Advancing the conductivity-permselectivity tradeoff of electrodialysis ion-exchange membranes with sulfonated CNT nanocomposites

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1. Introduction

Ion-exchange membranes (IEMs) are polymeric films with charged moieties, which allow the selective transport of oppositely-charged counterions and retention of like-charged co-ions and electrically neutral species [1]. IEMs are widely utilized in environmental and energy applications [2–5], such as desalination, wastewater treatment, energy harvesting from salinity gradient, and fuel cells. A crucial limitation of IEM-based processes is the low ionic conductivity, $\sigma$, of conventional ion-exchange membranes [6]. The large contribution of the IEMs to the overall resistance of the membrane stack elevates ohmic losses in the circuit that detrimentally lowers the energy efficiency [7–9]. Additionally, the low conductivity also slows process kinetics by diminishing ion flux.

Efforts to enhance the intrinsic conductivity of conventional polymeric IEMs are constrained by a tradeoff relationship between conductivity and permselectivity, $\alpha$, the ability of the membrane to select for counterion passage while repelling co-ions. Empirical evidence from recent studies indicate that an increase in ionic conductivity unavoidably lowers the permselectivity, resulting in a tradeoff between the two key membrane performance parameters [Fig. 1, with vertical axis of intrinsic resistivity, the reciprocal of conductivity, is lowered with greater blending of sCNTs fillers, decreasing by approximately 25% with 20 w/w% incorporation of sCNTs, while permselectivity is effectively unchanged across the different degrees of sCNT incorporation (within 2% variation). Compared with pristine membranes, the conductivity-permselectivity tradeoff line of the fabricated nanocomposite membranes is advantageously advanced, thus improving overall performance. Further characterization and analysis show a percolating network of carbon nanotubes is achieved in the polymer matrix with 10 w/w% sCNTs incorporation. We posit that the improved effective ionic conductivity is attributed to the interconnected sCNT network reducing the tortuosity of the ion transport path. This study demonstrates the promise of percolating 1D nanomaterial networks to potentially advance the conductivity-permselectivity tradeoff governing conventional IEMs.
chemical moieties remain neutrally charged [16]. Other approaches to increase IEC also incidentally increases membrane swelling degree and dilutes the effective charges per unit weight of dry membrane. However, raising IEC also raises membrane resistance in aqueous solution [32, 33]. However, the role of matrix is not specifically studied and, thus, the potential to advance conductivity-permselectivity tradeoff of ion-exchange membranes has not been fully explored.

This study presents the development and characterization of a new type of nanocomposite cation exchange membrane (CEM). The nanocomposite CEMs were fabricated by incorporating sulfonic acid-functionalized carbon nanotubes (sCNTs) in sulfonated poly(2,6-dimethyl-1,4-phenyleneoxide) (sPPO) polymer matrix, employing the solvent evaporation method. The influence of swelling degree (SD) on the resistivity of fabricated membranes was evaluated by thoughtful control of the heating duration during fabrication to achieve different extents of membrane hydration. The impacts of sCNT loading on the intrinsic resistivity and permselectivity of nanocomposite membranes were then investigated, and the conductivity-permselectivity tradeoff of nanocomposite IEMs was compared to control membranes without sCNT addition. Electrochemical impedance spectroscopy (EIS) analysis of the dry membrane resistance and scanning electron microscopy (SEM) were employed to examine the network of 1-dimensional nanomaterial within the membrane. This work investigates the potential of rational nanomaterials utilization to advance the conductivity-permselectivity tradeoff governing conventional IEMs.

2. Materials and methods

2.1. Materials and chemicals

Pristine multiwalled carbon nanotubes, CNTs, (20–30 nm outer diameter, 5–10 nm inner diameter, 10–30 μm length, 95% purity) were purchased from Cheap Tubes Inc. (Cambridgeport, VT) and used as received. Concentrated sulfuric acid (H2SO4, 98%), acetic anhydride, methanol, sodium hydroxide, chloroform, dimethyl sulfoxide (DMSO), and sodium chloride were acquired from Fisher Scientific (Pittsburgh, PA), whereas chlorosulfonic acid was procured from Sigma-Aldrich (St. Louis, MO). All chemicals are reagent grade and used as received. Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was acquired from Sigma-Aldrich and used as received. Indium foil was obtained from Alfa Aesar (Ward Hill, MA). Deionized (DI) water was purified with a Milli-Q system (Millipore Co., Burlington, MA). Polytetrafluoroethylene (PTFE) membrane disc filters (0.2 μm pore size, 47 mm diameter) were acquired from Fisher Scientific.

2.2. Nanocomposite ion-exchange membrane fabrication

2.2.1. Sulfonation and characterization of carbon nanotubes

Sulfonated nanomaterials have been incorporated into polymeric matrices for ion- and proton exchange membranes [34–41]. Sulfonation of the multiwalled CNTs using acetyl sulfuric acid was adopted from a previous study [42]. 20 mL concentrated sulfuric acid was slowly added to 40 mL acetic anhydride placed in an ice-water bath and vigorously stirred for 30 min. 40 mg pristine CNTs (pCNTs) were added to the mixture and sonicated for 30 min in ice-water bath. The mixture was then stirred at 80 °C for 24 h. The resulting product was diluted by 200 mL DI water, vacuum-filtered with PTFE membrane, and washed by DI water and methanol for three times each. The sulfonated CNTs (sCNTs), depicted in Fig. 2A, were then dried in a vacuum oven at 80 °C for 12 h. To assess the degree of CNT sulfonation, X-ray photoelectron spectroscopy, XPS (Phi 5500 XPS, PerkinElmer, Inc., Waltham, MA) was employed to characterize the chemical composition of pCNTs and sCNTs. Mg was used as the X-ray source with a work function of 4.5 eV, and AugerScan software was used for data collection, curve fitting, and quantitative analysis.

2.2.2. Sulfonation of PPO polymer

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was used as the backbone polymer of the IEMs in this study, with sulfonate as the negatively charged functional groups (Fig. 2B). The chemistry to
shredded into small pieces and washed with DI water multiple times until pH of the rinse water was higher than 4. After washing, the poly methanol solution was evaporated in a glass tray for 24 h to form a layer was cast onto a glass sheet using a casting knife with gate height set at 2.2.3. Membrane casting

A solution of sPPO was prepared and sCNTs were then mixed into the DMSO solution to remove residual solvents. To obtain membranes with different sPPOs and sCNTs links two chains with

2.2.2. Membrane casting

Sulfonated PPO polymer was dissolved in DMSO to obtain 19 w/v% casting solutions. Then, sCNTs were mixed into the DMSO solution to achieve 0–20 w/v% relative to sPPO. The sCNT-dispersed solution was immersed in an ultrasonic bath for 40 min before casting. Solvent evaporation method was employed for IEM fabrication [1]. The solution was cast onto a glass sheet using a casting knife with gate height set at ≈1.0 mm. The cast film was dried in a vacuum oven at 80 °C for 24 h to remove residual solvents. To obtain membranes with different swelling degree, the samples were further heated at 95 °C for between 24 and 48 h. Heat-induced self-condensation between sulfonic groups on sPPOS and sCNTs links two chains with −SO2− and hence eliminates a portion of −SO3H functional groups [47]. The loss of sulfonic groups lowers the density of fixed −SO3H functional groups and reduces the membrane hydrophilicity [1]. Additionally, the increased crosslinking in the polymer matrix confines the volume of water sorption [48]. These two effects reduce hydration ability of the IEMs.

2.3. Membrane characterization

2.3.1. Swelling degree

Swelling degree (SD) defines the ability of the IEM matrix to absorb water. The membrane was soaked in DI water for 24 h. Excess water on the sample was carefully removed and the wet weight (W wet) was recorded. The dry weight of the membrane (W dry) was determined after drying for 24 h in a vacuum oven at 60 °C. SD is calculated using [49]:

\[
SD = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{wet}}} \times 100\%
\]

2.3.2. Ion exchange capacity

Ion-exchange capacity (IEC) refers to the specific capacity of the IEM to hold exchangeable counterions and is generally expressed as the number of fixed charges per unit weight of dry membrane [1]. Acidity of the protonated membrane sample was used to determine the IEC of cation exchange membranes (CEMs) fabricated in this study [49]. To protonate all the functional groups, the membrane was immersed in 1 M HCl solution for 24 h and washed quickly with DI water. The sample was then soaked in 50 mL of 1 M NaCl aqueous solution for 24 h, exchanging H+ within the IEM matrix with Na+. 25 mL of the soaking solution was titrated with 0.01 M NaOH using phenolphthalein as indicator. The membrane was dried using the procedure described earlier and the weight, W dry was recorded. IEC is calculated with

\[
\text{IEC} = \frac{2C_{\text{NaOH}} V_{\text{NaOH}}}{W_{\text{dry}}}
\]

where C NaOH and V NaOH are concentration and volume of the titrated NaOH solution, respectively. Coefficient of two denotes the volume ratio of initial NaCl soaking solution (50 mL) to titrated sample (25 mL).

2.3.3. Morphology

To prepare membrane for imaging that are representative of the swollen state, the fabricated IEM coupons were soaked in 1 M NaCl for at least 24 h. The water-swollen IEMs were then dipped into liquid nitrogen for ≈40 s. Using tweezers, the membranes were carefully snapped in half to expose the cross-section. The samples were mounted onto specimen holders with carbon tape. To eliminate undesired static electric charge effect, ≈10 mm Au coating was applied before imaging. The samples were analyzed with scanning electron microscopy, SEM (SIGMA VP, Carl Zeiss, Germany).

Electrochemical impedance spectroscopy (EIS) with an electrochemical workstation (Interface 1010E, Gamry Instruments, Warminster, PA) was utilized to characterize the membranes at dry state [50, 51]. Newly fabricated membranes were soaked in 1 M NaCl solution overnight then dehydrated in vacuum oven for 12 h. The dry membranes were sandwiched between Au-coated coin electrodes (16 mm diameter) and scanned with alternating current over the frequency range from 1 Hz to 1 MHz.

2.3.4. Area specific resistance and resistivity

An electrochemical test setup based on a four-electrode cell system was used for resistance measurements [1]. The two chambers of the cell (≈16 mL in each chamber) were separated by a 2 cm × 2 cm membrane coupon. The terminal working electrodes are Pt-coated Ti mesh (4 cm × 4 cm). Two Ag/AgCl reference electrodes (BASI RE-5B, Bioanalytical Systems, Inc., West Lafayette, IN), positioned 7 mm apart and straddling the IEM, measures the potential difference across. Membrane resistance was measured using an electrochemical workstation (Interface1010E). The chambers of the test cell were filled with 1 M NaCl electrolyte solution. A scanning direct current was applied, from 1 to 10 mA (i.e., current density of 0.25–2.5 mA/cm2) in increments of 1 mA, and voltage drop across the membrane was recorded. Each current step was maintained for 10 s during which the voltage drop was sampled 10 times. The slope of voltage drop as a function of current density (dV/di), after subtracting the blank test reading (dV blank/di), i.e., recorded resistance without IEM, yields the area specific resistance (ASR) of the membrane:

\[
\text{ASR} = \frac{dV}{di} - \frac{dV_{\text{blank}}}{di}
\]

Wet thickness of the membranes, l, was determined using a digital micrometer. The area specific resistance normalized by wet thickness returns the membrane intrinsic resistivity, ρ, which is the reciprocal of conductivity, σ, i.e., ρ = ASR/l = σ–1.

2.3.5. Permeselectivity

Permeselectivity, α, describes the selectivity of the IEM for counterion transport over co-ions. The same test cell and electrochemical workstation employed for resistance characterization were used for permeselectivity measurements. The static method was adopted [1], which utilizes the potential difference across the membrane separating two solutions of different concentrations to determine the apparent
permselectivity, $\alpha$. In this study, 0.1 and 0.5 M NaCl solutions were circulated on opposite sides of the IEM. The potential difference between the two Ag/AgCl reference electrodes, $\psi_{\text{measured}}$, was averaged over 15 min after it had stabilized (fluctuations were within 0.1 mV over 5 min) [52–54]. Offset potential between the reference electrodes, $\psi_{\text{offsets}}$, was measured in 0.5 M NaCl solution with the same stabilization criterion. Junction potential difference between the two reference electrodes, $\psi_{\text{junction}}$, across 0.5 and 0.1 M NaCl solutions was estimated as 7.9 mV using the activity-corrected form of the Henderson equation [52]. Theoretical Nernst potential ($\psi_{\text{theoretical}}$) between 0.5 and 0.1 M NaCl solutions was calculated as 37.9 mV [11]. Solution-phase transport numbers for counterion, $t_{\text{ct}}$, and co-ion, $t_{\text{co}}$, which are Na$^+$ and Cl$^-$ in this study, were calculated as 0.396 and 0.604, respectively [55]. Apparent permselectivity is determined by [56]:

$$
\alpha = \frac{\psi_{\text{measured}} - \psi_{\text{offsets}}}{2 t_{\text{co}}} + 1 - 2 t_{\text{co}}.
$$

(4)

3. Results and discussion

3.1. Characteristics of sulfonated CNTs

Multiwalled carbon nanotubes were functionalized using acetyl sulfuric acid, decorating the outer wall of the nanotubes with sulfinic acid functional groups. XPS was employed to analyze the surface elemental compositions of the pristine and sulfonated carbon nanotube, pCNT and sCNT, respectively, and the survey spectra are presented in Fig. 3. Both spectra of pCNT and sCNT show a sharp carbon peak at binding energy of 285 eV [57], as expected for the carbon-based nanomaterial (labeled C1s in Fig. 3A). The peaks at around 450 eV are the signal of the indium foil substrate [57]. Around the characteristic binding energy of oxygen (O1s, ~532 eV) [57], both spectra display a peak for oxygen components: pCNT presents a weak peak for C–O and C=O defects on carbon nanotubes, whereas the sCNT spectrum exhibits a stronger signal due to additional S=O and S–OH functional groups produced in the sulfonation reaction.

The major difference between the spectra of pCNT and sCNT lies in the sulfur peak region (~168 eV) [57]. In the S2p spectrum of pCNT (Fig. 3B), no sulfur signal can be identified, i.e., as expected, sulfur is not present in pCNT. In contrast, a sulfur peak is observed in the S2p spectrum of sCNT and can be decomposed into S2p\(_{1/2}\) at 169.48 eV and S2p\(_{3/2}\) at 167.71 eV (Fig. 3C) [57]. Specifically, the binding energy of the sulfur peak matches the features of sulfate (168–171 eV) [57], thus validating the presence of sulfinic acid groups on the carbon nanotubes.

Quantitative analysis of surface elemental composition was carried out by combining multiplex scan results with the relative sensitivity factors of each element [57]. The atom ratio and weight percentage of the elements for pCNT and sCNT are summarized in Table 1. The O and S ratios of peak area to sensitivity factor is normalized by C to determine the atom ratios. The atom ratio is converted to weight percentage by factoring in the atomic weight of each element. Dividing the mass fraction of S in the sCNT by the molecular weight of S (32 g/mol) yields the effective IEC of the sulfonated carbon nanotubes. Mass concentration of sulfur in sCNT is around 3.5%, whereas no sulfur was detected in pCNT. In contrast, a sulfur peak is observed in the S2p spectrum of sCNT, whereas no sulfur signal can be identified, i.e., as expected, sulfur is not present in pCNT. The sulfur peak region (~168 eV) [52], no sulfur can be identified, i.e., as expected, sulfur is not present in pCNT. The sulfur peak of non-sulfonated pCNT and sCNT, respectively: A) full XPS spectra survey, B) S signal of non-sulfonated pCNT, and C) S peak of sCNT.

To investigate the impact of functionalization on CNT stability in casting solution, pCNTs and sCNTs were sonicated in casting solvent of DMSO for 3 min to obtain well-dispersed suspensions (Fig. 4). After 10 h, pCNTs aggregated and settled to the bottom, while sCNTs remained stable in DMSO for more than 3 months. This result confirms that sulfonation enhances the dispersibility of CNTs in DMSO, which can facilitate the incorporation of nanotubes into the polymer matrix of the

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**Table 1**

XPS atomic analysis of pristine and sulfonated carbon nanotube, pCNT and sCNT, respectively.

|        | Peak area | Atom ratio (C:O:S) | Weight percentage (C%:O%:S%) | IEC of $\text{SO}_3^-$ (meq/g) |
|--------|-----------|--------------------|-------------------------------|-----------------------------|
| pCNT   | 13,997    | 2,557              | 1 : 0.076 : 0                 | 90.8 : 9.8 : 0              | –                         |
| sCNT   | 12,768    | 4,186              | 1 : 0.136 : 0.016             | 81.7 : 14.8 : 3.5           | 1.1                       |
membranes, resistivity rose from 86 to 622 $\Omega \text{cm}$. As depicted in Fig. 5, the intrinsic resistivities of both CNT-mixed and control IEMs are negatively correlated with SD, in agreement with the theoretical framework for IEM transport [14]. The rise in membrane resistivity is especially pronounced as SD falls below $\approx 30\%$. Comparing the $\rho$ and SD data shows that incorporation of sCNTs leads to reduced membrane resistivity across the SD range investigated (blue circle symbols are generally to the lower left of orange square symbols). For instance, at swelling degree $\approx 45\%$, membranes without sCNTs exhibit an average resistivity of 169 $\Omega \text{cm}$, while addition of 20 w/w% sCNT to the membrane lowered $\rho$ to 112 $\Omega \text{cm}$ (33.7% decrease). This resistivity reduction of the nanocomposite IEMs is more amplified at lower swelling degrees, especially when SD is less than $\approx 20\%$.

The inverse relationship between SD and $\rho$ can be modeled based on ion transport analysis presented in our previous study [14]:

$$ f_w = \frac{SD}{SD + \phi^*_p} \quad \text{(5)} $$

$$ \rho = \lambda \left( 2 - f_w \right)^2 \quad \text{(6)} $$

where $f_w$ is the volume fraction of water in ion-exchange membrane and is related to SD through dry polymer density, $\phi^*_p$ (Eq. (5)). The influences of fixed charge density, ion diffusivity, and counterion condensation are aggregated into fitting parameter, $\lambda$, to enable simplification of the analysis by isolating the confounding effect of $f_w$ (or, equivalently, SD) without needing to separately quantify the individual influence of the different phenomena [14,61]. The experimental data of resistivity and SD for the nanocomposite and control membranes are fitted to Eqs. (5) and (6), shown in Fig. 5 as blue and orange dashed lines, respectively. The fitted $\rho$-SD trendlines enable direct quantitative comparison of IEM resistivity by excluding the free volume effect. Down and leftwards shift of the $\rho$-SD curve after sCNTs incorporation is clearly evident. The fitting parameter $\lambda$ for sCNT nanocomposite membranes and control membranes are 3.16 and 5.07, respectively, indicating that the blending of 20 w/w% sCNT favorably lowers resistivity by $\approx 38\%$ for the same $f_w$. Therefore, the introduction of rationally functionalized carbon nanotubes as fillers to the polymer matrix is a swelling degree-independent approach to advantageously improve IEM ionic conductivity.

3.3. Nanocomposite IEM resistivity drops with greater loading of sCNT

The impacts of different sCNT loading on membrane structural properties and performance parameters were further investigated. Weight ratio of sCNT to composite, i.e., polymer matrix and sCNTs, was tuned from 0 to 20 w/w% using the membrane fabrication protocol described in Section 2.2, except the heating time at 95 °C is fixed at 24 h to produce membranes with similar swelling degree. Digital images, structural properties of wet thickness, $l$, ion-exchange capacity, IEC, and
swelling degree, SD, and electrochemical parameters of area specific resistance, ASR, intrinsic resistivity, ρ, and permselectivity, α, are presented in Table 2 for the sPPO-only and sCNT-incorporated membranes. Experimental variations of IEC and SD between the membranes with different sCNT loadings are largely attributed to the inherent capricious tendency of the condensation reaction of sulfonic groups during membrane fabrication.

The polymeric membranes without CNT, i.e., controls, are translucent yellowish thin films. Incorporation of sCNTs tinged the membranes black, with increasing CNT loading resulting in progressive intensification of opacity. The uniformity of the 2.0, 10, and 20 w/w% sCNT membranes, without aggregated CNT bundles visible, corroborates the excellent dispersion of nanotubes in the membrane matrix. Thickness of membranes at water-swollen state with 0–20 w/w% sCNT loading ranged from 75 to 105 μm. Ion-exchange capacity, which describes the density of membrane fixed charges, of 1.48–1.84 meq/g were measured for the fabricated IEMs, comparable to the typical range of 1–3 meq/g reported in literature for commercial and lab-fabricated IEMs [6]. Generally, IEC drops with the incorporation of sCNTs. This decrease in IEC is attributed to the difference in degree of functionalization between the sulfonated carbon nanotubes and the charged polymer. The equivalent −SO3H capacity of the lab-functionalized sCNTs is ≈1.1 meq/g (Table 1), whereas IEC of the sPPO polymer matrix is higher at around 1.84 meq/g (equivalent to IEC of the polymer-only control membranes). Therefore, the mixing of sCNT fillers into the polymer matrix effectively dilutes the density of fixed functional groups and, hence, lowers the overall membrane IEC. Increasing sCNT loading also, in general, reduces the swelling degree of fabricated nanocomposite membranes. Adding sCNTs to the sPPO polymer lessened SD from 53.8% to 42.3–49.9%, as the nanocomposite membranes are rendered less hydrophilic due to the diminished IEC [1] and membrane hydration capacity is, therefore, depressed.

The influence of sCNT loading on IEM membrane performance was characterized by electrochemical measurements of area specific resistance, ASR, membrane intrinsic resistivity, ρ, and apparent permselectivity, α (Table 2). Specifically, intrinsic resistivity, the reciprocal of conductivity, is ASR normalized by I and is, hence, an intensive property of the IEM, i.e., independent of dimensions and amount of material. Therefore, by excluding the confounding factor of inherent experimental variations in membrane thickness, ρ is a more accurate and insightful parameter to quantify the effects of sCNT addition. Intrinsic resistivity and permselectivity data of Table 2 are presented in Fig. 6 as a function of sCNT loading (red square symbols, left vertical axis, and green circle symbols, right vertical axis, respectively).

Fig. 6 shows an overall decreasing trend in intrinsic resistivity, from 163 to 122 Ωcm, of the nanocomposite membranes with increasing amount of sCNT incorporation. Resistivity of the 2.0 w/w% sCNT IEMs are only marginally lower than the polymer-only membranes (−1.2%). However, a sharp reduction in ρ of 23% (relative to control) is observed between 2.0 and 10 w/w%, followed by a further gentle decrease from 10 to 20 w/w% (−25% compared to 0 w/w%). The steep drop-off in resistivity between 2.0 and 10 w/w% is possibly caused by the formation of a percolating carbon nanotube network [24,25,62], where the CNTs are continuously connected across the membrane thickness. The contiguous network of CNT fillers within the polymer matrix and the percolation threshold of nanotubes loading at which the lattice forms are further discussed in Section 3.5. In contrast to the declining resistivity trend, the membrane apparent permselectivity, α, a measure of IEM selectivity for counterion transport over co-ion, is practically preserved across the sCNT loadings investigated (Table 2 and Fig. 6). Compared to the sPPO-only control membranes, α of the nanocomposite IEMs with 2.0–20 w/w% differs by <2.0%, indicating permselectivity of the fabricated membranes is effectively not influenced by the incorporation of sCNTs. Therefore, the blending of sulfonated CNTs filler into the sPPO polymer matrix yields enhanced ionic conductivity without compromising counterion selectivity in the nanocomposite IEMs. The impact of sCNT addition on conductivity-permselectivity tradeoff is further analyzed in Section 3.4.

Mixing the lab-functionalized sCNT into the membrane incidentally lowers SD and IEC (Table 2). The equivalent fixed charge density, which is the concentration of fixed charged moieties in water swollen membrane matrix (calculated as IEC×ρw/SD, where ρw is the density of water), of the 20 w/w% sCNT membranes also dropped from 3.42 to 3.30 eq/L water sorbed, compared to 0 w/w% samples. For conventional ion-exchange membranes, the drop in SD and IEC would deleteriously elevate ionic resistivity [14,15,60], because of i) diminished effective ion diffusivity at lower swelling degrees, thus causing an inverse

### Table 2

| sCNT weight percent | 0 w/w% | 2.0 w/w% | 10 w/w% | 20 w/w% |
|---------------------|--------|----------|---------|---------|
| Thickness, l [μm]   | 86 ± 7 | 75 ± 8   | 105 ± 3 | 98 ± 5  |
| IEC [meq/g]         | 1.84   | 1.54     | 1.66    | 1.48    |
| SD [%]              | 53.6   | 42.3     | 49.9    | 44.9    |
| ASR [Ω·cm⁻²]        | 1.39 ± 0.04 | 1.21 ± 0.06 | 1.31 ± 0.03 | 1.19 ± 0.04 |
| ρ [Ω·cm]            | 163 ± 5 | 161 ± 8  | 125 ± 3 | 122 ± 4 |
| α [-]               | 0.862  | 0.858    | 0.862   | 0.845   |
relationship between $\rho$ and SD (explained earlier in Section 3.2) [14,59] and ii) the fall in IEC, and equivalently fixed charge density, reduces the concentration of mobile counterions inside the membrane, which are the main current carriers, thus resulting in smaller ion fluxes and, correspondingly, larger resistivity [14,60]. Despite the unfavorably decreased SD and IEC of the nanocomposite IEMs, incorporation of sCNT still improved ion permeability and reduced resistivity, signifying the conductivity enhancements are caused by a different mechanism that arises from the presence of 1-dimensional nanomaterial filler in the polymer matrix. Section 3.5 further examines this underlying phenomenon.

### 3.4. Incorporation of sCNTs advances the IEM conductivity-permselectivity tradeoff

High conductivity and high permselectivity are desired in IEMs for fast and efficient charge separations. A previous theoretical study on IEM transport established that conductivity, $\sigma$, can be improved by raising swelling degree but permselectivity, $\alpha$, is detrimentally compromised, i.e., varying SD produces a tradeoff between conductivity and permselectivity [14]. The role of water uptake in IEM $\sigma$-$\alpha$ tradeoff relationship was also observed by empirical studies [7,58,59]. To investigate the effect of sCNT fillers on the SD-controlled conductivity-permselectivity tradeoff, 20 w/w% sCNT nanocomposites and sPPO-only membranes with different SD were prepared by purposefully altering the fabrication condition of heating duration.

Fig. 7 shows the permselectivity falls as conductivity increases with higher SD for both the sCNT-incorporated and control membranes (blue circle and orange square symbols, respectively). For membranes with sCNT fillers, permselectivity declines from 0.914 to 0.845, whereas conductivity is elevated from 0.300 to 0.885 S/m. The same negatively correlated trend is observed for the control samples: $\alpha$ decreases from 0.902 to 0.837 while $\sigma$ increases from 0.252 to 0.662 S/m. Linear regression on permselectivity and conductivity of nanocomposites and sPPO-only membranes are indicated by blue and orange dashed lines, respectively. Both trendlines exhibit negative slopes with similar gradients of $-0.115$ and $-0.112$ for sPPO-only control membranes and sCNT-incorporated membranes, respectively. As depicted in Fig. 7, integrating sCNT into the polymer matrix of cation exchange membranes shifts the conductivity-permselectivity tradeoff line outwards, to the top right, i.e., for the same conductivity, nanocomposite IEMs have higher permselectivity than polymer-only membranes.

The results indicate the incorporation of sCNT can advance the conductivity-permselectivity tradeoff that constrains conventional ion-exchange membranes. Unlike the common strategy of introducing more fixed charged functional groups into the membrane polymer matrix to bolster performance, the thoughtful dispersion of sCNT to produce nanocomposite IEMs enhances $\alpha$ and $\sigma$ even though IEC is adversely lowered. This implies that performance improvements are likely due to other structural changes caused by the addition of sCNT fillers, and is further investigated in the next Section.

### 3.5. Conductivity improvements are attributed to percolating network of sCNTs in IEM polymer matrix

SEM micrographs of the sPPO-only membranes (top row, A-C) and nanocomposites with 20 w/w% sCNTs (bottom row, D-F) are presented in Fig. 8. Fig. 8A and D show the planar surface, Fig. 8B and E display the IEM cross-sections, and Fig. 8C and F are further zoomed-in cross-sectional views (10,000, 500, and 50,000 $\times$ magnification, respectively). Surface of the control sPPO thin film is dense and relatively flat (Fig. 8A). A similar nonporous and smooth morphology is observed in the cross-sectional views of Fig. 8B and C (flakes and small shreds of polymer Fig. 8B are artefacts of sample preparation when the membrane is snapped to expose the cross-section). The dense morphology is also observed in the polymer matrix of the 20 w/w% sCNT membranes (Fig. 8D–F) but, additionally, CNTs are visible (bright rods and dots as the nanotubes are electrically conducting). The 1D nanomaterials are clearly seen protruding out of the membrane surface and are especially prominent in the cross-sectional micrographs (Fig. 8E and F). The width of the rods observed in the SEM micrographs is measured to be $26.8 \pm 2.3$ nm (averaged by 6 readings), corresponding well with the manufacturer’s specifications of 20–30 nm outer diameter. The generally even distribution of bright rods and dots further substantiates the uniform dispersion of CNTs within the polymer matrix of the nanocomposite IEMs, consistent with the digital images of Table 2. SEM micrographs of the 10 w/w% sCNT IEMs (results not shown) are visually similar to the 20 w/w% samples, albeit with a lower density of nanotubes, i.e., lesser bright rods and dots.

Electrochemical impedance spectroscopy (EIS) tests were conducted on the membranes in dry state to probe the electrical conductivity with different sCNT loading. Changes in the net electrical conductivity measured provide information on the dispersion of electrically-conductive CNT fillers within the relatively insulating polymer matrix [26,63]. Fig. 9 shows the through-plane conductivity of membranes (logarithmic scale) as a function of weight percent of sCNT incorporation. Note that EIS conductivity is a measure of the conductivity of electrons across the membrane and is different from the hydrated conductivity (i.e., IEM in aqueous solution) discussed earlier, which represents ionic conductivity in electrolyte solutions. Dry conductivity, $\kappa$, of the pristine polymeric membrane, determined from the fitting of EIS impedance results, is $2.57 \times 10^{-3}$ S/m. $\kappa$ initially rises to $8.25 \times 10^{-5}$ S/m for the 2.0 w/w% sCNT IEM and then increases by almost 4 orders of magnitude to $5.57 \times 10^{-3}$ S/m for 10 w/w% sCNT. Doubling the sCNT loading further to 20 w/w% yields a comparatively modest elevation of $\kappa$ to $2.15 \times 10^{-2}$ S/m. The dry conductivity trend is in agreement with the percolating network explanation postulated earlier in Section 3.3: when CNT loading increases beyond a certain threshold, the 1D nanotubes form an uninterrupted network that enables the continuous transport of electrons across the membrane thickness through the electron-conducting CNTs [26,63], thus resulting in a drastic increase in electrical conductivity. Increasing the CNT loading beyond the percolating threshold produces a diminishing return in conductivity enhancement [24,25,62]. From the data of Figs. 6 and 9, the threshold at which the contiguous lattice of CNT filler is formed is estimated to be between 2.0 and 10 w/w%. Therefore, the impedance
characterization of dry state membranes and cross-sectional SEM micrograph analysis corroborate that a percolating nanotube network was achieved in 10 and 20 w/w% sCNT IEMs.

Based on the structure-property analyses of SEM imaging and EIS conductivity characterization, we deduce that the improved conductivity-permselectivity performance at adequately high 1D nano-material loading is due to the formation of a percolated CNT network when the filler exceeds the percolation threshold. We postulate that the contiguous and interconnected network of nanotubes across the nano-composite IEM thickness favorably shortens the effective transport pathway for ions (illustrated by Fig. 10). In pristine membranes, i.e., without sCNT incorporation, the polymer chains are entangled, thus forming compact clusters [64]. We conjecture that the sCNTs embedded in the polymer matrix disrupt the compact polymer packing, loosening the structure to create shortcuts for ion electro-diffusion. Thus, the transport pathway is less tortuous and the effective ion diffusivity is correspondingly improved. In addition, the sCNTs of 5–10 nm inner diameter can function as fast ion conduction channels by allowing transport of hydrated ions inside the inner most tube [65], possibly contributing to the improvement of ion permeability.

Permselectivity, on the other hand, is not significantly impacted by the CNT incorporation. This is because the sulfonic acid moieties functionalized onto the sCNTs contribute to the IEC/fixed charge density of the membrane. In contrast, control membranes incorporated with 20 w/w% pristine CNTs, i.e., carbon nanotubes without negatively charged sulfonate moieties, possess appreciably lower permselectivity (approximately 4%) compared to IEMs with 20 w/w% sCNT membranes under the same fabrication conditions. The lowered $\alpha$ of the pCNT nano-composite IEMs can lead to an additional 20% co-ion leakage in electrodialysis-based applications, relative to membranes incorporated with sCNT. The charge exclusion effect of nanocomposite membranes with sulfonated carbon nanotubes is better preserved and, hence, selectivity for counterions is not detrimentally affected.

4. Concluding remarks

In this study, we developed novel nanocomposite ion exchanges
membranes with percolated 1D nanomaterial network, i.e., sulfonated PPO polymer matrix incorporated with sulfonated carbon nanotube fillers. Unlike common conventional IEM fabrication approaches that tune the performance parameters through altering IEC or SD [1,15], the nanocomposite membranes with percolated nanotubes fabricated here demonstrate a new strategy to reduce membrane resistance while maintaining permselectivity, to advance the overall conductivity-permselectivity tradeoff line. The intrinsic resistivity of the nanocomposite IEMs is favorably lowered by as much as 25% with up to 20 w/w% incorporation of sCNT. The percolation of carbon nanotubes inside the nanocomposite membranes is corroborated by scanning electron microscope analysis and electrochemical impedance spectroscopy characterization. We postulate that the increase in effective ion conductivity is due to the interconnected network of sCNT reducing the tortuosity of the ion diffusion path. This study demonstrates the potential of rational utilization of nanomaterials to advance the conductivity-permselectivity tradeoff governing conventional IEMs. However, additional investigations are needed to demonstrate that the approach can be extended to improve current best-performing IEMs (indicated by green dotted line of Fig. 7). Future studies to investigate the effect of nanotubes properties, such as, diameter, length, functionality, and aspect ratio, can further enhance the performance of nano-composite ion-exchange membranes. The IEM fabrication platform can be extended to other nanomaterials, such as nano-dots, -wires, and -sheets, to produce different matrix-filler nanocomposites.

CRediT authorship contribution statement

Hanqing Fan: Conceptualization, Methodology, Formal analysis, Investigation, Data curation, Software, Writing - original draft, Writing - review & editing, Visualization. Yuxuan Huang: Methodology, Data curation, Formal analysis, Investigation, Writing - original draft, Writing - review & editing. Ngai Yin Yip: Conceptualization, Methodology, Formal analysis, Writing - original draft, Writing - review & editing, Funding acquisition, Supervision.

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