Reactive and Functional Polymers 178 (2022) 105336

Contents lists available at ScienceDirect

Reactive and Functional Polymers

journal homepage: www.elsevier.com/locate/react

Development of a new route for cation exchange membrane fabrication by using GO reinforced styrenated oil

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ARTICLE INFO

Keywords:
Cation exchange membrane
Polystyrene
Styrenated oil
Graphene oxide

ABSTRACT

A novel route was developed for cation exchange membrane (CEM) fabrication by using GO reinforced styrenated oil polymeric structure and the impact of polymer type (PS/PS-oil), graphene oxide amount (0.5,1,3, and 5 wt%), and sulfonation time (6,12, and 24 h) on the characteristics of prepared membranes (contact angle, water uptake, ion exchange capacity, DS(%), electron conductivity) were investigated for the first time in the current study. The results showed that higher values of water absorption, ion exchange capacity, and electron conductivity were obtained for GO-PS-oil-based membranes compared to GO-only PS based membranes under all experimental conditions. Also, it was seen that ion-exchange capacity and water uptake capacity were directly related to the GO amount and sulfonation time of the polymer. The maximum value obtained for ion exchange capacity was 7.7 meq/g for 5%GO incorporated-PS-oil based membrane sulfonating for 24 h. The obtained IEC values for all experimental conditions in this study are relatively high compared to other PS based membranes studied in the literature. The membrane's electrochemical characteristics (conductivity, flux and permeability) were also determined in an electrodialysis test cell. All obtained results indicated that CEM fabricated by this new approach could be utilized for electrodialysis applications in the future.

1. Introduction

Developing new polymeric membranes for cation exchange membranes (CEM) is an active area of research since they are widely utilized in essential applications, including fuel cells, seawater desalination, precious metal recovery from wastewater, diffusion dialysis, ultrapure water, and electrodialysis [1–5]. The fouling problem of the membrane can emerge as a major drawback during these processes. The surface of the membrane can be modified by blending, grafting, nanoparticle incorporation, and surface chemical reaction to solve this problem for long-term flux stability in membrane technologies [6–13]. Among the membrane applications, electrodialysis (ED), which is the basic process of electrochemical separation, has an increasing interest for investigators as it has different applications, which many of these are related to separation and reuse i) obtaining drinking water, ii) removing salt from seawater iii) separating and concentrating acids iv) recovering metal salts from industrial wastewaters [14–16]. Ion exchange membranes (IEM) play a critical role in electrodialysis, and the efficacy of electrodialysis is highly reliant on the characteristics of ion-exchange membranes. For this reason, to improve electrodialysis performance, many studies on ion exchange membranes with enhancing features such as ion exchange capacity, proton conductivity, water content, mechanical strength, and chemical stability have been carried out by using polymeric blends [17]. An essential part of these studies on IEM in literature involves polystyrene (PS)-based membranes since sulfonated polystyrene and its copolymers could be widely used to enhance the crucial properties of membranes in IEM fabrication [17–19]. The performance of the polymeric formulation which is used for membrane technologies depends on the degree of their miscibility. At this point, the thermodynamic interaction of PS and its copolymers with different polymers has been studied and evaluated in terms of the, χ, Flory−Huggins interaction parameter (or the related binary interaction energy density) in the literature [20–24]. Although these types of PS-based CEMs belong to improved features, they have still disadvantages; i) having low ion exchange capacity (IEC), ii) demonstrating brittle behavior for casting membranes due to the structure of polystyrene, iii) possessing lower C—H bond (chemical) stability [25–27]. To overcome these challenges, graphene oxide (GO) has been used for the

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https://doi.org/10.1016/j.reactfunctpolym.2022.105336
Received 16 May 2022; Received in revised form 24 June 2022; Accepted 4 July 2022

preparation of specific membranes with sufficient properties since it can be easily modified chemically due to being the variety of oxygen-containing functional groups (hydroxyl, carboxyl, and epoxy groups). It has unique properties including a high specific surface area, electrical conductivity, high mechanical stability, and flexibility [28–31]. For example, P. Kulasekaran et al. produced the membrane with enhancing thermal stability and ionic conductivity by incorporation of GO into sulfonated polystyrene-*block*-poly(ethylene-*ran*-butylene)-block-polystyrene polymer matrix [32]. In another study carried out by R. Rudra et al., ‘in situ’ polymerized sulfonated polystyrene and glutaraldehyde cross linked polyvinyl alcohol including GO was used in the membrane preparation process for improving proton conductivity and IEC in the fuel cell application [33]. Yan Zhao et al. also constructed the selective separation membranes based on graphene oxide and sulfonated amino-polystyrene nanospheres for ED applications [34]. Although membranes including GO have been produced in the other studies as exemplified above, there is no study on the GO incorporated into styrenated oil polymeric structure which was developed as a novel route for the fabrication of a cation exchange membrane for the first time in this study.

Triglyceride oils could be easily polymerized with vinyl monomers such as styrene owing to their double bonds [26,35,36]. Furthermore, they are exceptional in controlling both elasticity and plasticity within a single main chain structure [37]. When the thermodynamic interaction (Flory−Huggins interaction parameter,χ,) between polystyrene and triglyceride oil derivates (long-chain poly(n-alkyl acrylates)) was investigated, it was seen that while the χ parameter is found to be independent of the alkyl side chain length (n) for large values of n, it depends on the temperature of the system [38]. Herein, to utilize the advantages of oils, sunflower oil, one of the triglyceride oils, was polymerized with styrene to produce the organic part of CEM and then GO reinforced into this polymeric structure for the inorganic part of CEM. It envisages that while sunflower oil which is a renewable resource provides more flexible membranes and thus protects fracture of the membrane by inserting soft oil moiety into CEM's structure, GO improves the ion exchange capacity of the membrane along with its chemical and mechanical stability. Therefore, oil and GO will contribute to the improvement of the CEM's properties owing to their superior features. In addition to the development of the novel approach for CEM production, the effect of sulfonation time which is a necessary and essential process to achieve notably high ion exchange capacity in the CEM preparation and GO amount was also investigated on the membrane properties including ion exchange capacity, water uptake capacity, contact angle and electron conductivity. Furthermore, the membrane's electrochemical properties (conductivity, ion permeability, and flux of ions) were measured in the electrodialysis test cell.

The obtained results from the related tests showed that CEM with enhancing properties could be produced by this new route. Especially the obtained ion exchange capacity (IEC) values are higher when compared to that of other PS-based membranes in the literature [39–41]. Both oil and GO contributed to improving water uptake capacity and IEC of membrane owing to their functionalities. It was also observed that the increase in the sulfonation time and GO amount have much more effect on the membrane properties in the case of PS-oil based membrane. Based on these findings, it is worth noting that the sulfonated GO incorporated styrenated oil-based membrane has future potential for electrodialysis applications.

2. Materials and methods

2.1. Materials

Commercially purchased sunflower oil was used as the oil component. Styrene (St, 99%, Merck) was passed through a basic alumina column to remove the inhibitor. Benzoyl peroxide, which was used as the initiator, dimethylformamide (DMF) used as the solvent, and xylene were purchased from Merck. Phenyl isocyanate, ethanol, methanol, divinylbenzene, potassium nitrate (KNO_3), potassium permanganate ($KMnO_4$), hydrochloric acid (HCl), hydrogen peroxide (H_2O_2, 30% by weight), and sulphuric acid (H_2SO_4, 98% by weight) were also obtained from Merck and used without purification. Graphite (powder <20 μm, synthetic) was purchased from Sigma-Aldrich.

2.2. Membrane preparation

2.2.1. Production of graphene oxide

Graphene oxide was obtained by using a modified Hummers method from graphite powder [42]. Firstly, 1 g graphite and 0.5 g KNO_3 were slowly added into the concentrated 23.3 mL of H_2SO_4 and kept in an ice bath. After a while, 3 g $KMnO_4$ was added little by little into the mixture under continuous stirring. Next, the mixture flask was placed into the sand bath at 35 °C and stirred for 30 min. Subsequently, 50 mL of distilled water was poured into the mixture and stirred at 90 °C for 15 min. Following this, 167 mL of distilled water and 5 mL of 30% H_2O_2 were added cautiously into the solution flask. The prepared warm mixture was transferred to conical Eppendorf tubes and then centrifuged at 6500 rpm for 10 min. The product was filtered and washed with 10% by volume HCl until the particles disappeared in the liquid fraction. Then, the tubes were placed in an oven for 48 h at 65 °C for drying.

2.2.2. Preparation of modified graphene oxide

To improve the compatibility between the GO particles and the PS-oil matrix and GO dispersibility in *N*,*N*-dimethylformamide (DMF), the surface of GO particles was modified with isocyanate through hydroxyl groups of GO (Fig. 1). For modification, 250 mg of dried graphene oxide powders were blended with 25 mL of dehydrated dimethylformamide (DMF) in a 50 mL Schlenk flask in an inert atmosphere. After providing an inert atmosphere, 2 mL of phenyl isocyanate was added to the system. Next, the mixture was churned for 3 h with an ultrasonic stirrer and then for 24 h with a magnetic stirrer. Modified GO powders were obtained from the resultant solution by using centrifugation and then the powders were washed with DMF several times for purification [43].

2.2.3. Fabrication of GO reinforced PS-oil based membrane

GO reinforced PS-oil based membrane was fabricated in three main steps: In the first step, styrenated oil (PS-oil) was produced according to the classical method specified in the literature [36,44]. The reaction was carried out by mixing sunflower oil (55 mL), styrene (45 mL), divinylbenzene (1.9 mL), xylene (43 mL) and benzoyl peroxide which was used as an initiator (0,6 g) at 150 °C for 24 h in an inert atmosphere. In the second step, the solution of modified GO particles at different ratios (0.5, 1, 3, and 5 wt% relatives to PS-oil) in DMF was added to the reaction mixture obtained in the first step and mixed until GO particles dispersed well. In the third step, the modified GO-PS-oil mixture dropped into a large amount of ethanol for the precipitation of the desired product. The obtained precipitate was washed several times with ethanol to further purification. Then, the resulting viscous solution was employed onto the support material (polyethylene) by using a film applicator to prepare the cation exchange membrane.

2.2.4. Production of GO reinforced PS based membrane

For comparison, only PS was produced according to the literature [45]. The polymerization process of styrene was carried out by using benzoyl peroxide (5% wt) as an initiator at 70 °C for 24 h. Then, the same procedure explained above in detail was applied for the preparation of GO reinforced PS based membrane.

2.2.5. Sulfonation of GO-PS-oil based and GO-PS based membranes

The fabricated GO-PS-oil based and GO-only PS based membranes were sulfonated by immersing into 98% H_2SO_4 solution at 25 °C for various durations (6, 12, 24 h). Then, sulfonated membranes were washed with distilled water to remove excess sulphuric acid solution

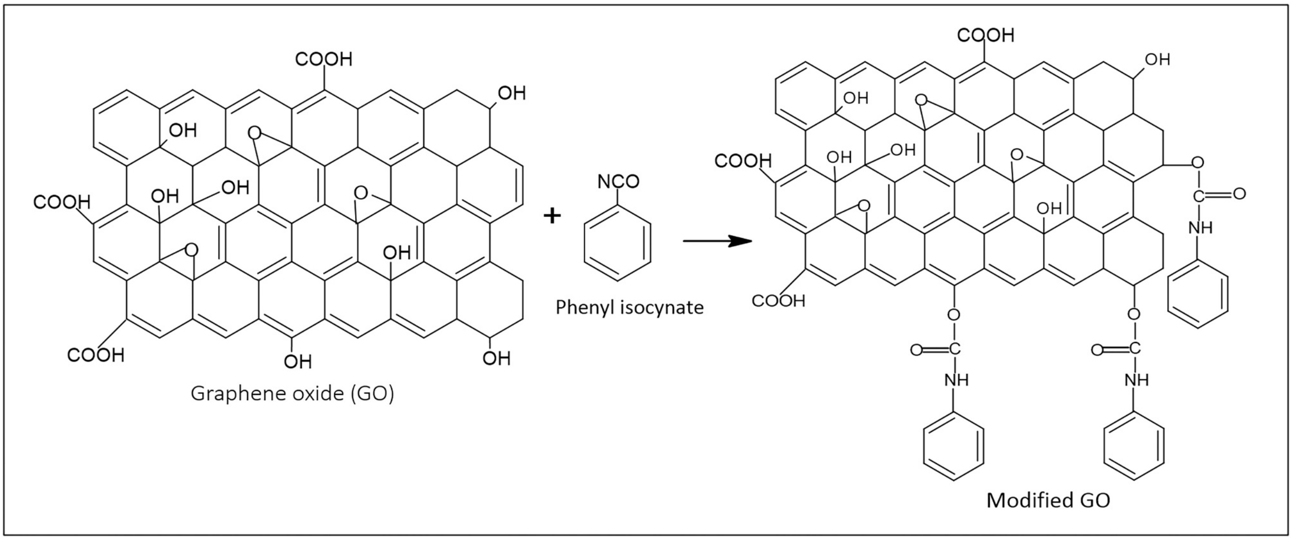

Fig. 1. Production of modified graphene oxide.

[46–48].

2.3. Membrane characterization

2.3.1. Chemical structure and morphological analysis

PS, PS-oil, GO reinforced PS-oil and sulfonated GO reinforced PS-oil produced at each stage were characterized by Fourier transform infrared spectroscopy (FT-IR) using the Bruker *Vertex* 70 *V* branded device. The samples were scanned within the wavenumber range of 0–4000 cm^{-1}. In addition, SEM analysis was performed to examine the prepared membrane morphologically using a Zeiss sigma 300 scanning electron microscope.

2.3.2. Contact angle

Contact angles were determined using a Biolin Scientific Attension Theta Brand device on prepared membranes. The contact angle is the angle created between the solid surface and the liquid in contact or the measure of a solid's wettability by a liquid. The solid's surface free energy determines the drop shape and contact angle on solid surfaces. The sessile drop method was used to measure the contact angle of the prepared membranes. This method determined the contact angle using a horizontal beam comparator by dropping 5 μL of water onto the surface through a 0.10 mL syringe.

2.3.3. Water uptake capacity

The prepared membranes were kept in an aqueous solution for 24 h at room temperature. After this period, the membrane was carefully taken out from the solution, and dried using absorbent paper to remove the water absorbed on the surface of the membrane. Following that, the wet weight of the membranes was determined. The water uptake capacity was calculated using the Eq. (1) given below [49].

$$Water\ uptake\% = \frac{(\mathrm{W}_{wet} - W_{dry)}}{W_{dry}} \times 100 \tag{1}$$

2.3.4. Ion exchange capacity

To determine the ion exchange capacity of the membranes, the prepared membranes were immersed in 50 mL of 0.1 N NaOH solution at room temperature for 2 h. During this time, H^+ ions change places with Na^+ ions. After removing the membranes from the NaOH solution, it was titrated with 0.1 N HCl, andthe ion exchange capacity was calculated as below (Eq. (2)):

$$IEC = \frac{(M_{NaOH}.V_{NaOH}.n_{NaOH}) - (M_{HCl}.V_{HCl}.n_{HCl})}{W_{membrane}} \tag{2}$$

M and *V* are the molar concentration and volume of the solutions, respectively, while $W_{membrane}$ is the weight of the membrane and n is the valance factor.

2.3.5. Degree of sulfonation

The degree of sulfonation (DS) can be calculated by using IEC obtained from the titration method which was explained in the ion exchange capacity section. The DS of fabricated membranes based on polystyrene was determined by the following Eq. [46];

$$DS\ (\%) = \frac{The\ molecular\ weight\ of\ repeat\ unit\ of\ PS\ x\ IEC}{1000 - the\ molecular\ weight\ of\ the\ SO3H\ group\ x\ IEC} \times 100 \tag{3}$$

2.3.6. Electron conductivity

Conductivity measurements were carried out by the Source Meter Keithley 2400 device. I/*V* measurements were made around ten times, and the average was calculated. The conductivity was determined with the following equations;

$$\rho = 2\pi sFR \tag{4}$$

$$\sigma = 1/\rho \tag{5}$$

ρ: resistivity (ohm.cm), s: probe spacing (0,2 cm), F: Correction Factor, R:V/I = Resistance (ohm), σ:conductivity (S/cm).

2.3.7. Determination of the electrochemical properties of the produced membrane in the electrodialysis test cell

The electrochemical characteristics of the created membrane were determined in an electrodialysis system (PCCell BED 1–4 GmbH, Heusweiler, Germany) which is formed by the electrodialysis cell and two tanks as shown in Fig. 2. This system is equipped with online control and data acquisition units. The current-voltage is applied and controlled by a DC power supply in this system. The cell consists of a cathode and anode which are comprised of mixed metal oxides coated with titanium and cation exchange membrane (CEM). Additionally, there are two support materials on both sides of the cation exchange membrane to regulate the flow inside the cell [50]. While one of the tanks in the experiment set is filled with 0,1 M NaCl solution, the other is full with 0,01 M NaCl solution. For tests, firstly, the prepared membrane was placed in the cell. Following that, the solutions in the tanks were transferred to both sides

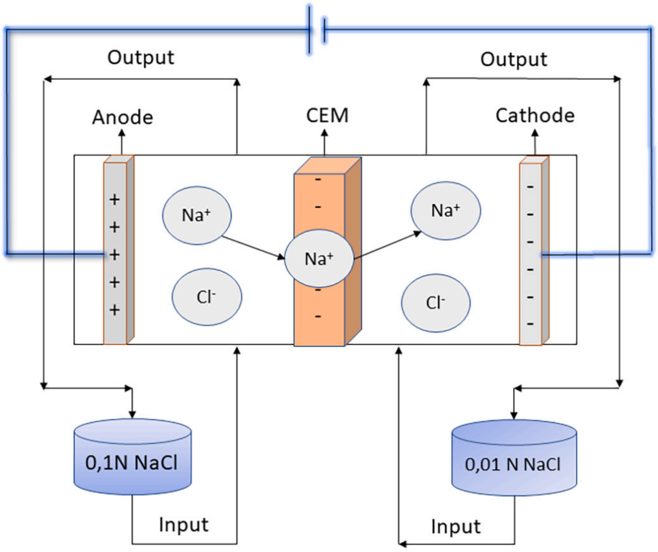

Fig. 2. The flow chart of the electrodialysis system.

of the cell at a flow rate of 15 L/h using the peristaltic pumps in the experimental apparatus. The power supply was then set to 3 A, and the experiment was started to predicate the produced membrane's electrochemical properties including conductivity, ion permeability, and flux measurements in an aqueous solution. The conductivity meter in the experiment system was used to measure conductivity on both sides. When the conductivity of the concentrated side dropped to 2mS/cm, the experiment was terminated. For the ion permeability and flux measurements, Na molarity on the diluted side was measured every 10 min via the titration method. Titration was performed by taking a certain amount of solution and using 0,001 M HCl solution. The flux was calculated with the following equation;

$$N_{ion} = \frac{n_t - n_0}{A.t} \tag{6}$$

n_t: the amount of Na in catholyte compartment at any time (moles), n_o: the amount of Na in catholyte compartment at the beginning (moles), A: active area of the cation exchange membrane used in the cell (64 cm^2), t: time (hour).

3. Results and discussions

GO reinforced PS-oil-based cation exchange membrane was fabricated in this study. The developed novel route was described as both a schematic diagram (Fig. 3) and a reaction mechanism (Fig. 4). To ascertain the optimum conditions for preparing the new cation exchange membrane, the firstly experiment plan was created utilizing the polymer type (PS/PS-oil), sulfonation time (6, 12, 24 h), and graphene oxide ratio (0.5, 1, 3, and 5 wt%) as the parameters. Before incorporation into the polymeric structure, the surface of GO particles was modified with phenyl isocyanate owing to the presence of hydroxyl groups in its structure to improve the compatibility between the GO particles and the PS-oil structure. Phenyl isocyanate generates $\pi - \pi$ interactions with the phenyl group on the polymer (polystyrene) surface [51]. This modification also increased GO dispersibility in *N*,*N*-dimethylformamide (DMF) [43].

3.1. Membrane characterization

The cation exchange membrane was structurally and morphologically characterized using FT-IR and SEM analyses. Fig. 5a shows the FT-IR analysis of the produced polystyrene. The first peak at a wavelength of 3024 cm $^{-1}$ seen here is the aromatic C—H stretching vibration in the polystyrene structure. The next three peaks (1600, 1492, and 1450 cm^{-1}) are aromatic C—H bond stretching vibrations. The peaks at 1026, 906, 750, 694 and 538 cm^{-1} correspond to C - H deformation vibration [52]. 1600 cm^{-1} peak indicates the C═C vinyl group. All these peaks are characteristic of polystyrene which confirms polymerization reaction has been completed effectively, resulting in the formation of polystyrene [53].

Fig. 5b shows the FT-IR image of the prepared PS-oil (styrenated oil). As it is apparent, the peaks at 2924 and 2854 cm^{-1} confirm –C-H stretch, and the peak at 1739 cm^{-1} confirms the double bonds. The peaks at 1600, 1452, and 1377 cm^{-1} correspond to –C-C stretch (aromatic chain) and –C-H stretch (Alkyl). The absorption peak at 1155 cm^{-1} shows = C-H bend. –C=C-H_2 vinyl group is seen at 908 cm^{-1}. The peak at 756 cm^{-1} peak corresponds to the = C-H bending. These peaks in the FT-IR spectrum are characteristic peaks of styrenated oil [54], indicating that PS-oil was produced successfully.

Fig. 5c confirmed the modification of GO with isocyanate and the incorporation of modified GO into the polymeric structure. While there are the characteristics peaks related to GO and PS-oil in the spectrum, successful bonding of the phenyl isocyanate onto the GO surface is also verified by the presence of the peaks at 1648 and 1554 cm^{-1}, which are attributed to the stretching vibration of the phenyl ring and collaborative stretching vibration between amide esters or carbonates and C—N, respectively [43].

Sulfonation of GO incorporated-PS-oil based membrane was confirmed by FT-IR spectroscopy. As shown in Fig. 5d, the peaks

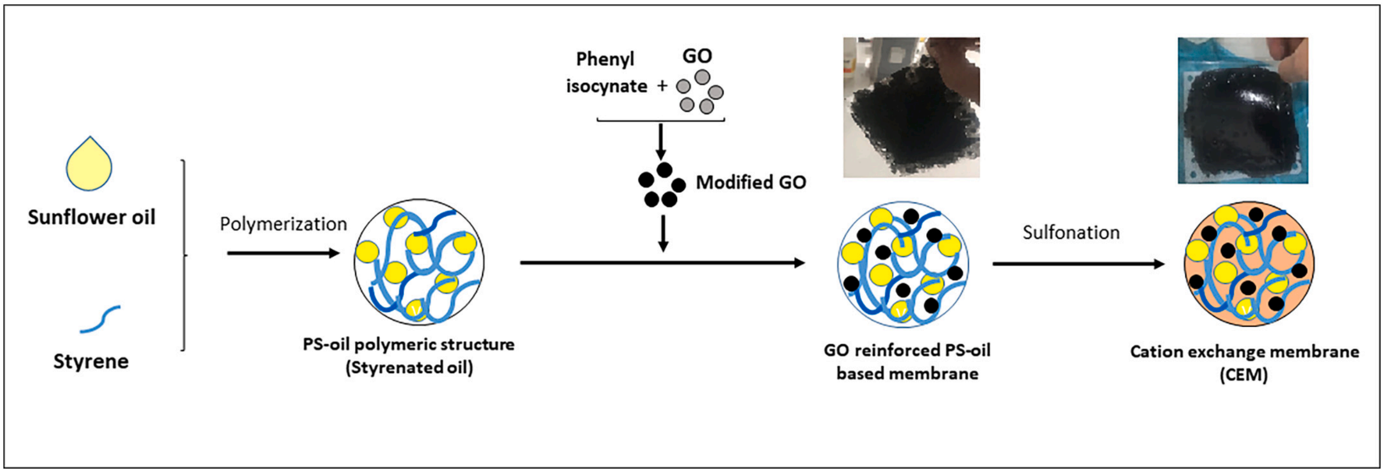

Fig. 3. Schematic diagram for the production of GO reinforced PS-oil-based cation exchange membrane.

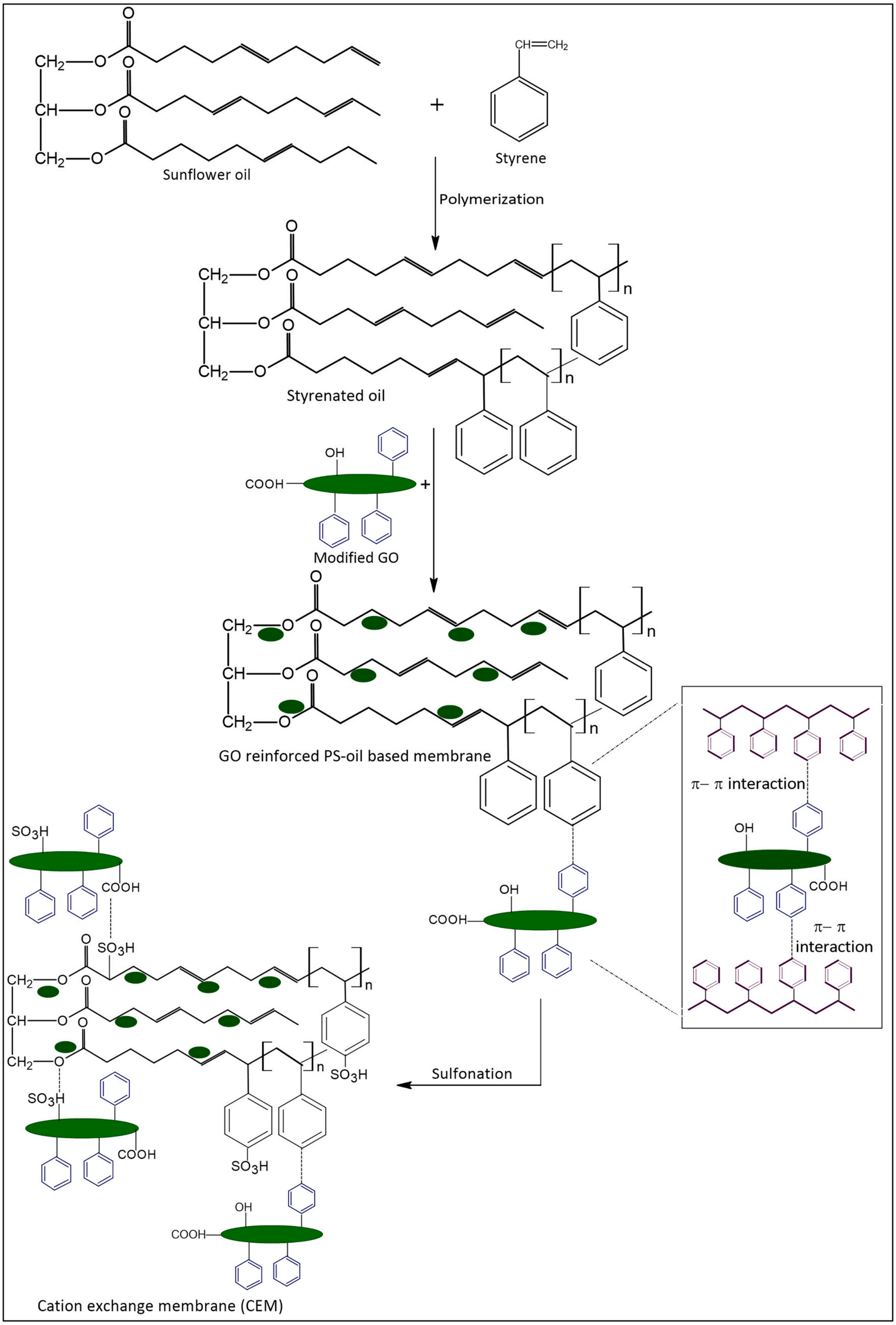

Fig. 4. Reaction mechanism for the production of GO reinforced PS-oil-based cation exchange membrane.

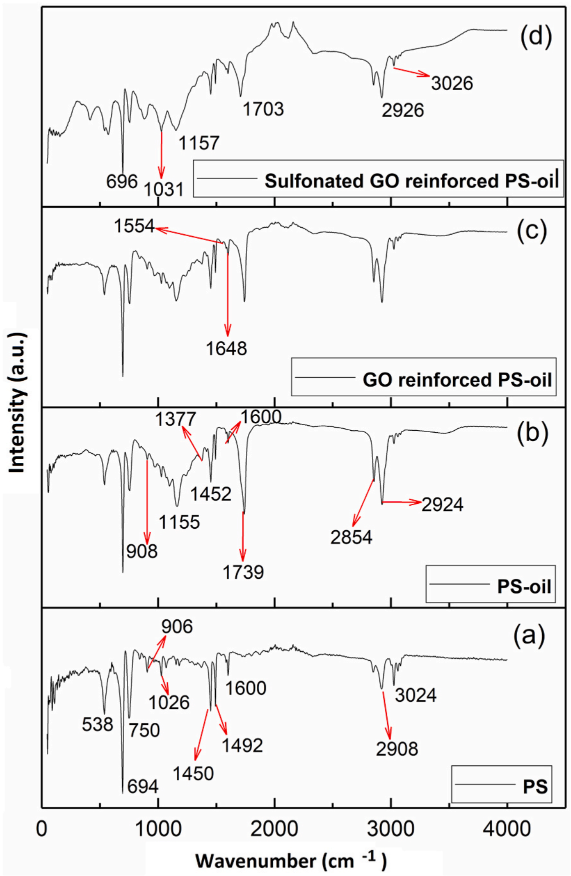

Fig. 5. FT-IR spectra of PS (a), PS-oil (b), GO reinforced PS-oil (c) and sulfonated GO reinforced PS-oil (d).

between 500 and 1350 cm^{-1} appeared after the sulfonation process, which confirms the presence of multiple sulfonic groups such as O=S=O, S═O, $S(=O)_2OH$, $-SO_3H$, S-O-C and C—S in the structure. Additionally, the peak at around 3024 cm^{-1} was broader by incorporating the hydroxyl groups of sulfonic acid into GO-PS-oil structure after sulfonation [17,47,48,55].

The surface and cross-section images of sulfonated GO reinforced PS-oil based membrane were captured by SEM analyses and displayed in Fig. 6. The surface of the membrane has roughness and there are holes in the membrane structure as seen from the image acquired from the surface and cross-section. According to this image, it can be stated that the produced cation exchange membrane has a porous structure morphologically.

3.2. Contact angle

Water management is critical for cation exchange membranes since water molecules serve as the primary proton carriers. Therefore, cation exchange membranes are desired to be hydrophilic. Because this feature increases the contact of water molecules with the membrane [56,57]. The contact angles of prepared membranes were measured and the results were shown in Fig. 7 as a graph. As shown, the membrane surfaces became more hydrophilic with increasing sulfonation time. The contact angle of water drops fell due to the improved wetting character of the polymer surface due to the hydrophilic structure of sulfonic acid groups. This case was also confirmed by contact angle photos of PS-oil-3%GO for different sulfonation times (Fig. 8). In sample codes, S6h, S12h and S24h demonstrate the sulfonation time of the membrane for 6 h, 12 h and 24 h, respectively.

Although the effect of GO on the contact angle could not be observed as a specific trend, the diminishing trend in the contact angle was broadly seen by increasing GO amount up to 3 wt%, especially for PS-oil based membranes.

3.3. Water uptake capacity

Membranes are required to contain a specific amount of water since water molecules are the essential proton carriers in membranes [58]. On the other hand, the retained water should not induce membrane swelling or overflowing [59,60]. To evaluate the effect of sulfonation time and GO amount on the water uptake capacity, the membranes fabricated by using different sulfonation times (6, 12, and 24 h) including 3%wt GO and different GO amounts (0.5, 1, 3, and 5 wt%) sulfonating for 24 h were selected for the measurements. As can be observed from Fig. 9, the water uptake capacity increased by the increment of sulfonation time due to the hydrophilic nature of sulfonyl groups [41,42,61,62,63]. The increase in the modified GO amount incorporated into the structure also enhanced the water uptake capacity of the membranes since modified GO not only has hydrophilic groups such as hydroxyl group but also can be sulfonated owing to its epoxy and/or hydroxyl groups [64]. When compared to the water uptake capacity of only PS based and PS-oil based membranes each other, it was recognized that PS-oil based membranes have higher values for all conditions than those of PS-based membranes, although the oil portion in the membrane structure has a hydrophobic feature. This result can be explained that modified GO particles could be more homogeneously distributed into the PS-oil based membrane since modified GO having carboxyl, hydroxyl and phenyl groups could interact with both polystyrene and oil portion owing to π-π and dipol-dipol intermolecular interactions, respectively in the polymeric structure (Fig. 4), which enhances the water uptake capacity of the membrane [43,51,64]. Additionally, it can be mentioned that i)there can be an interaction between the acid sites/protons of SO_3H groups and the oxygen atom in the ester linkage of triglyceride oil structure ii) there can be carried out nucleophilic substitution reaction between β carbon of triglyceride oil structure with sulphuric acid, which enhanced dipol-dipol interactions between oil and functional groups (carboxyl and hydroxyl) of modified GO by increasing the polarity of oil structure [65,66]. Thus, the cluster of sulfone groups could be prevented resulting in an increase of the water uptake capacity [66].

Another point that should be emphasized is that although sulfonation time increased, there is no significant improvement in the water uptake capacity of pristine GO-PS-based membrane. This case can be explained by a competitive effect: on the one hand, the number of sulfonyl groups increases; on the other hand, accumulation of these groups begins to form by increasing sulfonation time, which induces a hinderic effect for water uptake into the polymeric structure.

3.4. Ion exchange capacity

The polymer matrix's ion exchange capacity (IEC) is considered a measure for the number of ion-exchange groups present. Since proton transfer depends on the ion-exchange groups, IEC is a direct and accurate estimate of proton conductivity [67]. Fig. 10 and Table 1 show the ion exchange capacities of the membranes produced in this study. The results indicated that the ion exchange capacity enhanced by increasing of graphene oxide ratio in the membrane structure. For example, while the IEC value for PS-oil-1%GO-S24h is 5.44 meq/g, this value is 7.58 meq/g for PS-oil-3%GO-S24h. This increase can be explained that the ion exchange capacity of the membrane depends upon the water uptake capacity and functional group present in the membrane structure. GO reinforced membrane contains a variety of functional groups due to the incorporation of GO, which provides more active sites for the transport of the proton. In the meantime, since more water molecules in the membrane act as a medium for proton movement, the higher water uptake ability enhances ion exchange capacity.

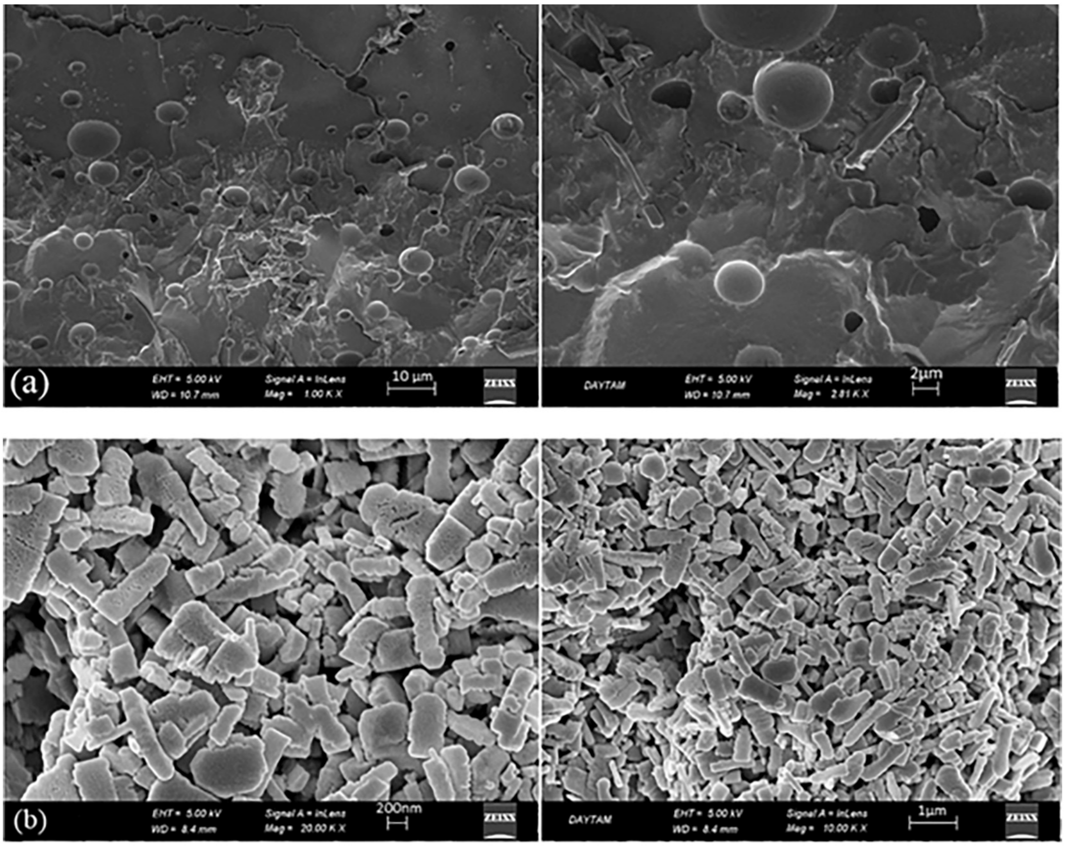

Fig. 6. Surface (a) cross-section (b) SEM images of 3 wt% GO reinforced PS-oil based membrane sulfonated for 24 h.

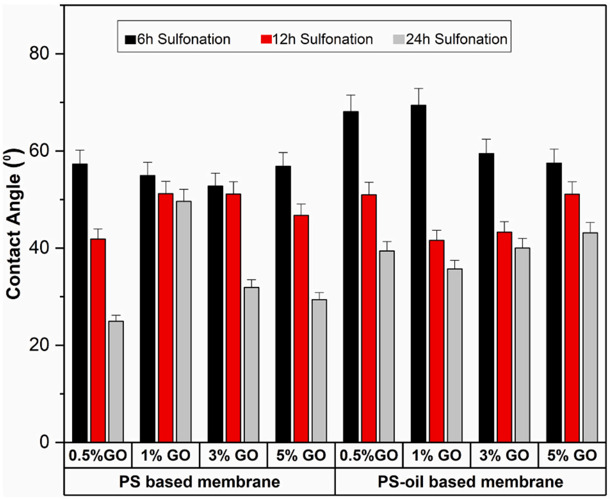

Fig. 7. The effect of both GO amount and sulfonation time on the contact angle of the produced membranes.

When the effect of sulfonation time on the IEC was observed, it was found out that the IEC of the produced membranes improved by increasing with a sulfonation time since the higher concentration of the sulfonic groups fixed in the structure is available to be exchanged with the sodium ions in solution by the evaluating sulfonation time. As seen in Table 1, while the IEC of PS-oil-3%GO-S6h was found to be 2.94 meq/g, this value improved to 4.92 meq/g and 7.58 meq/g for PS-oil-3%GO-S12h and PS-oil-3%GO-S24h, respectively.

As pristine PS based and PS-oil based membranes are compared with each other in terms of IEC, it is obvious that PS-oil based membranes have much higher IEC values than that of pristine PS based membrane and sulfonation time has much more effect on the IEC of PS-oil based membrane at the all experimental conditions (Table 1). These results can be attributed to two important points: i) triglyceride oil can also be sulfonated during the sulfonation step by means of nucleophilic substitution reaction between β carbon of triglyceride oil structure with sulphuric acid [65]. This contribution implements the presence of more sulfonyl groups (SO_3H) and a higher number of movable protons in membrane structure, leading to higher IEC. Additionally, the interaction between oil and sulfonyl groups is to preserve the cluster of -SO_3H groups as explained water uptake section [66]. ii) the aggregation of GO particles may be prevented by means of interaction of GO particles with both polystyrene and oil portion through π-π and dipol-dipol intermolecular interactions in the membrane structure and thus more homogenous distribution of GO within PS-oil based membrane could be provided compared to just PS-based membrane resulting in an increase the IEC [43,51,64].

When all the obtained results are evaluated, it is worth pointing out that the IEC value of membranes produced by the new approach in this study is higher than that of the other PS-based membranes in the literature [39,40,63,68].

3.5. *Degree of Sulfonation (DS)*

The membranes fabricated by using different sulfonation times (6 and 12 h) were selected for the calculation of DS. The obtained DS results and IEC, water uptake, contact angle values the of same membranes determined in previous sections were given in Table 2 to show the relationship between sulfonation degree (DS) and IEC, water uptake, contact angle. As seen from the table, the IEC and water uptake increased with the increase of DS due to the presence of more hydrophilic sulfonic acid groups in the membrane structure. This is consistent

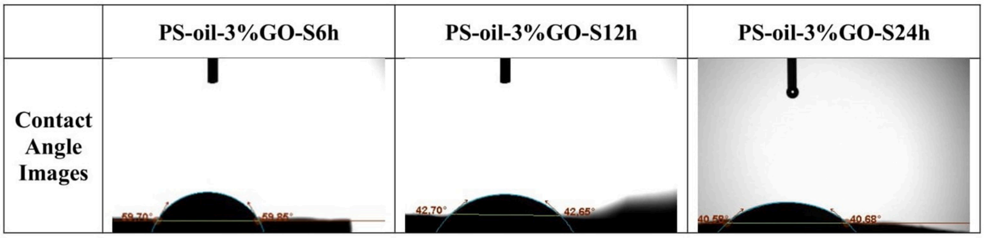

Fig. 8. Contact angle images of PS-oil-based membranes including 3 wt% GO for different sulfonating times.

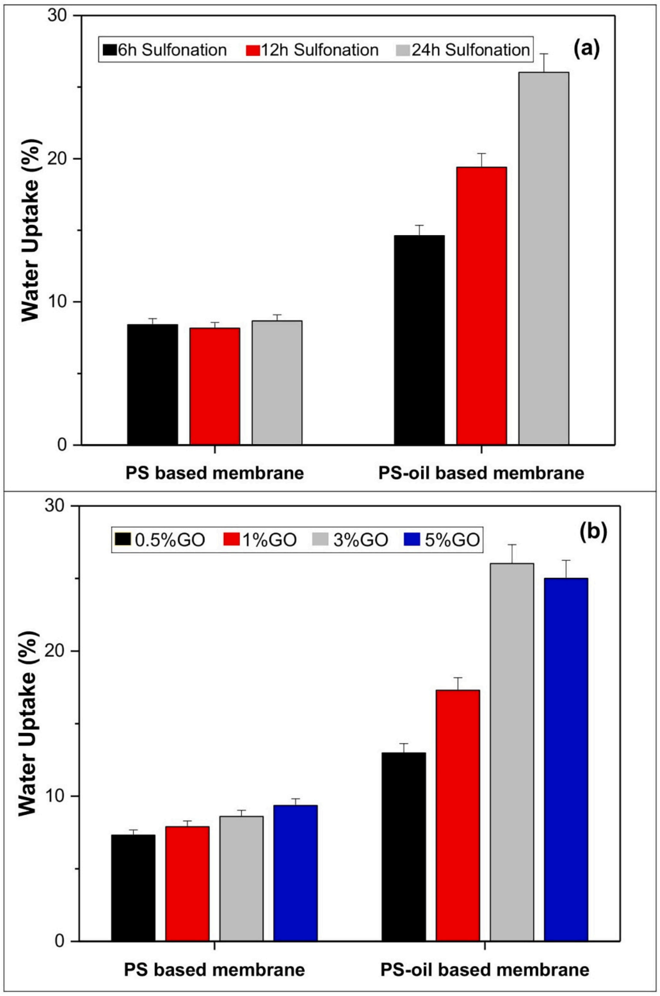

Fig. 9. The effect of sulfonation time for 3 wt% GO (a) GO amount for 24 h sulfonation (b) on the water uptake capacity of the produced membranes.

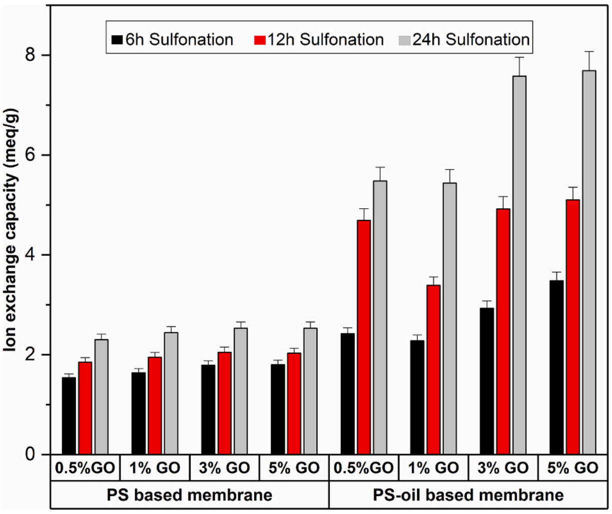

Fig. 10. The effect of both GO amount and sulfonation time on the IEC of the produced membranes.

Table 1
The effect of both GO amount and sulfonation time on the IEC of the produced membranes.

Ion exchange capacity (meq/g)			
Sulfonation time	6 h	12 h	24 h
PS-0.5%GO	1,54	1,85	2,35
PS-1% GO	1,65	1,96	2,44
PS-3 %GO	1,79	2,06	2,53
PS-5%GO	1,80	2,05	2,54
PS-oil-0.5%GO	2,42	4,69	5,49
PS-oil-1%GO	2,28	3,39	5,44
PS-oil-3%GO	2,94	4,92	7,58
PS-oil-5%GO	3,48	5,11	7,70

Table 2
Degree of sulfonation of PS-oil-based membranes including 3 wt% GO for different sulfonating times.

Sample	DS(%)	IEC	Water uptake	Contact angle
PS-oil-3%GO-S6h	40,01	2.94	14.62	59.00
PS-oil-3%GO-S12h	85.20	4.92	19.40	42.00
PS-oil-3%GO-S24h	204	7,58	26,03	40.00

with the decreasing of contact angle of the membranes with higher DS, indicating higher hydrophilicity.

It should be noted that especially, the calculated DS (204%) for PS-oil-3%GO-S24h confirmed that the oil portion and GO aside from styrene in the membrane structure were also sulfonated during the sulfonation process.

3.6. Electron conductivity

The utilization of conducting additive makes the membrane more ion-selective, thus allowing separation selectivity for anions or cations of different valences [69]. To determine the effect of the amount of GO having conductive feature on the electron transport, the conductivity measurements were carried out for the membranes including different GO amounts (0.5, 1, 3 and 5 wt%) using an impedance analyzer. As can be seen from the conductivity test results (Table 3), the highest conductivity was obtained for PS-oil-3%GO-S24h membrane as 1.07×10^{-7} S/cm. While the conductivity increased with GO amount up to 3 wt%, a decrease in conductivity was observed in case 5 wt% GO, especially for pure PS based membranes. The increase in electrical conductivity with the GO content can be explained by the rise in the specific surface area of the graphene layer in the membrane [70]. GO particles create electron

Table 3

Electron conductivity results of fabricated membranes.

Sample code	Conductivity(S/cm)
PS-0.5%GO-S24h	4.49E-08
PS-1% GO-S24h	6.44E-08
PS-3 %GO-S24h	7.46E-08
PS-5%GO-S24h	5.34E-08
PS-oil-0.5%GO-S24h	7.41E-08
PS-oil-1%GO-S24h	1.03E-07
PS-oil-3%GO-S24h	1.10E-07
PS-oil-5%GO-S24h	1.02E-07

pathways and thus provide conductivity to the membrane's structure. However, as GO amount exceeds a certain amount, agglomeration of GO can occur, which has an unfavorable impact on conductivity because this accumulation destroys the homogeneous distribution of GO and eliminates the planar network [71].

Table 3 reveals that when the conductivity of PS-based and PS-oil-based membranes was compared, the PS-oil-based samples were found to be more conductive overall. This situation can be attributed that the presence of oil within the membrane structure could have enhanced the more homogeneous distribution of GO particles.

3.7. Electrochemical properties of the prepared membrane in the Electrodialysis test cell

PS-oil-3%GO-S24h membrane was chosen for electrochemical tests including the conductivity, ion permeability, and flux of ions in the test cell. Fig. 11a shows the conductivity values on both sides of the test cell. As seen from the figure, while the conductivity of a 0,1 M NaCl solution declined with time, the conductivity of a 0,01 M NaCl solution increased over time. Because of the voltage given from the power source on the concentrated side, the NaCl compound is separated into Na and Cl, and the Na^+ ion passes to the other side, and Cl leaves the solution as a gas. As the Na^+ ions passing to the diluted side increased, the conductivity increased. On the concentrated side, the conductivity declined due to the decrease in the Na^+ ions [72]. Hosseini et al. investigated the permeability of the Na^+ ion of the membrane and achieved comparable results to ours in this study [73]. This result has proven that Na^+ passed through the cation exchange membrane obtained in this study.

Fig. 11b shows the molarity change of Na^+ ion with time. On the diluted side, the molarity of the Na^+ ion was measured by the titration method. It was observed that the molarity of the Na^+ ion increased slowly until about 30 min in the diluted solution of NaCl, which was 0.01 M in the beginning, and then there was seen a rapid climb in the molarity. Since the ion concentration is low in the catholyte compartment at the beginning, the catholyte resistance becomes high. As can be also seen from the Fig. 11c, this high resistance makes it difficult to

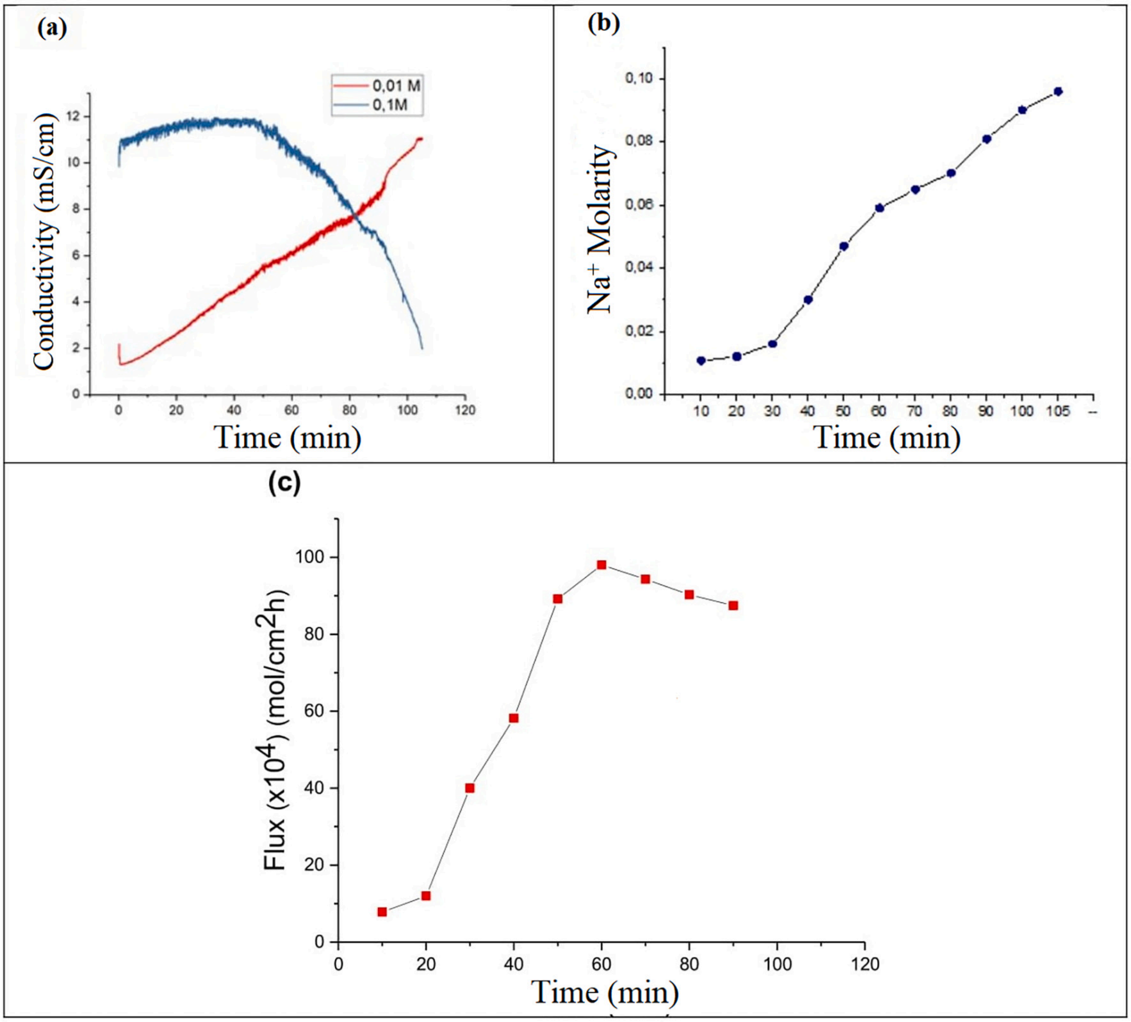

Fig. 11. Change in the conductivity with time concerning the test cell (a), change in Na^+ molarity (ion permeability) (b) flux of ions (c) for diluted side within time.

transfer ions from the anolyte to the catholyte compartment. After a while, the resistance in the catholyte compartment begins to decrease, which leads to an increase in ion transfer. This result demonstrated that conductivity and ion transfer across the membrane are linked to each other. All these outcomes (Fig. 11) show the promise that the prepared membrane can be used as an ion-exchange membrane.

4. Conclusions

In current study, a new route for CEM fabrication by using GO reinforced styrenated oil was developed and the produced membranes were evaluated in terms of water uptake capacity, contact angle, ion exchange capacity, and electron conductivity for the first time in the literature. The obtained results showed that both oil portion and GO contributed to improving the membrane properties. Additionally, as the effect of sulfonation time and GO amount on these properties was investigated, it was seen that the increase in the sulfonation time and GO ratio provided the higher values for all properties, especially ion exchange capacity. GO-incorporated PS-oil based membranes yielded higher IEC value (7.70 meq/g) compared to that of other PS-based membranes in the literature. Furthermore, GO-PS-oil based membrane was examined in electrodialysis test cell for determination of membrane's electrochemical properties including conductivity, ion permeability, and flux of ions measurements in an aqueous solution. All results showed that this research on PS-oil based CEM would have an impact on further investigations of cation exchange membranes for different electrodialysis applications.

CRediT authorship contribution statement

Mehmet Semih Bingöl: Data curation, Methodology, Formal analysis, Investigation, Writing – original draft, Visualization, Writing – review & editing. **Osman Nuri Ata:** Data curation, Methodology, Formal analysis, Investigation, Writing – original draft, Visualization, Writing – review & editing, Funding acquisition, Project administration. **Neslihan Alemdar:** Conceptualization, Data curation, Methodology, Project administration, Formal analysis, Investigation, Writing – original draft, Visualization, Writing – review & editing, Supervision.

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.

Acknowledgment

We would like to express our deep gratitude to the Research Fund of the Atatürk University, Turkey (BAPKO: Project No: PRJ2015/145) for financial support.

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