

Supplementary information

Short thermal treatments of carbon felts for copper-based redox flow batteries.

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1. Resistivity measurements

The electrical resistivity of carbon felts was measured with a two-probe technique. The sample (3.1 mm thickness) was placed between two PTFE spacers. The electrical contact was taken with Cu strips. Different compressions were achieved by placing calibrated weights on the samples. The spacers allow avoiding short circuits with the calibrated weights. After applying the load, a current of 10 mA was applied. The sample was left 5 minutes before taking the voltage value with a multimeter. The electrical resistivity of the materials was obtained according to Ohm's law and the geometry of the measurement system.

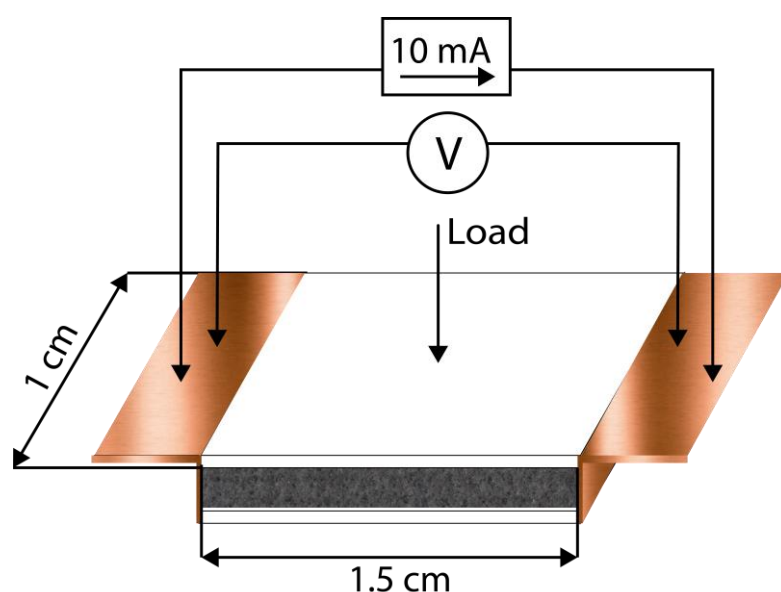


Figure S1. Experimental apparatus for resistivity measurements at different compression.

2. FTIR spectra

The spectra of rayon-based carbon felt before and after the thermal treatment are reported in Figure S2a. The spectra exhibit a broad band at 3434 cm^{-1} due to the O-H vibration, bands at 2919 and 2848 cm^{-1} of C-H stretching. At 1736 and 1638 cm^{-1} are present the C=O and C=C stretching followed by the -CH bending at 1370 cm^{-1} . At wavenumber between 1000 cm^{-1} and 1300 cm^{-1} are present the vibration of C-O and C-C.

After the thermal treatment, the material presents a decrease of intensity of C=C vibrations and an increase of the C=O vibration intensity. Thus, the thermal treatment in air results in an oxygen-enrichment of the material. In figure S2b, the FTIR spectra of the PAN-based carbon felts C=C band

decrease with the thermal treatment while the CH₂ bending, C-C stretching, and C-H stretching increase. Also, the C-O and C=O increase with respect to the C=C band with the thermal treatment. For PAN-based CF, XPS analyses are also reported in Figure 3.

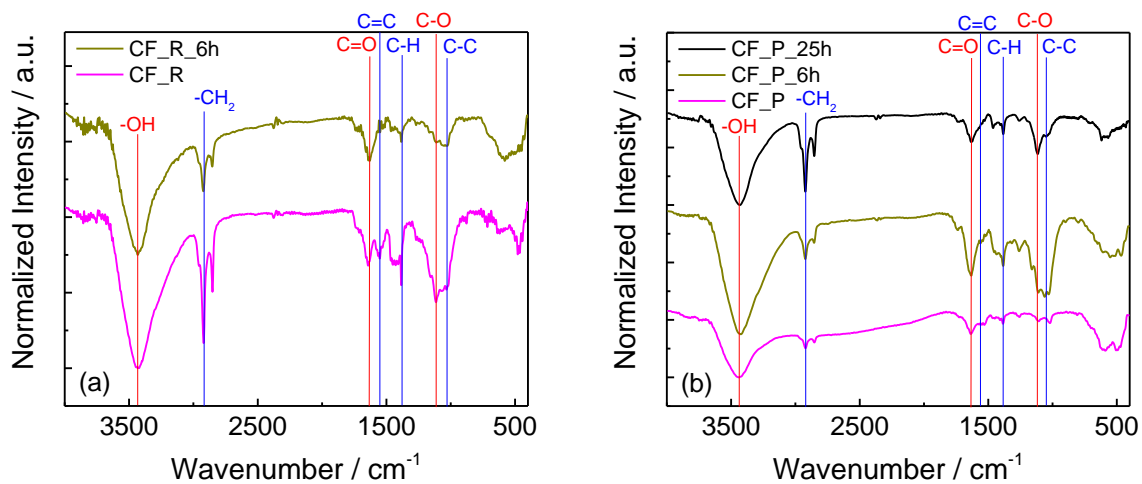


Figure S2. FTIR spectra of (a) CF_R and CF_R_6h, and (b) CF_P and CF_P_6h and CF_P_25h.

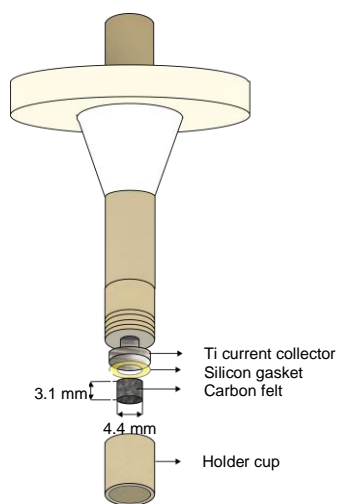


Figure S3. Electrode holder of conventional cell.

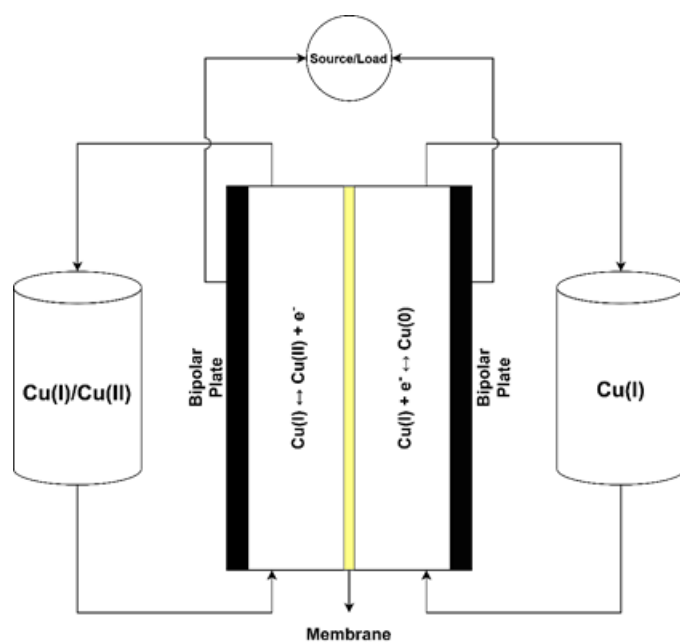
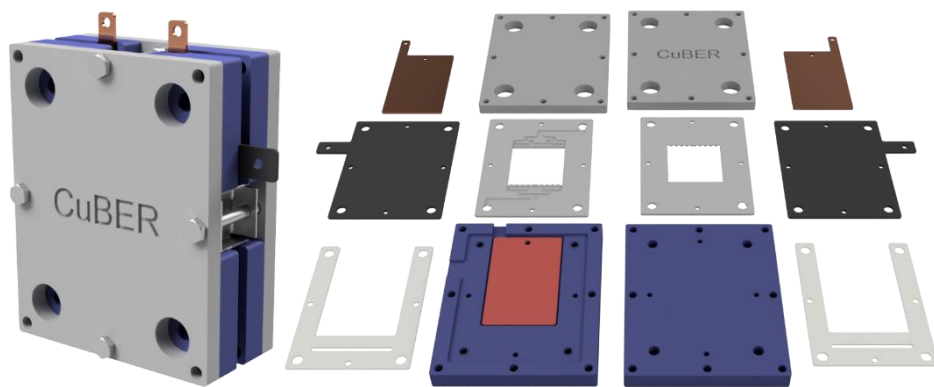


Figure S4. Redox flow cell

3. XPS spectra

In Figure S5 the full survey XPS spectra of CF_P, CF_P_6h, and CF_P_25h shows the characteristic peaks of C1s and O1s at 284 eV and 532 eV, respectively. Increasing the treatment duration, the signal relative at the O1s increases indicating the higher presence of oxygen groups in the material.

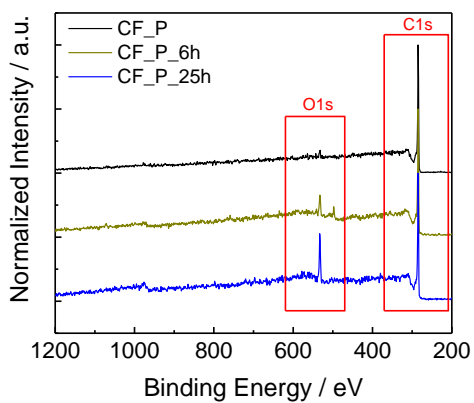


Figure S5. XPS survey spectra of polyacrylonitrile-based carbon felts.

4. Cyclic Voltammetry in conventional three-electrode cell

In concentrated solution, the higher density and viscosity permit to obtain some voltammetric cycles also with CF_R and CF_R_6h before the electrode loses the electrical contact with the current collector, as it happens with more diluted and, hence, less viscous solutions. The CVs on rayon-based carbon felts in concentrated solution are reported in Figure S6. The CF_R displays a resistive behaviour similar to CF_P, and CF_R_6h shows peak separation similar to CF_P_6h. The lower currents of CF_R_6h are probably due to the lowest effective area, given the highest mass lost with 6h-thermal activation. The electrochemical tests confirm that polyacrylonitrile-based carbon felts give better results than rayon-based felts.

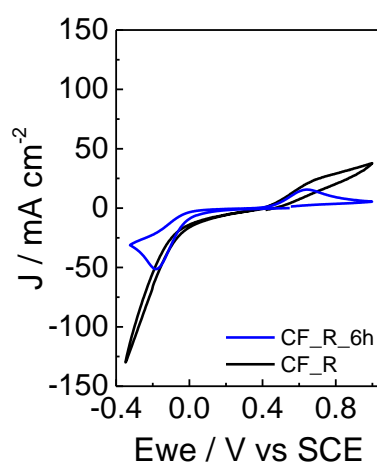


Figure S6. CVs at 10 mV s^{-1} and 40°C of pristine, and thermally treated rayon-based carbon felts in $2 \text{ M CuCl}_2 - 6 \text{ M HCl}$ solution.

Figure S7 reports stability test by repeated CVs (50 cycles) of CF_P (a), CF_P_6h (b) and CF_P_25h (c) to evidence if poisoning phenomena occur over cycling in presence of chloride ions. The CVs were carried out at 100 mV s^{-1} at 40°C in $5 \text{ mM CuCl}_2 - 1 \text{ M HCl}$ solution.

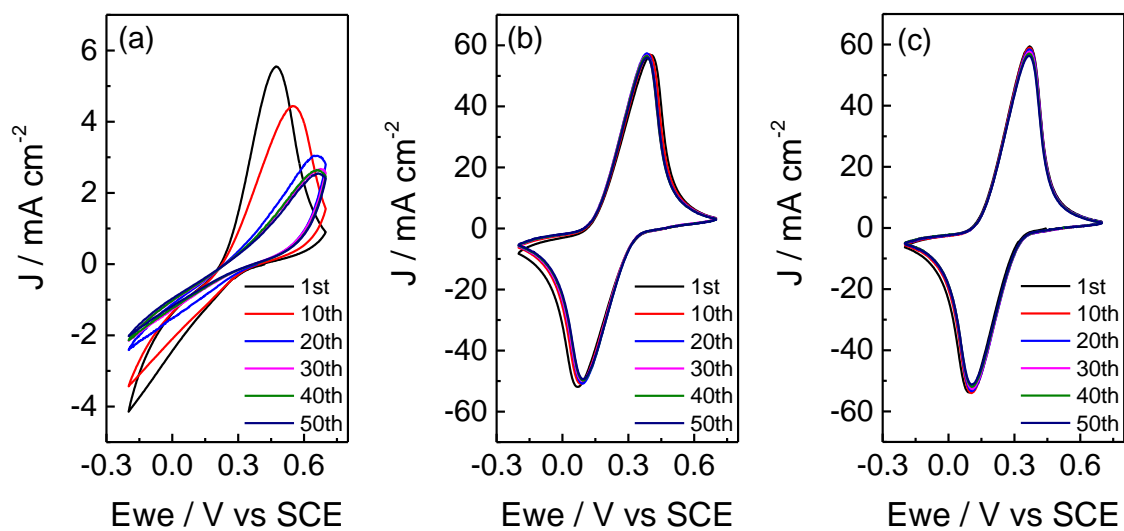


Figure S7. CVs in 5 mM CuCl_2 – 1 M HCl at 100 mV s^{-1} and $40 \text{ }^\circ\text{C}$ of CF_P (a), CF_P_6h (b), and CF_P_25h (c).