

Highly electrocatalytic flexible nanofiber for improved vanadium-based redox flow batteries cathode electrodes

Cristina Flox,^{*a} Cristian Fàbrega,^a Teresa Andreu^a, Alex Morata^a, Marcel Skoumal^a, Javier Rubio-Garcia^a and Juan Ramón Morante^{a,b}

^a *Departament of Advanced Materials for Energy, Catalonia Institute for Energy Research (IREC), c/Jardins de les Dones de Negre, 1, 2nd floor, 08930 Sant Adrià del Besòs, Spain. Fax: +34 9335 63802; Tel: +34 9335 62615; E-mail: cflox@irec.cat*

^b *Departament d'Electrònica, Universitat de Barcelona, c/Martí i Franquès 1, 08028 Barcelona, Spain.*

Synthesis of as-carbonized NFs

As-prepared spinning solution was performed using polyacrylonitrile (PAN) powders ($M_w = 150\,000\text{ g mol}^{-1}$, Sigma Aldrich) and N,N-dimethylformamide (DMF) as a solvent (Panreac) without further purification. The 10wt.% PAN in DMF solution was prepared at 80 °C under constant stirring for 2 h until complete dissolution. The solution was then filled in the syringe terminated by stainless steel needle ($\varnothing_{\text{int}} : 0.6\text{ mm}$; $\varnothing_{\text{ext}} : 0.9\text{ mm}$) and was placed in an electrospinning equipment (Nanotechnology Solutions, Yflow[®]) applying a flow rate of 2.2 ml h^{-1} .

The electrospinning process was carried out by applying a high positive voltage to the polymer solution via the syringe needle tip and the collector. The electrospun fibers were collected as a thin web by the collector wrapped in aluminum foil. The electric field (E), distance (d) between the needle tip to the collector and collection time (t) are shown in the table S1 for each NF synthesized. The electrospinning process was very stable and was carried out with continuously control of the Taylor cone by means of a camera (Figure S1).

Table S1. Experimental condition for all as-electrospun NFs prepared

As-electrospun NFs	Collector type	Rotating rate (r.p.m.)	E(kV cm ⁻¹)	d (cm)	t (h)
NF1	plane		1.3	11	3
NF2	Rotating	500	1.5	8	9
NF3	Rotating with with a motion along the rotating axis	500	1.5	8	24



Figure S1. Electrospinning equipment (Nanotechnology Solutions, Yflow[®]).

The conversion of each PAN as- electrospun NFs to carbon NFs involves thermal treatments (i.e. stabilization and carbonization processes) using a conventional tubular furnace. The oxidative stabilization of as-electrospun NF process was carried out at 270° C for 7.30 h under air atmosphere controlled (see the TGA results) in order to induce dimensional stability of the carbon NF. This process is accompanied by a change in color from white to reddish-brown. Finally, when the as-stabilized NFs web was thermally treated at 800 or 1000° C in nitrogen atmosphere for 1 h, the black as-carbonized NFs was obtained exhibiting a high carbon yield (80-90%).

Thermogravimetric analysis was carried out with PerkinElmer (TGA 4000) analyzer. The constant weight loss during 7 h at 270 °C in air atmosphere of all-NFs synthesized was evident and shown in Figure S2, indicating the well-stabilized process was achieved.

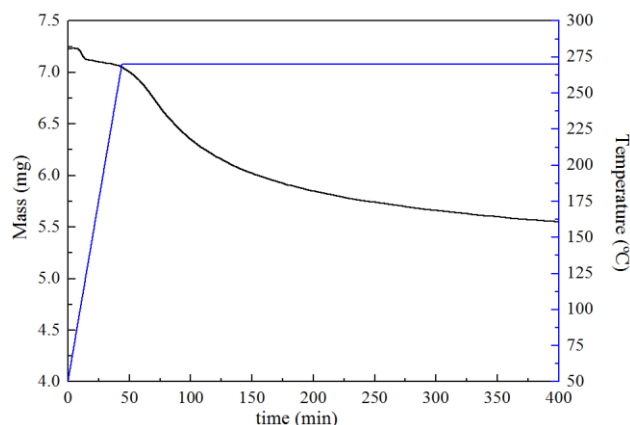


Figure S2. TGA analysis of the as-electrospun NFs in air atmosphere.

Characterization Techniques

-The morphology of the NF electrodes was examined using a Field Emission Scanning Electron Microscope (FE-SEM) Zeiss Serie Auriga.

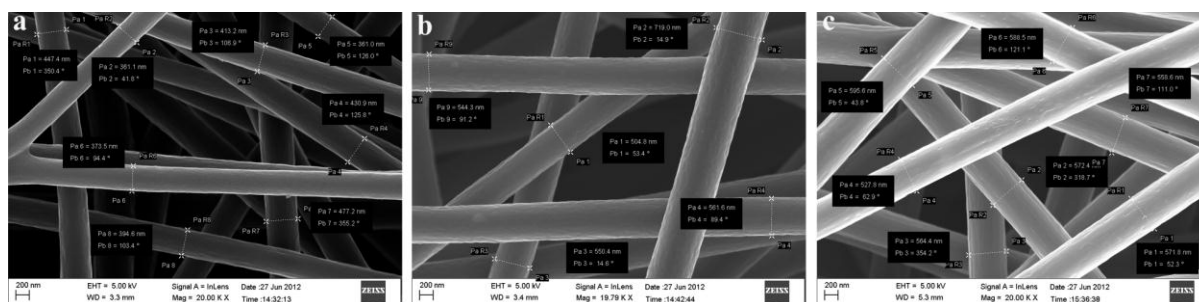


Figure S3. Diameter distribution of as-carbonized PC (a), RC (b) and PRC (c) treated at 1000 °C.

-Cross section of all NF electrodes determined by FE-SEM SEM being 28.83, 39.16, 51.18 μm for the PC, RC and PRC electrode respectively.

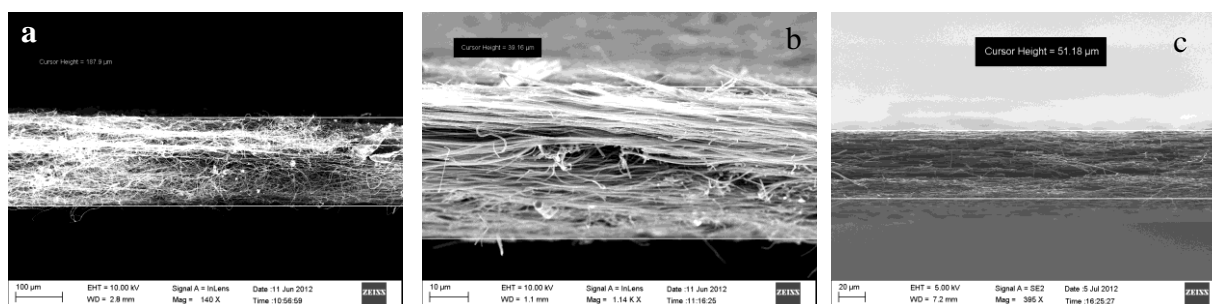


Figure S4. Cross section of PC (a), RC (b) and PRC (c) electrodes

- Electrical conductivity measurement was determined by means of reverse of resistivity. The resistivity was determined by in-plane resistance and cross-section measurements. The in-plane resistance was measured in parallel and perpendicular direction to the alignment of the RC and PRC-NF using 4-probe test equipment (EverBeig SP4). The direction of the maximum and minimum conductivity axes must be known to apply this technique. Those perpendicular axes were determined by measuring the resistance of the samples at different angles. Measurements on PAN felts were carried out in 5x5 cm samples with a constant thickness of 0.5 cm. For the PC-NF and PAN-felt Van der Pauw method was used to measure the in-plane resistivity conductivity of the samples. No compressive force was applied for the PAN-felt electrode measurement. A high anisotropy in conductivity was observed in some cases, most probably due to the fiber alignment. For this reason, the measurements were carried out following the procedure described by Kazani, G *et al.* (Textile Research Journal, 2011, 0, 1) and Price W, et al. (Journal of Physics D: Applied Physics, 1972, 5, 1127).

- The chemical composition changes of the surface of the d-PAN electrodes were analyzed by X-ray photoelectron spectroscopy (XPS) using a PHI instrument model 5773 Multitechnique with Al K α radiation (1486.6 eV).

Table S2. Relative quantities (%) of C-groups for NF.

	PC-800	RC-1000
N-pyridinic (%)	64.6	32.1
N-pyrrolic (%)	35.4	10.9
N-quaternary (%)	-	53.3
N-oxide (%)	-	3.8

Table S3. Relative quantities (%) of N-groups for NF

	PC-800	RC-1000
C-sp2 (%)	45.6	60.2
C-sp3 (%)	40.8	24.0
C-Carbonyl (%)	10.9	9.5
C-Ketonic (%)	-	1.2
C-Carboxyl	2.7	5.1

- Electrochemical characterization was carried out in a standard three-electrode glass cell with nitrogen gas used to deaerate all the solutions. The Hg/Hg₂SO₄/K₂SO₄ (sat.) electrode was used as the reference electrode, being placed into a Luggin capillary, and a platinum wire was employed as the counter electrode. Each electrode was used as working electrode with 1 and 1.5 cm² geometric area for the NF and PAN-felt (thickness 5 mm), respectively. 30 mL of 0.5 mol dm⁻³ VOSO₄ (Alfa Aesar) solution in 3 mol dm⁻³ H₂SO₄ (Sigma Aldrich) were used as the aqueous electrolyte, being all the electrodes soaked into it for 24 h before use. Each experiment was repeated at least five times to verify the repeatability.

Carbonization temperature influence on electrocatalytic activity towards positive half-cell in VRFB

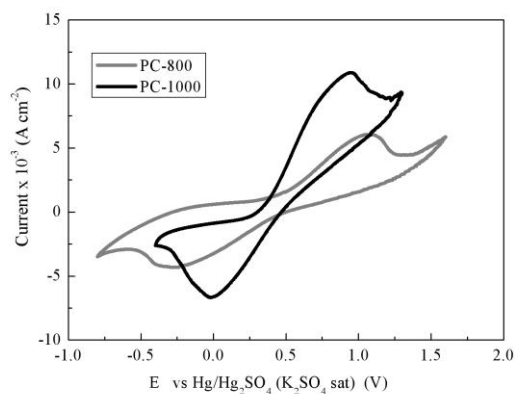


Figure S5. CVs recorded for PC-800 and PC-1000.

Electrochemical activity of the PAN-felt electrode towards the $\text{VO}_2^+/\text{VO}^{2+}$ redox couples under 5mV s^{-1}

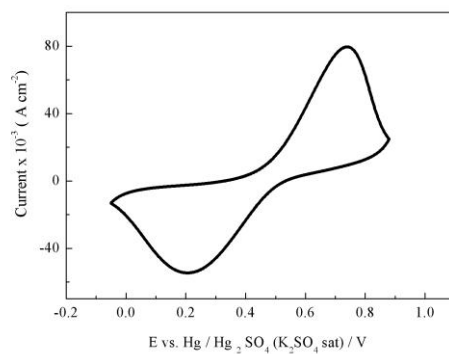


Figure S6. CV at 5mV s^{-1} of commercial PAN felt electrode in $0.5\text{ mol dm}^{-3}\text{VO}_2^+$ solution in $3\text{ mol dm}^{-3}\text{H}_2\text{SO}_4$.

The electrochemical parameters of the RC-1000 electrode towards $\text{VO}_2^+/\text{VO}^{2+}$ redox couples under different scan rates

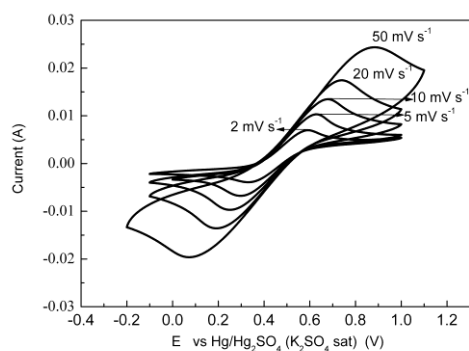


Figure S7. Cyclic voltammograms of the RC-1000°C electrode at different scan rates

Table S4. Electrochemical parameters obtained from Fig.S7 for RC-1000

Scan rate (mV s^{-1})	I_{pa}/I_{pc}	ΔE
50	1.06	0.80
20	1.09	0.55
10	1.10	0.42
5	1.13	0.34
2	1.07	0.26

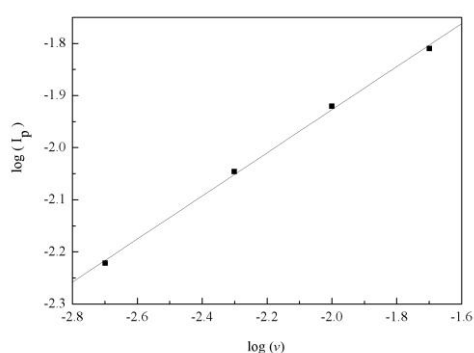


Figure S8 $\log(I_p)$: anodic peak current) vs. $\log(v)$: scan rate) for RC-1000 electrode.

A linear relationship was obtained with slope values of 0.42 for RC- 1000 electrode. Ideally, the slope should approach 0.50 under semi-infinite diffusion conditions where the diffusion of vanadium ions from bulk solution to the electrode surface is rate limiting. This small deviation from the theoretical 0.5 value can be explained by the nature of the electrodes analyzed which is porous and could introduce deviations due to different diffusion gradients on the surface of the electrode. Also, the Randles-Sevcik equation is adequate to be used for diluted solutions. Nevertheless, a very good linearity was observed for all studied system.

Electrochemical impedance spectroscopy measurement towards positive half-cell in VRFB

Electrochemical impedance spectroscopy (EIS) measurements were performed by applying an AC voltage of 5 mV amplitude in the frequency range of 0.1-100 kHz at room temperature.

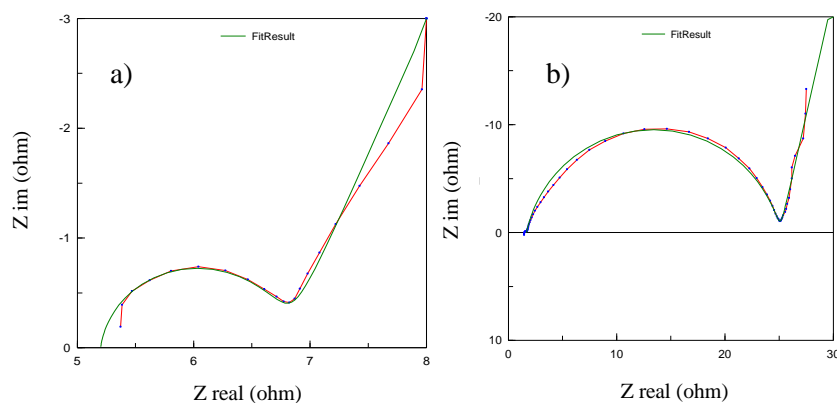


Figure S9. Nyquist spectra of electrodes obtained in $0.5 \text{ mol L}^{-1} \text{ VOSO}_4$ and $3 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solutions at anodic potentials of (a) RC-1000 and (b) PAN- felt.

FE-SEM images of the NFs showing the porosity of the electrode

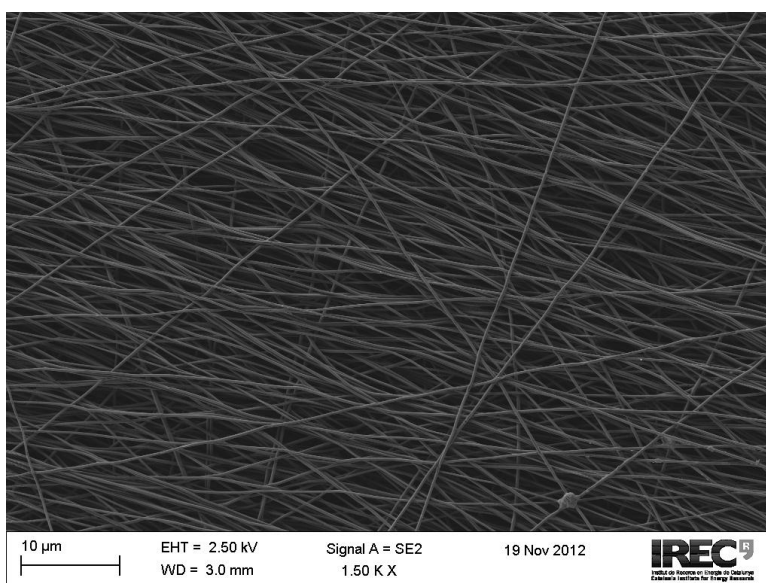


Figure S10. FE-SEM image of the PRC-1000 electrode.