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Graphene–PSS/L-DOPA nanocomposite mixed matrix cation exchange membranes for electrodialysis desalination

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Abstract

This research reports the fabrication of nanocomposite cation exchange membranes (CEMs) by incorporating negatively charged graphene-based nanomaterials into a non-charged poly(vinylidene fluoride) (PVDF) matrix using a mold-casting technique developed in-house. Graphene oxide (GO) or reduced graphene oxide (rGO) nanosheets were modified into ion exchange group carriers using a sulfonic group-bearing agent based on poly(sodium 4-styrenesulfonate)/3,4-dihydroxy-L-phenylalanine (PSS/L-DOPA) (SGO or SrGO). Such modified nanosheets provide the ion exchange capabilities in SGO/PVDF and SrGO/PVDF nanocomposite CEMs, respectively. Both nanocomposite CEMs displayed lower linear swelling ratios which are good for membrane stability. This was due to the presence of the nanomaterials which acted as pore fillers and increased the stiffness of the nanocomposite membranes. The ion exchange capacity (IEC) and permselectivity of the SGO/PVDF_45 CEMs were slightly higher than the values for the SrGO/PVDF_45 CEM. It was found that the SrGO additive increased the area resistance of the nanocomposite CEM. However, SrGO/PVDF_45 CEM demonstrated a higher current efficiency (7.5% higher than SGO/PVDF_45), which could be attributed to the improved electronic conductivity of rGO. It was found that both nanocomposite CEMs performed well in electrodialysis experiments to achieve the substantial salt removal rates, although the energy consumption results of the novel nanocomposite CEMs were higher than the conventional polymeric CEM. The above research results have successfully demonstrated the concept of fabricating nanocomposite cation exchange membranes (CEMs) for electrodialysis applications by employing negatively charged graphene-based nanomaterials as ion exchange carriers.

Keywords: Graphene oxide, reduced graphene oxide, nanocomposite ion exchange membranes, electrodialysis desalination

1 Introduction

Ion exchange membranes (IEMs) have received great attention from the research and industrial communities due to their role in electromembrane processes, which range from energy production to desalination. Given the rapid increase in demand for fresh water, technologies such as electromembrane desalination processes have been used to meet the fresh water needs of society. Electromembrane desalination processes, which include electrodialysis (ED)¹⁻⁷ and membrane capacitive deionization (MCDI),⁸⁻¹² use the electrochemical potential difference in an ionic solution as the driving force for ionic transport through IEMs. IEMs are then able to carry out salt removal by preferentially allowing the flow of oppositely charged ions through them, while preventing the passage of similarly charged ions.

The development of IEMs with desirable electrochemical and physico-chemical properties for efficient fresh water production is therefore important. Numerous strategies have been investigated to prepare IEMs with superior properties for enhanced electromembrane desalination performance. These strategies include:¹³⁻¹⁵ variation of charged functional groups on the polymer backbone of the IEM, modification of the IEM's surface, combination of different polymers to take advantage of their desirable properties, inclusion of chemical additives, and cross-linking to improve mechanical stability. Another emerging approach for improving the properties of IEMs is the incorporation of nanomaterials into polymeric matrices of IEMs to produce nanocomposite IEMs.¹⁶⁻¹⁸ However, until recently, it was found in the nanocomposite IEMs literature that nanomaterials have been used only as a minor additive (nanomaterial content varied between 0.5 - 15 wt.% of the IEMs) to improve the IEMs' physical properties, whereas the ion exchange capabilities were derived primarily from charged polymeric materials.^{16,19-21} Since nanomaterials can be functionalized with charged groups and also serve as ion conducting channels, the use of nanomaterials to provide ion exchange properties should be investigated. This had not been reported until we successfully

demonstrated the concept in our recent work where a nanocomposite cation exchange membrane (CEM) was prepared based on modified graphene oxide (SGO) nanosheets and inert polyvinylidene (PVDF).²² Having demonstrated a proof of concept, the possibility of using reduced GO has not been investigated yet; particularly the exploration of the implications of the difference in nanostructure of chemically reduced graphene oxide nanosheets, such as partial removal of oxygen containing groups and reduction of interlayer spaces, on the CEM properties and performance.

Properties that make graphene-based nanosheets suitable for nanocomposite ion exchange membranes include: (1) they are 2D nanosheets with high surface area; (2) they have high dispersibility in many organic solvents used for preparing casting solutions; (3) they have high mechanical and thermal stability; and (4) they form ion conducting channels for ionic transport facilitation.^{16, 23, 24}

Figure 1 Electrodialysis cell and components of the fabricated nanocomposite CEMs.

L-DOPA has catechol groups which possess strong adhesion to many surfaces.²⁵ PSS has a high content of sulfonic-acid groups for ion exchange. By electrostatically coupling PSS and L-DOPA together, a sulfonic-group incorporating agent is produced which is able to form non-covalent bonds with the surfaces of the graphene-based nanosheets. Strong adhesive capabilities are observed for molecules with a high concentration of 3,4-dihydroxyphenylalanine (L-DOPA). L-DOPA is an amino acid which marine mussels secrete for strong adhesion to wet surfaces.²⁵ L-DOPA forms strong covalent and non-covalent bonds with the surface of numerous types of materials²⁶ including PSS,²⁷ and graphene oxide.²⁸ The formation of polydopamine involves the polymerization of dopamine via auto-oxidation to form dopamine-quinone and 5,6-dihydroxyindole.²⁹ Similarly to the dopamine, L-DOPA self-polymerizes to form poly(L-DOPA)³⁰. The poly(L-DOPA) can attach to PSS by physical co-adsorption to produce an adsorbed layer [ref]. While the catechol groups, from poly(L-DOPA), enable the adhesion of the sulfonic-group incorporating agent to the graphene-based nanosheets.²⁸

GO was evaluated in our previous research work for improving the properties of IEMs. Zheng et al. demonstrated the incorporation of chemically reduced GO (rGO) into polymeric matrices for the purpose of reducing membrane swelling.³¹ Since rGO has less oxygen containing functional groups, it is expected to produce membranes with less swelling (and consequently more stability), and possibly higher electronic conductivity. By reducing GO, improvement may be achieved in both membrane structure and electronic properties. Furthermore, the impact of the reduction in the interlayer space of rGO can also influence the fabricated nanocomposite CEMs.

In this research, we investigate the effects of using as-prepared GO and chemically-reduced rGO to prepare ion exchange nanocomposites and incorporate them in inert PVDF polymer, and to assess the electrodialysis performance of the resultant nanocomposite CEMs. PVDF was selected as the polymeric membrane material because of its chemical stability and robustness.

It has been extensively used in membrane fabrication, and its membranes have demonstrated exceptional permeability, selectivity, and stability in water treatment applications.^{32, 33}

Reduced graphene oxide (rGO) or graphene oxide (GO) were modified using PSS/L-DOPA modifying agent to produce SrGO- and SGO-based CEMs (Figure 1). Different weights of the SrGO were incorporated into a fixed amount of PVDF to yield SrGO/PVDF with varying SrGO loadings. The higher loading of the SrGO in the polymer matrix will lead to an increase of the ion exchange capacity of the fabricated nanocomposite CEMs. The effect of the various loadings was investigated. SGO/PVDF CEM and plain PVDF membranes were also prepared for comparison of membrane structure and electrochemical properties. Most importantly, electrodialysis assessments were conducted on the nanocomposite CEMs to evaluate their suitability for electromembrane desalination processes.

2 Materials and Methods

2.1 Materials

Graphite flakes were bought from Bay Carbon Inc. (USA). Tris(hydroxymethyl)aminomethane, potassium permanganate (KMnO₄), sodium nitrite (NaNO₂), hydrogen peroxide (H₂O₂), hydrochloric acid (HCl), potassium chloride (KCl), poly(vinylidene fluoride) (PVDF), sodium sulfate (Na₂SO₄), sodium hydroxide (NaOH), *N*-methyl-2-pyrrolidone (NMP), L-ascorbic acid, 3,4-dihydroxy-L-phenylalanine (L-DOPA), sulfuric acid (H₂SO₄), and poly(sodium 4-styrenesulfonate) (PSS; 30 wt.% in H₂O) were obtained from Sigma Aldrich. Ethanol was purchased from Honeywell (USA). DI water was used throughout the experiments.

2.2 Preparation of GO and rGO

Graphene oxide was prepared from graphite powder by the modified Hummers method.³⁴ 240 mL of concentrated H₂SO₄ was cooled in an ice bath for 40–45 min. 2 g of graphite powder and 1 g of NaNO₂ were added to the chilled concentrated H₂SO₄ and stirred for 15 min. 12 g of KMnO₄ was slowly added to the mixture. Then the solution was stirred for 45 min. The solution was put into a water bath at 35 °C and stirred for 2 h. Then the solution was put in an ice bath, after which 250 mL DI water was slowly added. Then the solution was stirred continuously at room temperature for 2 h. Afterwards, 500 mL DI water was added to the solution. Then H₂O₂ was slowly added until the color of the solution became golden yellow. The solution was vacuum filtered to obtain graphite oxide cake. The mud was then washed twice with 400 mL dilute HCl solution (1:10 by volume). Then the mud was washed twice with 500 mL DI water. 500 mL DI water was added to the graphite oxide cake. This graphite oxide dispersion (8 g/L) was then exfoliated using a probe ultrasonicator to produce graphene oxide (GO).

To prepare chemically reduced GO (rGO), GO was reduced by mixing with 0.1 g L-ascorbic acid and stirring continuously for 24 h (Figure 3a).³⁵ L-ascorbic acid has been reported as a green and mild reducing agent used for reducing GO.^{36, 37} The solution turned from brown to black in color. The reduction of GO to rGO was indicated by the change in coloration from brown to black. FTIR characterization confirmed the reduction.

2.3 Preparation of PSS/L-DOPA-based sulfonic group-incorporating agent

1.5 g L-DOPA was added to 750 mL Tris-HCl buffer solution (pH 8.4) and continuously stirred at room temperature for 1 h. The L-DOPA dissolved and the solution turned from colorless to dark brown. This was followed by addition of 15 mL PSS and stirring at room temperature for 24 h to produce a PSS/L-DOPA modifying agent. A scheme is shown in Figure 2. This sulfonic-

group incorporating solution was later used to modify GO and rGO. The sulfonic groups provide negative charges for ion exchange. The catechol groups, which possess high adhesive properties, are responsible for the coupling of the modifying agent to the GO and rGO nanosheets.

Figure 2 Scheme for the preparation of the PSS/L-DOPA sulfonic group incorporating agent.

2.4 Modification of GO and rGO via electrostatically coupling with PSS/L-DOPA

The incorporation of sulfonic groups on GO and rGO was achieved via mixing with PSS/L-DOPA modifying agent (Figure 3b). 150 mL GO dispersion was added to a beaker, and 150 mL rGO dispersion was added to a separate beaker. Then 750 mL sulfonic group incorporating agent was added to each beaker and stirred at room temperature for 48 h. Afterwards, the solutions were centrifuged multiple times and washed with DI water several times. The

165 recovered PSS/L-DOPA modified GO (SGO) and PSS/L-DOPA modified rGO (SrGO) were
 166 each diluted with 500 mL DI water and exfoliated using a probe ultrasonicator. The resultant
 167 SGO and SrGO dispersions were then freeze dried to obtain dry and spongy SGO and SrGO.
 168 By using the obtained dry and spongy SGO or SrGO, a casting solution of uniform consistency
 169 and dispersion could be easily achieved. Coagulation and aggregation of the casting solution
 170 would be avoided, therefore ensuring the casting of good quality membranes.

Figure 3 (a) Reduction of GO to rGO. (b) Preparation of PSS/L-DOPA modified GO (SGO) and PSS/L-DOPA modified rGO (SrGO).

2.5 Fabrication of Nanocomposite CEMs

To fabricate the nanocomposite CEMs, casting solutions with compositions shown in Table 1 were first prepared. The membranes were then cast using the mold-casting method as previously described.²² A schematic depiction of the fabrication process is shown in Figure 4.

Table 1 Composition of casting solutions used to fabricate the SGO/PVDF and SrGO/PVDF nanocomposite CEMs

Membrane	PVDF (g)	SGO (g)	SrGO (g)	NMP (mL)	Nanomaterial loading, as percentage of dry membrane (wt.%)
SGO/PVDF_45	1.5	1.2	-	45	45
SrGO/PVDF_45	1.5	-	1.2	45	45
SrGO/PVDF_55	1.5	-	1.8	45	55
SrGO/PVDF_65	1.5	-	2.8	45	65

PVDF was added to NMP and heated at 55 °C with continuous stirring for 4 h. Then the heating was stopped and the solution was stirred at room temperature. In separate beakers, SGO or SrGO was added to NMP and exfoliated in an ice bath for a total of 10 min at 1 min intervals. Then the PVDF/NMP solution was mixed with the SGO/NMP or SrGO/NMP and stirred for 72 h to attain uniform mixing. The membrane thickness was controlled by ensuring a fixed amount of casting solution was used to cast each membrane sample. To achieve this, a syringe was used to administer 8 mL of the casting solution into the mold-casting setup. The mold-casting set-up comprised an aluminum square mold (7 × 7 cm internal dimension) placed on top of a silicon wafer. To prevent leakage of the casting solution, double clips were used to fasten the mold-casting setup. Then the mold-casting setup was placed in an oven at 50 °C for 4 days for temperature-induced phase inversion. The membrane samples were then placed in a water bath to peel off the membranes from the silicon wafer.

To illustrate the effects of SrGO or SGO on the membrane morphology and structure, plain PVDF membranes were also prepared using the same procedure as described above, but without the addition of SGO or SrGO nanosheets to the polymeric matrix.

Figure 4 Fabrication of SGO/PVDF and SrGO/PVDF nanocomposite CEMs using the mold-casting method.

2.6 Characterization of Prepared Nanomaterials and Nanocomposite CEMs

Raman spectroscopy was carried out with a Witec Alpha 300 RAS. An excitation wavelength of 532 nm was used for all Raman characterizations. Fourier-Transform Infrared (FTIR) spectroscopy was carried out using the Attenuated Total Reflectance (ATR) accessory of a Bruker Vertex 80v FTIR spectrometer in transmittance mode. Scanning electron microscopy

(SEM) images were obtained using a FEITM Nova NanoSEM 650. The membrane samples were coated with gold/palladium (Au/Pd) prior to imaging analyses. Elemental analyses and mapping were done by energy-dispersive X-ray spectroscopy (EDS). The equipment used for the EDS analyses was FEI Quanta 3D FEG, and the software used was TEAMTM EDS.

To carry out linear swelling ratio and water uptake measurements, the dry membrane samples (of known weights and lengths) were first soaked in DI water for 24 h. Then their new lengths and weights were measured. The linear swelling ratio^{38, 39} and water uptake were calculated according to Equations (1) and (2), respectively.

$$\text{Linear swelling ratio} = \frac{L_w - L_d}{L_d} \times 100\% \quad (1)$$

where L_w is the length of the wet membrane and L_d is the length of the dry membrane.

$$\text{Water uptake} = \frac{m_w - m_d}{m_d} \times 100\% \quad (2)$$

where m_w is the mass of the wet membrane and m_d is the mass of the dry membrane.

Water contact angle measurements were taken using a Kyowa Dropmaster water contact angle goniometer, model DM-501. The software for analysis was FAMAS. For each membrane sample, 12 measurements were taken and the average was used as the final value.

Ion exchange capacity (IEC) was determined by the traditional acid–base titration technique.^{22,}

⁴⁰ Briefly, membranes were converted to H⁺ form by soaking in 50 mL 1 M HCl for 24 h. The weights of the membranes were measured prior to soaking. Afterwards, the membranes were washed several times with DI water to rinse off excess HCl (To confirm that there was no more HCl present, AgNO₃ was added to the wash water and carefully observed for the absence of white precipitates). Then the membranes were transformed into the Na⁺ form by immersing in 50 mL 1 M NaCl for 24 h. In this step, H⁺ ions were displaced into the solution. The membrane-

soaked solution was then titrated against 0.01 M NaOH to evaluate the concentration of H⁺ ions within the solution. The IEC was calculated using Equation (3).

$$IEC = \frac{V_{NaOH} C_{NaOH}}{m_{dry}} \quad (3)$$

where V_{NaOH} is the volume of NaOH solution used in the titration, C_{NaOH} is the molar concentration of the NaOH consumed during the titration, and m_{dry} is the mass of the dry membrane.

The permselectivity can be defined as an IEM's ability to preferentially allow oppositely charged ions to pass through. It is a measure of the fraction of oppositely charged ions (in relation to the total amount of ions) that pass through an IEM under an electrical potential difference. In an ideal case, an IEM would only allow oppositely charged ions pass through, and so have a permselectivity value of 1.

The permselectivity measured in terms of transport number were obtained from chronopotentiometry tests as previously described.⁴¹ The setup for the chronopotentiometry tests is shown in **Error! Reference source not found.a**. Prior to the measurements, the sodium form of the membrane sample was immersed in 0.1 M NaCl for 24 h. The membrane sample was held using a plastic sandwich with a round exposed area of 0.196 cm². The reference and sensing electrodes used were Ag/AgCl electrodes, while the working and counter electrodes used were platinum mesh electrodes. 50 mL 0.1 M NaCl solution was filled into each compartment of the test cell. The solution was stirred continuously throughout the tests. Acquisition of the chronopotentiometric curves was achieved using a PGSTAT302N potentiostat/galvanostat (Metrohm Autolab, Netherlands; Software: Nova1.11), operated in galvanostatic mode at a current of 4 mA. The transition time was determined at the point of inflection of the chronopotentiometric curves. The modified Sand equation was used to obtain the permselectivity (Equation (4)):⁴²

$$P = \frac{|z| \cdot F \cdot D^{0.5} \cdot \pi^{0.5} \cdot C}{2 (1 - t_i) \cdot \frac{I}{A} \cdot \tau^{0.5}} \quad (4)$$

where P is the permselectivity, $|z|$ is the absolute charge of the sodium ion ($|+1|$), F is the Faraday constant ($96,485 \text{ A s mol}^{-1}$), D is the diffusion coefficient ($1.48 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) and t_i is the transport number (0.396) of the sodium ion in 0.1 M NaCl,⁴² C is the concentration of the sodium ions (0.1 M), I is the applied current (4 mA), A is the exposed membrane area (0.196 cm^2), and τ is the transition time. The chronopotentiometry measurements were performed in duplicates using two different pieces from the same membrane sheet. The transition time was measured in both directions (positive and negative current) to eliminate any possible effects of electrode inequivalence. The permselectivity values were obtained as an average of four runs.

Figure 5 (a) Electrochemical test cell used for chronopotentiometry and electrochemical impedance spectroscopy measurements. (b) Membrane stack assembly in ED cell. (c) Process diagram of the electrodialysis experiment setup.

The membrane area resistance was measured by electrochemical impedance spectroscopy (EIS) using the test cell as shown in **Error! Reference source not found.a**. In this case, 50 mL 1.0 M NaCl was filled into each compartment. There was no stirring of the solutions during the tests. Before the EIS tests, the membrane was soaked in 1.0 M NaCl. The EIS tests were run using a PGSTAT302N, a potentiostat/galvanostat with FRA32M frequency response analyzer. All tests were performed using a 0.1 mA amplitude AC signal at 50 different frequencies from 1 mHz to 1 kHz. The EIS measurements were performed in duplicates using

the same membrane pieces as in the chronopotentiometry tests. The area resistance was obtained after equivalent circuit fitting and after correction with the resistance of the empty cell. The exposed membrane area was 0.196 cm^2 in all tests. Equation (5) was used to determine the area resistance of the membrane samples.

$$R_A = (R_{m+sol} - R_{sol}) \cdot A \quad (5)$$

where R_A is the membrane area resistance, R_{m+sol} is the resistance of the membrane in the solution, R_{sol} is the resistance of the empty cell, and A is the membrane area.

2.7 Electrodialysis Assessment

Electrodialysis (ED) tests were conducted to assess the salt removal rate, current efficiency and energy consumption of the fabricated nanocomposite CEMs. The electrodialysis experiments were performed using an electrodialysis setup which consisted of a PCCell Micro BED System (see **Error! Reference source not found.c** for schematic diagram) with three closed-loop liquid circulation circuits for diluate, concentrate and electrode electrolyte solutions.

Sensors for electrical conductivity (EC), temperature and flow in the diluate and concentrate circuits were connected to a control system, operated by a computer. This allowed for the control, monitoring and data acquisition of the process. The liquids were contained in graduated polypropylene cylinders and were pumped through the ED cell. The cell holder contained the electrodes.

From each sample type, the nanocomposite CEM (cut into $40 \text{ mm} \times 60 \text{ mm}$ rectangular shape) was punched and assembled in a cell stack together with a standard AEM (type PC Acid 60 OT) (**Error! Reference source not found.b**). An additional CEM (PC S100) was included at the cathode side to prevent the migration of sulfate ions from the cathode chamber into the concentrate compartment. The experiments were performed in batch mode with circulated

diluate and concentrate solutions, consisting of NaCl solution with initial concentration of 0.1 M (brackish water). A DC current was applied between the electrodes, which led to flow of the anions (Cl^-) through the AEM to the concentrate compartment adjacent to the anode and flow of the cations (Na^+) to the concentrate compartment adjacent to the cathode.

The decrease of EC in the diluate due to decrease of salt concentration and the increase of conductivity in the concentrate due to increase of salt concentration, was recorded by the control system. The parameters of the experimental setup are shown in Table 2.

For each nanocomposite CEM sample, 3 consecutive ED runs were performed. For comparison, an additional run with a standard reference CEM (type PC S100) at the position of the sample nanocomposite CEM, was performed. Each ED run generated a data set of EC, temperature and flow rate for diluate and concentrate, as well as voltage and current values, collected for 2 s time intervals. Volumes were read manually every 5 min.

NaCl concentrations were automatically calculated from the EC of the solution assuming direct proportionality. The EC was measured by electrical inductive conductivity sensors (JUMO CTI-500, from JUMO, Germany). The EC values were automatically temperature-compensated to 25 °C. Prior to each experiment, the diluate and concentrate circuits were rinsed with DI water until the conductivity dropped below 0.1 mS/cm. For each run, fresh NaCl solutions were filled into the diluate and concentrate circuits until conductivities corresponding to 0.1 M NaCl were reached. The electrode electrolyte was also replaced at every new experiment.

Table 2 Parameters for electrodialysis experiment

Parameter	Value
Active membrane area	6.5 cm ²
Spacer thickness	0.4 mm
Thickness of PC S100 CEM (wet condition)	0.072 mm
Thickness of PC Acid OT AEM (wet condition)	0.95 mm
Electrode electrolyte	8.5% Na ₂ SO ₄ solution
Diluate (volume and initial concentration)	100 mL 0.1 M NaCl
Concentrate (volume and initial concentration)	100 mL 0.1 M NaCl
Applied Voltage (Max)	30 V
Applied Current (Max)	0.65 A
Diluate flowrate	6.5–7.2 L/h
Concentrate flowrate	3.7–4.5 L/h

The current and voltage were automatically adjusted by the computer. A low resistance of the system limits the current to 0.65 A, while the voltage is below 30 V. A high resistance limits the voltage to 30 V, while the current falls below 0.65 A. The reason for constant current is that the ED experiments are easily controlled and evaluated with constant current, while a voltage limit is necessary in order to protect the cell from overheating and to avoid too high voltages at the electrochemical interfaces.

The current was started after 2 min stabilization of the flow. After a run time of 40 min, the current was switched off and the system was allowed to settle down for another 6 min. Three consecutive experiments were performed immediately one after another without disassembly of the cell. The overall charge (in units of Faraday: 1 F = 96,487 A s mol⁻¹) was automatically evaluated and stored by the measurement and control software. Evaluation of the current efficiency and power consumption was done using Equations (6) and (7) respectively.

$$\text{Current efficiency} = \frac{V_D |\Delta C_D| F}{\int I dt} \quad (6)$$

$$\text{Power consumption (kJ/g)} = \frac{\int U I dt}{V_D |\Delta C_D|} \quad (7)$$

where V_D is the volume of the diluate, ΔC_D is the change in concentration of the diluate, F is Faraday constant 96,487 A s mol⁻¹, I is the applied current, U is the applied voltage and t is the duration of the experiment.

The salt removal was also evaluated according to the Equation (8) below:

$$\text{Salt removal (\%)} = \frac{C_i - C_f}{C_i} \times 100 \quad (8)$$

where C_i and C_f are the initial and final salt concentrations of the diluate solution.

3 Results and Discussion

3.1 Nanocomposite Membrane Stability

Attempts were made to fabricate nanocomposite IEMs with nanomaterial loadings higher than 45 wt.%. This was done with the objective of increasing the density of ion exchange functional groups in the nanocomposite CEMs. In line with this, SrGO/PVDF nanocomposite CEMs with SrGO loadings of 55 wt.% and 65 wt.% were prepared. We however discovered that these membranes (with loadings higher than 45 wt.%) had multiple cracks right after the temperature-induced phase inversion. Therefore the SrGO/PVDF_55 and SrGO/PVDF_65 nanocomposite CEMs were unfit for use as membranes for electromembrane processes. However, the nanocomposite CEMs with loadings of 45 wt.% were in good shape, without any cracks (see Figure 6). As a result, only SGO/PVDF_45 and SrGO/PVDF_45 were considered for characterization.

Figure 6 Fabricated nanocomposite CEMs: (a) SGO/PVDF_45; (b) SrGO/PVDF_45. Only the nanocomposite CEMs with 45 wt.% loadings were in good shape without cracks.

3.2 FTIR and Raman spectroscopy analyses

The Raman spectroscopy analyses of the GO, rGO, SGO and SrGO are shown in **Error! Reference source not found.a**. The D and G bands at $\sim 1340\text{ cm}^{-1}$ and $\sim 1585\text{ cm}^{-1}$, respectively, are typical for graphene-based nanomaterials.⁴³⁻⁴⁵ The appearance of these bands, therefore, confirms that the nanosheets are graphene-based. The intensity of the ratio of the D and G bands (I_D/I_G) for GO is 1.029 and 1.015 for rGO. The decrease in I_D/I_G ratio, although by a small margin, suggests a lower amount of basal plane defects in the rGO sample.⁴⁶

The FTIR spectroscopy analyses are shown in **Error! Reference source not found.b** and c. The typical spectrum and characteristic bands for GO are displayed in Figure 7b. After reduction to rGO, the peaks for the oxygen-containing functional groups were absent. The transformation of GO to rGO is confirmed by the absence of the OH deformation peak and C-O stretch peaks in the rGO spectra (**Error! Reference source not found.b**).⁴⁷⁻⁴⁹ The results of the FTIR analyses are in agreement with available literature on GO and rGO.^{50, 51} In **Error!**

354 **Reference source not found.**c, sulfonic group bands are present for the modified SGO, SrGO,
 355 SGO/PVDF_45 and SrGO/PVDF_45.⁵²⁻⁵⁵

356 This confirms the presence of sulfonic groups in the modified nanosheets and fabricated
 357 nanocomposite CEMs.

Figure 7 (a) Raman spectroscopy of nanomaterials. (b) FTIR spectroscopy of GO and rGO.
 (c) FTIR spectroscopy of modified nanosheets and fabricated nanocomposite CEMs

359 3.3 Structural and Elemental Analysis of Prepared Membranes

360 Figure 8 shows the top surface and cross-sectional views of the membrane samples. The
 361 morphologies of the SGO/PVDF_45 and SrGO/PVDF_45 differ from that of the plain PVDF
 362 membrane, owing to the high loading of SGO and SrGO nanosheets which represent 45 wt.%
 363 of the nanocomposite CEMs. Cross-sectional images revealed a stacked structure in the
 364 SGO/PVDF_45 and SrGO/PVDF_45, while the plain PVDF membrane had a typical globular
 365 structure. From the images, it can be seen that the 2D nanosheets of SGO and SrGO were well

oriented and stacked in layers during the casting and setting process and resulted in denser membranes with a visible stacked-sheet structure. The thickness of the SGO/PVDF₄₅ was $99 \pm 4 \mu\text{m}$, while that of the SrGO/PVDF₄₅ was $71 \pm 2 \mu\text{m}$. The SGO/PVDF₄₅ was thicker than the SrGO/PVDF₄₅, although both their casting solutions had a similar composition in terms of proportion of polymer, solvent and nanomaterial used (i.e. 1.5 g PVDF: 45 mL NMP: 1.2 g nanomaterial). Moreover, the same volume of casting solution was used to cast both types of membranes. The lower thickness observed for SrGO/PVDF₄₅ can be attributed to the rGO nanosheets. In producing rGO, the oxygen containing functional groups were removed from GO; resulting in a reduction in the interlayer distance between the nanosheets and a higher tendency for restacking.³⁵ This reduced interlayer distance resulted in SrGO/PVDF CEMs with a lower thickness than their SGO counterparts.

EDS analyses show the elemental composition of the membranes (Figure 9). The sulfur map confirms the presence of $-\text{SO}_3^-$ functional groups in both types of nanocomposite CEMs. Furthermore, the absence of hotspots demonstrates that there was no agglomeration of the SGO or SrGO nanosheets in the nanocomposite CEMs. Since nanomaterial agglomeration can lead to sites of failure in nanocomposite membranes,^{56,57} the absence of nanomaterial agglomeration suggests membrane stability. Nevertheless, it was found that uniform dispersion of SrGO in the SrGO/PVDF₄₅ CEM was achieved as shown by the absence of aggregates in the EDS map (Figure 9k). This confirmed that SrGO was thoroughly dispersed in the casting solution despite its lower concentration of oxygen functional groups.

Figure 8 SEM images of fabricated membranes. Top surface views of (a) SGO/PVDF_45; (b) SrGO/PVDF_45; (c) plain PVDF. Cross-sectional views of (d) SGO/PVDF_45; (e) SrGO/PVDF_45; (f) plain PVDF.

Figure 9 Composite and elemental maps and EDS spectrum: (a-f) for SGO/PVDF_45; (g-i) for SrGO/PVDF_45.

3.4 Wettability and Electrochemical Properties of Membranes

The water uptake results are shown in Table 3. It is found that SrGO/PVDF_45 showed significantly lower water uptake than SGO/PVDF_45. This is because the SrGO/PVDF_45 surface was less hydrophilic because of the rGO component, which possessed lesser amounts

of oxygen functional groups as compared to GO, so less hydrogen bonds were formed on the surface of the materials in the aqueous environment.⁵⁸

Table 3 Wettability properties and IEC of nanocomposite CEMs

Nanocomposite CEM	Water uptake (%)	Linear swelling ratio (%)	IEC (meq/g)
SGO/PVDF_45	255.10 ± 0.21	1.51 ± 0.01	0.61 ± 0.03
SrGO/PVDF_45	60.14 ± 0.01	0.84 ± 0.01	0.54 ± 0.02

The fabricated nanocomposite membranes were shown to have low linear swelling ratios (Table 3), similar to results obtained for a previously reported CEM.²² A lower linear swelling ratio is observed for the SrGO/PVDF_45 in comparison to the SGO/PVDF_45. This is in line with the water uptake results, as GO is more hydrophilic than rGO and is expected to swell considerably more than rGO.³¹ The presence of the nanomaterials in both SGO/PVDF_45 and SrGO/PVDF_45 allows more interfacial interactions within the porous membrane structure and also acts as pore fillers that increase the stiffness of the nanocomposite membrane, thus resulting in lower linear swelling ratio than the more swelling non-nanocomposite counterpart.⁵⁹

Water contact angle measurement results are shown in **Error! Reference source not found.a**. The surfaces of SrGO/PVDF_45 and SGO/PVDF_45 are found to be hydrophilic, whereas the surface of PVDF is hydrophobic. This is expected due to the hydrophilic nature of the GO as well as chemically reduced rGO nanosheets. Moreover, GO has more oxygen containing functional groups than rGO, which also explains why the surface of SGO/PVDF_45 was more hydrophilic with lower water contact angle than that of the SrGO/PVDF_45.

Figure 10 (a) Water contact angle results for PVDF, SrGO/PVDF and SGO/PVDF membranes. (b) Area resistance and permselectivity of the SGO/PVDF_45 and SrGO/PVDF_45 nanocomposite CEMs.

The measured IEC values are shown in Table 3. The IEC value of SGO/PVDF_45 is in line with previously reported work.²² Both nanocomposite CEMs exhibited relatively low IEC but were within close proximity to values of some commercial CEMs reported in literature i.e. CSMCRI HGC heterogeneous CEM (0.67–0.77 meq/g).⁶⁰ SGO/PVDF_45 had a higher IEC than SrGO/PVDF_45. This may be due to the presence of more negatively charged carboxylic functional groups on the planes of GO nanosheets, additional to the sulfonic groups, which can contribute to ion exchange.

For SGO/PVDF_45, the permselectivity and area resistance values were found to be 0.96 ± 0.04 and $27.5 \pm 16.5 \Omega \text{ cm}^2$, respectively. While the permselectivity and area resistance of the SrGO/PVDF_45 CEMs were 0.92 ± 0.04 and $46.3 \pm 3.2 \Omega \text{ cm}^2$, respectively (see **Error! Reference source not found.**b). As the nanocomposite CEMs were made of similar composition, except for the type of nanomaterial, the difference in the permselectivity and area resistance values can be attributed to the differences between the nanomaterial additives (i.e.

SGO or SrGO). Since SGO has been confirmed to be more hydrophilic and also carries extra negatively charged groups such as hydroxyl groups for ion exchange, the impact on the permselectivity and area resistance is expected to be more when compared to SrGO. This may explain why SGO/PVDF_45 exhibited higher permselectivity and lower area resistance than SrGO/PVDF_45. Moreover, the smaller interlayer distance between the rGO nanosheets resulting from chemical reduction alongside with lower swelling may restrict the passage of ionic species through the membrane which is therefore reflected in the higher area resistance of SrGO/PVDF_45.³⁵ The area resistance of the SGO/PVDF_45 CEM was higher than previously reported.²²

3.5 Assessment of the Nanocomposite CEMs in an Electrodialysis Cell

Error! Reference source not found.b shows the change in current with time for the CEMs during the electrodialysis tests. It can be seen that the current decreased with time as a result of the diminishing conductivity of the diluate compartment. When the diluate conductivity decreased, the cell resistance became higher and the voltage increased up to the limit voltage. Beyond this point, the voltage was kept constant by decreasing the current. Starting from identical initial salinity values of the NaCl solution, the electrical conductivity (EC) of the diluate steadily decreased upon starting of current and the EC of the concentrate increased – which is expected for an electrodialysis process.⁴⁰ When the current was cut, the EC remained constant which suggests conserved structural integrity of the membranes and no mixing of the compartments through membrane defects. The concentration profile for the diluate and concentrate sections is displayed in **Error! Reference source not found.**c. The rate at which the salt concentration changed was almost linear for all three CEMs, and plateaued as time progressed.

Figure 11 (a) Experimental setup for ED tests (Source: PCCell GmbH, Lebacher Str. 60, 66265 Heusweiler, Germany). (b) Current – time curves for the electrodesialysis tests with different CEMs. (c) Salt concentration changes in diluate and concentrate during electrodesialysis experiments with different CEMs. (d) Current efficiency and salt removal of fabricated nanocomposite CEMs and reference CEM during electrodesialysis test.

The suitability of the fabricated nanocomposite CEMs for electrodesialysis is evaluated by determining the current efficiency, salt removal rate and energy consumption. These parameters are influenced by the membrane properties and the operating conditions of the

experiment. Current efficiency values of 0.67 ± 0.05 , 0.72 ± 0.05 and 0.73 were obtained for SGO/PVDF_45 CEM, SrGO/PVDF CEM and the reference CEM (type PC S100) respectively (grey columns in **Error! Reference source not found.**d). The current efficiency of the SrGO/PVDF_45 was higher by 0.05 than that of the SGO/PVDF_45, and comparable to the reference CEM. This higher current efficiency could be attributed to the improved electronic conductivity of rGO. The high electronic conductivity of rGO has been well reported in literature, and is considerably larger than that of GO.⁶¹ Whereas, GO has more lattice imperfections and attached functional groups on its planes, which explains the vastly lower electronic conductivity. As an electromembrane such as cation exchange membrane, its overall separation performance not only relies on the relative ionic affinity of the ionic species being separated to the polymer, but also relates to the current efficiency which is based on the electrical potential generated by passing given current through the membrane.^{62, 63} The more electronic conductive membrane materials will enhance such electrical potential. The presence of rGO in SrGO/PVDF_45 could enhance the current utilization and lead to the increased current efficiency.

The average salt removal results are displayed in **Error! Reference source not found.**d (red columns). The salt removal results show comparable performance of the fabricated nanocomposite CEMs ($86 \pm 2\%$ for SGO/PVDF_45 and $82 \pm 1\%$ for SrGO/PVDF_45) and the reference (PC S100) CEM (89%). These results demonstrate that the fabricated nanocomposite CEMs are as effective as the commercial CEM during electrodialysis desalination runs.

Table 4 contains the energy consumption for salt removal rates for the reference CEM (49 kJ/g), SGO/PVDF_45 (67.1 ± 3.9 kJ/g) and SrGO/PVDF_45 (68.3 ± 3.9 kJ/g) during electrodialysis tests. The energy consumption of salt removal for both nanocomposite CEMs were at similar levels, although higher than the value recorded for the reference CEM. As the IEC of these nanocomposite CEMs are proportional to the charge carrying-nanomaterials

loadings, which is limited to 45% at present, further increase of either the charge density or the loading of the nanomaterials in the CEMs will increase its IEC, and could reduce the energy consumption.

Table 4 Energy consumption for salt removal for fabricated nanocomposite CEMs and the reference CEM

CEM	Energy consumption (kJ/g)
SGO/PVDF_45	67.1 ± 3.9
SrGO/PVDF_45	68.3 ± 3.9
Reference (PC S100)	49.0

The SrGO/PVDF_45 CEM demonstrated some advantageous properties with a 7.5% higher current efficiency, as well as the 0.67% less swelling than that of SGO/PVDF_45 CEM. However, the removal of the oxygen functional groups led to rGO nanosheets with smaller interlayer space, consequently increasing restrictions in the nanoconducting channels for ion transport as demonstrated by the lower area resistance and permselectivity values. Both nanocomposite CEMs demonstrated encouraging results for electrodialysis.

4 Conclusions

Modified GO and rGO nanosheets were incorporated into a non-charged membrane matrix to create nanocomposite CEMs for electrodialysis. GO and rGO were modified to sulfonic group-bearing SGO and SrGO, using a combination of 3,4-dihydroxy-L-phenylalanine (L-DOPA) and poly(sodium 4-styrenesulfonate) (PSS). 45 wt.% of SGO, and 45, 55, and 65 wt. % of SrGO, were added into PVDF matrix to produce SGO/PVDF and SrGO/PVDF nanocomposite CEMs, respectively. A mold-casting technique was used to fabricate the nanocomposite CEMs. It was found that only the nanocomposite CEMs with 45 wt.% were crack-free and were appropriate for use as CEMs. The use of nanomaterial content above 45 wt.% resulted in

cracked and deformed nanocomposite CEMs. There was no agglomeration observed in either the SGO/PVDF_45 or SrGO/PVDF_45 CEMs.

Both nanocomposite CEMs displayed lower linear swelling ratios, which are good for membrane stability. This was due to the presence of the nanomaterials in both SGO/PVDF_45 and SrGO/PVDF_45 which acted as pore fillers and increases the stiffness of the nanocomposite membrane. When comparing the effects of SGO versus SrGO additives, the IEC and permselectivity of the SGO/PVDF_45 CEMs were slightly higher than values for the SrGO/PVDF_45 CEM. It was found that the SrGO nanosheets increased the area resistance of the SrGO/PVDF_45 CEM nanocomposite CEM. However, the SrGO/PVDF_45 CEM demonstrated a higher current efficiency, which could be attributable to the improved electronic conductivity of rGO.

It was found that both nanocomposite CEMs performed well in electrodialysis experiments to achieve the substantial salt removal rate (SGO/PVDF_45 CEM (86 %) and SrGO/PVDF_45 CEM (82 %)), although the energy consumption of the novel nanocomposite CEMs was higher than the conventional polymeric CEM (PC S100). The above research results have successfully shown the concept of fabricating nanocomposite cation exchange membranes (CEMs) for electrodialysis applications by incorporating negatively charged graphene-based nanomaterials in a non-charged polymeric matrix, where the ion exchange capacity solely relies on the SGO or SrGO nanosheets. Additionally, these ion exchange group carriers of SGO or SrGO nanosheets can also be incorporated into existing charged ion exchange polymeric matrix, to enhance the performance of CEMs in electrodialysis in future research.

Conflict of interest

The authors declare no conflict of interest.

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