



Mining Critical Metals from Seawater by Subnanostructured Membranes: Is It Viable?

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Abstract: The continuous demand for energy-critical elements such as lithium, cobalt, uranium and so on will soon exceed their availability increasing further their significance of geopolitical resources. Seawater is a relevant, not conventional source of critical metals. Synthetic membranes with subnanometer pores are the core of processes such as desalination for separating solutes from water. These membrane processes have achieved remarkable success at industrial level. However, stateof-the-art desalination membranes cannot selectively separate a single metal ion from a mixture of ions. In this review the challenges of membranes with subnanometer pores to selectivity discriminate among different metal ions are briefly discussed. The key points of the molecular-level mechanism that contribute to energy barrier for ions transport through subnanometer pores are highlighted to provide guidelines for the design of single-metal ion selective membranes.

Keywords: critical metals scarcity; seawater desalination; membrane processes; subnanometer membranes; single-ion selective membranes

1. Introduction: Setting the Scene

Seawater is a relevant and not yet exploited source of metals (Table 1). Most of the critical metals and elements that are utilized in industry and energy fields such as conversion and storage are obtained through the mining of mineral ores [1]. As known, mining has a heavy environmental footprint because of the significant amounts of land, energy, and water necessary and lot of wastes produced [1]. The advances from one side in industrial ecology, which focuses on the production processes of goods and services trying to mimic a natural system by conserving and reusing resources [2] and water purification (e.g., desalination) from another side have acquainted that seawater, brines and industrial wastewater are relevant sources of critical metals [3–5].

An exemplary case is that of lithium, whose sharp demand increase (265,000 tons in 2015 and to 498,000 tons in 2025 [7]) is due to its large use for lithium batteries or electronic devices. Even though lithium reserves are enough for the market demands, the future offers a different, uncertain scenario because of the difficult conventional technologies to extract litium from the resources, which require high cost investement and in many cases are distributed around the globe in less accessible regions. In this framework, seawater with reserve of lithium estimated at 230,000 millions tons (Table 1, entry 5) represents a relevant resource not limited to geographic boundaries. The main drawbacks of extracting lithium ions (Li⁺) from seawater are the low concentration of ~ 0.2 ppm (Table 1, entry 5) and the coexistence of other similar monovalent ions, i.e., sodium (Na⁺) and potassium (K⁺) ions. Traditional approach to extract Li⁺ from brine and seawater consists of three main steps: (i) concentration (solar evaporation, adsorption, diffusion dialysis), (ii) purification (solvent extraction, ion exchange or adsorption) and (iii) precipitation by adding Na₂CO₃ [7,8]. Recent studies showed interest on developing effective technologies for the extraction of lithium from seawater and salt-lake brines, which is crucial for sustainable lithium reuse in battery industries [9–11]. Uranium is another example of critical metal: recovery of uranium is of critical importance for the continued energy security of many nations [12].



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Copyright: © 2022 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Ocean water contains ~4.3 billion tons of uranium (Table 1, entry 10). The key evaluation criteria for uranium extraction include selectivity, kinetics, capacity, and sustainability [13]. As for lithium, the extraction of uranium from its high salinity background is extremely challenging because of the low uranium concentration in seawater (Table 1, entry 10), and because of the the difficult separation from other cations such as Na⁺ and calcium (Ca²⁺) ions, abundant in seawater [14–16]. Abney et al. [17] comprehensively reviewed materials for recovery of seawater uranium, in particular inorgamic materials, polymer adsorbents, nanostructured materials such as metal-organic frameworks [18,19], porousorganic polymers, and mesoporous carbons. However, cost analysis showed that the performance of these adsorbents in terms of selectivity and recyclability is not enough compared to that of terrestrial mining for economically viable uranium extraction [20,21].

Entry	Element	Ionic Radius (nm)	Metal-Oxygen Internuclear Distance in Water (nm)	Terrestrial Reserves (×10 ⁶ Tonnes) [6]	Seawater Concentration (mg/L) [6]	Dissolved Metals in Seawater (×10 ⁶ Tonnes) [6]
1	Cu	0.057 (Cu ²⁺⁾	0.196/0.240	690	0.0009	1170
2	Ni	0.055 (Ni ²⁺)	0.217	74	0.0066	8580
3	V	$\begin{array}{c} 0.079 \ (\mathrm{V}^{2+}) \\ 0.0640 \ (\mathrm{V}^{3+}) \\ 0.058 \ (\mathrm{V}^{4+}) \\ 0.054 \ (\mathrm{V}^{5+}) \end{array}$	$\begin{array}{c} 0.405 \ [V(H_2O)_6]^{2+} \\ 0.388 \ [V(H_2O)_6]^{3+} \\ 0.382 \ [VO(H_2O)_5]^{2+} \\ 0.378 \ [VO_2(H_2O)_4]^+ \end{array}$	14	0.0019	2470
4	Мо	0.069 (Mo ³⁺)	0.225	11	0.010	13,000
5	Li	0.059 (Li ⁺)	0.204	13	0.178	231,400
6	Co	0.065 (Co ²⁺)	0.209	7.2	0.00039	507
7	Nb	0.072 (Nb ³⁺)		4.3	0.000015	1.3
8	Ag	0.15 (Ag ⁺)	0.232	0.52	0.00028	364
9	Au			0.054	0.000011	14.3
10	U	0.073 (U ⁶⁺)	0.246 [UO ₂ (H ₂ O) ₅] ²⁺	5.9025	0.0033	4290

Table 1. Critical Metals in Terrestrial Reserves and Oceans.

Membrane technology is worldwide recognized as fundamental for a sustainable growth due to its low direct energy consumption because of the absence of phase transformations, reduced indirect energy consumption through the recycling and reuse of raw materials and secondary materials minimizing the formation of waste [22].

Membranes, which are the core of membrane processes, can be symmetric and asymmetric and their structure varies from porous to nonporous (so-called dense) (Figure 1).



Figure 1. Schematic of: (top) symmetric membranes (porous symmetric and dense symmetric); (bottom) asymmetric membranes (**a**)porous skin layer on a porous sublayer; (**b**) selective, dense skin layer on a porous sublayer; (**c**) selective dense coating layer on a porous sublayer).

On the basis of pore size, membranes can separate microbial pathogens such as bacteria and protozoa $(1-10 \ \mu\text{m})$, gas and ions $(0.1-1 \ \text{nm})$. So the range of interest for metal ions separation from seawater mixture is that of subnanometer pore size (<1 nm) (Figure 2). The current interest to use mebranes for metal ions separation is confirmed by the publication of various reviews such as that by Wang et al. [23] on the application of polymeric, inorganic and mixed matrix membranes for the separation of alkali and alkaline earth metal ions.



Figure 2. Membrane filtration spectrum.

2. Separation of Metal Ions by Conventional Membranes

Separation technologies based on sub/nanostructured membranes, i.e., membranes with nanopores or "free volume elements" in the case of polymer membranes [22,24,25] with diameters widts smaller than 100 nm, can be classified according to the separation driving force. A hydraulic pressure difference (ΔP) must be applied to overcome the osmotic pressure difference between the feed and the permeate and separate the mixture components in reverse osmosis (RO) and nanofiltration (NF). Typically, the nanopores for RO and NF are on the order of 0.5 nm and 1–5 nm, respectively.

In forward osmosis (FO) and dialysis (D), the driving force is a concentration difference and in electrodialysis (ED) is an electro-potential difference.

Among the membranes processes mentioned above, narrow NF (molecular weight cut-off, MWCO, ranging from 0.2–1 kDa) has been used for Li extraction from a lithiumbearing brine. NF requires a heavy pre-treatment stage to overcome the drawbacks of inorganic fouling and scaling and diluting the brine with large quantity of freshwater. In polymeric NF steric exclusion is not as prominent as in RO membranes and electrostatic effects significantly influences solute transport: the combination of Donnan exclusion, steric hindrance and dielectric exclusion controls the mass transfer [26]. By using negatively charged NF membranes, which according to Donnan effect, reject anions while they are not able to separate solutes with positive charges [27], the separation of Li⁺ from Na⁺ was unsatisfactory. In the recent review by Wang et al. on separation of alkali/alkaline earth metal [23] no membranes for the separation Li^+/Na^+ are mentioned. Experimental [28] and simulation studies [29] demonstrated the contribution of electric transport through a NF membrane and confined subnanometer pore, respectively. Noteworthy, the fixed negatively charge in NF membranes can repel with different extent even like-charge ions (Figure 3) [28] confirming that a deep understanding of transport mechanism (see below next paragraph) is necessary to design solute-solute selective membrane.



Figure 3. Mechanism of the exclusion of a monovalent anion by a NF membrane. (**A**) A smaller anion with a higher charge density (e.g., fluoride, F⁻) is surrounded by a stronger hydration shell than a larger anion with a lower charge density (e.g., chloride, Cl⁻). (**B**) Anions partially dehydrated enter into the membrane pores. Adapted with permission from [28]: Copyright 2022, American Chemical Society.

A variety of positively charged NF membranes were prepared with the aim to obtain lithium selectivity higher than that observed with negatively charged NF membranes (Table 2). Different nitrogeneous bases such as polyethyleneimine (PEI) [27], ethylenediaminetetraacetic acid (EDTA) [30], and 1,4-bis (3-aminopropyl) piperazine (DAPP) [31] were used.

Membrane Materials	Salt Rejection (%)	Ref.
PIP-MWCNTs-PEI-PES	96.9 to MgCl ₂	[27]
PDA-MWCNTs/PEI/PSf	91.5 to MgCl ₂	[32]
MWCNTs/PEI/PSf	93.5 to MgCl ₂	[33]
EDTA/TFC	84.6 to MgCl ₂	[30]
DAPP/TFC	70.4 to MgCl ₂	[31]
	7011 to higely	[01]

Table 2. Selected positively charged NF membranes for metal ion removal.

The other conventional membrane process of interest for Li extraction is ED. In fact ED using ion exchange membranes (IEMs) has been used for desalination and ions separations. However, conventional IEMs are not able to separate Li⁺ ions to meet industry requirements: ED could be used to separate Li⁺ from high Mg²⁺ concentrated brine, but not with K⁺ and Na⁺ in the feed [34], making the problem of selective separation of Li⁺ from other monovalent ions still unresolved. Very recently, Uiliana et al. [35] proposed new ED subnanostructured membranes based on porous aromatic frameworks (PAFs) entrapped into IEMs of sulfonated polysulfone (sPsf): exceptionally selective capture by ED process has been observed for Hg²⁺, Cu²⁺ and Fe³⁺. The reasons for such successful results, i.e., single-species membrane selectivity as well as their implications are underscored in this review as discussed below.

3. Towards Single-Species Selective Membranes

The nanostructured membranes required for mining valuable metals from seawater to be competitive with existing conventional processes should transport single ions (e.g., Li⁺) and reject other ions (e.g., Na⁺), i.e., should have high ion-ion selectivity (single-species selectivity). Ion-ion selectivity in current synthetic membranes is relatively limited. In

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fact, in the past years, many efforts have been addressed to develop membranes with high water-salt selectivity, i.e., ultra-high water-solute selectivity with the final aim to ensure higher water quality avoiding post-treatment steps owing to the high retention of all the solutes [36]. Interfacial polymerization (IP) (one of the most used membrane fabrication techniques) to fabricate thin-film composite (TFC) membranes [37], has been developed and performed to improve water-solute selectivity, but without control of the pores to produce ion-ion-selectivity.

The recent paper by Uiliana et al. [35] represents a pivotal study in the direction and design of single-species selective membranes. Membranes with improved solute-solute selectivity, can be designed only by understanding of the molecular level mechanism for solute transport under subnanometer confinement.

"It is well known that ions behave drastically differently in nano-scale confined environments" [38]. Nanopore transport at the single pore level has been investigated recently thanks to the advent of sophisticated readout mechanisms able to probe fluidic motion and mass transport in the pores [39].

Ion transport through subnanometer pores is composed of two consecutive steps. The first is partitioning into the pore. The second is intrapore diffusion. Salt ions first partition into the polymer matrix, then diffuse through the membrane pore because of a chemical potential gradient (solution-diffusion theory [36,38]). Hence, both these steps should contribute to the overall energy barrier. Ion dehydration and ion interaction with pore walls dominate the energy barriers for partitioning into the pore and intrapore diffusion, respectively [39,40].

A scheme of the energy barrier for ions transport through subnanometer pores of a polyelectrolyte multilayer NF membrane is given in Figure 4.



Figure 4. Description of energy barriers to ion transport through a polyelectrolyte multilayer NF membrane. At the membrane-water interface (**a**), there is the main energy barrier because ions undergo dehydration before they enter into the pores (**b**). The ions overcome further energy barriers as they hop between charged groups of the membrane (**c**). Reproduced with permission from [40]: Copyright 2022, Elsevier.

The main energy barrier lies at the membrane-water interface, where ions undergo dehydration before they enter the pore (Figure 4a,b) as discussed below. The ions experience further energy barriers as they move through the membrane (Figure 4a) and hop between charged groups of the membrane (Figure 4c).

3.1. Molecular Level Mechanism: Partitioning into the Pore (Ion Dehydration Energy Barrier)

As known during the dissociation of salts into ions in medium with high dielectric constants such as water, there is the formation of hydration shells around the dissolved ions. This produces two relevant consequences for the transport through subnanometer membrane pores:

- (i). increase of the ion size due to water shell, thus hindering hydratated ions transport through membranes with lower pores size;
- (ii). masking of the bare ion due to the solvation shell, thus hampering its recognition by the pore, which is fundamental for achieving ion-ion selectivity.

When the ion enters a pore smaller than the hydrated ion, the water shell is often removed [39–41]. This dehydration of ions is part of the permeation energy barrier (Figure 4a,c) and can be used to rationalize observed selectivity for similar monovalent ions in subnanometer pores: ions with a high ratio charge/radius (i.e., smaller ions) have higher hydration energy and hence hold their hydration shell more tightly experiencing a higher energy barrier [40]. Dehydration energy barriers occur at pore size where the hydrated ion size is higher than the pore size.

3.2. Molecular Level Mechanism: Intrapore Diffusion (Ion-Pore Walls Interaction Energy Barrier)

After partial dehydration and partitioning from on dielectric (the solution bulk) into another (the pore) (Figure 4) dehydrated ions interact with the pore walls materials. These interactions can energetically compensate for the dehydration step thus reducing the energy price paid for partitioning. So confined diffusion of ions inside the pore is the result of consecutive barriers that hinders the transport (the energy profiles in Figure 4a). These barriers arise from the physical interactions between solutes and membrane surfaces and chemical affinity of solute to the membrane pore walls.

3.3. Ion-Ion Selectivity: A Subdle Balance between Partitioning and Intrapore Diffusion

The selectivity depends on the relative contribution of ion partitioning into the membrane and its diffusion through the membrane to the overall energy barrier. Higher ion affinity to the membrane material will promote partitioning into the membrane pore, but reduces diffusion through the membrane and viceversa.

During partitioning ions undergo dehydration, which corresponds to an energy barrier (E_H) (Figure 4a,b). After the dehydrated ions enter into the pores, interactions with the polymer matrix can stabilize them, resulting in energy compensation for dehydration (E_S) (Figure 4a,c). This phenomenon is well defined in IEMs where interactions between the ions and oppositely charged groups in the membrane compensate for the dehydration step. These interactions of the ions with the membrane pore walls are ion-specific and therefore, one of the key components to reach the goal of single-species selectivity [42]:

$$\Delta E_k = E_H - E_S \tag{1}$$

 ΔE_k provides the overall energy changes during partition. The overall energy barrier for ions transport (E_P) is the sum of the energy change during the partition step (ΔE_k) and the energy barrier of intrapore diffusion (E_D):

$$E_{\rm P} = E_{\rm D} + \Delta E_{\rm k} \tag{2}$$

Zhou et al. [40] obtained 5.2, 3.6, 1.8 and 0.5 kcal mol⁻¹ as values of ΔE_k for NaF, NaCl, NaBr and NaI, respectively. in accordance with the decrease of hydration energy from F⁻ (smaller) to I⁻ (larger). The energy barriers for intrapore diffusion (E_D) were found to be 14.2, 14.6, 15.2 and 15.6 kcal mol⁻¹ for NaF, NaCl, NaBr and NaI, respectively. The similarity among these values means that the energy barrier during Na⁺ intrapore diffusion dominates the energy barrier for the intrapore diffusion of the salt due to the presence of negatively charged groups distributed through the polyamide selective layer, i.e., deproto-

nated carboxyl groups (-COO⁻) [39,43] (Figure 4c). Therefore, the strong attraction between deprotonated carboxyl groups on the membrane subnanostructured pores (binding sites) and Na⁺ cations is the source of the high energy barrier for positively charged ions intrapore diffusion (E_D) in Equation (2) [42]. In contrast, the intrapore diffusion of F⁻, Cl⁻, Br⁻, I⁻ inside the pores is less hindered because of their repulsion with -COO⁻ groups [43,44].

Above all, the comparison between the values of ΔE_k and E_D obtained by Zhou et al. [40] for current TFC membranes characterized by an active layer thickness of ~200 nm shows that E_D governs E_P for ion permeation through relatively long subnanometer pores.

4. Conclusions: Learn from Nature

In conclusion, are there some guidelines to fabricate single species selective membranes?

The biological K^+ channel, which is able to transport K^+ ions 10,000 times faster than Na⁺ ions [45] could give the anwer for the design of membranes with single-species selectivity necessary for metal ions separations [46].

- (1) Pore lenght: the K⁺ channel is a ultra-thin layer of 12 Å, a quarter of the entire lenght of the channel spanning the lipid layer. A longer path with high affinity for the target ion could result in its higher transport hindrance compared to other solutes with low affinity, thus lowering selectivity. However, an extremely thin selective layer could result in higher permeation of undesired solutes;
- (2) Pore size: a pore size (d_p) smaller than the size of the hydrated solute (d_h) to induce solute dehydration and larger than the size of the non-hydrated solute (d_s) to avoid steric effects and facilitate permeation, i.e., $d_s < d_p < d_h$;
- (3) Selective binding sites: in the K⁺ channel binding sites, which are too small for dehydrated Na⁺, fit properly the size of dehydrated K⁺ [47]. As discussed above regarding partitioning and intrapore diffusion, these interactions stabilize K⁺ ions;
- (4) Short distance between two binding sites: this feature produces repulsive forces between bound K⁺ ions lowering the energy barrier of K⁺ permeation (intrapore diffusion) and assuring its high permeance [48].

Taking into account the above key points, what strategies of membrane fabrication are possible?

The first one is the incorporation of selective "receptors" such as MOFs into polymeric membrane as in the recent study by Uliana et al. [35] mentioned above: PAF (a subfamily of MOFs)-incorporated IEMs are able to capture Hg^{2+} meanwhile competing ions (Na⁺, K⁺, Mg²⁺, Ca²⁺, Ba²⁺, Mn²⁺, Fe³⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺ and Pb²⁺) pass through the membrane resulting in >97 to 99% feed desalination. Ionophores naturally occur in biological system to facilitate transport of specific ions through lipid membranes. Coordination chemistry is the tool to produce "receptors", which bind specific species to form a host-guest complex. This strategy has been adopted in interesting literature studies based on subnanometer polymeric membranes [35,49,50].

The second possible strategy lies in tuning pore size and chemical functionality of materials such as 2D graphene sheets, graphene oxide (GO) [51] and carbon nanotubes (CNTs).

"Tight control of CNT fabrication for making batches of CNTs with narrow diameter distribution or monochiral chemistry offers the potential for angstrom-level selectivity of molecules based on size" [52]. Scalability, expected cost at commercial scale, and difficulty of using subnanometer CNTs for membrane fabrication represent the main obstacles in the fabrication of membranes consisting of CNTs entrapped through a dense polymer membrane [53]. Recently McGinnis et al. [54] reported the first commercial prototype of CNT-based membranes featuring sub-1.27-nm-diameter CNTs into nonporous PSf film for both water and gas transport. However, desalination by RO or FO using such CNT membranes is still not possible because it requires reduction in the size of the CNTs used, going from an internal diameters of a maximum of 1.24 nm in this study to below 0.72 nm,

which is the size of hydrated diameter of Na⁺. So, the longtrip for single species selective membranes based on new materials started.

The third strategy concerns the fabrication of 2D nanofluidic membranes with electrically conductive nanosheets such as MXene nanosheets into laminar membranes with interlayer channels of sub-1 nm (comparable to those of hydrated ion diameters) [55]. MXene is another family of 2D materials with the form of $M_n + 1X_nT_x$, where M represents an early transition metal, X represents carbon or nitrogen, n = 1, 2, or 3, T represents surface groups (-O, -OH, and/or -F), and x is the number of terminating groups. In contrast with 2D GO-based materials, MXene membranes have intrinsically high electronic conductivity, strong van der Waals attraction force for the swelling resistance in aqueous solution, and regular channels with ample functional groups [56,57]. The results reported in literature show that these membranes can provide a strategy to construct devices for highly efficient on-demand ion transport [55].

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