

Supporting Information

Increasing the electrolyte salinity to improve the performance of anion exchange membrane water electrolyzers

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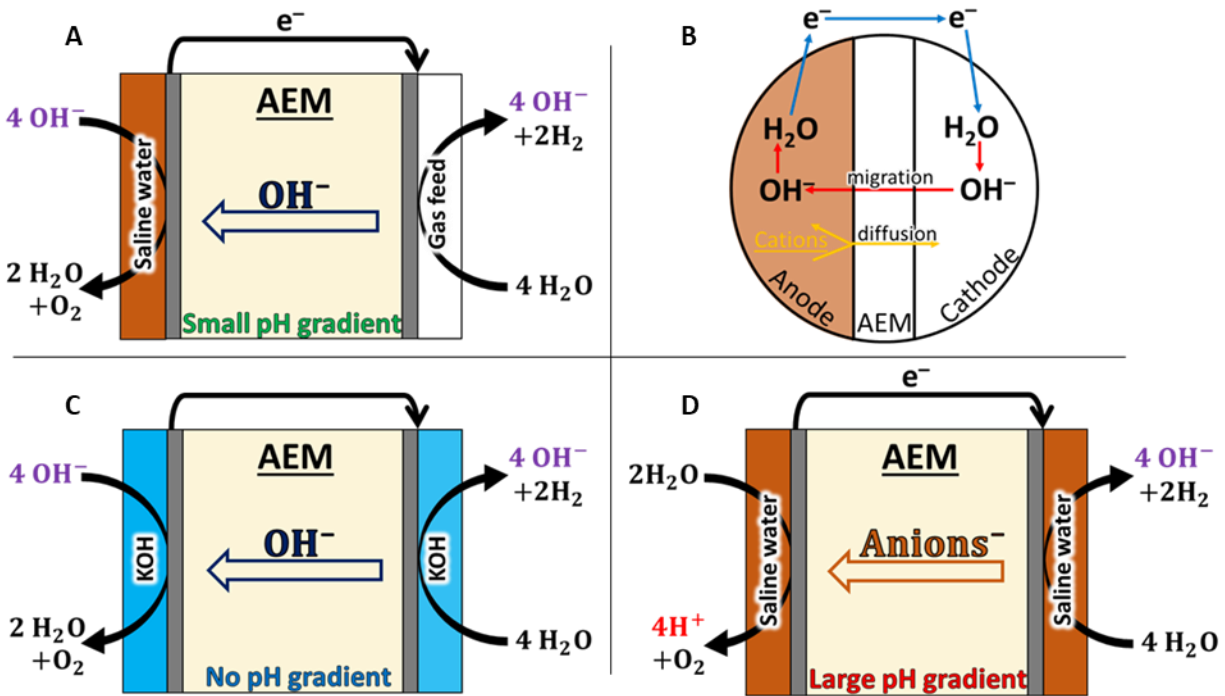


Figure S1. Comparison of predominant ion transport in anion exchange membrane water electrolyzer configurations fed solutions with different ion content. (A) Using slightly saline solutions in anode-fed only configurations increase solution conductivity and electrode surface area utilization while (B) minimizing competing ion transport through the membrane by favoring migrations of hydroxide ions from the cathode and reducing cation diffusion from the anode compared to typical AEM water electrolyzer configurations fed (C) concentrated KOH or (D) saline solutions at the anode and cathode.

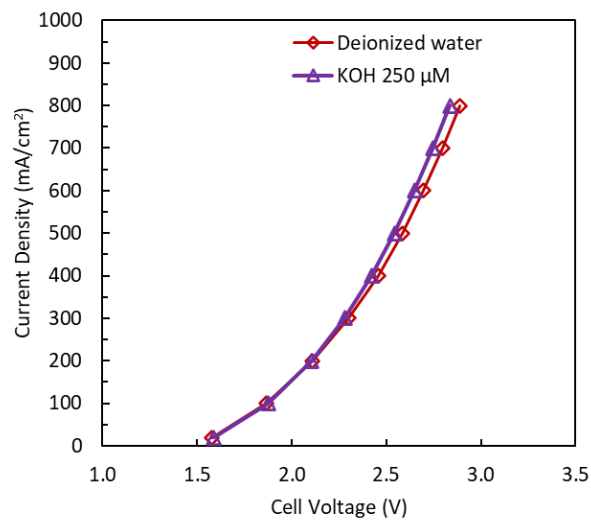


Figure S2. Performance comparison of the AEM electrolyzer fed 250 μM KOH and deionized water. The small potassium hydroxide concentration was used to enable stable pH measurement of the anolyte over time, which was drifting and not reproducible with deionized water due to the absence of ions in solution.

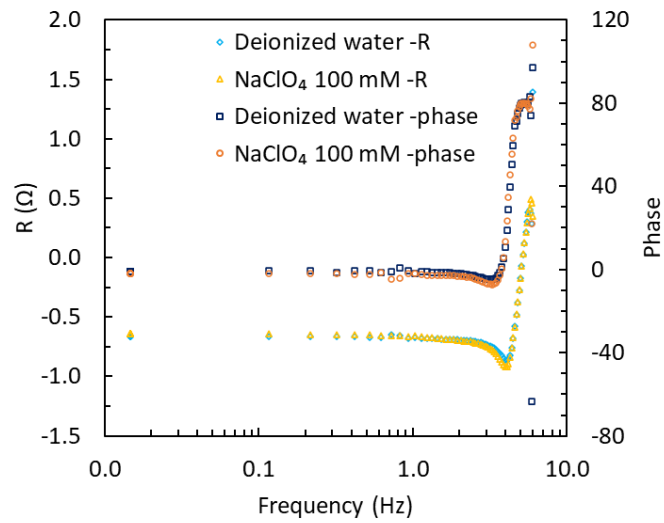


Figure S3. Bode plot of the EIS spectra of the dry cathode configuration fed deionized water or NaClO₄ 100 mM in the anolyte.

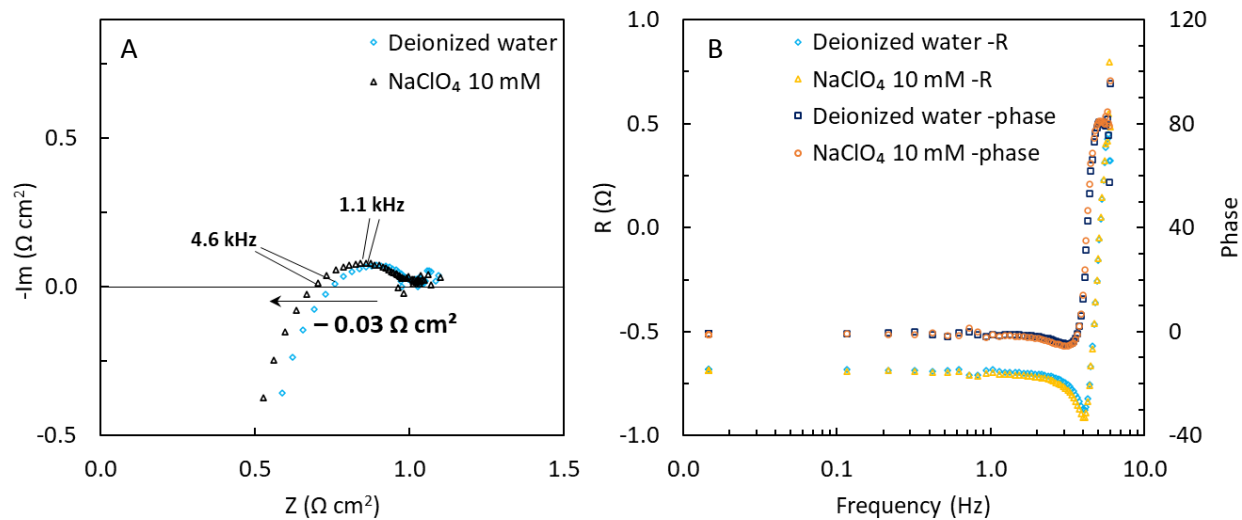


Figure S4. Nyquist and Bode plots of the EIS spectra of the dry cathode configuration fed deionized water or NaClO₄ 10 mM in the anolyte.

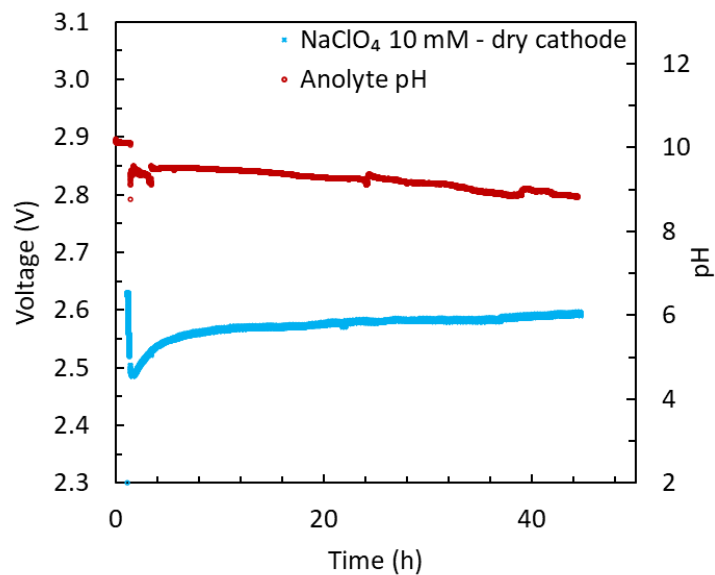


Figure S5. Increasing the operating time of the electrolyzer in the dry-cathode configuration do not result in a sensibly change of performance after the initial 20h of operation, indicating that using saline anolyte increases also long-term performance compared to deionized water.

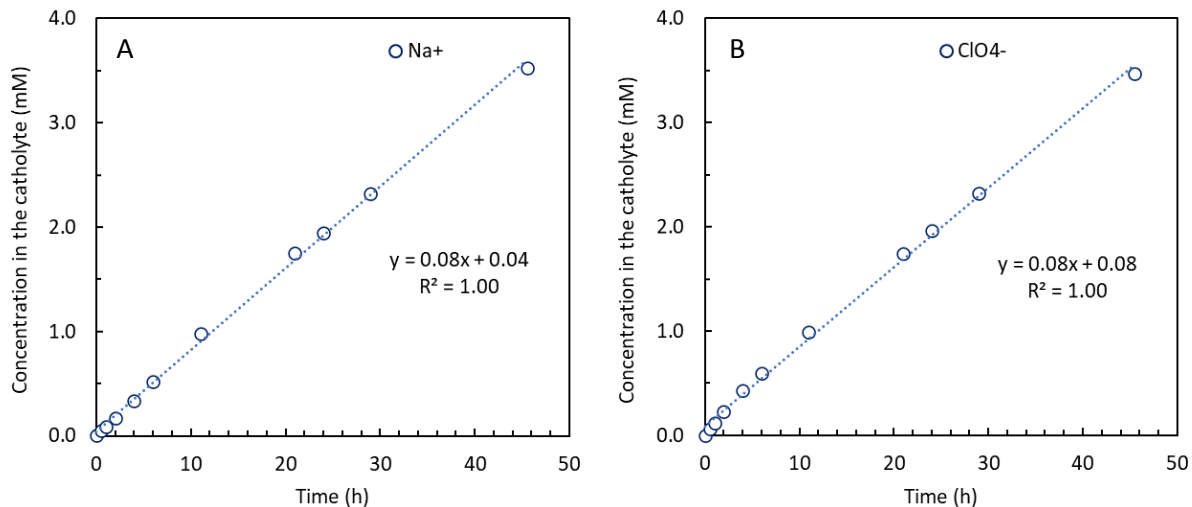


Figure S6. (A) Sodium diffusion through the AEM. Anolyte was 100 mM NaClO₄ and catholyte was deionized water. During sodium diffusion in the absence of current, charge balance was maintained by the transport of perchlorate ions from anolyte to catholyte. Such transport could not occur in the presence of an electric field due to the transport of electrons which facilitate migration of negative charges from the cathode to the anode. Anolyte and cathode were recirculated at 25 mL/min and the cell was maintained at 55 °C.

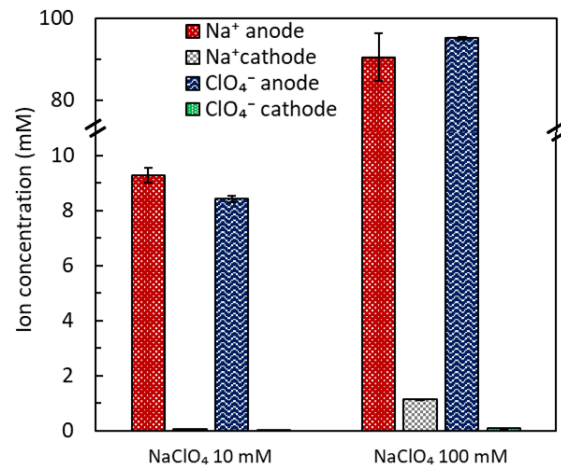


Figure S7. Ion crossover after 20 h of operation at a 50 mA/cm² current density. NaClO₄ 10 mM or 100 mM was fed to the anolyte while deionized water was recirculated on the cathode. The concentration of perchlorate ion diffusing in the catholyte was negligible, however, particularly with 100 mM NaClO₄ anolyte, up to 1.13 ± 0.00 mM of Na⁺ was detected in the catholyte. To maintain electroneutrality, a proton should diffuse from cathode to anode, resulting in pH decrease of the anolyte.

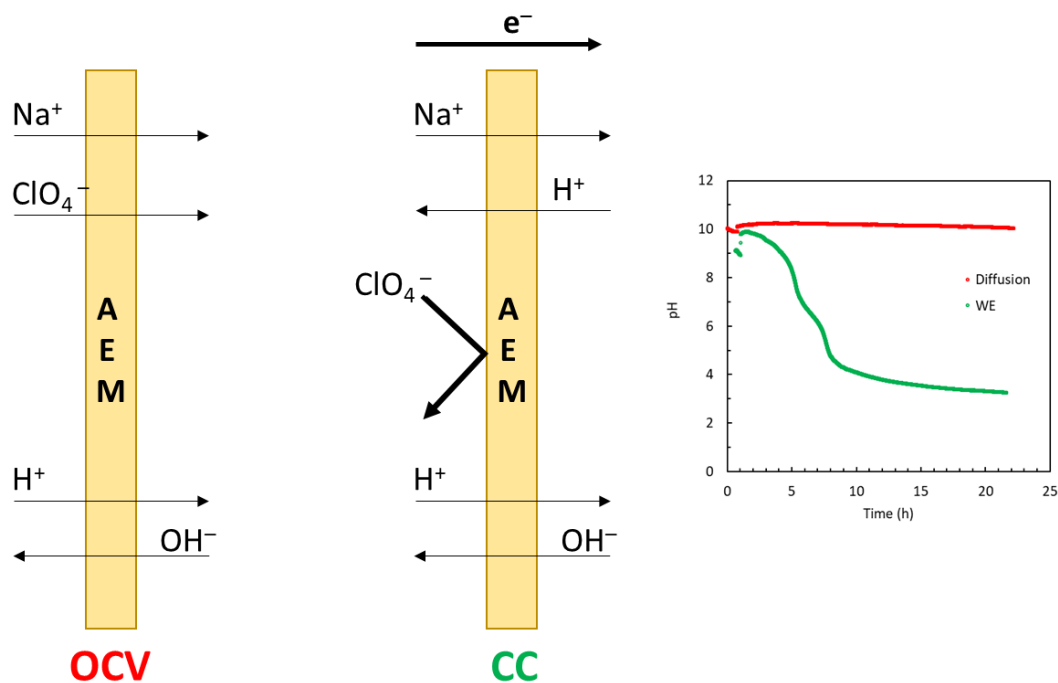


Figure S8. Mechanism controlling ion transport during open circuit voltage (OCV) and closed circuit (CC) configuration. At OCV there is no electric field, Na^+ diffuses through the AEM and its transport is accompanied by ClO_4^- transport to maintain electroneutrality. In CC operation mode, the charge transported by the electrons avoids ClO_4^- transport and the charge transported by Na^+ diffusion from anode to cathode is balanced by H^+ diffusion from cathode to anode. Therefore, in OCV configuration, $\text{Na}^+/\text{ClO}_4^-$ diffusion do not produce pH changes while in CC operation, Na^+/H^+ transport generates large pH gradients in the cell.

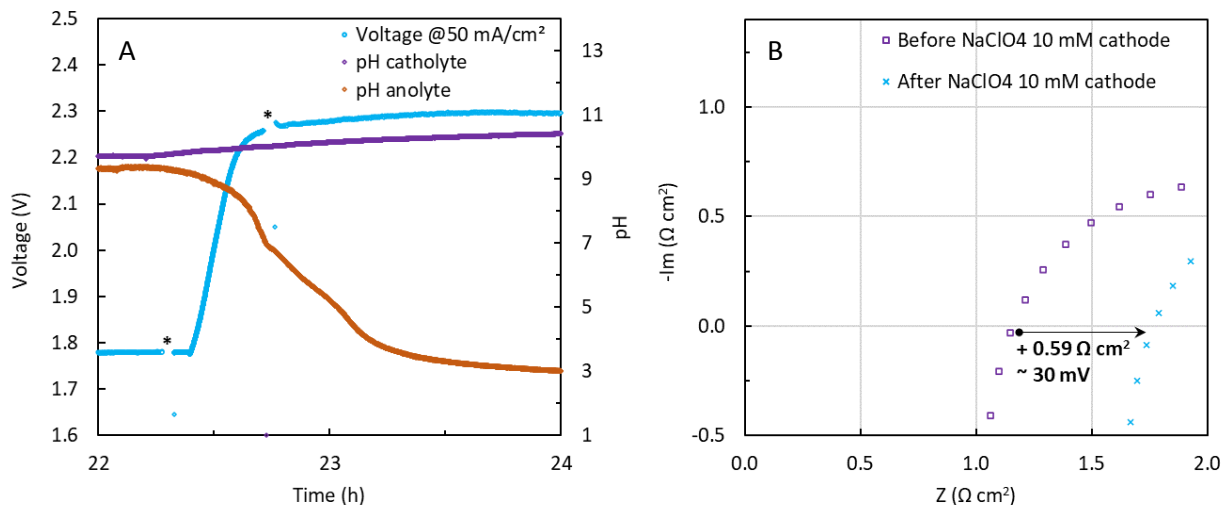


Figure S9. (A) Cell voltage and electrolyte pH change due to the addition of 10 mM NaClO₄ in the catholyte of a liquid catholyte AEM electrolyzer at 50 mA/cm². Adding salts in the cathode in a near-neutral pH solution facilitate the transport of perchlorate ions from cathode to anode, displacing the hydroxide ions and producing large pH gradients in the cell. (B) The transport of perchlorate ions in the cell is also accompanied by a large increase in the ohmic resistance likely due to the fact that perchlorate ion conductivity in the membrane is smaller than hydroxide ion conductivity.