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Assessing the Long-Term Stability of Anion Exchange Membranes for Electrochemical CO₂ Reduction

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Abstract: *Materials and cell components used in CO₂ electrolysis have largely been adapted from technologies initially developed for water electrolysis and fuel cells. However, electrochemical CO₂ reduction introduces distinct material challenges due to the unique chemical environment in this process. In this study, we conducted ex-situ 1000-hour stability tests on commonly used anion exchange membranes, exposing them exclusively to electrolytes and organic molecules used or produced during CO₂ electrolysis, at concentrations relevant to and compatible with post-separation processes. Notably, 15% w/w n-propanol and 5 M acetic acid caused complete dissolution or partial disintegration of the membranes unless crosslinking is present and remains stable throughout the test. When the membranes stayed physically intact, most of them exhibited excellent chemical stability in alkaline medium containing alcohols or formic acid which were confirmed by vibrational spectroscopy and ion exchange capacity measurements. However, exposure to alcohol- and acid-containing solutions led to substantial increase in swelling and water uptake, with potential implications for mechanical stability, ion/product crossover, and compression management of adjacent components. The potential effects of CO₂ electroreduction products on membrane stability, their subsequent impact on electrolyzer performance and mitigation strategies are discussed.*

Keywords: *anion exchange membranes, CO₂RR, durability, ion exchange capacity, vibrational spectroscopy, electrochemical CO₂ conversion.*

INTRODUCTION

Ion exchange membranes (IEMs) are essential components in many modern electrochemical systems.¹ Over the past decade, significant advancements have been made in improving the (electro)chemical and mechanical properties and stability of anion exchange membranes (AEMs).² Much of this progress has been driven by the demands of water electrolysis, electrodialysis, and fuel cell applications, with a focus on enhancing their stability in alkaline and oxidative environments.³⁻⁵ Most electrochemical carbon dioxide reduction reaction (CO₂RR) studies have adopted the same

types of AEMs, as many of these studies are conducted in neutral to alkaline media, where the predominant charge carriers are anions, such as OH^- and CO_3^{2-} .^{2, 6, 7} The effect of OH^- on the chemical stability of AEMs has been heavily investigated, particularly in the context of alkaline water electrolysis and fuel cells.^{2, 8} CO₂RR environments may present additional challenges beyond alkalinity, primarily due to the formation of organic products such as alcohols and acids.^{9, 10} These products can interact with the membrane, potentially affecting its chemical stability and performance over time. As a result, membranes in CO₂RR systems must withstand not only the alkaline conditions but also the presence of various organic products, which can introduce further degradation pathways.

The stability of AEMs under CO₂RR conditions has received relatively little attention, despite its critical importance in advancing CO₂ conversion technologies. However, this topic has garnered significant attention in the context of alcohol fuel cells, where alcohols such as methanol and ethanol are used as fuel sources.¹¹ Understanding the effect of alcohols on membrane materials in alcohol fuel cells is crucial, as alcohol permeation can lead to reduced efficiency, degradation of membrane properties, and potential crossover effects. Exposure to alcohols may lead to increased swelling due to higher water uptake which may lower the mechanical properties and increase the permeability of the membranes.¹²⁻¹⁴ In some polymers, excessive swelling from water and alcohol absorption compromises structural integrity and can even lead to complete dissolution of the membrane.^{15, 16} In relation to CO₂RR, Hasa et al. conducted a study on various membrane types to evaluate ethanol crossover during electrochemical carbon monoxide reduction (COR) and establish correlations with key membrane properties.¹⁷ A subsequent accelerated stability study at 500 mA/cm² over 6 hours revealed significant differences in the chemical stability of various functional groups within the membranes. On the other hand, the focus of many CO₂RR studies has been on enhancing selectivity toward alcohol production, rather than achieving a more concentrated stream

of products that could challenge membrane stability.¹⁸ In short-duration experiments or those where the electrolyte is frequently refreshed, the concentrations of alcohols produced are typically too low to significantly impact the membrane's properties.¹⁹ However, as the systems are scaled to larger cell sizes, down-the-channel product concentrations inevitably increase, leading to higher accumulation along the flow path.^{20, 21} In addition, ultimately, these processes may need to achieve a substantial concentration of alcohols to reduce separation costs and make the technology economically viable. For instance, fermentation processes typically produce ethanol concentrations in the 8-20 wt % range, with lower concentrations potentially making the process economically unviable.^{22, 23} A base case scenario assumed a concentration of liquid products around 10 wt % to provide a consistent framework for evaluating the economic and technical feasibility of CO₂ electrolysis.²⁴ Nevertheless, recently, Robb et al. achieved a 12.4 wt % of ethanol by adding a porous layer between the catalyst layer and AEM to accelerate evaporation of ethanol while slowing down water transport from the anode.²⁵ This configuration was subjected to a 12-hour stability test to assess its performance. In addition, new post-separation techniques are being explored to concentrate dilute ethanol streams, which may offer potential benefits for improving the durability of catalyst layers and AEMs.²⁶

Moreover, many studies have focused on catalysts that primarily generate CO or acids in the form of salts, such as formate or acetate. These products are more likely to influence the transport properties of the membrane, rather than its long-term durability. These have led most studies to prioritize investigating the membrane's role in influencing performance aspects like ion and water transport, product selectivity, crossover and carbonation rather than addressing its long-term stability under CO₂RR conditions.^{6, 17, 27, 28} Nonetheless, formic and acetic acid is one of the few liquid products has been produced in concentrated amounts during CO₂RR. Using porous ion-exchange resin between the IEM layers, researchers were able to prepare formic and acetic acid at moderate

to high concentrations (10-95 wt %). This configuration takes advantage of the AEM primarily interacting with the formate ion, which is subsequently converted into formic acid within the porous ion-exchange resin layer.^{29, 30} On the other hand, MEA-based scalable systems typically produce lower formic acid concentrations, often below 1 M, while concentrations of 2-5 M are preferred for efficient separation processes.³¹⁻³³ The exposure of AEMs to CO₂RR products as well as the concentration of CO₂RR products, are dictated by reactor design, integration with downstream processes, and the post-separation techniques employed. Since the impact of prolonged exposure to CO₂RR products on membrane durability remains unexplored, we propose that conducting initial ex-situ stability tests with CO₂RR products would be highly beneficial for the advancing field.

In this study, we exposed various types of commercial membranes to the primary liquid products of CO₂RR in the presence and absences of salts, i.e. KOH and K₂CO₃ for an extended duration of 1000 hours, and subsequently characterize key properties, including ion exchange capacity (IEC), ionic conductivity, water uptake, and swelling. In addition, we conducted a comprehensive characterization of AEMs using infrared (IR) and Raman spectroscopy to gain detailed insights into the chemical structural changes occurring within the membranes. Notably, in 15 wt % n-propanol and 5 M acetic acid, AEMs either dissolved completely or became physically disintegrated, except for the crosslinked ones, which remained intact as long as the crosslinks did not degrade. Ethanol and formic acid were less detrimental to the polymers, although they induced significant swelling, which in turn, had a pronounced effect on water uptake and ionic conductivity. In parallel, we discuss the potential implications of exposing AEMs to CO₂RR and COR products, focusing on how these changes may influence their electrochemical properties and long-term durability in CO₂/CO electrolyzers.

EXPERIMENTAL SECTION

Materials and Chemicals: Self-supporting anion exchange membranes (AEMs), Piperion® (20 µm), were obtained from Fuel Cell Store. Similarly, ORION CMX AEMs, also 20 µm and self-supporting, were sourced from Orion Polymer. Reinforced AEMION+® membranes, featuring a woven PEEK support structure and a thickness of 75 µm, were acquired from Ionomr. Additionally, crosslinked AEMION+ membranes, with thicknesses ranging from 40 to 60 µm, were provided by Ionomr. 1-N-propanol (ACS reagent, ≥99.5%) and ethyl alcohol (ACS reagent) were both purchased from Sigma-Aldrich. Acetic acid (glacial, ReagentPlus®, ≥99%) and formic acid (reagent grade, ≥95%) were also obtained from Sigma-Aldrich. Dimethyl sulfoxide-d₆ (99.9 Atom% D) was sourced from Cambridge Isotope Laboratories. Sodium chloride (99.5%, analytical grade) was obtained from Thermo Scientific Chemicals. Potassium carbonate (ACS reagent, ≥99.0%) and sodium nitrate (ReagentPlus®, ≥99.0%) were purchased from Sigma-Aldrich. Potassium hydroxide pellets (analytical grade, EMSURE®) were sourced from Merck. 0.1 mol/L (0.1 N) silver nitrate solution (Titrisol®) was purchased from Sigma-Aldrich. All experiments were conducted using Milli-Q Deionized (DI) water with a resistivity of 18.2 MΩ·cm.

Stability Tests: Polypropylene (PP) bottles (125 mL) and glass bottles with PTFE linings (250 mL) were washed with 1 M KOH, followed by three rinses with deionized (DI) water prior to testing. All membranes were also triple washed with DI water and ion-exchanged to the chloride form by soaking in 1 M NaCl overnight before being placed into the test solutions. A variety of test solutions were prepared, including deionized (DI) water with no added electrolyte, 1 M KOH, and 1 M K₂CO₃, with and without 15% w/w ethanol and n-propanol and added to PP bottles. Additionally, 5 M solutions of formic acid and acetic acid were prepared for the stability tests and added to the glass bottles. The

test conditions were summarized in the Supporting Information (Table SI1). Four pieces of membrane, each measuring 6 x 6 cm, were placed into separate bottles containing the respective test solutions and then placed in an oven at 80 ± 2 °C for testing. The membranes were left to sit in the sealed bottles at the specified conditions for the next 1000 hours. After the tests, the membranes were allowed to cool to room temperature while still in the test solutions. The membranes were then removed, triple washed with deionized (DI) water, and subsequently placed in 1 M NaCl solution. The NaCl solution was replenished three times, once per day, over three consecutive days. All membranes were stored in 1 M NaCl solution prior to further characterization. All membranes were dried in a desiccator at room temperature, unless otherwise specified, for characterizations that required drying.

IEC measurements: The chloride-exchanged membranes were dried at 60 °C, weighed, and placed into vials. NaNO_3 solution was then added to each vial to ion-exchange the membranes with nitrate. The chloride ions released into the solution were subsequently ready for titration. The chloride ions were titrated with a 0.1 N AgNO_3 solution using a Mettler Toledo (MT) T90 auto-titrator. Three separate 1 M NaCl solutions were used to check calibration and generate error bars for the measurements. Based on the chloride ion activity in the solution, a titration curve was constructed (Figure SI1). The volume at the equivalence point, combined with the concentration of the silver nitrate solution and the weight of the membrane, IEC of the membrane, indicating the number of ionic groups present.

Water Uptake measurements: Water uptake of the AEMs was measured using dynamic vapor sorption (DVS) with a TA Instruments Q5000. The chloride-exchanged membranes were dried at 60 °C, weighed, and placed in platinum sample pans. The weight change of the AEMs was monitored by exposing the membranes to varying relative humidity (RH) levels (0%, 20%, 40%, 60%, 80%, and 95%) for 1 hour at a fixed temperature of 60 °C, over two absorption and desorption cycles. The as-received

membranes were measured three times using this procedure to generate error bars. The water uptake (%) in grams of H₂O per gram of dry polymer was calculated using Equation 1.1,

$$\text{Water Uptake(\%)} = \frac{W - W_0}{W_0} \times 100 \quad 1.1$$

where, W_0 is the dry weight of the polymer measured at the end of the drying step and W is the wet weight of the polymer measured at the end of each step.

Ionic conductivity measurements: The chloride-exchanged membranes were cut into 5 x 50 mm pieces using a die cutter and the thickness of the membranes were measured by a micrometer in the hydrated state. These membranes were then placed in a four-point in-plane conductivity cell with parallel platinum electrodes spaced 6.4 mm apart. The AEMs were equilibrated at 95% RH in an environmental chamber (Test Equity, 1000H series) at 60 °C for 1 hour prior to each of the five consecutive electrochemical impedance spectroscopy (EIS) measurements. EIS measurements were performed using a Solartron 1470 multi-channel potentiostat, over a frequency range of 10 to 10⁵ Hz at an amplitude of 10 mV (Figure SI2). Ionic conductivity (σ) of the membranes was calculated via,

$$\sigma = \frac{L}{A \cdot R} \quad 1.2$$

where, L is the distance between the inner electrodes (cm), A is the cross-sectional area of the sample (cm²), R is the measured resistance (Ω).

Swelling measurements: Chloride-exchanged membranes were cut into 2 x 2 cm pieces using a die cutter. The membranes were then dried overnight in a desiccator, and the final thickness and width were measured in the dried state using micrometers. Volume swelling (%) of the membranes were calculated via,

$$\text{Volume swelling}(\%) = \frac{V_{wet} - V_{dry}}{V_{dry}} \times 100$$

1.3

Where V_{wet} is the volume of the membranes in the hydrated state and V_{dry} is the volume of the membrane in the dry state.

Spectroscopic characterization and analysis: Raman spectra of chloride-exchanged membranes were collected using an XploRA Plus Raman microscope over the range of 600–3600 cm^{-1} . The membranes were placed onto microscope slides, and spectra were acquired for Piperion and Orion membranes using a 638 nm laser and 2.1 cm^{-1} resolution. For Aemion polymers, a 785 nm laser and 2.1 cm^{-1} resolution were used. IR spectra were collected in attenuated total reflectance (ATR) mode using a Thermo Nicolet 6700 Fourier transform infrared (FTIR) spectrometer equipped with a DTGS detector. The spectra were acquired at a resolution of 4 cm^{-1} over the range of 600–3600 cm^{-1} . Both

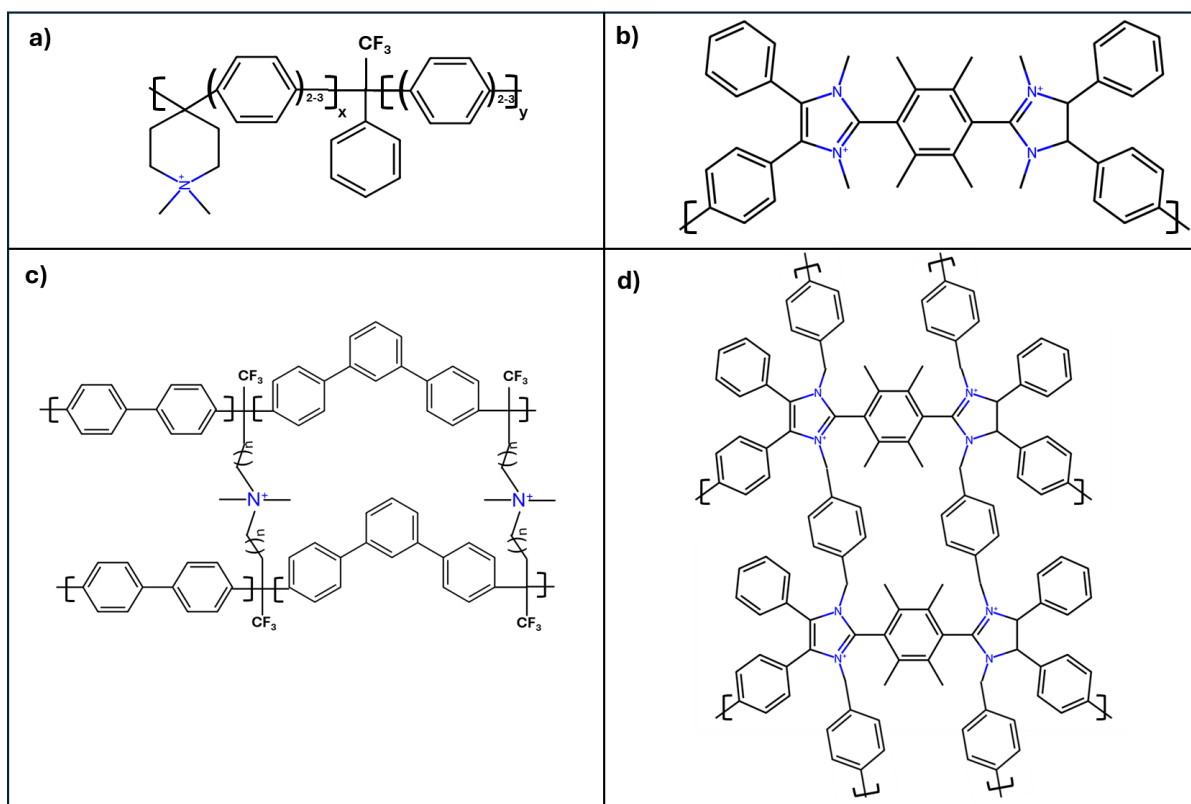


Figure 1: Chemical structures of studied AEMs **a)** Piperion **b)** Aemion **c)** Orion **d)** Crosslinked Aemion. The exact polymer structure may vary slightly from the schematic shown, as full structural details are not always disclosed by the manufacturer.

IR and Raman spectra were background-corrected using the Adaptive Iteratively Reweighted Penalized Least Squares (airPLS) algorithm.³⁴ Density functional theory (DFT) calculations were employed to optimize the geometries of the functional groups in the anion exchange membranes (AEMs) and to compute their vibrational spectra. All calculations were carried out using the ORCA 5.0.4 software package. The model compounds were optimized, and their normal modes were analyzed using the r2SCAN-3c method, a composite electronic-structure approach that has high accuracy and is computationally efficient.³⁵ This method incorporates Grimme's D4 dispersion corrections and utilizes the def2-mTZVPP basis set. The absence of imaginary frequencies in the results confirmed that the optimized structures are true minima on the potential energy surface. The IR intensities of the vibrational modes were calculated based on the changes in the transition dipole moment during vibrational motion. Raman activities were determined by numerically differentiating the polarizabilities along the normal coordinates and are proportional to the mean polarizability.

RESULTS AND DISCUSSION

The structures of the membranes examined in this study are illustrated in Figure 1a-d. Piperion can be considered a main-chain type polymer composed of methylated piperidinium cations and an aryl backbone. This membrane has recently attracted considerable attention for its remarkable performance in MEA-based cells in different applications.^{36, 37} Its high carbonate conductivity, combined with excellent mechanical stability, even at reduced thicknesses, makes it an ideal candidate for CO₂RR applications.^{36, 38} Orion polymers are crosslinked materials featuring a rigid poly(phenylene) backbone with quaternary ammonium groups attached via pendant aliphatic side chains. While quaternary ammonium groups are typically prone to degradation through SN₂ reactions and Hofmann elimination, the presence of alkyl side chains helps stabilize the positive charge^{39, 40}. Aemion polymers are cutting-edge materials developed by stabilizing the imidazolium ring. This was achieved by incorporating bulky and/or electron-withdrawing groups and removing

beta hydrogens to prevent degradation pathways.⁴¹ To address their generally suboptimal mechanical properties, these polymers can be reinforced with a mesh of polytetrafluoroethylene (PTFE).⁴² They exhibited excellent chemical stability in alkaline fuel cells and CO₂ electrolyzers^{28, 43} and crosslinking techniques have been employed to further enhance their mechanical strength.

Figure 2 presents the IEC results for the AEMs after 1000 hours in their respective solutions at 80 °C. N/A indicates conditions that resulted in complete or partial dissolution and physical disintegration of the membrane, making further characterization impossible (Figure SI3 and SI4). Notably, 15% n-propanol and 5 M acetic acid proved to be the most destructive environment for the AEMs. The crosslinked membranes, i.e. Orion and Aemion, survived in 15% n-propanol and Acetic acid solutions. However, crosslinked Aemion dissolved when electrolytes were present in addition to alcohols, likely due to degradation of the crosslinked structure, as will be shown below. We noted that higher concentrations of alcohols may cause immediate dissolution such as Piperion, which dissolves within a day at room temperature above 50 % ethanol and 20% n-propanol (Figure SI5). In

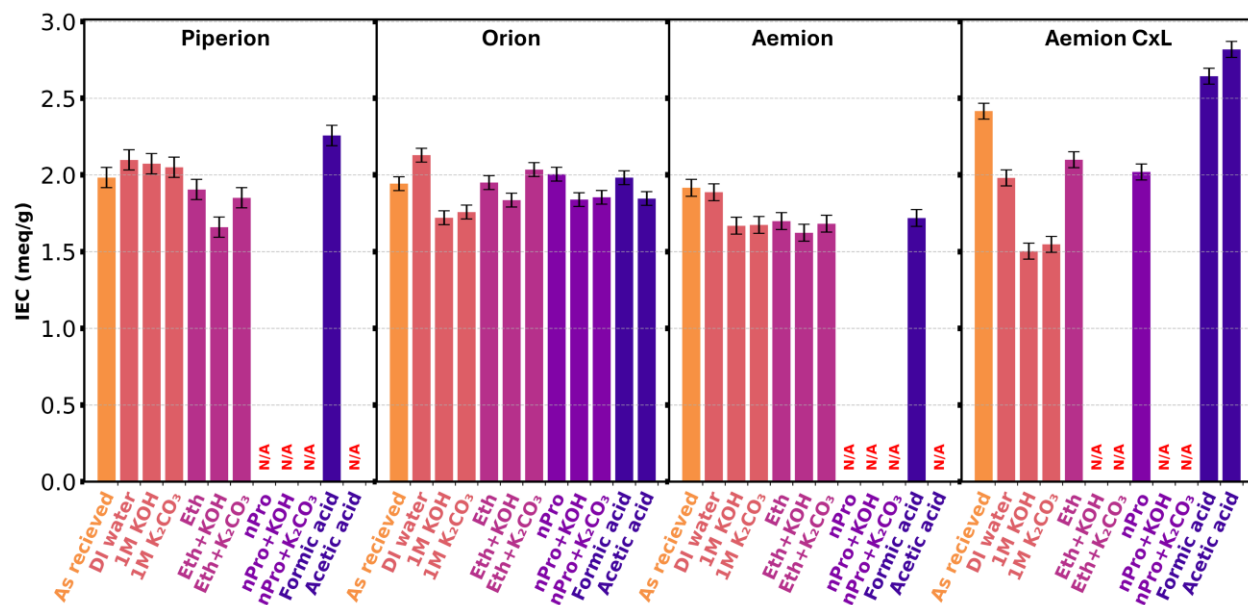


Figure 2: IEC values of membranes after 1000-hour exposure at 80°C to various electrolyte and organic molecule compositions. Solutions with ethanol and n-propanol are at 15% w/w. Concentration of formic and acetic acid are 5 M while KOH and K₂CO₃ electrolytes are 1 M.

linear and branched polymers, chains can remain connected through physical interactions, even in the absence of chemical crosslinking. This allows the polymer matrix to remain cohesive, even when undergoing significant expansion during water uptake. However, when alkyl groups are attached to the hydroxide group, such as in ethanol and n-propanol, solvent molecules may interact with the hydrophobic polymer backbone, potentially causing plasticization and partial or complete dissolution of the polymer chains. This interaction appeared to be more favorable in the case of n-propanol, likely due to its longer alkyl chain. In contrast, crosslinked polymers are more resistant to dissolution due to the presence of covalent bonds between chains, which provide structural integrity and stability, even in the presence of solvents.⁴⁴ The addition of alcohols into test solutions containing electrolytes did not cause an apparent loss in IEC or revealed a clear trend for all the membranes, whereas acids generally result in slightly higher IEC values possibly due to protonation of residual tertiary amides. Except for crosslinked Aemion, the membranes retained high IEC after exposure to electrolytes and CO₂RR products. This stability reflects the fact that these materials were originally engineered and rigorously optimized for alkaline water-electrolysis, where protection of the ionic groups against degradation is a key design criterion. The IEC results, along with the vibrational spectroscopy findings, will be discussed later in the text.

Water uptake and volume swelling values after 1000 hours at 80 °C are presented in Figure 3a and 3b, respectively. Unlike the IEC results, there was a noticeable effect and trend in the impact of alcohols and acids on the water uptake and swelling behavior of AEMs, albeit to varying extents. Piperion exhibited the most distinct change upon exposure to ethanol and formic acid and absorbed significantly more water and exhibited a corresponding dramatic increase in swelling. Alcohols can enhance the mobility of polymer chains, leading to changes in the spacing between hydrophobic and hydrophilic domains. This process increases porosity and creates additional free space, causing the polymer to absorb more water and swell more.^{45,46} Crosslinking can restrict chain

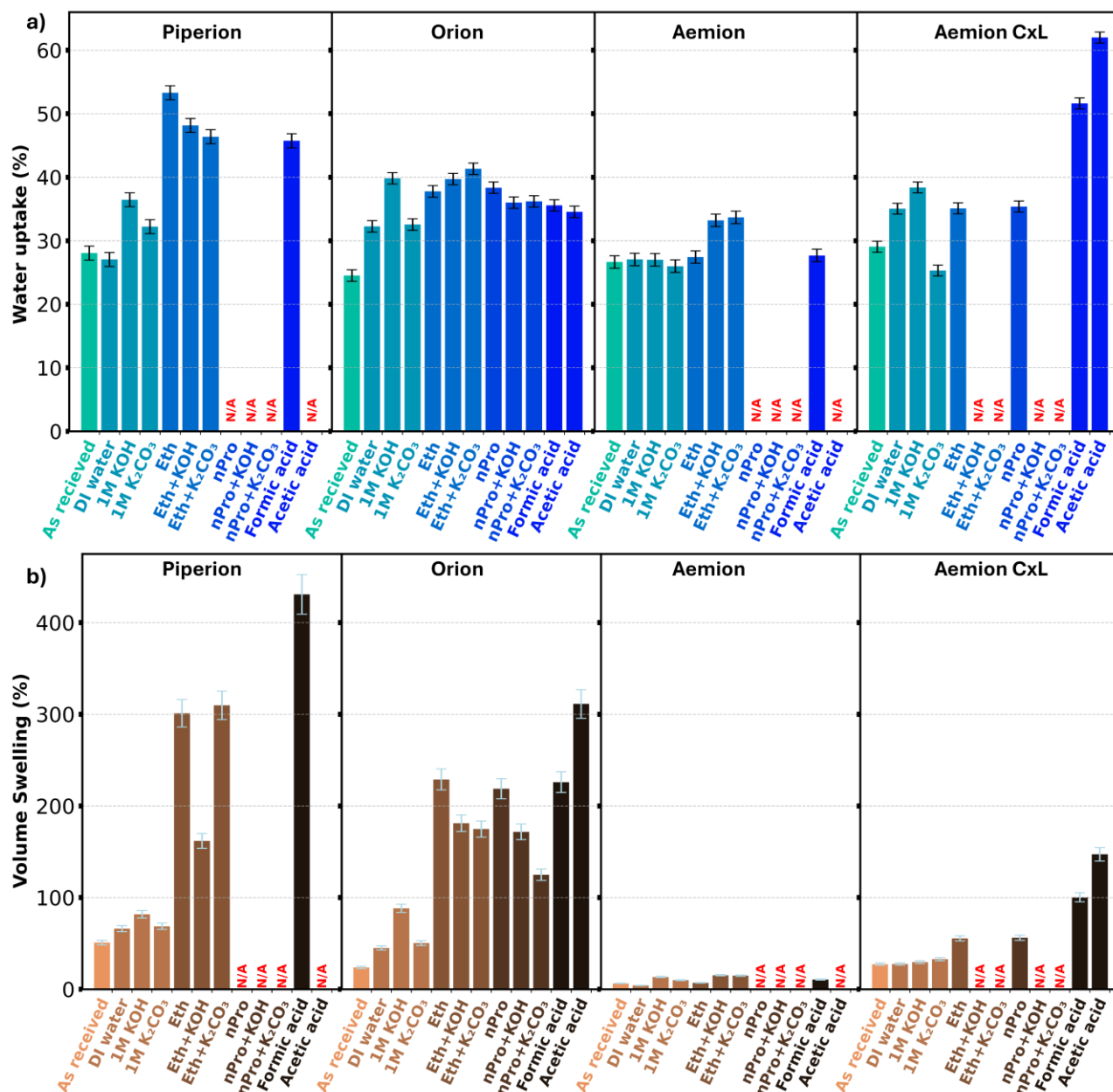


Figure 3: (a) Water uptake and (b) Volume swelling of membranes after 1000-hour exposure at 80°C to various electrolyte and organic molecule compositions. Solutions with ethanol and n-propanol are at 15% w/w. Concentration of formic and acetic acid are 5 M while KOH and K₂CO₃ electrolytes are 1M. Water uptake was measured at 60°C and 95 %RH in Cl⁻ form.

mobility, providing a buffer against excessive water uptake and swelling, which might partially explain

the relatively lower dimensional changes and water uptake observed in Orion membranes.^{30, 47}

During operation, AEMs experience repeated cycles of swelling and shrinking, introducing hydrothermal stress. Even when AEM is chemically stable, excessive swelling can lead to the

formation of cracks and pinholes within the membranes, which are major contributors to long-term failure.⁴⁸⁻⁵⁰ Increased swelling in anion exchange membranes can lead to greater porosity, which can also significantly increase the crossover of ions and reaction products.⁵¹ On the other hand, remarkably, the Aemion polymer exhibited minimal changes in water uptake behavior and swelling upon exposure to alcohols or acids which can potentially be explained by the presence of reinforcement within the membrane.⁴³ By serving as an internal scaffold, the PTFE mesh reinforcement effectively counteracts the polymer's expansion and uniformly distributes stress throughout the material.⁵²⁻⁵⁴ This can provide a big advantage for long term mechanical stability CO2RR experiments where alcohols and acids are produced in substantial amounts. However, reinforcement of membranes can increase thickness swelling, reduce ion conductivity, alter tortuosity and introduce additional challenges and costs with manufacturing of the membranes.^{55, 56} Due to significant degradation, it was challenging to directly correlate the changes in water uptake and swelling behavior of crosslinked Aemion with its exposure to alcohols and electrolytes.

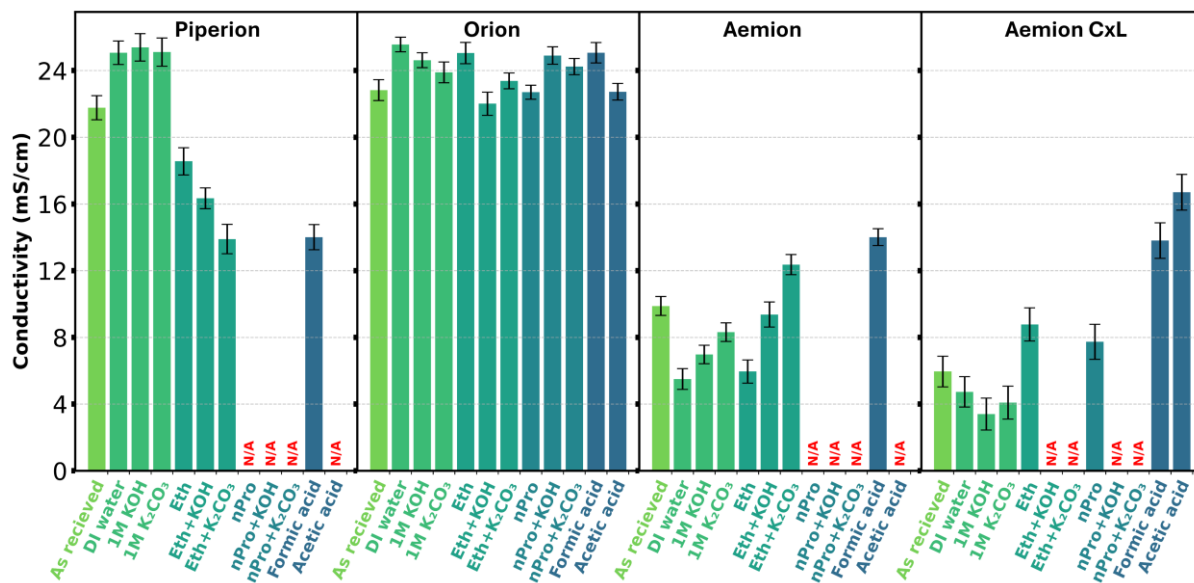


Figure 4: Ionic conductivity of membranes after 1000-hour exposure at 80°C to various electrolyte and organic molecule compositions. Solutions with ethanol and n-propanol are at 15% w/w. Concentration of formic and acetic acid are 5 M while KOH and K₂CO₃ electrolytes are 1M. In-plane ionic conductivity was measured at 60°C and 95 % RH in Cl⁻ form.

Nevertheless, swelling behavior was still evident, when exposed to acidic solutions, in which the crosslinked polymer maintained its chemical stability.

In Figure 4, the in-plane ionic conductivity of the AEMs are presented after 1000 hours of exposure at 80 °C in their respective test solutions. A clear trend emerged for Piperion membranes, where exposure to ethanol and formic acid significantly reduced ionic conductivity. This decline occurred despite a marked increase in water uptake and swelling, and no significant change in IEC, in ethanol containing solutions as previously shown (Figure 2 and 3). This outcome deviates from the typical expectation that increased swelling and water uptake enhance water-based ionic conductivity. This suggests that, while swelling generally promotes ion transport by improving water uptake, excessive swelling in this case disrupted the membrane's ionic transport network. Poly(aryl piperidinium) polymers, being main-chain-type AEMs, are known for their challenges in assembling well-organized ionic domains.⁵⁷ These membranes often require a high density of ionic groups to achieve appreciable conductivity. We propose that the excessive swelling caused by ethanol and formic acid led to a highly dispersed and isolated ionic microstructure, which was no longer effectively connected. As a result, ion transport pathways became inefficient, ultimately leading to reduced ionic conductivity. Through-plane swelling of these membranes, resulting in a significant increase in thickness, can also lead to ohmic losses at high current densities even if the ionic conductivity remains unchanged. On the other hand, Orion polymer did not show any trend or clear changes in conductivity upon exposure to alcohols even though there was noticeable swelling upon exposure to alcohols as shown in Figure 3. This can be attributed to crosslinking exist in this polymer which protects the structure of the ionic channels and prevents them from swelling excessively and becoming dispersed.⁵⁸ Despite swelling in alcohol, the structure can maintain its hydration levels, which might explain the lack of change in conductivity. This indicates that the swelling largely reflects nonproductive matrix expansion, e.g. polymer relaxation or void formation, rather than the

development of more connected ion conducting domains. In contrast, the Aemion membrane exhibited a noticeable enhancement in ionic conductivity when comparing solutions containing ethanol to those without ethanol. Although ethanol slightly promoted water absorption, the changes in water uptake across these conditions were not consistent, indicating that increased conductivity cannot be explained by water uptake alone. To further assess structural changes, the membranes were also examined in their dry state after the 1000-hour exposure (Figure SI6). Membranes exposed to ethanol-containing environments consistently displayed higher dry swelling than those treated with DI water or other mild conditions, suggesting a greater degree of irreversible structural expansion. These differences were not captured in the equilibrium swelling data, which compares the wet and dry dimensions of the membranes. This may partially explain the discrepancies observed between the trends in swelling, water uptake, and conductivity, particularly for the Aemion and Orion membranes. For crosslinked Aemion, in-plane conductivity positively correlates with both IEC and volume swelling (Figure SI7). The increase in conductivity observed in samples exposed to only alcohols, despite a small loss in IEC, likely arises from enhanced swelling and increased segmental mobility of the polymer chains, which facilitate ion transport. In contrast, under more aggressive alkaline conditions, the pronounced decreases in IEC and vibrational markers indicate a substantial loss of functional groups and crosslinks, which likely dominates the conductivity response.

All the AEMs were characterized before and after stability tests using IR and Raman spectroscopy, with DFT calculations aiding in the interpretation of the vibrational data. The Raman and IR spectra of tested Piperion membranes are presented in selected regions in Figure 5a and 5b, respectively. The N–C (quaternary) symmetric stretching vibration, coupled with methyl and methylene deformation modes, around 707 cm^{-1} in the Raman spectra was used as a marker to assess the stability of the piperidinium group (Figure 5a). The vibrational motion associated with this

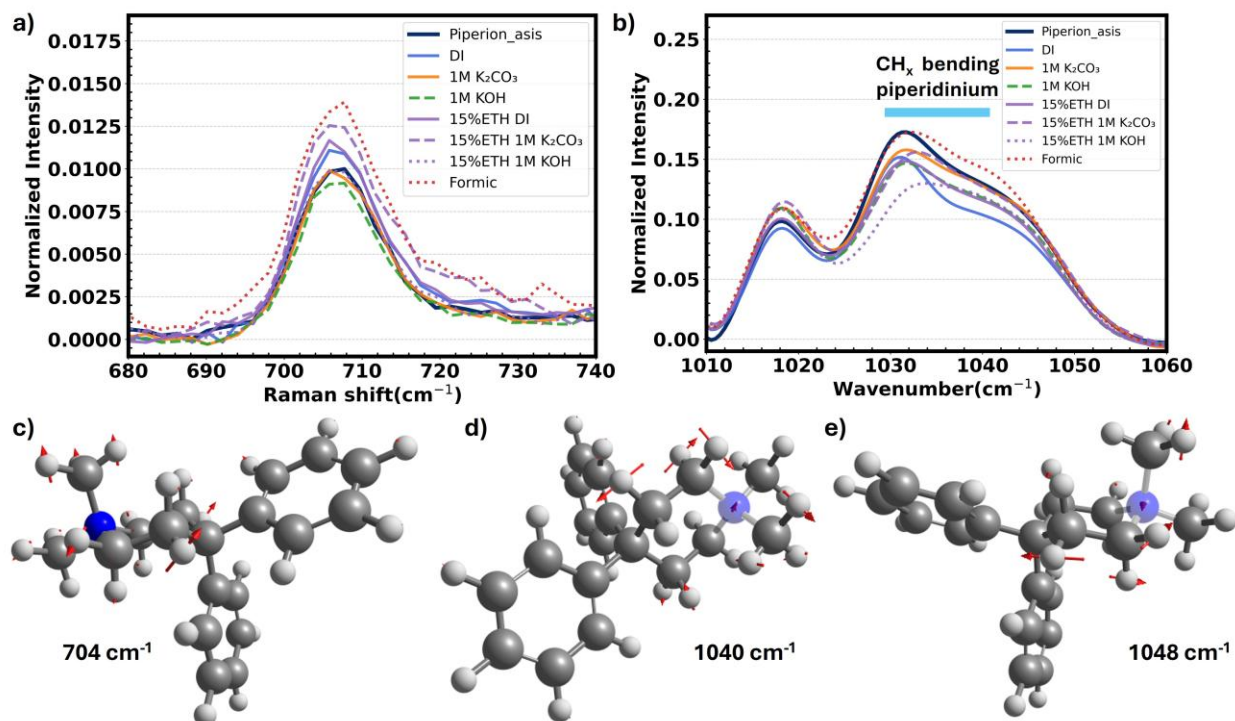


Figure 5: Selected regions of **a)** Raman and **b)** infrared spectra of Piperion membranes after 1000-hour exposure at 80°C to various electrolyte and organic molecule compositions. **c)** Corresponding Raman-active vibrational mode predicted to be around 704 cm^{-1} by DFT. **d)** and **f)** Corresponding infrared-active vibrational modes predicted to be around 1040 and 1048 cm^{-1} , respectively.

peak, along with the corresponding vectors, is illustrated in Figure 5c, and its presence in the Raman spectra of 1,1-dimethylpiperidinium chloride provided confidence in assigning this peak to the corresponding vibration.⁵⁹ Specifically, the 15% ethanol-KOH sample, which showed the greatest IEC loss, also exhibited the most pronounced decrease in the 707 cm^{-1} intensity. In contrast, the membrane exposed to formic acid, which retained the highest IEC, showed the highest intensity of this band. This indicates that the band is sensitive to substantial decomposition of the piperidinium moiety. For the remaining conditions, the corresponding changes in IEC were comparatively small and fell near the measurement variability. Therefore, the associated Raman intensity changes are modest and should be interpreted with caution. The reduced intensity of this peak in the membranes prior to testing, i.e. as is membrane, suggests that it may be influenced by residual impurities or minor variations in background spectral correction, despite the use of advanced spectral correction

techniques. To further validate our observations, we shifted our focus to another set of moderate-intensity peaks in the IR spectra, around the $1030\text{--}1045\text{ cm}^{-1}$ region, which are useful for tracking the ionic groups of Piperion (Figure 5b). These set of overlapping peaks correspond to bending vibrations of CH_3 and CH_2 groups coupled with piperidinium ring. DFT calculations predicted the IR-active modes to occur around 1040 and 1048 cm^{-1} (Figure 5d and 5e). A similar trend was observed in the IR spectra, where the CH_x -bending vibrations of the piperidinium group showed noticeably lower intensity for the 15% ethanol-KOH sample compared to formic acid, consistent with the relative changes seen in the 707 cm^{-1} Raman band. In addition, these peaks are particularly sensitive to the number and type of substituents on the nitrogen atoms of the piperidinium ring (Figure SI8). Notably, the relative intensity of the higher-frequency peak is significantly greater in the 1-methylpiperidinium ion compared to the 1,1-dimethylpiperidinium ion and 1-methylpiperidine, highlighting the influence of the substituent configuration on the vibrational characteristics. Additionally, this peak shifts to a higher frequency in the 1,1-dimethylpiperidinium ion. Utilizing vibrational analysis combined with IEC results, we propose that the membranes initially contained a small fraction of 1-methylpiperidine groups before the tests that were not fully methylated. Upon exposure to formic acid, these groups became protonated. When the membranes were exposed to an alkaline medium, a slight degradation of the piperidinium/piperidine ring occurred which appears to proceed at a faster rate when the ethoxide ion is present in the test mixture. The NMR data further supported this observation, showing characteristic allylic protons, which are indicative of Hofmann elimination occurring in the piperidinium groups of membranes exposed to alkaline conditions (Figure SI9).⁶⁰ Although it remains unclear whether this behavior indicates an initial drop followed by continuous degradation, the overall extent of degradation was minimal, indicating that Piperion exhibited good chemical stability. Therefore, dissolution in n-propanol and acetic acid, along with excessive swelling

upon exposure to ethanol and formic acid, appears to pose a more significant challenge than chemical stability.

Ionic groups Orion polymer exhibited excellent stability based on IEC measurements which was also supported by Raman spectra given in Figure 6a. Similar to piperidinium group, the quaternary ammonium group symmetrical NC_4 stretching coupled with deformations of methyl and methylene groups can be a good indication of stability. This peak shifted to higher frequencies, $\sim 750 \text{ cm}^{-1}$, due to being attached to alkyl chain when compared to cyclic piperidinium group and predicted by DFT calculations around 756 cm^{-1} (Figure 6b). The minimal variation in the intensity of this peak along with the IEC results strongly indicate that the decomposition of the quaternary ammonium

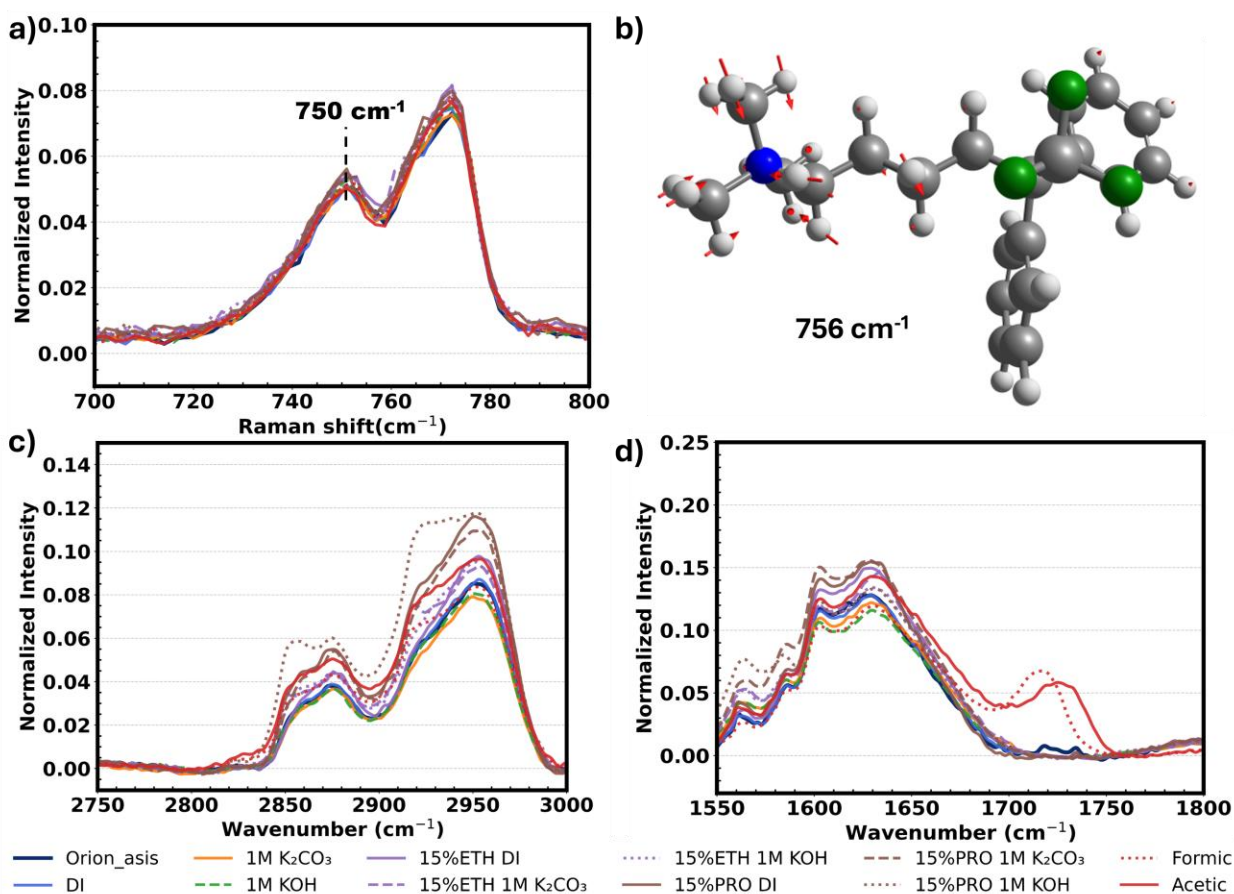


Figure 6: a) Selected region of Raman spectra of Orion membranes after 1000-hour exposure at 80°C to various electrolyte and organic molecule compositions. b) Corresponding Raman-active vibrational mode predicted to be around 756 cm^{-1} by DFT. c) and d) Selected regions of IR spectra of Orion membranes after 1000-hour exposure at 80°C to various electrolyte and organic molecule compositions

group remained negligible across all tested conditions. On the other hand, the IR spectrum indicated a substantial amount of test solutions trapped within the polymer matrix, particularly evident in the cases of n-propanol and formic acid (Figure 6c and 6d). We approached the high frequency CH_x stretching region in Figure 6c with care, as its lower relative intensity is likely related to the reduced sensitivity of the DTGS detector at higher wavenumbers. This diminished sensitivity increases the region's susceptibility to fluctuations, particularly when impurities are present, making it more prone to noticeable variations in the spectral response. Nevertheless, the increase in stretching vibrations of CH₃ and CH₂ was evident in membranes exposed to n-propanol. Furthermore, the removal of n-propanol was notable after drying at 80°C, while additional extensive washing steps did not result in a significant difference (Figure SI10). For n-propanol, it is unclear whether it engages in significant physical interactions with the polymer molecules, such as the formation of propoxide ions in an alkaline medium, or if its effects are primarily due to a dense polymer network that restricts or slows the diffusion of the molecules. On the other hand, the existence of the carbonyl stretching vibration in the membranes that are exposed to acids (Figure 6d), a substantial amount of formic and acetic acid remained confined within the polymer matrix, even after additional washing steps and drying at 80°C, persisting in its acidic form (Figure SI11). It is most likely that either the carbonyl group of formic acid was interacting with the quaternary ammonium group, or the formate ion was interacting through one of its oxygen atoms with the quaternary ammonium group.

In the comparison of the Raman spectra of Aemion and crosslinked Aemion, a peak around 667 cm⁻¹ stands out as a relatively isolated Raman-active feature (Figure 7a). This peak has been

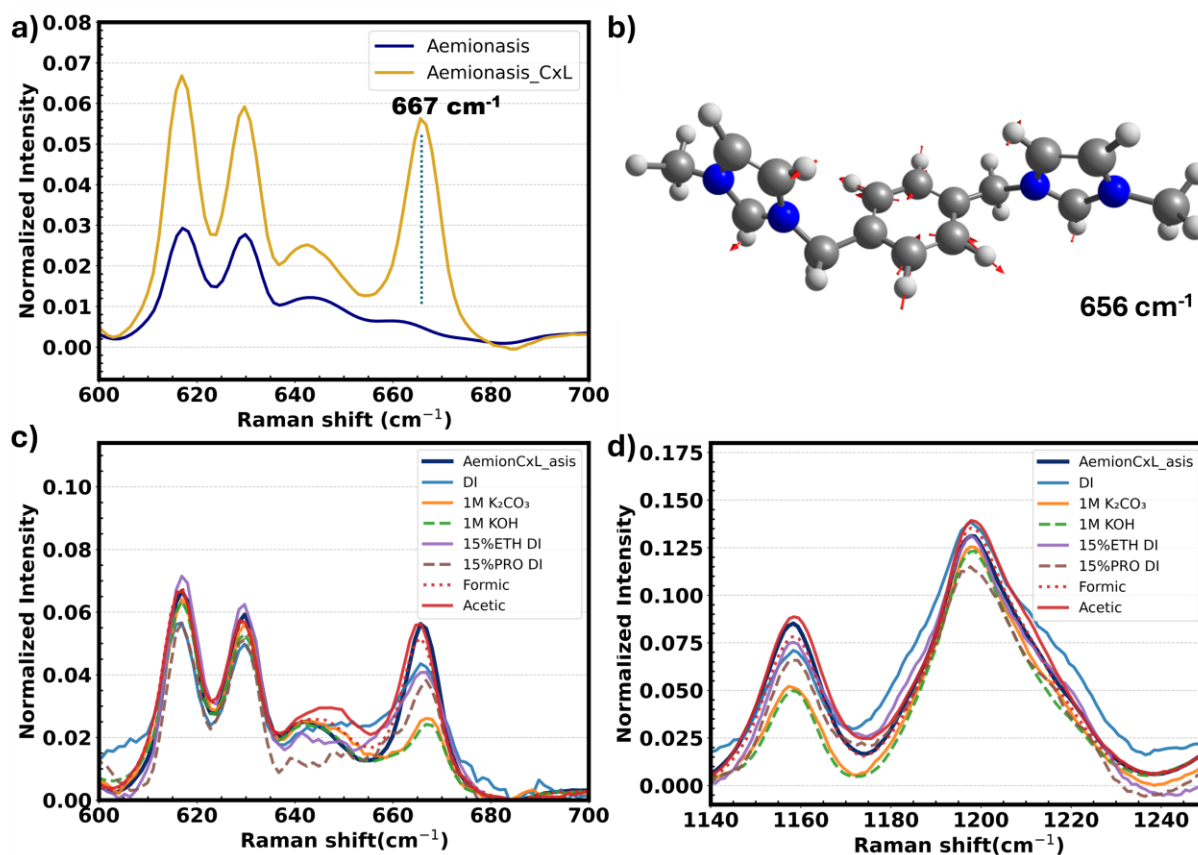


Figure 7: **a)** Comparison of crosslinked and not crosslinked Raman spectra of Aemion in selected regions **b)** the assigned vibrational mode for the stand-out peak in crosslinked Aemion calculated to be around 656 cm^{-1} by DFT. **c)** and **d)** Selected region of Raman spectra of crosslinked Aemion membranes after 1000-hour exposure at 80°C to various electrolyte and organic molecule compositions.

assigned to the in-plane bending of the phenylene group that connects the two imidazolium groups, as shown in Figure 7b, based on DFT calculations ($\sim 656\text{ cm}^{-1}$) and can serve as an indicator for tracking the progress and stability of the crosslinking. Based on IEC results and visual observations (Figure 2 and Figure SI3), there were strong indications of possible degradation in crosslinked Aemion compared to its non-crosslinked counterpart. This hypothesis was further supported by the Raman measurements, the decrease in the intensity of the phenylene vibration correlated strongly with the loss of IEC in the crosslinked Aemion (Figure 7c). A similar trend was noticeable in the higher frequency vibrations of the crosslinker phenylene, particularly around 1158 cm^{-1} (Figure 7d). Notably, decomposition also occurred thermally without electrolytes, reinforcing the consistency among IEC, Raman data, and visual observations. The loss of crosslinking observed in the Raman spectrum likely

explains the dissolution of crosslinked Aemion in n-propanol and ethanol when an electrolyte is present. The degradation rate appeared to accelerate significantly when electrolyte was present, and as the polymer loses a substantial amount of crosslinking, it becomes more susceptible to physical dissolution. The pronounced IEC reduction and weakened Raman bands observed in samples exposed to KOH and K_2CO_3 indicate degradation initiated by hydroxide and carbonate ions. In contrast, membranes exposed only to ethanol or n-propanol showed minimal IEC loss, primarily associated with minor thermal decomposition of the crosslinker, which appeared to be slightly unstable even under neutral conditions. This limited degradation agrees with the strong ionic attack observed in alkaline media, confirming that the main degradation mechanism arises from reactive ionic species rather than from solvent or temperature effects alone.

Extensive research has been conducted on imidazolium ions and imidazolium-based polymers, focusing on enhancing the stability of the ionic groups. This has been achieved by systematically modifying nearly all the carbon and nitrogen atoms within the imidazolium groups with various substituents, aiming to improve their overall stability. Crowding at the C2 position is essential for stability, as it helps protect the imidazolium ring from OH^- attack, making it less susceptible to degradation.^{61 62} Similarly, substituting the C4 and C5 positions is also crucial for preventing deprotonation reactions and enhancing the stability of imidazolium ions, further protecting the structure from degradation.^{63,64} Last but not least, electron-donating groups attached to these nitrogens generally enhance the cation's stability by reducing the overall positive charge density.^{65, 66} The relative stability of these cations is influenced not only by the nature of the substituent groups but also by their specific combinations. For instance, some studies focus on modifying the C2 position or the nitrogen atoms of the imidazolium ring while leaving the C4 and C5 positions unsubstituted, whereas others introduce additional substitutions at the C4 and C5 positions to further modulate electron distribution and steric factors. Even though these different

combinations might lead to slightly different results and conclusions, the extensive amount of research conducted has yielded clear guidelines indicating that strategic substitutions at these positions can yield more stable imidazolium cations.⁴¹ The latest generation of state-of-the-art Aemion membranes are based on polyarylene imidazoliums, which incorporate a tetramethylbenzene group at the C2 position to provide steric hindrance against degradation. Additionally, aryl groups attached to the C4 and C5 positions facilitate charge delocalization within the imidazolium rings. These polymers have demonstrated outstanding stability in 10 M KOH at temperatures ranging from 80 to 100 °C for extended periods of time.^{67, 68}

Raman spectroscopy provided useful information regarding the crosslinker yet the intensity of the imidazolium vibrations, which are coupled with CH_x bending vibrations, is generally lower

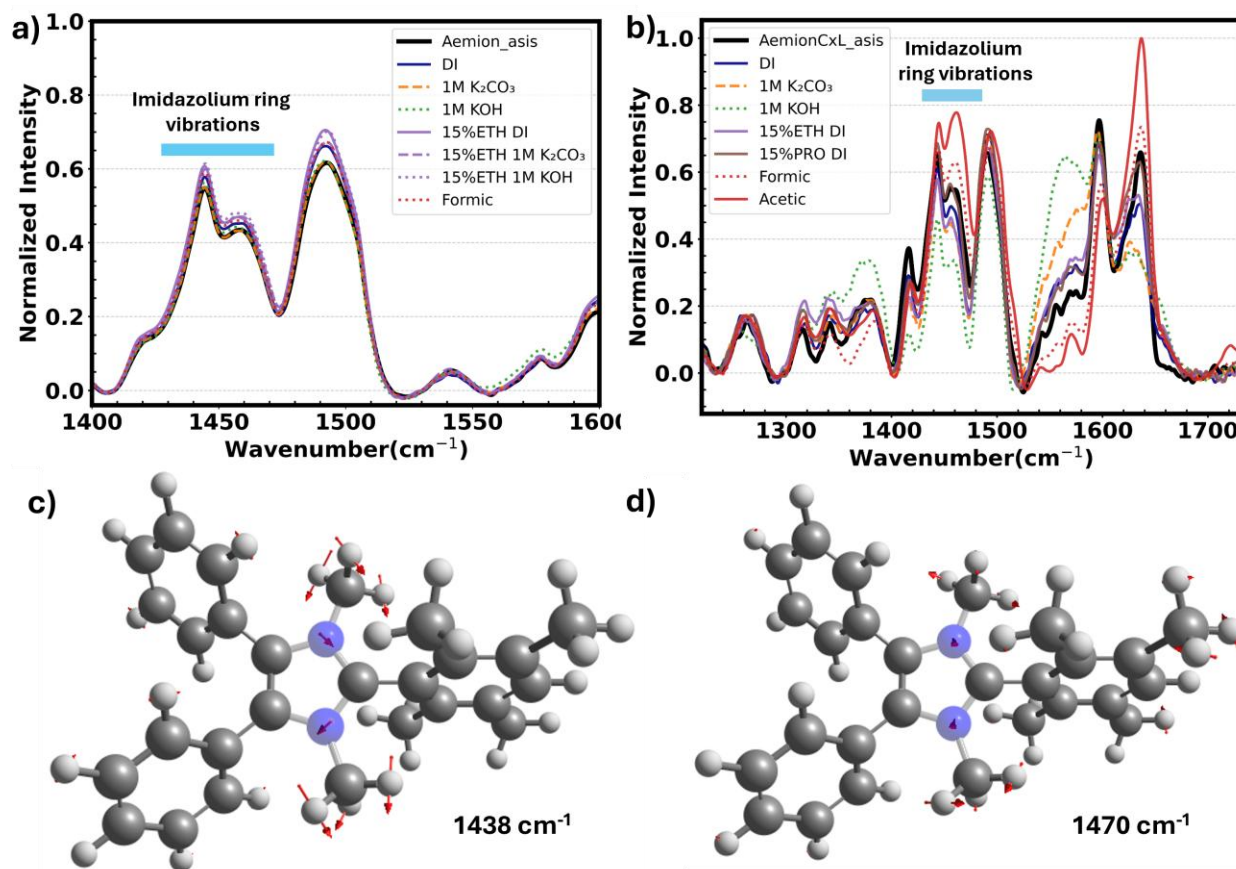


Figure 8: Selected region of IR spectra of **a)** not crosslinked and **b)** crosslinked Aemion membranes after 1000-hour exposure at 80°C to various electrolyte and organic molecule compositions. **c)** and **d)** Corresponding infrared-active vibrational modes predicted to be around 1438 and 1470 cm⁻¹, respectively.

compared to the aromatic ring vibrations. IR spectroscopy offers highly effective insights into the stability of the imidazolium ring in this context. In the spectral region between 1400-1500 cm^{-1} , multiple CHx bending vibrations were present, originating from the attached methyl groups as well as neighboring benzyl and phenyl groups, each exhibiting different degrees of coupling with the imidazolium ring (Figure 8a and 8b). Specifically, the IR absorption bands observed at approximately 1443 and 1460 cm^{-1} in both Aemion polymers are attributed to imidazolium ring vibrations coupled with bending modes of the attached methyl, with DFT calculations predicting these vibrations to occur around 1440 and 1469 cm^{-1} (Figure 8c and 8d). There is only a slight decrease in the intensity of this peak in alkaline conditions in non-crosslinked Aemion, specifically in 1 M KOH and 1 M K_2CO_3 . However, these changes are minimal and do not allow for a definitive conclusion, indicating that the membranes demonstrate strong overall chemical stability. Conversely, the substantial decrease in the intensity of these peaks in crosslinked Aemion strongly indicated that degradation of the imidazolium ring occurs alongside the loss of crosslinking. Consistent with the Raman spectra, this degradation was significantly more rapid in an alkaline medium, while the intensity of these peaks remained higher in polymers tested under acidic conditions. The unexpectedly poor chemical stability of crosslinked Aemion membranes suggests that the introduction of a benzyl group during the crosslinking process may play a role in destabilizing the imidazolium group. However, this structural modification generally confers significant stability in alkaline media when the C2 position was protected and the C4 and C5 positions of imidazolium cations were substituted with mesitylene and phenyl groups.⁶⁹ Therefore, we believe the strain introduced by crosslinking the bulky and substituted imidazolium groups may contribute to instability. When the imidazolium cations, with highly substituted benzyl and two phenyl groups, are linked via a rigid crosslinker, they are forced into close proximity, causing steric clashes. This overcrowding distorts bond angles within the rings, making the imidazolium ring more prone to bond cleavage or rearrangement. Using a more flexible

crosslinking agent could potentially yield an AEM with outstanding chemical and mechanical stability.

The color of the crosslinked Aemion membranes shifted from yellow to orange upon exposure to heat or alkaline conditions, likely due to the formation of extended conjugation in the chemical structure that absorbs visible light (Figure SI3). IR spectroscopy revealed several features that either increased or decreased in intensity during the decomposition of crosslinked Aemion, suggesting the presence of specific chemical changes associated with the resulting degradation products. Specifically, the quadrant stretching modes of the benzene rings, observed between 1600 and 1650 cm^{-1} , were significantly more prominent in the crosslinked polymer (Figure SI12). This increased intensity is likely due to the crosslinker itself, which lacks a center of inversion, or to the conformational changes induced in the polymer backbone upon crosslinking. The observed decrease in this peak in alkaline medium was accompanied by the emergence of a broad peak around 1570 cm^{-1} , a lower intensity shoulder at 1665 cm^{-1} , and a notable increase in the peak near 1375 cm^{-1} . The degradation of imidazolium compounds primarily proceeds through elimination or ring-opening mechanisms at the C2 carbon, leading to a range of products with varying oxidation states.⁴¹ Given the two phenyl groups connected at the C4 and C5 positions, the transition in color from yellow to orange and the change in the IR spectra suggested that the imidazolium ring primarily undergoes oxidative cleavage. This process potentially formed a variety of compounds, including amides, diketones, and dicarboxylic acids, with phenyl and/or tetramethyl benzyl groups attached.⁷⁰⁻⁷² The exact identification of these degradation products is complex and beyond the scope of this study. Strategies to enhance membrane stability should include designing more flexible crosslinking agents to minimize chemical degradation, particularly in alkaline and alcohol-rich environments.

This study explored the effects of CO₂RR liquid products on commonly used AEMs in the presence of various electrolytes. While most membranes exhibited robust chemical stability under

the test conditions, non-crosslinked membranes like Piperion and Aemion experienced complete dissolution in solutions containing n-propanol and acetic acid. Although ethanol and formic acid were less damaging to the physical integrity of the membranes, they cause extensive swelling in both Piperion and Orion membranes. This excessive swelling might pose a risk to membrane durability by inducing localized stress, pinhole formation, and tears, which can result in mechanical failure of the AEMs. Additionally, excessive swelling significantly increases the membrane thickness, which can introduce additional ohmic resistance at high current densities unless accompanied by increased water uptake and enhanced ionic conductivity. The combination of swelling and high water uptake might also play a crucial role in increasing ion and product crossover during CO₂ electrolysis, potentially affecting overall performance. To address these issues, AEMs originally designed for water electrolysis and fuel cells may require specific modifications to better suit CO₂RR applications when liquid products are formed. Lastly, it is important to note that these polymers, often used as ionomers in their lower molecular weight forms, may encounter similar challenges.

Supporting Information

Compositions of test solutions, potentiometric titration curves of Piperion membranes, Nyquist plots of Orion membranes, visual comparisons of membranes and solutions after stability testing, solubility tests, correlations of properties for crosslinked Aemion membranes, calculated IR stick spectra of piperidinium and piperidine compounds, NMR spectra of Piperion membranes after 1000 h testing, and IR spectra comparisons of Orion and Aemion membranes before and after washing and drying (PDF).

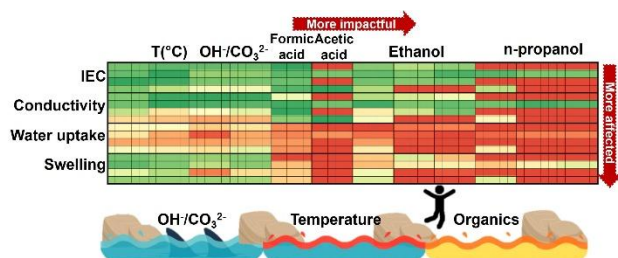
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