

Supporting Information

Using a vapor-fed anode and saline catholyte to manage ion transport in a proton exchange membrane electrolyzer

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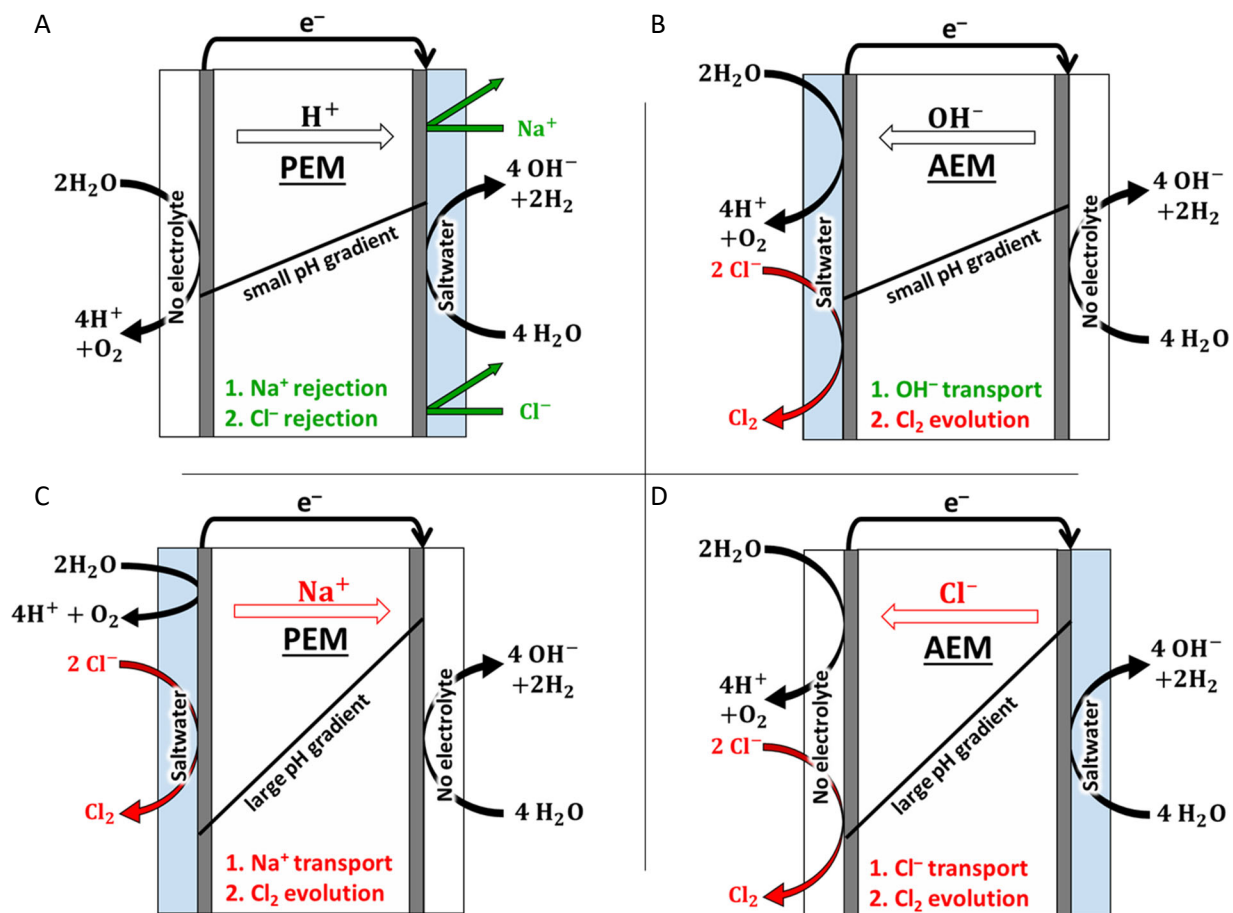


Figure S1. The direction of the electric field and the charge of the membrane can be used to limit the transport of competing ions through the cell, minimizing the development of large concentration gradient in the electrolyzer and the evolution of large amounts of Cl_2 . Only a vapor-fed electrolyzer with a PEM (A) can be used to concurrently reject Cl^- ions and minimize Na^+ intrusion with the aid of the electric field. To favor the migration of OH^- over Cl^- an AEM can be used fed with a liquid electrolyte only at the anode (B), however, the Cl^- present in seawater will still be in contact with the anode. Using a liquid electrolyte in the anode of a PEM electrolyzer (C) allows to provide plenty of water for the OER at the anode, but will favor the evolution of Cl_2 at the anode and Na^+ migration across the PEM, developing large concentration gradients in the cell. A liquid catholyte in an AEM electrolyzer (D) would favor the migration of Cl^- rather than OH^- from cathode to anode.

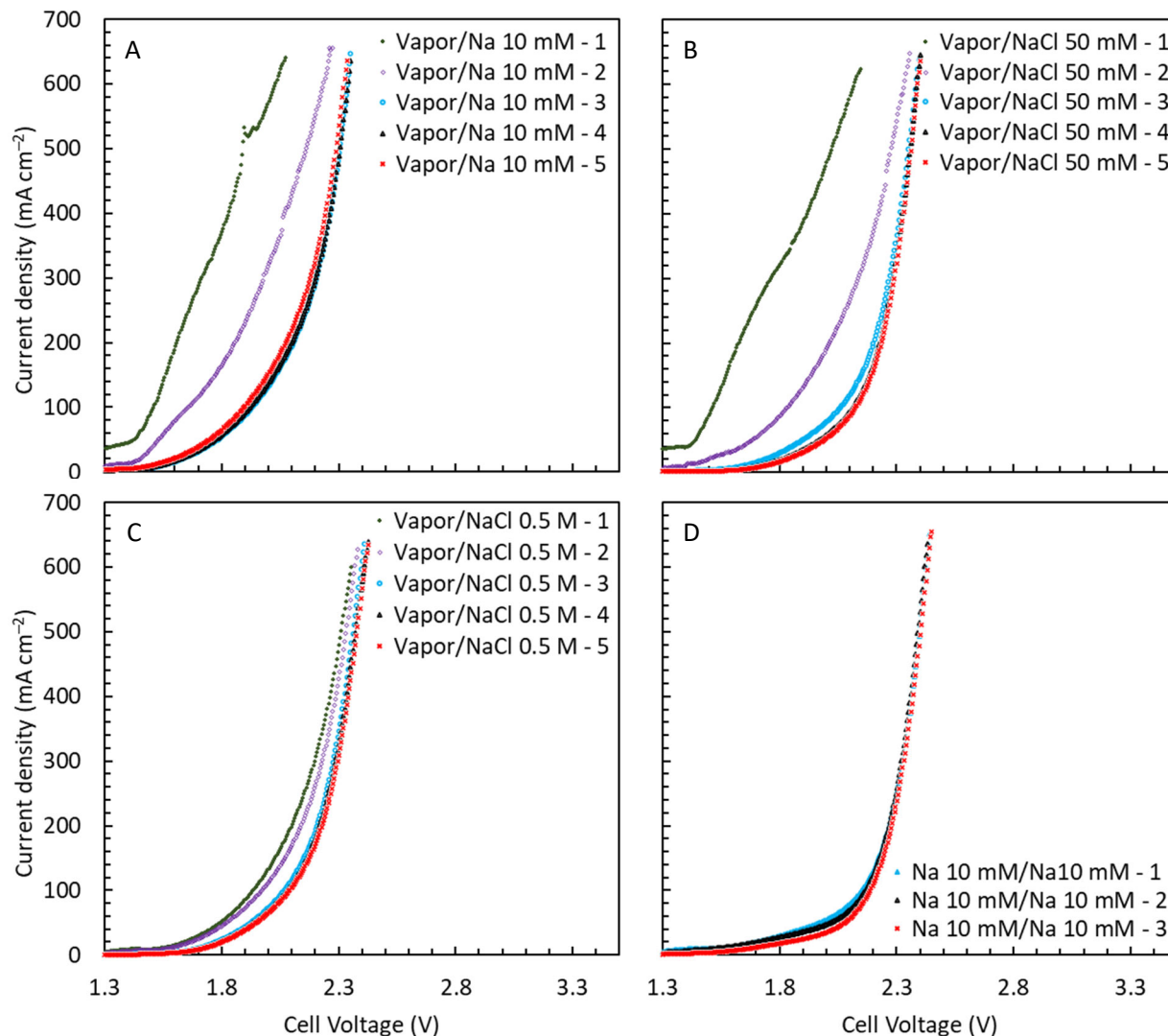


Figure S2. Shifts in the vapor-fed electrolyzer performance depending on the sodium concentration in the catholyte over time compared to the liquid-anode configuration. The overpotential from the LSVs of the (A) Vapor/NaClO₄ (10 mM) and (B) Vapor/NaCl (50 mM) largely increased from one LSV to the next, likely due to the diffusion of the sodium ions from cathode to anode, favoring the development of larger concentration gradient over time. With higher concentrations of NaCl (0.5 M), the overpotential at the beginning of the test was larger than that obtained with smaller sodium concentration (A, B), suggesting that the sodium diffusing in the PEM depends by the sodium concentration in the catholyte. The liquid-anode electrolyzer fed NaClO₄ 10 mM in the anolyte showed a large and stable overpotential over time.

The EIS analysis revealed large changes in the electrolyzer resistance based on the different feeding configurations and sodium contents at the same applied potential (Figure S3). Sodium contamination increased the ohmic resistance, but at a lower extent for the vapor-anode compared to the liquid-anolyte. For example, the ohmic resistance of the gas-anode electrolyzer was $0.27 \Omega \text{ cm}^2$ compared to $0.29 \Omega \text{ cm}^2$ for the liquid anode electrolyzer. The spectrum of the DI/DI and vapor/DI electrolyzer configurations were similar, showing the same overall resistance of $0.15 \Omega \text{ cm}^2$ and a similar ohmic resistance of $0.18 \Omega \text{ cm}^2$. The ohmic resistance obtained here was slightly larger than that typically reported for electrolyzers using Nafion 212, likely due to the application of the catalyst layer onto electrode current collector rather than directly onto the membrane and the use of a non-platinized Ti felt as anode current collector.¹

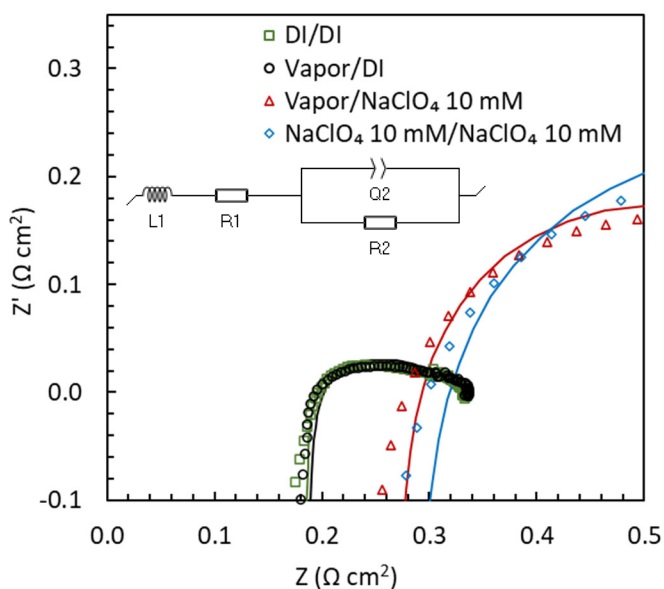


Figure S3. EIS spectra at 1.7 V for each different electrolyzer configuration 1.7 V. The solid lines represent the fitting to the data. The fitting circuit is reported in the inset.

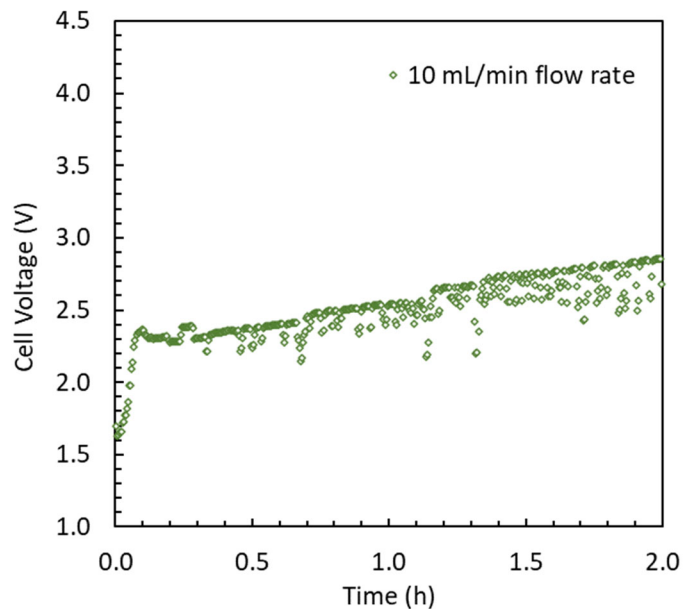


Figure S4. In the vapor-fed anode configuration, decreasing the flow rate of the liquid catholyte and of the vapor in the anode chamber from 25 mL min^{-1} to 10 mL min^{-1} resulted in erratic performance and a large increase in the cell overpotential, likely due to the insufficient transport of water molecules in the anode chamber, which cannot sustain the high water consumption by the OER.

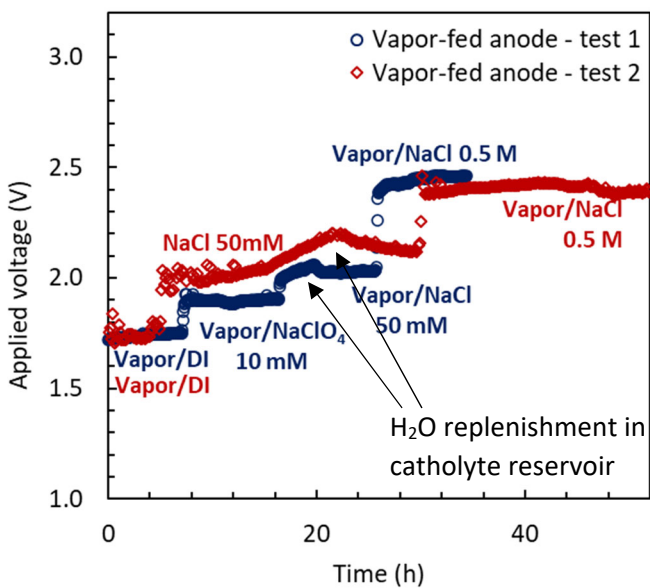


Figure S5. Long-term performance of the vapor-fed anode electrolyzer with different concentration of salts fed at the cathode. For this experiment we used NaClO_4 10 mM to allow comparison with the $\text{NaClO}_4/\text{NaClO}_4$ liquid-fed electrolyzer and NaCl at different concentration (50 mM and 0.5 M) to investigate the Faradaic efficiency toward the OER and the CER. With Nafion 212 as a separator, the increase in the cell voltage was 0.16 V when NaClO_4 10 mM was added in the catholyte of the vapor-fed anode electrolyzer, compared to a much larger increase of 0.67 V when NaClO_4 was fed to both the anolyte and the catholyte of the electrolyzer. The increase in the voltage was 0.28 V with NaCl 50 mM (3 g L^{-1}) and 0.70 V with NaCl 0.5 M (30 g L^{-1}), however, the negative charge of the PEM allowed to reject the chloride ions in solution and produce a Faradaic efficiency exceeding 90% (Figure S5, Figure 3D). The voltage slightly increased overnight in the two tests due to the evaporation of the liquid catholyte, which in turn increased the concentration of ions in solution. When the initial volume was reestablished by adding DI to the catholyte, the cell voltage decreased.

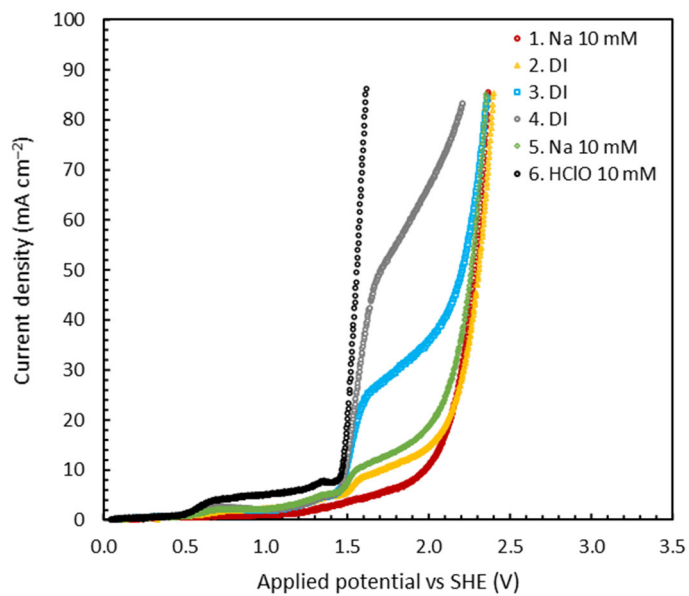


Figure S6. Impact of sodium contamination on the electrolyzer performance measured through LSVs with Nafion 117 and the liquid electrolytes fed on anode and cathode. Switching from NaClO₄ 10 mM to DI (1 to 4) progressively reduces the cell overpotential, while feeding again NaClO₄ 10 mM increases back the cell potential. Using HClO₄ 10 mM avoids overpotential issues due to sodium contaminations.

Sodium ion transport in the vapor-fed anode configuration.

There are two possible ways a sodium ion can diffuse from cathode to anode. A sodium ion can diffuse through the PEM as Na^+ (Figure S7A). This will not diminish the performance as the transfer of an Na^+ from cathode to anode should be balanced by the diffusion of one H^+ from anode to cathode to maintain the electroneutrality. Thus, once under the effect of the electric field, the Na^+ will diffuse back from the anode to the cathode, electron transport from anode to cathode will be balanced by a “net” transport of one H^+ from anode to cathode. However, sodium ions can diffuse in the anode chamber also as NaCl . Briefly, when the concentration of ions in contact with a membrane is similar or larger than the ionic strength of the membrane, the negative charges of the sulfonated moieties are saturated by the positive charges of the ions in solution, in this case Na^+ . The saturation of the charges produced a “shielding effect”, allowing Cl^- , which has the same charge of the PEM and should be theoretically rejected, to diffuse from cathode to anode.²⁻⁴ Again, to maintain electroneutrality the diffusion of a Cl^- ion must be accompanied by the diffusion of a positive charge in the same direction. If Na^+ diffuses from cathode to anode with a Cl^- , and then under the effect of the electric field, diffuses back to the cathode, it produces a pH imbalance which diminish the electrolyzer performance (Figure S7B). Using a denser membrane with larger concentration of fixed charges will more effectively reject the chloride ions, limiting the co-transport of Na^+ and avoiding the development of large pH imbalances across the PEM.

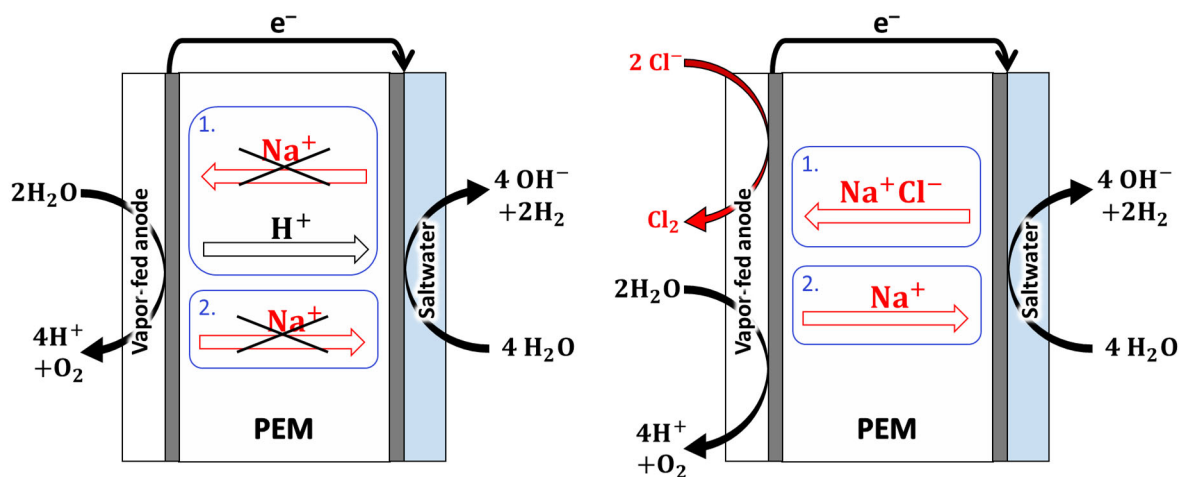


Figure S7. Mechanisms of sodium transport in the vapor-fed electrolyzer. (A) The diffusion of Na^+ from cathode to anode is balanced by the diffusion of an H^+ in the opposite direction. The back diffusion of the Na^+ to balance charge will not result in pH imbalance across the PEM. (B) The transport of an Na^+ and a Cl^- will have detrimental effects on the electrolyzer performance. The Cl^- will be oxidized at the anode and generate chlorine while the Na^+ transport will favor the development of pH imbalances as an H^+ will be generated at the anode but not removed and an OH^- will be generated at the cathode but not neutralized.

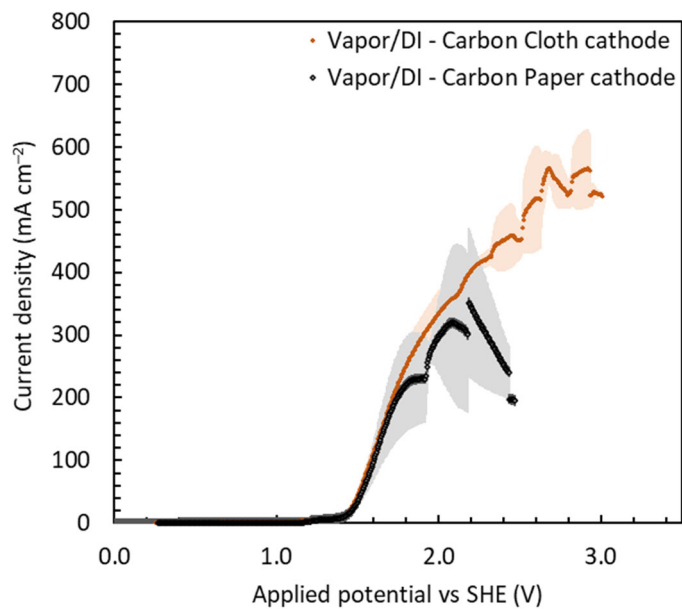


Figure S8. Impact of the cathode support material on the performance of the vapor-fed electrolyzer with Nafion 117 as a separator between anode and cathode. Carbon cloth as a cathode catalyst support layer allowed more water to diffuse from cathode to anode, resulting in limiting current density of 600 mA cm⁻² compared to only 360 mA cm⁻² with a more hydrophobic carbon paper catalyst support.

Literature cited

1. Bernt, M., Schröter, J., Möckl, M. & Gasteiger, H. A. Analysis of gas permeation phenomena in a PEM water electrolyzer operated at high pressure and high current density. *J. Electrochem. Soc.* **167**, 124502 (2020).
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