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Clay Reimagined: Phyllosilicates as Future Membrane Technologies

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Abstract text. Membrane technologies have made critical advances in resource recovery, water purification, and energy systems. However, it is difficult to systematically tune properties of traditional polymer membranes, and researchers have struggled to deliver challenging, advanced separations using these platforms. In recent years, membranes based on two-dimensional (2D) materials have drawn attention for molecular-scale separations due to their unique properties, most notably their tunable nanoscale interlayer properties. Among the diverse family of 2D materials, phyllosilicates, a broad class of naturally abundant clay minerals, offer significant advantages in cost and scalability over synthetic 2D materials, positioning them as promising candidates for advanced membrane technologies. We discuss their inherent structural and chemical properties, strategies for tailoring selective transport pathways, and recent advancements across applications including ion separation, water treatment, and energy conversion. Finally, we outline key challenges and opportunities to guide future research in leveraging phyllosilicate membranes for high-performance separation technologies.

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1. Introduction

Chemical separations are extremely energy-intensive and account for 10–15% of global energy consumption.[1] Specifically, separations which depend on thermal processes (such as distillation) are responsible for ~80% of that energy cost. Shifting from thermal techniques to more energy-efficient membrane-based technologies could reduce these separations' energy intensity by an estimated 90%, resulting in a ~7–11% reduction in global energy consumption and improving energy security.[1-2] To date, membrane technologies have been applied to a broad spectrum of energy- and water-related applications, including reverse osmosis (RO), wastewater treatment, battery systems, gas separations, organic solvent nanofiltration, and membrane-based fuel cells and electrolyzers.[3-6]

Membrane technologies are also attractive for emerging separation applications, such as the recovery of critical metals from aqueous sources.[1, 7-8] Metals including lithium, magnesium, and many transition metals are in high demand for energy technologies but have limited supply and low recycling rate.[7-8] Recovering these high-value metals from brine, waste streams, or seawater is an attractive prospect for improving energy security and efficiency. Since critical metal cations are often only present in dilute concentrations alongside many other ions, they cannot be effectively recovered from water using thermal separations. Membranes capable of precise size- or charge-based separations, in contrast, are well-suited for recovering these valuable resources. Traditional membranes based on polymeric materials generally struggle to deliver this level of precision.

Two-dimensional (2D) materials, a family of crystalline materials consisting of atomically thick layers, have recently drawn attention as potential source materials for separation membranes. 2D materials can be exfoliated (or etched) and restacked into lamellar membranes, which consist of many two-dimensional flakes separated by regular interlayer spaces on the order of 0.3–1 nm. These spaces, or nanochannels, make 2D materials ideal candidates for nanofiltration (separations involving solutes ~0.2–10 nm in diameter). Nanofiltration membranes have been developed from a wide range of 2D materials, including graphene and its derivatives, MXenes, transition metal dichalcogenides, and the emerging class of phyllosilicates.[9-14]

Among these 2D material systems, phyllosilicates occupy a particularly interesting space. As naturally abundant clay minerals, they offer distinct advantages in cost, availability, and chemical versatility. In this perspective, we examine phyllosilicate minerals as 2D building blocks for laminar membranes, discussing fabrication strategies, recent advances in separation and energy applications, and opportunities for future research. We begin by reviewing the inherent properties of phyllosilicate minerals that make them attractive for laminar membrane design.

1.1. Phyllosilicate Minerals

Phyllosilicates are the most common type of clay minerals. Clay minerals are composed of fine particles (typically defined with an upper limit of 2 to 4 μm) and are generally plastic at the appropriate water content but harden upon drying or firing.[15-16] Clay minerals are formed by natural processes such as the weathering of silicate rocks; they are found in various sources such as soils, marine and continental sediments, volcanic deposits, and geothermal fields.[17-18] Due to their widespread natural occurrence, substantial deposits of phyllosilicate minerals can be found in nearly every region of the world, including North America, South America, Africa, and Asia (**Figure 1**).

As their name suggests (from the Greek *phyllon*, meaning leaf), phyllosilicates have a sheet-like structure with uneven edges formed by tetrahedral and octahedral layers.[19] The abundance and environmental compatibility of phyllosilicates, combined with their structural properties, provide significant advantages in cost and scalability over synthetic 2D van der Waals layered materials for membrane development. Producing synthetic 2D materials often requires expensive precursors, strict environmental controls, and high-temperature and/or pressurized synthesis methods such as chemical vapor deposition. By contrast, natural phyllosilicates are inexpensive, abundant, and require relatively simple and low-energy processing methods, resulting in lower production costs. **Table 1** presents a comparison of the major existing types of 2D materials used for membrane technologies and their properties, highlighting the advantages of phyllosilicate-based membranes.

Table 1. Comparison of the chemistry, interlayer spacing, stability, cost, and environmental compatibility of the leading 2D materials for membrane technologies. Material costs were obtained from Sigma-Aldrich for non-exfoliated and exfoliated graphene oxide, MAX phase powders, MoS_2 and WS_2 powders, and raw phyllosilicates.

	Graphene oxide	MXenes	Transition metal dichalcogenides	Phyllosilicates
Component elements	C, H, O	C, N, transition metals (Ti, V, Mo, etc.), surface groups (Cl, F, O, etc.)	S, Se, Te, transition metals (Mo, W, etc.)	Al, Si, O, H, Li, Na, K, Mg, Ca, transition metals (Fe, Cu, etc.)
Interlayer spacing (nm)	~1.0 – 7.0	~0.1 – 1.1	~0.3 – 1.1	~0.3 – 2.0
Stability in water (without crosslinkers)	Hours	Days	Days	Varies (hours – weeks)
Stability in water (with crosslinkers)	Days – weeks	Weeks	Weeks	Weeks – months
Raw material cost ($/kg)	$5,000 – $100,000	$10,000 – $15,000	$600 – $2,000	$5 – $80
Environmental concerns	Possible cytotoxicity	Synthesis involves HF or other strong acids	Synthesis involves solvothermal methods	None known

Beyond their economic advantages, there are also environmental impact benefits of phyllosilicate minerals. Polymeric membranes are in general also cost-effective and easy to fabricate, but their production results in undesirable emissions.[20] Leveraging naturally derived phyllosilicates would enable membrane technologies to substantially reduce their environmental footprint while also enhancing membrane performance and properties.

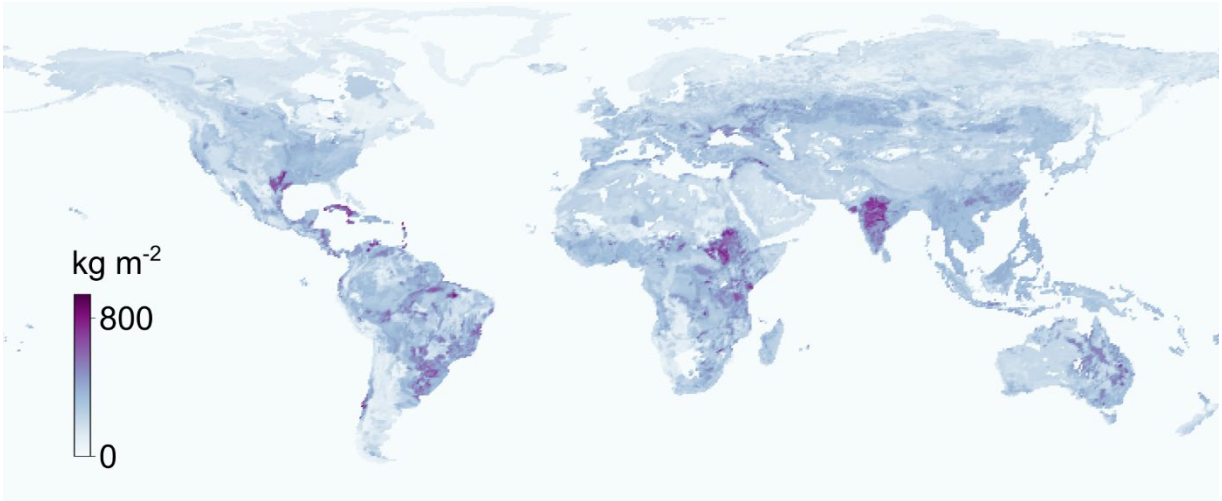

Figure 1. The geographic distribution of phyllosilicate minerals in the soil column. The weight of five phyllosilicate groups (kaolinite, illite/mica, smectite, vermiculite, chlorite) per unit area (kg m^{-2}) is shown. The global soil clay mineral dataset published in 2016 was used to produce the map.[21]

1.2. History of Clay Research

Clay materials have been important to human civilization since prehistoric times as construction materials. Modern clay research has been active for approximately 100 years; it was accelerated by the discovery of bentonite in North America and Europe in the early 20th century. Early clay scientists discovered that clay minerals were crystalline and could be dehydrated.[22] From the 1920s to the 1940s, scientists used tools such as X-ray diffraction and electron microscopy to reveal the structure of clay minerals such as kaolinite, micas, and montmorillonite. In the 1950s to 1970s, clay science was applied on an industrial scale with the advent of clay-based catalysts for organic reactions and catalytic cracking. In the late 20th century, many new clay materials (such as pillared clay minerals, modified clays, and layered double hydroxides) were developed and used for environmental, medical, and electrochemical applications.[22]

Although clay research has an extensive history, the ability of clay minerals to be exfoliated into 2D layers (and subsequently assembled into membranes) was only explored in recent years.[23] Within the past decade, several types of 2D clay nanosheets have been synthesized by delaminating phyllosilicate minerals, such as montmorillonite, kaolinite, and vermiculite.[24] While clay nanosheets were soon applied to membrane science, early studies used 2D phyllosilicates only as fillers or minor components in mixed-matrix membranes.[25-26] More recently, phyllosilicate nanosheets have been directly used to fabricate laminar (layered) membranes for molecular-scale separations, sometimes with crosslinking agents.[27-28] 2D phyllosilicates continue to rapidly generate interest as potential membrane materials due to their many advantageous properties, such as their abundance, stability, and tunable transport channels.

2. Tunability of Transport Channels

2.1. Inherent Properties of Phyllosilicates

As illustrated in **Figure 2a**, phyllosilicate structure consists of stacked layers composed of tetrahedral sheets (formed by silicon coordinated in a tetrahedral arrangement with oxygen) and octahedral sheets (comprised of metal cations such as Mg, Al, or Fe coordinated octahedrally with oxygen or hydroxyl groups). In 1:1 phyllosilicates (e.g., kaolinite), each layer consists of one tetrahedral and one octahedral sheet. In contrast, 2:1 phyllosilicates (e.g., smectites, vermiculite, and micas) have an octahedral sheet sandwiched between two tetrahedral sheets. During their geological formation, isomorphic substitution commonly occurs within both tetrahedral and octahedral sheets, where central cations are replaced by lower-valency cations. This substitution generates a net negative surface charge, which is balanced by interlayer cations to preserve charge neutrality and structural stability. This layer charge is a fundamental property that influences many physicochemical characteristics of phyllosilicates. Its magnitude and distribution vary among different minerals depending on the type and location of substitution. For instance, smectites and vermiculite exhibit relatively low layer charge, leading to weaker interlayer binding. This allows water to penetrate and swell the layers, and facilitates cation hydration and exchange, resulting in high cation exchange capacity (CEC). In contrast, micas possess higher layer charge, producing strong interlayer interactions. Their interlayer cations are tightly held, often dehydrated, and not readily exchanged, which inhibits swelling and renders their CEC nearly zero.

Like other 2D materials, phyllosilicates can be exfoliated and restacked to form 2D laminar membranes, where the interlayer galleries (**Figure 2b**) serve as transport pathways that can be tuned for selective ion or molecule transport. Transport within 2D interlayers can be categorized as either in-plane or out-of-plane (**Figure 2b**). While in-plane transport has been explored in nanofluidic devices to harness the selectivity of phyllosilicate interlayer galleries,[29-30] practical membrane separation typically operates in the out-of-plane direction. This orientation leverages the inherently tortuous transport pathways, which enhance defect tolerance by preventing membrane imperfections from forming continuous, percolating channels. Phyllosilicates with exchangeable interlayer cations, such as smectites and vermiculite, are especially well-suited for membrane fabrication due to the ease of exfoliation. This is typically achieved via liquid-phase exfoliation, where interlayer cations are replaced by larger ones to weaken electrostatic interactions, followed by agitation (e.g., sonication) to delaminate the layers into individual flakes.

While more challenging, even non-swelling phyllosilicates like mica and kaolinite can be exfoliated and fabricated into membranes.[31-33] Successful exfoliation in these systems often hinges on strategies that reduce interlamellar binding, such as surface functionalization or modification of the layer charge.

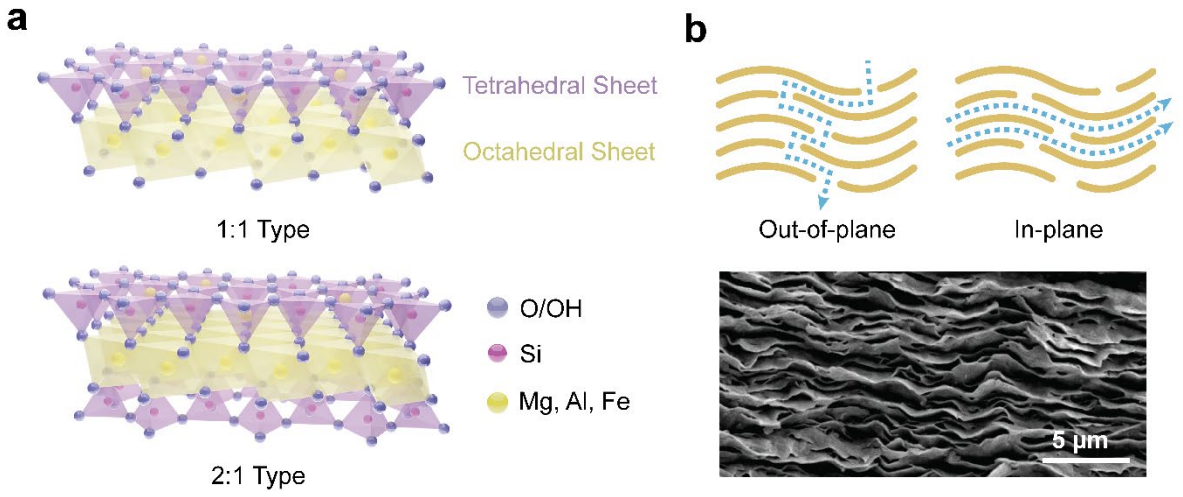

Figure 2. (a) Crystal structure of phyllosilicates. (b) Laminar phyllosilicate membrane structure and cross-sectional scanning electron microscopy image.

2.2. Modifying Phyllosilicate Membranes for Selective Transport

Membranes constructed from 2D materials hold significant promise for selective ion or molecule transport, owing to the highly tunable nature of their interlayer channels. In 2D laminar membranes, selectivity arises from a combination of Donnan exclusion, size-based sieving, and specific binding interactions.[34] Donnan exclusion, driven by fixed surface charges, enables preferential transport of counter-ions while excluding co-ions, making it particularly effective for separating ions of different valencies. In critical mineral recovery applications, positively charged membranes are preferred to distinguish between cations of varying valencies.[35-36] For ions with similar charge and valency, size exclusion becomes essential. This mechanism relies on engineering sub-nanometer transport pathways, where partial dehydration of ions within confined interlayers introduces a complex interplay between steric hindrance and hydration energy barriers.[37] Beyond charge and size, chemical affinity offers an additional degree of tunability. Functional groups such

as carboxyl (-COOH), amine (-NH_2), and thiol (-SH) can selectively interact with target ions through coordination or complexation—for instance, -COOH groups show strong affinity for lead ions[38]—offering opportunities for enhanced selectivity via tailored interfacial chemistry.

To enable targeted ion selectivity in phyllosilicate membranes, it is essential to first address their stability in aqueous environments. Owing to their weak interlamellar interactions and the hydrophilic nature of surface hydroxyl groups, phyllosilicate membranes are prone to disintegration in water—the same property that facilitates their easy exfoliation.[24] Therefore, enhancing interlayer binding during or after membrane fabrication is key to improving water stability. This can be achieved through several strategies: (i) electrostatic interactions, by crosslinking or intercalating positively charged species such as multivalent cations[39-41], small molecules (e.g., diamines)[12, 28], or polymers (e.g., polyethyleneimine, PEI)[42-43]; (ii) covalent bonding, as in the case of pillared clays[44-45], where rigid metal oxide pillars are introduced to form direct bonds with phyllosilicate flakes, effectively suppressing swelling and locking the interlayer spacing—an approach recently adapted for membrane fabrication[46]; and (iii) external confinement, where membranes are physically sealed with materials like silicone or epoxy to prevent delamination, a strategy previously also demonstrated with graphene oxide (GO) membranes.[47-48] These stabilization strategies can give phyllosilicate membranes water stability similar to or exceeding other types of 2D materials.[49-51]

Once stable, transport channels can be further tailored for specific separation mechanisms. Phyllosilicate membranes originally carry negative surface charge. In order to separate cations for critical resource recovery by Donnan exclusion, the surface charge of phyllosilicate membranes can be tuned through intercalation of positively charged species (e.g., PEI) into the interlayers[42], or through lattice doping to reduce the intrinsic layer charge (e.g., Li-doped muscovite)[52]. In some cases, a combined strategy—reducing original charge while introducing additional charge—has proven effective, as demonstrated in doped pillared clay membrane systems.[46]

For size exclusion, there are two approaches to creating confinement. The interlayer spacing can be tuned by introducing molecular crosslinkers or spacers with varying sizes.[12, 28] While direct crosslinking with small molecules to achieve sub-nanometer channels has not yet been realized in

phyllosilicate systems, related work in laminar membranes based on other 2D materials, such as thiourea-crosslinked graphene oxide (GO), can provide valuable design insights.[53] Alternatively, intercalation of bulky species within the nanochannels (e.g., polymers) can reduce effective channel size by occupying free volume, though often at the expense of permeability.

Lastly, chemical affinity-based selectivity can be introduced through intercalation of functionalized polymers (e.g., sulfonated poly(vinyl alcohol) (SPVA) with sulfonic acid groups)[54] or via surface functionalization[55] of phyllosilicate flakes. Surface functionalization can be achieved by electrostatic intercalation of small molecules[56]—an approach commonly used in organoclays—or by silanization reactions targeting surface hydroxyl groups[57-59]. Together, these strategies offer a versatile platform for engineering phyllosilicate membranes with tunable transport properties suited for complex ion separations.

3. Recent Research Progress and Emerging Applications for Phyllosilicate Membranes

3.1. Resource Recovery

2D laminar membranes are specifically attractive for critical resource recovery applications. Among critical minerals, lithium recovery from various water sources—such as wastewater and salt lake brines—is of particular importance, as water bodies represent the largest lithium reserves and demand is surging due to the growth of the electric vehicle market.[60] However, extracting lithium from aqueous environments is challenging due to the presence of coexisting ions, particularly sodium and magnesium, often at much higher concentrations. Membrane-based lithium extraction has therefore focused on achieving selective separation from these competing ions, each requiring distinct separation mechanisms. For example, positively charged membranes can separate divalent magnesium ions from monovalent lithium ions via Donnan exclusion. Polyethyleneimine (PEI)-intercalated montmorillonite membranes have demonstrated enhanced Li/Mg selectivity by introducing positive surface charges through PEI intercalation.[42] In contrast, separating lithium from sodium—both monovalent cations—requires precise control over channel size and chemical affinity. For instance, alumina-pillared vermiculite membranes, after doping, exhibited reduced pore sizes, which improved Li/Na separation by hindering the transport of the larger sodium ions.[46] Additionally, SPVA-intercalated vermiculite membranes showed enhanced

Li/Na selectivity, attributed to the stronger binding affinity of lithium ions toward sulfonic acid groups.[54] By rationally designing and engineering transport pathways, phyllosilicate membranes hold promise for the selective recovery of other critical and strategic materials, including nutrients and rare earth elements (REEs).

3.2. Water Purification

Membrane technologies have been increasingly applied to water purification in order to address global water scarcity and combat pollution. Urgent research goals for membrane-based water purification include achieving high selectivity and fouling resistance.[61] Additionally, water purification membranes must meet a number of basic requirements, such as long-term stability in water, resistance to chemical/thermal degradation, and high rejection for toxins, heavy metals, and organic waste.

2D-material-based membranes are attractive for water purification due to their sub-nanometer pore/channel size, which can remove many pollutants by size exclusion and achieve high selectivity. They also possess good chemical and thermal stability. To date, 2D materials including graphene oxide, transition metal dichalcogenides, and MXenes have been studied for water purification applications.[62-64]

Recently, phyllosilicate membranes have also joined the library of 2D-material-based membranes applied to water purification. For instance, cobalt-functionalized vermiculite membranes have shown high water permeance and can degrade several organic pollutants through oxidation.[55] Additionally, iron phyllosilicates have been used as catalysts in membranes to degrade dyes and organic solutes in simulated wastewater.[65] Phyllosilicate membranes may also be able to overcome challenges faced by other 2D materials, which can suffer from poor stability in water or difficulties in chemical functionalization. Crosslinked vermiculite membranes exhibit robust water stability[46], which is seldom reported for other classes of 2D-material-based membranes, and phyllosilicates have the potential for superior selectivity due to their finely tunable interlayer spacing and numerous modes of functionalization.

3.3. Gas Separation Applications

Membranes have been in use for gas separations for over 45 years. Industrial gas separation membranes typically consist of a thin (< 1 μm) selective layer on top of a porous support that provides mechanical strength. Due to this requirement, gas separation membrane materials must be able to be processed into thin films with large areas.[66] Research goals for gas separation membranes are similar to those for aqueous separation membranes, such as increased selectivity, permeance, and fouling resistance. Several 2D materials, including graphene oxide, transition metal dichalcogenides, and MXenes, have recently been applied to gas separation membranes.[67-69]

Phyllosilicate membranes for gas separations may improve on existing technologies due to their low cost, stability, and wide array of possible intercalants (tunable interlayer spacing). Some initial efforts have been made with phyllosilicate-polymer composite membranes (for example, montmorillonite/polydimethylsiloxane and layered AMH-3 silicate/cellulose acetate composites) for CO_2/CH_4 separation.[70-71] Additionally, polyethyleneimine has been used as an intercalant in pristine vermiculite membranes, yielding high permeance and CO_2/CH_4 selectivity.[72] However, the research space for phyllosilicate-based gas separation membranes remains open. Major research gaps include applying these membranes to other separations beyond carbon capture, studying the effects of various linkers on dry membrane performance and gas selectivity, and scaling up phyllosilicate membranes to industrial gas separation modules.

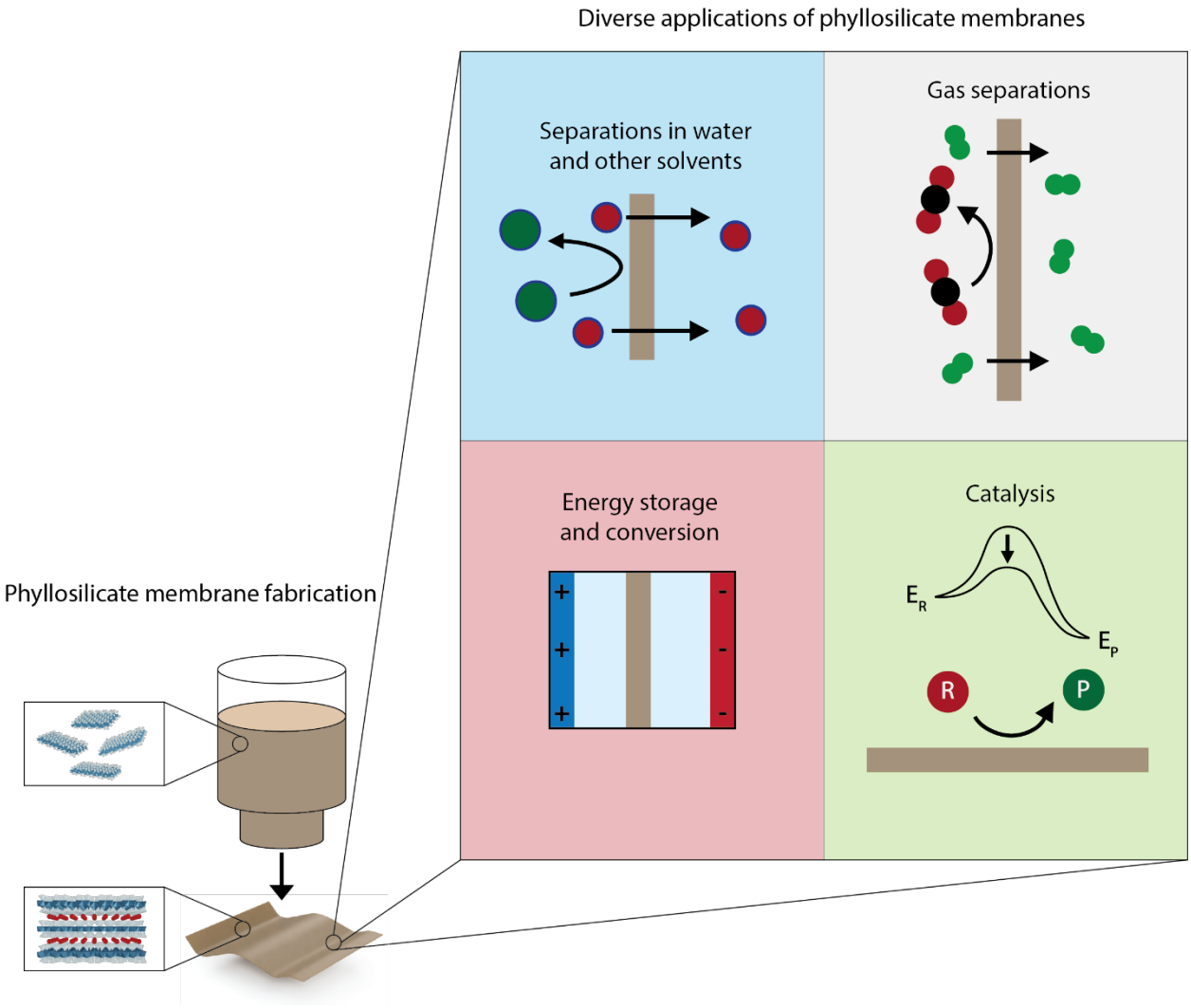

Figure 3. The tunable interlayer spaces, diverse chemistry, and environmental compatibility of phyllosilicate membranes make them suitable for applications including aqueous separations, gas separations, energy storage and conversion, and catalysis.

3.4. Energy Conversion Applications

Beyond their critical roles in direct separation applications such as resource recovery and water purification, phyllosilicate-based membranes can provide alternative approaches in energy conversion technologies owing to their selective transport, thermal stability, structural tunability, and environmental advantages. For example, phyllosilicates' selective ion transport properties can be leveraged for osmotic energy conversion, where the energy of mixing released when salt water meets freshwater is captured for beneficial use. As energy demands grow and traditional sources

face limitations, alternatives such as "blue energy" systems are increasingly gaining attention. Conventional membranes used for osmotic energy harvesting face challenges such as low power density due to their limited water and ion transport capabilities.[73-74] Fundamental studies with ion-selective nanoporous membranes made from single-layer 2D materials such as graphene[75] and MoS_2[76] have demonstrated highly effective osmotic power generation, with an exceptional power density of 10^6 W m^{-2} for single-channel MoS_2 membranes.

Laminar membranes made from 2D nanosheets provide scalability for large-area membrane fabrication while still possessing uniform and continuous nanoscale pores/channels. Various 2D materials have been fabricated into laminar membranes for osmotic power generation, including graphene oxide[77-78], MoS_2[79], MXene[80], and phyllosilicate-based membranes. Kaolinite membranes effectively generate osmotic energy at a rate competitive with graphene oxide membranes[77], with a maximum output power density of 0.18 W m^{-2}.[32] Similar osmotic power density was also reported for montmorillonite membranes.[81] Recently, composite membranes with phyllosilicate minerals have also shown promising osmotic power generation capabilities.[82-83] However, deeper understanding of the relationships between phyllosilicate membranes' composition, structure, and ion transport is urgently needed to further improve membrane design and fully harness the vast library of natural phyllosilicate minerals for efficient osmotic energy applications.

Water evaporation is a ubiquitous process that can also generate electricity by converting thermal energy from the ambient environment. 2D laminar membranes are promising materials for hydrovoltaic energy harvesting, due to their charged surfaces that promote electrokinetic effects and interlayer spaces that allow electric double layer overlap. When confined water flows through a nanochannel with a diameter less than water's Debye length, continuous capillary-driven movement leads to streaming potentials and sustained power output. A pioneering study with carbon black showed that centimeter-sized membranes could generate a stable voltage of up to 1 V and peak power of 53 nW under ambient evaporation.[84] Since then, various 2D materials including layered double hydroxides,[85] 2D AlOOH,[86] MXene,[87] and MoS_2[88] have been fabricated into laminar membranes for water-evaporation-based electricity generation. Recently, phyllosilicate (vermiculite) membranes also achieved a stable voltage of 1 V,[89] and

heterostructure membranes with vermiculite and halloysite nanotubes demonstrated the combined use of two natural clays to generate open-circuit potentials up to 406 mV.[90] Yet, phyllosilicate membranes remain a largely underexplored resource; further research is currently needed to employ the rich diversity of phyllosilicate minerals for high-efficiency, scalable, and sustainable hydrovoltaic devices.

3.5. Catalysis applications

Due to their high surface area, tunable interlayer properties, and robust structural and thermal stability, phyllosilicates have been widely explored as platforms for catalysis. While pristine phyllosilicates are typically catalytically inert, incorporating active species into their structure enables a broad range of catalytic applications.[91] These include acid/base-driven organic transformations,[92] the hydrogen evolution reaction (HER),[93] oxygen evolution reaction (OER),[94] CO_2 reduction,[95] and water splitting,[96] where the confined interlayer spaces can function as microreactors. Both synthetic and natural phyllosilicates have been employed in these roles. For instance, synthetic phyllosilicates with catalytically active transition metal cations (e.g., Fe, Ni, Co, Cu) in the octahedral layers can be prepared via co-precipitation under hydrothermal conditions, yielding materials with excellent catalytic performance and thermal stability.[97]

Utilizing natural phyllosilicates as catalytic supports offers a more cost-effective alternative. One notable example is K10, an acid-activated montmorillonite that has been commercialized for acid-catalyzed reactions such as esterification and C–C bond cleavage.[98-99] Another major class involves pillared clays, where catalytically active metal oxide pillars (e.g., Al_2O_3, ZrO_2, TiO_2) are inserted between phyllosilicate layers.[100] These pillars expand the interlayer spacing, enhance structural stability against swelling, and introduce additional catalytic functionality—such as photocatalysis from TiO_2 pillars. Integrating catalytically active phyllosilicate materials into membranes presents new opportunities to couple membrane transport with catalytic reaction processes in confined architectures.

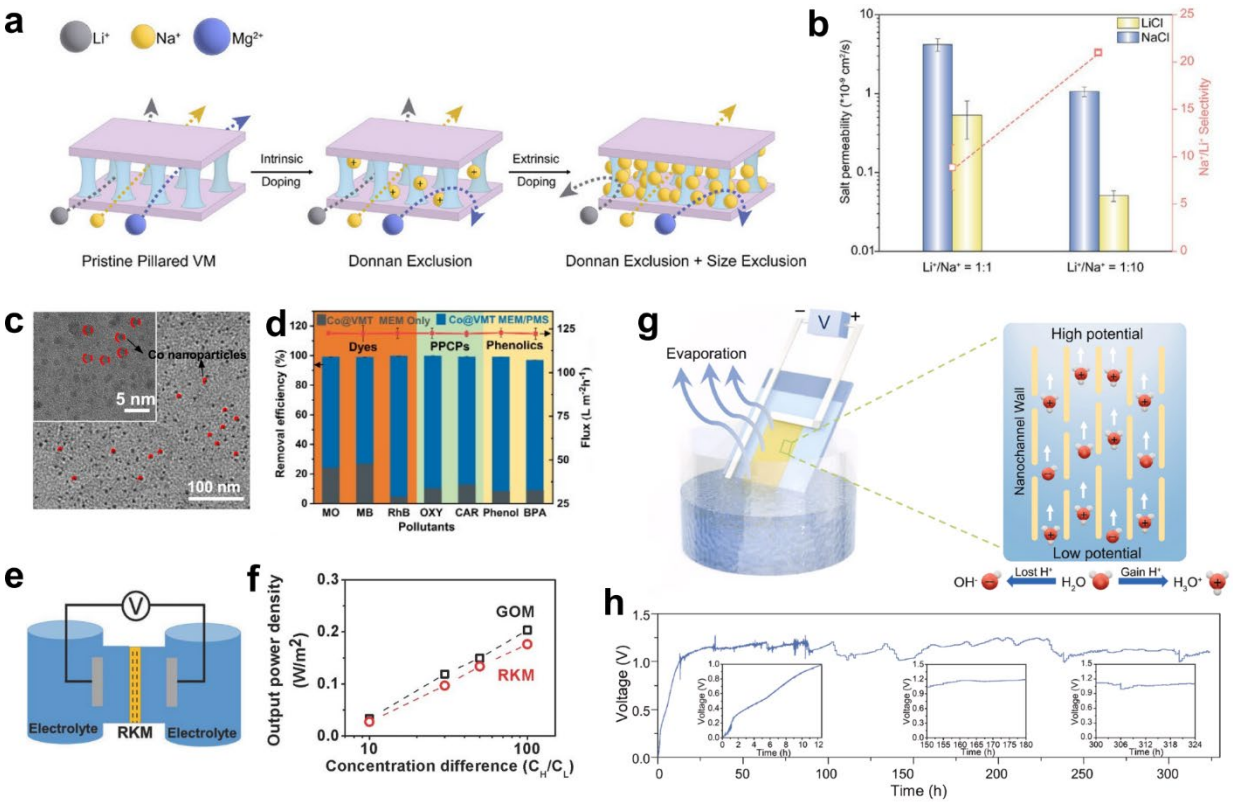

Figure 4. Phyllosilicate membranes in various applications. a) Schematic illustration of ion sieving mechanism and b) binary Na^+/Li^+ diffusion in doped pillared vermiculite membranes. a,b) Reproduced under the terms of the CC-BY-NC 4.0 license.[46] Copyright 2025, UChicago Argonne, LLC. Advanced Materials published by Wiley-VCH GmbH. c) HRTEM image of cobalt-functionalized vermiculite (Co@VMT) nanosheets and d) removal of different organic pollutants by fabricated Co@VMT membrane coupled with peroxymonosulfate. c,d) Reproduced under the terms of the CC BY 4.0 license without any changes.[55] Copyright 2024, The Author(s), published by Springer Nature. e) Experimental setup schematic of voltage-driven ionic transport through reconstructed kaolinite membrane (RKM) and f) its osmotic power generation compared with graphene-oxide membranes (GOM). e) f) Reproduced with permission.[32] Copyright 2017, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. g) Schematic illustration of a vermiculite-based nanofluidic device for water evaporation-induced electricity generation and h) measured voltage-time curve for continuous voltage output. g) h) Reproduced with permission.[89] Copyright 2025, Elsevier.

4. Outlook for the Future

4.1. Future Innovations in Membrane Technology using Phyllosilicate Minerals

Fully inorganic phyllosilicate membranes offer significant potential advantages for organic solvent nanofiltration (OSN) applications. Conventional polymeric membranes often suffer from poor chemical stability in harsh organic solvents. For instance, traditional polymers such as cellulose, nylon, and PVDF are prone to dissolution or swelling in polar aprotic solvents like N,N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO).[101] By contrast, phyllosilicate membranes, owing to their fully inorganic layered structures, offer exceptional stability and resistance to chemical attack, even under aggressive solvent conditions.[40] Additionally, they offer an anticipated cost advantage over traditional ceramic membranes, which, although highly stable, are typically expensive to fabricate due to the need for high-temperature processing. For instance, the price of commercial alumina ceramic membranes typically ranges from $500 to $1,000 per m^2.[102] In contrast, the cost of phyllosilicate raw materials is negligible. For example, montmorillonite averages only $97 per ton on the commodity market,[103] and requires minimal processing under mild conditions for membrane fabrication.

Beyond their potential application in OSN, another intriguing aspect of phyllosilicate membranes is the opportunity to explore their intrinsic selectivity. Different degrees of isomorphic substitution can result in varying layer charge densities within the same phyllosilicate.[104] Moreover, different phyllosilicate types naturally possess distinct interlayer cations, which can further influence molecular transport and separation behavior. For example, magnesium ions predominantly occupy the interlayer spaces of vermiculite, whereas sodium and calcium ions are more common in montmorillonite. Such specific cation affinities have been observed even after material reconstruction, suggesting a strong link to surface structural features, such as the chemistry and geometry of siloxane rings that create cavities within the layers.[30] Importantly, the large number of phyllosilicate minerals and their distinct characteristics in molecular transport is only the first building block of membrane composition. Varying the membrane thickness and using different cross-linking agents, dopants, and surface functionalizing molecules each add another layer of parameter space to further fine-tune the transport properties. By effectively exploring the high-dimensional chemical and structural space of phyllosilicate membranes, one can realize cost-

effective, highly specific, and customizable production of "designer membranes" tailored for specific applications. High-throughput automated experimentation combined with machine learning will help navigate this vast design space to accelerate the development of next-generation phyllosilicate-based membranes. Emerging approaches like inverse design,[105] where desired membrane properties guide the selection of specific mineral chemistries and fabrication parameters, could further streamline the on-demand production of membranes tailored precisely for specific applications.

Another emerging research direction is the integration of phyllosilicates with other 2D materials to achieve synergistic properties. MXenes are one such family of 2D materials that may benefit from integration into phyllosilicate hybrid membranes. Pristine MXene membranes have numerous desirable properties, including good selectivity for several ion separations (including the removal of heavy metals and large molecules), excellent conductivity, high mechanical strength, and reported performance enhancement in sunlight due to the photothermal effect.[106-108] However, they suffer from stability issues over long time scales due to hydrolysis and oxidation, and the tendency of MXene nanochannels to swell in the presence of water can limit separation effectiveness.[109-111] Hybrid membranes fabricated using both phyllosilicate and MXene flakes (as well as crosslinkers) could leverage the conductivity and mechanical advantages of MXene while retaining the water stability and well-controlled interlayer spacing of phyllosilicates. Hybrid phyllosilicate membranes incorporating other 2D materials are also attractive. For instance, phyllosilicates could benefit from the high water permeability and monovalent salt rejection capability of graphene oxide[112], or from transition metal dichalcogenides' suitability for functionalization and pore size engineering[63]. Any type of 2D-material-based hybrid membrane would also benefit from the low cost and environmental compatibility of phyllosilicates.

4.2. Current Challenges with Phyllosilicate Membranes

While significant progress has been made throughout the last decade, achieving stable and tunable surface chemistry in phyllosilicate membranes with a diverse library of moieties remains a challenge. In contrast to other non-swelling two-dimensional materials, phyllosilicate membranes without crosslinkers often exhibit poor water stability due to their hydrophilic surfaces and weak

interlamellar binding. As a result, surface functionalization strategies commonly employed to tune membrane transport properties in other 2D materials do not necessarily lead to the formation of stable channels in phyllosilicate membranes. To date, most strategies for modifying the 2D interlayer spaces of phyllosilicates have relied on intercalation through van der Waals or electrostatic interactions, as commonly seen in organoclays. However, these approaches often fail to eliminate swelling behavior and can significantly reduce permeate flux.[42, 113] Although silanization has been widely applied for the functionalization of silicate surfaces, the majority of the hydroxyl groups in phyllosilicates are located on flake edges or beneath the basal planes that are inaccessible, leading to limited functionalization density.[58] Future work therefore should focus on exploring new chemistries or mechanisms that enable stable and direct functionalization of phyllosilicate surfaces, improving structural stability and chemical affinity to enhance the membrane selectivity, lifetime, and overall performance.

In addition, like many other 2D materials, phyllosilicates tend to be more brittle than polymers due to their limited flexibility and layered structure, making them more susceptible to fracture under stress. Future research could address this limitation by exploring alternative separation driving forces, such as electrodialysis, which imposes lower mechanical stress, or by developing composite membranes that combine the molecular/ion selectivity of phyllosilicates with enhanced mechanical robustness.

Another challenge with phyllosilicate membranes is the purity of the raw precursor materials. Naturally sourced minerals often contain contaminants or foreign materials, which introduce significant complexity into the membrane system and increase batch-to-batch variation. For quality control and reproducibility, more effort towards developing scalable and cost-effective purification methods will be necessary. A common purification process involves two main steps: (i) removal of unwanted components through physical or chemical treatments, such as the decomposition of carbonates, and (ii) sedimentation-based fractionation to eliminate coarse impurities (e.g., quartz) that may be trapped within non-exfoliated phyllosilicate aggregates.[114] While complete purification processes can be time-consuming, standardized purification protocols can be developed tailored to specific phyllosilicate types to perform efficient enrichment processes at an industrial scale. For instance, oxidation treatments for organic contaminants might not be

necessary for phyllosilicates from geological sources like bentonites or kaolins, which often contain minimal organic materials. Alternatively, membrane design strategies could incorporate a higher tolerance for variations in source material purity, reducing the need for stringent purification without compromising membrane performance. For example, blending strategies can be used to mix materials from multiple sources to reduce batch-to-batch variability. Buffer stocks of high-quality sources or high purity synthetic phyllosilicate produced via hydrothermal synthesis can be used for blending.[115]

Demonstration of scaled up processing and manufacturing will be critical for assessing the technological viability of these materials. Conventional fabrication strategies, including vacuum filtration, are inherently low-throughput and often require handling of large liquid volumes. Formulation of precursors and process optimization for more scalable and high-throughput fabrication techniques such as dip coating, blade coating, and slot-die coating should be further explored to improve uniformity and reproducibility of phyllosilicate membranes in scaled-up production. The development of high-throughput automated membrane testing platforms, potentially in combination with machine learning, is also an attractive strategy for accelerating the exploration of the complex compositional/structural design space of phyllosilicate membranes.

Furthermore, scale-up development must move beyond small, flat-sheet formats to transition phyllosilicate membranes from laboratory research to real-world applications. Module-scale fabrication will be necessary to integrate phyllosilicate membranes into commercially viable systems. Large-area and high-speed solution coating techniques such as dip coating, slot-die coating, and spray coating are compatible with roll-to-roll (R2R) manufacturing systems. In R2R processing, thin film structures are continuously deposited onto a flexible web moving at a constant speed between rotating rollers. Coating methods developed during early scale-up efforts can be integrated with additional fabrication steps (e.g., drying and annealing) within the R2R system. This transition from batch processing to continuous fabrication enables phyllosilicate membranes to be produced in a moving roll format, substantially increasing production speed and scalability suitable for industrial scale production. Future research should also investigate operational models benefiting from the low cost of phyllosilicates. For example, membranes could be periodically replaced to maintain optimal performance without requiring extensive regeneration processes;

recycling and waste treatment protocols for phyllosilicate membranes is another potential research focus.

4.3. Integration of Phyllosilicate Membranes with Emerging Technologies

Phyllosilicate membranes hold great potential as multifunctional components in a wide range of emerging technologies. For example, phyllosilicate laminates have been already adapted for various critical roles in next-generation energy storage technologies.[116-118] Specifically, phyllosilicates have been gaining interest as alternative lithium hosts in Li-ion battery electrodes. Their hydrophilic surfaces and low energy barriers for Li-ion diffusion, combined with tunable interlayer spacing, offer high specific surface area and support rapid Li^+ transport. Various phyllosilicate minerals such as montmorillonite,[119] vermiculite,[120-121] and saponite[122] have been fabricated into laminar membranes, demonstrating promising Li^+ transport performance even under challenging conditions such as high sulfur content.

Additionally, phyllosilicates' ion-selective pathways have enabled their use as separators in lithium-sulfur batteries. The surface charge of phyllosilicate membranes helps hinder the diffusion of polysulfides between electrodes while promoting fast Li transport.[123-124] High in-plane proton conductivity observed in vermiculite and montmorillonite membranes also highlights their potential as alternative proton exchange membranes for fuel cells.[29, 125] Furthermore, 2D phyllosilicate nanosheets show promise as components in composite electrolyte membranes. [126-130] Their superior ionic conductivity, thermal stability, and mechanical rigidity compared to polymer counterparts can contribute to improving the performance and safety of electrolyte membranes.

Beyond energy applications, phyllosilicate membranes could play transformative roles in many other emerging technologies. In the field of next-generation electronics, phyllosilicates' dielectric properties, channel tunability, and non-toxicity make them attractive and cost-efficient candidates for soft substrates in flexible and wearable electronic devices. Polymers can serve as flexible linkers, while phyllosilicate sheets boast high mechanical strength and thermal stability.[131] Moreover, as they are considered to be nontoxic and non-irritant materials, phyllosilicate

membranes offer valuable benefits in biotechnology. Their high surface area, tunable nanochannel charge and size, and biocompatibility make them good candidates for alternative drug delivery systems.[132] Also, phyllosilicate minerals are known to have blood-clotting properties,[133] making them suitable for skin tissue engineering applications.[134]

The environmental compatibility and abundance of phyllosilicate membranes further position them as sustainable alternatives for agriculture technologies. Previous studies have demonstrated phyllosilicate minerals' potential in this field.[135] For example, potassium-bearing phyllosilicate minerals have been used to treat potassium deficiency in soil, serving as sustainable alternatives to conventional fertilizers.[136] Phyllosilicates' absorption properties for pollution control, such as the uptake of heavy metals from contaminated soil, have also been reported.[137-138] These properties can be leveraged to develop phyllosilicate membranes for agricultural applications (for instance, permeable barriers to prevent contaminant leaching while also enriching soil), offering environmental benefits for the future.

5. Conclusion

Building on a long history of clay research, recent advances in using exfoliated phyllosilicates for 2D laminar membranes suggest their unique and promising opportunities for advancing membrane technologies. Early demonstrations of their critical roles in various membrane applications, such as direct separations and energy conversion, illustrate the importance of phyllosilicate minerals as 2D materials for laminar membranes. The inorganic nature of phyllosilicate membranes offers unique advantages for OSN applications, while their naturally occurring rich material library combined with interlayer gallery tuning strategies enable highly customizable membrane design for ion transport and separations at a low cost. By bridging the gap between laboratory-scale discovery and large-scale applications, phyllosilicate membrane systems have the potential to provide on-demand membrane solutions for various industries. Several challenges remain for phyllosilicate membranes, including achieving stable surface chemistry via novel functionalization strategies, improving mechanical robustness, and handling impurities in raw materials. Addressing those challenges will lead to future innovations in membrane technologies and improve our understanding of fundamental molecular-level interactions that govern membrane selectivity in

layered materials. Phyllosilicates offer a pathway to the next generation of high-performance, cost-efficient, and environmentally friendly membrane systems.

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Conflict of Interest Statement

The authors declare no conflict of interest.

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The table of contents entry:

Recent advancements in membrane technologies based on two-dimensional (2D) materials have drawn attention for molecular-scale separations owing to these materials' tunable nanoscale interlayer properties. Phyllosilicates, natural and abundant layered clay minerals, have emerged as scalable and cost-effective candidates. This work explores recent developments related to phyllosilicate membranes, including strategies to tailor selective transport pathways, novel applications, challenges, and future directions.

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Clay Reimagined: Phyllosilicates as Future Membrane Technologies

ToC figure