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**Polymer Films** 

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## **Bimodal Ionic Conduction through Polymer Films due to Nano Confinement**

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Abstract: Kinetic and selectivity of ionic conduction through polymer films is a key factor in the function of many systems including membrane technology, energy devices, sensors, and corrosion. Typically, the ionic conduction is accelerated by increasing the ionic strength of the electrolyte. However, counterintuitively, polymer films with very high electrochemical impedance demonstrate the opposite effect, i. e. ionic conduction slows down by increasing the ionic strength of the electrolyte. This bimodal nature of ionic conduction was discovered five decades ago and yet the mechanism has remained poorly understood. This minireview explains the long-standing anomaly through the lens of recent advances in nano-confinement electrochemistry. Emerging evidence shows that changes in solvation shells occurs due to the size of the channel through which ionic diffusion takes place. These solvation shells can significantly affect the mobility of ions, their interactions with functional groups of the polymer, and the overall conductivity of the electrolyte. At dimensions only a few nanometers, partially hydrated ions form stronger bonds with polymer slowing down the ionic conduction. Increasing ionic strength will add ion-pairing interactions further reducing ions mobility. The interplay of solvated ions, polymer chemistry, and ionic content offer an explanation for the anomalous bimodal ionic conduction.

# 1. Historical Accounts of Ionic Conduction Through Polymer Coatings

The structure and transport mechanism of nano-confined water and ions represent a critical area of research with significant implications across various scientific disciplines. The significance of this phenomenon lies in its potential applications in areas such as developing highly selective membranes and nanofluidics for ion separation and biosensing, electrocatalysis, membrane technology in battery and energy conversion and understanding of biological systems, to name a few.<sup>[11]</sup> An interplay of nano confinement scale, water-ion-surface charge and ionic content determines the ion transport kinetics.<sup>[2]</sup> The precise control over the mode and kinetic of ionic conduction enables more efficient and selective systems in various applications that rely on the central role of nanostructured films.<sup>[3]</sup>

Nano confinement is a pivotal concept for the understanding of ionic conduction through protective polymer coatings that signify effectiveness as a barrier layer. Reactive polymers are the main matrix materials that impart structural properties and cohesion to polymer composites and polymer coatings. Yet, modern crosslinked polymers cannot fully prevent ionic or moisture transport because they are naturally polar, being formed from reactive species, and include regions of low crosslink density due to the stochastic nature of network formation.<sup>[4]</sup> One of the earliest hypotheses, proposed by Mayne,<sup>[5]</sup> explained the mechanism of ionic conduction through polymer films by considering polymers comprised of two distinctive phases. The hypothesis suggests that the passage of ions takes place through the bulk matrix of the film but there are regional differences within the film with regards to ionic permeability.<sup>[6]</sup> In nature, polymer films are electrochemically inhomogeneous with two distinct conduction mechanisms for ions.<sup>[7]</sup> Changes in the electrochemical impedance of the film indicate the mode of ionic conduction. The first mode was identified as a direct relationship between the impedance of the film and that of the external solution, hence named direct or "D" type, i.e., film impedance increases with increasing resistance of the solution and vice versa. The second mode was the inverse or "I" type conduction, where the impedance of the film was inversely correlated with the solution resistance, i.e., the impedance of the film increases with increasing ionic content of the solution and vice versa. Figure 1 depicts the typical change in the impedance exhibited by D and Itype polymer films due to the difference in ionic content in the electrolyte.

A series of studies investigated the effect of ions in electrolyte,<sup>[7]</sup> thickness of the film, temperature,<sup>[9]</sup> addition of micro-particles<sup>[10]</sup> and types of organic solvents<sup>[11]</sup> on the D/I type ratio of polymer films. The film impedance was typically measured on a large number of samples to statistically determine the fraction of D- or I-type behaving films. D-type areas appeared more frequently with decreasing film thickness, at temperatures above the glass transition temperature, and due to the presence of solvent in the system. The latter suggested that solvents may interfere with the process of cross-linking was later corroborated by other work.<sup>[12]</sup> Furthermore, a series of studies revealed the major impact of polymer type on its D/I-type behaviour.<sup>[10,13,14]</sup> Of particular importance were the findings of White et al.<sup>[14]</sup> that showed slightly higher water uptake and lower localised hardness of D-type areas.

Mayne and Scantlebury hypothesised that the D-type area only occupies a small fraction of film, but this area has a remarkably higher permeability and thus dominates the overall diffusion rate.<sup>[15]</sup> The team determined that D-type conduction cannot be attributed to macro capillaries unless these are of molecular dimension. For example, a typical value of 10<sup>8</sup> ohm.cm<sup>2</sup> for a D-type coating in 1 N KCl yields in about 1,000 Å radii for the pore.<sup>[15]</sup> However, there was no evidence, either microscopically or in relation to the Donnan equilibrium, that such pores existed. Years later, numerical simulations and mathematical modelling con-

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*Figure 1.* Illustration of bimodal (two distinct types) of ionic conduction in polymer films. (a) Inverse (I type) conduction occurs when the resistance of the film run counter to, and direct (D type) conduction occurs when the impedance follows that of, the external solution. (b) Effect of KCl concentration on the impedance of D and I type model (alkyd) film. The impedance of D-type film drops as the ion concentration in the electrolyte increases, whereas the impedance of I-type film that increases with higher ion concentration. Adapted with permission from.<sup>[8]</sup> Copyright © 1971 Society of Chemical Industry.

firmed the theory that D-type areas are a small fraction of the polymer film, randomly distributed, dominating the ionic conduction through the film.<sup>[16,17]</sup>

The impedance behaviour of the film being a function of ion concentration (Figure 1) also leads to a conclusion that the water content of the film is a controlling factor of ion transport. It was proposed that the ionic conduction in Itype regions depends on the osmotic pressure of the external solution. In concentrated solutions, the osmotic solvent depletion of the film leads to increasing impedance. It was





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suggested that the water activity plays a key role in ionic conduction through I-type coatings, whilst the ionic strength controls the transport through D-type coatings where the size of the conduction pathway is remarkably bigger.<sup>[7]</sup> This hypothesis, proposed more than five decades ago is yet to be confirmed or rejected by scientific proof and the aim of this minireview is to re-examine the hypothesis through the lens of recent advances in nanoconfinement electrochemistry.

#### 2. Spatially Resolved Perspective of Heterogenous Conduction Modes

State-of-the-art microscopy techniques resolve molecular structures down to atomic scale. However, common spatially resolved microscopy techniques primarily examine the top layer of the film, while the conduction pathway in D-type areas is determined by the chemical structure along the entire length of the (presumed) nano-pore. Therefore, the majority of current microscopy techniques cannot access the depth of channels to explain the conduction mechanism. Nonetheless, a myriad of microscopy-focused studies has been published with a focus on deeper insight into the structure of nano-pore/defects in polymer coatings and the mechanism of ionic transport. The most relevant techniques reported so far span from wire-beam electrode, localised fluorescence microscopy, AFM-IR (atomic force microscope-infrared spectroscopy) to scanning electrochemical microscopy.

Wire beam electrodes, in essence, a multi-array of miniaturised metal electrodes (Figure 2a), were the first attempt to achieve a closer look at the local distribution of D- and I-type areas. These studies gave an improved

perception of the inhomogeneous distribution of D-type area randomly across the polymer films<sup>[18]</sup> and how some fabrication parameters, such as thickness and crosslinking density of the film, shift the D/I-type behaviour.<sup>[19]</sup> Wire beam electrodes have the unique advantage of direct through-film impedance measurement. However, the scale at which the wire beam electrode resolves local impedance, i. e., hundreds of micrometre square at best, is far larger than the scale of ionic pathways. Few other microscopy techniques, though unable to directly measure impedance, can visualise ion conduction pathways indirectly via probing localised ion clusters or water uptake on the surface. The ion clusters can be probed by localised fluorescence microscopy using ion-specific chromophores for chloride<sup>[20]</sup> and Ca2+[21] both visualising diffusion of ions through small discrete sites in the coating film, reaffirming Mayne's hypothesis. Figures 2b&c demonstrate planar (2b) and cross-sectional (2c) views of a discrete Ca<sup>2+</sup> cluster in an epoxy polymer film acquired by localised fluorescence microscopy. The number of these higher diffusion sites increases with decreasing ionic concentration or increasing water activity of the exposure electrolyte.<sup>[21]</sup> Such behaviour signifies an I-type characteristic.

Localised clusters of water are also strongly linked with the diffusion mechanism and D/I-type behaviour. The original Mayne hypothesis proposes that water activity dominates the ionic conduction through I-type domain of a polymer film. Localised water uptake in a polymer film changes the morphology of the surface. These water clusters may be detected as localised protrusion of the surface profile. Among the techniques capable of in situ profilometry, scanning electrochemical microscopy has been used with limited success to visualise early roughening of the surface due to localised water uptake and inherent inhomo-



*Figure 2.* Methodologies used to spatially resolve the innate inhomogeneity and distribution of ionic pathways in polymer films: (a) wire beam electrode, (b & c) localised fluorescence microscopy,<sup>[27]</sup> (d & e) scanning electrochemical microscopy,<sup>[27]</sup> and (e & f) AFM-IR.<sup>[26]</sup> (a) shows the architecture of a wire beam electrode comprised of metal "pins" inserted into a block of polymer. (b & c) show planar and cross-sectional view of fluorescent marker ion (Ca<sup>2+</sup>) in an epoxy film following exposure to 0.1 M CaCl<sub>2</sub>, showing isolated domains of Ca<sup>2+</sup> concentrated clusters. (d & e) show in situ scanning electrochemical microscopy visualising localised roughening of polymer film due to discrete domains of higher water uptake before and after 24 h immersion in 0.1 M KCl solution. (f & g) show AFM topography and IR spectroscopy map at 3300 cm<sup>-1</sup> in 65% relative humidity representing localised domains of higher polymer-water H-bonds. Reprinted with permission from.<sup>[26]</sup> Copyright © 2010 Elsevier Science. Reprinted with permission from.<sup>[27]</sup> Copyright © 2012 Elsevier.

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geneity of the polymer film.<sup>[22]</sup> Figure 2d&e represent an example, where the roughening of a polyurethane film in 0.1M KCl solution occurs after 24 hours due to water cluster formations that is probed in negative feedback mode. A more wholesome methodology was used later by Lyon et al., combining AFM with IR spectroscopy to map nanoclusters of water in polymer coatings of varying chemistry.<sup>[23-26]</sup> AFM-IR provided the first evidence at a meaningful scale to indicate the size and distribution of D-type domains. Nanoscale softened regions were found to absorb more water, which was accompanied by a greater degree of hydrogen bonding. For a model epoxy coating, these regions surprisingly coincided with a higher degree of cross-linking attributed to increasing unoccupied space (i. e., free volume) in the polymer. Figure 2f&g depicts AFM-IR height and corresponding IR amplitude ratio images of an epoxy polymer film after exposure to two different relative humidity conditions. The IR amplitude ratio (Figure 2g) corresponds to  $3300 \text{ cm}^{-1}$  under  $65 \% \text{ RH}/3300 \text{ cm}^{-1}$  under 35 % RH representing the increased absorbance of the OH stretch peak due to water sorption. This confirms that the increase in OH stretch absorbance is associated with localised "bumps" that were identified to have higher degrees of crosslinking.

Ion conduction pathways form as the ion and its hydration shell traverse the film; hence channels are required to hold a significant amount of free water (not hydrogen-bonded to the polymeric network).<sup>[24]</sup> This is consistent with the two-stage water absorption mechanism, in which the Fickian diffusion kinetics (driven by ion concentration gradient) is followed by polymer relaxation and adjunction of isolated pockets of free volume forming a continuous "micro-void" channel. Almost the entire body of research in this area has focused on elaborating the structure and mechanism of ionic conduction through D-type regions. This is justified as the D-type regions are primarily responsible for the failure of polymer coatings, particularly in protective applications. It also signifies the poorly understood conduction mechanism through I-type regions. Next section will address this gap in knowledge.

#### 3. Interplay of Water-Ion-Surface Charge Signify Conduction Mode Through Nanopores

Water structure and transport of ions in nanoconfined spaces is of fundamental importance not only in polymer chemistry but also in nanopore sensors, filtration membrane and even biological systems. Nano confinement represents a pivotal gap in understanding how these systems operate at the molecular level. In the absence of effective empirical approaches, the majority of studies in this area resorted to theory and simulation to explain the changes in the structure of water and hydrated ions as they move through nanopores. Simulation methods, and in particular molecular dynamic simulation, have attained deeper insight into the multivariant mechanism of ionic conduction.

Molecular dynamic simulations suggest that the waterwater H-bonds per molecule decrease from 3.0 in bulk to ~1.8 inside the nanochannel in a model polyamide matrix smaller than 6 nm diameter<sup>[28]</sup> (Figure 3a). Corroborated by other work,<sup>[29]</sup> the depletion in water-water H-bonds is compensated by the formation of new H-bonds with hydrophilic functional groups inside the polymer matrix (e.g. (CO)OH-water, (NH)CO-water, and NH<sub>2</sub>-water H-bonds herein). The interplay of water-water and ion-water bonds in the bulk solution and inside nanochannels of a model polymer are schematically depicted in Figures 3b,c&d. Note that the functional groups considered in this simulation are common in many polymeric materials used for coating such as polyimide, polyester, alkyd, epoxy, polyurethane to name a few. These new polymer-water H-bonds are longer lasting and stronger than the water-water H-bonds which in part results in reduced diffusion coefficient of water to about half inside the nano-channels compared to that of the bulk. This



*Figure 3.* (a) Profiles of the average numbers of the water–water and water-polymer H-bonds (< n >) per water molecule against the z, size of nanopore.<sup>[28]</sup> (b) shows water molecules and ions inside polymer cavities: oxygen atoms (red), hydrogen atoms (white), cations (cyan), anions (yellow), and polymer matrix (orange). The backbone of polymer matrix mostly consists of carbon atoms. The hydration of a cation as well as the hydrogen bonding of the surrounding water molecules are compared in (c) bulk water and (d) inside a segment of the pore. The red dashed lines indicate interactions between the cation and oxygen atoms of water or the polymer surface (e. g., carboxyl groups). The blue dashed lines indicate the hydrogen bonds between individual water molecules.<sup>[31]</sup> Reprinted with permission from.<sup>[31]</sup> Copyright © 2022 American Chemical Society. Reprinted with permission from.<sup>[28]</sup> Copyright © 2018, American Chemical Society

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is recently corroborated experimentally by Quasi-Elastic Neutron Scattering, further explaining how water diffusion in polyamide membrane depends on size and activation energy.<sup>[30]</sup>

The first physical observation of ions partially shedding hydration shell to pass through nanochannels was reported by Lu et al..<sup>[32]</sup> The team used in situ liquid Time-of-flight secondary-ion mass spectrometry (ToF-SIMS) to examine the dehydration of three alkali metal cations, Li<sup>+</sup>, K<sup>+</sup>, and Na<sup>+</sup> during transport in nanochannels within a model polyamide membrane with sub-nanometer pores. The authors show that for a model  $Na^+$  ion in bulk solution, hydration species of  $(H_2O)_nNa^+$  with n=1-6 and average of n=3.03 being the highest proportion of hydration species. This is smaller than previously reported values of n=4- $8^{[33,34]}$  and far less than the n  $\approx$  50 approximated by polymer coating chemists.<sup>[4]</sup> This partial shedding of water molecules from ion solvation shells allowed alkali-metal ions to permeate through the membrane with pores smaller than their solvated size. Compared to bulk water, the waterwater hydrogen bonding is weak inside the pores, and water can be arranged in a single file.<sup>[35]</sup> Ions, which are partially dehydrated, interact with the pore surface.

Their molecular dynamics (MD) simulation results, in line with experimental data, demonstrate that the ionic mobility of the hydrates (of various cations) is the ratelimiting parameter in ion transport in channels larger than the size of solvated ions.<sup>[32]</sup> The so-called "viscous effect", defined as the electrostatic interaction of charged partially hydrated ions with the polar functional groups on the polymer within the nanopore (Figure 4a&b), governs the ion transport through channels smaller than the size of solvated ions. In their model, electrostatic interactions with carboxyl groups inside the membrane preferentially slows down the transport of the mono- and dihydrates. These insights were also inferred earlier via MD simulation, e.g., for a model polyamide membrane indicating that water molecules show heterogeneous diffusivities and converge adjacent to polar groups resulting in rejection of ion transport in channel size smaller than  $\sim 6-7$  nm (Figure 4c).<sup>[36]</sup> Yet, it is noteworthy that results of Lu et al.<sup>[32]</sup> are the first-ever physical evidence, unequivocally confirming the hypothesis proposed more than five decades ago by Mayne.<sup>[7]</sup>

#### 4. Conductivity in Long Range Defines the Overall Mode of Ion Conduction: From 2D to 3D

Every evidence, whether by MD simulation or experiments, explaining the characteristics of ions and water in nanochannels is limited to a short, sub-micrometer scale. However, in real life applications polymer films can be tens of micrometres thick. Therefore, the short-scale studies that focus on the ion-water-polymer interaction in a few nanometers range (2D) cannot be directly extended to the ionic conduction mechanism across the length of a film (3D). We resort to the hypothesis of interconnected pockets/channels to explain the conductivity that transverse the thickness of polymer film. The theory of interconnected pockets of water (Figure 5a) have been extended previously to explain the Dtype (non-sterically limited) ion diffusion through polymer films.<sup>[16,24]</sup> A similar mechanism may be valid for the nanoscale diffusion model. Recent experimental<sup>[37]</sup> and numerical<sup>[30,36,38]</sup> studies suggest that water molecules travel as clusters through a network of pores that are transiently connected (Figure 5b).

The model of interconnected nanovoids presumes the existence of interconnected nano-pockets of lower crosslinking density as a pathway for the diffusion of water and ions.<sup>[36]</sup> Accelerated diffusion of water molecules is observed (by MD simulation) within the less cross-linked domains of a model polyamide matrix.<sup>[36]</sup> However, the assumption used in this model contradicts the recent findings of Morsch et al. (informed by AFM-IR) that suggested an interconnected network of higher crosslinking domains heterogeneously distributed in the bulk of an epoxy polymer with a localised nodular topology.<sup>[25]</sup> Whether the bulk matrix of polymer is of lower or higher crosslinking density remains a subject of debate. Nonetheless, despite the difference in nature, the



*Figure 4.* (a & b) Steric effect on the mechanism of ion transport across a polyamide membrane.<sup>[32]</sup> Ion mobility is the key factor in transport of solvated ions smaller than the size of the pore (a), whereas the polymer-ion interactions, and dehydration dominating the transport of solvated ions larger than the size of the pore (b). (c) Density profile of water, polymer atoms, and ions (Na<sup>+</sup> and Cl<sup>-</sup>) across a model polyamide polymer membrane.<sup>[36]</sup> Reprinted with permission from<sup>[32]</sup> Copyright © 2021, American Chemical Society. Reprinted with permission from<sup>[36]</sup> Copyright © 2016, American Chemical Society.

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*Figure 5.* Water and ions diffusion pathways via a network of (a) Micro.<sup>[16]</sup> and (b) nano-<sup>[36]</sup> cavities. The microcavity model was proposed by multilayered films characterized experimentally and modelled mathematically. The nano-cavity model is assumed in MD simulation showing water molecules (red dots) inside polymer matrix (green), and ion and water pathway through interconnected nano-cavities (red pockets).<sup>[39]</sup> (c) represents the length scales associated with the water jumps and void sizes in the nano-interconnected network model. Reprinted with permission from.<sup>[16]</sup> Copyright © 2017 Elsevier. Reprinted with permission from.<sup>[36]</sup> Copyright © 2016, American Chemical Society. Reprinted with permission from.<sup>[31]</sup> Copyright © 2022 American Chemical Society.

interconnected network of the localised second phase exhibited higher water uptake, forming interconnected pockets of water cluster as an ionic conduction pathway.<sup>[24]</sup>

MD simulation suggests that transport through the interconnected network is assisted by "jumps" advancing the water molecule  $\sim 1 \text{ nm}$  along the membrane during  $\sim 1 \text{ ns}$ . The length scales associated with water jumps and void sizes are shown in Figure 5c with double arrows. The time scale associated with the jumps is on the order of picoseconds. The average jump length is  $\sim 3 \text{ Å}$ .<sup>[31,39]</sup> Furthermore, the result of the simulation (Figure 4c) indicates that the ionic diffusion is impeded once the pore size reduces to lower than ~6-7 nm. This result agrees with other MD studies predicting diffusion-limiting pore size of ~6 nm for water molecules due to the higher density of temporary polymerwater H-bonds.<sup>[28]</sup> This phenomenon puts the scale in perspective and explains the abrupt changes in the mode of ionic diffusion due to structural variations that interrupt the connectivity of pockets by more than a few Å. Examples of structural variation are changes in the thickness of the film, type and rate of solvent removal, and addition of nonporous solid particles, all of which are shown to have a significant impact on the conduction mode.

An increase in the concentration of ion also has a secondary effect on the type of ions-water pairs that forms in the solution. An increase in concentration of ions leads to formation of solvent shared ion pairs structure where counter ions (e. g.,  $Na^+$  and  $Cl^-$ ) share a water molecule. This structure is signified by slowing down of the vibrational/rotational dynamics of ion pairs due to the stiffening of water hydrogen bonds in the hydration shell of solvated ions and it manifests in an anomalous fluorescence emission as reported in the case of KCl, NaCl, HCl & NaOH.<sup>[40,41]</sup>

A joint study of electrical conductivity and MD simulation of NaCl transport through nanopores with a wide spectrum of electrolyte concentration range spanning from 10–7 M all the way up to 4 M showed that the ion mobility in nanopore/channels continuously decreases as the electrolyte concentration increases.<sup>[42]</sup> The combination of factors; the low mobility of surface-bound ions in the Stern layer,

plus enhanced pairing and collisions between partially dehydrated ions of opposite charges are the key reason for the reduced ion mobility inside a nanopore.<sup>[42,43]</sup> These insights help explain the ionic resistance in nanocavities inside polymer coatings and shed new light on this long-standing puzzle.

#### 5. The Significance of Heterogeneous Ion Diffusion Through Polymer: D-type Domains are not "Defects", I-type Behaviour is not a "Myth"

The importance of electrochemical inhomogeneity of polymer coatings to the protective and barrier efficiency afforded by the coating is well-established. It is common knowledge that the protective coatings fail primarily due to ion and water permeation through the film, resulting in unimpeded electrochemical redox reactions under the barrier film that leads to complete failure of the system. The failure mode, due to localised blistering or because of total disbondment, depends on the type and rate of water and ions diffusion as well as the level of porosity of the film.<sup>[44-46]</sup> Domains of the film with higher permeability to water and ions are associated with initiation sites of the blistering and delamination as well as localised degradation of the film.<sup>[47,48]</sup>

Among the factors that introduce inhomogeneity to the coatings, the intrinsic hydrophilicity of the polymer is a key factor. Experimental evidence shows that the polarity of resin dominates the equilibrium water content, while the free volume is the main factor for diffusion coefficient and activation energy of water sorption.<sup>[49]</sup> One important implication is that the hydrophilicity of the film increases water (and thus ions) transport in D-type domains due to the increased water uptake into the local (D-type) clusters. In contrast, hydrophilicity has the reverse effect in I-type domain through increased temporary polymer-water H-bonds. A large body of previous work reports that increasing reactive and hydrophilic groups of the polymer accelerate water and ion flux through the film.<sup>[50]</sup> Yet complementary

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data at the nanoscale, informed by experiments and simulations, suggest that the high hydrophilicity of the polymer inhibits water transport due to the increased density of polymer-water hydrogen bonds.<sup>[28]</sup>

## 6. Nanoconfinement Dictates Transport Mechanism in Nanochannels

Fluid dynamics in capillaries and nanofluidic channels are significantly influenced by the interplay between confinement effects, surface properties, and the high surface-to-volume ratios inherent at the nanoscale.<sup>[51,52]</sup> Capillary forces dominate these systems, enabling spontaneous liquid imbibition and controlled transport. In nanofluidic channels, surface forces such as van der Waals interactions, hydration effects, and the overlapping of electrical double layers influence fluid behaviour in ways not observed at macroscopic scales.<sup>[53]</sup>

In contrast to typical insulating polymeric materials, conducting constructs such as Mxene, carbon nano tubes (CNT), and graphene establish electrical double layer (EDL) on the surface of the wall inside the nanochannels. The formation of EDL dominates ionic transport within these structures. When channel sizes approach the Debye length, the surface conductance becomes the primary contributor to transmembrane ionic conductance, emphasizing the importance of surface charge in nanofluidic devices.<sup>[54,55]</sup>

The dynamics of capillary filling, often described by the Washburn equation, reveal that nanoscale confinement alters fundamental parameters like viscosity and contact angle while maintaining the validity of classical scaling laws.<sup>[56]</sup> Studies have also shown that confinement effects, such as changes in viscosity, contact angles, and capillary pressures, influence unusual transport behaviour.<sup>[57,58]</sup>

#### 7. Summary and Outlook

The polar nature of polymer coatings, typically comprised of reactive chemical groups, constitutes an inherently inhomogeneous network with multitude of hydrophilic functional groups. These functional groups present hydrogen bonding sites within nano-channels that give rise to temporary bonding with water that may or may not replace water-water H-bonds. In narrow channels of a few nanometers in size, the higher polarity increases electrostatic temporary bonding between the ions and channel walls, slowing down the diffusion of ions. In channels larger than the size of fully solvated ions, the electrostatic interaction between the ions and polymer and temporary H-bonds between polymerwater is minimal.

The formerly poorly understood phenomenon of D- and I-type behaviour is now clarified and explained as nonsterically limited and sterically limited ion diffusion modes. We stress that the D-type domains are not "defects", and Itype behaviour is not a "myth". D-type domains are of a sub-micrometer nature with channel size above the size of the solvated ions. This is also the reason that different ions (e. g.,  $K^+$  vs Na<sup>+</sup>) show slightly different electrochemical impedance when used to measure the ionic resistance of Dtype film in particular. Ion mobility is the dominant mechanism in determining the diffusion dynamics through D-type film. Higher polarity of the polymer attracts more water, swelling and broadening of the pathways, leading to higher conductivity. In contrast, the presence of polar functional groups in the polymer has the opposite impact on the rate of ion diffusion in sterically limited channels. The so-called "viscous" effect slows down the mobility of the ions due to partial shedding of water from the hydration shell and replacing them with temporary electrostatic bonds.

This minireview revisits the phenomenon of D- and Itype behaviour of polymer films with new insights from state-of-the-art analytical techniques. There are still many unknowns, particularly with respect to the long-term behaviour of the film. Polymer relaxation, plasticisation, hydrolysis and swelling over time can change the size of the nanopore and, thus a mode of ionic conduction. This phenomenon has been indicated in the past by long-term examination of I-type films and transformation of I-type into D-type triggered by deprotonation (i. e. high pH). However, the specific molecular changes during this transformation, changes in functional groups and reciprocal impact on the water and ion transport are still largely unknown.

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#### **Conflict of Interest**

The authors declare no conflict of interest.

#### **Data Availability Statement**

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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- [2] L. X. Wang, S. L. Huang, P. Wu, X. R. Liu, C. Sun, B. Kang, H. Y. Chen, J. J. Xu, *Angew. Chem. Int. Ed.* **2023**, *62*, DOI 10.1002/anie.202315805.
- [3] I. M. F. Tanimoto, B. Cressiot, S. J. Greive, B. Le Pioufle, L. Bacri, J. Pelta, *Nano Res.* **2022**, *15*, 9906–9920.
- [4] S. G. Croll, Prog. Org. Coat. 2018, 124, 41–48.
- [5] J. E. O. Mayne, Official digest 1952, 24, 127-136.
- [6] D. Greenfield, J. D. Scantlebury, J. Corros. Sci. Eng. 2000, 3, paper 5.
- [7] E. M. Kinsella, J. E. O. Mayne, Br. Polym. J. 1969, 1, 173-176.
- [8] J. E. O. Mayne, J. D. Scantlebury, Br. Corros. J. 1971, 3, 237– 239.
- [9] E. M. Kinsella, J. E. O. Mayne, J. D. Scantlebury, Br. Polym. J. 1971, 3, 41–43.
- [10] J. E. O. Mayne, J. D. Scantlebury, Br. Corros. J. 1971, 3, 237– 239.
- [11] J. E. O. Mayne, in Advance in Corrosion Protection by Organic Coatings III (Eds.: J. D. Scantlebury, M. W. Kendig), Electrochemical Society, Cambridge, UK, 1989, pp. 1–7.
- [12] S. S. Jamali, D. J. Mills, Corros. Eng. Sci. Technol. 2013, 48, 489–495.
- [13] D. J. Mills, J. E. O. Mayne, in *Corrosion Control by Organic Coatings* (Ed.: H.Jr. Leidheiser), NACE International, Bethelehem, PA, USA, **1981**, pp. 12–17.
- [14] M. L. White, D. J. Mills, H. Jr. Leidheiser, in *Corrosion Protection by Organic Coatings* (Eds.: M. W. Kendig, H.Jr. Leidheiser), Electrochemical Society, San Diego, Calif., **1986**, pp. 208–216.
- [15] J. E. O. Mayne, J. D. Scantlebury, Br. Polym. J. 1970, 2, 240– 243.
- [16] S. S. Jamali, T. Suesse, S. Jamali, D. J. Mills, Y. Zhao, Prog. Org. Coat. 2017, 108, 68–74.
- [17] S. S. Jamali, P. Mokhtarian, D. J. Mills, Prog. Org. Coat. 2015, 87, 20–27.
- [18] Y. J. Tan, Prog. Org. Coat. 1991, 19, 89-94.
- [19] C.-I. Wu, X. Zhou, Y. J. Tan, Prog. Org. Coat. 1995, 25, 379– 389.
- [20] P. Moongkhamklang, S. R. Taylor, Prog. Org. Coat. 2003, 46, 259–265.
- [21] S. R. Taylor, F. Contu, R. Santhanam, P. Suwanna, Prog. Org. Coat. 2012, 73, 169–172.
- [22] R. M. Souto, Y. González-García, J. Izquierdo, S. González, Corros. Sci. 2010, 52, 748–753.
- [23] S. Morsch, Y. Liu, S. B. Lyon, S. R. Gibbon, ACS Appl. Mater. Interfaces 2015, acsami.5b10767.
- [24] S. Morsch, S. B. Lyon, P. Greensmith, S. D. Smith, S. R. Gibbon, *Faraday Discuss.* 2015, 180, 527–542.
- [25] S. Morsch, S. B. Lyon, S. Gibbon, M. Irwin, J. Appl. Polym. Sci. 2022, 139, 1–9.
- [26] S. Morsch, S. Lyon, S. D. Smith, S. R. Gibbon, Prog. Org. Coat. 2015, 86, 173–180.
- [27] R. G. Duarte, S. González, A. S. Castela, M. G. S. Ferreira, R. M. Souto, *Prog. Org. Coat.* **2012**, *74*, 365–370.
- [28] N. Zhang, S. Chen, B. Yang, J. Huo, X. Zhang, J. Bao, X. Ruan, G. He, *J. Phys. Chem. B* **2018**, *122*, 4719–4728.
- [29] M. Ding, A. Szymczyk, A. Ghoufi, J. Membr. Sci. 2016, 501, 248–253.
- [30] F. Foglia, B. Frick, M. Nania, A. G. Livingston, J. T. Cabral, *Nat. Commun.* 2022, 13, DOI 10.1038/s41467-022-30555-6.
- [31] M. Heiranian, R. M. Duchanois, C. L. Ritt, C. Violet, M. Elimelech, *Environ. Sci. Technol.* 2022, 56, 3313–3323.

[32] C. Lu, C. Hu, C. L. Ritt, X. Hua, J. Sun, H. Xia, Y. Liu, D. W. Li, B. Ma, M. Elimelech, J. Qu, J. Am. Chem. Soc. 2021, 143, 14242–14252.

Angewandte

Chemie

- [33] H. Ohtaki', T. Radnai, *Structure and Dynamics of Hydrated Ions*, **1993**.
- [34] B. M. Rode, C. F. Schwenk, T. S. Hofer, B. R. Randolf, *Coord. Chem. Rev.* 2005, 249, 2993–3006.
- [35] A. Horner, F. Zocher, J. Preiner, N. Ollinger, C. Siligan, S. A. Akimov, P. Pohl, *Sci. Adv.* **2015**, *1*, DOI 10.1126/ sciadv.1400083.
- [36] T. Wei, L. Zhang, H. Zhao, H. Ma, M. S. J. Sajib, H. Jiang, S. Murad, J. Phys. Chem. B 2016, 120, 10311–10318.
- [37] T. E. Culp, B. Khara, K. P. Brickey, M. Geitner, T. J. Zimudzi, J. D. Wilbur, S. D. Jons, A. Roy, M. Paul, B. Ganapathysubramanian, A. L. Zydney, M. Kumar, E. D. Gomez, *Science* (1979) **2021**, 371, 72–75.
- [38] L. Wang, J. He, M. Heiranian, H. Fan, L. Song, Y. Li, M. Elimelech, Sci. Adv. 2023, 9, eadf8488.
- [39] W. Gao, F. She, J. Zhang, L. F. Dumée, L. He, P. D. Hodgson, L. Kong, J. Membr. Sci. 2015, 487, 32–39.
- [40] A. M. Villa, S. M. Doglia, L. De Gioia, A. Natalello, L. Bertini, J. Phys. Chem. B 2022, 126, 2564–2572.
- [41] A. M. Villa, S. M. Doglia, L. De Gioia, L. Bertini, A. Natalello, J. Phys. Chem. Lett. 2019, 10, 7230–7236.
- [42] J. Ma, K. Li, Z. Li, Y. Qiu, W. Si, Y. Ge, J. Sha, L. Liu, X. Xie, H. Yi, Z. Ni, D. Li, Y. Chen, J. Am. Chem. Soc. 2019, 141, 4264–4272.
- [43] Z. Li, Y. Qiu, Y. Zhang, M. Yue, Y. Chen, J. Phys. Chem. C 2019, 123, 15314–15322.
- [44] M. L. White, H. Vedage, R. D. Granata, H. Jr Leidheiser, Ind. Eng. Chem. Prod. Res. Dev. 1986, 25, 129–132.
- [45] D. A. Worsley, D. Williams, J. S. G. Ling, Corros. Sci. 2001, 43, 2335–2348.
- [46] E. P. M. van Westing, G. M. Ferrari, F. M. Geenen, J. H. W. de Wit, Prog. Org. Coat. 1993, 23, 89–103.
- [47] F. Zou, D. Thierry, Electrochim. Acta 1997, 42, 3293-3301.
- [48] M. Szociński, K. Darowicki, K. Schaefer, J. Coat. Technol. Res. 2012, 1–8.
- [49] L. Li, Y. Yu, Q. Wu, G. Zhan, S. Li, Corros. Sci. 2009, 51, 3000–3006.
- [50] N. S. Sangaj, V. C. Malshe, Prog. Org. Coat. 2004, 50, 28-39.
- [51] P. Abgrall, N. T. Nguyen, Anal. Chem. 2008, 80, 2326–2341.
- [52] P. N. N.-T. Abgrall, Nanofluidics, ARTECH HOUSE, 2009.
- [53] S. Kim, H. Choi, B. Kim, G. Lim, T. Kim, M. Lee, H. Ra, J. Yeom, M. Kim, E. Kim, J. Hwang, J. S. Lee, W. Shim, *Adv. Mater.* **2023**, *35*, DOI 10.1002/adma.202206354.
- [54] A. Awati, R. Yang, T. Shi, S. Zhou, X. Zhang, H. Zeng, Y. Lv, K. Liang, L. Xie, D. Zhu, M. Liu, B. Kong, *Angew. Chem. Int. Ed.* **2024**, *63*, DOI 10.1002/anie.202407491.
- [55] L. Ding, M. Zheng, D. Xiao, Z. Zhao, J. Xue, S. Zhang, J. Caro, H. Wang, *Angew. Chem. Int. Ed.* **2022**, *61*, DOI 10.1002/ anie.202206152.
- [56] F. H. Kriel, R. Sedev, C. Priest, Isr. J. Chem. 2014, 54, 1519– 1532.
- [57] L. Zhang, X. Yu, Z. Chen, J. Li, G. Hui, M. Yang, R. Yu, *Chem. Eng. J.* **2021**, 409, DOI 10.1016/j.cej.2020.128113.
- [58] S. Zhang, R. Song, H. Zeng, N. Wu, H. Duan, L. Wang, *Droplet* 2024, 3, DOI 10.1002/dro2.110.

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## Minireview



### Minireview

#### **Polymer Films**

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Bimodal Ionic Conduction through Polymer Films due to Nano Confinement



#### r<sub>pore</sub> > r<sub>solvated ion</sub>

This minireview revisits the phenomenon of nano-confined ion conduction through polymer films. Ions diffuse through polymer films in two distinct modes depending on the nano-structure and free space for the passage of

hydrated or partially hydrated ions. The size of pathway and how it compares to the size of hydrated ion determines whether ions must shed water from the solvation shell which in essence governs the mode of ionic conduction.