

Supporting information to:

Nafion membranes for power generation from physiologic ion gradients

Carolina Pierucci^{a,e}, Lorenzo Paleari^b, James Baker^{a,c,e}, Christian Sproncken^{a,e}, Matilde Folkesson^a, Justus Wesseler^a, Andela Vracar^a, Andrea Dodero^{a,e}, Francesca Nanni^b, José Augusto Berrocal^{a,f}, Michael Mayer^{a,e,*}, Alessandro Ianaro^{a,d,e,*}.

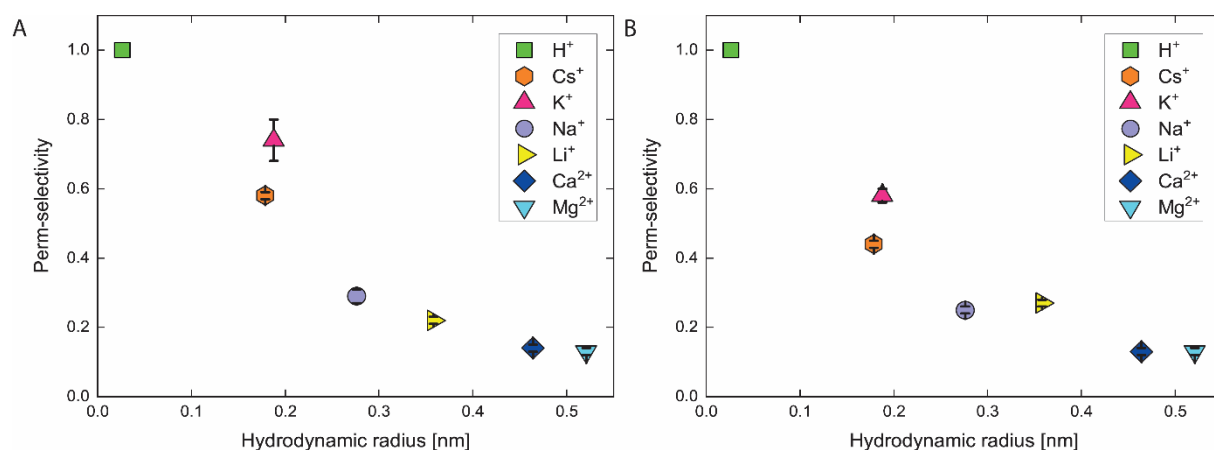


Figure S1 – Perm-selectivity calculated by measuring the open circuit voltage for all salts vs HCl (e.g., HCl vs CsCl; HCl vs KCl; HCl vs NaCl; HCl vs LiCl; HCl vs CaCl₂; HCl vs MgCl₂; all solutions of monovalent salts were 1 M and all solutions of divalent salts were 0.5 M) in relation to the apparent hydrodynamic radius for A) Nafion 115 and B) Nafion Xion.

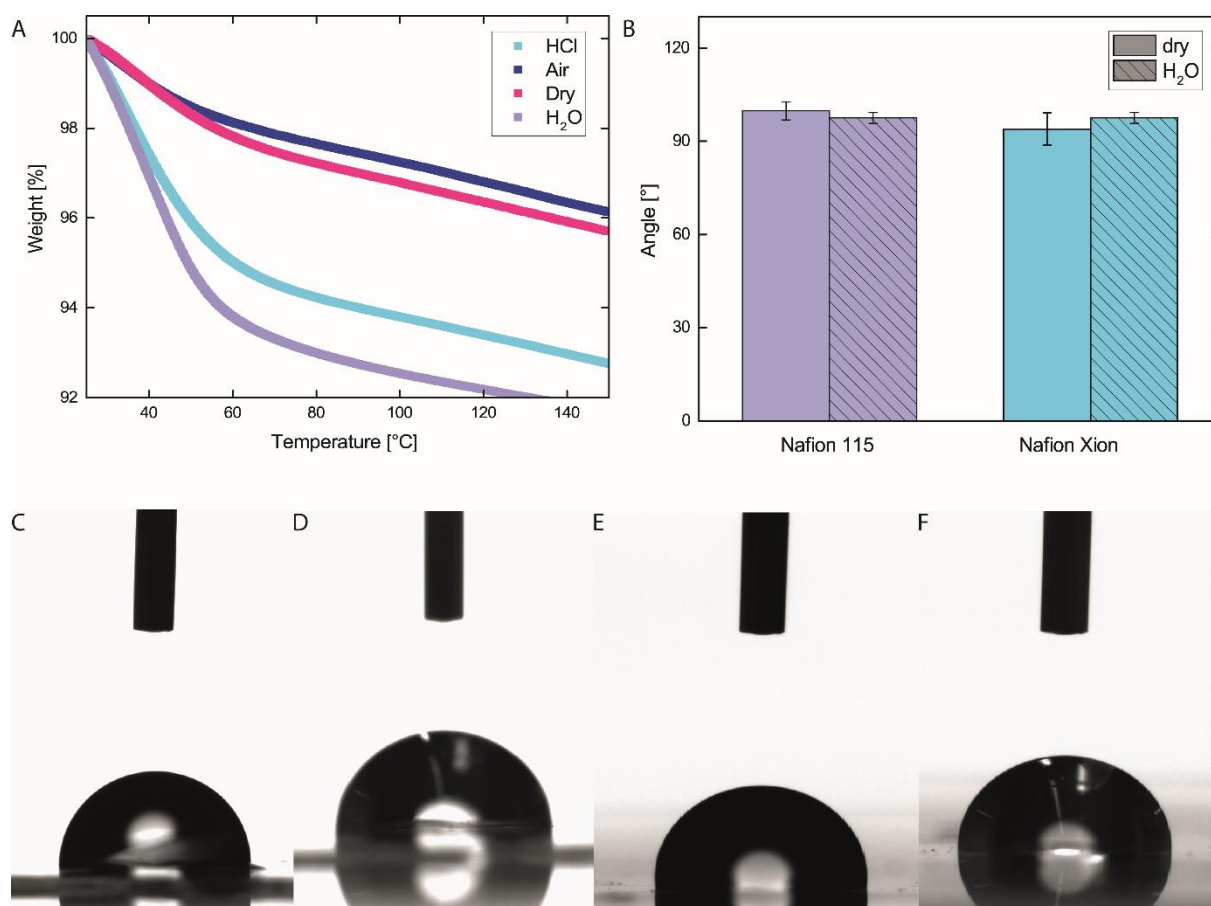


Figure S2 – A) Thermogravimetric analysis of four samples of Nafion 115 that were kept in distilled water for two hours, heated in the oven at 60 °C for two hours, and then they were differentiated, putting one sample in milliQ water (H₂O), one sample in a HCl 1 M solution (HCl), one at air (air) and the last one has been dried in a desiccator under vacuum (dry); all of them for two days. B) Median values of the measured contact angles for both Nafion membranes (n = 3 for each sample): all four samples were kept in distilled water for two hours, heated in the oven at 60 °C for two hours, then two samples were dried in a desiccator under vacuum (dry) while the other two samples were placed in milliQ water (H₂O). Right before the measurement, the samples were removed from the water and residual water was removed by tissue paper. The obtained pictures of each sample are reported: C) Nafion 115 dry; D) Nafion 115 H₂O; E) Nafion Xion dry; F) Nafion Xion H₂O.

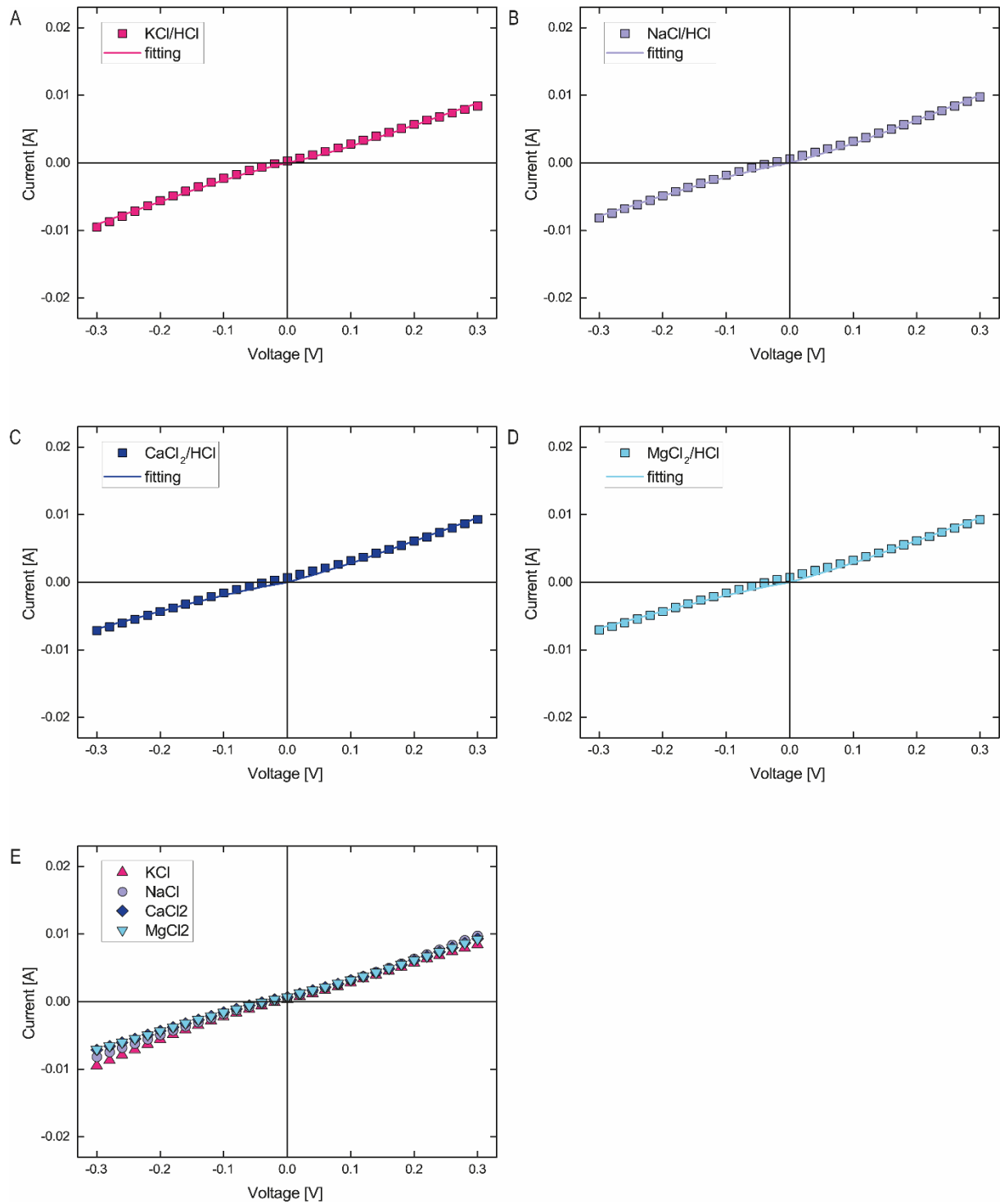


Figure S3 - Asymmetric I-V curves related to Nafion 115 for all couples of salts i.e., A) KCl vs HCl; B) NaCl vs HCl; C) CaCl₂ vs HCl; D) MgCl₂ vs HCl; the curves show the transmembrane current as a function of the applied voltage. Each graph shows the measured I-V curve represented by the symbols (the different salts are at negative voltages while HCl is always at positive voltages); the solid lines refer to the fitting of the measured I-V curves of the salt under analysis. E) comparison of all asymmetric I-V curves.

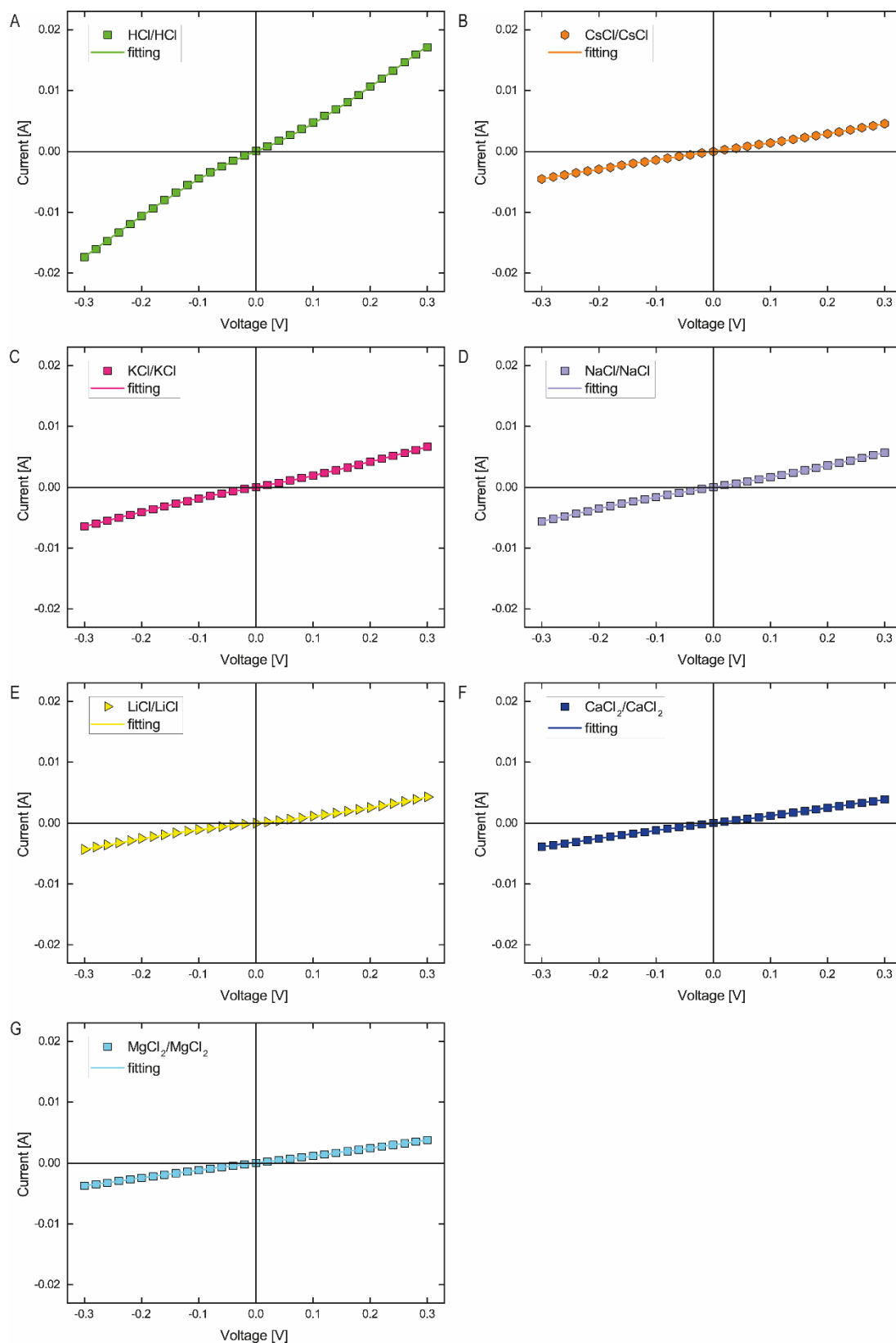


Figure S4 - Symmetric I-V curves related to Nafion 115 for all salts i.e., A) HCl vs HCl; B) CsCl vs CsCl; C) KCl vs KCl; D) NaCl vs NaCl; E) LiCl vs LiCl; F) CaCl₂ vs CaCl₂; G) MgCl₂ vs MgCl₂. The curves show the transmembrane current as a function of the applied voltage. Each graph shows the measured I-V curve represented by the symbols, and the solid line refers to its fitting.

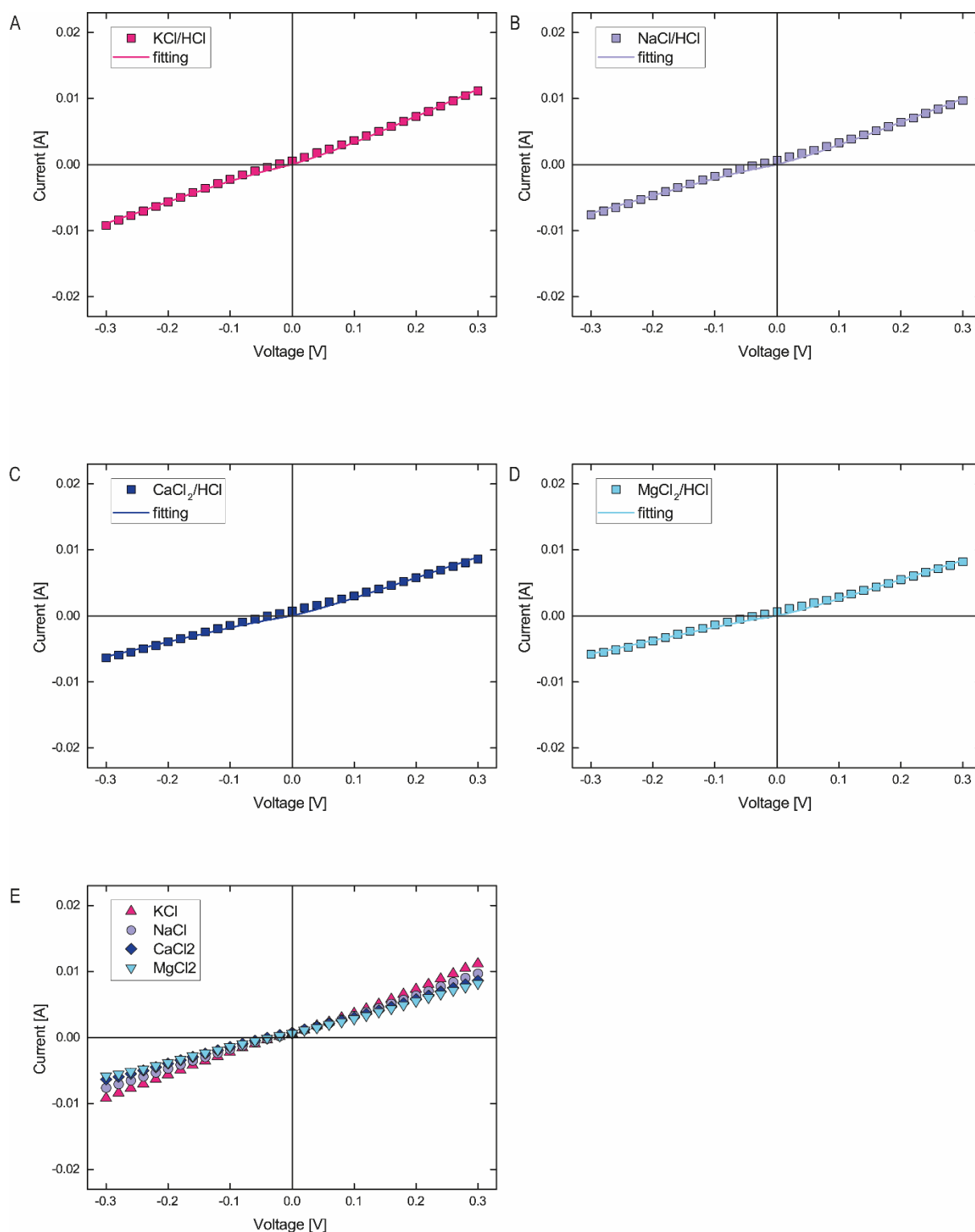


Figure S5 - Asymmetric I-V curves related to Nafion Xion for all couples of salts i.e., A) KCl vs HCl; B) NaCl vs HCl; C) CaCl₂ vs HCl; D) MgCl₂ vs HCl; the curves show the transmembrane current as a function of the applied voltage. Each graph shows the measured I-V curve represented by the symbols (the different salts are at negative voltages while HCl is always at positive voltages); the solid lines refer to the fitting of the measured I-V curves of the salt under analysis. E) comparison of all asymmetric I-V curves.

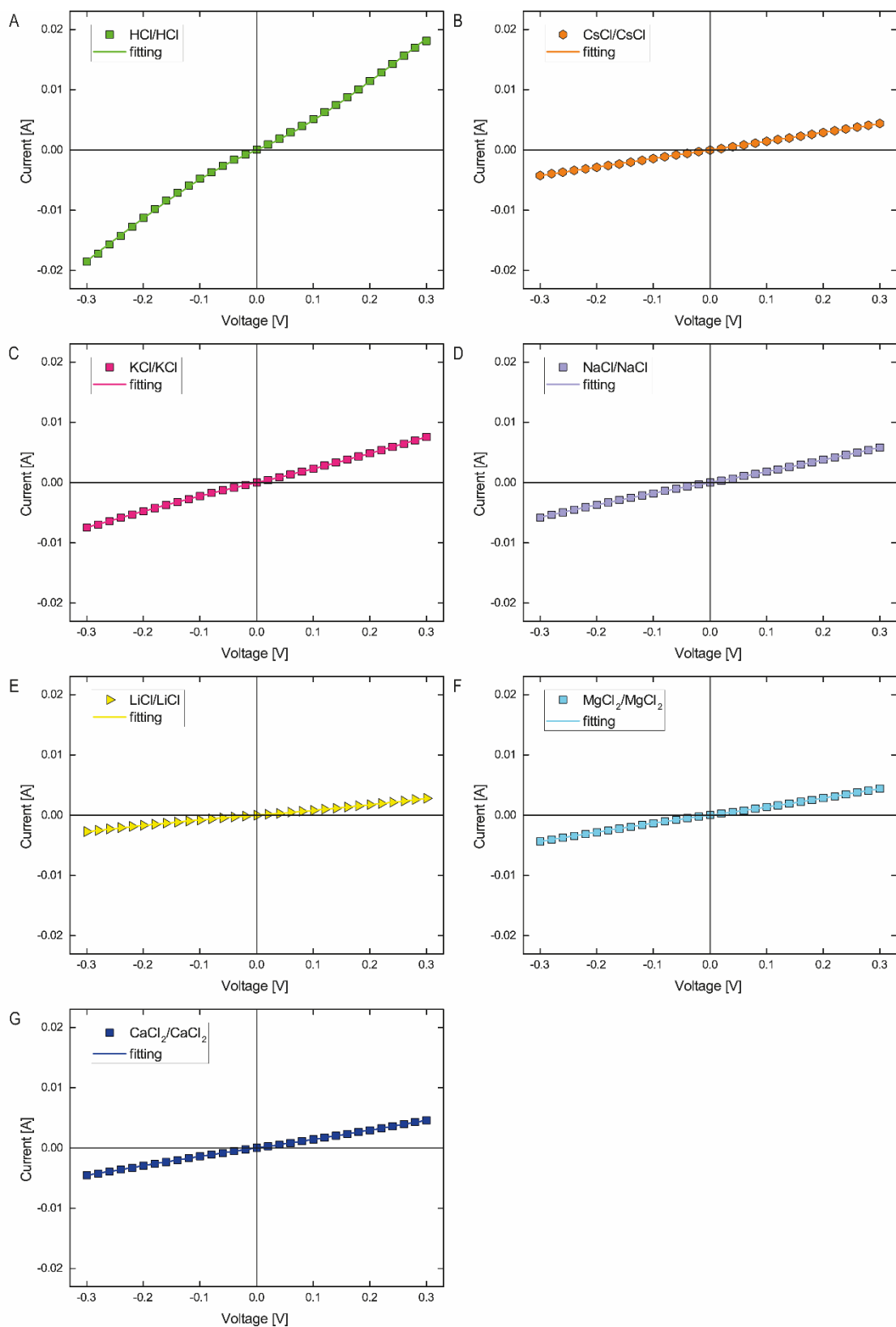


Figure S6 - Symmetric I-V curves related to Nafion Xion for all salts i.e., A) HCl vs HCl; B) CsCl vs CsCl; C) KCl vs KCl; D) NaCl vs NaCl; E) LiCl vs LiCl; F) CaCl_2 vs CaCl_2 ; G) MgCl_2 vs MgCl_2 . The curves show the transmembrane current as a function of the applied voltage. Each graph shows the measured I-V curve represented by the symbols, and the solid line refers to its fitting.

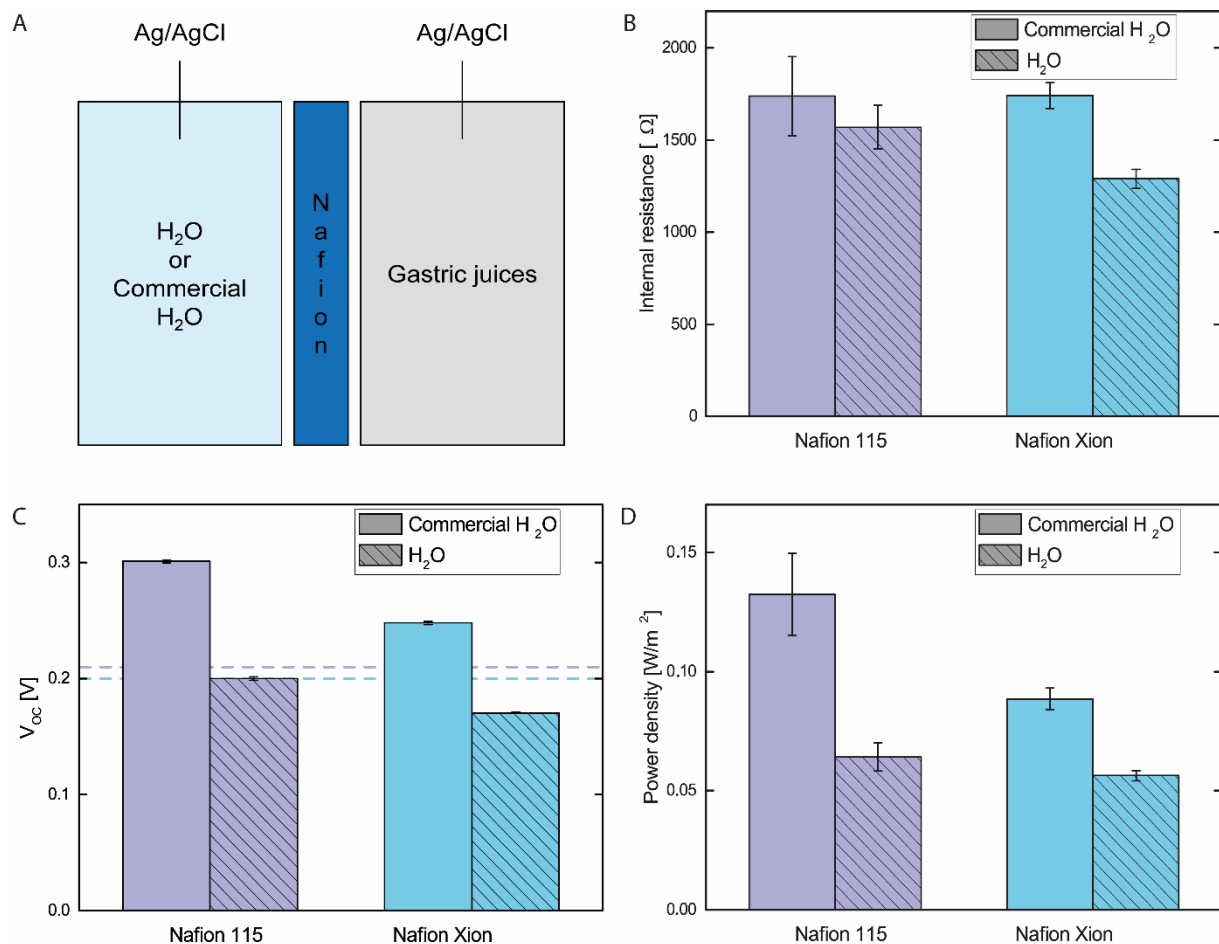


Figure S7 - A) Schematic representation of the cell used to measure the voltage across Nafion membranes using gastric juices as ion-rich solution vs H₂O or the commercially available Tavina water as ion-poor solution. B) Comparison of the internal resistances obtained with both Nafion 115 and Xion with the setup reported in Figure SI 6A; C) comparison of the open circuit voltages. The lines in the graph show the estimated transmembrane potentials using the GHK equation: i) the dark blue dashed line refers to Nafion 115 with H₂O and gastric juices; ii) the turquoise dashed line refers to Nafion Xion with H₂O and gastric juices. D) Comparison of the power densities calculated from the internal resistances and open circuit voltages as described in the Methods section.

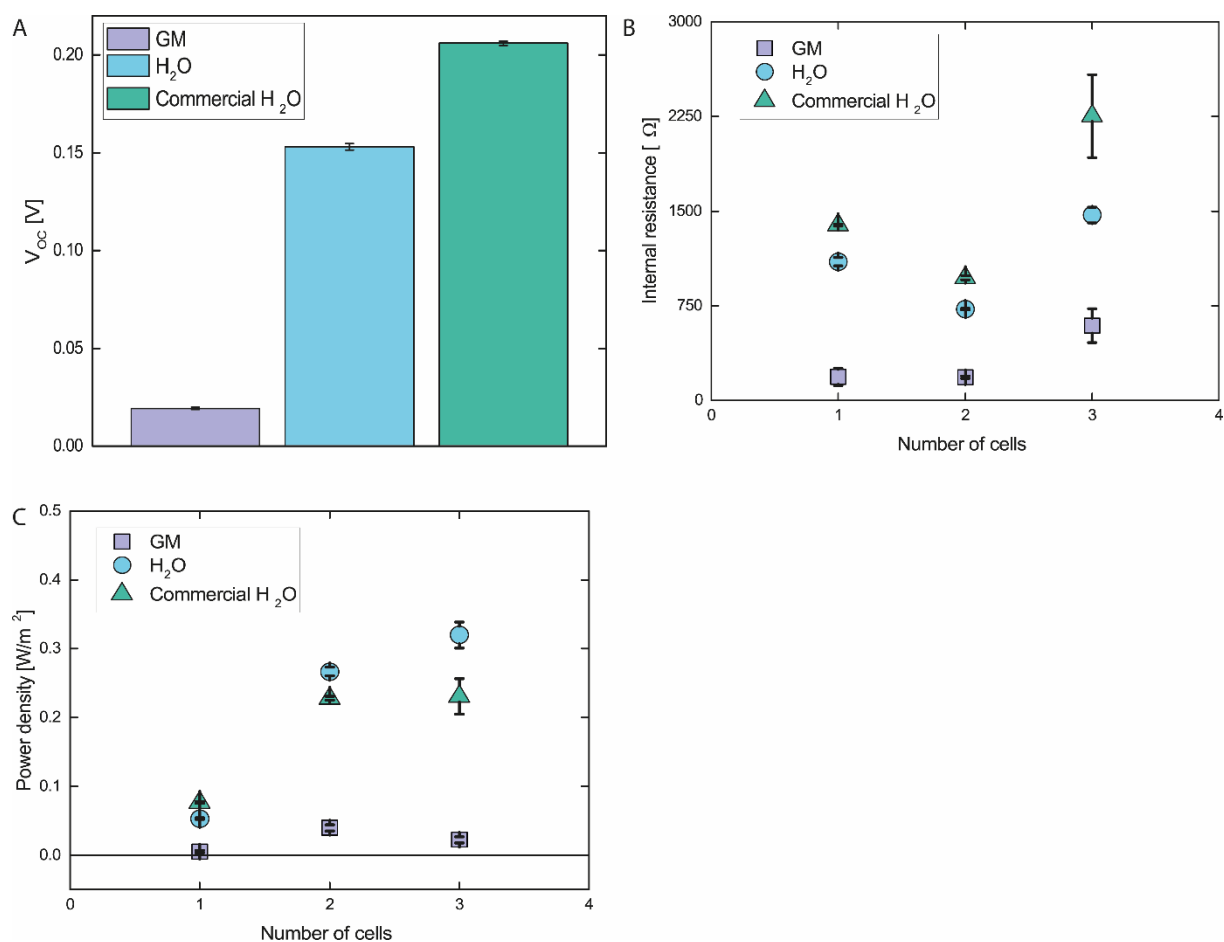


Figure S8 – A) Comparison of the open circuit potentials obtained with Nafion® 115 in a RED cell with the setup reported in Figure 4E main text. B) Comparison of the internal resistances as a function of the number of stacked cells; C) Comparison of the power densities as a function of the number of stacked cells calculated from the internal resistances and potentials following equation 6.

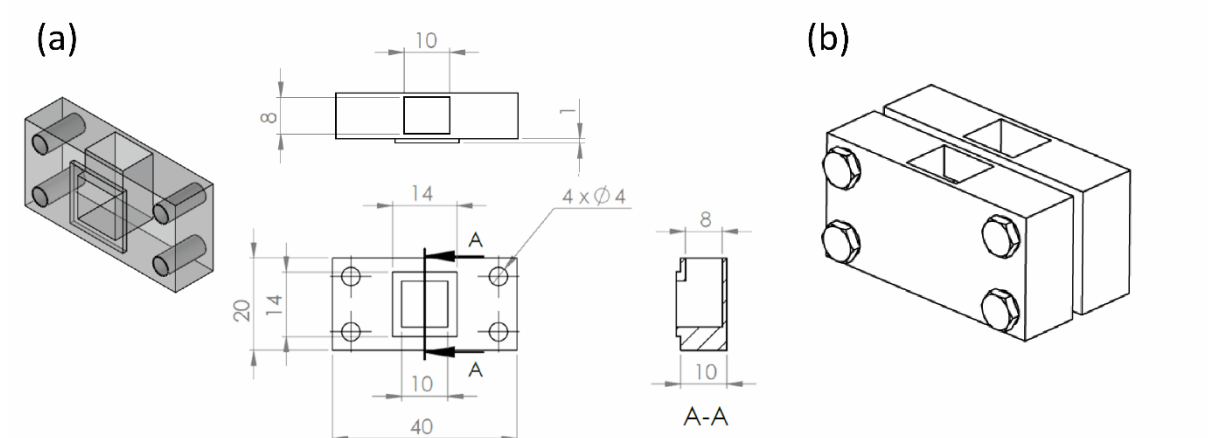


Figure S9 – Design of the 3D printed cell used for the electrical characterization of the membranes. The modular design consists of two terminal plates assembled together via M4 bolts and nuts (Figure b). Each plate presents a 10 mm² through cubic blind hole (Figure a), to allow the ions to exchange through the membrane, which is inserted and clamped with expanded Teflon gaskets between the two plates.

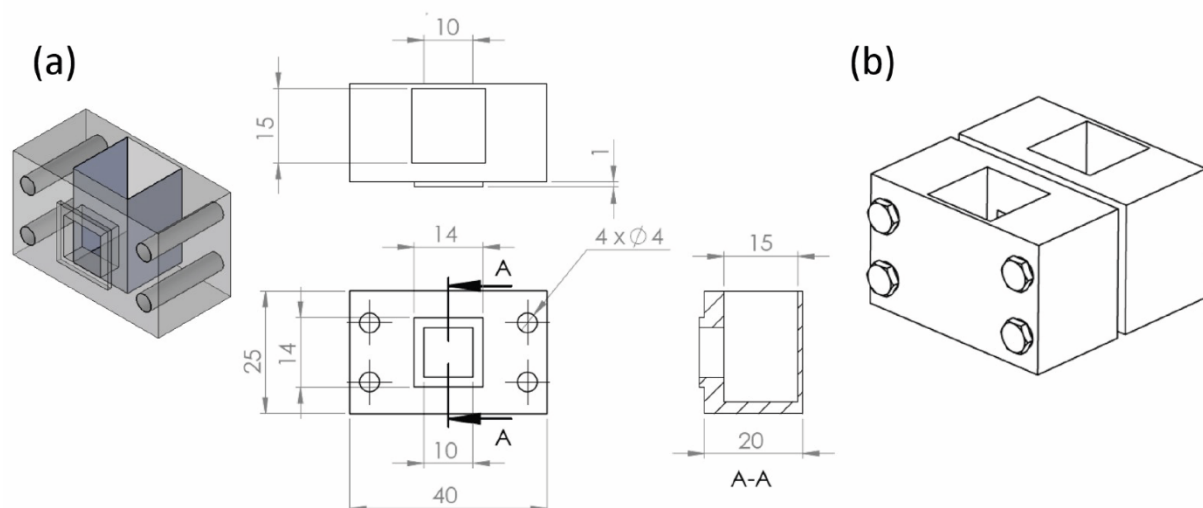


Figure S10 – Design of the 3D printed cell used for the electrical characterization of the membranes that also allows for the measurement of the pH. The modular design consists of two terminal plates assembled together via M4 bolts and nuts (Figure b). Each plate presents a 10 mm² through squared blind hole (Figure a), to allow the ions to exchange through the membrane, which is inserted and clamped with expanded Teflon gaskets between the two plates.

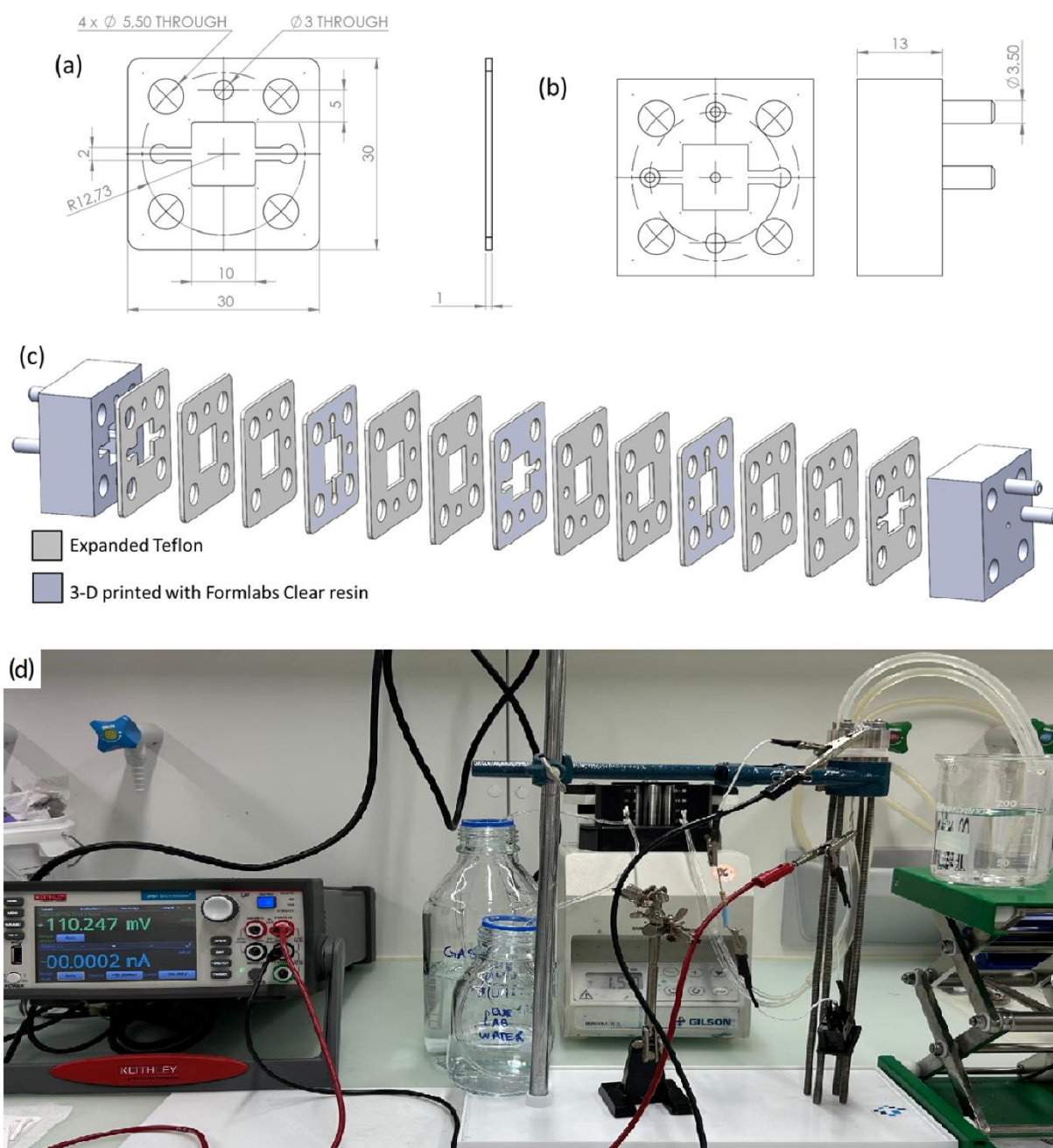


Figure S11 - Model of the 3D printed cell used to assemble a prototype of the electric organ (RED with multiple cells connected in series) where water and gastric solutions have been flowed. The modular design consists of two terminal plates (Figure b) that allow the insertion of Ag/AgCl electrodes and of the solutions, and multiple intermediate plates (Figure a) assembled together via threaded bars. Each plate presents a 10 mm² through hole (or blind hole, in the case of the terminal plates) to allow the ions exchange through the membranes, which are inserted and clamped with compressed expanded Teflon gaskets between the plates. c) Scheme of the assembled cell with expanded Teflon gaskets. d) Picture of the setup for the measurements under flow.

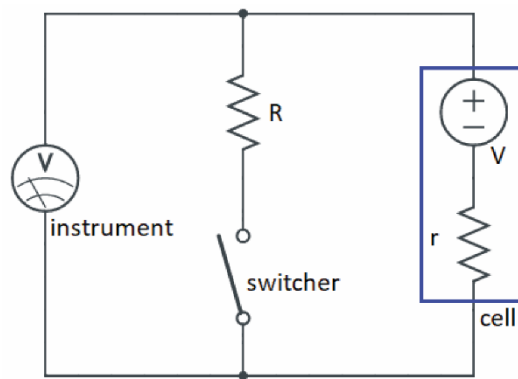


Figure S12 – Equivalent circuit used to estimate the open circuit voltage, the internal resistance and the power density of the system. The cell with both the internal resistance (r) and its electromotive force (V) is displayed in the blue box. The instrument can measure either the potential difference across the external load (R) or the open circuit voltage (V_{oc}) according to the switcher position.

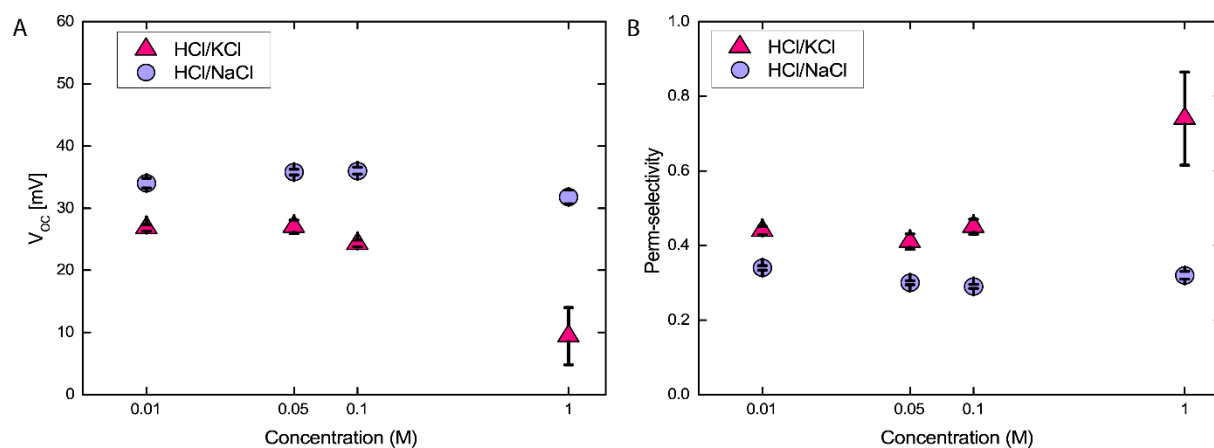


Figure S13 – A) Open circuit voltages measured at different concentrations of the two monovalent salts i.e., HCl vs KCl and HCl vs NaCl; B) Calculated perm-selectivity from the voltages reported in Figure A for the two monovalent salts.

Table S1 – Measured contact angles for both Nafion membranes.

Nafion 115		Nafion XION	
Dry	H ₂ O	Dry	H ₂ O
99.8 ± 2.9	97.5 ± 1.8	93.9 ± 5.2	93.7 ± 1.6

Table S2 – Calculated resistances from the slopes of the asymmetric I-V curves for all the salts. The resistances have been separately calculated for potentials < 0 and for potentials > 0. During the measurements the pH was also recorded.

Asymmetric	Nafion XION				Nafion 115			
	V < 0		V > 0		V < 0		V > 0	
Salt	pH	Resistance [Ω]	pH HCl	Resistance [Ω]	pH	Resistance [Ω]	pH HCl	Resistance [Ω]
KCl	6.4	30.4 ± 0.4	0.1	24.2 ± 0.1	6.4	29.5 ± 0.9	0.1	29.8 ± 1.3
NaCl	6.0	36.9 ± 0.1		27.9 ± 0.2	6.0	32.7 ± 0.3		27.9 ± 1.0
CaCl ₂	6.7	44.0 ± 0.8		31.4 ± 0.6	6.7	38.9 ± 1.0		29.0 ± 0.6
MgCl ₂	6.3	47.7 ± 1.8		33.8 ± 0.5	6.3	43.7 ± 3.5		31.5 ± 2.0

Table S3 – Calculated resistances from the slopes of the symmetric I-V curves for all the salts.

Symmetric		Nafion XION	Nafion 115
Salt	pH	Resistance [Ω]	Resistance [Ω]
HCl	0.1	13.3 ± 0.3	14.3 ± 0.2
KCl	6.4	38.2 ± 2.7	42.9 ± 2.8
NaCl	6.0	47.6 ± 0.6	44.5 ± 1.5
CaCl ₂	6.7	59.4 ± 1.1	73.1 ± 0.3
MgCl ₂	6.3	58.9 ± 5.7	76.9 ± 3.0