

Carbon flow electrodes for continuous operation of capacitive deionization and capacitive mixing energy generation

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Electronic Supplementary Information

1. Nitrogen Gas Sorption Analysis of Activated Carbon

Prior to gas sorption measurements, the activated carbon sample was kept under vacuum (1 mbar) at 150 °C for 16 h. The porosity was analyzed using N₂ gas sorption at -196 °C up to 1 P/P₀ using an Autosorb iQ MP (Quantachrome Instruments, Germany). BET SSA values were calculated using the multipoint-BET method in the linear range from 0.01-0.20 P/P₀.¹ As seen from **Fig. S1A**, the shape of the YP50-F isotherm is of type I (according to IUPAC classification), indicating dominant presence of micropores (i.e., < 2nm). Total pore volumes were derived from the cumulative pore volume using the quenched solid density functional theory (QSDFT).² A model assuming slit-shaped pores was used to obtain pore size distribution data of activated carbon used in this study, see **Fig. S1B**.

2. Raman Spectroscopy of the Activated Carbon

Raman spectroscopy was carried out on an inVia Raman Spectrometer (Renishaw) using an excitation wavelength of 514 nm with ≤ 2 mW output power on the sample and a 50x magnification objective lens (numeric aperture: 0.75). The focus plane spot size of the laser beam was approximately 2 μ m and the spectral resolution ranged from 0.8 to 1.3 cm⁻¹ within the studied Raman shift range using a grating of 2400 lines/mm.

The Raman spectra showed a typical spectrum for amorphous carbon, with various degrees of ordering, see **Fig. S1C**.

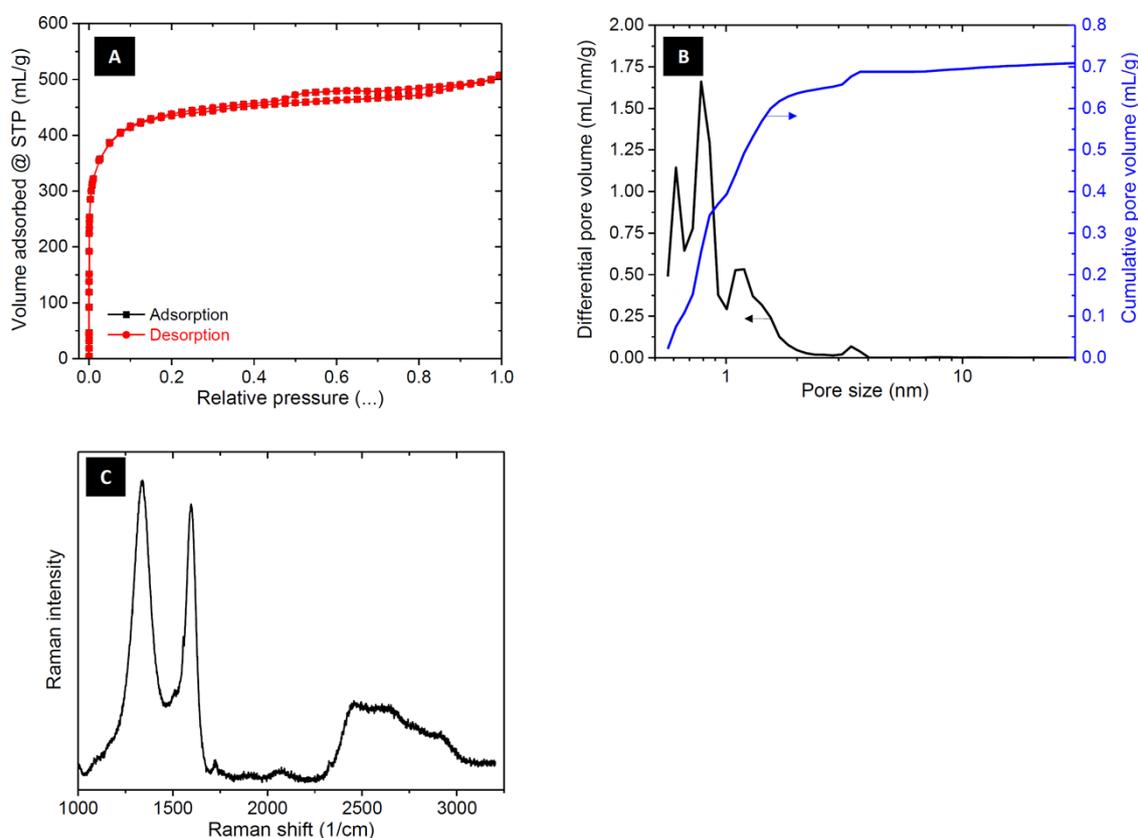


Fig. S1. Characterization of the Kuraray YP50-F activated carbon sample employed in this work. a) Nitrogen gas sorption isotherm, b) cumulative pore size distribution, and c) Raman spectra.

2. Preparation and chemical modification of PE//p(St-co-DVB) capillaries

Low density polyethylene pellets were swollen using the mixture of styrene and divinylbenzene containing dissolved benzoyl peroxide and subjected to interpolymerization process using Brabender mixer at 90 °C for 5 h. Weight ratio of polyethylene to styrene/divinylbenzene was kept at 7:3. Fixed amount of crosslinker (2 wt%) and initiator (1 wt%) was used in relation to styrene. After completing the process, the modified pellets were homogenated in an one-screw extruder at 150 °C and cut to the 5 mm pellets. The cylindrical shape of the interpolymer was formed in the next extruder equipped with a suitable die.³ Next, chemical modification was carried out by soaking cylindrical capillaries in 20 % solution of chlorosulfonic acid in dichloroethane for 3 h. After the chlorosulfonation process, dichloroethane, dioxane and methanol were used for washing. In the following step capillaries were soaked for 24 h at room temperature either in 20 % ethelenedimanie (EDA) in dioxane to obtain anion exchange properties or in 20 % NaOH in water to obtain membranes with cation exchange properties. In the next step ion-exchange membranes were washed with water and alternatively immersed in 0.5 M solutions of NaOH and HCl for 30 min. In order to preserve ion exchange properties both types of membranes were soaked in 50:50 water:glycerol solution overnight and dried at room temperature. Two types of ion-exchange membranes were obtained: CEM with sulfonic groups and AEM with amido-amine groups, see **Table 1**. The preparation of the AEM used in this study does not use harmful reactants, see Ref. ⁴, where interpolymer capillaries were chloromethylated by chloromethyl methyl ether in presence of SnCl₄ catalyst. In addition, the number of modification steps is significantly reduced as chlorosulfonated derivative can be used for preparation of either CEMs or AEMs.

Table. 1 Characteristics of the cylindrical ion exchange membranes.

Membrane	Ion-exchange capacity (mmol/g)	Water content (%)	Outer diameter (mm)	Wall thickness (µm)
Cation exchange (sulfonic groups)	2.59 - 2.62	50-58	2.3 - 2.5	150
Anion exchange (amidoamine groups)	1.17 - 1.22	21-27	2.3 - 2.5	150

3. Measurements of the carbon slurry electrical conductivity

A resistive flow-through cell was used to characterize the electrical conductivity of carbon slurry, see **Fig. S2**. This cell consisted of two titanium plates placed 4.4 mm apart, with each of the Ti electrodes having equal size ($a_{\text{plate}} = 5.6 \text{ cm}^2$). This cell allowed us to study the influence of carbon content on the electrical conductivity during flow cell operation.

In short, measurement procedure was based on applying constant cell voltage, $V_{\text{cell}} = 50 \text{ mV}$, for the duration of $t = 600 \text{ s}$ and measuring the resulting electrical current I_{slurry} (average value measured in the period of 500 to 600 s was used in Eq. 1). Next, carbon slurry electrical conductivity was calculated according to

$$\sigma = \frac{I_{\text{slurry}} - I_{\text{water}}}{V_{\text{cell}}} \cdot \frac{d_{\text{plate}}}{a_{\text{plate}}} \quad (\text{S1})$$

where I_{water} refers to current value when no carbon particles were present in a solution and where d_{plate} and a_{plate} are the distance between the plates and area of one plate respectively. Water conductivity measured at $V_{\text{cell}} = 50 \text{ mV}$ was equal to 0.04 mS/cm . We had not expected such a large electrical conductivity of the water. Apparently, some faradaic reactions take place, even at the cell voltage of 50 mV .

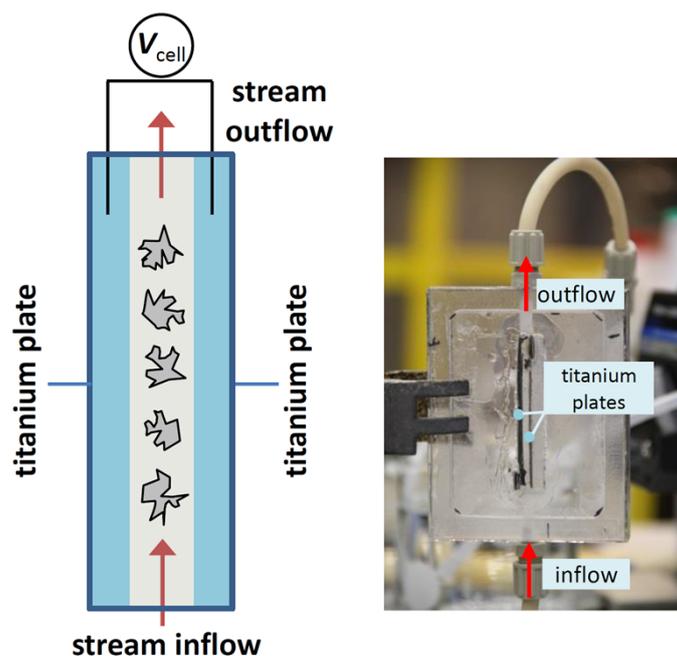


Fig. S2. Schematic view and image of the set-up used to measure electrical conductivity of a carbon slurry.

4. Measurements of the carbon slurry viscosity

Viscosity analysis of the carbon flow electrodes was performed using a modular compact rheometer (Physica MCR 300, Austria) in a rotational concentric cylinder at room temperature. All measurements were performed using as an electrolyte 100 mM NaCl solution.

Briefly, **Fig. S3A** indicates that with increased carbon mass loading, flow characteristics of carbon slurries are changed. With increased shear rate, decrease in the viscosity for all tested carbon slurries was observed. Moreover, significant increase of a flow carbon electrode viscosity at relatively small shear rates was observed for carbon loading higher than 15 wt%. This may be the result from strong particle-particle interactions occurring at low shear rates. Also, we see in **Fig. S3B** a very strong increase in viscosity when using 100 mM of NaCl instead of DI water while keeping the mass loading of carbon particles constant; this increase is enhanced when increasing the weight percent of carbon.

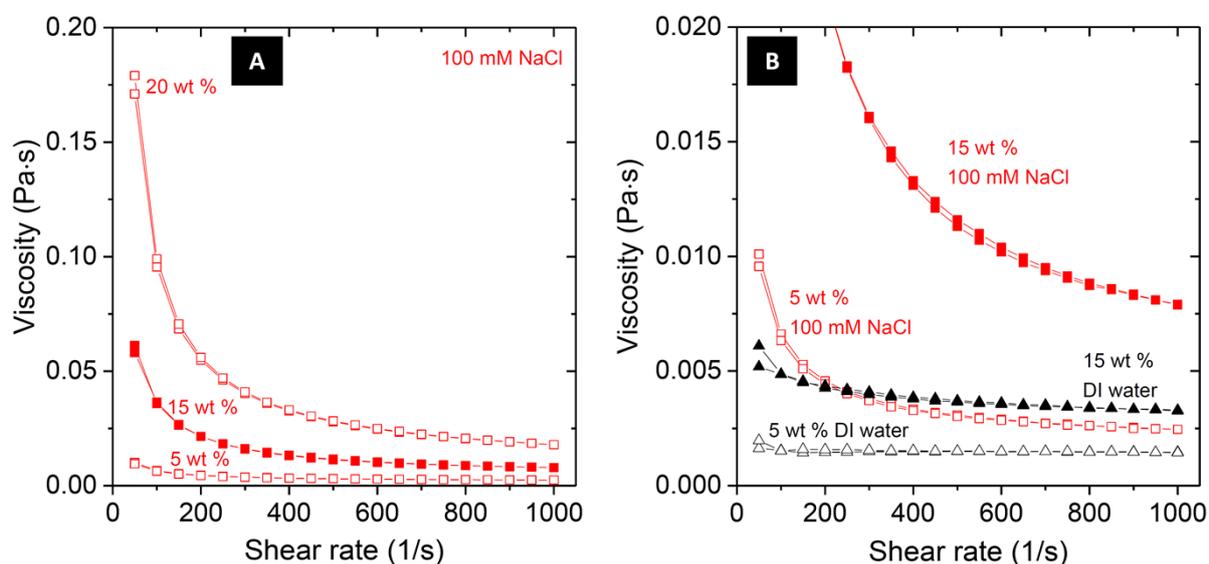


Fig. S3. Viscosity versus shear rate of carbon slurries with different carbon mass loadings and electrolyte composition.

4. CDI performance stability

CDI was operated in continuous mode using different amounts of carbon loading. After an initial run-in phase (ca. 20 min), all carbon loadings yielded a stable performance (tested for a total of 60 min).

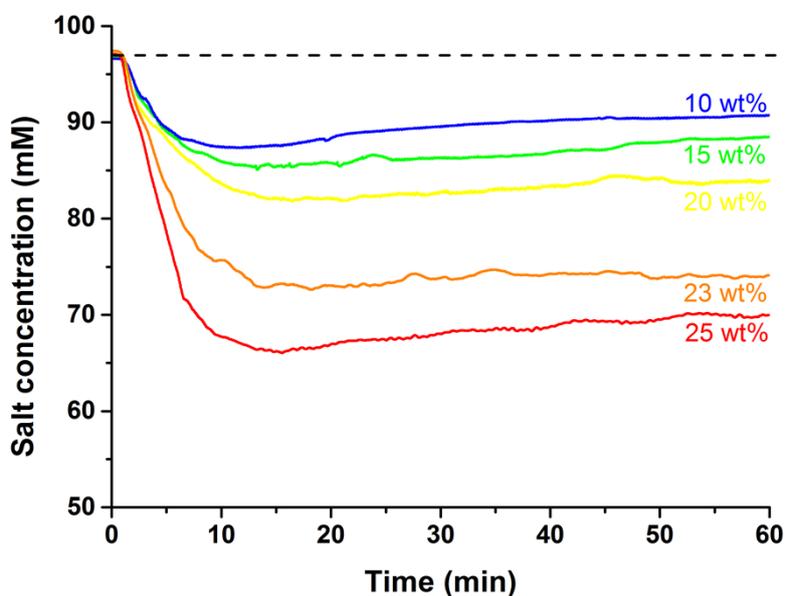


Fig. S4. Salt concentration versus time showing the performance stability when using different carbon mass loadings for continuous mode CDI.

References

1. British Standards, BS ISO 9277 Determination of the specific surface area of solids by gas adsorption - BET method, 2010.
2. P. I. Ravikovitch and A. V. Neimark, *Langmuir*, 2006, **22**, 11171-11179.
3. G. Pożniak and W. Trochimczuk, *Die Angewandte Makromolekulare Chemie*, 1984, **127**, 171-186.
4. G. Pożniak and W. Trochimczuk, *Journal of Membrane Science*, 1990, **49**, 55-68.