

Background

Perfluorosulfonic acid (PFSA) membranes are cation exchange membranes composed of a polytetrafluoroethylene backbone with sulfonated side chains. The fluorinated backbone provides chemical stability, while negatively charged sulfonic acid groups create hydrated ionic domains for cation transport.

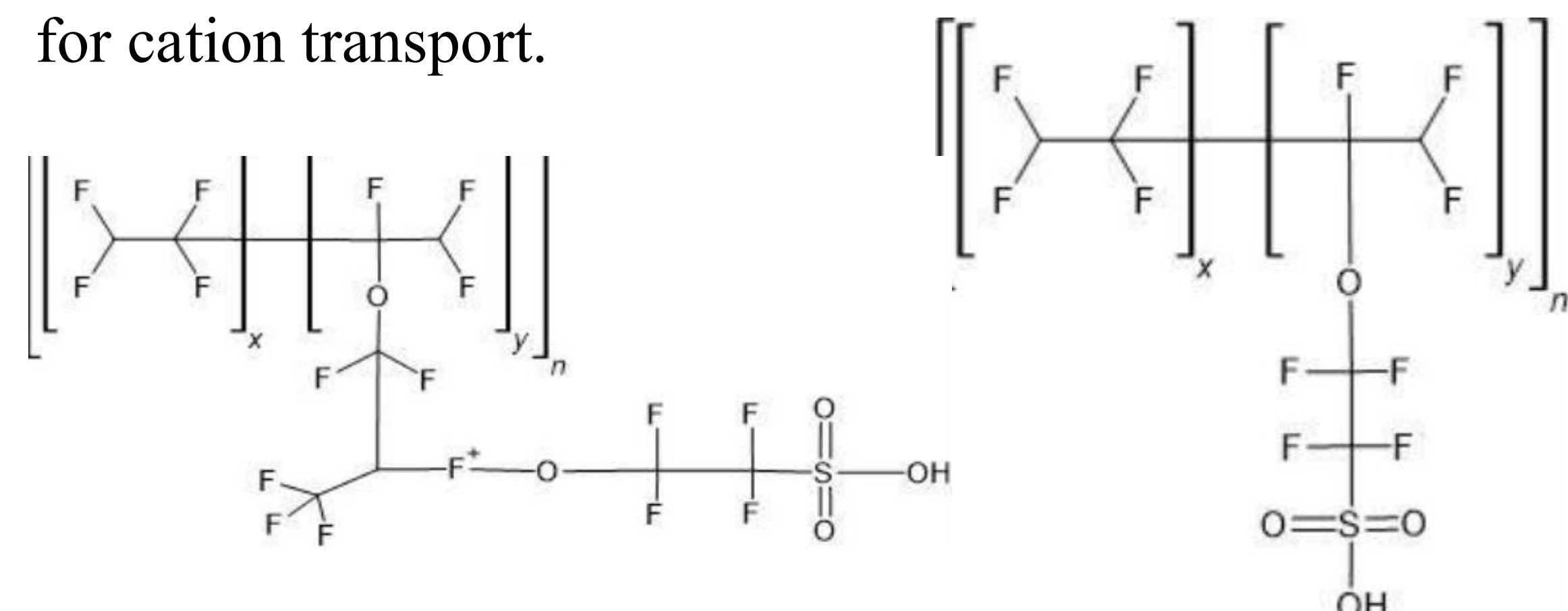


Figure 1. Molecular Structure of protonated Nafion 115 (left) and Aquivion E98-09S (right)

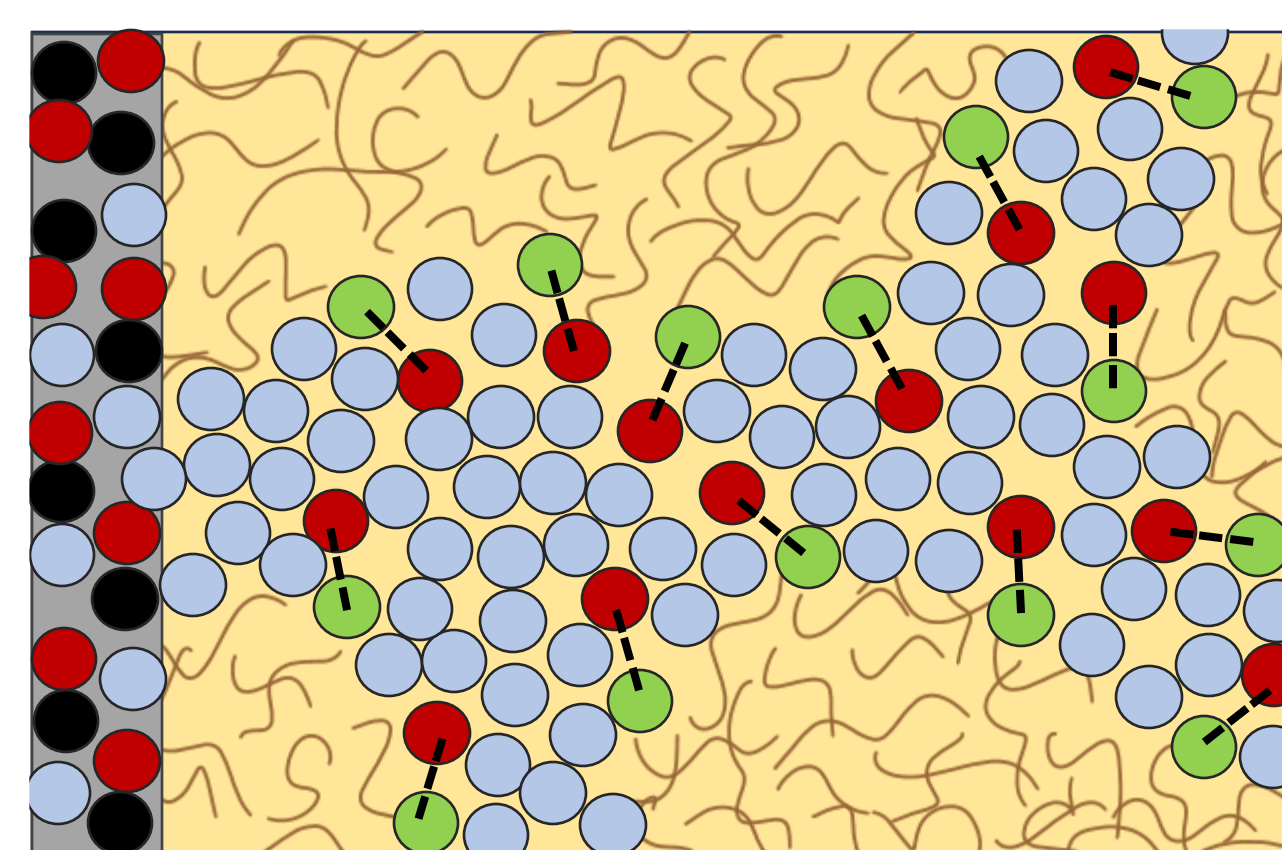
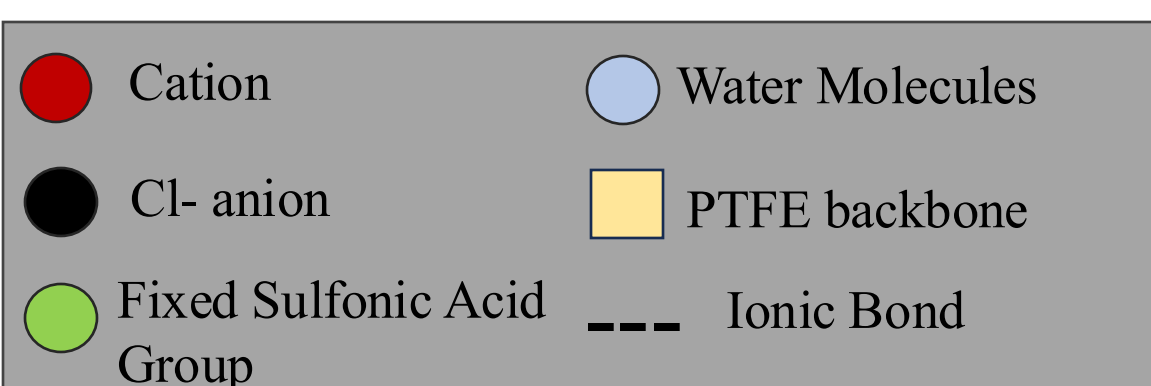
Motivation

High abundance of multivalent ions in **industrial and environmental brines**³ result in

- Processing challenges
- Opportunities for resource recovery

Ion transport in PFSA membranes is affected by:

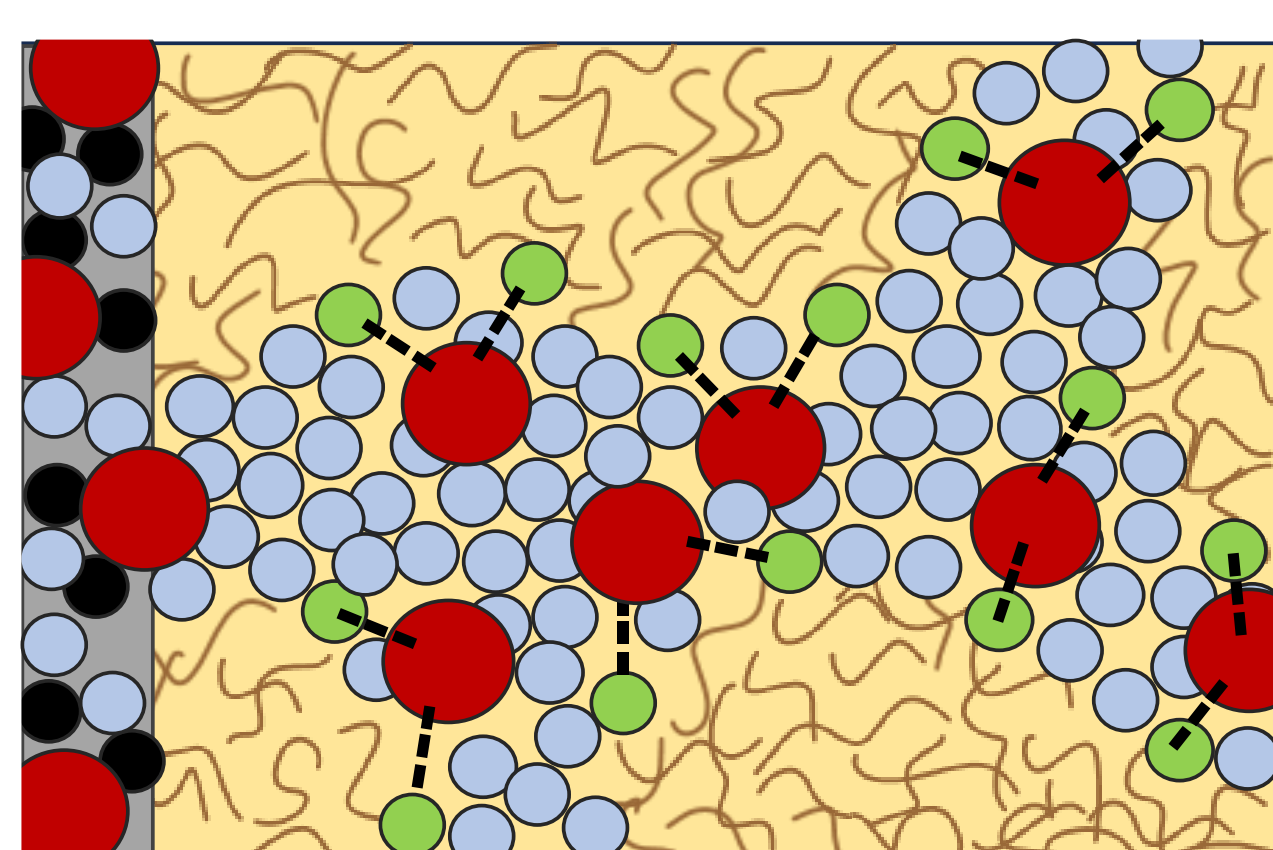
- Donnan Exclusion
- Electrostatic Interactions
- Hydration Shell



Larger cations like Mg^{2+} and Ca^{2+} behave differently than monovalent ions due to

- Higher charge number
- Larger hydration shells
- Stronger interactions within ionic domains

Schematic of Divalent Ions in CEM Membrane

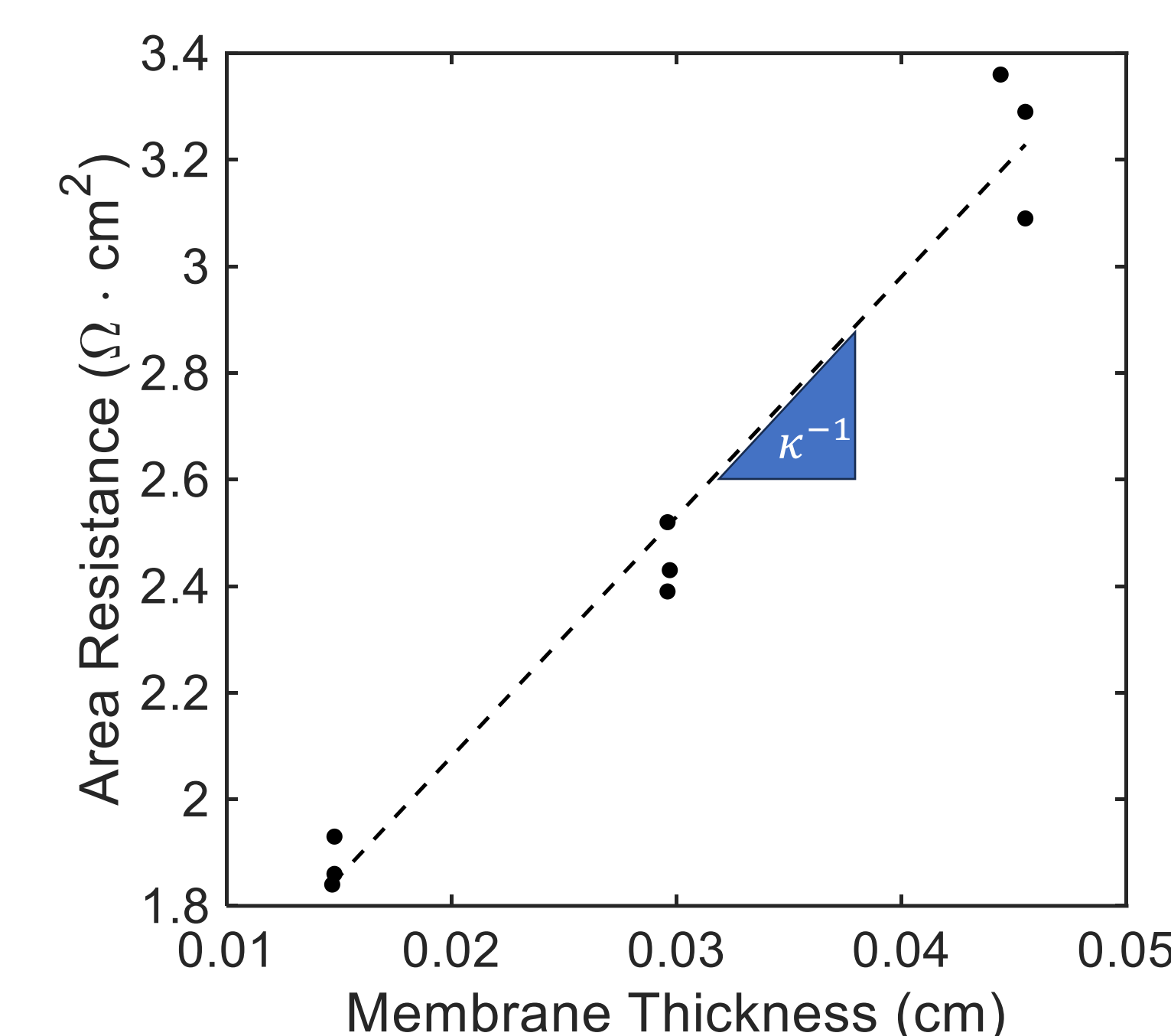


Analysis & Results

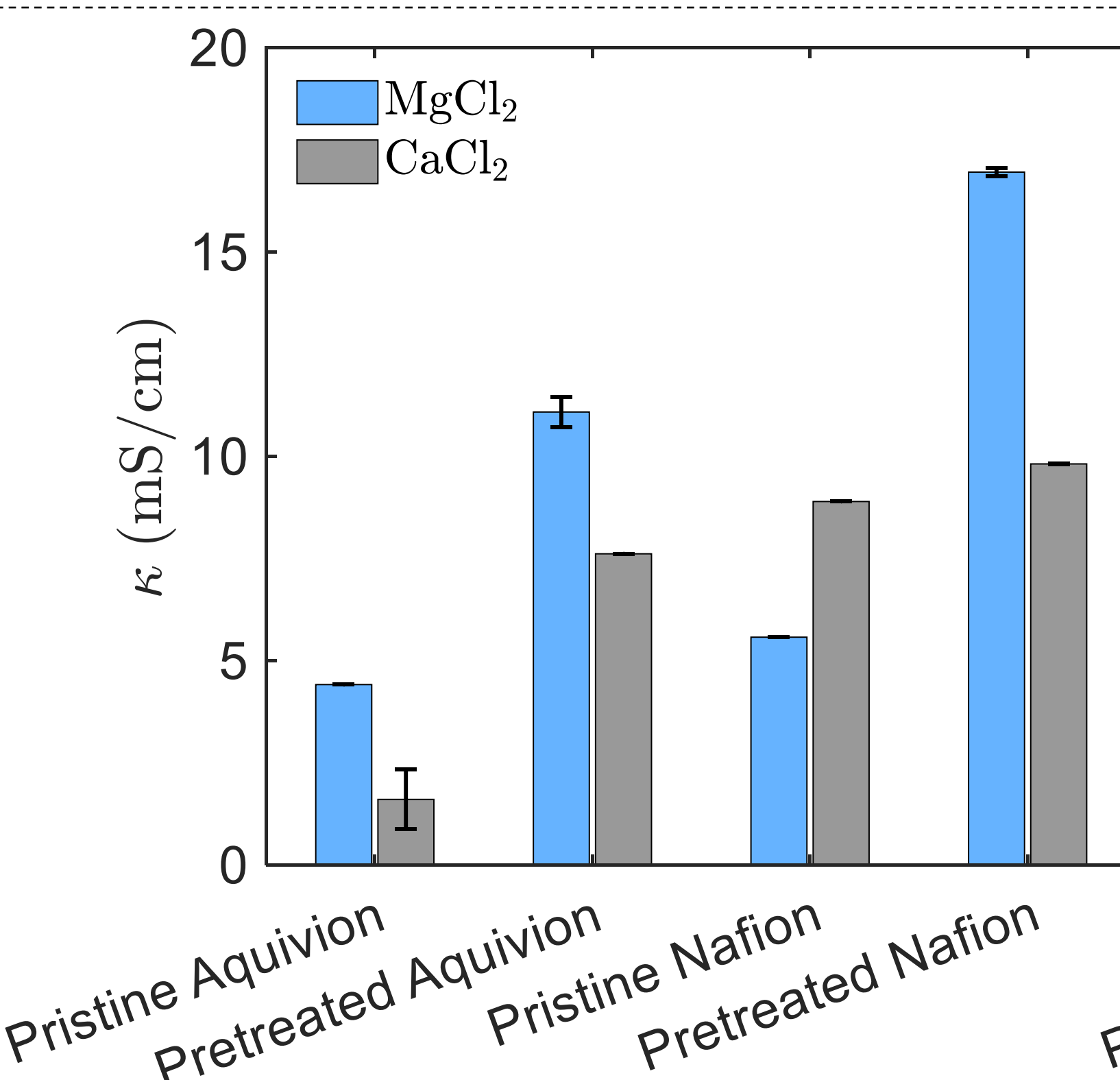
Ionic conductivity

Ion transport under an applied electric field

- **Electrochemical impedance spectroscopy (EIS)** with the stacking method determines membrane bulk resistance.
- Increases with increasing water content to a maximum due to dissociation and increasing ion mobility
- Decreases at high water content due to ion dilution.



***Higher conductivity** indicates more efficient cation transport

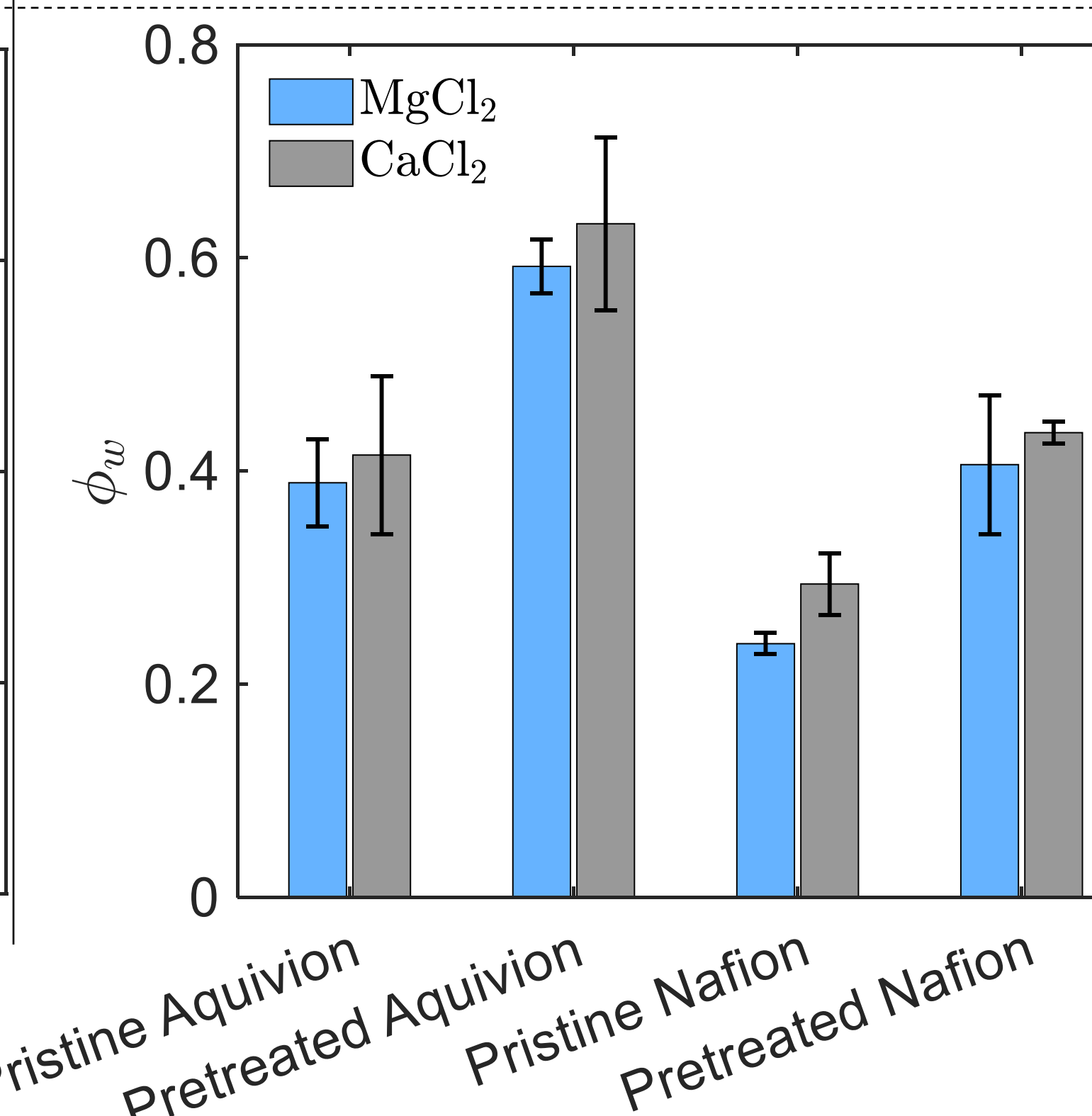
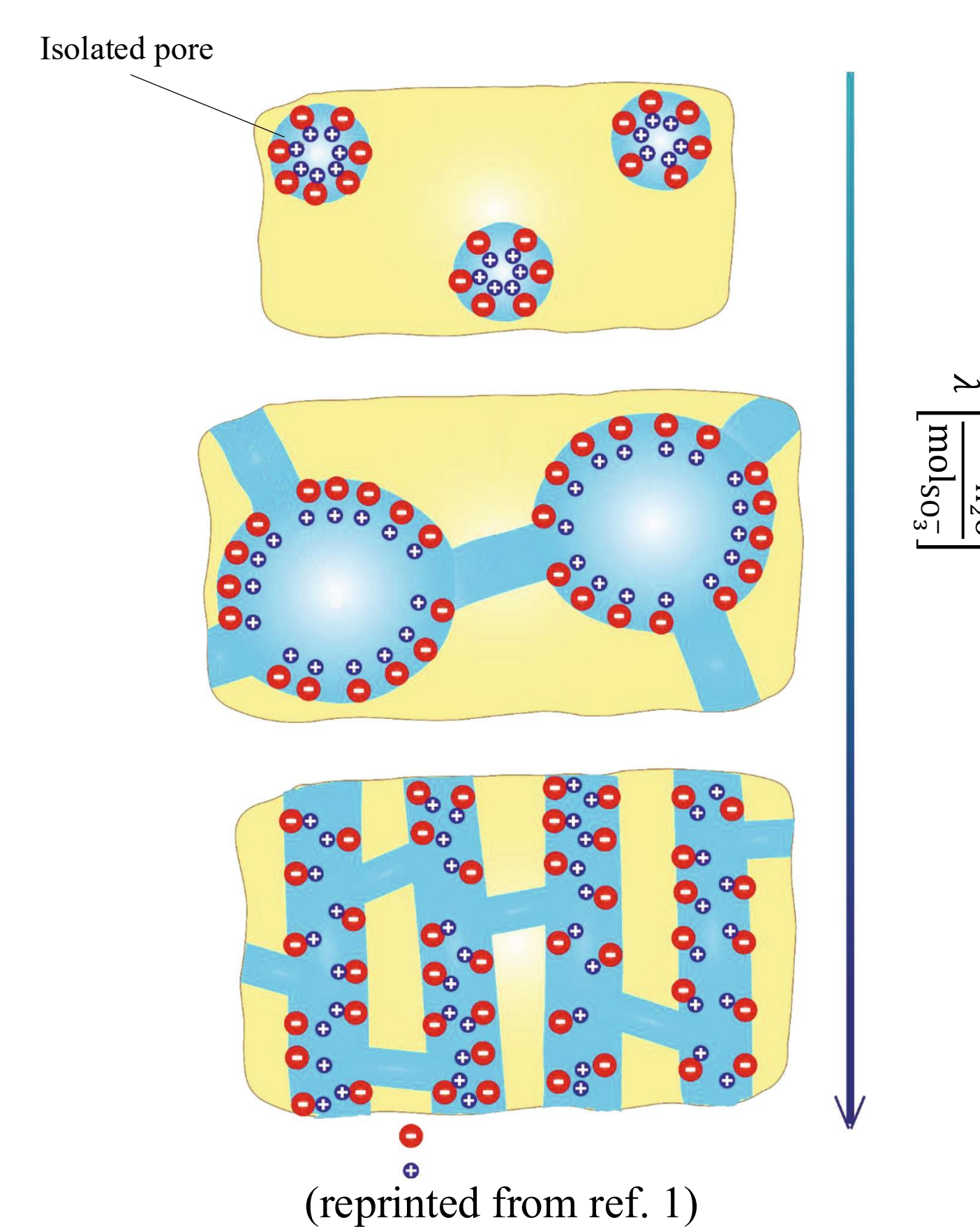


Water Content

Water volume fraction (ϕ_w) dictates swelling and hydration of ionic domains

- Solvates sulfonic acid groups
- Expands **hydrophilic transport channels**
- Dilutes charge at high levels

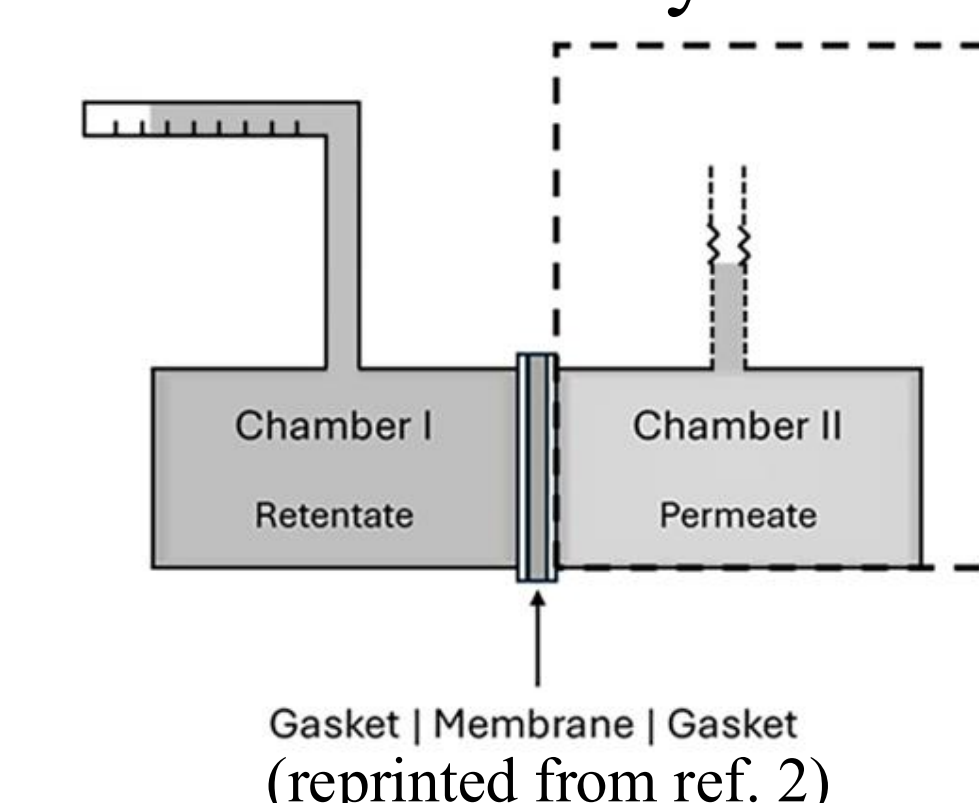
Ion transport primarily occurs through these hydrated channels.



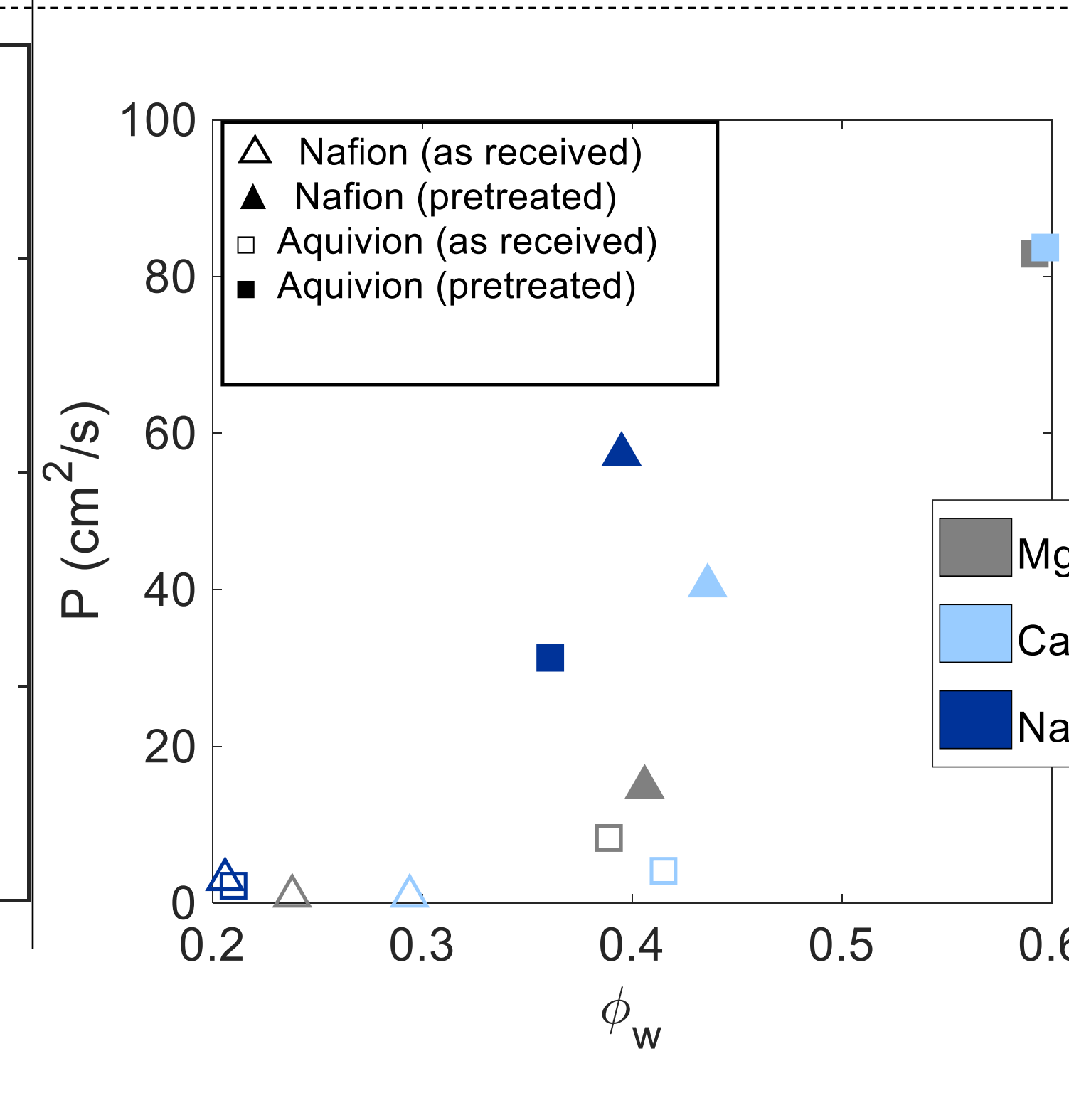
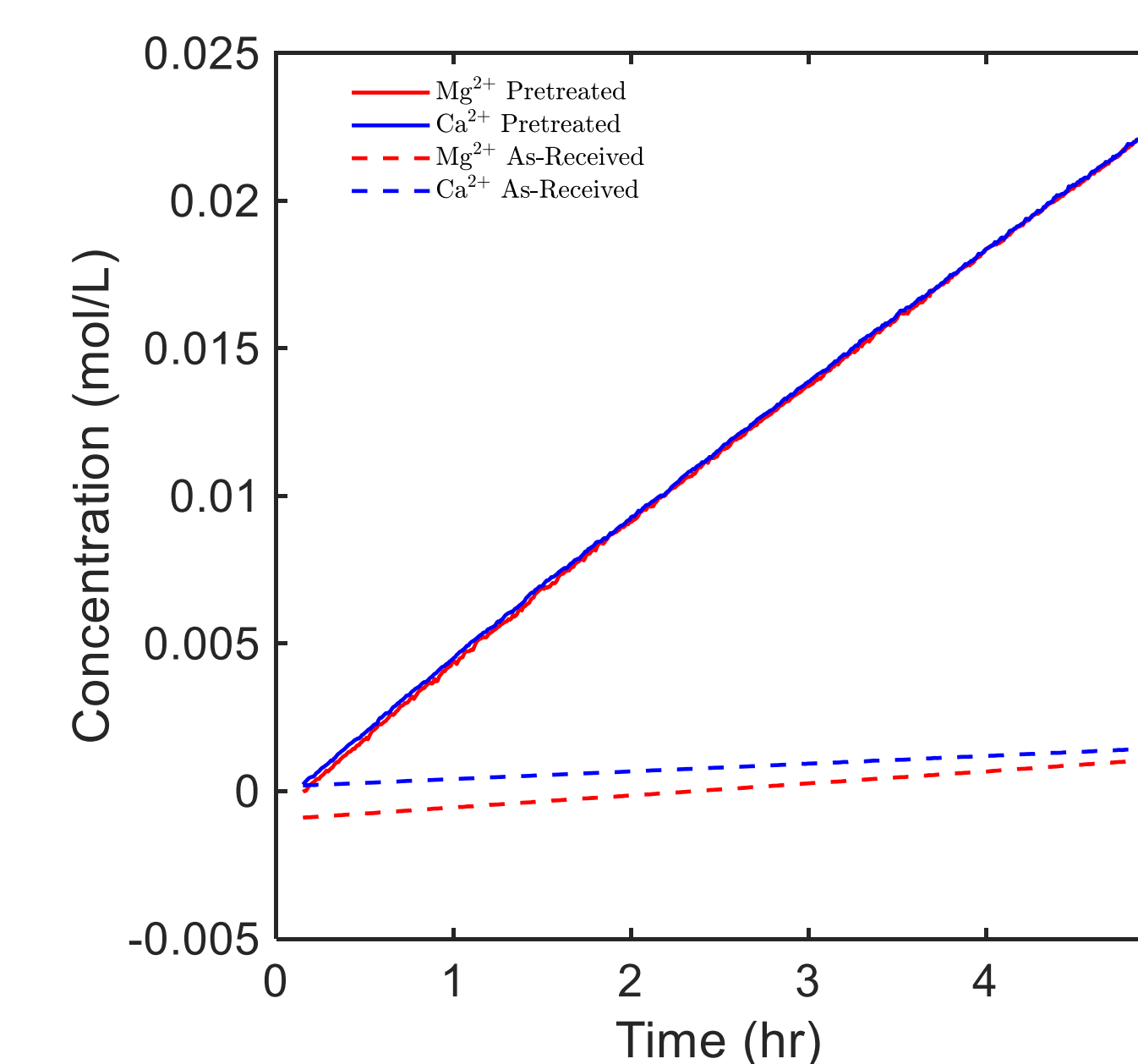
Permeability

Ion transport through a membrane due to concentration gradient

- Key for membrane separation
- **Increases with ϕ_w**
- Measured in side-by-side cell



- Track transient permeate solution conductivity and convert to concentration via calibration



Conclusions

• **Aquivion showed higher water uptake but lower ionic conductivity than Nafion.**

Transport efficiency appears to depend more on ionic domain morphology and connectivity than water content alone.

• **Mg²⁺ systems exhibited higher ionic conductivity than Ca²⁺ systems.**

The smaller ionic radius and higher charge density of Mg²⁺ may enable greater mobility in hydrated ionic domains.

• **CaCl₂ systems showed higher membrane water content.**

The larger hydration structure of Ca²⁺ may introduce more associated water into the membrane, increasing swelling.

• **Pretreated Aquivion (MgCl₂, CaCl₂) showed higher permeability than Na⁺ systems in both membranes.**

Increased permeability coincided with higher water volume fraction, indicates enhanced transport under highly hydrated conditions.

Future Work

- Extend transport studies to additional multivalent cations to further investigate charge density and hydration effects.
- Characterize membrane morphology to directly link structure to conductivity and permeability

Acknowledgments

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References

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- (2) Kim, K.; Hallinan, D. T. Charged polymer membrane processing and its impact on membrane separation. *Frontiers in Membrane Science and Technology* 2025, Volume 4 - 2025, Review. DOI: 10.3389/fmst.2025.1688243.
- (3) González, A.; Choque, G.; Grágeda, M.; Ushak, S. (2025). Membrane-Assisted Electrochemical Removal of Mg²⁺ and Ca²⁺ from Lithium Brines: Effects of Temperature and Current Density Through a

This work demonstrates that while Nafion supports more efficient cation transport, short-side-chain Aquivion membranes exhibit unexpectedly high multivalent ion permeability under highly hydrated conditions, highlighting the critical role of membrane morphology and water uptake in governing Ca²⁺ and Mg²⁺ transport in PFSA systems.