	2	3.45	79.1	11.7	5.6	1.9	1.7
RY-EO	20	12.7	58.0	18.4	10.1	5.3	8.2
RY-oMWCNTs	37	9.9	66.7	14.9	7.0	4.1	7.3
RY-GrO	25	13.7	59.0	19.2	9.3	4.9	7.6

Aiming to further understand the role of oxygenated functional groups on the electrocatalytic activity towards vanadium faradaic processes, in a second study we investigated the influence of electro-oxidation and electro-reduction treatments performed in different acidic media (H<sub>2</sub>SO<sub>4</sub> or HNO<sub>3</sub> solutions), on their subsequent electrochemical response towards VO<sup>2+</sup>/VO<sub>2</sub><sup>+</sup> and V<sup>3+</sup>/V<sup>2+</sup> redox reactions [2]. The chemical and electrochemical properties of the modified felts were studied (Figures 3 and 4), concluding that two key parameters affect the vanadium reaction catalysis: the depth and oxidation degree of the fibres. An aggressive treatment with HNO<sub>3</sub>, a strong oxidizing agent, leads to a deep oxidation of the fibre and the development of a high

density of oxygenated functional groups, mainly C=O, which hinder the redox reactions of vanadium, especially for the faradaic reactions from the catholyte. A moderate electro-oxidation treatment in sulphuric acid provides the adequate type (mainly –OH and –COOH) and proportion oxygen functional groups to achieve the best electrochemical performance on VRFBs. A slight increment of the oxygen content has positive impact not only in the improvement of the wettability of the felt, but also has a relevant role on its electrochemical behaviour, providing available and stable active sites that promote the kinetics of the anodic/cathodic redox processes and facilitate the electron and oxygen atom transfer for the vanadium ions.

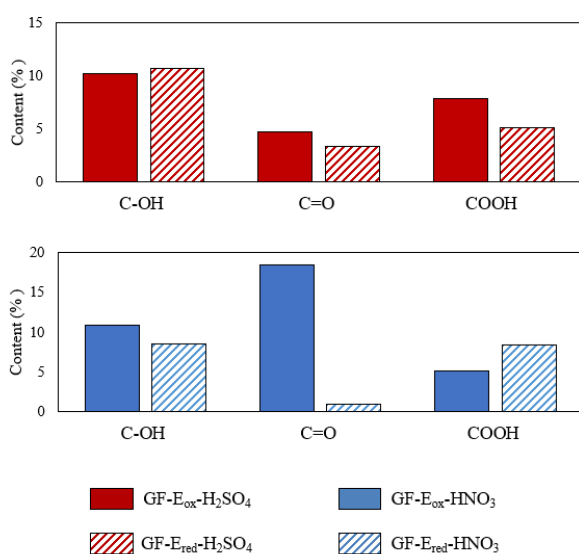
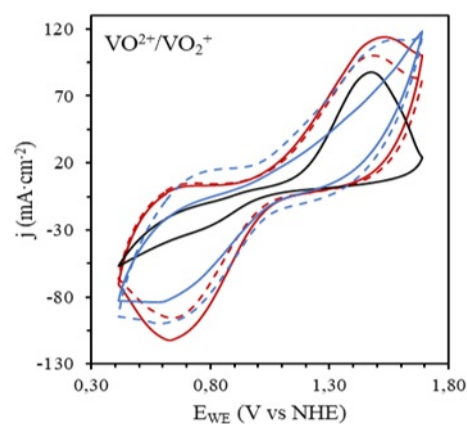


Figure 3. Evolution of the oxygen functional groups percentages determined by XPS for felts after electrooxidation (plain) and electroreduction (striped) treatments in H<sub>2</sub>SO<sub>4</sub> (a) and HNO<sub>3</sub> (b) media.



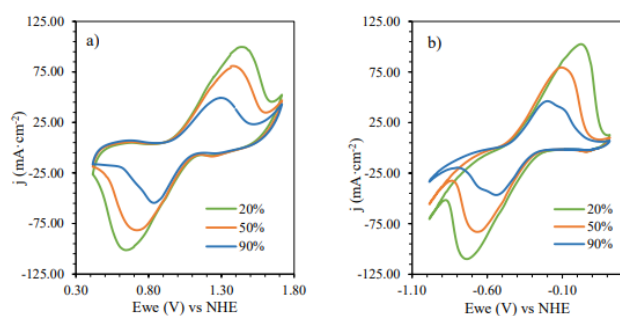
— GF — GF-E<sub>ox</sub>-H<sub>2</sub>SO<sub>4</sub> - - GF-E<sub>red</sub>-H<sub>2</sub>SO<sub>4</sub>  
— GF-E<sub>ox</sub>-HNO<sub>3</sub> - - GF-E<sub>red</sub>-HNO<sub>3</sub>

Figure 4. CVs recorded, at 50 mVs<sup>-1</sup> and towards positive potential values, on the felts electrochemically oxidized and reduced in 1.0 M H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> solutions with 0.05 M VOSO<sub>4</sub>/1.0M H<sub>2</sub>SO<sub>4</sub> as electrolyte. CVs corresponding to the starting material (GF) were also included for comparative purposes.

Regarding the appropriate characterization of the modified materials, our last study discusses the influence of two key parameters (the compression percentage of the working electrode and the relative position of the three electrodes in the whole cell set-up) on cyclic voltammetry and impedance measurements of carbon-based felts towards vanadium redox reactions [3] demonstrating the impact of both, the felt compression percentage (CP) (**Figure 5**) and the relative position of the three electrodes setting up the cell (WE, RE and CE) used for carrying out the electrochemical experiments under static conditions. Regarding the felt CP, researchers have to find a compromise between avoiding electrolyte leakages and ensuring an appropriate current collector/WE/electrolyte contact, thus providing quality electrochemical signals and data (optimized at CP = 50 % in this work). On the other hand, when assessing the most suitable allocation of the electrodes set up of the electrochemical cell, the relative positions of both, the RE and the CE with respect to the WE have to be also evaluated and fixed, as this parameter also has a marked impact on the electrochemical measurements. Thus, both of them should be placed close to the WE in order to decrease the uncompensated electrical resistance, which negatively impacts of the development of the redox processes of interest thus underestimating the performance of the tested electrodes. The results obtained provide reliable information which could be useful when planning electrochemical tests for assessing active electrode materials towards vanadium redox reactions (or even other chemistries).

[3] García-Alcalde, L., González, Z., Concheso, A., Blanco, C., Santamaría, R., Impact of electrochemical cells configuration on a reliable assessment of active electrode materials for Vanadium Redox Flow Batteries, *Electrochimica Acta*, 2022; 432, 141225.

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**Figure 5.** CVs recorded on TTGF electrodes at three different compression percentages, in a 0.05M  $\text{VOSO}_4/1.0\text{M}$   $\text{H}_2\text{SO}_4$  solution at scan rates of  $20 \text{ mVs}^{-1}$ , for  $\text{VO}_2^+/\text{VO}_2^+$  (a) and  $\text{V}^{3+}/\text{V}^{2+}$  (b) redox reactions.

## RELATED PUBLICATIONS

[1] García-Alcalde, L., González, Z., Barreda, D., G. Rocha, V., Blanco, C., Santamaría, R., Unraveling the relevance of carbon felts surface modification during electrophoretic deposition of nanocarbons on their performance as electrodes for the  $\text{VO}_2^+/\text{VO}_2^+$  redox couple, *Applied Surface Science*, 2021; 569, 151095.

[2] García-Alcalde, L., Concheso, A., G. Rocha, V., Blanco, C., Santamaría, R., Z. González, Influence of the oxygen surface functionalities introduced by electrochemical treatment on the behavior of graphite felt electrodes in VRFBs, *Batteries*, 2022; 8 281.