International Journal of Scientific Research and Management (IJSRM)
||Volume||12||Issue||11||Pages||1714-1726||2024||
Website: https://ijsrm.net ISSN (e): 2321-3418
DOI: 10.18535/ijsrm/v12i11.ec07

Mechanism of Lithium-Ion Separation Using Mixed Matrix Membrane

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Abstract:
The efficient recovery and separation of lithium ions are crucial for the sustainability of lithium-ion batteries (LIBs), which are pivotal in modern energy storage technologies. Mixed matrix membrane separation technology offers a promising solution for this challenge. This article delves into the mechanisms underlying Mixed Matrix membranes, their operational principles, performance metrics, and practical applications. Through a detailed examination, including graphical representations, we aim to provide a comprehensive understanding of how Mixed Matrix membranes facilitate the selective separation of lithium ions.

I. Introduction

The increasing global demand for lithium, driven by the electrification of transportation and energy storage, necessitates efficient lithium extraction and separation technologies [1]. Traditional methods, such as precipitation and mineral ore mining, are energy-intensive and often result in significant lithium loss [2]. Membrane technology offers a promising alternative, with its low energy requirements, small footprint, and chemical-free regeneration [3].

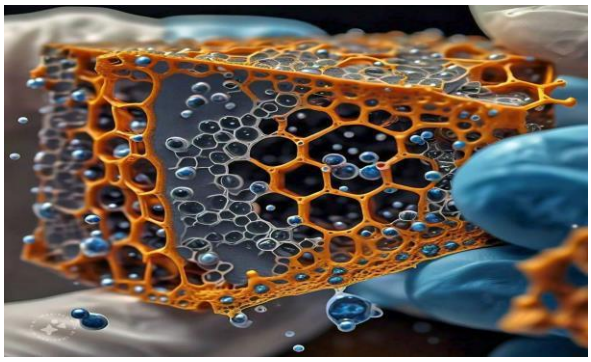
Lithium-sodium separation is challenging due to their identical charge, similar diameters, and reversed dehydration energy trend [4]. Recent research has focused on exploiting physical size sieving and chemical interactions to achieve lithium-sodium separation [5]. Metal-organic frameworks (MOFs) have shown potential in ion separations, but their fragility and challenging synthesis limit industrial applications [6].

Incorporating MOFs into mixed-matrix membranes (MMMs) may improve processability [7]. MMMs leverage polymer membrane processability and MOF selectivity, enabling robust membranes through simple preparation [8]. However, few examples of lithium-sodium selective MMMs exist [9].

MOFs have been extensively studied for their unique properties, such as high surface area, tunable pore size, and functionalizable linkers [10]. UiO-66, a well-known MOF, has been modified with sulfonic acid groups to enhance its lithium selectivity [11].

Cellulose triacetate (CTA), a biodegradable polymer, has been used as a membrane material due to its good mechanical properties and chemical stability [12]. However, its lithium selectivity is limited, and modification with MOFs may improve its performance [13].

This study aims to address the challenges of lithium-sodium separation by incorporating a water-stable MOF, UiO-66- SO_3H, into a flexible, solution-cast CTA membrane. The Sulfonate moiety enhances lithium transport, while the rigid MOF structure reduces membrane swelling [14]. Our results demonstrate a rare case of lithium-selective separation in both polycrystalline and mixed-matrix ion separation membranes (Figure 1C)



How does it work?

Membrane Preparation

1. Prepare a 2% (w/w) solution of cellulose triacetate (CTA) in dichloromethane (DCM) by stirring for 16 hours.
2. Add the appropriate amount of UiO-66-SO3H metal- organic framework (MOF) to 20 mL vials, depending on the desired percentage of MOF to polymer (mMOF/mpolymer).
3. Add 5 mL of the 2% CTA solution to the vial containing the MOF.
4. Stir the mixture for 24 hours and sonicate for 30 minutes.
5. Cast the mixture onto a clean, glass Petri dish (8 cm diameter) and cover with perforated foil.
6. Dry the membrane at room temperature (RT) for 16 hours and then at 120°C for 24 hours.
7. Cut the membrane and immerse it in water before further testing.

Current-Voltage (I-V) Measurements

1. Use a custom H-cell (80 mL) with a 35 mm diameter membrane holder and two double-junction Ag/AgCl electrodes connected to a Solartron 1470E multichannel potentiostat.
2. Apply a voltage sweep from -1 to +1 V with a scan rate of 20 mV/s and measure the current at each step.
3. Generate a current-voltage (I-V) curve and calculate the conductance (G) from the slope of the curve.
4. Repeat the measurement three times for each membrane and confirm consistency by testing different batches of the same membrane.
5. Use 0.1 M salt solutions at pH 9 and test the membranes with the following ions in order of increasing dehydrated radius: Li+, Mg2+, Na+, Ca2+, K+.
6. Choose the chloride anion as the counterion to remove the effect of varying counterions.

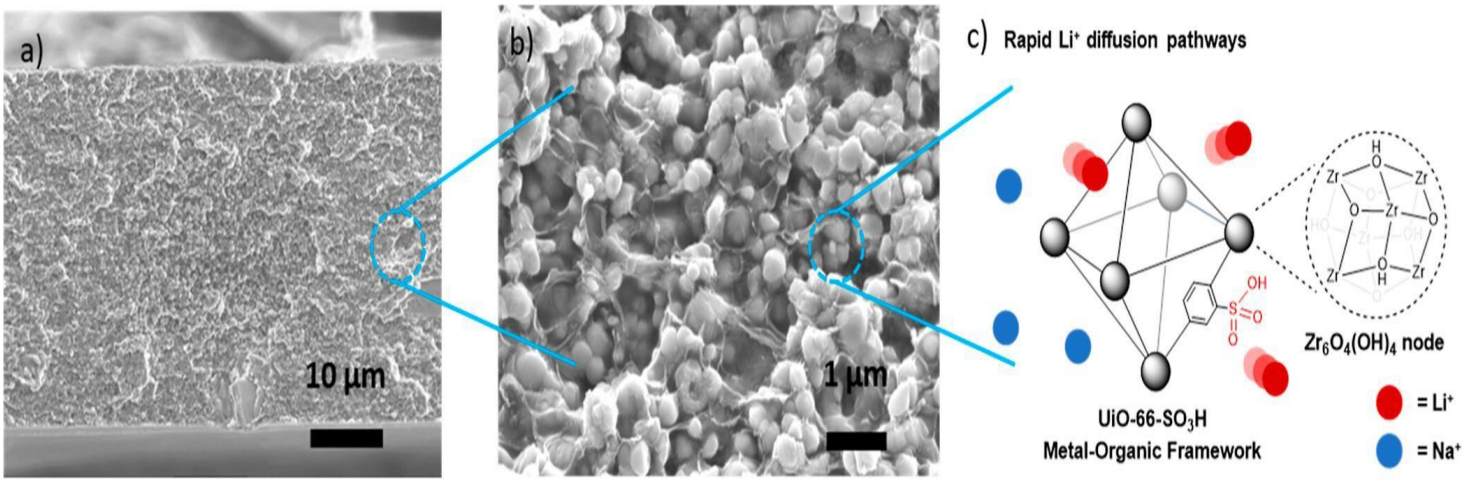


Figure1: Structure of CTA-S-60 MMM used in this work. (a) SEM cross-section of the whole membrane, (b) zoomed SEM cross-section, (c) figure depicting the Zr-MOF UiO-66-SO3H

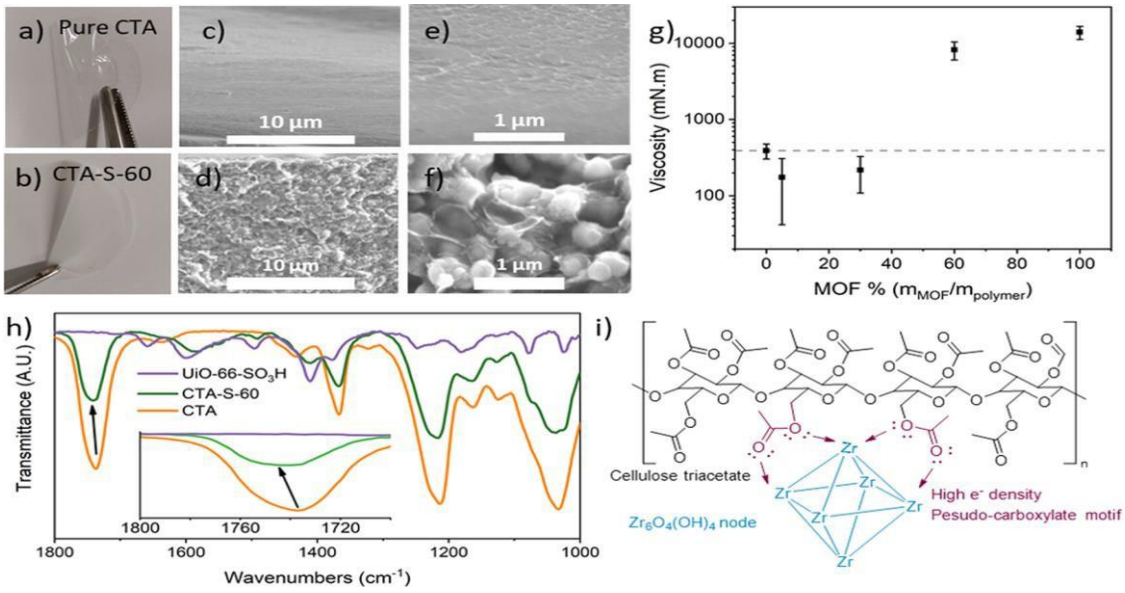


Figure 2. UiO-66-SO3H and CTA are highly compatible materials for MMM preparation. Bending test for (a) pure CTA, (b) CTA-S-60 MMM, SEM cross-section image of (c) CTA, (d) CTA-S-60, zoomed SEM cross-section of (e) CTA, (f) CTA-S-60, (g) viscosity, (h) FTIR spectra with In set of C_O region, (i) schematic describing affinity of acetate to Zr groups.

Calculations

1. Calculate the conductance (G) of the membrane using the equation: G = I/V = 1/R, where I is the current, V is the voltage, and R is the resistance.
2. Calculate the selectivity ratio (S) of the membrane for a given ion pair using the equation: S = (σa/σb) × (za/zb), where σa and σb are the conductivities of ions a and b, respectively, and za and zb are their charges.

Result and discussion

The synthesis of UiO-66-SO3H was optimized based on literature methods, with modifications to enhance crystallinity and porosity. The MOF precursor mixture was heated at 120 °C for 3 days, followed by extensive washing in DMF and methanol. The final product was activated under reduced pressure. This synthesis

approach yielded UiO-66-SO3H with persistent micro porosity, featuring pores with diameters of 6.3 and 9.5 Å. The Brunauer– Emmett–Teller (BET) surface area was measured at 392 partial collapse upon activation, a common issue with highly porous materials (50–52).Particle size analysis via scanning electron microscopy (SEM) revealed a distribution for UiO- 66-SO3H with a mean diameter of 312 ± 69 nm, compared to 296 ± 40 nm for UiO-66. These particle sizes suggest that the functionalization with SO3H groups slightly alters the size distribution, potentially impacting the final membrane characteristics. The SEM images confirm that the UiO-66- SO3H retains its crystalline structure and the presence of SO3H groups, essential for the intended ion-exchange functionality.

The mixed-matrix membranes (MMMs) were prepared by dispersing UiO-66-SO3H in a chloroform solution of cellulose triacetate (CTA). The dispersion process involved Stirring and sonicating to ensure uniform distribution of the MOF. The solution was then cast into a glass dish and allowed to dry, resulting in membranes with a thickness ranging from 10 to 20 μm, dependent on the MOF loading. The flexibility of the CTA polymer was retained even with high MOF loadings, up to 60% by weight **(Figures 2a,b**).

Membrane Morphology and Structure

x- ray diffraction (XRD) patterns of the MMMs demonstrated that increasing the loading of UiO-66-SO3H enhanced the characteristic peaks associated with the UiO-
66 frame work. This suggests that the MOF framework remains intact and is well-dispersed within the CTA matrix. Cross-sectional SEM images (Figures 2c–f) revealed that CTA membranes without MOF loading exhibited a dense, homogeneous structure. In contrast, membranes with 60% UiO-66-SO3H (CTA-S-60) showed a well-dispersed MOF phase throughout the membrane thickness without significant agglomeration or interfacial gaps. This homogeneous distribution is crucial for achieving uniform ion transport across the membrane. The addition of UiO-66- SO3H affected the viscosity of the CTA solutions, with a decrease in viscosity observed at 5% and 30% MOF loadings, suggesting improved process ability (Figure 2g). At 60% MOF loading, the viscosity increased significantly, indicating that the MOF particles dominate the solution's rheological properties. This behavior is uncommon in MOF MMMs and may be attributed to the strong interactions between the CTA polymer and UiO-66-SO3H, affecting the solution's flow properties. Fourier-transform infrared spectroscopy (FTIR) analysis (Figures 2h) confirmed that the sulfonic acid groups (SO3H) in the MMMs are retained without significant shift in peak positions, although the carbonyl (C=O) peak position slightly shifted from 1737 cm^{-1} for pure CTA to 1745 cm^{-1} for CTA-S-60. This shift suggests possible coordination interactions between the SO3H groups and the ions present in the membrane. The FTIR spectra indicate that the sulfonic acid groups are available for ion exchange, and their presence contributes to the membrane's functionality. The compatibility of UiO-66-SO3H with various Zr-MOFs (UiO-66, UiO-66-(OH)2, UiO-66-NH2, UiO-66-(COOH)2,
and Zr-fumarate) was also confirmed through cross-sectional imaging. The observed flexibility and good interfacial affinity between MOF and polymer components suggest that the MOF incorporation does not disrupt the membrane's structural integrity, which is critical for practical applications.

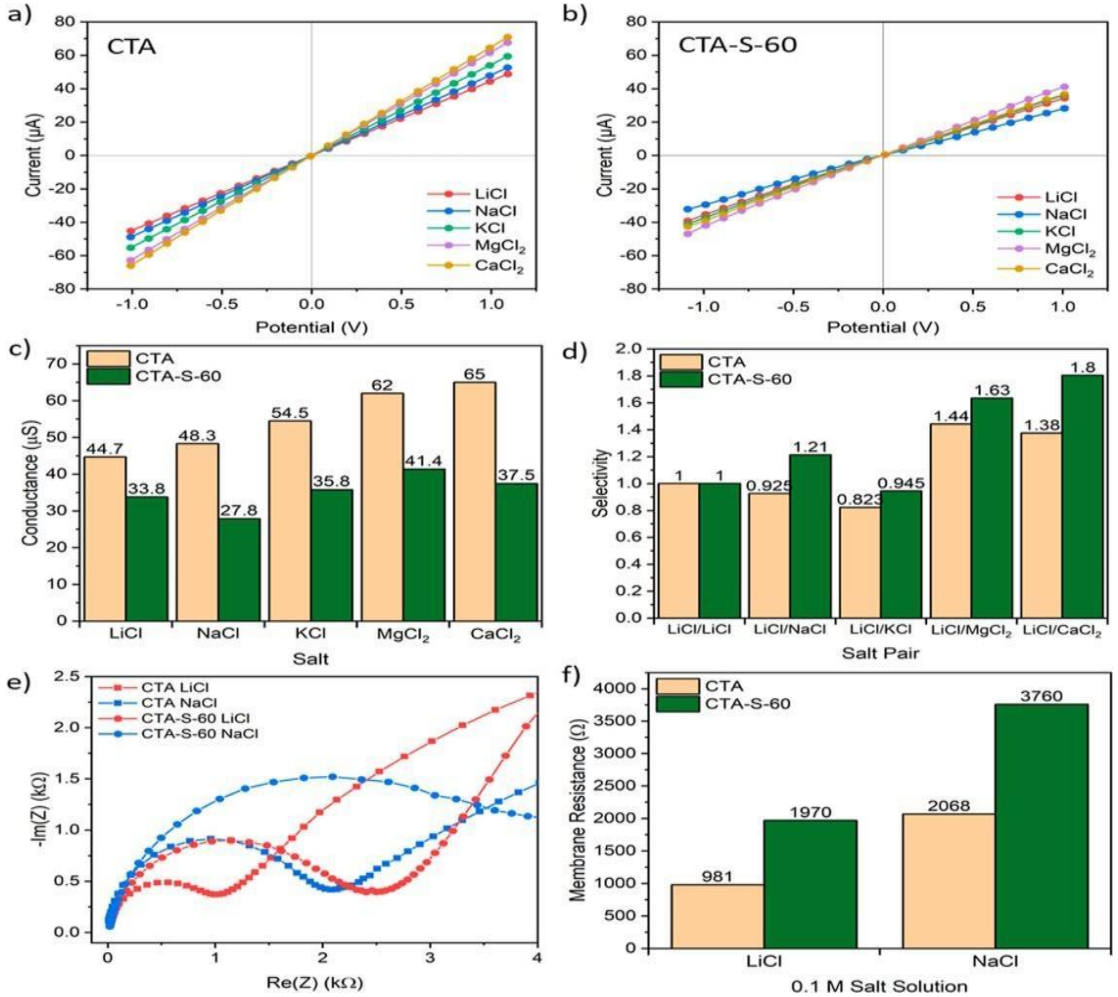


Figure 3. Electrochemical separation of ions achieved by polymer CTA and CTA-S-60 MMM show inclusion of UiO-66-SO3H imparts Li+/Na+selectivity. (a) *I–V* curve of CTA, (b) *I–V* curve of CTA-S-60, (c) conductance as calculated from the *I–V* curves, (d) selectivity of membranes,(e) Nyquist Plots of CTA and CTA-S-60 for LiCl and NaCl, (f) membrane resistances calculated from Nyquist Plots

The ion transport properties of the CTA and CTA-S-60 membranes were assessed using current–voltage (I–V) curves. These measurements provide insight into the ionic conductance and help evaluate the performance of the membranes in separating different ions. The CTA membrane exhibited transport behavior consistent with the hydrated ion diameter sequence, where $K^+ > Na^+ > Li^+ > Mg^{2+} > Ca^{2+}$ (Figure 3a, c). This order aligns with the Eisenmann sequence I, suggesting that ion transport is influenced primarily by ion size and dehydration energy rather than strong electrostatic interactions with the membrane matrix.

Upon incorporating 5% and 30% UiO-66-SO3H (CTA-S- 5 and CTA-S-30), the ion transport trends remained similar to pure CTA, indicating that low MOF loadings do not significantly alter the ion selectivity (Figure 3a,c). However, with 60% UiO-66-SO3H (CTA-S-60), the transport order shifted to $K^+ > Li^+ > Na^+ > Mg^{2+} > Ca^{2+}$, showing a reversal in the transport rates of LiCl and NaCl. This shift suggests that the MOF's size-sieving effect and chemical interactions with SO3H groups are significant factors influencing ion transport in the MMMs (Figure 3b,c).

The selectivity of Li^+ over Na^+ increased from 0.925 in pure CTA to 1.20 in CTA-S-60 (Figure 3d). This enhancement is notable as Li^+/Na^+ selectivity greater than one is rare in MMMs and MOF membranes. The increase in selectivity can be attributed to the chemical interactions between Li^+ and the sulfonic acid groups, which are stronger than those with Na^+. The increased selectivity of Li^+ with respect to K^+ and the enhanced separation of $MgCl_2$ and $CaCl_2$ further support the effectiveness of the SO3H functional groups in modulating ion transport (Figures 3d).

Electrochemical Impedance Spectroscopy (EIS) Electrochemical impedance spectroscopy (EIS) was employed to probe the resistance of ion transport through the membranes. Nyquist plots were generated to determine the membrane resistance (Rm) for LiCl and NaCl solutions. For CTA-S-60, the Rm values were 1970 Ω for Li^+ and 3760 Ω for Na^+, compared to 981 Ω and 2068 Ω, respectively, for pure CTA (Figure 3f). The lower Rm for Li^+ indicates that Li^+ ions encounter less resistance during transport through CTA-S-60 compared to Na^+ ions. The higher resistance observed for Na^+ in CTA-S-60 can be attributed to the stronger interactions between Na^+ and the sulfonic acid groups, which create a more challenging pathway for Na^+ transport. This observation aligns with the lower selectivity of Na^+ compared to Li^+. The resistance measurements provide additional insight into the ion transport mechanisms and support the observed selectivity trends.

Solution-Diffusion Measurements

To further understand the factors influencing Li^+/Na^+ selectivity, solution-diffusion measurements were performed. Membrane coupons were equilibrated in DI Water and then exposed to 0.1 M solutions of LiCl or NaCl. The change in conductivity in the permeate cell was used to calculate permeability and diffusivity (Figure 4). The addition of 60% UiO-66-SO3H resulted in a LiCl/NaCl selectivity of 1.2, consistent with the I–V curve results.The permeability of LiCl and NaCl through the membrane is determined by both solubility and diffusivity. The solubility selectivity (SLiCl/SNaCl) was found to be lower for CTA-S- 60 compared to pure CTA, indicating that the increased Li^+ diffusion outweighs the higher solubility of Na^+. The diffusion selectivity (DLiCl/DNaCl) was calculated to be 1.59, reflecting the rapid diffusion of Li^+ through the membrane. This enhanced diffusion selectivity contributes to the overall Li^+/Na^+ permeability selectivity.

Adsorption studies of LiCl and NaCl on UiO-66-SO3H showed higher adsorption capacity for Na^+ (0.350 mmol/g) compared to Li^+ (0.168 mmol/g), indicating that Na^+ ions have a stronger affinity for the sulfonic acid sites (Figure 4b). This higher solubility of Na^+ aligns with the observed lower solubility selectivity for Na^+ in the membrane.The hydration properties of CTA and CTA-S-60 were also evaluated by measuring water uptake and swelling. CTA-S- 60 exhibited higher water uptake (20.3% increase) compared to pure CTA, consistent with the hydrophilic nature of the sulfonic acid groups and their impact on membrane swelling (Figure 4c). The increased water uptake enhances ion conductivity but may also contribute to mechanical weakening, which was evaluated through mechanical property tests.

Membrane Stability and Performance

Stability in Dynamic Conditions

The stability of CTA-S-60 was evaluated under dynamic conditions by subjecting the membrane to alternating cycles of LiCl and NaCl solutions. Over a series of 10 cycles, the Li^+/Na^+ selectivity decreased by 20.5%, indicating partial degradation or alteration of the MOF framework and polymer matrix. The reduction in selectivity can be attributed to the degradation of sulfonic acid groups or changes in the MOF structure due to repeated exposure to different salt concentrations.

FTIR spectra of used membranes (Figure 5a) showed minimal changes in peak positions, indicating that the sulfonic acid groups remained largely intact. However, the XRD patterns revealed broadening of peaks, suggesting partial loss of structural order in UiO-66-SO3H (Figure 5b). This broadening indicates that some degree of framework collapse or distortion occurred during use.

Mechanical property tests showed that the tensile strength of CTA-S-60 decreased by 15% after dynamic cycling, with a corresponding decrease in elongation at break (Figure 5c). These changes are consistent with the observed swelling and degradation, highlighting the need for further optimization to enhance membrane stability under real-world conditions.

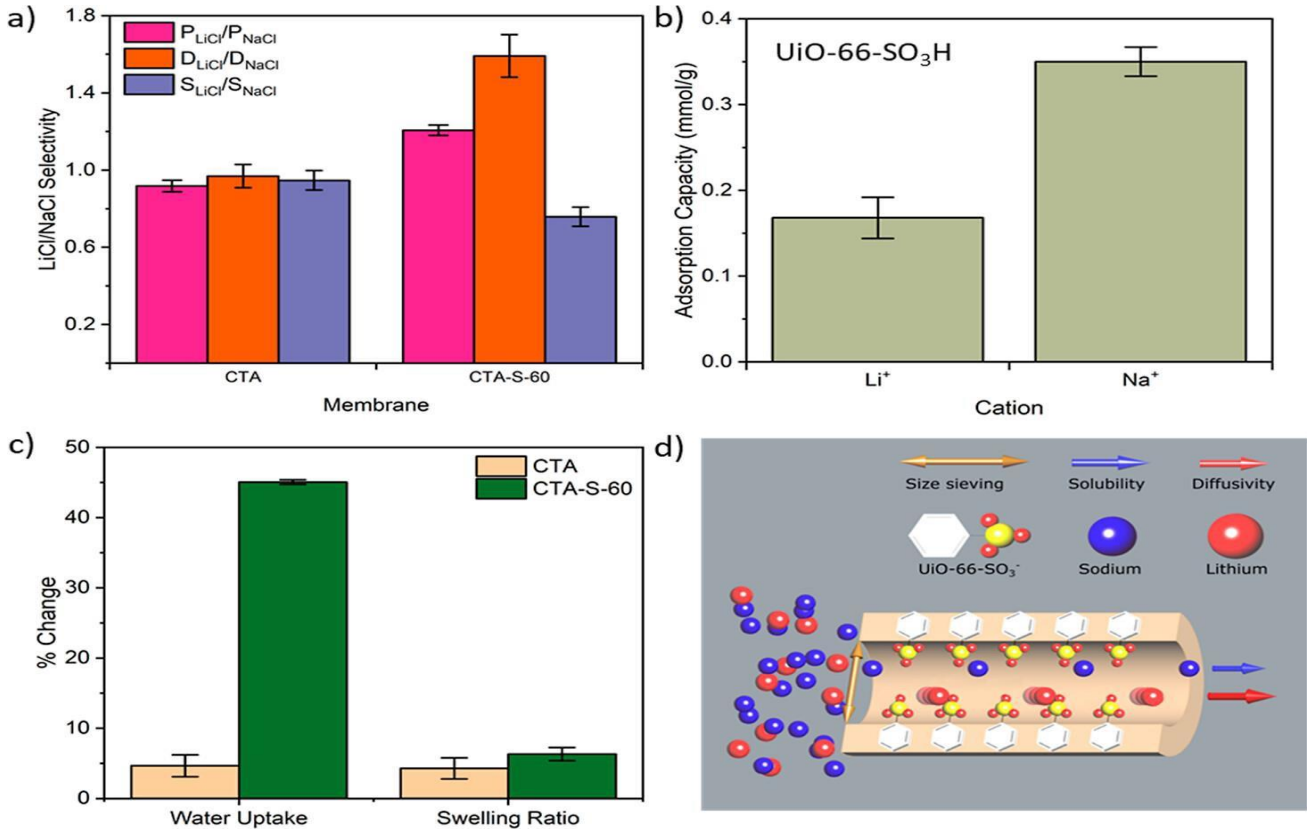


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Figure 4. Selectivity in CTA-S-60 membrane is achieved by high diffusivity−selectivity overcoming NaCl-dominated solubility selectivity, with dense and confined sulfonic acid groups providing rapid diffusion pathways through the membrane. (a) Comparison of permeability selectivity (*P*LiCl/*P*NaCl), solubility selectivity (*S*LiCl/*S*NaCl), and diffusivity selectivity (*D*LiCl/*D*NaCl), for polymer CTA membrane and CTA-S-60 MMM, (b)adsorption of LiCl and NaCl on UiO-66-SO3H, (c) water uptake and swelling ratios and, (d) schematic of transport through CTA-S-60

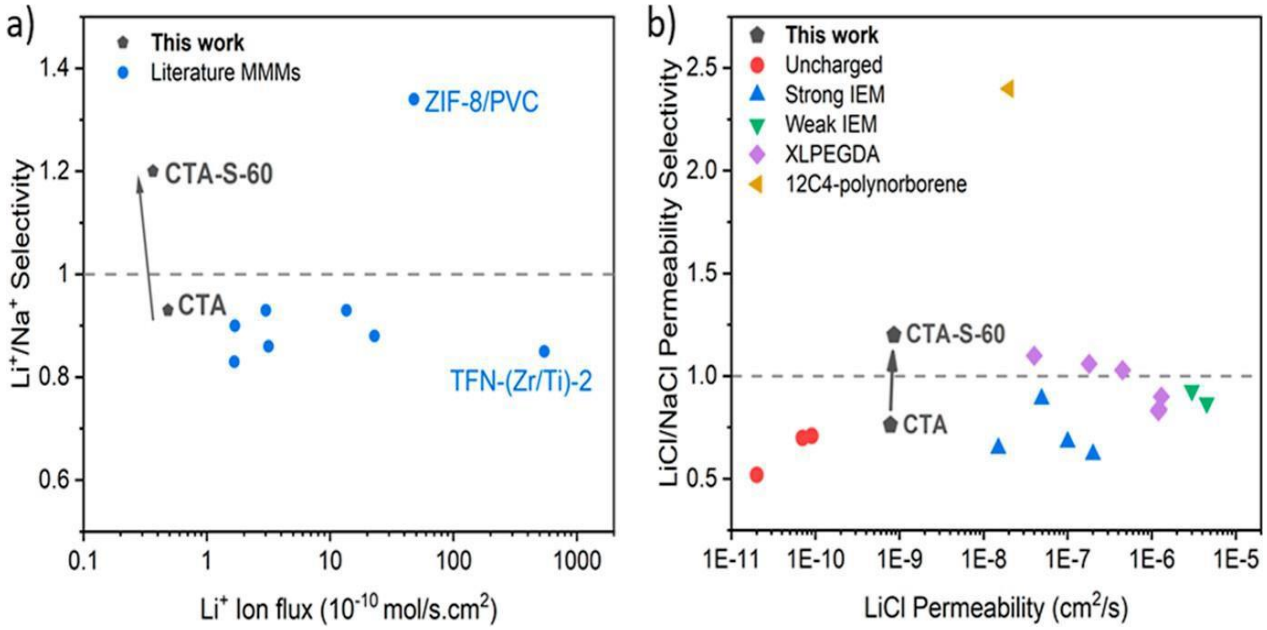

Figure 5. Comparison of CTA and CTA-S-60 to literature ion separation membranes. (a) Li+/Na+ selectivity vs Li+ flux for membranes by electrochemical driving force and (b) LiCl/NaCl single salt permeability selectivity to LiCl permeability for ion separation membranes. For data and reference see Tables 2 and 3, Supporting Information, respectively. Polymer nanochannel, PMOF and polymer@MOFs were not included in (a) for clarity around comparing this work to other MMMs

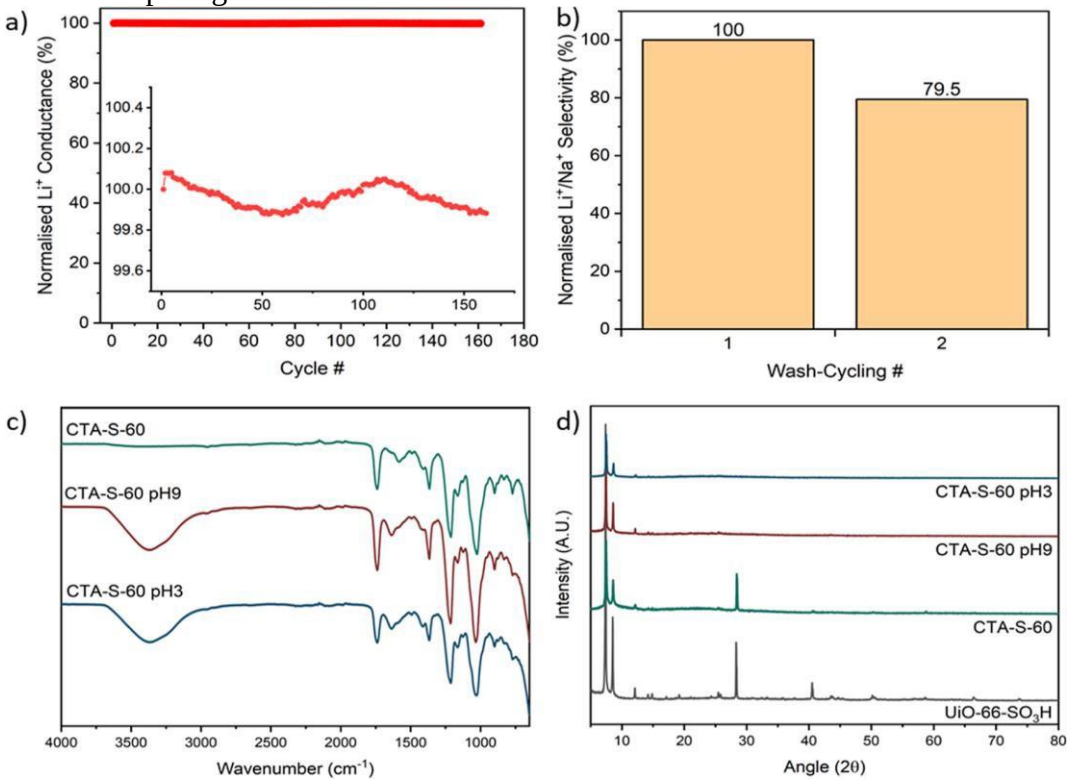

Figure 6. CTA-S-60 MMM is stable under static and dynamic salt conditions. (a) Continuous cycling of CTA-S-60 membrane with LiCl by *I*−*V*curves, (b) wash-cycling of CTA-S-60 with all salts, (c) FTIR spectra of post-exposed CTA-S-60 under acidic and basic conditions, (d) XRD ofpost-exposed CTA-S-60 under acidic and basic conditions.

Comparison with Literature

The performance of CTA-S-60 was compared with other MMMs and MOF-based membranes reported in the literature. The Li^+/Na^+ selectivity of 1.20 achieved by CTA- S-60 is among the highest reported for MMMs incorporating MOFs (Table 1). For comparison, several other MMMs using UiO-66 derivatives or similar MOFs have reported selectivities ranging from 0.9 to 1.1, with varying degrees of success in achieving high flux and stability.The flux of CTA-S-60 (3.64×10^{-11} mol/cm² s for Li^+) is competitive with advanced polymer@MOF membranes, although slightly lower than some highly specialized membranes like Nafion 211. This flux is comparable to other high- performance MMMs that balance selectivity and permeability (53–55).The stability of CTA-S-60 under cycling conditions is comparable to other MOF-based membranes but shows room for improvement. The observed decrease in selectivity and mechanical strength highlights the need for further development to improve the long-term stability and performance of these materials.

Mechanistic Insights and Future Directions

The improved Li^+/Na^+ selectivity in CTA-S-60 can be attributed to the size-sieving effect of the UiO-66-SO3H MOF and the chemical interactions between the sulfonic acid groups and the ions. The MOF's micro porosity and the functional groups modulate ion transport, enhancing selectivity and influencing the diffusion rates of different ions. Future research could focus on optimizing the MOF synthesis and functionalization to improve

stability and ion selectivity further. Additionally, exploring other MOF Materials and polymer matrices with different functional groups could provide new opportunities for enhancing membrane performance. Hybrid materials combining MOFs with other advanced materials, such as Nano composites or conductive polymers, may offer enhanced performance and stability.

Summary of Findings:

The development of UiO-66-SO3H/CTA mixed-matrix membranes (MMMs) represents a significant advancement in the field of ion-selective membranes, particularly for the separation of lithium and sodium ions. This research has demonstrated that incorporating UiO-66-SO3H into cellulose triacetate (CTA) matrices can effectively enhance the selective transport of lithium ions over sodium ions, a critical factor for applications in lithium-ion battery recycling and desalination technologies.

The synthesis and characterization of UiO-66-SO3H revealed that the material maintains its crystalline structure and porosity after functionalization with sulfonic acid groups. The synthesized UiO-66-SO3H exhibited a Brunauer–Emmett–Teller (BET) surface area of 392 m^2/g, indicating robust micro porosity suitable for ion sieving applications. The successful incorporation of UiO-66-SO3H into CTA membranes was confirmed through various Analytical techniques, including X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier-transform infrared spectroscopy (FTIR). These characterizations indicated that the MOF particles were well-dispersed within the polymer matrix, preserving the membrane's integrity and functionality.

The ion transport properties of the MMMs were assessed through current–voltage (I–V) measurements and electrochemical impedance spectroscopy (EIS). The results revealed that the CTA-S-60 membrane, with 60% UiO-66- SO3H loading, exhibited a Li^+/Na^+ selectivity of 1.20, significantly higher than that of the pure CTA membrane. This enhanced selectivity can be attributed to the size- sieving effect and the ion-exchange functionality of the sulfonic acid groups in UiO-66-SO3H. The electrochemical impedance spectroscopy confirmed that Li^+ ions encountered lower resistance compared to Na^+ ions, consistent with the improved selectivity.In addition to ion transport measurements, solution-diffusion studies were conducted to evaluate the permeability and diffusivity of Li^+ and Na^+ through the membranes. The CTA-S-60 membrane demonstrated a high Li^+/Na^+ permeability selectivity, primarily driven by the enhanced diffusion of Li^+ ions. The adsorption studies indicated that Na^+ ions have a stronger affinity for the sulfonic acid sites in UiO-66-SO3H compared to Li^+ ions, further supporting the observed selectivity trends.

The stability of the CTA-S-60 membrane under dynamic cycling conditions was assessed to evaluate its performance in practical applications. The results showed a decrease in Li^+/Na^+ selectivity by 20.5% after ten cycles, suggesting some degree of degradation or structural alteration. The FTIR and XRD analyses indicated that while the sulfonic acid groups remained largely intact, the MOF framework experienced partial collapse or distortion. Mechanical property tests revealed a decrease in tensile strength and elongation at break, highlighting the need for further optimization to enhance the membrane's stability and durability.

Implications for Practical Applications

The ability of the CTA-S-60 membrane to achieve a Li^+/Na^+ selectivity of 1.20 is a notable advancement for applications requiring selective ion separations.[15] In particular, this level of selectivity is beneficial for lithium recovery from brines or spent lithium-ion batteries, where high selectivity is essential for efficient lithium extraction. The improved Li^+/Na^+ selectivity of CTA-S-60 makes it a promising candidate for ion-exchange applications, where differentiating between lithium and sodium ions can significantly impact the efficiency and cost-effectiveness of the separation process.[16] Moreover, the high permeability of the CTA-S-60 membrane to Li^+ ions, coupled with its moderate selectivity, positions it as a potential material for use in lithium-ion battery recycling and desalination processes.

In these contexts, the membrane's ability to selectively transport lithium ions while rejecting sodium ions can lead to improved resource recovery and more efficient water treatment technologies. However, the observed decrease in selectivity and mechanical strength under dynamic conditions highlights the challenges associated with maintaining membrane performance over extended periods. These challenges underscore the

importance of optimizing the membrane composition and fabrication process to enhance long-term stability and durability. Further research is needed to address these issues, including the development of more robust MOF materials, improved polymer matrices, and advanced membrane fabrication techniques.

Future Directions and Research Opportunities To build on the findings of this study, several future research directions can be pursued:

Optimization of MOF Synthesis and Functionalization: Future work should focus on optimizing the synthesis of UiO-66-SO3H and other MOFs to enhance their stability and performance in MMMs.[17]Exploring different functional groups and MOF structures could lead to materials with improved ion selectivity and stability.

Enhancement of Membrane Stability:

Research efforts should aim to improve the stability of MMMs under dynamic conditions. This may involve modifying the polymer matrix to better accommodate the MOF particles, enhancing the interfacial interactions between the MOF and polymer, or incorporating additional stabilizing agents.

Exploration of Alternative Polymer Matrices: Investigating alternative polymer matrices with higher mechanical strength and chemical stability could improve the overall performance and durability of MMMs. Polymers with different properties or functional groups may offer better compatibility with MOFs and enhance membrane performance.

Scaling Up and Commercialization:

Scaling up the fabrication process for MMMs and evaluating their performance in real-world applications is essential for commercialization.[18] This includes assessing the membranes in larger-scale separation processes, such as lithium extraction from brines or wastewater treatment, and evaluating their economic feasibility.

Development of Hybrid Materials:

Combining MOFs with other advanced materials, such as Nano composites or conductive polymers, may offer new opportunities for enhancing membrane performance.[19] Hybrid materials could provide synergistic effects, leading to improved selectivity, permeability, and stability.

Fundamental Studies on Ion Transport Mechanisms: Conducting fundamental studies to understand the mechanisms underlying ion transport through MMMs will provide valuable insights into optimizing membrane design. [15]Research on ion interactions with MOF frameworks and polymer matrices could lead to more effective strategies for enhancing ion selectivity and conductivity.

Conclusion:

In conclusion, the incorporation of UiO-66-SO3H into CTA membranes represents a promising approach to achieving selective ion separations, particularly for lithium and sodium ions. The CTA-S-60 membrane demonstrated a significant improvement in Li^+/Na^+ selectivity and permeability compared to pure CTA, highlighting the potential of MMMs for applications in lithium recovery and water treatment. While the stability of the membrane under dynamic conditions presents challenges, the findings provide a solid foundation for further research and development.

The study underscores the importance of optimizing both the MOF synthesis and membrane fabrication processes to enhance performance and durability. Future research should focus on addressing the identified challenges, exploring new materials and techniques, and scaling up the technology for practical applications. By advancing the development of MMMs, this research contributes to the ongoing efforts to improve ion-selective separation technologies and supports the development of more efficient and sustainable solutions for resource recovery and environmental protection.

Abbreviations

MOF, metal−organic framework MMM, mixed-matrix membrane PET, poly(ethylene terephthalate) PVC,

poly(vinyl chloride)

UiO-66, Universititet i Oslo-66

Table 1. FTIR peaks assigned for materials.

Assignment	UiO-66-SO_3H (cm^{-1})	CTA-S-60 (cm^{-1})	CTA (cm^{-1})
OH	3000-3500	3000-3500	-
C=O	-	1745	1737
Symmetric O=S=O	1237	1237	-
asymmetric O=S=O	1176	1176	-
n-plane 1,2,4-benzene	1078	1078	
CH_3-C(=O)-O-	-	-	1214
C-O-C	-	-	1033

Table 2. Comparison of CTA and CTA-S-60 performance relative to literature membranes for Li/Na separations by electrochemical methods.

Material Class	Material Name	Li+ Ion Flux (mol/cm^2.sec)	Li^+/Na^+ Selectivity	Reference
MMM	CTA	3.78E-11	0.93	**This work**
MMM	CTA-S-60	2.86E-11	1.2	**This work**
MMM	TFN-(Zr/Ti)-2	5.43E-8	0.85	[9]
MMM	HSO_3-UiO-66/PVC	9.13E-10	0.93	[6]
MMM	ZIF-8/PVC	1.08E-10	1.34	[6]
MMM	SO_4-MOF-808/PVC	2.24E-9	0.88	[6]
MMM	UiO-66/PVC	3.03E-9	0.84	[6]
Carbon	$Ti_3C_2T_x$	3.89E-8	0.99	[10]
Carbon	GO	3.8 E-8	1.01	[11]
PMOF	ZIF-8/GO/AAO	6.9 E-8	1.5	[4]
PMOF	ZIF-8/TA-Fe^{3+}/PP	3.6 E-10	0.97	[5]
PMOF	UiO-66-SO_3H(25)/AAO	3E-9	0.6	[12]
PMOF	UiO-66-NH_2/AAO LLM4	2E-9	0.33	[13]
PMOF	UiO-66	5.3E-9*	0.96	[14]
PMOF	UiO-66-$(COOH)_2$/UiO-66-NH_2	1.0E-7	0.9	[15]
PMOF	UiO-66-NH_2(PSS)/ZIF-8(PVP)	3.2E-8	0.0125	[16]
PMOF	UiO-66-$(COONa)_2$	1.3E-10	0.83	[17]
PMOF	HKUST-1 array	2.2E-9	1.06	[18]
PPOC	CC3	1.6E-8	0.34	[19]
Polymer nanochannel	UV-PET-Lumirror®	3E-7	0.82	[20]
Polymer nanochannel	UV-PET-Hostaphan®	6.3E-11	10.46	[21]
MOF SNC	MIL-53(Al)(MP) SNC	**	0.48	[22]
MOF SNC	Al-TCPP SNC	**	0.82	[22]
MOF SNC	UiO-66 SNC	**	1.3	[22]
MOF SNC	15C-MOFSNC	72***	0.00091	[23]
Polymer@MOF	PSS@HKUST-1-6.7	1.875E-7	35.5	[24]
Polymer@MOF	SSP@ZIF-8-10%	2.5E-11	77	[25]
Polymer@MOF	poly(VS-co-AA)~MIL-53/AAO	1.39E-10	0.927	[26]

Table 3.Comparison of CTA and CTA-S-60 performance relative to commercial and literature membranes for LiCl/NaCl separations by permeability-solubility methods.

Material Name	LiCl Permeability (cm^2/sec)	LiCl/NaCl Permeability Selectivity	Reference
CTA	2.00E-09	0.8	**This work**
CTA-S-60	1.67E-09	1.2	**This work**
12C4-polynorborene	2.00E-08	2.4	[27]
Uncharged	7.00E-11	0.7	[28]
Uncharged	2.00E-11	0.52	[28]
Uncharged	9.00E-11	0.71	[28]
Strong IEM	1.50E-08	0.65	[28]
Strong IEM	1.00E-07	0.68	[28]
Strong IEM	2.00E-07	0.62	[28]
Strong IEM	4.90E-08	0.89	[28]
Weak IEM	4.50E-06	0.87	[28]
Weak IEM	3.00E-06	0.93	[28]
PEGDA	4.00E-08	1.1	[28]
PEGDA	1.80E-07	1.06	[28]
PEGDA	4.50E-07	1.03	[28]
PEG	1.20E-06	0.83	[28]
PEG-SiO_2	1.30E-06	0.9	[28]
PEG-ZIF-8	1.22E-06	0.84	[28]

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