Lithium Ion Separation **Hot Paper**

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Polystyrene Sulfonate Threaded through a Metal–Organic Framework Membrane for Fast and Selective Lithium-Ion Separation

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Abstract: *Extraction of lithium ions from salt-lake brines is very important to produce lithium compounds. Herein, we report a new approach to construct polystyrene sulfonate (PSS) threaded HKUST-1 metal–organic framework (MOF) membranes through an in situ confinement conversion process. The resulting membrane PSS@HKUST-1-6.7, with unique anchored three-dimensional sulfonate networks, shows a very high* Li^+ *conductivity of* $5.53\times10^{-4}\,S\,cm^{-1}$ *at 25°C,* $1.89\times10^{-3}\,S\,cm^{-1}$ *at 70°C, and* Li^+ *flux of* $6.75\,mol\,m^{-2}\,h^{-1}$*, which are five orders higher than that of the pristine HKUST-1 membrane. Attributed to the different size sieving effects and the affinity differences of the* Li^+*,* Na^+*,* K^+*, and* Mg^{2+} *ions to the sulfonate groups, the PSS@HKUST-1-6.7 membrane exhibits ideal selectivities of 78, 99, and 10296 for* Li^+/Na^+*,* Li^+/K^+*,* Li^+/Mg^{2+} *and real binary ion selectivities of 35, 67, and 1815, respectively, the highest ever reported among ionic conductors and* Li^+ *extraction membranes.*

Lithium has been widely utilized in lithium batteries, ceramics, light and strong metal compounds.[1a] Salt-lake brines are the primary lithium resource from which about 60% of lithium compounds are produced.[1b] It is thus very important to extract high purity lithium ions from salt-lake brines. Although there has been extensive research and some methodologies/techniques have been realized, such as solvent extraction, salting out, ion-exchange, precipitation, nanofiltration, and adsorption to extract lithium ions,[3,4] economic, environmentally friendly, and highly selective and efficient methods have still not been realized because of the co-existence of the large amount of the chemically similar and interfering Mg^{2+}, Na^+, and K^+ ions in salt-lake brines.[1c,d,2,3]

It has been revealed that natural protein ionic channels show extraordinary selective and efficient ions transportation arising from the highly specific control of ionic interactions in the confined pores.[4] Motivated by these discoveries in natural systems, scientists have been trying to mimic them and thus to target some artificial materials for highly selective and efficient ions transportation.[5] Based on the affinity of sulfonate groups to alkaline and alkaline-earth metal ions, the sulfonate networks have been implemented in Nafion membranes for fast ion transportation but with very low selectivity, mainly due to the irregular free-spaces and/or ion paths of wide size distributions which have limited the size sieving effects for the separations of these hydrated metal ions.[6] At the same time, a number of artificial organic and inorganic porous materials have been designed and synthesized for ionic nanofluidics over the past few years.[5]

Porous metal–organic frameworks (MOFs) have been rapidly emerging as a very powerful platform to construct multifunctional materials.[7] Their tunable pore sizes and functionalities have also enabled them to be promising materials for ion conductors and transporters.[8] Current studies have been largely focused on the enhancement of proton conductivity with much less attention to the conductivity of alkaline and alkaline-earth ions, mainly in the form of pressed-pelleted MOFs.[8–12]

Polymer/MOF composites and or mixed-matrix membranes are superior to traditional pure MOF membranes.[13] They take advantage of the properties of polymer membranes, such as easy processing, and of MOF membranes including tunable pores and functional surfaces, which can not only minimize the transportation of extrinsic guest species (gas and ions) but can also tune sieving effects and optimize permeance, making them particularly promising for practical applications. Herein, we use a linear polymer polystyrene sulfonate (PSS) with ample sulfonate groups (about four sulfonate groups/nm)[6] to construct a PSS@HKUST-1 membrane and then to further introduce sulfonate groups to direct the recognition of alkaline and alkaline-earth metal ions. The resulting PSS@HKUST-1 membrane has the above mentioned features, which enable it to exhibit outstanding performance for the highly fast and selective lithium-ion separation.

The PSS@HKUST-1 membrane was synthesized via a solid confinement conversion process from a thin film of copper hydroxide nanostrands (CHNs)[14] coated with PSS at room temperature (Scheme 1). The negatively charged PSS firmly assembled on the surface of highly positively charged copper hydroxide nanostrands (CHNs)[14d–f] (Figure S1a in the Supporting Information) before the copper hydroxide nanostrands were transformed into HKUST-1. The element analysis results show that there is no sodium ion in the PSS/CHNs composite thin film (Figure S1b), which indicates that the sodium ions of the polystyrene sulfonate sodium salt have been completely replaced by the positively charged copper ions from CHNs. When the solid PSS/CHNs thin film was

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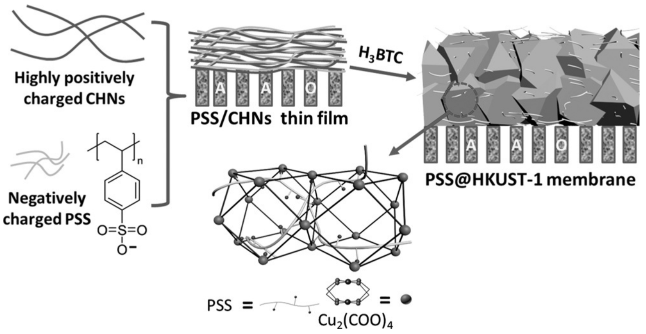

Scheme 1. Preparation of PSS-threaded HKUST-1 membranes. CHNs = copper hydroxide nanostrands. AAO = anodic alumina, the gray bars are the anodic alumina oxide membrane.

immersed into a H_3BTC solution in water/ethanol (water/ethanol volume ratio 1:1), the HKUST-1 layer formed first on the top surface. Because the PSS molecules are well encapsulated into the HKUST-1 crystals (the formation of the first HKUST-1 layer can block PSS to escape from PSS/CHNs to the solution) a very nice PSS@HKUST-1 membrane was readily constructed.

To investigate the effect of the PSS content on the resulting membranes, PSS@HKUST-1 with different PSS content of 0.07, 0.7, 3, 6.7, 10, 20, and 40 wt.%, named as PSS@HKUST-1-007, PSS@HKUST-1-07, PSS@HKUST-1-3, PSS@HKUST-1-6.7, PSS@HKUST-1-10, PSS@HKUST-1-20 and PSS@HKUST-1-40, respectively, were prepared (Figure S2, see detail in Supporting Information). Figure 1 a,b show the SEM images of an 8 μm thick, intergrown and continuous PSS@HKUST-1-6.7 membrane. The cross-section element mapping image shows that sulfur is uniformly distributed in the whole membrane (Figure 1 c,d), and pure HKUST-1 crystal phase was formed (Figure 1 e and Figure S3). As expected, both the BET surface area (1213 m^2 g^{-1}) and pore size (0.62 nm) of the PSS@HKUST-1-6.7 (Figure S4) are smaller than 1370 m^2 g^{-1} and 0.67 nm of pristine HKUST-1,[14] respectively, because of the incorporation of the PSS molecules into the HKUST-1 channels. FTIR spectra (Figure 1 f and Figure S5) indicate that the characteristic peaks of sulfonate groups in pure PSS at 1191 and 1129 cm^{-1} are slightly shifted to 1205 and 1130 cm^{-1} in PSS@HKUST-1 membranes, possibly because part of the sulfonate groups of PSS has interacted with the fifth accessible Cu^{2+} sites in the HKUST-1 crystal.[13c]

The zeta potential of the PSS@HKUST-1 membranes was more negative than that of pristine HKUST-1 (−15.1 mV; Figure S6). It becomes more negative with the increase of the PSS content, indicating that the surface of the PSS@HKUST-1 membrane is more negatively charged, which can enforce the capture for the positively charged cations from solutions and thus transport metal cations into the HKUST-1 pores through PSS networks.

The cationic conductivities of PSS@HKUST-1 and pristine HKUST-1 membranes were measured for a membrane-based device[15] sealed by polydimethylsiloxane (PDMS; Figure S7, see detail in supporting information) in metal chloride aqueous solution at 25 °C (Figure 2). All of the PSS@HKUST-1 membranes show much higher Li$^+$ ion conductivities than that of pristine HKUST-1 one (Figure 2 a,b). The PSS@HKUST-1-007 has a two orders higher Li$^+$ conductivity than that of pristine HKUST-1. When PSS content was increased to 6.7 wt.%, PSS@HKUST-1-6.7 membrane exhibits the highest Li$^+$ conductivity of 5.53×10^{-4} S cm^{-1}, five orders higher than 3.799×10^{-9} S cm^{-1} of pristine HKUST-1. Further increase of the PSS content led to the reduced Li$^+$ conductivity. This is because further PSS content led to some obvious cracks and/or voids in the corresponding membranes (Figure S2 e–g).

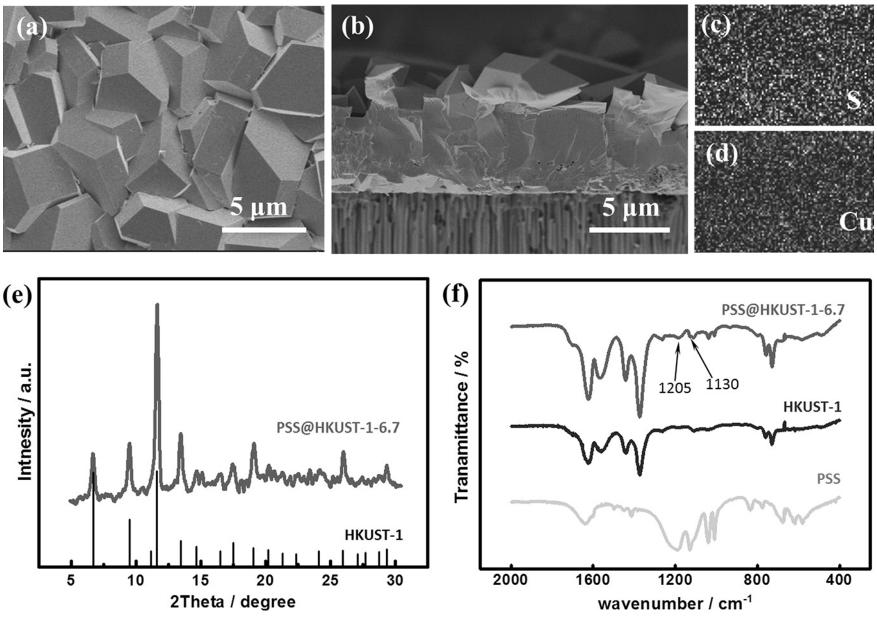

Figure 1. a) Surface, b) cross-section SEM images, c) S element and d) Cu element mapping; e) XRD patterns of PSS@HKUST-1–6.7 and pristine HKUST-1; f) FTIR spectra of PSS@HKUST-1–6.7, pristine HKUST-1 membrane, and PSS.

The Li$^+$ ion conductivity through the PSS@HKUST-1–6.7 membrane immediately increased to the saturated level at the LiCl concentration of 0.05 M, indicating a sign of surface charge-governed transport (Figure 2 c and Figure S8).[15b] The same phenomena were also observed for Na$^+$, K$^+$, and Mg^{2+} ions transportations (Figure 2 c and Figure S9).

The Li$^+$ ionic conductivity through the PSS@HKUST-1–6.7 membrane follows an Arrhenius-like behavior with an activation energy of 0.21 eV (Figure 2 d). The low activation energy suggests that Li$^+$ ion transport through the PSS@HKUST-1 membranes is via a Grotthuss mechanism.[11,16] The charge is transported by the coordinated hopping of Li$^+$ between sulfonate groups of PSS (with interval of about 0.25 nm)[6] threaded through the

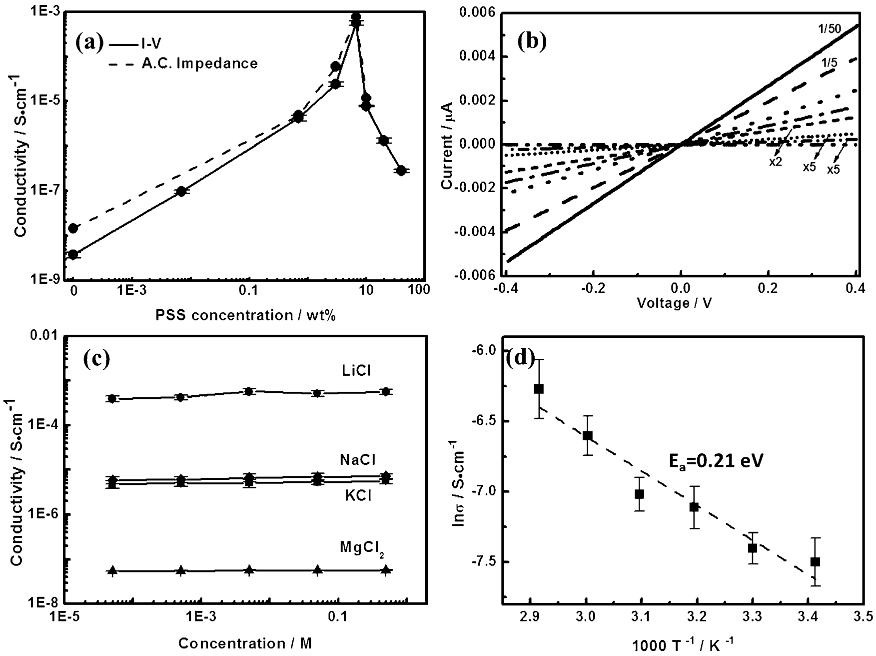

Figure 2. a) Li-ion conductivity through membranes of the pristine HKUST-1 and PSS@HKUST-1 with different PSS contents, in 0.5 M LiCl electrolyte, calculated from the corresponding *I–V* curves in (b). b) *I–V* curves of pristine HKUST-1 (—••—••) and PSS@HKUST-1 with PSS contents of 0.07 wt. % (–•–•), 0.7 wt. % (•••••), 3 wt. % (–––), 6.7 wt. % (——), 10 wt. % (· — · —), 20 wt. % (-----), and 40 wt. % (· · · ·). c) Ionic conductivity of PSS@HKUST-1–6.7 in LiCl, NaCl, KCl, and $MgCl_2$ at different ion concentrations. d) Li-ion conductivity of PSS@HKUST-1–6.7 in 0.5 M LiCl at different temperature.

cavities of HKUST-1. The Li^+ ion conductivities ($5.53\times10^{-4}\,S\,cm^{-1}$ at 25 °C, $1.89\times10^{-3}\,S\,cm^{-1}$ at 70 °C) are remarkably high. In fact, they are even comparable to the proton conductivities reported in MOFs-based materials,[8–12] albeit the size of hydrated Li^+ is much larger than that of the proton ion.[6a]

The PSS@HKUST-1–6.7 membrane systematically exhibits much higher ionic conductivities for Li^+ than for Na^+, K^+, and Mg^{2+} (about two orders higher than those of Na^+ and K^+ ions, and four orders higher than those of Mg^{2+}), as shown in Figure 2c and Figure S9. The ionic conductivity ratios between different cations are typically considered as the ideal separation factors, and are 78, 99, and 10296 for Li^+/Na^+, Li^+/K^+, and Li^+/Mg^{2+}, respectively.

The ionic conductivities through these membranes measured by alternating current impedance (Figure 2a, Figure S10 to Figure S12) are in agreement with the values calculated by *I–V* curves. The Li^+ ionic conductivity of a pressed PSS@HKUST-1–6.7 pellet is $0.0139\,S\,cm^{-1}$ (Figure S13b) which is higher than that of the well-intergrown PSS@HKUST-1–6.7 membrane, indicating that the voids between the grains dominate the ionic conductivity in the pressed-pelleted samples.

As mentioned in the introduction, separation of Li^+ ions from salt-lake brines is a very important while challenging process. Such high separation factors indicate that the PSS@HKUST-1–6.7 membrane has great potential to fulfill this challenging task. We further explored the PSS@HKUST-1–6.7 membrane for the separation performances of binary ion mixtures through inductively coupled plasma mass spectroscopy (ICP-MS) (See detail in the Supporting Information and Table S1). The separation selectivities for the binary ions of Li^+/Na^+, Li^+/K^+, Li^+/Mg^{2+}, are 35, 67, and 1815 (Figure 3a), respectively, with a Li^+ flux of $6.75\,mol\,m^2\,h^{-1}$. The separation selectivities of Li^+/Na^+ of 35 and Li^+/K^+ of 67 are to our knowledge the highest ever reported for membranes.[1–4,6] The selectivity of Li^+/Mg^{2+} is even much higher (Figure 3b, Table S2).[1d,3d,g,h,6c] This is the first reported ionic flux for MOF-based ionic conductors. The flux of lithium ions through PSS@HKUST-1–6.7 membrane is comparable to that of specific molecular functionalized liquid–liquid membranes with a thickness of 100 μm.[1d] As shown in Figure 3b and Table S2, PSS@HKUST-1–6.7 membrane is superior to other reported membranes when the conductivity, flux, and selectivity are evaluated together.[1d,3d,g,h,6c]

For porous separation membranes, both size-sieving effects and specific interactions between the target species and membranes play important roles for the separation performance.[17] The metal ions in this separating process are in the forms of hydrated ones, with hydrated diameters of Li^+, Na^+, K^+, Mg^{2+} of 0.76, 0.72, 0.66, and 0.86 nm,[6a] respectively (Figure 3c). The pore entrance of HKUST-1 is 0.9 nm,[12b] greater than the sizes of these hydrated alkaline metal ions, so the size-sieving effect might contribute less to the higher selectivity of Li^+ over Na^+, and K^+. It has been established that the permselectivities of Li^+, Na^+, and K^+ in the sulfonated poly(ether sulfones) cation exchange membrane follow the order $Li^+ > Na^+ > K^+$, and are governed by their corresponding binding affinity to sulfonate groups (normalized to Li^+) of 1.0, 1.98, and 2.90, respectively (Figure 3c).[6a,c] Higher binding affinity results in easier condensation of the cation–sulfonate pairs, and more difficult for dissociation for fast transportation, so the ionic conductivities of the PSS@HKUST-1–6.7 membrane follow the order $Li^+ > Na^+ > K^+$ as well. The binding affinity of sulfonate groups to Mg^{2+} ions is 3.18,[6a] much larger than that of 1 to Li^+. Furthermore, the size of Mg^{2+} hydrate (0.86 nm) is larger than that of Li^+ one (0.76 nm). Both the size sieving effect and the binding affinity contribute to the significantly high selectivity factor of Li^+ over Mg^{2+}.

The PSS@HKUST-1 membranes exhibited much higher stability against water than the HKUST-1 membrane. They are stable after immersing in water for two months, indicating their promise for lithium-ion separation. Apparently, the PSS has protected the most labile and accessible Cu^{2+} sites, then stabilized the framework. This is very important for practical applications.

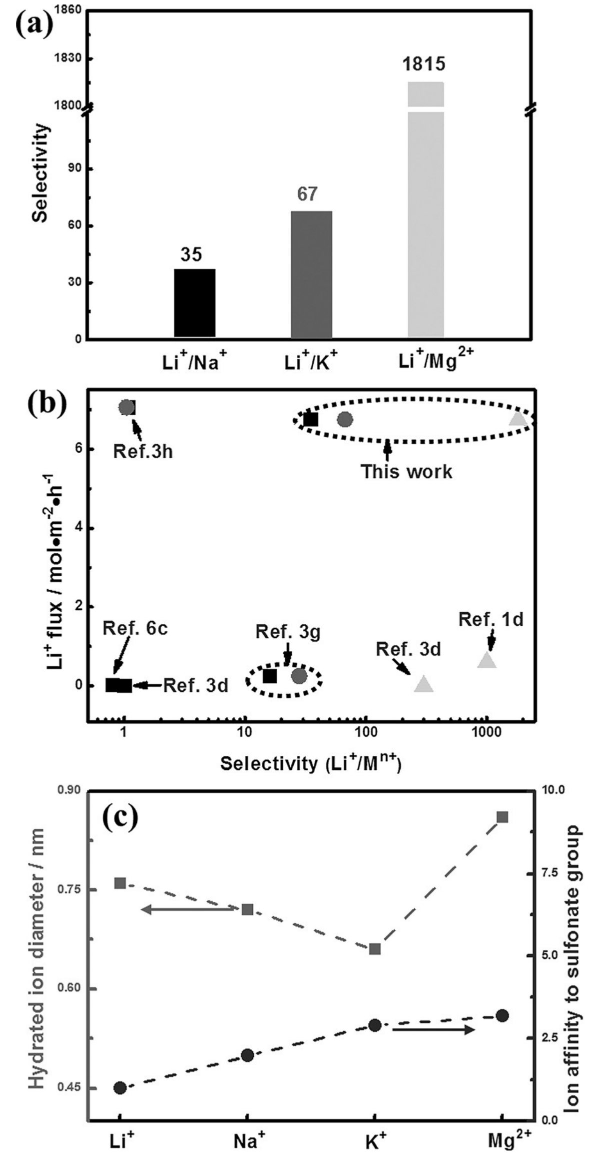

Figure 3. a) Binary ion selectivities of PSS@HKUST-1–6.7 in 0.5 M LiCl and 0.5 M M^{n+}Cl$_n$ electrolytes. b) The performance in the separation of binary ion mixtures by the PSS@HKUST-1–6.7 membrane for Li$^+$ over Na$^+$, K$^+$, and Mg^{2+}, and that of other membranes. Li$^+$/Na$^+$ (square); Li$^+$/K$^+$ (circle); Li$^+$/Mg^{2+} (triangle). c) The hydrated ion diameters (squares) and ion affinities (circles) to sulfonated group related to that of Li$^+$ of Li$^+$, Na$^+$, K$^+$ and Mg^{2+}.

In conclusion, we construct intergrown and continuous PSS threaded HKUST-1 membranes through a solid confinement conversion process. The linear polymer polystyrene sulfonate (PSS) not only significantly improves the water stability of HKUST-1 but also forms 3D networks of sulfonic groups for ion transportation. As a result of the different binding affinity of Li$^+$, Na$^+$, K$^+$, and Mg^{2+} to the sulfonate groups, and their different hydrated ion size diameters, the PSS@HKUST-1–6.7 membrane presents: a) very high Li$^+$ conductivity of 5.53×10^{-4} S cm^{-1} 25 °C and 1.89×10^{-3} S cm^{-1} at 70 °C (five orders higher than that of the pristine HKUST-1); b) outstanding selectivity for Li$^+$ over Na$^+$, K$^+$, and Mg^{2+} with binary ion separation factors of 35, 67, and 1815, respectively; c) low activation energy of 0.21 eV and fast Li$^+$ ion flux. The approach we developed herein can be applied to the fabrication of various other polymer-functionalized MOF-based membranes. The outstanding performance of the PSS@HKUST-1–6.7 membrane makes it a very promising material for the efficient extraction of lithium ions from salt-lake brines.

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