

Increasing the Electrolyte Salinity to Improve the Performance of Anion Exchange Membrane Water Electrolyzers

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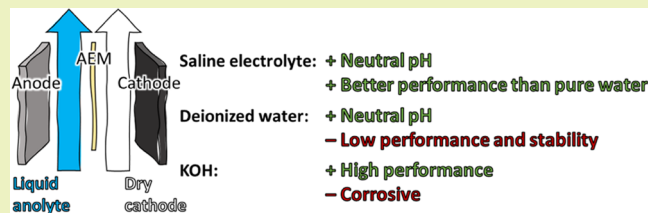
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Supporting Information

ABSTRACT: Direct operation of anion exchange membrane water electrolyzers (AEMWEs) with near-neutral pH feeds avoids the use of highly alkaline and corrosive solutions. However, using neutral pH solutions currently faces fundamental operational challenges that diminish performance and reduce long-term stability due to poor solution conductivity and low hydroxide ion concentration. Here, we showed that amending near-neutral pH solutions with low concentrations of alkali metal salts in a dry-cathode configuration substantially improved performance and stability. Adding NaClO_4 (10 mM) to the anolyte reduced the operating voltage by 0.19 to 2.58 V at 500 mA/cm^2 compared to non-saline solutions (2.77 V). However, further increases in the feed salt concentration (100 mM NaClO_4) reduced performance (2.64 V) due to a greater co-ion diffusion through the anion exchange membrane. Electrolyzer performance was further improved by utilizing salts with high conductivity such as KNO_3 . Using a saline anolyte reduced ohmic resistance, resulting in smaller applied voltage and energy consumption for hydrogen generation, while the combined effect of the membrane charge and the electric field direction in the dry-cathode feed configuration minimized ion crossover. Thus, increasing the salinity of near-neutral pH solutions represents a cost-effective strategy to improve the performance of AEMWE compared to ultrapure electrolytes, minimizing risks and costs associated with recirculating highly alkaline solutions.

KEYWORDS: green hydrogen, electrolysis, ion transport, anion exchange membrane water electrolyzer, saline electrolytes, solution pH, solution conductivity



INTRODUCTION

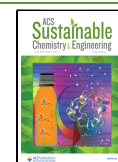
Green hydrogen produced by water electrolysis and powered by renewable energy plays a prominent role in the decarbonization of the energy, chemical, and transportation sectors.^{1,2} Anion exchange membrane (AEM) electrolyzers recently emerged as potential alternatives to the traditional alkaline and proton exchange membrane electrolyzers, relying on the transport of hydroxide ions between the electrodes and combining the low gas permeability of polymer membranes with the capability to use non-platinum group metal electrocatalysts.^{3,4} Initial attempts at improving AEM electrolyzer performance were focused on developing stable and high-performing membranes and electrocatalysts.⁵ Lately, electrolyte type and composition are being recognized as critical elements in the balance of plant for the implementation of AEM electrolyzers at the commercial scale.^{5–9} Most of the studies reporting efficient catalysts and stable membranes have been conducted using highly alkaline solutions to provide both high conductivity and minimize membrane degradation. However, there are several disadvantages in the use of caustic solutions rather than neutral pH media as electrolytes, such as corrosion and shunt current issues, as well as the hazards and costs associated with handling alkaline solutions (\$800/t KOH)^{7,8,10,11} compared to diluted electrolytes or deionized water.

Operating AEM electrolyzers with neutral pH media or deionized water represent a chemistry and engineering challenge, but solving these issues will advance AEM water electrolysis toward sustainable and safer industrial applications by avoiding the use of highly corrosive solutions.^{3,8,12} The solution conductivity directly impacts the ohmic resistance, and the low conductivity of deionized water reduces performance compared to concentrated alkali solutions.^{7–9,13} Previous studies have shown that shifting from a 0.3 M KOH electrolyte to deionized water increased the ohmic resistance by 52%, from 0.041 to 0.062 Ω at 500 mA/cm^2 , due to the lower solution conductivity of deionized water compared to that of KOH.⁸ Small spacings between the membrane and the catalyst particles can substantially contribute to ohmic resistance when using deionized water rather than concentrated hydroxide ion solutions, resulting in lower catalyst utilization and an increase in cell resistance.¹⁴ Moreover, electrolytes with neutral pH contain a small concentration of

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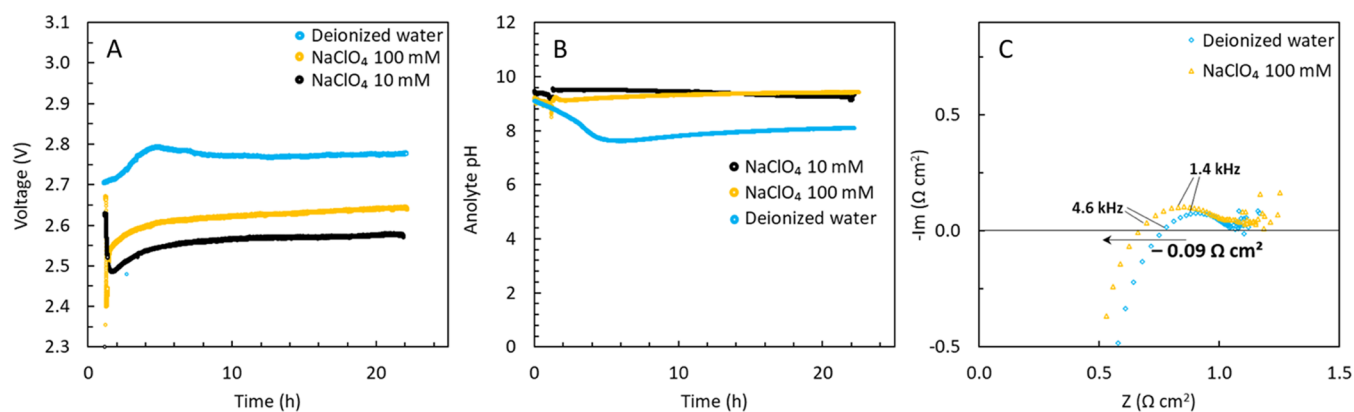
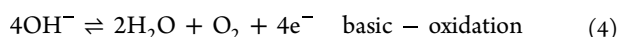
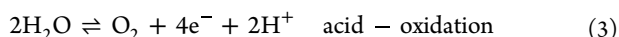
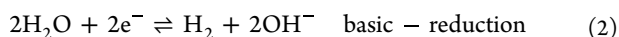
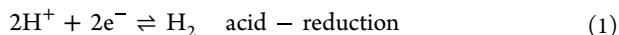


Figure 1. Performance of the anion exchange membrane water electrolyzer in the dry-cathode configuration fed with anolytes with different salinity. (A) Performance of the saline anolyte-fed electrolyzer at 500 mA/cm^2 and (B) corresponding anolyte pH. The voltage decrease in (A) after approximately 1 h of operation indicates when salts were added to the electrolytes. (C) Impact on the EIS spectra of addition of salts (100 mM NaClO_4) in the anolyte. The Bode plot of the EIS spectra as well as the NaClO_4 10 mM spectrum are reported in the Supporting Information (Figures S3 and S4).

hydroxide ions that are critical for both the oxygen evolution (OER) and hydrogen evolution (HER) reactions, as shown in the following equations (eqs 1–4)



Oxidation reactions in environments with low concentrations of hydroxide ions ($\text{pH} \sim 9$ [OH^-] = $10 \mu\text{M}$) likely proceed through the acidic route (eq 3) rather than the basic pathway (eq 4) due to the high concentration of H_2O (55 M) in solution compared to OH^- . A recent simulation study indicated that while in high (13) and low (0) pH solutions, the bulk and local pH values at the reaction site are similar, large deviations occur in near-neutral pH solutions (pH 8–9), where the local anode pH approaches 2 in the mass-transfer boundary layer even for moderately low current densities (30 mA/cm^2).¹⁵ Low anodic local pH combined with high cathodic pH increases cell voltage due to the Nernst equation by 64 mV/pH at $55 \text{ }^\circ\text{C}$.¹⁶ An increase in the cell voltage due to pH gradients and high ohmic resistance exacerbate the oxidative stress on the anode environment, resulting in faster degradation of the ionomer and reducing the stability of the cell.^{6,17}

Increasing the conductivity of non-corrosive electrolytes fed to AEM electrolyzers through salt addition has the potential to diminish ohmic resistance, increase catalyst utilization, and therefore reduce applied voltages and energy consumption at high current densities. Furthermore, operation with conductive solutions at circumneutral pH reduces hazards compared to caustic electrolytes, potentially diminishing operational expenditures. However, caution must be used to avoid contamination of the membrane with competing anions displacing OH^- to balance the charge (Figure S1). Competing ions can interact more strongly than OH^- with the positive charges in the membrane, reducing membrane conductivity and producing pH gradients between the electrodes.^{18–20} Here, we systematically investigated the impact of the addition of metal salts to near-neutral pH solutions on AEM water

electrolyzers using sodium perchlorate as a model salt due to its stability in an aqueous environment.²¹ We combined ion chromatography and electrochemistry to unravel the ion transport mechanism in dry-cathode and liquid-catholyte configurations. Dry-cathode layouts have been previously reported to maximize long-term performance by reducing chemical degradation and facilitating gas removal from the cathode.²² Finally, we compared the performance of dry-cathode configurations fed with deionized water or different salt solutions (sodium perchlorate, sodium bicarbonate, potassium nitrate) and tap water. The results of this work advance the current understanding of ion transport in AEM electrolyzers and the impact of the feeding configuration, providing new insight into the effect of the electrolyte type and composition on electrochemical performance.

EXPERIMENTAL SECTION

Materials and Electrolyzer Operation. Pt black (Fuel Cell Store) sprayed on carbon paper was used as the cathode, while Ir nanoparticles (American Elements) on an ultrathin titanium porous transfer layer were used as an anode catalyst. Anode and cathode electrodes (5 cm^2) were prepared following a previously published method using PiperION as an ionomer (Fuel Cell Store).⁷ The final catalyst loading was $2.0 \pm 0.5 \text{ mg/cm}^2$ for both electrodes. The membrane was an anion exchange membrane (PiperION, $80 \mu\text{m}$; Fuel Cell Store) conditioned accordingly to the manufacturer's instructions and washed with deionized water prior to use. Electrodes and the membrane were assembled in the stack (Dioxide Materials; Ti anode bipolar plate and Ni cathode bipolar plate) and a torque wrench was used to tighten the screws to 6 N m at a 2 N m increment.

Initial tests with $18.2 \text{ M}\Omega \text{ cm}$ deionized water resulted in low reproducibility and large variability of the pH measurement due to the absence of ions in the electrolytes. Further tests indicated that KOH $250 \mu\text{M}$ produced performance comparable to deionized water while enabling stable pH measurements, and it was therefore used in any subsequent tests (Figure S2). Salts (NaClO_4 , KNO_3 , NaHCO_3) were added at different stages of analysis directly in the anolyte. The pH of the electrolytes was continuously monitored over time (ET042 eDAQ, Australia). The solution conductivity was routinely measured with a Mettler Toledo conductivity meter (S47 SevenMulti). The anolyte and catholyte were recirculated in the respective electrode chambers at 25 mL/min . In the dry-cathode configuration, only the overhead of the catholyte reservoir was recirculated. The anolyte, catholyte, and cell were maintained at $55 \text{ }^\circ\text{C}$ for the duration of the experiment.

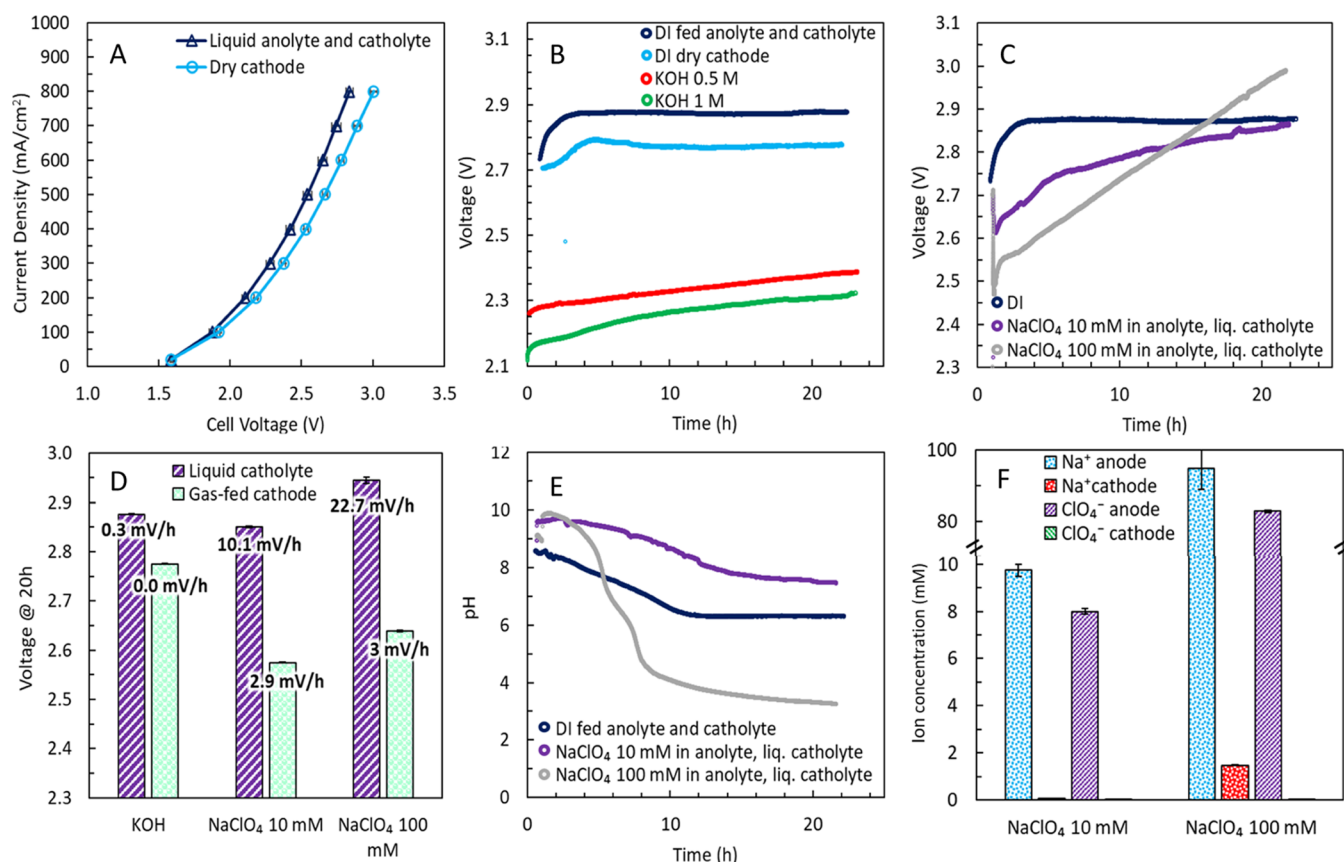


Figure 2. Performance of liquid-anolyte and liquid-catholyte AEM electrolyzers. (A) Polarization test of the liquid-anolyte and catholyte configuration compared to the dry-cathode mode and (B) corresponding cell voltage over time at 500 mA/cm². Salts were added to the anolyte, while deionized water was recirculated in the catholyte. (C) Impact of the addition of salts on the voltage of liquid-anolyte and liquid-catholyte electrolyzers. The voltage decrease after approximately 1 h of operation indicates when salts were added to the electrolytes. (D) Voltage degradation rate of the liquid-anolyte and catholyte versus dry-cathode configurations. (E) Change in anolyte pH during the chronoamperometry analysis. (F) Ion concentration after 20 h of operation in the liquid-anolyte and catholyte configuration.

Ion Transport Analysis. Samples were collected at different times directly from anolyte and catholyte reservoirs and analyzed with ion chromatography to investigate the ion transport mechanism in the cell. The diffusion of sodium ions through the membrane in the absence of an electric field was determined by assembling the cell as specified above and not applying any current through it. All of the ion concentration measurements were conducted in duplicate.

Electrochemical Tests. The cell was conditioned according to a previously published method.⁷ Polarization curves were conducted with a VMP3 potentiostat (5 A booster) by recording the voltage at 20, 100, 200, 300, 400, 500, 600, 700, and 800 mA/cm² for 2 min each. At the end of the polarization curve, EIS spectra were recorded at 1.7, 1.9, 2.1, and 2.3 V. Chronoamperometries were performed at 500 or 50 mA/cm². EIS spectra were recorded before and after the addition of salts in the electrolytes at the voltage corresponding to the applied current density.

RESULTS AND DISCUSSION

Improving Electrolyzer Performance Requires Optimization of Salt Concentration in the Anolyte. Addition of sodium perchlorate to the anolyte in the dry-cathode configuration improved the electrolyzer performance by reducing the operating cell voltage from 2.77 to 2.57 V with 10 mM NaClO₄ at 500 mA/cm² (Figure 1A). Further increasing the salt concentration from 10 to 100 mM slightly reduced the performance, as shown by a higher cell voltage of 2.64 V, although both potentials were lower than those using deionized water. This voltage increase with the 100 mM

solution was likely due to the charge balanced by the transport of sodium or perchlorate ions through the membrane, producing local pH changes next to the anode and cathode, despite a stable bulk pH of the anolyte over the course of the analysis (Figure 1B).

The lower cell voltage of saline-fed electrolyzers was only partially due to a decrease in the high-frequency resistance calculated from electrochemical impedance spectra (EIS). For example, the resistance based on the high-frequency region intercept of the x-axis (Figure 1C) decreased by 0.09 Ω cm² at 500 mA/cm² after addition of 100 mM NaClO₄ in the anode feed, corresponding to a maximum voltage reduction of only 0.05 V, approximately one-third of the observed voltage drop (0.13 V). Modeling studies have previously indicated that using electrolytes with high conductivity rather than deionized water in AEM electrolyzers enables a larger utilization of the electrocatalytic surface area by providing additional pathways for hydroxide ion transport and favoring bubble removal during gas evolution.¹⁴ For example, it was reported that replacing a deionized water electrolyte with high conductivity and alkaline solution such as 1 M KOH increased the electrochemical surface area by approximately five times by facilitating ion transport from the catalyst particles not in the immediate vicinity of the membrane and ionomer. Thus, in a similar way, it is likely that the addition of salts to the electrolyte enabled a more efficient utilization of the catalysts

compared to low-conductivity electrolytes by increasing solution conductivity and decreasing ohmic resistance.¹⁴ The lower voltage of the dry-cathode electrolyzer fed with 10 mM NaClO₄ in the anolyte was maintained during operation for >40 h, indicating that saline electrolytes can improve long-term performance (Figure S5).

Dry-Cathode Configurations are Needed to Operate Effectively with Saline Electrolytes. Liquid-anolyte and catholyte configurations fed with low-conductivity electrolytes outperform the dry-cathode setup in initial polarization tests, with a cell voltage 0.17 V lower at the highest current density of 800 mA/cm² (Figure 2A). However, in chronoamperometry tests, the dry-cathode configuration required a cell voltage 0.11 V lower than the liquid-anolyte and catholyte feeding mode at the same current density (500 mA/cm²; Figure 2B). It was previously reported that the superior performance of the dry-cathode configuration could be induced by a uniform cathode utilization, facilitated by a more efficient diffusion of the H₂ bubbles generated on the electrode in a gas chamber compared to a liquid electrolyte.²² Additionally, it was hypothesized that the dry-cathode configuration facilitated the evolution of a local high electrode pH next to the cathode, improving the HER kinetics.

Adding salts into the anolyte in a liquid-catholyte configuration decreased the performance and produced large variations in the cell voltage over time. Amending the anode electrolyte with 10 mM NaClO₄ in the liquid-anolyte and liquid-catholyte (deionized water) configuration produced erratic performance and a fast increase of the cell voltage in the first 20 h of operation, despite an initial decrease of the applied voltage. For example, the voltage was 2.70 V after 4 h of operation, 0.17 V smaller than that fed with deionized water (2.87 V). However, the voltage quickly increased to 2.85 V after 20 h, similar to that obtained with no salts in the solution. Further increasing the salt concentration to 100 mM NaClO₄ resulted in an even larger initial voltage drop (2.60 V, 4 h) accompanied by more unstable performance over time (2.96 V, 20 h) (Figure 2C). Therefore, adding salts to the anolyte of the AEM electrolyzer is an effective strategy to improve performance compared to deionized water feeds only in the dry-cathode configuration. The dry-cathode configuration with a salty anolyte resulted in performance decay approximately 1 order of magnitude smaller than those of the liquid-catholyte operation mode of 2.9 mV/h compared to 10.1 mV/h for 10 mM NaClO₄ and of 3.0 mV/h compared to 22.7 mV/h for 100 mM NaClO₄, likely due to generation of smaller pH gradients across the membrane (Figure 2D).

Salts addition in the electrolyzer configuration where anode and cathode were both fed liquid electrolytes produced a decrease in performance due to large pH changes. The anolyte pH rapidly decreased when 100 mM NaClO₄ was added to the solution, from 9.9 to 4.1 in less than 10 h of operation, while the catholyte pH change was minimal (~0.7 unit of pH, Figure 2E). A much smaller pH change was observed with less (pH from 9.4 to 8.6) or no salt (pH from 8.4 to 6.8) in the anolyte. Variations in the electrolyte pH can have a large impact on the electrochemical performance of a cell. Based on the Nernst equation, at 55 °C, each unit of pH difference will produce a cell voltage change of approximately 0.06 V; therefore, in our configuration, a pH difference of 6 units of pH was responsible for an increase in the applied voltage of approximately 0.38 V. Additionally, a variation in the local pH can negatively affect the kinetics of an electrochemical reaction, for example, the

OER is typically favored in a basic pH compared to an acidic environment. Thus, pH changes in our system have not only thermodynamic but also kinetic implications and could likely be identified as a critical factor in the performance degradation of the liquid-anolyte and liquid-catholyte configuration.

Diffusion Controls the Transport of Sodium Ions through the Membrane. The evolution of the pH gradient in the cell was due to the transport of positive ions through the anion exchange membrane, even though this membrane should selectively transport negatively charged ions and reject cations based on the high ion exchange capacity and positively charged moieties. When 100 mM NaClO₄ was fed to the anode, the sodium ions diffused through the membrane, accumulating in the cathode chamber. We determined through ion chromatography that the concentration of sodium ions leaked in the catholyte after approximately 20 h was 1.48 ± 0.02 mM, slightly larger than the concentration of H⁺ accumulated in the anolyte over the same period of time (~0.5 mM) based on the pH of the anolyte solution. Therefore, for each sodium ion diffusing from the anode chamber to the cathode chamber, approximately one proton accumulated in the anolyte, driving the development of a large pH gradient over time as the sodium ions accumulated in the cathode chamber. To balance the charge due to sodium transport through the membrane and maintain electroneutrality, protons diffused from the cathode to the anode. The transport of positive ions is not typically considered important in AEM electrolyzers due to the membrane charge, which rejects positive ions and favors the transport of negative ions, such as hydroxide; but this transport cannot be neglected here due to the presence of salts.

The negative charge carried by the electrons from the anode to the cathode needs to be balanced by migration of positive ions in the same direction or negative ions in the opposite. Therefore, we initially hypothesized that sodium transport was facilitated by the electric field, pulling Na⁺ from the anode to the cathode to maintain electroneutrality. Further analysis demonstrated that sodium ion transport occurred primarily by diffusion and not migration. In the absence of an electric field, when all other parameters were maintained equal, the sodium ion concentration in the cathode chamber after 20 h was 1.80 ± 0.05 mM (Figure S6), slightly larger than that obtained in the presence of the electric field. These results were further confirmed by an additional experiment at a low current density of 50 mA/cm² and therefore with a weaker electric field, where the concentration of sodium ions in the catholyte after 20 h of continuous operation was 1.13 ± 0.00 mM (Figure S7). Migration, as well as diffusion, is driven by the concentration gradient. Therefore, the absence of sodium ion migration can likely be explained by a local high pH in the cathode chamber, which facilitates the migration of hydroxide ions from the cathode to balance charge rather than sodium from the anode. Perchlorate ions were effectively rejected and their accumulation in the cathode chamber was minimal (<0.1 mM).

The predominant role of diffusion on sodium transport explains the superior performance of the dry-cathode configuration over the liquid cathode and liquid-catholyte mode. During dry-cathode operation, a thin aqueous layer is formed in the cathode chamber between the electrode and the membrane, presumably of only a few microliters in volume. Sodium ions can diffuse from the anolyte through the membrane to the thin aqueous layer in the cathode chamber during operation. However, with diffusion controlling sodium transport, the concentration gradient across the membrane

dictates the amount of sodium ions diffusing. Therefore, only a few sodium molecules diffusing through the AEM minimize the concentration gradient due to the small liquid volume next to the cathode. In contrast, when a catholyte with a volume of a few hundreds milliliters is used, the sodium ions diffusing through the membrane are continuously diluted in the electrolyte, maintaining a high Na^+ concentration gradient between the anolyte and the catholyte. The large transport of sodium ions through the membrane reduces the anolyte pH, resulting in lower electrolyzer performance and stability.

The dry-cathode configuration fed with a salty anolyte produced superior performance compared to the liquid-catholyte operation mode with equal salt concentrations in the anolyte by coupling the advantages of higher solution conductivity with limited sodium diffusion through the membrane, reducing local pH gradients. For example, assuming a final concentration of sodium ions in the catholyte of 1.5 mM and a catholyte volume of 500 μL in the dry-cathode configuration, only 0.75 μmol of sodium ions diffuse through the membrane, 3 orders of magnitude smaller than that with 500 mL of the catholyte (750 μmol), producing a minimal perturbation in the anode pH (final pH of 6 for the dry cathode vs 3 for the liquid catholyte based on one H^+ accumulation for each Na^+ diffusing; Figure 3). The perform-

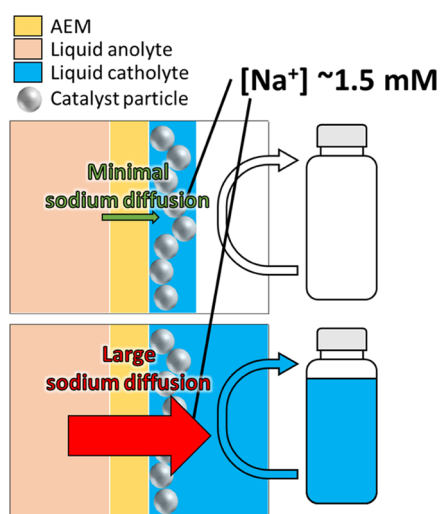


Figure 3. Schematic of the impact of the catholyte volume on sodium diffusion. Assuming a final concentration of sodium ions in the catholyte of 1.5 mM, the smaller electrolyte volume of the dry-cathode configuration reduces the number of moles of sodium ions diffusing through the membrane, avoiding the development of large local pH gradients.

ance of the 100 mM NaClO_4 dry-cathode electrolyzer was worse than that of the cell fed with 10 mM NaClO_4 likely due to a larger sodium diffusion through the AEM with the larger salt concentration, producing a slightly larger pH gradient and therefore requiring higher voltage input at similar current densities (Figure 1A).

Changing Electrolyte Conductivity Directly Impacts Electrolyzer Performance. The potential of using less expensive but potentially less stable salts other than perchlorate was examined for the dry-cathode configuration fed with solutions of NaHCO_3 or KNO_3 , or tap water. After 20 h of continuous operation, the electrolyzer fed with KNO_3 required the smallest cell voltage input (2.53 V) compared to the

perchlorate control (10 mM NaClO_4 , 2.57 V) and NaHCO_3 (2.66 V). All these electrolyzers performed better than the same system using a non-saline anolyte (2.77 V) (Figure 4).

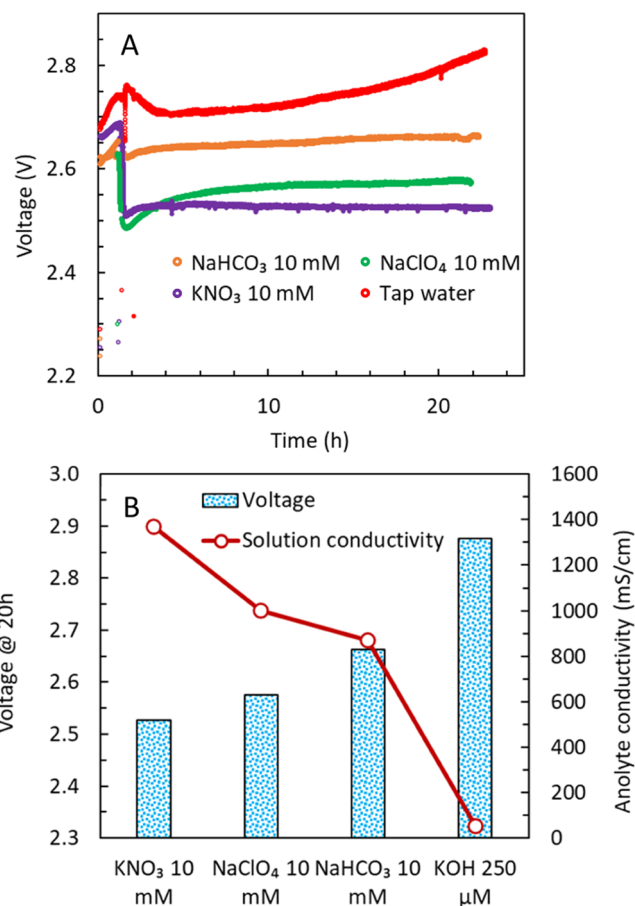


Figure 4. Impact of electrolyte composition on the performance of dry-cathode AEMWE at near-neutral pH. (A) Long-term test at an applied current of 500 mA/cm^2 . The voltage decrease after approximately 2 h of operation indicates when salts were added to the electrolytes. (B) Impact of the anolyte conductivity on the cell voltage. The higher the solution conductivity, the smaller (less energy consumption) the cell voltage after 20 h of operation.

The electrolyzer performance with the different salts was in agreement with the solution conductivity of each component. For example, the solution containing 10 mM KNO_3 , producing the best performance, had the highest solution conductivity of 1370 $\mu\text{S}/\text{cm}$, followed by NaClO_4 (999 $\mu\text{S}/\text{cm}$) and NaHCO_3 (871 $\mu\text{S}/\text{cm}$), indicating that the final solution conductivity dictates the performance gain due to the addition of salt to the anolyte (Figure S8). The test with tap water produced erratic performance and a large voltage increase from 10 to 20 h of operation, likely due to the precipitation of salts on the electrodes.

Implications of the Use of Saline Electrolytes on the Electrolyzer Performance and Operation. Typically, water electrolyzers are operated with ultrapure electrolytes to avoid the contamination of the membrane and the development of undesired reactions.¹⁰ Proton exchange membrane electrolyzers, leveraging the high conductivity of Nafion and the intimate connection between the catalyst and the membrane in zero-gap cells, do not need highly conductive and low pH electrolytes to operate and are typically fed with deionized

water. Applying heat and pressure between the support and the membrane avoids the development of gaps between catalyst particles and the ionomer, while the electrolyte flowing behind the membrane–electrode assembly provides water for the electrochemical reactions. In AEM electrolyzers, using a hot-pressing method to physically connect the catalyst and the membrane is not always feasible due to the low thermal stability of the anion exchange ionomer.²³ Therefore, it is not possible to develop a membrane–electrode continuum, leading to the formation of gaps between the catalyst and the membrane.²⁴ Filling these gaps with high-conductivity electrolytes avoids the development of preferential pathways for charge transport during electrolysis. Typical electrolytes contain high concentrations of hydroxide ions to maintain a stable and high pH throughout the cell and provide the reagents needed for the anodic OER. Here, we found that diluted saline solutions can be used in AEM electrolyzers to decrease ohmic resistance and improve performance compared to deionized water or ultrapure solutions.

Using saline solutions in AEM electrolyzers could potentially simplify operation and diminish risks, minimizing operational costs. Current water purification technologies can effectively remove unwanted ions and contaminants from water. However, energy consumption to produce highly desalinated water greatly increases as the concentration of ions to be removed diminishes.^{25,26} For example, reverse osmosis (RO) can purify seawater and bring ion concentration down to the millimolar range with an energy efficiency close to the thermodynamic limit. However, producing ultrapure water suitable for water electrolyzers requires additional technologies with high energy demand such as ion exchange or electro-deionization, where the ions in solution are replaced with H⁺ and OH⁻ from concentrated sulfuric acid and potassium hydroxide, respectively, or from water splitting. Thus, the direct use of electrolytes with a low concentration of salts in solution can be appealing for reducing the water purification steps that contribute to both the energy consumption and complexity of system operation, with greater reason if the use of such electrolytes is accompanied by better performance and a lower cell voltage as shown here. Future studies should focus on identifying the impact of different salt compositions on the electrocatalytic reactions, including long-term analysis, and determining the effect of the operational variables such as the electrolyte flow rate, temperature, and applied voltage on the performance as well as the membrane composition and thickness. A thinner membrane will exhibit a larger ion crossover than a thicker membrane due to the larger concentration gradient of the ions across the membrane, which is the driving force for diffusion. Additionally, cost and safety considerations need to be taken into account when considering the potential use of saline electrolytes compared to concentrated hydroxide ion solutions.

CONCLUSIONS

Amending the anode electrolyte with specific salts improved the AEM electrolyzer performance in the dry-cathode configuration as shown by a decrease in the cell voltage. This improvement was directly related to the solution conductivity, which decreased the required applied voltage due to a decrease in the ohmic resistance. The dry-cathode configuration enabled better performance and lower applied voltage compared to using a liquid catholyte by avoiding the buildup of large pH gradients across the membrane. The main

mechanism controlling co-ion transport was diffusion and not migration, despite the strength of the electric field. The transport of sodium through the membrane was accompanied by the accumulation of protons in the anode chamber, and reducing the catholyte volume in the dry-cathode configuration diminished the amount of sodium ions transported and therefore avoided the development of large pH gradients.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.3c01245>.

Schematic of ion transport mechanisms; Bode and Nyquist plots of the EIS spectra for deionized water and NaClO₄ 10 and 100 mM; impact of electrolyte feeding type and configuration on performance and solution pH; and ion concentration from diffusion and migration as a function of the current density (PDF)

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Notes

The authors declare no competing financial interest.

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