OPEN ACCESS

EDITORIAL

Nanoconfined ion transport: Common foundations driving innovative theories and transformative applications

Qiang Wang and Zhiguo Qu*

MOE Key Laboratory of Thermo-Fluid Science and Engineering, School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an 710049, China

*Correspondence: E-mail: zgqu@mail.xjtu.edu.cn

Received: December 8, 2024; Accepted: January 8, 2025; Published Online: January 11, 2025; https://doi.org/10.59717/j.xinn-energy.2024.100075

Citation: Wang Q. and Qu Z. (2025). Nanoconfined ion transport: Common foundations driving innovative theories and transformative applications. *The Innovation Energy* **2**:100075.

Nanoconfined ion transport plays a central role in both natural biological processes and artificial devices designed for energy conversion and storage. The Nernst–Einstein relation proposed over a century ago offers a universal relevance between ionic diffusion coefficient and its mobility in aqueous solutions, serving as the cornerstone of classical ion transport theories. However, ion transport within nanoconfined spaces deviates significantly from that in open spaces due to complex interface-scale-structure effects, challenging the validity of this relationship. This editorial begins by highlighting the limitations of classical ion transport theories in the context of the unique mass transfer processes observed in biological ion channels. It then delves into the underlying mechanisms and common foundations that govern ion binding and migration in nanochannels. The focus is then shifted from individual ions to collective behaviors of multiple ions, aiming to illuminate the historical evolutions and innovative advancements in theories used to capture the occurrence states and transport features of ions in nanoconfined spaces. Additionally, we examine transformative applications where ions act as charge and energy carriers, and the operating principles and improvement strategies of ion-based devices are discussed upon the representative osmotic energy conversion. An outlook is finally provided on the research prospects in nanoconfined ion transport.

EMERGING CHALLENGES OF NERNST–EINSTEIN RELATION

Figure 1 highlights the common foundations, innovative theories, and transformative applications of nanoconfined ion transport. The

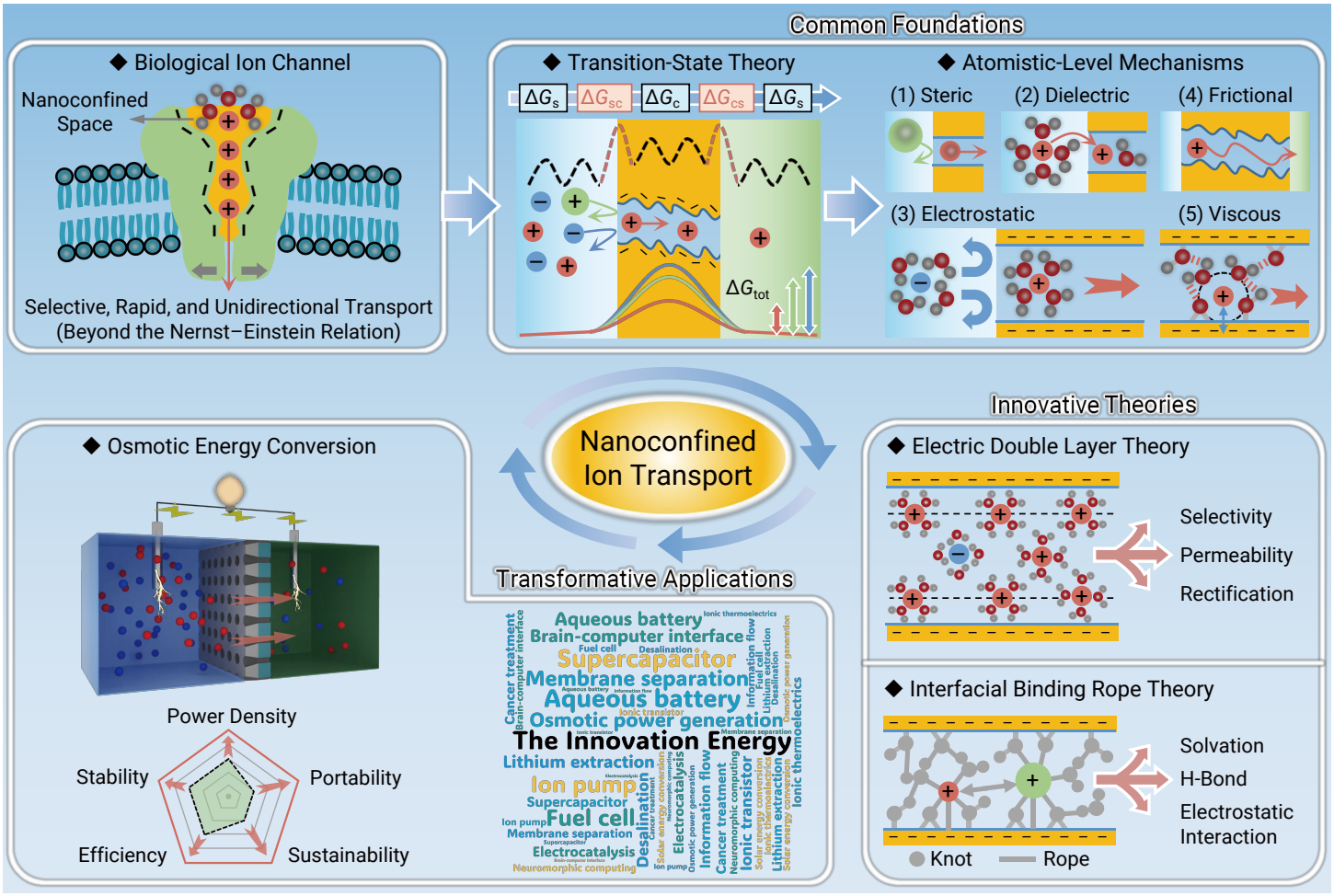

Figure 1. Common foundations, innovative theories, and transformative applications of nanoconfined ion transport.

Nernst–Einstein relation established over a century ago suggests that ionic microscopic motion is determined by random collisions with neighboring molecules, regardless of the type of macroscopic driving force.[1] This relation is applicable to aqueous solutions in open or weakly confined spaces, forming the foundation for classical ion transport theories such as the Poisson–Nernst–Planck equation.

However, from an atomic-scale perspective, ions in aqueous solutions are surrounded by water molecules and exist in a hydrated state. Meanwhile, ion transport in nanoconfined environments rather than in open spaces is the common process for energy and species transfer in natural systems. For

instance, trees utilize naturally aligned cellulose nanofibers to transport ions along their growth direction for nutrient delivery. Biological membranes employ channel proteins to construct selective and gated channels with nanoconfined spaces, thereby enabling the selective, rapid, and unidirectional transport of specific ions driven by a transmembrane electrochemical potential gradient. Hence, ion transport through such nanochannels differs significantly from that in open spaces, due to cooperative factors including ionic interactions with surroundings, geometric and charge properties of channel surface, as well as operational conditions like driving force and external stimuli. These complexities place nanoconfined ion transport beyond the description of classical Nernst–Einstein relation.

COMMON FOUNDATIONS OF NANOCONFINED ION TRANSPORT

The ion transport process through nanoconfined channels can be described by the empirical transition-state theory. In detail, diversified driving forces (e.g., concentration and potential gradients) can be unified as an electrochemical potential gradient. This gradient drives ions to break their interactions with surroundings, so that ions move to the next position and bind with new media in subsequent environments, thus forming an elementary step of ion transport. Ion migration through the entire nanochannel is a continuous relay of multiple elementary steps. These processes can be described by kinetic barrier networks,[2] which account for distinct energy barriers encountered during ion transport. The networks include the diffusion barrier within solutions (ΔG_s), the partition barrier into the channel (ΔG_{sc}), the diffusion barrier within the channel (ΔG_c), and the partition barrier out of the channel (ΔG_{cs}). The total energy barrier (ΔG_{tot}) ultimately determines ion permeability, and the discrepancies in these barriers between ions are responsible for ion selectivity.

With an atomistic-level insight, several mechanisms can determine the energy barriers for ion transport through nanochannels. They include steric hindrance, dielectric effects, and electrostatic interactions at the channel entrance, as well as friction and viscosity effects within the channel. Specifically, ions face significant resistance when migrating from bulk solutions into channels with nanoconfined spaces. When the channel height is smaller than the hydrated ion, the confinement effect reorganizes or removes the ion hydration shell, leading to partial dehydration and energy consumption. Hence, high-resolution nanochannels can exploit these mechanisms to distinguish among ions with distinct sizes. Furthermore, as counter-ions carry an opposite charge to the channel walls, electrostatic attraction can partially offset the energy required for ion dehydration, allowing counter-ions to enter the channel with lower energy barriers. In contrast, electrostatic repulsion between the walls and co-ions creates huge energy barriers and blocks co-ion transport, thus establishing selectivity between counter-ions and co-ions. Moreover, frictional and viscous effects become prominent once the partially dehydrated ions enter the channel. Specifically, the frictional effect arises from the atomistic-scale random collisions between ions and surroundings, including adjacent ions, water medium, and channel walls. The viscous effect specifically refers to physicochemical interactions between hydrated ions and channel walls, including hydrogen bonding, electrostatic attraction, and bond formation. These interactions induce chemical affinity and impede ion transport in the channel.

In summary, these kinetic barrier networks and atomistic-level mechanisms form the common foundations of nanoconfined ion transport processes in both natural biological systems and artificial devices. The well-tailored ion constitutions, nanochannel properties, and operating conditions can modulate the relative dominance of various energy barriers and mechanisms in localized regions, thus addressing the requirements of ion transport characteristics in different application scenarios.

INNOVATIVE THEORIES OF NANOCONFINED ION TRANSPORT

When the focus shifts from individual ions to the collective behaviors of multiple ions, ion distribution in nanochannels is described by the electric double layer (EDL) theory. Specifically, solid–liquid contact triggers electron transfer and functional group dissociation, resulting in the electrified channel surface. Ions form an EDL near the surface due to electrostatic interaction and thermal motion. The Gouy–Chapman–Stern (GCS) model proposed in 1924 introduces a Helmholtz plane to divide the EDL into a Stern layer occupied by tightly packed counter-ions and a diffuse layer containing loosely distributed ions. The Grahame model born in 1947 further considers ionic solvation and specific adsorption, and the Bockris–Devanathan–Muller (BDM) model proposed in 1963 then recognizes the water dipole–surface interaction in the interfacial region. These models serve as milestones in describing the occurrence states and transport properties of aqueous ions through nanoconfined channels. Other refined EDL models continue to emerge with advancements in experimental characterization and computational techniques.

The above EDL theories provide valuable guidance for modulating nanoconfined ion transport in energy conversion and storage devices. For instance, when the channel height is smaller than twice the EDL thickness, the EDL is overlapped and allows numerous counter-ions to selectively migrate through the channel. When the channel geometry or surface charge is asymmetric, ions exhibit rectification effects and diode-like unidirectional migration, significantly increasing the net ion flux. Upon such understanding, various strategies are effective to break the trade-off between ion selectivity and permeability in nanochannels. On the solution side, factors such as ion composition, concentration, and temperature can be adjusted to enhance ion migration and improve ion permeability. On the channel side, chemical modifications and size adjustments (e.g., height, length, and roughness) of the walls can be implemented to identify target ions and improve ion selectivity.[3] Additionally, external stimuli (e.g., light, electric field, and magnetic field) deserve to be introduced to manipulate ion migration direction. Combining multiple driving forces (e.g., concentration, temperature, and potential gradients) is particularly recommended to maximize ion flux. For instance, heating the channel's low-concentration side creates a temperature gradient opposite to a concentration gradient, thereby accelerating ion transport and maximizing ion selectivity simultaneously.

Although current EDL theories can rationalize the trade-off mechanisms governing ion transport in nanochannels, they fail to fully explain several experimental phenomena. For example, a temperature gradient across nanochannels can induce the Soret effect and ion thermal diffusion, and current research reveals two contrasting behaviors. Hydrated ions may diffuse either from high to low temperatures or from low to high temperatures, depending on integrated factors such as ion concentration and temperature value. The origin and direction of ion migration remain unresolved scientific mysteries. Atomistic-level investigations are necessary to uncover the charge distribution features of hydrated ions at solid–liquid interfaces, which could provide critical insights. Moreover, local physical fields in nanochannels give rise to diverse interfacial effects on hydrated ions near walls, such as dynamic hydration structures, hydrogen bonding networks, and chemical reactions. Such effects create ion transport behaviors with directional preferences that lie beyond the explanatory scope of EDL theories.

Accordingly, current theories on ion transport in nanoconfined spaces remain incomplete. The innovative theories that integrate multiple mechanisms are imperative to fully bridge the structure-performance relationship of ion transport in nanochannels. As a preliminary attempt, researchers propose an interfacial binding rope theory to clarify ion transport mechanisms in sub-nanochannels.[4] The underlying basis of such theory lies in an atomic-scale insight into interfacial phenomena in nanoconfined channels. Under this circumstance, this theory connects atomic-scale interactions in confined environments with the spatial configurations and dynamic behaviors of hydrated ions, including the solvation structures, hydrogen bonding networks, and electrostatic interactions. The current–potential response and surface charge density are important metrics in experiments, which contribute to the understanding of such nanoconfined ion transport theory. This theory is confirmed through first-principles calculations and experimental characterization of charged properties of nanochannels, providing valuable insights for improving the selective ion migration in experiments. This theory can further guide the experimental design and improve the output performance of osmotic energy conversion, especially for the arrangements of salt concentration, working temperature, and pH value. This achievement broadens the nanoconfined ion transport theory for systems involving the coexistence of multiple ions.

TRANSFORMATIVE APPLICATIONS UPON NANOCONFINED ION TRANS-

PORT

Compared to electrons, ions provide tailorable properties (e.g., charge, size, and solvation capability) based on task-specific screening. Hence, inspired by the biomimetic concept, the mechanisms and features of nanoconfined ion transport are uniquely suited for the design of transformative energy conversion and storage devices. For instance, ion transport driven by concentration gradients across channels is exploitable to harvest osmotic energy from seawater, salt lakes, and wastewater, addressing the electricity demands of islands and high-altitude regions. When a temperature gradient serves as the driving force, low-grade heat from solar energy and industrial processes can be harnessed for multi-energy coupled ionic thermoelectric generation. The performance metrics include thermopower and energy conversion efficiency. Meanwhile, the high-precision structural design of nanochannels facilitates electrochemical energy storage through ion intercalation.[5] It also enables the extraction of valuable metal ions from industrial wastewater based on the selectivity of ions with distinct sizes and valences. Nanoconfined ion transport is even superior in multifunctional integration, offering promising applications in environmental protection, information processing, and biomedical science.

Taking osmotic power generation as an example, its central process involves multiphysical and multiscale heat-mass transfer within nanoporous membranes, thereby converting the renewable salinity-gradient energy into electricity. Current research mainly focuses on developing membrane materials that combine high selectivity and high ionic flux from a material science perspective. To advance this field, it is crucial to establish scientific criteria for aligning ionic mass flow with energy flow and address theoretical gaps in nanoconfined heat-mass transfer. Furthermore, more efforts are necessary to delve into the atomistic-level ion friction in nanoconfined environments, overcome the selectivity-permeability trade-off of ion transport, and explore passive and active strategies to regulate power generation performance. The ultimate goal of osmotic power generation is to develop the technology with optimized power density, efficiency, stability, portability, and sustainability, thereby meeting the electricity demands in practical applications.

PROSPECTS FOR NANOCONFINED ION TRANSPORT RESEARCH

Although significant achievements have been made in fundamental research and cutting-edge applications of nanoconfined ion transport, the future development of this field still faces several unresolved challenges. At present, the significant technical challenges lie in experimental techniques and underlying mechanisms, which deserve to be focused in future research. Specifically, in terms of experimental techniques, scalable synthesis methods and high-resolution characterization tools are needed to predict other unique phenomena at solid–liquid interfaces. For ion transport mechanisms, innovative theoretical frameworks are required to bridge the knowledge gap concerning the structure and dynamic behaviors of ions and water molecules in nanoconfined spaces. These frameworks will help quantify the relative contributions of various atomistic-level mechanisms to the total energy barrier of ion transport through nanochannels. Regarding performance prediction, the integrated evaluation system and accurate prediction model are vital to capture the time-dependent behaviors of ion transport. To address these challenges, interdisciplinary collaboration together with a forward-looking perspective is indispensable for energy science, materials science, physical chemistry, engineering, and nanotechnology. Multi-insight research is valuable to cover first-principles calculations, molecular simulations, machine learning, experimental characterization, and system integration. Long-term exploration is essential in the research field of nanoconfined ion transport, ultimately driving the development of ion-related technologies.

REFERENCES

1. Li Z.W., Misra R.P., Li Y.H., et al. (2023). Breakdown of the Nernst-Einstein relation in carbon nanotube porins. *Nat. Nanotechnol.* **18**:177–183. DOI:10.1038/s41565-022-01276-0
2. Kingsbury R.S., Baird M.A., Zhang J.W., et al. (2024). Kinetic barrier networks reveal rate limitations in ion-selective membranes. *Matter* **7**:2161–2183. DOI:10.1016/j.matt.2024.03.021
3. Chen L., Shi G.S., Shen J., et al. (2017). Ion sieving in graphene oxide membranes via cationic control of interlayer spacing. *Nature* **550**:415–418. DOI:10.1038/nature24044
4. Liu Q., Wang Q., Qu Z.G., et al. (2023). Interfacial binding rope theory of ion transport in sub-nanochannels and its application for osmotic energy conversion. *Nano Energy* **113**:108545. DOI:10.1016/j.nanoen.2023.108545
5. Chen W.S., Gu J.J., Liu Q.L., et al. (2022). Two-dimensional quantum-sheet films with sub-1.2 nm channels for ultrahigh-rate electrochemical capacitance. *Nat. Nanotechnol.* **17**:153–158. DOI:10.1038/s41565-021-01020-0.

FUNDING AND ACKNOWLEDGMENTS

This work was supported by the National Science Foundation for Distinguished Young Scholars (No.52025065). The funders had no role in study design, data collection and analysis, decision to publish, or preparation of the manuscript.

AUTHOR CONTRIBUTIONS

All authors contributed to the manuscript and approved the final version.

DECLARATION OF INTERESTS

The authors declare no competing interests.