

Energy-Efficient Nanostructured Ion Exchange Membranes from Functionalized Poly (2,6-Dimethyl-1,4-Phenylene Oxide)

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Summary: Highly energy efficient and ion permeable ion exchange membranes are in high demand in many modern sectors to clean water, transform energy, and store energy in devices like electro-dialyzer, fuel cells, and batteries. However, greater resistance and reduction in ion permeation of conventional membranes dictate the desire for nanostructured functional ion exchange membranes. This project proposes the fabrication of ion exchange membranes using electroactive nanostructured polyaniline incorporation into ion exchange materials, electrostatically interaction between polymer and nanostructured electroactive material overcomes the problem of high resistance and less ion permeation. Solution casting and post-drying techniques are used for membrane casting. Nanostructured electroactive material helps to increase ionic conduction thus reducing 17% resistance for functional cation exchange membrane (FCEM) and 12% for functional anion exchange membrane (FAEM) also assisting to increase ion permeation. Hydrophilic nanostructured polyaniline electroactive material holds more water and increases water uptake. Cross-linking increases stability as well as reduces 17% and 8% swelling degrees for FCEM and FAEM respectively. Besides the electrochemical property offers an increase limiting current density of 38%, 23% for FCEM and FAEM respectively, and 19% higher desalination performance than non-nanostructured sulfonated polyphenylene oxide (CEM) and quaternized polyphenylene oxide (AEM) membranes.

Keywords: Ion exchange membranes, Saline water treatment, Nanostructured polyaniline, Functionalized polyphenylene oxide.

Introduction

The development of innovative materials for energy storage and conversion applications has attracted a lot of attention due to the rising worldwide need for clean and sustainable energy sources. Ion exchange membranes (IEMs) have become one of them, and are now essential parts of many electrochemical systems, such as fuel cells, electro dialyzers, redox flow batteries [1] and for wastewater treatment plants [2, 3]. The qualities and features of the IEMs used have a significant impact on the effectiveness and functioning of these devices [4]. Ion exchange membranes with improved ion conductivity, selectivity, and stability have been designed and created during the past few years. Furthermore, there is a significant motivation to increase the energy efficiency of these membranes since their function in electro dialysis processes directly affects the efficiency of the entire system [5-7]. Ion-conducting channels, which are generally found in ion exchange membranes (IEMs), are composed of ion exchangeable pendent sites [6-10]. It is feasible to obtain efficient ion transfer

via increasing ion exchanging sites (sulfonate groups) in main chains [10, 11]. A key technique is regulating membrane structure, also termed as self-assembling of the exchange sites, that creates well-specified electrostatic channels, as indicated for the membranes made of sulfonated copolymer have multiblock clusters and comb-shaped grafts [12-16]. Although the effectiveness of ionic permeation is increased by the increase of ion exchange sites but at the expense of membrane stability (increased membrane swelling) and vice versa. Manufacturing highly energy efficient, stable (less swollen membranes), and more ion-permeable polymeric membranes is technically challenging to circumvent the stability- energy efficiency tradeoff in IEMs.

Fabricated polyaniline (PANI-EB) emeraldine base nanostructured material has shown promise as potential components of the upcoming high-performance IEM generation. PANI is a potential material because it has special qualities including

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strong electrical conductivity [12, 13], superior mechanical strength, semi-crystalline polymer [17], nontoxic, stable and highly hydrophilic [18]. PANI can be added to IEMs' polymeric matrix to modify the membrane physio-chemical characteristics [17, 19] for better electrochemical performance [18, 20].

The Electrostatic Ionic Bonding Theory is proposed as the fundamental theory behind the design and production of nano-structured functional ion exchange membranes, which include functional cation exchange membranes (FCEMs) and functional anion exchange membranes (FAEMs). The integration of sulfonated polyphenylene oxide (SPPO) and quaternized polyphenylene oxide (QPPO) polymers, which are differentiated by their strong ion exchange capability and high swelling tendency, is the foundation of our method. In addition, the incorporation of Nano-structured polyaniline emeraldine base (PANI-EB) contributes to the establishment of electrostatic interactions inside the nanostructured functionalized membranes. This strategic integration improves the nanostructures hydrophilicity, increasing their capacity for water retention as they pass through the assembled sulfonate and amine groups. Simultaneously, this arrangement improves ion penetration by reducing resistance at ion-conducting sites. Notably, the polyaniline nanostructures securely immobilize the SPPO and QPPO elements via electrostatic forces. This leads in the production of long-lasting scaffolds, which effectively preserves the integrity of the ionic channels while alleviating worries about membrane swelling and instability over long periods of time.

Experimental

Materials

Quaternized Poly (phenylene oxide) (QPPO) and Sulfonated Poly (phenylene oxide) (SPPO) are received from A. M scientific group Pakistan. Aniline, ammonia peroxydisulfate (APS), dimethylformamide (DMF), NaCl, HCl

NaOH, Phenolphthalein, were reagent grade and obtained from A. M scientific group Pakistan. Deionized water used for all aqueous solutions.

Preparation of PANI nanostructures and Fabrication of ion exchange membranes (IEMs)

Oxidative chemical polymerization was used to create polyaniline nanostructures. Separately, aniline and ammonia peroxydisulfate (APS) were dissolved in 1 M HCl. Ammonia peroxydisulfate (APS) was gradually added to aniline after agitation.

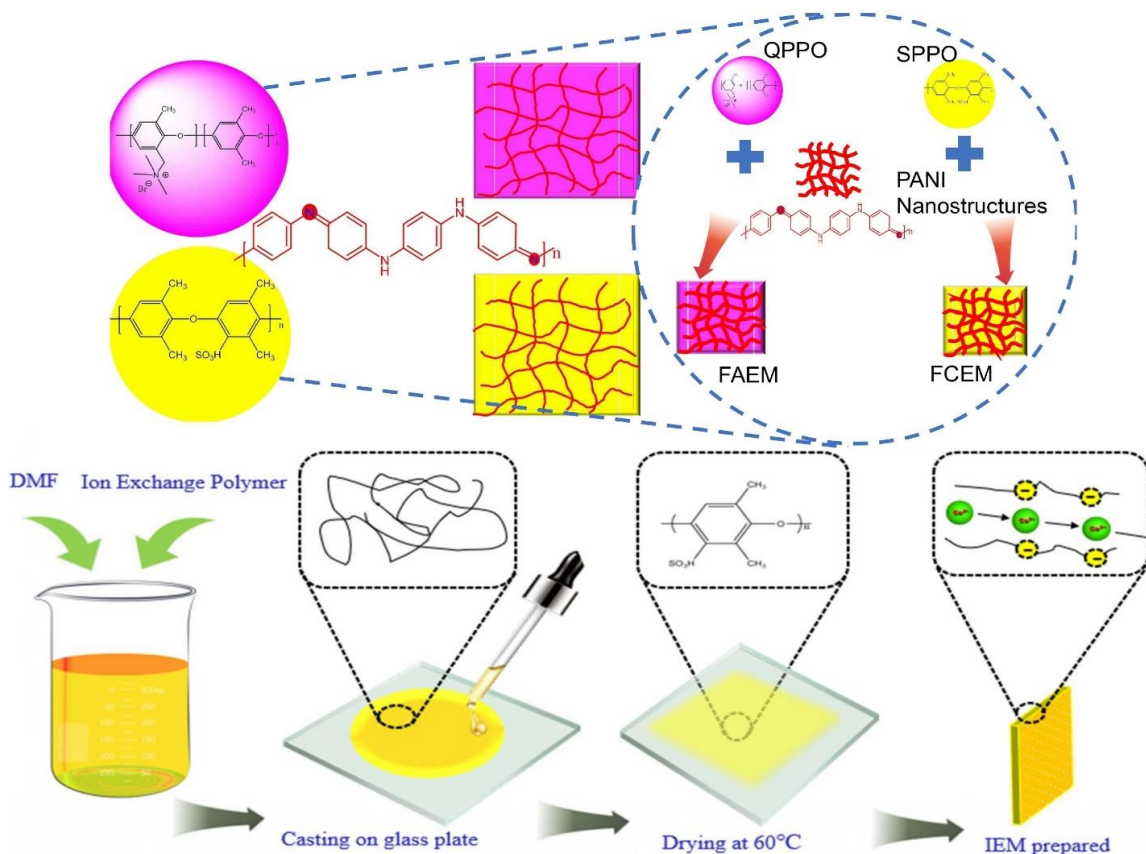
Precipitates of dark green polyaniline emeraldine salt form. Using 1 M ammonia, they were filtered, rinsed, and dedoped. The PANI-EB precipitates those formed were dried and kept in desiccators for subsequent use (Scheme 1). The noodled form of SPPO was washed with deionized (DI) water to prepare solution for cation exchange membranes. This cleaning process was continued until a pH 7 neutral filtrate is obtained. The cleaned SPPO was next dried in an oven at a temperature of 60 °C for 24 h until there is no further loss of weight. After dissolving 1 g of dried SPPO for CEMs (Scheme 1) and QPPO (Powder) for AEMs in 9 ml DMF (Fig. 1a) and stirring continuously for 12 h, a homogeneous solution is obtained (Fig. 1b). The ratio of nanostructured PANI-EB to SPPO and QPPO in (DMF) was kept constant for all membranes at 1:10:15 % weight to weight to obtain optimized characteristics. Solutions for Cation and anion exchange membranes were then placed in a centrifugation and ultra-sonication bath to ensure that it is dispersed evenly throughout the solution. Following full homogenization, the ion exchange polymer solution was uniformly poured onto the glass plates. Methanol washing was used to prepare the glass plates (Fig. 1c). The glass plate was balanced and adjusted for constant thickness prior to production. The glass plate was then heated on a hot plate to 55 °C (Fig. 2a and 2b). The homogenized ion-exchange polymer solution was applied to the glass plate with a dropper, achieving complete coverage within the plate boundaries (Fig. 1d, 1e, and 1f). The heated plate with the coated solution was left undisturbed for 8 h after the casting procedure to allow solvent evaporation. When the solvent had completely evaporated, membrane was gently removed from the glass plate (Fig. 2c and 2e) and preserved for further analysis.

Physiochemical analysis of membranes

Water uptake of membranes

Water uptake is an extremely valuable measure for assessing the hydrophilicity of membranes [24]. For this test, both the cation and anion exchange membranes were cut into 1:4 cm strips (Fig. 2d and Fig. 2f). The samples of membranes were dried at 55 °C for 20 h weigh as W_{dry} , and after that placed in DI water for the next 24 h. The membranes were reweighed as W_{wet} following a gentle wiping to remove any surface water. Utilizing the following Equation, membrane water uptake was calculated using Eq. 1 [25].

$$\% \text{ WU} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \quad (1)$$



Scheme-1: Schematic illustration for the fabrication of nanostructured functional ion exchange membranes.

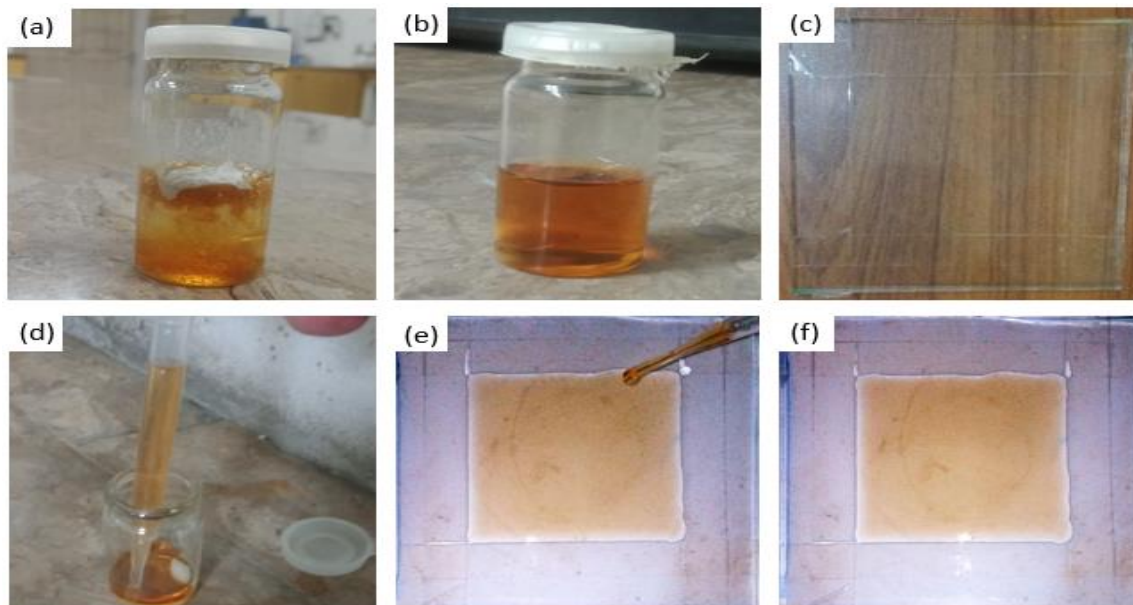


Fig. 1: Preparation of solution and casting on glass plate (a) 9ml DMF and 1-gram QPPO material in glass vial for stirring, sonication and centrifugation. (b) Homogenized QPPO solution (c) glass plate prepared by cleaning and using glass tape. (d) Dropper used to drop solution on glass plate. (e, f) solution casted on glass plate.

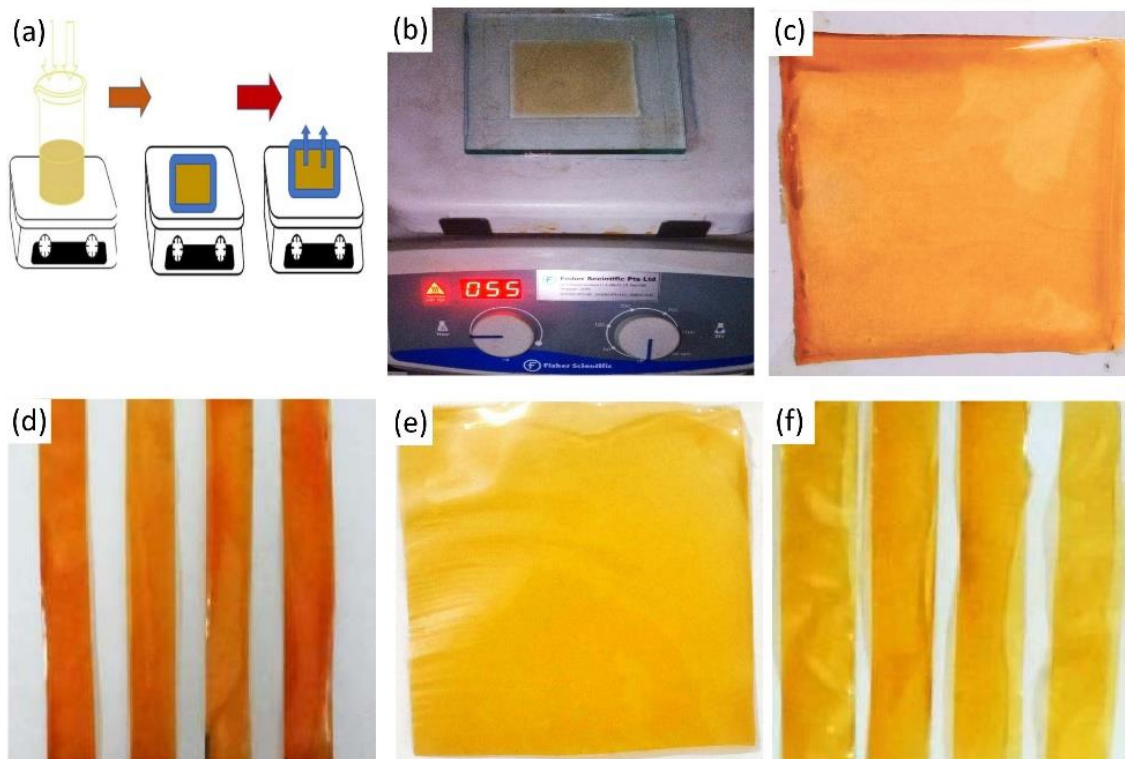


Fig. 2: Fabrication of ion-exchange membranes. (a) Scheme to cast IEM (b) glass plate with cation exchange polymer solution placed on hot plate at 55°C. (c) CEM removed from glass plate. (d) CEM cut into 1:4 cm strips for physio-chemical characterization. (e) AEM removed from glass plate. (f) AEM cut into 1:4 cm strips for physio-chemical characterization.

Swelling of the Membranes

The swelling of the membranes, which is another critical characteristic for comprehending the dimensional stability of membranes in an aqueous environment, is a significant variable. The membranes rectangular strips ($4 \times 1 \text{ cm}^2$) were soaked at room temperature (25 °C) for 48 h in DI water. The average thickness of three sets of samples of swollen membranes (t_{wet}) was determined using digital thickness gauge. Afterward, all the samples were dried in a drying oven for 20 h at 60 °C, then dried samples thickness was measured using Eq. 2 [25].

$$\% \text{ Swelling} = \frac{t_{\text{wet}} - t_{\text{dry}}}{t_{\text{dry}}} \times 100 \quad (2)$$

Membranes ion exchange capacity (IEC)

An acid-base titration method is used to calculate the membranes IEC [4]. To exchange hydrogen ions (H^+) and hydroxyl ions (OH^-) for sodium ions (Na^+), samples of membranes were submerged in 2 M NaCl for 70 h. Produced HCl and NaOH was titrated with 0.0103 M NaOH and H_2SO_4 respectively. Phenolphthalein was used as an

indicator to measure the release of protons from protonated membranes in NaCl solution to determine the concentration of hydrochloric acid (HCl). IEC values for three value of samples were computed using the Eq. 3 and 4 [26, 27].

$$\text{IEC (CEM)} = \frac{V_{\text{base}} \cdot M_{\text{base}}}{W_{\text{dry}}} \quad (3)$$

$$\text{IEC (AEM)} = \frac{V_{\text{acid}} \cdot M_{\text{acid}}}{W_{\text{dry}}} \quad (04)$$

Where W_{dry} is the weight of the test samples for dried membranes evaluated at weight balance. C_{NaOH} and V_{NaOH} are the concentration of the NaOH solutions and titrating volume, respectively [28].

Electrochemical analysis:

At room temperature, the responses of the fabricated nanostructured ion exchange membranes to direct current stimulation were studied using the four-compartment I-V setup from DADA WEETECH PVT. Ltd., Pakistan. The results are displayed as characteristic curves of current voltage (Fig. 6a). The arrangement consists of four compartments, with two commercial Nafion® 115 membranes dividing the intermediate

compartments from the anode and cathode chambers at either end. As a result, the testing fluid near the test membranes is shielded from electrode reactions. 0.5 M sodium chloride (NaCl) was used to test the membranes, which have an effective area of 7.06 cm², and 0.5 M sodium sulfate (Na₂SO₄) was used to rinse the electrodes. Flow-controlled pumps were employed to continuously circulate the fluids inside each compartment to prevent the solution concentration polarization impact during the entire operation. Before testing, the membranes under investigation were balanced in the test solution for more than 24 h. When conducting current-voltage (I-V) testing, a DC power supply (HSPY-120-03) increased direct current density progressively. Using a digital multimeter and a set of silver-silver chloride (Ag/AgCl) electrodes that were placed about a millimeter from the membrane surface through angled capillaries to reach the membrane surfaces, a steady voltage was observed across the testing membrane every 50 to 60 s. For all of the membranes, the typical current-voltage (I-V) curves were produced, which included the three zones of Ohmic, non-ohmic, and plateau length.

Saline water Desalination performance

An electrodialysis stack consists of an anion exchange membrane and a cation exchange membrane. The cathode and anode provide an electrical potential, and the membrane stack sits in the middle of this electrical potential hierarchy between the two. Between the cation-exchange and anion-exchange membranes, a feed flow of ion-containing material is introduced. In this chamber of a cation exchange membrane, an anion-exchange membrane (AEM) prevents cations from accessing the cathode (CEM). These anions are barred from the anode by a cation-exchange membrane, which mixes the cations with anions traveling in the opposite direction. Consequently, they are maintained in the same compartment as the cations. In the "dilute" compartment, cations and anions are depleted from the left and right compartments. Astonishingly, ions can cross the concentration gradient to reach the concentrated state. In Fig. 3, the configuration of an electrodialysis unit, in the center of the ED unit, the cation exchange membrane (effective surface area: 7.06 cm²) is positioned. Silicone rubber gaskets separated adjacent anion exchange membranes and all the ED unit plates to prevent solution leakage. The assembled ED unit consists of four compartments, sequentially from anode to cathode: anode, diluting, concentrating, and cathode. As a test solution, simulated water with 4300 TDS is employed. Both diluting and concentrating compartments receive 200 mL of the equimolar simulated water samples for the desalination procedure. As an electrode cleaning

solution, 200 ml of 0.5 M Na₂SO₄ is cycled between the anode and cathode compartments. All solution streams are constantly cycled at a very constant flow rate. Electrostatic ionic flow through the ED unit is studied at a direct current density of 10 mA cm⁻² (potentially applied between the two electrodes). The duration of the desalination process is 240 min. Every 40 min, the performance of the ED unit is checked from the diluting compartment using a TDS measurement device Hanna TDS meter.

Morphological characterization

Morphological analysis was successfully done through digital optical microscope (LEICA DM 2700 P). Microscope was used to determine the nanostructured functional ion exchange membranes surface and cross-sectional morphology. For understanding, the resulting topography result is given in Fig. 4. Surface and cross-sectional views of membranes were taken from dry membranes.

Results and Discussion

Morphological characterization of fabricated Membranes

To research materials and assess their microscopic qualities, surface examination is a crucial step. Using an optical microscope, the surface properties of synthesized non-nanostructured and nanostructured ion exchange membranes were examined in this work. The surface characteristics of the material may be imaged and analyzed with great resolution using the digital optical microscope. The smooth and uniform surface shown in the microscope photos suggested the surface characteristics across various sections of the sample (Fig. 4a and 4b). The material was well-prepared and homogenous. The surface uniformity and homogeneity of the samples were shown by the microscope pictures. A high degree of uniformity and consistency in the material composition and structure was suggested by the absence of notable differences in samples that were functionalized poly (2,6-dimethyl-1,4-phenylene oxide) membranes including nanostructured polyaniline (PANI). The PANI nanoparticles morphology within the membranes was made visible by the digital optical microscope (Fig. 4b). The microscopy pictures revealed the existence of nanoparticles in a range of sizes that were spherical or irregularly shaped. Cross-sectional analysis showed that there was a homogeneous dispersion of PANI nanoparticles across the membrane matrix. The findings showed that the PANI nanoparticles had a good level of matrix integration, pointing to robust interactions between the two elements.

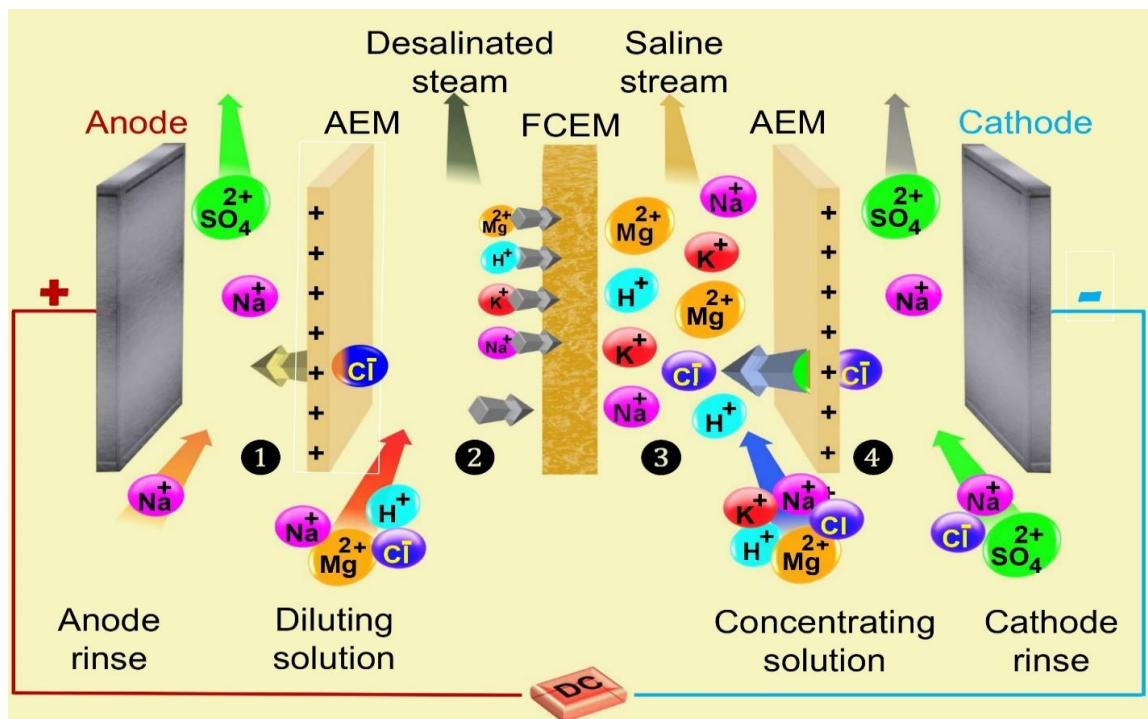


Fig. 3: ConFigure of Electrodialysis cell. Comprises four chambers anode, diluting, concentrating and cathode rinse from left to right. 0.5 M Sodium sulphate (Na_2SO_4) solution is used for electrodes rinse. Between diluting and concentrating chambers which comprises commercial anion exchange membranes (AEM, Neosepta®) our nanostructured functional cation exchange membrane is present. Simulated waste water is run in both diluting and concentrating chambers.

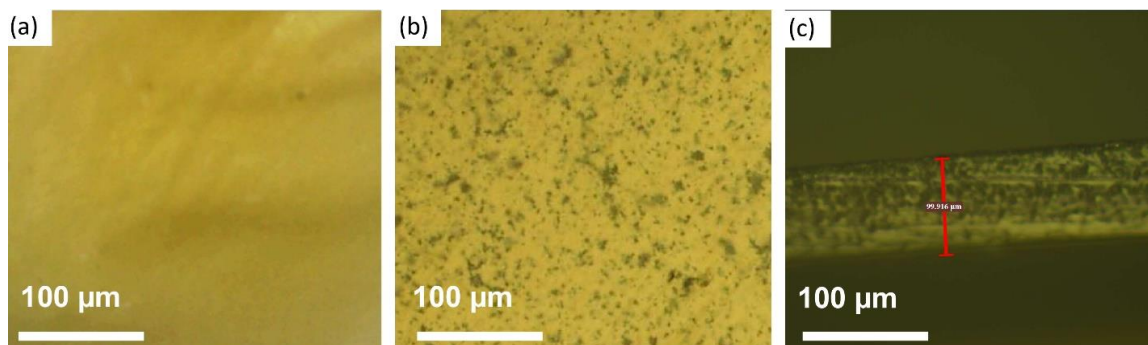


Fig. 4: Morphological analysis of membranes (a) Surface morphology of non-nanostructured ion exchange membranes (b) surface morphology of nanostructured functional ion exchange membrane having uniform distribution of nanostructures (c). Cross-sectional thickness of functional nanostructured ion exchange membrane.

Water Uptake and Volumetric Expansion

IEMs are involved in ion conduction and mechanical characteristics, water uptake and swelling are critical. In general, increased water uptake improves the ionic conductivity and flexibility of membranes, but it also causes increased volumetric expansion (observed from swelling in thickness and

linear expansion), which can compromise its dimensional stability. As a result, adequate water uptake is required to provide strong ionic conductivity and membrane mechanical stability. Water uptake of (SPPO)FCEM is larger than (QPPO)FAEM, as shown in Fig. 5 since water absorption increases specifically with the incorporation of the Polyaniline groups hydrophilicity [30].

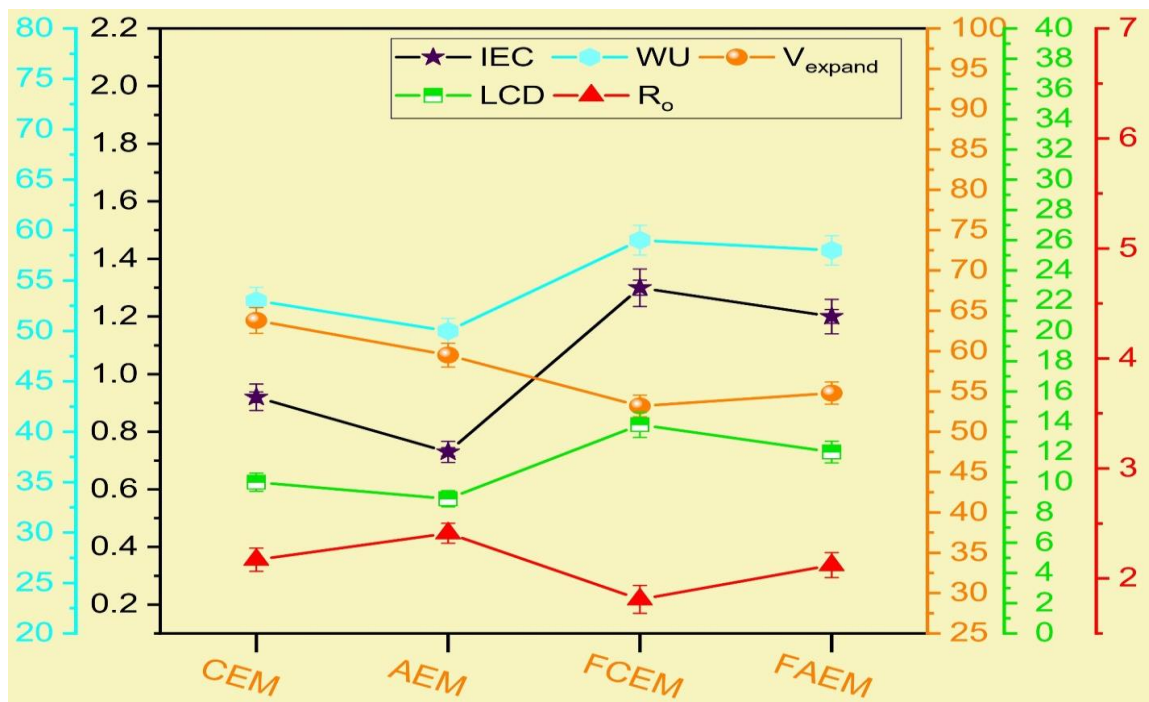


Fig. 5: Physio-chemical evaluation of nanostructured functional ion exchange membranes. Increase in ion permeation and water uptake and decrease in swelling degree than non-nanostructured function ion exchange membranes (CEM and AEM). Reducing resistance and increase in limiting current density for nano-structured functional ion exchange membranes (FCCEM and FAEM).

Ion Exchange Capacity

The SPPO (CEM) membranes combined with PANI shown an improved ion exchange capacity in comparison to the pure SPPO membranes, according to the acid-base titration study. The ion exchange capacity (IEC) of the PANI-incorporated SPPO membranes was calculated to be 1.2 meq/g, showing a greater IEC attributable to the inclusion of PANI nanoparticles. Similar to this, the acid-base titration investigation showed that the addition of PANI increased the ion exchange capacity of QPPO membranes. In comparison to the QPPO membranes without PANI, the IEC of the PANI-incorporated AEM membranes was found to be 1.1 meq/g, showing an increased ion exchange capacity.

This analysis identifies any discrepancies between the two membrane types and sheds light on how the polymer matrix affects ion exchange capacity. Overall, the acid-base titration research showed that the addition of PANI enhanced the ion exchange capacity of both CEM and AEM membranes. The extra ion exchange sites offered by PANI nanoparticles are responsible for this enhancement. The observed IEC values demonstrate the increased ion exchange capacity in the membranes with PANI

incorporation quantitatively, suggesting their potential for a range of applications requiring effective ion transport and selectivity.

Excellent Electrochemical Properties

Here, specific characteristic current-voltage (I-V) graphs demonstrate the electrostatic response of the membranes to penetrating ions, with the transmembrane potential decreasing correspondingly with the gradual rise in applied direct current density (Fig. 6a). The data are divided into three distinct parts by I-V curve analysis: the over-limiting, the current plateau, and the beginning (linear) section, also known as the "ohmic region." The reverse slope of the current-voltage (I-V) curves in the "ohmic area" provides the membranes resistance (R_o) to the transmembrane penetrating ions. The resistance of the FIEMs has greatly decreased, as shown by the computed resistances in cm², CEM=2.17, AEM=2.41, FCCEM=1.81, and FAEM=2.12. In particular, the typical FCCEM, FAEM, shows roughly 17% and 12% reduction in resistance to penetrating ions than the non-FIEMs. The FCCEM and FAEMs exhibit exceptionally very low electrical resistance (R_o) to the permeating ions when compared to the non-FIEMs membrane.

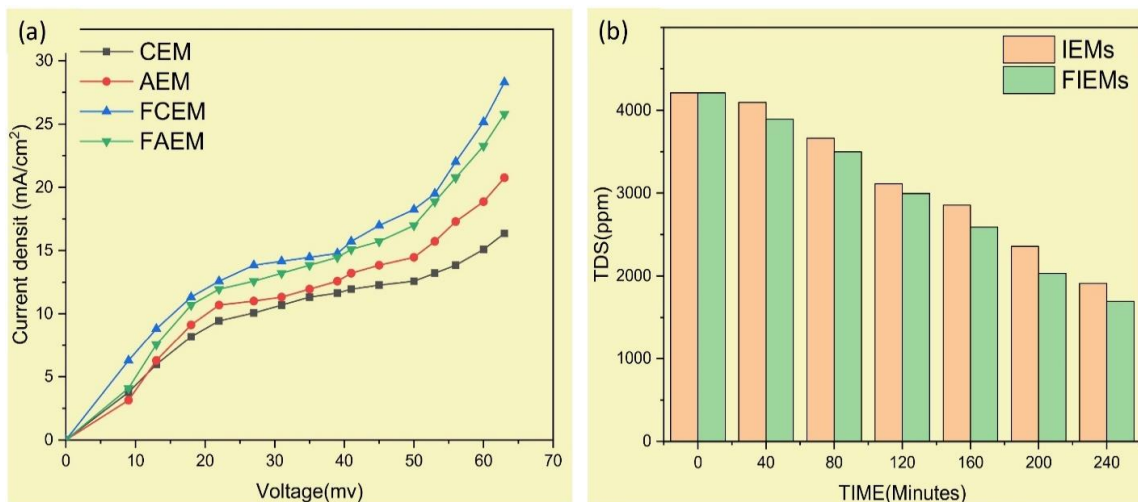


Fig. 6: Improved Electrochemical and Desalination performance for developed Nano-structured function ion exchange membranes. A) Current voltage curve represent high limiting current density and less resistance than non-Nano-structured functional ion exchange membranes. B) Nano-structured function ion exchange membranes offer 19% faster desalination performance than non-nanostructured function ion exchange membranes.

Saline water desalination performance

Saline water of 4300 TDS was used as the testing solution, using a conductivity meter (TDS), the effectiveness of the individual cell desalination process was assessed for 240 min, and with results being recorded every 40 min. The fabricated membranes demonstrate the fastest ion penetration of all the membranes as compared to the simple CEM and AEM ion exchange membrane at the same evaluating period, resulting in significant desalination 19% greater for FIEM in 240 min. The delegate FIEM membrane provided a comparably quick desalination capacity than the non-FIEM membrane. Desalination of saline water capacity is improved because the resistivity of the FIEMs is lower than that of the non-FIEMs (as illustrated in current voltage curves, Fig. 6a). Another condition for effective ion penetration across the ion exchange membranes is the homogeneous arrangement of the nano-structured PANI (as illustrated in morphological analysis in Fig. 4b). During transit hydrated ions boost their permeations, Moreover, the hydrophilic Polyaniline nano-structures can store much water. Simply said, FIEMs, in particular with uniform nano-structures distribution, low membrane resistance for ions penetration, higher water uptake, and minor membrane swelling, work together to produce an ultra-fast and consistent performance of desalination as in (Fig. 6b). These characteristics are especially desired for the effective large-scale processing of

extremely salinized water effluents in the steel, electroplating, and chlor-alkali industries.

Conclusion

Results indicate that the proposed nano-structured polyaniline and its systematic distribution within the ion exchange polymer matrix increase ion permeation and energy efficiency by reducing resistance. Moreover, the uniform distribution of nano-structured electroactive material increases stability, and cross-linking, and decreases swelling degree. Therefore, nanostructured functional ion exchange membranes offer less swelling higher water uptake, and ion permeation. Improved electrochemical properties also increase the limiting current density for FIEMs than non-FIEMs. Improved physio-chemical and electrochemical properties offer 19% faster desalination performance than non-functional IEMs. Moreover, simple solution casting and post-drying methods for membrane fabrication can be applied to the industrial-scale fabrication of Functional ion exchange membranes. Those can benefit several industrial processes such as pickling, electroplating, and chlor-alkali which discharges huge amounts of wastewater.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships

that could have appeared to influence the work reported in this paper.

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