Supplementary Materials

Determination of Battery Separator Permeability by Scanning Electrochemical Microscopy

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Figure S1 - Finite element simulation with COMSOL

Finite element simulation with COMSOL were performed to obtain a quantitative description of the impact of SPEEK modification on permeability to copper cation of Daramic membranes. We obtained a range of diffusion coefficient constants, *D*, by simulating SECM PSCs at 8 and 24 hours.

The geometry of the electrochemical cell was simulated as showed in **Figure S1A**, with the height of the membrane, represented as the rectangle in the middle of the upper and lower compartments, taken from the dimension of the wet membranes, Dar or Dar-SP100, as reported in **Table 1**. The mesh of the model was obtained as detailed in the Materials and Methods section employing the meshing function of COMSOL and adjusted to get continuous simulated concentration profiles. Meshing used for both Dar and Dar-SP100 separators is shown in **Figure S1B.**Finite element simulation was obtained at different time points and copper concentration profiles extracted along the coordinates of the red line in **Figure S1C**; no flux as boundaries conditions was set for the boundaries of the geometrical model of the cell, as depicted with blue lines in **Figure S1D**.

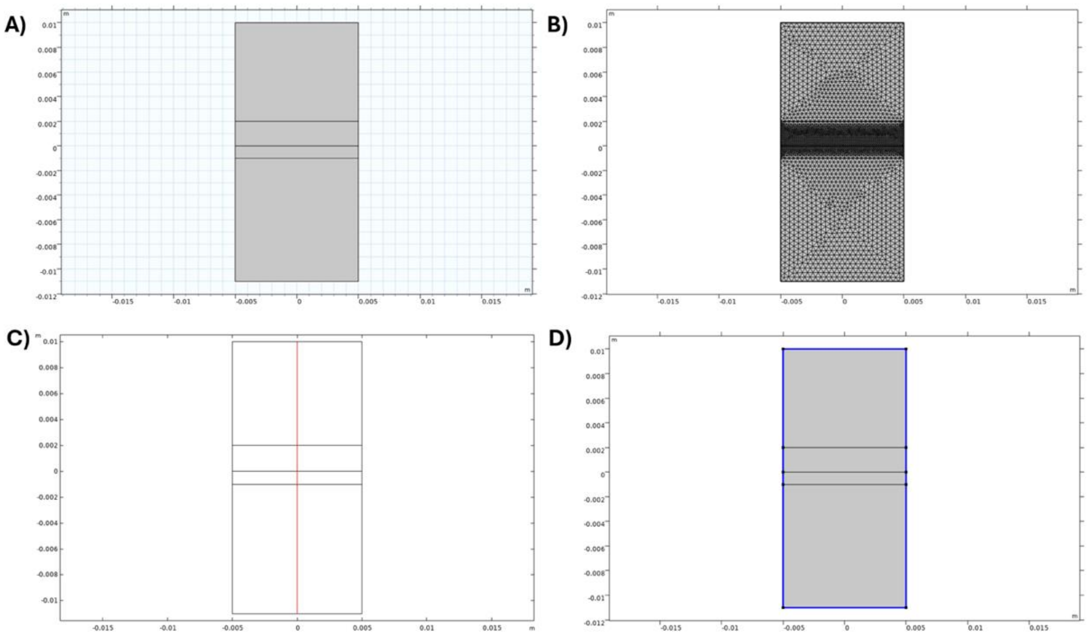

Figure S1 – Geometrical model of electrochemical cell employed in finite element simulation with COMSOL. **(A)** Upper and lower compartments were represented as 10 mm side squares divided by a rectangle, the separator, with the height as measured and reported in Table 1. In the upper compartment is shown the geometry of the refinement region, with a height of 2 mm and in contact with one side of the separator. (**B**) Meshing employed for the different compartments and for the refinement region. **(C)** The red line defines the coordinates at which concentration profiles were extracted to study simulated PSC. **(D)** Boundary conditions: blue lines highlight boundaries with no flux as set in the COMSOL simulation.

Figure S2 – Cu(II) concentration in bulk solution

To have a more impactful visualization of the copper concentration, the current recorded in the approach curve can be correlated to the active species concentration by **Equation S1**

$$i = 4nFrD_{Cu(II)}C^{O}_{Cu(II)} \qquad (S1)$$

where *n* is the number of electrons, *F* is the Faraday constant, *r* is the microelectrode radius, $D_{Cu(II)}$ is the diffusion coefficient ($1.2 \cdot 10^{-9}$ m^2/s) [1] and $C^{O}_{Cu(II)}$ is copper concentration. The copper concentration was verified spectroscopically to assess the diffusion coefficient used. The absorbance at 870 nm with a Perkin Elmer Lambda19 UV/Vis/NIR Spectrophotometer (PerkinElmer, UK) in quartz cuvettes with 1 mm optical path (OP). Absorbance and concentration values are reported in **Table S1**.

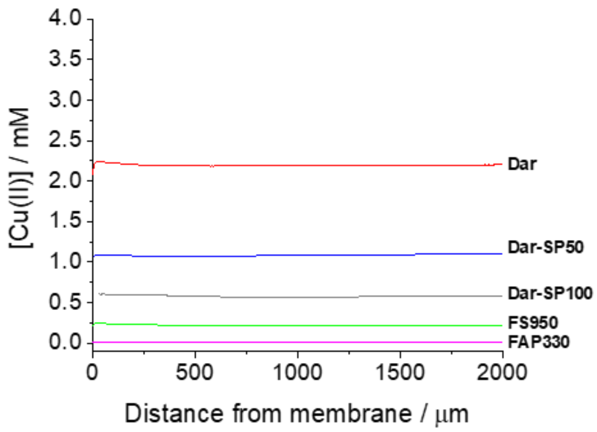

Figure S2 – PSC of a 10 µm Pt microelectrode in calcium chloride solution approaching the different tested membranes at 24 hours after assembling the cell.

Membranes	A	$[Cu(II)]_{opt}$ mM	$[Cu(II)]_{SECM}$ mM
FS 950	0.014	0.28	0.25
FAP330	/	/	0.02
DAR	0.116	2.14	2.21
DAR-SP50	0.140	2.80	2.70
DAR-SP100	0.055	1.10	1.08

Table S1. Copper concentrations $[Cu(II)]_{SECM}$ in the upper part of the SECM cell during the experiments after 24 hours obtained from the approach curves (500 µm from the membrane) and concentration $[Cu(II)]_{opt}$ values obtained from absorbance at 870 nm.

Figure S3 – S4 - Contact angles of the investigated membranes

Membrane wettability is one essential aspect of a well-performing membrane in an electrochemical cell. Ideally, in RFBs, the membrane should be wettable and ionic conductive for the charge carriers. Thus, the best membrane, being selective, should be highly compatible with aqueous systems. Wettability was evaluated by contact angle measurement, where the angle between a water droplet and the membrane surface is monitored by a camera (**Figure S3A-E**). Contact angle measurement is a qualitative way to evaluate whether the surface has hydrophobic or hydrophilic behavior, which is based on the effect of the different intermolecular interactions between the surface and a drop of water when the drop meets the surface, resulting in different surface tensions. For a surface exhibiting a hydrophobic character, the contact angles of an aqueous droplet are expected to be closer or even higher than 90°. Contrarily, a surface with hydrophilic properties shows contact angles smaller than 65°.[2] Dar membrane shows the most hydrophilic surface with angles c.a. 52°, and commercial CEM and AEM membranes show a more hydrophobic surface around 80°. From this point of view, membrane modification with SPEEK increases the hydrophobicity of the scaffold (Dar) with a result still lower than other IEMs.

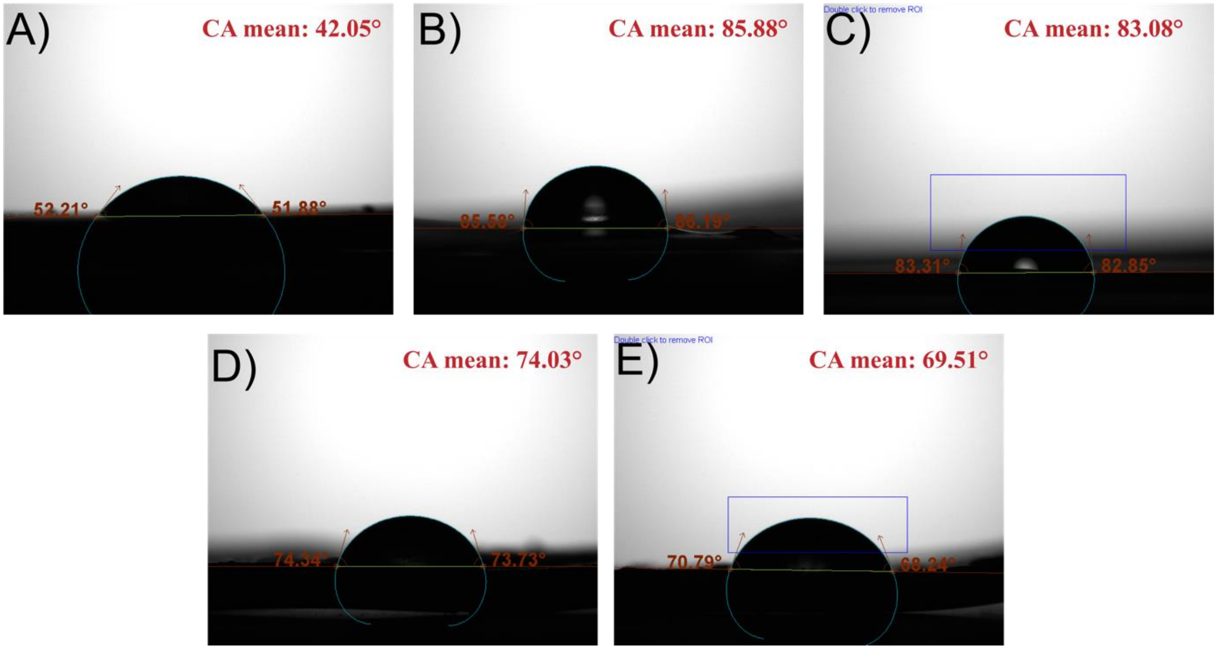

Figure S3 – Contact angle picture after 10 s from the water drops meeting with the surface of **(A)** Dar, **(B)** FS950, **(C)** FAP330, **(D)** Dar-SP50, **(E)** Dar-SP100.

Further details can be found by looking at the behavior of the contact angle during the time. On a wettable surface, the water drops are absorbed progressively and, correspondingly, the angle decreases. Contrarily, by increasing the hydrophobicity, surfaces tend to absorb the water drop slowly. **Figure S4** shows the variation in the contact angle in 10 seconds. The porous membrane (Dar) shows the highest hydrophilicity and wettable surface. Indeed, the starting angle of 57° progressively decreases, approaching 52°, demonstrating the high wettability of the surface. The FS950 CEM exhibits a more hydrophobic surface with an angle that increases due to a slight membrane deformation if wetted. It must be considered that all the selected membranes form angles with water lower than 90°, indicating a hydrophilic surface.

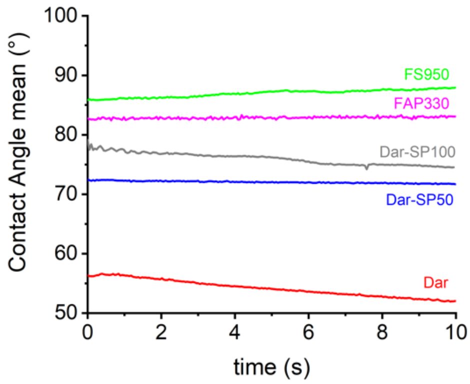

Figure S4 - Contact-angle variation vs time.

As shown by **Figure S4**, the coating of Dar with SPEEK increases its hydrophobicity, but Dar-SP100 shows a well-wettable surface, as can be seen by the continuous angle decreasing. Hence, in the SECM cell, it is wet slower than other membranes, showing lower permeability to Cu(II) on short time-scales (**Figure S4**) but potentially lower selectivity at long time-scales. Consequently, the Dar-SP100, which results competitive with the other CEMs, prevents the permeation of Cu(II) ions even if the amount of SPEEK is low.

Figure S5 – COMSOL studies on Daramic and Daramic SP-100 membranes

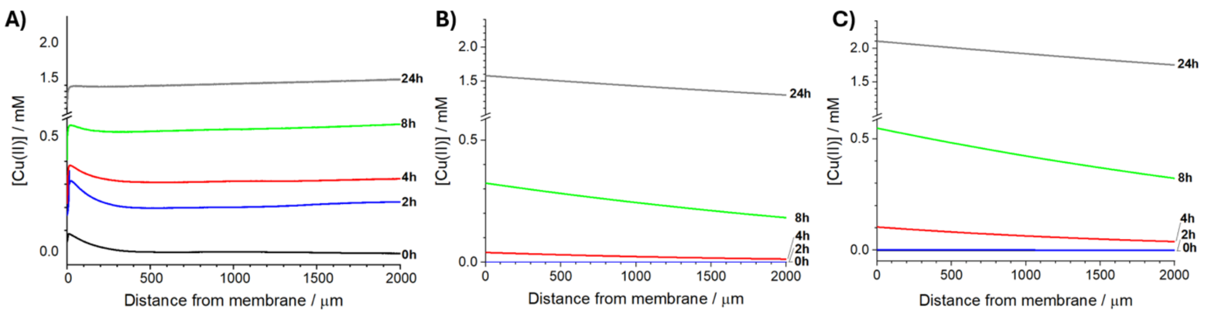

Figure S5 – (A) Concentration profiles obtained from PSCs for the Daramic membrane. **(B)** COMSOL simulation of the corresponding concentration profiles obtained using diffusion coefficient for copper $4 \cdot 10^{-12}$ $m^2 s^{-1}$ and **(C)** $5 \cdot 10^{-12}$ $m^2 s^{-1}$.

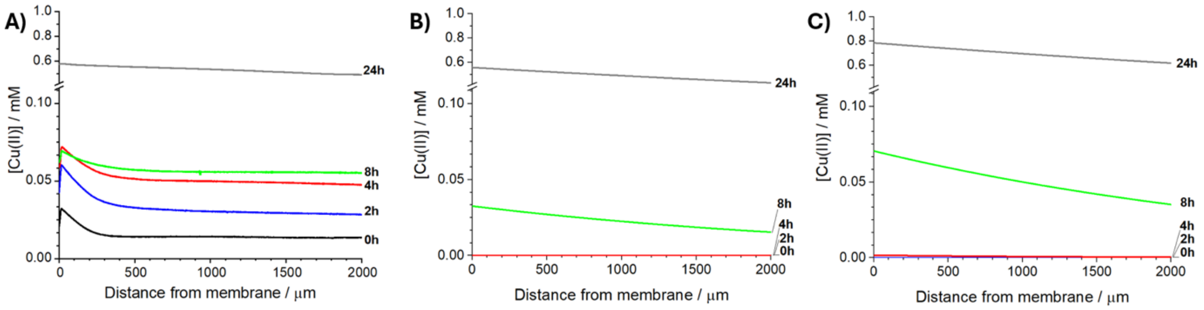

Figure S6 – (A) Concentration profiles obtained from PSCs for Dar-SP100. **(B)** COMSOL simulation of the corresponding concentration profiles obtained using diffusion coefficient for copper $2.5\cdot10^{-12}$ m^2 s^{-1} and **(C)** $3\cdot10^{-12}$ m^2 s^{-1}.

References

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