Potential dependent ionic sieving through functionalized laminar MoS₂ membranes

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Abstract

Laminar MoS₂ membranes show outstanding potential for practical applications in energy conversion/storage, sensing, and as nanofluidic devices. The re-stacking of exfoliated MoS₂ creates nanocapillaries between the layers of MoS₂ nanosheets. These MoS₂ membranes have been shown to possess a unique combination of ionic rejection properties, high water permeation rates, and long-term solvent stability, with no significant swelling when exposed to aqueous or organic solvents. Chemical modification of MoS₂ membranes has been shown to improve their ionic rejection properties, however the mechanism behind this improvement is not well understood. In this work, we elucidate the ion-sieving mechanism by the study of potential-dependent ion transport through functionalized MoS₂ membranes. The ionic permeability of the MoS₂ membrane is transformed by chemical functionalization with a simple naphthalene sulfonate dye (sunset yellow) and with a resultant attenuation of permeability by at least an order of magnitude, compared to the pristine MoS₂ membranes and permeability reported for graphene oxide and Ti₃C₂Tx (MXene) membranes. The effects of pH, solute concentration, and ionic size/charge on the ionic selectivity of the functionalized MoS₂ membranes are also reported. Understanding the mechanism of ionic sieving within functionalized MoS₂ membranes will enable future applications in electro-dialysis and ion exchange for water treatment technologies.

Two dimensional (2D) materials, in the form of laminar membranes, have been widely studied for water purification applications such as desalination, ion exchange, and electro-dialysis [1–3]. Recently, graphene and graphene oxide (GO), when formed into layers of randomly re-stacked nanosheets, have shown promise as membrane materials, demonstrating high rejection properties towards small ionic solutes while maintaining high water permeation rates due to a network of nanocapillary channels formed between the individual layered materials [3–6]. However, GO-based membranes are reported to be unstable when submerged in aqueous solutions because the membranes become swollen. GO membranes consequently have an enlarged interlayer spacing resulting in poor rejection properties [7, 8]. To overcome this, a number of membrane modification strategies have been developed, including additives to crosslink individual layers [8, 9] and physical confinement [3] to restrict the membrane’s swelling. Membranes modified by these approaches exhibited improved rejection properties but a decrease in the water flux. This drawback will hinder capacity for large scale exploitation in industry. Other 2D materials have also been reported as suitable candidates for the formation of laminar membranes, e.g. transition metal carbides/nitrides, MXenes (e.g. Ti₃C₂ and Ti₃CN), [10, 11] and transition metal dichalcogenides, TMDs (e.g. MoS₂ and WS₂) [12–14]. Deng et al [12] reported that MoS₂ laminar membranes showed good performance with high stability under extreme pH conditions, without any
significant expansion of the interlayer distance. These promising MoS$_2$ membranes are not only stable in a range of aqueous media but also show significantly higher water permeation rate than similar laminar membranes. Despite this promise there are few studies of ion transport through MoS$_2$ membranes; however recent reports have demonstrated improved ionic rejection, surpassing similar GO membrane, by chemical functionalization: the mechanism for this improvement is unclear. TMD laminar membranes are also capable of molecular sieving/separation performance for both organic vapour and liquid media, which lends them to further applications as membrane extreme conditions [12, 14].

Chemical functionalization is crucial in altering the desired surface chemistry of 2D materials, providing control over the membrane’s properties for use in various applications such as water treatment [1, 15], energy storage [16], and photocatalysis [17]. For water purification, we have previously described the functionalization of MoS$_2$ membranes with organic dyes, which exhibit an increase in water flux by a factor of four, with high ion rejection (~99%) when compared to membranes of pristine, exfoliated MoS$_2$, of comparable thickness [1]. These dye-functionalized MoS$_2$ membranes also showed ca. Five-fold increase in water flux compared to the previously described GO-based membranes [3, 4].

Ion transport through GO-based membranes under the influence of an applied potential has been studied previously by Hong et al [18], with the rejection resulting from the electrostatic repulsion and the size exclusion imparted by the negative surface charge and confinement by the nanochannels. These GO membranes were, however, of extremely limited applicability due to their aforementioned tendency to swell in aqueous solutions, leading to poor ionic rejection. Specifically, the interlayer spacing increases to nearly 70 Å when the membrane was completely soaked in deionized water [7].

In this work, we firstly investigated ion mobility through laminar MoS$_2$ membranes in the presence of an applied potential and salt concentration gradient. As-prepared functionalized membranes are stable in a range of aqueous solutions including acidic and basic media (no delamination was detected). The sunset yellow (disodium 6-hydroxy-5-[(4-sulfophenyl)azo]-2-naphthalenesulfonate; anionic dye) functionalized, laminar MoS$_2$ membranes (MoS$_2$/SY) show significant retardation of ion transport as well as significant size and charge-based selectivity, compared to pristine MoS$_2$ membranes, previously reported laminar membranes (GO and Ti$_3$C$_2$T$_x$), and commercial polymeric membranes (Nafion). A range of characterization techniques including optical microscopy, electron microscopy (scanning electron microscopy, SEM, and scanning transmission electron microscopy, STEM), powder x-ray diffraction (PXRD), x-ray photoelectron spectroscopy (XPS), and zeta ($\zeta$) potential measurements were employed to determine the quality of the MoS$_2$ membrane, along with its thickness, stability, chemical composition, and surface charge. Moreover, MoS$_2$/SY membranes were also characterized as a function of permeate concentration and solution pH, thereby demonstrating their excellent cation selectivity at low permeate concentration and alkaline conditions.

The ionic mobility of dye-functionalized MoS$_2$ membranes was measured as shown schematically in figure 1(a); after first using the functionalization procedure described in our previous work (see figures S1 and 2) [1]. Briefly, 1 mM sunset yellow (SY) was used to functionalize the laminar MoS$_2$ membranes, they were then cleaned to remove any excess dye molecules until no remaining dye was detected, by UV–visible absorption spectroscopy and electro-spray mass spectroscopy. Detailed characterization of the pristine and dye-functionalized MoS$_2$ membranes are provided as supporting information. Figure 1(b) shows the experimental setup for ion transport in a variety of salt solutions, under a concentration gradient, with 100 mM and 10 mM in the feed and permeate reservoirs, respectively, using a four-electrode system [19–21]. The MoS$_2$ membranes were supported on polyvinylidene fluoride (PVDF) membranes during their pressure filtration driven by self-assembly as shown in figure 1(c). Figure 1(d) shows a cross-sectional SEM image of a MoS$_2$/PVDF membrane showing the laminar structure of the MoS$_2$ flakes, with a lateral size range of 200–300 nm. The high resolution plan view and cross-sectional SEMs are shown in figures S3 and 4, as well as energy dispersive x-ray (EDX) analysis mapping of Mo and S elements in figure S4. Figure 1(e) reveals the laminar structure of the stacked MoS$_2$ flakes using scanning transmission electron microscopy (STEM). The individual MoS$_2$ flakes are composed of ca. ~1–15 layers, with the majority being 3–5 layers thick (figure S5). The individual sheets are predominantly stacked horizontally, with some vertically-aligned, randomly oriented flakes also present. The capillary heights measured between individual MoS$_2$ flakes lie in the range 6–13 Å. The PXRD pattern of MoS$_2$/SY also indicates the membrane stability (no significant swelling) after exposure to aqueous solution as judged from the consistency of the (002) peak position, shown in figure S6.

The assembled MoS$_2$ membrane was inserted in a custom-made H-beaker cell consisting of two liquid reservoirs (30 mL) contacted with Pt electrodes and Ag/AgCl reference electrodes, connected to the main solution via 3M KCl agarose salt bridges inside Luggin capillaries (placed ~2 mm on either side of the membrane to minimize the membranes’ resistance) as shown in figure 1(b). Pt and Ag/AgCl electrodes in the feed chamber were connected to the counter and reference electrodes terminals of the potentiostat, whereas the corresponding electrodes in the permeate chamber were connected to the working and sense terminals.
The transmembrane potential was cycled using a triangular potential waveform from $-200 \text{ mV}$ to $200 \text{ mV}$ at a rate of $1 \text{ mV s}^{-1}$ with a reverse cycle to ensure there was no hysteresis in the response. Figure 1(f) shows the $I-V$ characteristics of different valence ions, measured at a constant concentration ratio (10 mM/100 mM). As a function of the size and charge of the ions, the membrane potential (zero-current potential, the applied potential at which there is no net flow of ions) decreased to a more negative potential with increasing cationic charge. The net current at zero applied voltage is indicative of different diffusion rates between cations and anions resulting in the shift of the $I-V$ response along the voltage axis for both the functionalized (figure 1(f)) and pristine MoS$_2$ membranes (figure S7). A negative current at zero applied voltage corresponds to the higher mobility of cations compared to the Cl$^{-}$ counter-ions, vice versa for a positive current as shown in figure 1(f). The $I-V$ responses indicated that the permeation properties of the MoS$_2$ membrane are transformed by dye functionalization. The effect of SY functionalization is clearly seen in figure 1(g), which reveals that the membrane conductance decreased significantly, with a related fall in the zero-current potential resulting in a two-fold reduction of ion mobility ratio as determined by the Goldman–Hodgkin–Katz (GHK) equation (equation (1)), compared to the pristine MoS$_2$. The conductance of salt with three different cationic charges (KCl, BaCl$_2$, and AlCl$_3$) has been plotted as a function of MoS$_2$/SY thickness as shown in figure 1(h). This analysis shows that the trivalent salt with larger hydrated cation radius (AlCl$_3$) has the highest conductance for a given membrane thickness. Moreover, the conductance values decreased dramatically with increasing membrane thickness, from 1 $\mu$m to 3 $\mu$m, but were only slightly lower for thicker (5 $\mu$m) membranes. This can be explained in terms of either an imperfect packing of the laminar MoS$_2$ membranes, as supported by the STEM image of the pristine MoS$_2$ membrane (figure 1(e)), or non-uniform dye functionalization of the thicker membrane [1], i.e. increased dye functionalization at the outer surface of the membrane, with limited dye diffusion through the inner MoS$_2$ membrane.

To quantify the influence of charge on ion transport through the MoS$_2$ membranes, $I-V$ measurements known as ‘drift-diffusion’ experiments were performed, as they are driven by both the diffusion due to concentration gradient and the applied potential difference [18, 22, 23]. The GHK equation, which
Assumes independence of the ion movements across a membrane, was used to express the cation/anion mobility ratio ($\mu^+ / \mu^-$) as shown in equation (1) [18, 24–26].

$$\frac{\mu^+}{\mu^-} = \frac{z_+^2}{z_-^2} \left( \frac{[C^-]_m}{[C^+]_m} \exp\left(\frac{-z_-F\Phi_m}{RT}\right) \right) \left( \frac{1 - \exp\left(\frac{z_+F\Phi_m}{RT}\right)}{1 - \exp\left(\frac{-z_-F\Phi_m}{RT}\right)} \right)$$

where $\Phi_m$ is the membrane potential (zero-current potential, often called the reversal potential), $[C^-]_m$ and $[C^+]_m$ are the concentration of anions and cations in the feed and the permeate reservoirs, respectively, $z_+$ and $z_-$ are the valences of cations and anions, respectively, and other symbols have their usual meanings. The mobility ratio, $\mu^+ / \mu^-$, of the pristine exfoliated and functionalized MoS$_2$ membranes were plotted using equation (1) as shown in figure 2(a). The mobility ratios of the pristine and functionalized cases decreased with increasing hydrated cation radii, which changed by over one order of magnitude from K$^+$ to Al$^{3+}$, after the chemical functionalization. This is in agreement with previous work studying ion transport through Ångström-scale slits [25]. Moreover, the individual mobility of cations ($\mu^+$) and anions ($\mu^-$) were calculated from the relation between ionic conductivity ($\sigma$) and ion mobility:

$$\sigma \approx F(C^+\mu^+ + C^-\mu^-).$$

The conductivity of chloride solutions was measured using a relatively high concentration of 0.1 M in both feed and permeate reservoirs (see tables S1 and 2 for a comparison of the ionic conductivity between the MoS$_2$ membranes and bulk chloride solutions), which allows the surface charge contribution to be neglected [18, 25, 27]. Figure 2(b) plots the ion mobility (filled circle and square) of the cations, and their corresponding chloride counter ions (open circle and square) within the MoS$_2$ membranes, as a function of hydrated cation radii [25, 28, 29] obtained by the combination of equation (2) and the calculated mobility ratio. The cation mobility ($\mu^+$) in laminar MoS$_2$ membranes decreased by ca. 10 and 100-fold for a pristine MoS$_2$ membrane and the dye-functionalized MoS$_2$ membrane, respectively, compared to ion mobility in bulk solutions (open and filled diamonds) [30]. Moreover, our measured ion mobilities are also compared to the literature values reported for the same type of laminar membranes (graphene oxide, see supporting information: figure S8, and Ti$_3$C$_2$T$_x$ (MXene) [11, 18] and porous separation membranes (Nafion-117 and Nafion XL perfluorosulfonic acid (PFSA) membranes) [31, 32] as shown in figure 2(b). This analysis indicated that a pristine MoS$_2$ membrane exhibited the retardation of ion transport of a similar magnitude to previously reported membranes. The variation of Cl$^-$ mobility was found to be within 15% and 20% for the pristine and the dye functionalization, respectively, estimated from average Cl$^-$ mobility for several ionic salt solutions. This finding is consistent with the variation in Cl$^-$ mobility found for transport through Ångström-scale slits (±15%) [25]. The cation mobility decreased with increasing hydrated cation radius, $R_H$, from K$^+$ to Al$^{3+}$ with the trend lines shown across cation radii, especially for MoS$_2$/SY. The dye-functionalized MoS$_2$ membrane not only

![Figure 2](image-url)
significantly suppressed ion transport through the membranes but also decreased the mobility for the cations with the larger hydrated radii. This is clearly revealed by comparing cation mobility between the functionalized and pristine MoS2 membranes, which correspond to ca. 9.5, 10.3, and 17.9-fold reduction in cation mobility for a range of mono-, di-, and trivalent cations, respectively, for the dye-functionalized MoS2 membrane compared to its pristine counterpart. By comparing similarly sized ions K\(^{+}\) (3.31 Å) and Cl\(^{-}\) (3.32 Å), \[28\] the potassium cations are seen to be transported through MoS2 membranes slightly more quickly than the chloride anion (K\(^{+}\)/Cl\(^{-}\) > 1), an effect attributed to the negatively charged surface of MoS2 membranes. This was observed for both pristine and dye-functionalized MoS2 membranes.

Furthermore, the transport through the MoS2 membranes was evaluated with different concentration of the permeate reservoirs, ranging from \(10^{-2}\) M to \(10^{-5}\) M, using KCl solution with a constant feed concentration at 0.1 M: the resultant current–voltage (I–V) responses are given in figure 3(a). By decreasing the KCl concentration on the permeate side, the diffusion current at zero applied voltage rapidly dropped due to the suppressed transport of Cl\(^{-}\) through the MoS2/SY membrane as shown in figure 3(b). To understand the effect of diffusive flux on the ion transport across the MoS2 membrane, we measured the zero-current potential, as well as the Cl\(^{-}\) mobility, for a variety of KCl permeate molarities as shown in figure 3(c). The Cl\(^{-}\) mobility through the MoS2 membrane dropped exponentially with decreasing salt concentration at the permeate side in agreement with previous literature using graphene oxide membranes \[18\], single-layer MoS2/graphene nanopores \[22, 23\], carbon/boron nitride nanotube, \[33, 34\] and nanochannel slits.

Figure 3. Concentration dependence of ion mobility. (a) I–V characteristics of the 3.01 ± 0.13 µm thick MoS2/SY membrane for KCl solutions at several permeate concentrations using a constant KCl concentration at the feed reservoir (100 mM). The inset shows a schematic of the drift–diffusion experiment at different permeate molarities (x mM). (b) The net ion current as a function of KCl concentration at the permeate reservoir. The red coloured line in (b) represents the trend in diffusion current as a function of KCl permeate molarity. (c) The zero-current potential (black line) and Cl\(^{-}\) mobility (red line) as a function of the permeate molarity. The Cl\(^{-}\) mobility was calculated using the combination of the GHK equation (equation (1)) and the ionic conductivity (equation (2)). The black and red coloured lines in (c) represent the trend in zero–current potential and Cl\(^{-}\) mobility, respectively, as a function of KCl permeate molarity. (d) Ion selectivity (%S) of the MoS2/SY membrane for K\(^{+}\) and Cl\(^{-}\) as a function of KCl permeate molarity. Error bars indicate standard deviation in our measurements of the zero–current potentials and ionic conductivity.
This is due to the effective surface charge of the membrane, which dominates membrane transport at the low salt concentration in the permeate reservoir [35, 36]. This suggestion is also supported by the zeta potential measurements showing that the SY-functionalized MoS$_2$ nanosheets are negatively charged at pH values around 7. The zero-current potentials scale with the logarithm of the permeate molarity, which results in the increase of the calculated K$^+$/Cl$^-$ mobility ratio (K$^+ >$ Cl$^-$). In addition, the ionic selectivity (S) at different permeate molarity can be deduced from the ionic mobility ($\mu_i$) defined as:

$$S = \left( \frac{\mu^+}{\mu^+ + \mu^-} \right) \times 100.$$  (3)

Figure 3(d) shows ion selectivity as a function of KCl concentration in the permeate reservoir. The selectivity for both ions (K$^+$ and Cl$^-$) are very similar (~50%) for the highest concentration ratio (10 mM/100 mM), and diverges with decreasing KCl concentration at the permeate side. This phenomenon can be explained by the increase of the surface zeta potential, due to the decrease of ionic strength as previously reported in pristine MoS$_2$ membranes [37]. The increasing zeta potentials result in repulsion between the negatively charged MoS$_2$/SY surface and Cl$^-$ ions.

To understand the role of the adsorption of hydrogen and hydroxide ions on the nanocapillary channels, and the consequent effect this has on membrane stability, the I–V responses of the membranes were measured for a constant KCl concentration for both sides (100 mM) for pH ranging from 3.4 to 10.8 as shown in figure 4(a). Figure 4(b) shows the ionic conductance of the dye-functionalized MoS$_2$/SY membranes as a function of pH values. The KCl conductance of the functionalized membrane slightly decreased in acidic media which corresponds to low adsorption of H$^+$ on the surface of the MoS$_2$/SY channels. By contrast,
the conductance increased sharply for basic media which indicated significantly higher OH\textsuperscript− adsorption on the Mo\textsubscript{2}S\textsubscript{2}/SY surfaces, resulting in an increase in negative charge density inside the nanochannels (see table S1 for bulk conductivity as a function of pH) [18, 38]. Similar behavior with increasing conductance at high pH has been reported for GO membranes [18], carbon nanotubes [38], and hBN nanochannels [25]. Iso-pH conditions were maintained for both feed and permeate reservoirs for this drift-diffusion experiment. Figure 4(c) shows the \textit{K}\textsuperscript{+}/Cl\textsuperscript− mobility ratio of the functionalized Mo\textsubscript{2}S\textsubscript{2} membrane and a pristine Mo\textsubscript{2}S\textsubscript{2} membrane as a function of pH. A pristine exfoliated Mo\textsubscript{2}S\textsubscript{2} membrane exhibited a small change in mobility ratios for a range of pH solutions with slightly increased at basic pH (K\textsuperscript{+}/Cl\textsuperscript− > 1) which indicated partial adsorption of hydroxide ions on the surface of the pristine Mo\textsubscript{2}S\textsubscript{2} channels. Interestingly, the mobility ratio of the dye-functionalized Mo\textsubscript{2}S\textsubscript{2} membrane decreased significantly at low pH values, which is consistent with some protonation of the Mo\textsubscript{2}S\textsubscript{2}/SY surface, lowering the absolute surface charge of Mo\textsubscript{2}S\textsubscript{2}/SY, as indicated by the zeta potential measurements (see figure S9). By increasing solution pH, the mobility ratio dramatically increased due to the greater extent of OH\textsuperscript− adsorption at the functionalized sites of the Mo\textsubscript{2}S\textsubscript{2}/SY surface. This significant change in mobility ratio reflects the role of functionalization in controlling the surface chemistry of Mo\textsubscript{2}S\textsubscript{2}, which in turn imparts the high cation selectivity of ~80% seen at basic pH which is necessary for nanofiltration. Figure 4(d) shows the K\textsuperscript{+} mobility increased and Cl\textsuperscript− mobility decreased (K\textsuperscript{+}/Cl\textsuperscript− ≫ 1) at high pH due to the influence of polarized water molecules around their hydration shells. This is attributed to preferential co-ordination of H\textsuperscript{+} and OH\textsuperscript− groups on the K\textsuperscript{+} and Cl\textsuperscript−, respectively [39]. This corresponds to an increase in the OH\textsuperscript− adsorption on the nanochannel’s surface at higher pH (see figure 4(b)); leading to a strong influence on the Cl\textsuperscript− transport on the Mo\textsubscript{2}S\textsubscript{2}/SY surfaces (higher Cl\textsuperscript− friction).

In addition, the change in surface chemistry after functionalization is reflected in changes in the water contact angle (WCA) in air, using ultra-pure water droplets placed on the surface of the Mo\textsubscript{2}S\textsubscript{2} membranes (see figure S10). The WCA of the Mo\textsubscript{2}S\textsubscript{2} membrane after functionalization (−68\textdegree) compares with a value of ~85\textdegree for the fresh, pristine Mo\textsubscript{2}S\textsubscript{2} membrane. This increase of hydrophilicity on dye functionalization may result from the increase in dye functionalization on the Mo-edge of Mo\textsubscript{2}S\textsubscript{2} (see HAADF-STEM in figure S5) due to the high number of defects created by the bath sonication process, which is also seen from the presence of Mo–N bonding determined by Raman and X-ray photoelectron spectroscopy (XPS) as shown in figures S11 and 12, respectively. Functionalized Mo\textsubscript{2}S\textsubscript{2} membranes were also soaked in different pH solutions (10\textsuperscript{−3}–10\textsuperscript{−5} M for HCl and KOH solutions) for a week and dried in a vacuum oven at room temperature. The functionalized acid-exposed Mo\textsubscript{2}S\textsubscript{2} membrane exhibits a constant WCA whereas a slightly lower WCA was seen for the membrane exposed to alkaline pH (10(8), which is again indicative of OH\textsuperscript− adsorption giving more hydrophilic material [40, 41].

In conclusion, the drift-diffusion technique has been applied to dye-functionalized Mo\textsubscript{2}S\textsubscript{2} membranes (Mo\textsubscript{2}S\textsubscript{2}/SY), revealing a strong reduction in ionic mobility, which is seen for a range of pH values, an experiment made possibly by the stability of the membrane materials. The ion mobility of the Mo\textsubscript{2}S\textsubscript{2}/SY membrane was reduced ca. Ten-fold, compared to the pristine Mo\textsubscript{2}S\textsubscript{2} membrane and other commercial membranes. Moreover, the molar conductivity decreased by over a factor of ~5 and ~50 for Mo\textsubscript{2}S\textsubscript{2}/pristine and Mo\textsubscript{2}S\textsubscript{2}/SY, respectively, compared to the bulk molar conductivity. Dye functionalization of Mo\textsubscript{2}S\textsubscript{2} membranes not only yields excellent charge/size selective ionic sieving but also enabled the tunability for cation selectivity of nearly 80% under alkaline conditions. Mo\textsubscript{2}S\textsubscript{2}/SY membranes show significantly improved ion rejection compared to those previously reported for GO, Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}, and porous polymeric membranes. Thus, the ability to alter the surface charge of the membranes via functionalization with organic molecules provides the capability to modulate ion transport selectively for technologies used in water purifications such as ion exchange membranes, specifically in applications for electro-dialysis and electro-deionization.

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Author contributions

MAB and RAWD conceived the experiment and designed research. WH prepared membranes and performed all ion transport measurements. PI assisted with analysis of current–voltage data, EP performed and analyzed electron microscopy.

Competing interests

A patent application relating to functionalized Mo\textsubscript{2}S\textsubscript{2} membranes has been filed by the University of Manchester.
Associated content

Supporting information

The supporting information is available free of charge on the website at (stacks.iop.org/TDM/7/015030/mmedia).

Materials and methods including silver/silver chloride agarose salt bridge preparation, membrane preparation and dye functionalization method; further membrane characterizations including SEM/EDX, STEM, XRD, Raman, XPS, zeta potential measurements, and water contact angle (WCA) experiments; further ion transport results through a pristine MoS$_2$ membrane and GO-based membranes including electrolyte and ionic conductivity measurements; ion mobility comparison between hydrated and nonhydrated cations; voltage drop across a bare PVDF membrane (PDF)

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References

[1] Hirunpinyopas W, Prestat E, Worrall S D, Haigh S J, Dryfe R A W and Bissett M A 2017 Desalination and nanofiltration through functionalized laminar MoS$_2$ membranes ACS Nano 11 11082–90
[2] Sun L, Huang H and Peng X 2013 Laminar MoS$_2$ membranes for molecule separation Chem. Commun. 49 10718–20
[3] Abraham J et al 2017 Tunable sieving of ions using graphene oxide membranes Nat. Nanotechnol. 12 546–50
[4] Joshi R K, Carbone P, Wang F C, Kravets V G, Su Y, Grigorieva I V, Wu H A, Geim A K and Nair R R 2014 Precise cationic control of interlayer spacing and insight into water solvation. Effective radii of hydrated ions J. Phys. Chem. C 118 11901–9
[5] Huang L, Zhang M, Li C and Shi G 2012 Scalable graphene-based membranes for ionic sieving with ultrahigh charge selectivity Nano Lett. 12 7782–32
[6] Kalinowski S and Fagaszewski Z 1995 A four-electrode potentiostat-galvanostat for studies of biliary lipid membranes Meas. Sci. Technol. 6 1050–3
[7] Ramachandraiah G and Ray P 1997 Electroassisted transport phenomenon of strong and weak electrolytes across ion-exchange membranes: chronopotentiometric study on deactivation of anion exchange membranes by higher homologous monocarboxylates J. Phys. Chem. B 101 7892–900
[8] Cseri L, Baugh J, Alabi A, AlHajai A, Zou L, Dryfe R A W, Budd P M and Szakely G 2018 Graphene oxide–polybenzimidazolium nanocomposite anion exchange membranes for electrodialysis J. Mater. Chem. A 6 24728–39
[9] Feng J, Wang J, Liu D, Yang C, Liu Y, Ruoff R S and Lei W 2018 Ultrafast molecule separation through layered WS$_2$ nanosheets Nano Lett. 18 8617–24
[10] Nightingale E R 1959 Phenomenological theory of ion sorption, Effective radii of hydrated ions J. Phys. Chem. 63 1381–7
[11] Lamprasertkun P, Hirunpinyopas W, Keerthi A, Wang B, Radha B, Bisset M A and Dryfe R A W 2019 Capacitance of basal plane and edge-oriented highly ordered pyrolytic graphite: specific effects of J. Phys. Chem. Lett. 10 617–23
[12] Yandex K, Tahir S, Michel T, Louber B, Manghi M, Bentin J, Picaud F, Palmeri J, Henn F and Jourdain V 2017 Voltage-activated transport of ions through single-walled carbon nanotubes Nanoscale 9 11976–86

membrane from two-dimensional molybdenum disulfide Nano Lett. 17 2342–8
[13] Hirunpinyopas W, Rodgers A N I, Worrall S D, Bissett M A and Dryfe R A W 2017 Hydrogen evolution at liquid|liquid interfaces catalyzed by 2D materials ChemNanoMat 3 428–35
[14] Sun L, Ying Y, Huang H, Song Z, Mao Y, Xu Z and Peng X 2014 Ultrafast molecule separation through layered WS$_2$ nanosheet membranes ACS Nano 8 6304–11
[15] Chen C, Wang J, Liu D, Yang C, Liu Y, Ruoff R S and Lei W 2018 Functionalized boron nitride membranes with ultrafast solvent transport performance for molecular separation Nat. Commun. 9 1902
[16] Liu Q-F, Chen G, Lin T-T and Yu Y 2015 Dye-functionalized graphene/polyaniline nanocomposite as an electrode for efficient electrochemical supercapacitor Compos. Sci. Technol. 115 80–6
[17] Huang J, Wang D, Yue Z, Li X, Chau D and Yang P 2015 Ruthenium dye N749 covalently functionalized reduced graphene oxide: a novel photocatalyst for visible light H$_2$ evolution J. Phys. Chem. C 119 27929–90
[18] Hong S, Constan C, Surmani Martins M V, Seow Y C, Guevara Carrió J A and Garaj S 2017 Scalable graphene-based membranes for ion sieving with ultrahigh charge selectivity Nano Lett. 17 7782–32
[19] Kalinowski S and Fagaszewski Z 1995 A four-electrode potentiostat-galvanostat for studies of biliary lipid membranes Meas. Sci. Technol. 6 1050–3
[20] Ramachandraiah G and Ray P 1997 Electroassisted transport phenomenon of strong and weak electrolytes across ion-exchange membranes: chronopotentiometric study on deactivation of anion exchange membranes by higher homologous monocarboxylates J. Phys. Chem. B 101 7892–900
[21] Cseri L, Baugh J, Alabi A, AlHajai A, Zou L, Dryfe R A W, Budd P M and Szakely G 2018 Graphene oxide–polybenzimidazolium nanocomposite anion exchange membranes for electrodialysis J. Mater. Chem. A 6 24728–39
[22] Feng J, Graif M, Liu K, Ovchinnikov D, Dumencedo C, Heiranian M, Nandigana V, Alhajai A, Radic R G and Radenovic A 2016 Single-layer MoS$_2$ nanopores as nanopower generators Nature 536 197–200
[23] Rollings R C, Kuan A T and Golovchenko J A 2016 Ion selectivity of graphene nanopores Nat. Commun. 7 11408
[24] Hille B 2001 Ion Channels of Excitable Membranes 3rd edn (Sunderland, MA: Sinauer) ch 14
[25] Esfandiar A, Radha B, Wang F C, Yang Q, Hu S, Garaj S, Nair R G, Geim A K and Gopinadhan K 2017 Size effect in ion transport through angstrom-scale slits Science 358 511–3
[26] Miedema H 2002 Surface potentials and the calculated selectivity of ion channels Biophys. J. 82 156–9
[27] Duan C and Majumdar A 2010 Anomalous ion transport in 2-nm hydrophilic nanochannels Nat. Nanotechnol. 5 548–52
[28] Nightingale E R 1959 Phenomenological theory of ion solvation, Effective radii of hydrated ions J. Phys. Chem. 63 1381–7
[29] Lamprasertkun P, Hirunpinyopas W, Keerthi A, Wang B, Radha B, Bisset M A and Dryfe R A W 2019 Capacitance of basal plane and edge-oriented highly ordered pyrolytic graphite: specific effects of J. Phys. Chem. Lett. 10 617–23
[30] Lide D R 2005 Handbook of Chemistry and Physics 85th edn (Boca Raton, FL: CRC Press)
[31] Steinna I A, Sipst P, Brevov I L, Pourcelly G and Yaroslavtsev A B 2004 Ion mobility in nafion-117 membranes Desalination 170 39–57
[32] Baker A M, Babu S K, Mukundan R, Advani S G, Prasad A K, Spernjak D and Borup R L 2017 Cerium ion mobility and transport through angstrom-scale slits J. Phys. Chem. Lett. 6 4026–31
[34] Siria A, Poncharal P, Biance A-L, Fulcrand R, Blase X, Purcell S T and Bocquet L 2013 Giant osmotic energy conversion measured in a single transmembrane boron nitride nanotube Nature 494 455
[35] Stein D, Kruihoff M and Dekker C 2004 Surface-charge-governed ion transport in nanofluidic channels Phys. Rev. Lett. 93 035901
[36] Schoch R B and Renaud P 2005 Ion transport through nanoslits dominated by the effective surface charge Appl. Phys. Lett. 86 253111
[37] Wang Z, Tu Q, Zheng S, Urban J J, Li S and Mi B 2017 Understanding the aqueous stability and filtration capability of MoS2 membranes Nano Lett. 17 7289–98
[38] Secchi E, Nígues A, Jubin L, Siria A and Bocquet L 2016 Scaling behavior for ionic transport and its fluctuations in individual carbon nanotubes Phys. Rev. Lett. 116 154501
[39] Strauss I, Chan H and Král P 2014 Ultrasound polarization chains induced by ions solvated in confined water monolayers J. Am. Chem. Soc. 136 1170–3
[40] Chen L, Xie H, Li Y and Yu W 2009 Carbon nanotubes with hydrophilic surfaces produced by a wet-mechanochemical reaction with potassium hydroxide using ethanol as solvent Mater. Lett. 63 45–7
[41] Ho T A, Papavassiliou D V, Lee L L and Striolo A 2011 Liquid water can slip on a hydrophilic surface Proc. Natl Acad. Sci. USA 108 16170–5