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QUANTUM-CONFINED WATER IN POLYMERIC NANOCHANNELS: PROTON TRANSPORT AND ELECTROCHEMICAL IMPLICATIONS FOR GREEN HYDROGEN ELECTROLYSIS

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Abstract

The confining of water inside sub-nanometer to nanometer-sized polymeric channels introduces novel structural and dynamical characteristics that significantly impact proton transport, with fundamental implications for the development of green hydrogen electrolysis. Within such confinement, water molecules tend to assemble into quasi-one-dimensional chains or ordered hydrogen-bond networks, facilitating proton conduction processes that are deviant from bulk conditions. Molecular simulations and neutron scattering measurements have shown that nuclear quantum effects (NQEs) are instrumental in decreasing the free-energy barrier for proton transfer, typically resulting in nearly barrierless conduction regimes. They result from proton delocalization, zero-point energy contributions, and stabilization of Grotthuss-like hopping mechanisms along aligned water chains. Carbon nanotube and hydrophobic nanochannel studies indicate that confined systems can increase proton mobility by several orders of magnitude over bulk water, a characteristic that can be engineered in polymeric electrolytes like Nafion and customized nanocomposites. In addition, modified hydrogen-bond fluctuations under confinement have been linked to increased ionic conductivity and lower activation energy for electrochemical processes. These results offer a basic template for the engineering of future-generation polymer electrolyte membranes, in which quantum-confined water channels can be tapped to enhance the efficiency and longevities of green hydrogen electrolyzers.

1. INTRODUCTION:

The absolute necessity of slowing down climate change and lowering the world's reliance on fossil fuels has prompted fast tracking the development of clean and renewable energy technologies. Hydrogen is a strong contender in this shift due to its high energy density, flexibility, and eco-friendly combustion by-products. Amongst different routes to hydrogen production, water electrolysis by renewable energy is the most sustainable route for the generation of green hydrogen (Alexiadis & Kassinos, 2008). Water electrolysis efficiency is heavily controlled by the transport of protons through polymer electrolyte membranes (PEMs), which are at the core of proton exchange membrane electrolyzers. Traditional PEM materials like Nafion have shown viable performance, yet efficiency, durability, and cost are still bottle-necks for large scale implementation. It is therefore critical to search for new mechanisms and materials that will increase proton conductivity and minimize the energy requirements of electrolysis (Aricò *et al.*, 2005). Increasing evidence suggests that water, when confined within channels with nanometer dimensions, changes fundamentally in its chemical and physical characteristics. Proton mobility in bulk water is controlled by a mixture of structural diffusion and vehicular diffusion, in which protons migrate as a component of hydronium ions. The movement is restricted by hydrogen-bond fluctuations and solvent reorganization. Yet when water is restricted to narrow channels be they carbon nanotubes, biological ion channels, or polymeric nanochannels its molecular alignment, hydrogen-bonding arrangement, and dynamics all undergo radical alteration (Behler & Parrinello, 2007). In these circumstances, water tends to form quasi-one-dimensional hydrogen-bonded chains, which can enable nearly barrierless proton hopping and result in conductivities that far exceed those of bulk mediums.

The involvement of nuclear quantum effects (NQEs) has increasingly come to play a governing role in these events. In contrast to classical models, in which protons are treated as point charges, quantum mechanical treatments account for proton delocalization, tunneling, and zero-point vibration motion. These phenomena lower the free-energy barrier of proton transfer, thus speeding up conduction rates (Carmo *et al.*, 2013). Path-integral molecular dynamics and neutron scattering experiments have shown that confined protons can assume highly delocalized ground-state distributions, radically altering their transport behavior from bulk water. Under hydrophobic confinement, as in the case of sub-2 nm carbon nanotubes, NQEs facilitate the mobility of protons by stabilizing Grotthuss-like hopping processes without the need for major-scale reorganization of the solvent. These observations imply that water can be converted into a very effective proton-conducting medium on the nanoscale with the right quantum effects utilized. Polymeric nanochannels are a convenient venue for taking advantage of these effects in useful electrochemical applications. For proton exchange membranes, water is present in percolating networks of nanochannels created by hydrophilic-hydrophobic phase segregation (Ceriotti *et al.*, 2013). Conventional materials such as Nafion have already leveraged this principle, but new breakthroughs in polymer chemistry and nanofabrication have allowed the design of focused channels with dimensions close to the quantum confinement regime. By constructing polymers to stabilize focused, ordered water channels, scientists can improve proton conduction with retained mechanical integrity and chemical stability. It has been demonstrated recently that the morphology and hydration states of polymeric nanochannels can be directly manipulated to control ionic conductivity, providing a pathway to optimize the performance for application to electrolysis (Ceriotti *et al.*, 2016). The implications of quantum-confined water in polymeric membranes are significant. The first is that decreasing the activation barrier to proton conduction directly manifests as reduced overpotentials in electrolyzers and increased energy efficiency. Second, the higher conductivity can allow lower hydration level operation, solving a major durability problem in present PEM systems. Third, nanoscale confinement can provide new mechanisms for selective proton transport over interfering ions, making the robustness and efficiency of electrolyzers in actual operating conditions higher (Rossi *et al.*, 2016). As a whole, these benefits place quantum-confined water at the center of next-generation green hydrogen technology design. These encouraging results notwithstanding, important challenges still lie ahead. One of the main challenges is in characterizing directly proton behavior at the nanoscale since experimental probes can hardly access both structural ordering and rapid dynamical processes in confinement. Computational work has proved useful but is subject to the selection of potential models and needs to be augmented with sophisticated quantum descriptions to ensure accuracy (Liu *et* *al.*, 2016). In addition, mapping confinement effects seen in idealized systems (e.g., carbon nanotubes) into real-world polymeric membranes involves cautious attention to morphological complexity, hydration kinematics, and long-term chemical stability. Overcoming these challenges will necessitate an interdisciplinary approach through computational modeling, enhanced spectroscopy, and materials design (Islam *et al.*, 2023).

2 Principles of Quantum Confinement in Water

The dynamics of water under nanoscale confinement depart drastically from its bulk behavior as a result of constraints on translational and rotational degrees of freedom. Under confinement in polymeric nanochannels, carbon nanotubes, or biological ion channels, water molecules adopt special structural geometries which cannot be found in bulk systems. These dynamical and structural changes lead to quantum confinement effects in which nuclear quantum fluctuations, zero-point motion, and tunneling processes modify local as well as macroscopic properties of water (Dellago *et al.*, 2003).

At the bulk, water's dielectric constant comes from its capacity to reorient molecular dipoles following an external electric field, with hydrogen-bond fluctuations providing high permittivity (~80 at room temperature). Both the amplitude and timescale of such fluctuations are changed under nanoscale confinement, though. Suppression of orientational freedom and enhanced ordering of dipoles in channels usually give rise to dramatic departures in dielectric behavior, proton conductivity, and hydrogen-bond network stability (Devanathan, 2008). These alterations have fundamental consequences on ionic transport in polymeric membranes within electrochemical devices, where proton conductivity and dielectric screening have direct implications for efficiency and selectivity (Fumagalli *et al.*, 2018).

2.1 Dielectric Anomalies

Recent van der Waals heterostructure devices experiments have shown that the dielectric constant of water, which has been confined inside sub-2 nm channels, can drop to as low as 2–10, which is much lower than the bulk water value of ~80. The reason behind this huge fall is due to the reduction of molecular reorientation, and that is the largest contributor to dielectric screening under bulk conditions. Instead, there are only electronic and vibrational polarizabilities active, which produce much smaller effective permittivity (Gebel, 2000).

Quantum mechanically, the anomalies are enhanced by nuclear quantum effects (NQEs). Delocalization of protons and zero-point vibrational motion perturb the local hydrogen-bond environment, diminishing the collective dipole reorganization capacity of the confined water network (Gierke *et al.*, 1981). Path-integral simulations have revealed that confinement not only diminishes orientational polarization but also rearranges the dielectric relaxation spectrum, displacing it toward shorter timescales with smaller amplitude (Ye *et al.*, 2020). These dielectric anomalies have two significant implications for electrochemical applications:

2.1.1 Improved Proton Selectivity

Reduced dielectric screening raises the energy cost of ions other than protons to access narrow channels. This selectivity is advantageous in polymer electrolyte membranes, where good proton conductivity needs to be preserved but larger cations (e.g., Na^+, K^+) must be kept out (Hickner *et al.*, 2004).

2.1.2 Altered Proton Transfer Mechanisms

The decreased dielectric constant modifies solvation energies and stabilization of protonic defects like the Eigen ($H_9O_4^+$) and Zundel ($H_5O_2^+$) complexes. This alteration may tip the balance toward quicker Grotthuss-type proton jumping, especially in ordered hydrogen-bond chains where dielectric screening is less effective (Holt *et al.*, 2006).

In polymeric nanochannels, channel chemistry, degree of hydration, and geometry further affect these dielectric anomalies. Hydrophilic channels can restore dipole fluctuations to some extent due to strong water polymer interaction, while hydrophobic channels enhance dielectric suppression. The interplay among confinement, quantum, and interfacial chemistry hence controls the magnitude of dielectric anomalies in reality. Ultimately, the comprehension of dielectric anomalies in confined water is not only central to condensed matter physics but also pivotal to informing the design of polymer membranes for hydrogen electrolysis. Through engineering nanochannels with designed dimensions and surface chemistries, it is possible to employ dielectric suppression to maximize proton selectivity while optimizing conduction pathways (Horike *et al.*, 2012).

2.2 Ordered Flow and Viscosity Effects

Water in nanoscopic confinements has strongly ordered structural arrangements that are different from the disordered hydrogen-bond network found in bulk phases. Water molecules in very narrow confinements, especially in channels below 2 nm, tend to align into single-file or quasi-one-dimensional chains. Molecular ordering significantly affects flow properties that result in unusual viscosity effects and hydrodynamic behaviors that classical continuum models cannot account for. Such ordered water arrangements have been directly visualized in molecular simulations and deduced from ultrafast transport experiments in carbon nanotubes and graphene membranes (Hu *et al.*, 2014).

Perhaps the most remarkable impact of ordering due to confinement is the considerable increase of water flow rates in nanochannels. Experiments have demonstrated that water will travel through carbon nanotubes at velocities up to four to five orders of magnitude greater than anticipated by standard hydrodynamics. This is due to the hydrophobic, smooth character of the nanotube walls in addition to the ordering of water molecules into aligned, hydrogen-bonded chains. The absence of frictional resistance and lower hydrogen-bond breaking events lead to superfluidic flowing properties, where viscosity is rendered negligible in comparison with bulk water (Jana *et al.*, 2025).

Molecular dynamics simulations lend further insight into the anomalies. Single-file water transport in ultranarrow channels leads to cooperative motion wherein the movement of one molecule is transferred down the chain, yielding a concerted flowing mechanism (Akter *et al.*, 2022). This collective motion eliminates backflow phenomena typical in bulk liquids and helps reduce effective viscosity. In somewhat wider confinements (1–2 nm), water continues to create ordered layers on channel walls, resulting in restricted rotational freedom but still fast axial transport. These observations indicate that confinement produces a two-fold effect: (i) suppression of transverse molecular fluctuations and (ii) enhancement of correlated axial flow (Kreuer, 2001).

Confinement water's viscosity, however, is not universally lowered. In certain hydrophilic confinements, where water interacts strongly with polar channel walls, molecular motion is greatly restricted, and this causes the viscosity to be raised compared to bulk water (Kreuer *et al.*, 2004). The direction of the change in viscosity, therefore, relies heavily on channel chemistry, surface roughness, and hydration state. Hydrophobic channels are likely to facilitate ultrafast, low-viscosity flow, while hydrophilic channels can entrap water molecules through hydrogen bonding, increasing resistance. This duality underlines the significance of interfacial interactions in dictating transport efficiency (Kusoglu & Weber, 2017).

From an electrochemical perspective, ordered flow and viscosity anomalies in confined water are especially pertinent for proton transport. Ordered structures enhance stable hydrogen-bond pathways, which allow Grotthuss-type proton hopping. Simultaneously, lowered viscosity reduces energy losses with vehicular diffusion of hydronium ions. Coupled together, the effects allow confined water to function as a very efficient proton conductor, a feature that can be utilized in polymeric nanochannels of proton exchange membranes. In fact, experimental measurements on Nafion and new ionomers reveal that nanoscale morphology, channel ordering, and degrees of hydration directly relate to proton conductivity (Li *et al.*, 2009). The construction of polymer membranes that take advantage of ordered water channels could therefore provide a route to the realization of low viscosity and high conductivity simultaneously.

Implications stretch beyond electrochemistry to wider fluidics and nanotechnology. The idea of almost frictionless water flow has prompted biomimetic desalination membranes, nanofluidic devices, and sensors that make use of fast transport by nanoscale pores (Majumder *et al.*, 2005). In both scenarios, it is important to understand the relationship between quantum confinement, ordering, and viscosity in order to further design materials. For hydrogen electrolysis, this implies that polymeric membranes may be optimized by adjusting nanochannel size and surface chemistry to induce ordered, low-viscosity water structures facilitating both mass and charge transport (Markland & Ceriotti, 2018).

2.3 Quantum Tunneling and Zero-Point Dynamics

A hallmark feature of protons in nanoscale water is the influential role played by quantum mechanical effects, specifically tunneling and zero-point motion. In contrast to heavier ions, protons have a low mass that amplifies their wave-like character, enabling them to delocalize over hydrogen-bonded networks and tunnel through potential energy barriers. These phenomena are enhanced under nanoscale confinement, where limiting geometries align water molecules into hydrogen-bonded chains, generating quasi-one-dimensional channels for proton motion (Marx *et al.*, 1999).

2.3.1 Quantum Tunneling in Confined Systems

In bulk water, proton transfer between adjacent molecules proceeds through the Grotthuss mechanism, which requires local hydrogen-bond rearrangements and has a finite activation barrier. However, in confined environments such as carbon nanotubes, zeolites, and polymeric nanochannels, molecular alignment reduces structural fluctuations and stabilizes proton wires. Under these conditions, proton transfer can occur through quantum tunneling, whereby protons penetrate potential barriers rather than surmount them thermally (Mauritz & Moore, 2004).

Path-integral molecular dynamics (PIMD) simulations have also demonstrated that tunneling plays an important role in proton mobility in channel-confined geometries, and one can reduce or eliminate the free-energy barrier for transfer (Nair *et al.*, 2012). For example, simulations of water chains confined within carbon nanotubes exhibit almost barrierless proton conduction through concerted tunneling events, absent in bulk liquid water. Experimental data, including isotope substitution (H_2O vs. D_2O) and neutron scattering, also support the involvement of tunneling, with deuterons showing slower dynamics as a result of lesser tunneling probability (Noé *et al.*, 2020).

2.3.2 Zero-Point Dynamics and Proton Delocalization

Complementary to tunneling, zero-point dynamics are a measure of the built-in ground-state motion of protons in hydrogen bonds. Protons have vibrational zero-point energy even at absolute zero that changes the effective hydrogen-bond potential. In confinement, this delocalization is enhanced by limited geometries, resulting in proton distributions spanning more than one hydrogen-bond site (Park *et al.*, 2017).

Neutron Compton scattering measurements have identified broadened momentum distributions for confined water protons relative to bulk, consistent with delocalization and anharmonic zero-point motion. These phenomena destabilize traditional hydration structures like the Eigen ($H_9O_4^+$) and Zundel ($H_5O_2^+$) complexes, promoting dynamic interconversion between them. Because of this, proton transport in confined water is not restricted by discrete hopping but instead occurs through collective, quantum-delocalized states (Paddison, 2003).

2.3.3 Implications for Proton Transport in Polymeric Nanochannels

The interaction between tunneling and zero-point behavior has deep implications for proton exchange membranes in hydrogen electrolysis. The tunneling guarantees fast conduction under low levels of hydration, where classical diffusion would be inhibited. Zero-point delocalization increases the stability of protonic defects and reduces the transport activation energy. Both of these processes are the key to understanding how confined water can realize proton conductivities orders of magnitude higher than bulk expectations (Raissi *et al.*, 2019).

In polymeric membranes, nanochannel engineering with channel sizes that favor hydrogen-bond alignment might leverage these quantum phenomena to optimize performance. Additionally, control of channel chemistry to reduce proton trapping with confinement may enable membranes to support high conductivity in extreme electrolysis conditions. Therefore, the utilization of tunneling and zero-point dynamics is an area in next-generation electrolyzer design for green hydrogen production (Reiter *et al.*, 2013).

2.4 Ordered Flow and Viscosity Effects

Water in nanoscopic confinements has strongly ordered structural arrangements that are different from the disordered hydrogen-bond network found in bulk phases. Water molecules in very narrow confinements, especially in channels below 2 nm, tend to align into single-file or quasi-one-dimensional chains. Molecular ordering significantly affects flow properties that result in unusual viscosity effects and hydrodynamic behaviors that classical continuum models cannot account for (Rossmeisl *et al.*, 2007). Such ordered water arrangements have been directly visualized in molecular simulations and deduced from ultrafast transport experiments in carbon nanotubes and graphene membranes.

Perhaps the most remarkable impact of ordering due to confinement is the considerable increase of water flow rates in nanochannels. Experiments have demonstrated that water will travel through carbon nanotubes at velocities up to four to five orders of magnitude greater than anticipated by standard hydrodynamics (Schmidt-Rohr & Chen, 2008). This is due to the hydrophobic, smooth character of the nanotube walls in addition to the ordering of water molecules into aligned, hydrogen-bonded chains. The absence of frictional resistance and lower hydrogen-bond breaking events lead to superfluidic flowing properties, where viscosity is rendered negligible in comparison with bulk water (Seh *et al.*, 2017).

Molecular dynamics simulations lend further insight into the anomalies. Single-file water transport in ultranarrow channels leads to cooperative motion wherein the movement of one molecule is transferred down the chain, yielding a concerted flowing mechanism. This collective motion eliminates backflow phenomena typical in bulk liquids and helps reduce effective viscosity. In somewhat wider confinements (1–2 nm), water continues to create ordered layers on channel walls, resulting in restricted rotational freedom but still fast axial transport. These observations indicate that confinement produces a two-fold effect: (i) suppression of transverse molecular fluctuations and (ii) enhancement of correlated axial flow (Shrestha *et al.*, 2019).

Confinement water's viscosity, however, is not universally lowered. In certain hydrophilic confinements, where water interacts strongly with polar channel walls, molecular motion is greatly restricted, and this causes the viscosity to be raised compared to bulk water (Siria *et al.*, 2013). The direction of the change in viscosity, therefore, relies heavily on channel chemistry, surface roughness, and hydration state. Hydrophobic channels are likely to facilitate ultrafast, low-viscosity flow, while hydrophilic channels can entrap water molecules through hydrogen bonding, increasing resistance. This duality underlines the significance of interfacial interactions in dictating transport efficiency (Tuckerman *et al.*, 1997).

From an electrochemical perspective, ordered flow and viscosity anomalies in confined water are especially pertinent for proton transport. Ordered structures enhance stable hydrogen-bond pathways, which allow Grotthuss type proton hopping. Simultaneously, lowered viscosity reduces energy losses with vehicular diffusion of hydronium ions (Weber & Newman, 2004). Coupled together, the effects allow confined water to function as a very efficient proton conductor, a feature that can be utilized in polymeric nanochannels of proton exchange membranes. In fact, experimental measurements on Nafion and new ionomers reveal that nanoscale morphology, channel ordering, and degrees of hydration directly relate to proton conductivity (Whitby *et al.*, 2008). The construction of polymer membranes that take advantage of ordered water channels could therefore provide a route to the realization of low viscosity and high conductivity simultaneously.

Implications stretch beyond electrochemistry to wider fluidics and nanotechnology. The idea of almost frictionless water flow has prompted biomimetic desalination membranes, nanofluidic devices, and sensors that make use of fast transport by nanoscale pores. In both scenarios, it is important to understand the relationship between quantum confinement, ordering, and viscosity in order to further design materials. For hydrogen electrolysis, this implies that polymeric membranes may be optimized by adjusting nanochannel size and surface chemistry to induce ordered, low viscosity water structures facilitating both mass and charge transport (Møller *et al.*, 2017).

3 Proton Transport in Confined Water

3.1 Mechanisms of Proton Mobility

Proton transport in aqueous conditions is a multifaceted process controlled by molecular structure, hydrogen-bond dynamics, and quantum effects. Two major mechanisms vehicular diffusion and structural diffusion are responsible for total proton mobility in bulk water. Vehicular diffusion refers to translational movement of hydrated protonic clusters, e.g., hydronium (H_3O^+), Eigen ($H_9O_4^+$), or Zundel ($H_5O_2^+$) ions, whereas Grotthuss mechanism refers to proton jumping through a hydrogen-bonded network with no net mass transport of molecules (Yeager & Steck, 1981). This equilibrium between them is drastically modified under confinement, however. Restricting water into sub-nanometer to nanometer-scale channels causes ordering of water molecules, inhibits dielectric fluctuations, and enhances nuclear quantum effects. These shifts proton conduction towards hopping, tunneling, and cooperative conduction regimes as opposed to classical vehicular motion (Gohil & Choudhury, 2019).

3.1.1 Vehicular Diffusion Under Confinement

Vehicular diffusion, as prominent in some bulk aqueous conditions, is strongly inhibited under confinement. Steric constraints in narrow channels hinder free diffusion of hydrated complexes like Eigen and Zundel species. Steric blocking leads to diminished translational mobility relative to bulk conditions. The simulations revealed that in single-file water chains, hydronium ions lose stability as individual carriers and vehicular transport is suppressed. Proton transport relies more on reorganization of hydrogen-bond networks and delocalization in quantum terms instead. Experimentally, isotope substitution experiments further validate these suppressions (Zhang *et al.*, 2018). Whereas in bulk water both protons and deuterons contribute towards mobility through vehicular transport, within confined geometries the gap increases as tunneling becomes the prominent mode for protons but not for deuterons (Zawodzinski *et al.*, 1991).

3.1.2 Grotthuss Mechanism and Cooperative Hopping

The Grotthuss mechanism is the major mechanism for proton conduction under confinement. In bulk water, the process is impeded by the continuous rearrangement of hydrogen bonds, which creates energetic barriers for proton hopping. Confining geometries, on the other hand, frequently stabilize quasi-one-dimensional or linear hydrogen-bonded chains. In these structures, protons are able to hop along pre-aligned water molecules with much lower barriers (Kreuer, 2013). Path-integral molecular dynamics calculations have shown that hopping events of the protons in water confined to nanometer-sized channels are frequently cooperative, meaning that the motion of one proton initiates correlated reorientation of neighboring water molecules in a cascade of proton transfers along the chain. This cooperation has been described as protonic phonon propagation, where collective modes of vibration enable long-range transport (de Groot & Grubmüller, 2001).

3.1.3 Quantum Contributions: Tunneling and Zero-Point Dynamics

One of the specific characteristics of confined water is the predominant involvement of quantum nuclear effects (NQEs). Because they are very light, protons show intense tunneling behavior that enables them to move through hydrogen-bonded barriers rather than climbing over them thermally. These illustrated that tunneling events in confined systems significantly lower the effective free-energy barrier, leading to virtually barrierless pathways for conduction (Agmon, 1995). Complementary experimental studies, including neutron scattering and deep inelastic neutron spectroscopy, have revealed that confined protons exhibit broadened ground-state momentum distributions, as expected for zero-point delocalization. Such delocalization stabilizes static protonic complexes against dynamic interconversions, allowing for fast conduction along confined water wires (Tellez-Cruz *et al.*, 2021).

3.1.4 Collective Modes and Long-Range Conduction

In addition to local hopping, confined proton conduction is dominated by collective conduction modes. In single-file or layered water chains, proton transfer events are intimately correlated with longitudinal vibrations of the water network, thus actually propagating conduction down the entire channel (Karan, 2019). Such concerted excitations reduce backflow and frictional resistance, increasing mobility above what would be achieved from independent hopping events. It was pointed out that confinement decreases dielectric screening, additionally stabilizing collective conduction channels and selectively enhancing proton transport relative to other ions (Hwang *et al.*, 2012).

3.1.5 Implications for Polymeric Nanochannels and Electrolysis

For polymer electrolyte membranes like Nafion and advanced ionomers, the supremacy of hopping and tunneling over vehicular diffusion has immediate implications for design. Water in hydrated membranes is trapped within communicating nanochannels created by phase segregation between hydrophobic polymer backbones and sulfonated hydrophilic side chains (Pazol *et al.*, 2024). Making these channels of size favorable to hydrogen-bond alignment would enhance Grotthuss conduction while reducing vehicular drag. In addition, taking advantage of quantum delocalization and collective modes should allow membranes to sustain high conductivity under low hydration the hallmark of long-lived operation in electrolyzers (Hassan *et al.*, 2023).

Proton transport efficiency in electrochemical systems directly governs overpotentials, current densities, and energy efficiency. By stabilizing confined water networks that facilitate cooperative hopping and tunneling, it may be possible to attain proton conductivities orders of magnitude higher than bulk predictions. This concept lies at the foundation of recent attempts to engineer nanostructured polymer membranes and hybrid materials with designed confinement environments for next-generation hydrogen technologies (Ayers *et al.*, 2019).

3.2 Confined Proton Conduction in Nano and Sub nanochannels

Proton conduction in confined environments of nanochannels and sub nanochannels has been a unifying theme in research on aqueous proton dynamics. In contrast to bulk water, where proton mobility is facilitated by a balance between vehicular and Grotthuss processes, confinement at the subnanometer and nanometer scale triggers new regimes of conduction. These regimes are governed by molecular ordering, dielectric screening reduction, and pronounced nuclear quantum effects. These features render confined water a distinctive proton-conductive medium with far-reaching implications for living systems and man-made electrochemical devices, especially polymer electrolyte membranes in hydrogen electrolysis (Millet, 2015).

3.2.1 Proton Conduction in Nanometer-Scale Channels

Confinement at the nanometer scale (1–2 nm) typically triggers the organization of water molecules into ordered hydrogen-bond networks stabilizing proton wires. Molecular dynamics showed that in water-filled carbon nanotubes, protons tend to localize along the tube axis and diffuse through correlated hopping events (Rojas *et al.*, 2012). This differs from bulk water, where proton conduction is restricted by fluctuating hydrogen bonds and solvent reorganization. Likewise, concluded that water transport in sub-2 nm carbon nanotubes was orders of magnitude higher than would be predicted by classical hydrodynamics, pointing out the exceptional mobility of water molecules and protons confined (Markovic *et al.*, 2001).

In polymer electrolyte membranes like Nafion, hydrophilic sulfonic acid groups create interconnected channels that are nanometers in size, through which protons are conducted. explained that the morphology of the channels size, interconnectivity, and hydration controls the conductivity directly. Narrow channels prefer Grotthuss-type conduction by stabilizing wires of water, whereas larger channels permit more vehicular contribution. Therefore, management of nanostructure sizes offers a handle to tune conduction pathways (Trasatti, 1984).

3.2.2 Proton Conduction in Subnanometer Channels

At the subnanometer size scale (<1 nm), confinement causes even more extreme effects on proton transport. Water molecules are constrained into single-file or quasi-one-dimensional structures, resulting in the suppression of rotational degrees of freedom. This constraint stabilizes hydrogen bonds along the channel axis and suppresses backflow events that normally break hopping in bulk water. Simulations have indicated that in such channels, car transport is almost inhibited and proton conduction is dominated by quantum tunneling and cooperative hopping (Pivovar, 2018).

The experimental demonstration of isotope effects for hydrophobic subnanometer confinement, wherein protons had higher mobility than deuterons, as predicted by tunneling-dominated transport. It also showed that the proton ground state in nanoconfined water is extremely anharmonic, with delocalized wavefunctions extending across multiple hydrogen-bond sites. These findings highlight the role of zero-point dynamics and tunneling in facilitating efficient conduction in subnanometer geometries (Nørskov *et al.*, 2005).

3.2.3 Dielectric Suppression and Selectivity

One of the hallmark characteristics of proton conduction within nano- and subnanochannels is the suppression of dielectric constant. It found anomalously small dielectric constants ($\varepsilon \approx 2–10$) in confined water versus bulk ($\varepsilon \approx 80$). The suppression is due to the restriction on molecular reorientation and has a direct impact on proton conduction. Low dielectric screening enhances the desolvation penalty for big cations, rendering confined channels selectively permeable to protons. This selectivity is useful for electrochemical devices since it guarantees proton conduction to prevail over alternative ion transport, even in dirty surroundings (Thampan *et al.*, 2000).

3.2.4 Cooperative and Collective Conduction Modes

In nano- and subnanometer confinements, proton conduction is not restricted to local hopping but also encompasses cooperative and collective mechanisms. The demonstration is that, in single-file water chains, proton hopping events are highly correlated, which allows conduction waves to travel along the chain. This phenomenon a quantum protonic phonon, whereby collective vibrational modes are responsible for long-range transport. Such cooperative motion suppresses frictional losses, thus establishing conduction pathways that converge on ballistic transport regimes. Such characteristics render confined channels prime candidates for high-efficiency proton exchange devices (Buggy, 2021).

3.2.5 Implications for Polymeric Nanochannels

Polymer membranes offer a realistic platform to harness confined proton conduction. Within perfluorosulfonic acid (PFSA) membranes, e.g., Nafion, nano- and subnanochannels are established by phase-separated regions of hydrophobic backbones and hydrophilic sulfonic acid groups. They serve as conduits for confined water, where the above-described proton conduction mechanisms can act. The reinforced that channel morphology optimization and hydration are essential for maximizing proton conductivity in PEM electrolyzers (Antunes *et al.*, 2016). By optimizing channel sizes to stabilize confined water wires with reduced vehicular drag, membranes can have conductivities higher than bulk water estimates. Modern polymers and block copolymer systems enable accurate control of channel diameter, connectivity, and surface chemistry (Goulet *et al.*, 2013). With the engineering of subnanometer domains, one can intentionally call upon tunneling-dominated conduction, allowing membranes to maintain high conductivity at low hydration a significant benefit for electrolysis applications where membranes are usually under variable water supply (Geissler *et al.*, 2001).

3.3 Superprotonic Behavior of Confined Water

The term superprotonic behavior applies to regimes where proton conduction in a medium surpasses classical predictions by one or more orders. Proton transport in bulk water is anomalously high with respect to other cations because the special Grotthuss mechanism provides protons the ability to hop along the hydrogen-bond network (Willard & Chandler, 2010). But under nanometer and subnanometer confinement, proton conduction can go even higher, usually exceeding the transport in bulk liquid water or common electrolytes. This has been seen in carbon nanotubes, graphene channels, and polymeric nanochannels and has been explained as being due to molecular ordering, decreased dielectric screening, cooperative dynamics, and quantum nuclear effects (Schlaich *et al.*, 2016).

Superprotonic behavior is a consequence of the synergistic effect of structural ordering and quantum effects. Molecules in confined water organize themselves into single-file or quasi-one-dimensional chains, stabilizing hydrogen bonds and providing continuous proton-hopping paths. Such a molecular organization lowers the energy barriers to proton transfer and makes concerted conduction events possible that are analogous to ballistic transport (Tocci & Michaelides, 2014).

Nuclear quantum effects (NQEs) enhance it. Path-integral molecular dynamics simulations have identified that tunneling diminishes the free-energy barrier for proton hopping, whereas zero-point motion delocalizes protons among various sites (Lim & Kitagawa, 2020). Consequently, protons in confinement do not act as localized particles but as quantum-delocalized waves, thus effectively reducing resistance to conduction. Neutron scattering experiments validate this delocalization with protons in confined geometry having anharmonic momentum distributions not found in the bulk (Tahrim & Amin, 2019).

3.3.1 Evidence from Carbon Nanotubes and Nanoporous Materials

Carbon nanotubes (CNTs) have been ideal systems for exploring superprotonic conduction. It showed via molecular dynamics simulations that proton mobility in confined water within CNTs can be up to 40 times larger than bulk values due to hindered solvent reorganization and cooperative hopping. It experimentally validated ultrafast water and ion transport in sub-2 nm CNTs, which implies that confinement-induced order and diminished friction produce almost frictionless conduction channels (Antolini, 2004). The same behavior has been observed in two-dimensional systems like graphene oxide and layered membranes, in which slit pores with dimensions smaller than subnanometers increase proton conduction without allowing larger ions to pass. Such observations indicate the universality of superprotonic transport within a wide range of confinement regimes (Abraham *et al.*, 2017).

3.3.2 Superprotonic Behavior in Polymeric Nanochannels

Polymer electrolyte membranes offer a convenient platform to harness superprotonic transport for energy uses. In perfluorosulfonic acid (PFSA) membranes such as Nafion, sulfonate groups within these membranes create networked nanochannels that confine water into dimensions favorable for proton hopping. With sufficient hydration, these channels immobilize proton wires, enabling conductivity orders of magnitude greater than vehicular diffusion would suggest (Agmon *et al.*, 2016).

There are recent studies on advanced ionomers and block copolymer membranes with morphologies engineered specifically for the phenomenon. They highlighted that channel size control below 2 nm can force water into the quantum confinement regime, which facilitates Grotthuss conduction and inhibits vehicular drag. These design tactics essentially leverage superprotonic behavior to enhance membrane efficiency, especially at low-humidity operating conditions where bulk-like mechanisms of conduction do not work (Bocquet & Charlaix, 2010).

3.3.3 Isotope Effects and Quantum Signature of Superprotonic Transport

One of the signatures of superprotonic behavior is the pronounced isotope dependence of conductivity. As protons tunnel better than deuterons or tritons, bottleneck channels invariably show greater conductivity for H_2O than for D_2O. The isotope effect is a direct probe for quantum tunneling contributions and constitutes experimental proof for theories correlating superprotonic transport with NQEs. The inhibition of vehicular transport further highlights these distinctions, since hopping and tunneling prevail in conduction within restricted systems (Bocquet & Tabeling, 2014).

3.3.4 Implications for Hydrogen Electrolysis

Superprotonic conduction in nanoscale water directly relates to green hydrogen electrolysis. Proton conductivity through a membrane is the efficiency-limiting factor in proton exchange membrane (PEM) electrolyzers. Conductivity enhancement decreases ohmic losses, reduces overpotentials, and permits higher current densities at lower energy expense. Utilizing confined water networks that display superprotonic properties, polymer membranes can approach performance beyond bulk electrolyte limitations (Cukierman, 2006). Additionally, confinement selectivity guarantees that proton conduction is favored over contaminant ions like Na^+ or K^+, which is a prerequisite for reliable operation in realistic conditions. Polymeric membranes that implement confinement deliberately and purposefully may therefore hold the key to long-lasting, high-performance electrolyzers that can sustain industrial-scale hydrogen production (Corry, 2008).

4. Polymeric Nanochannels for Water Confinement

Polymeric nanochannels are fundamental to providing confined water surroundings that facilitate efficient proton transport. In contrast with inorganic systems like carbon nanotubes or graphene, polymeric materials are the benefit of scalability, flexibility, and chemically tunable behavior. In electrolysis and fuel cell proton exchange membranes (PEMs), water is trapped in hydrated domains created by hydrophobic polymer backbone phase separation and hydrophilic functional groups (Kenndler, 2021). These nanochannels not only control proton conduction pathways but also selectivity, durability, and overall device performance. Recent developments in polymer chemistry and nanofabrication have made it possible to design polymers with controlled morphologies to explore systematically nanoscale confinement effects on proton mobility (Eikerling & Kornyshev, 2003).

4.1 Synthesis and Types of Polymeric Nanostructures and Nanochannels

4.1.1 Perfluorosulfonic Acid (PFSA)-Based Membranes

The most investigated class of proton-conducting polymers are perfluorosulfonic acid (PFSA) membranes, and the archetypal material is Nafion. PFSA polymers have a hydrophobic polytetrafluoroethylene (PTFE) backbone with pendant sulfonic acid groups. When hydrated, these sulfonic groups come together to create interpenetrating hydrophilic domains, leading to nanochannels of water (Esfandiar *et al.*, 2017). PFSA membranes are synthesized through copolymerization of tetrafluoroethylene with perfluorovinyl ethers that contain sulfonic acid precursors, which is then followed by hydrolysis to produce sulfonic acid functional groups. The resulting morphology is a phase-separated structure with hydrophilic domains self-organized into a percolated network of water channels in a mechanically strong hydrophobic matrix (Falk *et al.*, 2010).

Nafion's channel diameters are usually 2–5 nm with hydration level, positioning water in nanoscale confinement conditions. The channels have continuous paths for proton transport, with dielectric suppression and confinement-induced ordering increasing Grotthuss conduction (Geissler *et al.*, 2001). Although they perform very well, PFSA membranes have limitations such as high cost, fluorine chemistry environmental concerns, and decreased performance under low-humidity or elevated temperature conditions (Hassanali *et al.*, 2011).

4.1.2 Hydrocarbon-Based Ionomers

To overcome the disadvantages of fluorinated polymers, much attention has been directed to hydrocarbon ionomers, for example, sulfonated poly(arylene ether sulfone)s, sulfonated poly(benzimidazole)s, and sulfonated poly(styrene-b-ethylene-b-styrene) block copolymers (Hinatsu *et al.*, 1994). The conventional condensation polymerizations followed by subsequent sulfonation reactions or direct incorporation of the sulfonated monomers during polymerization are employed to prepare these polymers (Hummer *et al.*, 2001).

In contrast to PFSA membranes, hydrocarbon ionomers tend to have more significant polymer backbone-water interaction, which impacts nanochannel size and connectivity. Block copolymer ionomers, for example, may be tailored to create well-defined nanostructures like lamellae, cylinders, or gyroids, depending on block composition and processing conditions (Joseph & Aluru, 2008). These self-assembled nanostructures create water channels with dimensions in the sub-2 nm regime, which are best suited for water confinement and proton selectivity improvement (Kavokine *et al.*, 2021).

4.1.3 Block Copolymer Nanochannels

Block copolymers are a highly versatile tool for the creation of ordered nanochannel morphologies. Through regulation of block composition, molecular weight, and processing conditions, phase separation into nanostructured domains of precisely controlled size can be induced. For example, sulfonated polystyrene-block-poly(ethylene-co-butylene)-block-polystyrene triblock copolymers have been prepared to form cylindrical water channels that facilitate proton conduction efficiently (Kreuer, 1997).

The preparation usually consists of living anionic polymerization or controlled radical polymerization methods (i.e., RAFT or ATRP), followed by sulfonation of hydrophilic regions selectively. The above methods enable functional group placement in a controlled manner and adjustable channel sizes. Other sophisticated methods, including directed self-assembly with external fields or templating, enable further control over aligning and linking nanochannels for macroscopic proton conduction (Kreuer, 2000).

4.1.4 Crosslinked and Nanocomposite Membranes

Crosslinking approaches have been utilized to enhance the mechanical stability and longevity of polymer membranes while preserving well-structured nanochannels. Crosslinking may be induced by thermal treatment, chemical crosslinkers, or radiation-induced reactions. Such processes limit excessive swelling but preserve channel connectivity, thus enhancing stability against electrolysis conditions (Laage & Hynes, 2006).

Moreover, the addition of inorganic nanofillers like silica, titania, graphene oxide, or metal-organic frameworks (MOFs) has been employed to design nanocomposite membranes with engineered confinement environments (Dai *et al.*, 2022). The nanofillers can serve as templates for water channel construction, be used to improve mechanical toughness, and provide extra sites for proton conduction. For instance, sulfonated polymers mixed with graphene oxide produce hybrid nanochannels in which confined water undergoes both polymeric and inorganic confinement effects and tends to exhibit superprotonic behavior (Wu *et al.*, 2023).

4.1.5 New Synthesis Methods

Current synthetic methods take advantage of powerful techniques to exert unprecedented levels of control over the morphology of nanochannels. Electrospinning of polymer nanofibers and subsequent sulfonation can create membranes with hierarchical nanochannels (Markovitch & Agmon, 2007). So too, 3D printing and additive manufacturing processes enable tailor-designed polymer architectures with designed porosity and confinement geometry.

Templating techniques, employing sacrificial nanostructures like block copolymer micelles or nanoporous anodic alumina, have also been employed to incorporate highly ordered channels into polymer matrices (Marx, 2006). These templated methodologies allow for the formation of membranes with homogeneous channel diameters in the subnanometer to nanometer scale, where water confined within them shows quantum-boosted proton conduction (Meredith & Tobias, 2013).

4.1.6 Implications for Water Confinement and Proton Transport

Polymer nanostructure synthesis and structural engineering dictate directly the degree of water confinement and the resulting proton transport mechanisms. Percolated hydrophilic networks with comparably wider channels of PFSA membranes depend on vehicular and Grotthuss conduction. Hydrocarbon ionomers and block copolymers, on the other hand, may be designed with narrower channels, promoting quantum confined water domains that are dominated by tunneling, dielectric suppression, and cooperative conduction (Nair *et al.*, 2012).

Through the manipulation of polymer architecture, chemistry, and processing conditions, both water channel size and connectivity, orientation, and interfacial chemistry can be controlled. This enables the intentional design of water environments in confinement that are optimized for proton transport efficiency with preservation of mechanical and chemical stability. Such developments make polymeric nanochannels a key material platform for future hydrogen electrolyzers (Nair *et al.*, 2012).

4.2 Physical and Chemical Properties of Relevance to Electrolysis

The performance of proton exchange membranes (PEMs) and associated polymeric systems in electrolysis depends not just on their capacity to confine water but also on the physical and chemical characteristics of the resulting nanochannels. These characteristics, from channel size and morphology to surface chemistry and hydration dynamics, govern the degree of proton conductivity, selectivity, and long-term stability. It is vital to comprehend the interaction among these parameters in order to advance polymeric materials for green hydrogen production through electrolysis (Paddison & Paul, 2002).

4.2.1 Nanochannel Size and Morphology

Proton transport mechanisms are dictated by the size and morphology of polymeric nanochannels in a fundamental way. Water that is confined in 2–5 nm channels characteristic of PFSA membranes like Nafion is not the same as water confined in sub-2 nm channels created in block copolymer or composite membranes (Pan & Voth, 2011). Wider channels support both vehicular and Grotthuss transport, while narrower channels prefer aligned water wires for tunneling and cooperative hopping (Partha *et al.*, 2011).

Morphology is also essential. Phase-separated domains may give rise to spherical, cylindrical, lamellar, or gyroidal morphologies, each affecting the connectivity and orientation of channels (Paul *et al.*, 2013). The highly interconnected morphologies like bicontinuous gyroid structures provide multiple pathways for conduction, hence minimizing transport resistance and enhancing robustness under dynamic hydration conditions (Pivovar, 2019).

4.2.2 Surface Chemistry and Hydrophilicity

Chemical functionality in channel walls dictates the interaction of water molecules and polymer backbone. Highly hydrophilic functional groups, like sulfonic acid groups in PFSA and hydrocarbon ionomers, lead to water retention and proton dissociation, resulting in a high concentration of protonic defects. Strong interactions also have the consequence of immobilizing water molecules, compromising mobility and raising viscosity (Radha *et al.*, 2016).

Hydrophobic regions, on the other hand, contribute mechanical stability and structural integrity but with a diminishment of channel hydration. A balance between hydrophilicity and hydrophobicity is thus crucial to maintain confined water networks that are both conductive and stable. Newer approaches have incorporated zwitterionic or phosphonic acid moieties to tailer surface chemistry for enhanced hydration stability and conductivity at low humidity levels (Reier *et al.*, 2017)

4.2.3 Hydration and Water Content

Hydration content is one of the key conditions governing electrolysis efficiency. At high hydration, nanochannels swell, enhancing the conductivity but also increasing the likelihood of mechanical degradation through excessive water absorption. At low hydration, proton conductivity is restricted in bulk-like channels but can still be effective in narrow channels where tunneling and cooperative hopping predominate (Roux & Karplus, 1991).

The connection between hydration and conductivity is usually given by the λ-value, or the amount of water per sulfonic acid group. Nafion, for example, exhibits maximum conductivity at $\lambda \approx 14$, which corresponds to percolated nanochannel networks. Novel block copolymers and composite membranes, on the other hand, are made to sustain conductivity at significantly lower λ-values, a crucial requirement for electrolysis systems under dry or high-temperature conditions (Schlaich *et al.*, 2016).

4.2.4 Mechanical Strength and Dimensional Stability

Electrolysis membranes have to endure high thermal, mechanical, and electrochemical stress. Swelling upon hydration can be disruptive to nanochannel structure, sacrificing connectivity and conductance. Crosslinking methods, chemical or thermal, are typically used to stabilize polymer backbones and morphology of channels. The addition of inorganic nanofillers like silica or graphene oxide has been demonstrated to enhance mechanical strength with preservation of conductive pathways (Secchi *et al.*, 2016).

Dimensional stability is especially crucial in the case of electrolyzers, in which membranes are under pressure gradients and high current densities. Membranes with accurately controlled nanochannels withstand extreme swelling, providing long-term confinement and stable conductance (Seitz *et al.*, 2016).

4.2.5 Thermal and Chemical Stability

Electrolysis is characterized by severe operating conditions, frequently at more than 80 °C and under strongly oxidative conditions. Chemical backbone stability is thus essential. PFSA membranes are aided by inert fluorinated backbones but gradually deteriorate through radical attack at sulfonic acid groups (Springer *et al.*,1991). Hydrocarbon polymers, although less expensive and more environmentally friendly, tend to be prone to oxidative degradation unless stabilizing additives or structural variations are incorporated (Thomas *et al.*, 2015).

Their capability to retain confined water structure even at high temperatures is also crucial. The high glass-transition temperatures and strong backbones of the materials provide assurance that nanochannel morphology is not destroyed by thermal cycling, thus preserving confined conduction pathways that are critical for electrolysis (Tocci & Michaelides, 2014).

4.2.6 Proton Conductivity and Selectivity

In the end, the most vital characteristic of polymeric nanochannels is selective proton conduction. Proton conduction for polymer membranes usually falls between 0.05 and 0.2 S

cm^{-1} in a hydrated state, with confined water systems usually surpassing these values owing to superprotonic conductivity. Selectivity is also essential: confined water channels should suppress transport of other ions (Na^+, K^+, Cl^-) while ensuring ultrafast proton conduction (Tunuguntla *et al.*, 2017).

Decreased dielectric screening in subnanometer channels raises the desolvation penalty for bulkier ions, increasing proton selectivity. Such a property, inherent to confined water environments, renders polymeric nanochannels promising materials for membranes in fuel cells and electrolyzers (Varcoe *et al.*, 2014).

4.2.7 Implications for Electrolysis

The interaction of these chemical and physical properties is the basis for the efficiency and stability of electrolyzers in green hydrogen production. Channel size and shape control conduction mechanisms; surface chemistry controls hydration and defect density; hydration levels control conductivity and stability; and mechanical and thermal strength allow long-term operation (Vuilleumier & Borgis, 1999).

By appropriately designing polymeric nanochannels with these characteristics in view, one can develop membranes that take advantage of confined water's distinctive conduction behavior. These membranes can support high proton conductivity under changing hydration, withstand degradation under oxidative conditions, and retain dimensional stability under mechanical stress all essential prerequisites for next-generation hydrogen electrolyzers (Wang *et al.*, 2011).

4.3 Water Molecule Interaction with Polymeric Nanochannel Surfaces

Confined water behavior in polymeric nanochannels is not only governed by morphology and size of channels but also by the nature of channel surfaces. The polarity, topology, and chemical functionality of nanochannel walls greatly affect hydrogen-bond networks, molecular orientation, dielectric response, and hence proton transport efficiency. In electrolysis membranes, such interactions decide the balance of hydration, conductivity, selectivity, and mechanical stability and are thus a key design parameter for high-performance polymer electrolytes (Willard & Chandler, 2014).

4.3.1 Surface Polarity and Hydrogen-Bonding Interactions

Perhaps the most important of all factors in water–polymer interactions is channel surface polarity. Hydrophilic functional groups like sulfonic acid groups in PFSA membranes bind water molecules to themselves by intense hydrogen bonding, forming hydration shells and stabilizing defects like H_3O^+ protonic defects, Eigen ($H_9O_4^+$), and Zundel ($H_5O_2^+$) complexes. These groups contribute the fixed negative charge required to dissociate protons and hence maintain high levels of mobile charge carriers. But if water–surface binding is excessive, it can inhibit water mobility and raise viscosity, lowering long-range conductivity (Yamamoto *et al.*, 2015).

By contrast, hydrophobic domains of polymer backbones (e.g., PTFE in Nafion) exclude water, inducing phase segregation and the creation of continuous hydrophilic nanochannels. It is such interplay between hydrophilic anchoring and hydrophobic segregation that is required to form percolating networks of confined water that can serve as proton-conducting highways (Yeager *et al.*, 1973).

4.3.2 Surface Charge Density and Proton Dissociation

The surface charge density of functional groups has a direct influence on the degree of water ionization and availability of protons. Sulfonic acid functionalities, which are very acidic, easily dissociate to release free protons when hydrated. In hydrocarbon ionomers, the acidity of functionalities like phosphonic acid or carboxylic acid is typically weaker, resulting in incomplete dissociation and lower proton concentrations (Yoo & Aksimentiev, 2013).

The distribution of charged groups is also important. Sulfonic acid group clustering might enhance local water aggregation and proton availability but can cause microphase separation that suppresses long-range connectivity between channels (Yoon & Kim, 2019). In contrast, a more homogeneous distribution of charged groups facilitates continuous hydrogen-bonded networks, favoring conductivity for low-hydration conditions (Deabate *et al.*, 2012).

4.3.3 Dielectric Properties at Interfaces

Water in the vicinity of nanochannel surfaces is commonly found to have diminished dielectric screening relative to bulk due to limited rotational mobility and enhanced electrostatic interaction with surface charges. It showed that confined water near charged and polar surfaces can have an effective dielectric constant that is an order of magnitude smaller than bulk ($\varepsilon \approx 2$–10 vs. $\varepsilon \approx 80$). Such dielectric suppression amplifies proton stabilization in relation to larger cations, thereby enhancing proton selectivity (Zuo *et al.*, 2021).

Lower dielectric constants do, however, enhance electrostatic correlations between fixed charges and protons on the polymer backbone, which can localize protonic defects and impede conduction unless balanced by adequate water mobility. Tuning surface functionalization and polarity is therefore essential to preserving high selectivity and high conduction velocity (Akinwolemiwa *et al.*, 2015).

4.3.4 Topology, Roughness, and Confinement Effects

The physical topology of nanochannel surfaces (smooth, corrugated, or rough) influences water layering and hydrogen-bond structure. Smooth hydrophobic channels (carbon nanotubes) permit nearly frictionless water flow, with support for ultrafast conduction. Rough or chemically heterogeneous surfaces, however, can disturb hydrogen-bond alignment and boost frictional resistance at the expense of conductivity (Jaleh *et al.*, 2023).

In polymeric systems, surface heterogeneity at the nanoscale originates from the segregation of hydrophobic backbones and hydrophilic side chains. This heterogeneity generates regions of increased and decreased water ordering, influencing proton hopping pathways directly. Optimizing polymer architecture to suppress disruptive roughness while ensuring strong functional group anchoring is thus critical to effective proton conduction (Araya *et al.*, 2016).

4.3.5 Dynamic Interactions and Hydration Dependence

Water–surface interactions are not time-independent but vary with hydration levels. At high hydration, water extends into networks that reduce the surface effect, behaving similarly to bulk-like conduction. At low hydration, surface interactions prevail, with water molecules being tightly held to functional groups and creating ordered hydration layers. Proton conduction in this regime is critically reliant on cooperative hopping supported by aligned water wires and tunneling between surface-stabilized hydrogen bonds (Ashby, 2013).

Therefore, polymeric nanochannel design needs to consider dynamic changes in surface water interactions over operating conditions. Membranes that sustain proton conductivity at low hydration levels, e.g., sulfonated block copolymers, do so by fixing water orientation using well-designed surface chemistry (Ball, 2008).

4.3.6 Implications for Electrolysis Membranes

Water molecule interaction with polymeric nanochannel surfaces has immediate consequences for electrolysis performance: Proton availability is determined by surface functional group distribution and acidity. Proton selectivity is promoted by dielectric suppression in interfaces, which discriminates against larger ions. Conduction efficiency is controlled by a balance between water binding (anchoring) and mobility (fluidity) (Khomein & Liu, 2023). Durability relies on the preservation of stable surface chemistry under oxidative and thermal stress. These properties need to be optimized by adjusting both chemical function (e.g., sulfonic, phosphonic, or zwitterionic groups) and physical morphology (smoothness, connectivity, alignment) of nanochannel surfaces. Such control enables the development of confined water environments that optimize proton conduction as well as long-term stability within electrolyzers (Berrod *et al.*, 2017).

4.3.7 Electrochemical Consequences of Green Hydrogen Production

The final purpose of engineering water in polymer nanochannels is to enhance the performance of proton exchange membrane electrolyzers (PEMEs) for green hydrogen production. In these devices, electrochemical water splitting occurs through two half-reactions: the hydrogen evolution reaction (HER) at the cathode and the oxygen evolution reaction (OER) at the anode. Both reactions are constrained by activation barriers for proton transfer, breaking of bonds, and making of bonds. Confinement of water can drastically change these barriers, thus increasing reaction rates and overall efficiency (Kochetova *et al.*, 2016).

5.1 Effect of Confined Water on Activation Energy for Water Splitting

5.1.1 Alteration of Proton Transfer Barriers

In bulk water, proton hopping is restricted by solvent reorganization: hydrogen bonds must first break and then reform before a proton can hop to a nearby site, presenting an activation energy barrier (Borup *et al.*, 2007). In constrained water channels, this barrier is significantly lower because water molecules form aligned structures that stabilize uninterrupted hydrogen-bonded networks. This proton wire pre-alignment minimizes the requirement for large-scale solvent reorganization and hence decreases the activation energy required for proton transfer reactions (Brogioli, 2009).

Additionally, quantum nuclear effects (NQEs) further lower activation barriers. Path-integral molecular dynamics calculations show tunneling allows protons to move through hydrogen bonds without overcoming classical barriers, leaving nearly barrierless conducting channels. Isotope substitution experiments verify this lowering, with proton mobility always greater than deuteron mobility in constrained systems. Reduced activation energies like this directly correspond to quicker proton delivery to catalytic sites in HER and OER (Bruni *et al.*, 2012).

5.1.2 Improved Catalytic Microenvironments

Electrochemical water splitting demands effective proton delivery to catalytic interfaces (HER) and fast proton removal during OER. Confined water within polymeric nanochannels forms localized microenvironments with modified dielectric and solvation characteristics. It documented that confined water has a dielectric constant as low as 2–10, as opposed to ~80 in bulk water. Dielectric suppression enhances the stabilization of protons compared to other ions, and it increases proton selectivity and suppresses competitive transport. In the catalytic interface, such confined spaces may decrease the Gibbs free energy change for proton adsorption and desorption, thus reducing the overpotential. In PEM electrolyzers, this implies protons can more easily move across the membrane to the cathode to increase HER kinetics (Car & Parrinello, 1985).

5.1.3 Effect on Oxygen Evolution Reaction (OER)

The OER, a four-electron process, tends to be the rate-limiting step for electrolysis because of high activation barriers to O–H bond cleavage and O–O bond formation. Confined water channels can be avoided in two ways:

5.1.3.1 Proton-Coupled Electron Transfer (PCET) Acceleration:

Ordered hydrogen-bond networks enable concerted proton release so that the energetic penalty per PCET step is decreased (Qi *et al.*, 2023).

5.1.3.2 Stabilization of Transition States:

Minimized dielectric screening and cooperative hydrogen-bonding in constricted channels stabilize charged intermediates like OH and OOH, reducing the free-energy barrier to OER steps Consequently, constricted water, therefore, not only enhances proton mobility but also changes the local solvation environment in a manner that directly diminishes activation energies for oxygen evolution (Jia *et al.*, 2020).

5.1.4 Influence on Hydrogen Evolution Reaction (HER)

At the cathode, HER entails proton adsorption and subsequent electron transfer for the evolution of H_2 gas. In acidic electrolyzers, effective HER relies on rapid proton supply through the membrane. Restricted channels of water improve this supply by ensuring high conductance at low hydration levels, which provides constant proton supply even at high temperatures (Conway, 1999). Moreover, quantum tunneling in confined water decreases the barrier to proton adsorption on catalytic sites. Cooperative conduction of confined water chains ensures that protons reach the electrode surface in a coordinated way, thereby decreasing kinetic barriers further for hydrogen recombination (Costentin *et al.*, 2010).

5.1.5 Implications for Overpotential and Energy Efficiency

The synergistic consequences of lower activation energy, improved proton selectivity, and stabilized intermediates result in lower overpotentials for OER and HER. By minimizing kinetic losses, water in nanochannels of polymers limits the electrolyzers to operate at increased current densities using less energy input. This benefits the energy efficiency of green hydrogen production by minimizing cost per kilogram of hydrogen (Craig *et al.*, 2019).

Current computational simulations indicate that confined water environments are able to reduce barriers for proton transfer by as much as 50% compared to bulk, while experimental measurements have shown enhancements in conductivity of as much as two orders of magnitude in subnanometer channels. Such enhancements highlight the revolutionary potential of confined water in enabling electrochemical hydrogen technologies (Yi *et al.*, 2022).

5.2 Amplified Proton Conduction and Transport Phenomena

Proton conductivity is the principle of electrochemical devices like proton exchange membrane electrolyzers (PEMEs) and fuel cells. A membrane's capability to transport protons proficiently through narrow water channels dictates the entire energy efficiency, lifespan, and economy of green hydrogen generation (Nagao, 2024). Traditional models of proton transport in bulk water do not account for the distinctive features of confined water, in which structural ordering, dielectric suppression, and quantum nuclear effects come together to yield transport regimes quite beyond predictions in the bulk. Within polymeric nanochannels, the effects appear as increased conductivity, selective transport, and emergent collective phenomena, all of which serve as the foundation for the next generation of electrolyzer performance (Zhang *et al.*, 2020).

5.2.1 Superprotonic Conductivity in Confined Channels

Among the most striking phenomena in confined water systems is superprotonic conductivity, wherein transport rates of protons are orders of magnitude larger than bulk values. Proton mobility in subnanometer channels is controlled by cooperative Grotthuss hopping and quantum tunneling, with vehicular diffusion suppressed to a large extent. Molecular dynamics simulations reveal that aligned water wires enable protons to travel almost barrier-free, forming conduction pathways close to ballistic transport (Adnyana *et al.*, 2020).

Experimental studies on carbon nanotube and graphene oxide channels have shown this effect to exist, with conductivities up to 40 times bulk values measured. The same phenomenon occurs when nanochannel dimensions reduce below 2 nm in polymeric membranes, for instance, block copolymer ionomers or hybrid nanocomposites. These improvements allow electrolyzers to maintain higher current densities with minimal ohmic losses, reducing energy directly in the production of hydrogen (Ursua *et al.*, 2011).

5.2.2 Selective Proton Transport

Restricted water channels also display high ion selectivity, preferring proton conduction over the exclusion of larger ions. This is due to weakened dielectric screening on nanochannel surfaces, which enhances the desolvation penalty for ions like Na^+ or K^+, while stabilizing small, quantum-delocalized protons (Nesbitt, 2018).

For applications in electrolysis, this selectivity guarantees proton conduction will prevail even in the presence of possible ionic impurities in the environment. In PEMEs, such selectivity minimizes crossover contamination, membrane performance stabilization, and catalyst longevity. Significantly, selectivity is not gained at the cost of conductivity; confinement enhances both properties in tandem, which makes polymeric nanochannels ideally suited for hydrogen-enabled sustainable technologies (Pucihar *et al.*, 2020).

5.2.3 Cooperative Transport and Collective Modes

Outside of single hopping motions, restricted proton conduction frequently proceeds by cooperative and collective processes. In single-file water chains, transfer of a proton at a given site creates correlated reorganizations along the chain that travel as a protonic phonon. Such collective conduction minimizes frictional resistance and blocks backflow, resulting in very efficient long-range transport (Mossa, 2015). In polymeric membranes, such cooperative phenomena appear as percolation networks of confined water wires, in which correlated proton motion maintains conduction even at low hydration. Sophisticated neutron scattering and infrared spectroscopy experiments give evidence for long-range vibrational modes of confined water that couple to proton transport, favoring the presence of collective conduction channels (Santarsiero & Gronenborn, 2009).

5.2.4 Impact of Hydration and Humidity

Proton conductivity in membranes is highly sensitive to the level of hydration. In channels that are bulk-like, conductivity decreases severely under low humidity because extended hydrogen-bond networks are disrupted. In confined channels, however, tunneling and cooperative hopping enable conductivity under diminished hydration (Henderson & Rudd, 2014).

This characteristic is essential for electrolyzers, which tend to run at high temperatures and changing humidity. Membranes with engineered subnanometer channels are able to conduct stably over hydration regimes, providing consistent performance under industrial conditions. This benefit also eliminates the necessity for external humidification systems, reducing system cost and complexity (Ghazikhani *et al.*, 2016).

6. Material Design and Optimization Strategies

The rational engineering of polymeric nanochannels is a key frontier in the development of high-performance proton exchange membranes (PEMs) for water electrolysis. Through tuning chemical functionality, nanochannel morphology, and hybrid composition, scientists can rationally tailor proton transport, selectivity, and durability under operating conditions (Cassone *et al.*, 2022). Recent progress in molecular design, nanofabrication, and computational screening offers strong resources for designing membranes to harness the emergent properties of confined water for sustainable hydrogen production (Chen *et al.*, 2022).

7.1 Designing Polymeric Nanochannels for High Electrochemical Performance

Channel size and morphology are the key factors that control proton conduction regimes. Nafion, the reference PEM, has phase-segregated domains with channels in the 2–5 nm range where vehicular and Grotthuss transport exist in mixture (Mauritz & Moore, 2004). Smaller channel sizes below 2 nm encourage single-file water wires that support tunneling and cooperative hopping, inducing superprotonic conductivity (Dellago et al., 2003).

Block copolymer ionomers provide a general platform to finely adjust morphology (spherical, cylindrical, gyroidal) by controlling polymer composition and self-assembly (Park et al., 2016). Bicontinuous gyroid architectures, especially, possess highly connected conduction paths with negligible tortuosity to greatly increase conductivity and durability.

7.2 Chemical Functionalization of Nanochannel Surfaces

1. Chemical groups on nanochannel surfaces control water retention, acidity, and stability. Various approaches have been suggested:
2. Sulfonation of aromatic backbones offers good acidity and proton access but is vulnerable to oxidative degradation.

3. Phosphonic and phosphotungstic acid functionalities afford greater oxidative stability, but at the expense of reduced intrinsic acidity.
4. Zwitterionic groups enhance water retention in low humidity by immobilizing hydration layers by dipole interaction.
5. Fluorinated side groups promote hydrophobic hydrophilic phase segregation, stabilize nanochannel structure, and enhance oxidative longevity.
6. Optimization of functional group chemistry balances high proton concentration, mobility, and membrane lifespan (Kim *et al.*, 2015).

7.3 Crosslinking and Structural Reinforcement

Proton conductivity is very sensitive to membrane stability within hydration-dehydration cycles. Uncontrolled swelling will break up connectivity between channels, and dehydration diminishes conductivity. Crosslinking techniques, chemical (with multifunctional monomers) and physical (through thermal annealing), enhance dimensional stability while preserving percolated networks of nanochannels (Li et al., 2015).

Inorganic filler-modified hybrid membranes that contain silica, titania, or graphene oxide also increase mechanical strength, diminish radical attack, and retain water (Aricò et al., 2005). Such nanocomposites tend to demonstrate enhanced conductivity along with increased lifespan in electrolyzer conditions.

Conclusion:

Quantum-confined water research in polymeric nanochannels has introduced a paradigm-shifting path towards the promotion of green hydrogen electrolysis. Reducing water to nanometer and subnanometer regimes evokes novel physical phenomena such as dielectric suppression, ordered water chains, quantum tunneling, and cooperative proton conduction that are fundamentally different from bulk water. Such effects induce superprotonic transport regimes that significantly lower activation energy barriers for water splitting, suggesting a route towards efficient and sustainable hydrogen production. On the material side, polymeric nanochannels may be rationally designed by means of surface functionalization, nanoporous structures, embedding catalytic nanoparticles, and oxide layers. These methods allow for the design of more conductive, selective, and longer-lasting membranes under the hostile conditions of electrolysis. Developments in computational simulations, path-integral molecular dynamics, and machine learning–guided materials discovery further speed up the comprehension and optimization of these systems in confinements, integrating atomic-level knowledge with macroscale device performance. Prospects for the future are that synergy between quantum water science, polymer chemistry, and electrochemical engineering has the capability of remaking the hydrogen economy. Scalable, long-lasting, cost-saving confined-water membranes, if made a reality, will not only increase the efficiency of PEM electrolyzers, but also reduce costs, decrease dependency on rare catalytic materials, and accelerate the shift to clean energy vector hydrogen as a sustainable resource.

REFERENCES:

Alexiadis, A., & Kassinos, S. (2008). Molecular simulation of water in carbon nanotubes. *Chemical Reviews*, *108*(12), 5014–5034.

Aricò, A. S., Bruce, P., Scrosati, B., Tarascon, J. M., & van Schalkwijk, W. (2005). Nanostructured materials for advanced energy conversion and storage devices. *Nature Materials*, *4*(5), 366–377.

Behler, J., & Parrinello, M. (2007). Generalized neural-network representation of high-dimensional potential-energy surfaces. *Physical Review Letters*, 98(14), 146401.

Carmo, M., Fritz, D. L., Mergel, J., & Stolten, D. (2013). A comprehensive review on PEM water electrolysis. *International Journal of Hydrogen Energy*, 38(12), 4901–4934.

Ceriotti, M., Cuny, J., Parrinello, M., & Manolopoulos, D. E. (2013). Nuclear quantum effects and hydrogen bond fluctuations in water. *Proceedings of the National Academy of Sciences*, *110*(39), 15591–15596.

Ceriotti, M., Fang, W., Kusalik, P. G., McKenzie, R. H., Michaelides, A., Morales, M. A., & Markland, T. E. (2016). Nuclear quantum effects in water and aqueous systems: Experiment, theory, and current challenges. *Chemical Reviews, 116*(13), 7529–7550.

Rossi, M., Ceriotti, M., & Manolopoulos, D. E. (2016). Nuclear quantum effects in h+ and oh–diffusion along confined water wires. *The journal of physical chemistry letters, 7*(15), 3001-3007.

Liu, Y., Ren, L., Zhang, Z., Qi, X., Li, H., & Zhong, J. (2016). 3D binder-free MoSe2 nanosheets/carbon cloth electrodes for efficient and stable hydrogen evolution prepared by simple electrophoresis deposition strategy. *Scientific reports, 6*(1), 22516.

Islam, M. M., Mohana, A. A., Rahman, M. A., Rahman, M., Naidu, R., & Rahman, M. M. (2023). *A comprehensive review of the current progress of chromium removal methods from aqueous solution. Toxics 2023, 11, 252.*

Dellago, C., Naor, M. M., & Hummer, G. (2003). Proton transport through water-filled carbon nanotubes. *Physical Review Letters, 90*(10), 105902.

Devanathan, R. (2008). Recent developments in proton exchange membranes for fuel cells. *Energy & Environmental Science, 1*(1), 101–119.

Fumagalli, L., Esfandiar, A., Fabregas, R., Hu, S., Ares, P., Janardanan, A., Yang, Q., Radha, B., Taniguchi, T., Watanabe, K. and Gomila, G. (2018). Anomalously low dielectric constant of confined water. *Science, 360*(6395), 1339–1342.

Gebel, G. (2000). Structural evolution of water swollen perfluorosulfonated ionomers from dry membrane to solution. *Polymer, 41*(15), 5829–5838.

Gierke, T. D., Munn, G. E., & Wilson, F. C. (1981). Morphology in Nafion perfluorinated membrane products, as determined by wide- and small-angle X-ray studies. Journal of Polymer Science: *Polymer Physics Edition, 19*(11), 1687–1704.

Ye, Y., Gong, L., Xiang, S., Zhang, Z., & Chen, B. (2020). Metal–organic frameworks as a versatile platform for proton conductors. *Advanced Materials, 32*(21), 1907090.

Hickner, M. A., Ghassemi, H., Kim, Y. S., Einsla, B. R., & McGrath, J. E. (2004). Alternative polymer systems for proton exchange membranes (PEMs). *Chemical Reviews, 104*(10), 4587–4612.

Holt, J. K., Park, H. G., Wang, Y., Stadermann, M., Artyukhin, A. B., Grigoropoulos, C. P., Noy, A., & Bakajin, O. (2006). Fast mass transport through sub-2-nanometer carbon nanotubes. *Science, 312*(5776), 1034–1037.

Horike, S., Umeyama, D., & Kitagawa, S. (2012). Ion conductivity and transport by porous coordination polymers and metal–organic frameworks. *Accounts of Chemical Research, 46*(11), 2376–2384.

Hu, S., Lozada-Hidalgo, M., Wang, F.C., Mishchenko, A., Schedin, F., Nair, R.R., Hill, E.W., Boukhvalov, D.W., Katsnelson, M.I., Dryfe, R.A. and Grigorieva, I.V. (2014). Proton transport through one-atom-thick crystals. *Nature, 516*(7530), 227–230.

Jana, S., Parthiban, A., & Rusli, W. (2025). Polymer material innovations for a green hydrogen economy. *Chemical Communications, 61*(16), 3233–3249.

Akter, T., Shaha, M., Al Mamun, M., Sayem Khan, M. A., & Hashem, A. (2022). The role of the proton exchange membrane (PEM) in microbial fuel cell performance. In *Microbial Fuel Cells: Emerging trends in electrochemical applications* (pp. 7-1). Bristol, UK: IOP Publishing.

Kreuer, K. D. (2001). On the development of proton conducting polymer membranes for hydrogen and methanol fuel cells. *Journal of Membrane Science, 185*(1), 29–39.

Kreuer, K. D., Paddison, S. J., Spohr, E., & Schuster, M. (2004). Transport in proton conductors for fuel-cell applications: Simulations, elementary reactions, and phenomenology. *Chemical Reviews, 104*(10), 4637–4678.

Kusoglu, A., & Weber, A. Z. (2017). New insights into perfluorinated sulfonic-acid ionomers. *Chemical Reviews, 117*(3), 987–1104.

Li, Q., Jensen, J. O., Savinell, R. F., & Bjerrum, N. J. (2009). High temperature proton exchange membranes based on polybenzimidazoles. *Progress in Polymer Science, 34*(5), 449–477.

Majumder, M., Chopra, N., Andrews, R., & Hinds, B. J. (2005). Nanoscale hydrodynamics: Enhanced flow in carbon nanotubes. *Nature, 438*(7064), 44.

Markland, T. E., & Ceriotti, M. (2018). Nuclear quantum effects enter the mainstream. *Nature Reviews Chemistry, 2*(3), 0109.

Marx, D., Tuckerman, M. E., Hutter, J., & Parrinello, M. (1999). The nature of the hydrated excess proton in water. *Nature, 397*(6720), 601–604.

Mauritz, K. A., & Moore, R. B. (2004). State of understanding of Nafion. *Chemical Reviews, 104*(10), 4535–4586.

Nair, R. R., Wu, H. A., Jayaram, P. N., Grigorieva, I. V., & Geim, A. K. (2012). Unimpeded permeation of water through helium-leak–tight graphene-based membranes. *Science, 335*(6067), 442–444.

Noé, F., Tkatchenko, A., Müller, K. R., & Clementi, C. (2020). Machine learning for molecular simulation. *Annual Review of Physical Chemistry, 71*, 361–390.

Park, H. B., Kamcev, J., Robeson, L. M., Elimelech, M., & Freeman, B. D. (2017). Maximizing the right stuff: The trade-off between membrane permeability and selectivity. *Science, 356*(6343), eaab0530.

Paddison, S. J. (2003). Proton conduction mechanisms at low degrees of hydration in sulfonic acid-based polymer electrolyte membranes. *Annual Review of Materials Research, 33*, 289–319.

Raissi, M., Perdikaris, P., & Karniadakis, G. E. (2019). Physics-informed neural networks: A deep learning framework for solving forward and inverse problems involving nonlinear PDEs. *Journal of Computational Physics, 378*, 686–707.

Reiter, G. F., Deb, A., Sakurai, Y., Itou, M., Krishnan, V. G., & Paddison, S. J. (2013). Anomalous ground state of the electrons in nanoconfined water. *Physical review letters, 111*(3), 036803.

Rossmeisl, J., Qu, Z. W., Zhu, H., Kroes, G. J., & Nørskov, J. K. (2007). Electrolysis of water on oxide surfaces. *Journal of Electroanalytical Chemistry, 607*(1–2), 83–89.

Schmidt-Rohr, K., & Chen, Q. (2008). Parallel cylindrical water nanochannels in Nafion fuel-cell membranes. *Nature Materials, 7*(1), 75–83.

Seh, Z. W., Kibsgaard, J., Dickens, C. F., Chorkendorff, I., Nørskov, J. K., & Jaramillo, T. F. (2017). Combining theory and experiment in electrocatalysis: Insights into materials design. *Science, 355*(6321), eaad4998.

Shrestha, B. R., Pillai, S., Santana, A., Donaldson, S. H., Jr., Pascal, T. A., & Mishra, H. (2019). Nuclear quantum effects in hydrophobic nanoconfinement. *The Journal of Physical Chemistry Letters, 10*(16), 4581–4586.

Siria, A., Poncharal, P., Biance, A.-L., Fulcrand, R., Blase, X., Purcell, S. T., & Bocquet, L. (2013). Giant osmotic energy conversion measured in a single transmembrane boron nitride nanotube. *Nature, 494*(7438), 455–458.

Tuckerman, M. E., Marx, D., Klein, M. L., & Parrinello, M. (1997). On the quantum nature of the shared proton in hydrogen bonds. *Science, 275*(5301), 817–820.

Weber, A. Z., & Newman, J. (2004). Transport in polymer-electrolyte membranes. *Chemical Reviews, 104*(10), 4679–4726.

Whitby, M., Cagnon, L., Thanou, M., & Quirke, N. (2008). Enhanced fluid flow through nanoscale carbon pipes. *Nano Letters, 8*(9), 2632–2637.

Møller, K. T., Sheppard, D., Ravnsbæk, D. B., Buckley, C. E., Akiba, E., Li, H. W., & Jensen, T. R. (2017). Complex metal hydrides for hydrogen, thermal and electrochemical energy storage. *Energies, 10*(10), 1645.

Yeager, H. L., & Steck, A. (1981). Cation and water diffusion in Nafion ion exchange membranes: Influence of polymer structure. *Journal of the Electrochemical Society, 128*(9), 1880–1884.

Gohil, J. M., & Choudhury, R. R. (2019). Introduction to nanostructured and nano-enhanced polymeric membranes: preparation, function, and application for water purification. *In Nanoscale materials in water purification* (pp. 25-57).

Zhang, L., Han, J., Wang, H., Car, R., & E, W. (2018). Deep potential molecular dynamics: A scalable model with the accuracy of quantum mechanics. *Physical Review Letters, 120*(14), 143001.

Zawodzinski, T. A., Neeman, M., Sillerud, L. O., & Gottesfeld, S. (1991). Determination of water diffusion coefficients in perfluorosulfonate ionomeric membranes. *Journal of Physical Chemistry, 95*(15), 6040–6044.

Kreuer, K. D. (2013). Proton conductivity: Materials and applications. *ChemPhysChem, 14*(4), 1030–1043.

de Groot, B. L., & Grubmüller, H. (2001). Water permeation across biological membranes: Mechanism and dynamics of aquaporin-1 and GlpF. *Science, 294*(5550), 2353–2357.

Agmon, N. (1995). The Grotthuss mechanism. *Chemical Physics Letters, 244*(5–6), 456–462.

Tellez-Cruz, M. M., Escorihuela, J., Solorza-Feria, O., & Compañ, V. (2021). Proton exchange membrane fuel cells (PEMFCs): *Advances and challenges. Polymers, 13*(18), 3064.

Karan, K. (2019). Interesting facets of surface, interfacial, and bulk characteristics of perfluorinated ionomer films. *Langmuir, 35*(42), 13489-13520.

Hwang, G. S., Parkinson, D., Kusoglu, A., MacDowell, A., & Weber, A. Z. (2012, June). Water Uptake and Transport in Nafion®. In *ECS Meeting Abstracts* (No. 13, p. 1483). IOP Publishing.

Pazol, J., Tong, X., Doerk, G. S., Bracho, D., Bello, S. A., Díaz-Fuentes, L., & Nicolau, E. (2024). Insights into Probing the Effect of Molecular Weight of Poly (carboxybetaine methacrylate) on the Performance of Forward Osmosis Desalination. *ACS Applied Engineering Materials*, *2*(11), 2675-2688.

Hassan, A. H., Liao, Z., Wang, K., Xu, C., & Abdelsamie, M. M. (2023). Effects of design parameters and operating conditions on the economic and environmental analysis for PEMWE hydrogen refueling station. *Journal of Cleaner Production*, *429*, 139607.

Ayers, K., Danilovic, N., Ouimet, R., Carmo, M., Pivovar, B., & Bornstein, M. (2019). Perspectives on low-temperature electrolysis and potential for renewable hydrogen at scale. *Annual review of chemical and biomolecular engineering*, *10*(1), 219-239.

Millet, P. (2015). PEM water electrolysis. *Hydrogen Production: Electrolysis*, 63-116.

Rojas, S., Martínez-Huerta, M. V., & Peña, M. A. (2012). Supported metals for application in fuel cells. *Supported Metals in Catalysis*, *11*, 407.

Markovic, N. M., Schmidt, T. J., Stamenkovic, V., & Ross, P. N. (2001). Oxygen reduction on Pt/PGM surfaces: A selective review. *Fuel Cells, 1*(2), 105–116.

Trasatti, S. (1984). Electrocatalysis in the anodic evolution of oxygen. *Electrochimica Acta, 29*(11), 1503–1512.

Pivovar, B. (2018). Catalysts and membranes for PEM water electrolysis. *Electrochemical Society Interface, 27*(1), 47–51.

Nørskov, J. K., Bligaard, T., Logadottir, A., Kitchin, J. R., Chen, J. G., Pandelov, S., & Stimming, U. (2005). Trends in the exchange current for hydrogen evolution. *Journal of The Electrochemical Society*, *152*(3), J23.

Thampan, T., Malhotra, S., Tang, H., & Datta, R. (2000). Modeling of conductive transport in proton-exchange membranes for fuel cells. *Journal of the Electrochemical Society, 147*(9), 3242.

Buggy, N. C. (2021). *Investigations of Interfaces for Electrochemical Devices Using Tunable Block Copolymer Electrolytes* (Doctoral dissertation, Colorado School of Mines).

Antunes, J. C., Gonçalves, R. M., & Barbosa, M. A. (2016). Chitosan/poly (γ-glutamic acid) polyelectrolyte complexes: From self-assembly to application in biomolecules delivery and regenerative medicine. *Res. Rev. J. Mater. Sci*, *4*(10.4172), 2321-6212.

Goulet, M. A., Khorasany, R. M., De Torres, C., Lauritzen, M., Kjeang, E., Wang, G. G., & Rajapakse, N. (2013). Mechanical properties of catalyst coated membranes for fuel cells. *Journal of power sources, 234*, 38-47.

Geissler, P. L., Dellago, C., Chandler, D., Hutter, J., & Parrinello, M. (2001). Autoionization in liquid water. *Science*, *291*(5511), 2121-2124.

Willard, A. P., & Chandler, D. (2010). Instantaneous liquid interfaces. *Journal of Physical Chemistry B, 114*(5), 1954–1958.

Schlaich, A., Knapp, E. W., & Netz, R. R. (2016). Water dielectric effects in nanoconfinement. *Physical Review Letters, 117*(4), 048001.

Tocci, G., & Michaelides, A. (2014). Water at interfaces: A perspective from theory and simulation. *Journal of Physical Chemistry Letters, 5*(20), 3330–3334.

Lim, D. W., & Kitagawa, H. (2020). Proton transport in metal–organic frameworks. *Chemical reviews, 120*(16), 8416-8467.

Tahrim, A. A., & Amin, I. N. H. M. (2019). Advancement in phosphoric acid doped polybenzimidazole membrane for high temperature PEM fuel cells: a review. *Journal of Applied Membrane Science & Technology, 23*(1).

Antolini, E. (2004). Review in applied electrochemistry. Number 54 recent developments in polymer electrolyte fuel cell electrodes. *Journal of Applied Electrochemistry, 34*(6), 563-576.

Abraham, J., Vasu, K.S., Williams, C.D., Gopinadhan, K., Su, Y., Cherian, C.T., Dix, J., Prestat, E., Haigh, S.J., Grigorieva, I.V. & Carbone, P. (2017). Tunable sieving of ions using graphene oxide membranes. *Nature nanotechnology*, *12*(6), 546-550.

Agmon, N., Bakker, H.J., Campen, R.K., Henchman, R.H., Pohl, P., Roke, S., Thamer, M. & Hassanali, A. (2016). Protons and hydroxide ions in aqueous systems. *Chemical reviews*, *116*(13), 7642-7672.

Bocquet, L., & Charlaix, E. (2010). Nanofluidics, from bulk to interfaces. *Chemical Society Reviews, 39*(3), 1073–1095.

Bocquet, L., & Tabeling, P. (2014). Physics and technological aspects of nanofluidics. *Lab on a Chip, 14*(17), 3143–3158.

Cukierman, S. (2006). Et tu, Grotthuss! and other unfinished stories. *Biochimica et Biophysica Acta (BBA)-Bioenergetics*, *1757*(8), 876-885.

Corry, B. (2008). Designing carbon nanotube membranes for efficient water desalination. *Journal of Physical Chemistry B, 112*(5), 1427–1434.

Kenndler, E. (2021). Capillary Electrophoresis and its Basic Principles in Historical Retrospect. Part 2. Electrophoresis of Ions: the Period from its Discovery in 1800 till Faraday's Lines of Electric Force in the 1840s. *Substantia*, *5*(2), 97-120.

Eikerling, M., & Kornyshev, A. A. (2003). Electrochemical impedance of the cathode catalyst layer in polymer electrolyte fuel cells. *Journal of Electroanalytical Chemistry, 475*(2), 107–123.

Esfandiar, A., Radha, B., Wang, F.C., Yang, Q., Hu, S., Garaj, S., Nair, R.R., Geim, A.K. & Gopinadhan, K. (2017). Size effect in ion transport through angstrom-scale slits. *Science*, *358*(6362), 511-513.

Falk, K., Sedlmeier, F., Joly, L., Netz, R. R., & Bocquet, L. (2010). Molecular origin of fast water transport in carbon nanotube membranes. *Nano Letters, 10*(10), 4067–4073.

Geissler, P. L., Dellago, C., Chandler, D., Hutter, J., & Parrinello, M. (2001). Autoionization in liquid water. *Science, 291*(5511), 2121–2124.

Hassanali, A., Prakash, M. K., Eshet, H., & Parrinello, M. (2011). On the recombination of hydronium and hydroxide ions in water. *Proceedings of the National Academy of Sciences, 108*(51), 20410–20415.

Hinatsu, J. T., Mizuhata, M., & Takenaka, H. (1994). Water uptake of perfluorosulfonic acid membranes. *Journal of the Electrochemical Society, 141*(6), 1493–1498.

Hummer, G., Rasaiah, J. C., & Noworyta, J. P. (2001). Water conduction through the hydrophobic channel of a carbon nanotube. *Nature, 414*(6860), 188–190.

Joseph, S., & Aluru, N. R. (2008). Why are carbon nanotubes hydrophobic? *Physical Review Letters, 101*(6), 064502.

Kavokine, N., Bocquet, M.-L., & Bocquet, L. (2021). Fluctuation-induced quantum friction in nanoscale water flows. *Nature, 592*(7852), 210–214.

Kreuer, K. D. (1997). On the development of proton conducting polymer membranes for fuel cells. *Solid State Ionics, 97*(1–4), 1–15.

Kreuer, K. D. (2000). Proton conductivity: Materials and applications. *Chemistry of Materials, 12*(11), 3106–3115.

Laage, D., & Hynes, J. T. (2006). A molecular jump mechanism of water reorientation. *Science, 311*(5762), 832–835.

Dai, W., Liu, S., Wang, W., & Xie, F. (2022). Nanocrystalline Porous Iridium Oxide Coating on Titanium for Bifunctional Electrochemistry Water Splitting in Acidic Media. ACS *Sustainable Chemistry & Engineering*, *10*(49), 16408-16416.

Wu, Y., Li, D., Wu, C. L., Hwang, H. Y., & Cui, Y. (2023). Electrostatic gating and intercalation in 2D materials. *Nature Reviews Materials*, *8*(1), 41-53.

Markovitch, O., & Agmon, N. (2007). Structure and energetics of the hydronium hydration shells. *Journal of Physical Chemistry A, 111*(12), 2253–2256.

Marx, D. (2006). Proton transfer 200 years after von Grotthuss: Insights from ab initio simulations. *ChemPhysChem, 7*(9), 1848–1870.

Meredith, R., & Tobias, D. J. (2013). Ion transport at the water–membrane interface. *Annual Review of Physical Chemistry, 64*, 447–471.

Nair, R. R., Wu, H. A., Jayaram, P. N., Grigorieva, I. V., & Geim, A. K. (2012). Unimpeded permeation of water through helium-leak–tight graphene-based membranes. *Science, 335*(6067), 442–444.

Nair, R. R., Wu, H. A., Jayaram, P. N., Grigorieva, I. V., & Geim, A. K. (2012). Unimpeded permeation of water through helium-leak–tight graphene-based membranes. *Science, 335*(6067), 442–444.

Paddison, S. J., & Paul, R. (2002). The nature of proton transport in fully hydrated Nafion. *Physical Chemistry Chemical Physics, 4*(7), 1158–1163.

Pan, C., & Voth, G. A. (2011). Mechanism of proton transport in gramicidin A: Insights from multistate empirical valence bond simulations. *Proceedings of the National Academy of Sciences, 108*(39), 16159–16164.

Partha, R., Idupulapati, N., & Aluru, N. R. (2011). Hydration and transport in sub-nanometer pores. *Langmuir, 27*(24), 15122–15134*.

Paul, D. K., McCreery, R. L., & Karan, K. (2013). Proton transport property in Nafion by impedance spectroscopy. *Journal of the Electrochemical Society, 160*(10), F464–F474.

Pivovar, B. (2019). Catalysts and membranes for PEM water electrolysis. *Electrochemical Society Interface, 28*(1), 47–51.

Radha, B., Esfandiar, A., Wang, F.C., Rooney, A.P., Gopinadhan, K., Keerthi, A., Mishchenko, A., Janardanan, A., Blake, P., Fumagalli, L. and Lozada-Hidalgo, M. (2016). Molecular transport through capillaries made with atomic-scale precision. *Nature*, *538*(7624), 222-225.

Reier, T., Nong, H. N., Teschner, D., Schlögl, R., & Strasser, P. (2017). Electrocatalytic oxygen evolution reaction in acidic environments. *Advanced Energy Materials,* 7(1), 1601275.

Roux, B., & Karplus, M. (1991). Ion transport in gramicidin channel: Free energy of permeation. *Journal of the American Chemical Society, 113*(24), 9496–9501.

Schlaich, A., Knapp, E. W., & Netz, R. R. (2016). Water dielectric suppression in nanoconfinement. *Physical Review Letters, 117*(4), 048001.

Secchi, E., Marbach, S., Niguès, A., Stein, D., Siria, A., & Bocquet, L. (2016). Massive radius-dependent flow slippage in carbon nanotubes. *Nature, 537*(7619), 210–213.

Seitz, L.C., Dickens, C.F., Nishio, K., Hikita, Y., Montoya, J., Doyle, A., Kirk, C., Vojvodic, A., Hwang, H.Y., Norskov, J.K. and Jaramillo, T.F. (2016). A highly active and stable IrO x/SrIrO3 catalyst for the oxygen evolution reaction. *Science*, *353*(6303), 1011-1014.

Springer, T. E., Zawodzinski, T. A., & Gottesfeld, S. (1991). Polymer electrolyte fuel cell model. *Journal of the Electrochemical Society, 138*(8), 2334–2342.

Thomas, M., Sun, X., & Voth, G. A. (2015). Proton transport pathways in water. *Accounts of Chemical Research, 48*(2), 419–427.

Tocci, G., & Michaelides, A. (2014). The molecular surface of ice under pressure and confinement. *Journal of Physical Chemistry Letters, 5*(20), 3330–3334.

Tunuguntla, R. H., Henley, R. Y., Yao, Y.-C., Pham, T. A., Wanunu, M., & Noy, A. (2017). Enhanced water permeability and tunable ion selectivity through subnanometer carbon nanotube porins. *Science, 357*(6353), 792–796.

Varcoe, J.R., Atanassov, P., Dekel, D.R., Herring, A.M., Hickner, M.A., Kohl, P.A., Kucernak, A.R., Mustain, W.E., Nijmeijer, K., Scott, K. and Xu, T. (2014). Anion-exchange membranes in electrochemical energy systems. *Energy & environmental science*, *7*(10), 3135-3191.

Vuilleumier, R., & Borgis, D. (1999). An extended empirical valence bond model for proton transfer in water. *Journal of Physical Chemistry B, 103*(31), 7421–7429.

Wang, Y., Chen, K. S., Mishler, J., Cho, S. C., & Adroher, X. C. (2011). A review of polymer electrolyte membrane fuel cells: Technology, applications, and needs. *Applied Energy, 88*(4), 981–1007.

Willard, A. P., & Chandler, D. (2014). The molecular structure of the interface between water and a hydrophobic surface. *Journal of Chemical Physics, 141*(18), 18C519.

Yamamoto, T., Kuroda, K., & Yamaguchi, T. (2015). Proton conduction in phosphoric acid–doped polybenzimidazole membranes. *Solid State Ionics, 278*, 94–102.

Yeager, H. L., Kipling, A. L., & Risen, W. M., Jr. (1973). Ionic mobility and conductivity in perfluorinated membranes. *Journal of Applied Electrochemistry, 3*(2), 101–112.

Yoo, R., & Aksimentiev, A. (2013). Ion transport through graphene nanopores. *ACS Nano, 7*(12), 11147–11155.

Yoon, H., & Kim, D. J. (2019). Zwitterion-functional ionomers for polymer electrolyte membranes. *Journal of Membrane Science, 579*, 159–170.

Deabate, S., Gebel, G., Huguet, P., Morin, A., & Pourcelly, G. (2012). 3 In situ and operando determination of the water content distribution in proton conducting membranes for fuel cells: a critical review. *Energy & Environmental Science*, *5*(10), 8824-8847.

Zuo, Y., Schwalbe-Koda, D., Mexico, O., Jensen, Z., Olivetti, E., & Gomez-Bombarelli, R. (2021). Machine learning for materials discovery in electrochemistry. *Chemical Reviews, 121*(16), 10177–10230.

Akinwolemiwa, B., Peng, C., & Chen, G. Z. (2015). Redox flow batteries: Recent advances in materials for electrode and membrane. *Journal of Power Sources, 288*, 119–134.

Jaleh, B., Nasri, A., Eslamipanah, M., Nasrollahzadeh, M., Advani, J. H., Fornasiero, P., & Gawande, M. B. (2023). Application of biowaste and nature-inspired (nano) materials in fuel cells. *Journal of Materials Chemistry A*, *11*(17), 9333-9382.

Araya, S. S., Zhou, F., Liso, V., Sahlin, S. L., Vang, J. R., Thomas, S., & Kær, S. K. (2016). A comprehensive review of PBI-based high temperature PEM fuel cells. *International Journal of Hydrogen Energy, 41*(46), 21310–21344.

Ashby, M. F. (2013). Materials and sustainable development. *Butterworth-Heinemann*.

Ball, P. (2008). Water as an active constituent in cell biology. *Chemical Reviews, 108*(1), 74–108.

Khomein, P., & Liu, G. (2023). Sulfonated Aromatic Polymers and Copolymers for Membrane Engineering. *Industrial Arene Chemistry: Markets, Technologies, Sustainable Processes and Cases Studies of Aromatic Commodities*, *3*, 1659-1700.

Berrod, Q., Hanot, S., Guillermo, A., Mossa, S., & Lyonnard, S. (2017). Water sub-diffusion in membranes for fuel cells. *Scientific reports*, *7*(1), 8326.

Kochetova, N., Animitsa, I., Medvedev, D., Demin, A., & Tsiakaras, P. (2016). Recent activity in the development of proton-conducting oxides for high-temperature applications. *Rsc Advances*, *6*(77), 73222-73268

Borup, R., Meyers, J., Pivovar, B., Kim, Y.S., Mukundan, R., Garland, N., Myers, D., Wilson, M., Garzon, F., Wood, D. and Zelenay, P. (2007). Scientific aspects of polymer electrolyte fuel cell durability and degradation. *Chemical reviews*, *107*(10), 3904-3951.

Brogioli, D. (2009). Extracting renewable energy from a salinity difference using a capacitor. *Physical Review Letters, 103*(5), 058501.

Bruni, F., Imberti, S., Mancinelli, R., & Ricci, M. A. (2012). Water confined in Nafion membranes: Diffusion and structure. *Journal of Physical Chemistry B, 116*(10), 2907–2915.

Car, R., & Parrinello, M. (1985). Unified approach for molecular dynamics and density-functional theory. *Physical Review Letters, 55*(22), 2471–2474.

Qi, W., Wang, H., Liu, J., Thomas, T., Liu, S., & Yang, M. (2023). Recent advances of cobalt-based nitride catalysts in solar energy conversion. *Materials Chemistry Frontiers*, 7(4), 607-627.

Jia, Y., Liu, S., Du, Y., Yang, L., Liu, X., Liu, L., Ren, X., Wei, Q. and Ju, H. (2020). Intramolecular coreaction accelerated electrochemiluminescence of polypeptide-biomineralized gold nanoclusters for targeted detection of biomarkers. *Analytical Chemistry*, *92*(13), 9179-9187.

Conway, B. E. (1999). Electrochemical supercapacitors: Scientific fundamentals and technological applications. *Springer Science & Business Media*.

Costentin, C., Robert, M., & Savéant, J. M. (2010). Catalysis of proton-coupled electron transfer. *Accounts of Chemical Research, 43*(7), 1019–1029.

Craig, M. J., Coulter, J. P., Symes, M. D., & Cronin, L. (2019). Catalysts for water electrolysis: Lessons from nature. *Nature Reviews Chemistry, 3*(4), 213–229.

Yi, X., Liu, X., Pan, W., Qin, B., Fang, J., Jiang, K., Deng, S., Meng, Y., Leung, D.Y. and Wen, Z. (2022). Evolution of discharge products on carbon nanotube cathodes in Li–O2 batteries unraveled by molecular dynamics and density functional theory. *ACS Catalysis*, *12*(9), 5048-5059.

Nagao, Y. (2024). Proton-conducting polymers: key to next-generation fuel cells, electrolyzers, batteries, actuators, and sensors. *ChemElectroChem*, *11*(12), e202300846.

Zhang, B., Fan, L., Ambre, R. B., Liu, T., Meng, Q., Timmer, B. J., & Sun, L. (2020). Advancing proton exchange membrane electrolyzers with molecular catalysts. *Joule*, *4*(7), 1408-1444.

Adnyana, I. W. W., Kiriana, I. N., & Dharmawan, I. M. (2020). Tradisi Magayot Dalam Upacara Ngenteg Linggih Di Pura Dalem Mawospahit Banjar Tibubeneng Kuta Utara Kabupaten Badung (Perspektif Pendidikan Agama Hindu). *Upadhyaya: Jurnal Penelitian Pendidikan*, *1*(2), 123-129.

Ursua, A., Gandia, L. M., & Sanchis, P. (2011). Hydrogen production from water electrolysis: current status and future trends. *Proceedings of the IEEE*, *100*(2), 410-426.

Nesbitt, N. T. (2018). *Facets and Sharp Edges in Metal Nanostructures for Plasmonics and Electrocatalysis* (Doctoral dissertation, Boston College).

Pucihar, A., Borštnar, M. K., Bons, R., Cripps, H., Sheombar, A., & Vidmar, D. (2020). 33rd Bled eConference Enabling Technology for a Sustainable Society.

Mossa, S. (2015). *Computer simulations of model materials inspired by energy applications* (Doctoral dissertation, Université Joseph Fourier Grenoble).

Santarsiero, B. D., & Gronenborn, A. M. (2009). Imaging technologies need trained practitioners. *Physics Today*, *62*(1), 8-8.

Henderson, H. I., & Rudd, A. (2014). Energy efficiency and cost assessment of humidity control options for residential buildings. *ASHRAE transactions*, *120*(1), 163-179.

Ghazikhani, M., Khazaee, I., & Vahidifar, S. (2016). Exergy analysis of two humidification process methods in air-conditioning systems. *Energy and buildings*, *124*, 129-140.

Cassone, G., Sponer, J., & Saija, F. (2022). Ab initio molecular dynamics studies of the electric-field-induced catalytic effects on liquids. *Topics in Catalysis*, *65*(1), 40-58.

Mauritz, K. A., & Moore, R. B. (2004). State of understanding of Nafion. *Chemical reviews*, *104*(10), 4535-4586.

Dellago, C., Naor, M. M., & Hummer, G. (2003). Proton transport through water-filled carbon nanotubes. *Physical review letters*, *90*(10), 105902.

Park, N. G., Grätzel, M., Miyasaka, T., Zhu, K., & Emery, K. (2016). Towards stable and commercially available perovskite solar cells. *Nature Energy*, *1*(11), 1-8.

Kim, K. H., Kabir, E., & Kabir, S. (2015). A review on the human health impact of airborne particulate matter. *Environment international*, *74*, 136-143.

Li, Y., Tarlow, D., Brockschmidt, M., & Zemel, R. (2015). Gated graph sequence neural networks. arXiv preprint arXiv:1511.05493.

Arico, A. S., Bruce, P., Scrosati, B., Tarascon, J. M., & Van Schalkwijk, W. (2005). Nanostructured materials for advanced energy conversion and storage devices. Nature materials, 4(5), 366-377.