Electrodialysis Desalination of Brine Water with Simultaneous Recovery of Acid and Base

*Krishnaveni Venugopal [a] and Sangeetha Dharmalingam [a]**
a – Research Scholar, a – Assistant Professor*
[a, a] Department of Mechanical Engineering, Anna University, Guindy, Chennai 600025, Tamil Nadu, India, Tel: +91- 44- 2235 7763, Fax: +91 044 22357744*
Email: rvveni@gmail.com; sangeetha@annauniv.edu

Abstract: The desalination process parameters like current efficiency, energy consumption and acid-base production for the fabricated bipolar membrane electrodialysis unit (5 compartments of 120 cm^2 active areas) were investigated in this paper by using monopolar and bipolar based ion exchange membranes. Also the performance of the fabricated unit was assessed in terms of electrical conductivity, salinity and ion (sodium and chloride) concentrations. Polystyrene ethylene butylene polystyrene (PSEBS) was functionalized to prepare the mono and bipolar ion exchange membranes. In the case of bipolar membrane, polyvinyl pyrrollidone was used as the intermediate layer. The synthesized membranes were characterized using FTIR, SEM and TGA to evaluate them structurally, morphologically and thermally. Their water absorptions and contact angles were measured. A commercially procured ion exchange membrane made of polystyrene divinyl benzene was also evaluated for the purpose of comparison. The electrodialysis process using these ion exchange membranes reached a highest current efficiency of 43 % and 38 % with the energy consumption of 0.41Wh and 1.60 Wh for the synthesized and commercial membrane respectively.

Keywords: Brine water, Bipolar membrane, Membrane technology, Polyvinyl pyrrollidone, Water electrolysis.

I. INTRODUCTION

According to experts from different countries, the production of drinking water is not only a problem of science and technology but also a political problem due to its transformation in the immediate future into the global factor that will retard the world progress [1]. Desalination of brackish water, which is the source of drinking water in various world regions, is one of the large-scale applications of electrodialysis (ED). ED has attracted much attention from the academia and industry and also proved its advances in the fields of both separation and purification due to its diversity, sophisticated functions and technological compatibility [2]. Apart from these, ED can promote the comprehensive utilization of renewable resources and contribute to the sustainable development of humankind.

When it comes to the separation and production of organic acids, membrane based ED process is the most competitive technology because of its predominance in resource utilization and simultaneous supply of H^+ and OH^- ions without salt introduction or discharge, etc [2]. The water dissociation noticed in a conventional ED process decreases current efficiency (CE) and gives rise to scale troubles. Further the same attracts attention in a bipolar membrane electrodialysis (BPMED) process or in an electro-deionization process because it increases CE. The efficiency of the ED process strongly depends on the type of ion exchange membrane (IEM) chosen for the process. It was identified from the literature that to modify the existing membranes to meet the requirements in terms of electrochemical, ion exchange capacity (IEC), mechanical stability, thermal stability, transport characteristics and conductivity, powdered ion exchange resins (IER) are incorporated mechanically into the hydrophobic membrane matrix. Also the particle size distribution of the resin (different mesh size) and resin loading percentage have an influence over these properties.

Resin based IEMs show good dimensional stability compared to homogeneous membranes, which are the most desirable criteria for any commercially successful IEM. IEM with resin can be prepared through various methods such as calendaring or moulding. In the last few decades, membrane technologies have rapidly progressed and many researchers have focused on a special type of IEM called bipolar membrane (BPM) because of its inherent advantages. BPMED process is a combination of conventional ED and water dissociation feature due to the presence of intermediate layer (IL) in BPM that allows the production of acid and base from their corresponding salt solutions. In general, BPM can be prepared by two different techniques. In the first method, one side of the polymer membrane is selectively functionalized followed by the other side. The second method of lamination involves either hot pressing (using heat and pressure) or gluing (using an adhesive paste) both cation and anion exchange membranes together with or without an IL.

A BPM does not perform efficient water dissociation when prepared with anion exchange layer (AEL) and cation exchange layer (CEL) alone. To improve the water splitting effect of a BPM, a thin interfacial layer/contact region (IL), containing an immobilized water dissociation catalyst, is generally introduced between the charged AEL and CEL [3]. The contact region is not a well-defined separate layer; for

some membranes it is part of one or both ion selective membrane layers (CEL and AEL). Different types of ILs used by various investigators include a matrix material containing quaternary, non- quaternary amine group, weak acid and its corresponding base (such as pyridines, carboxylic acid, phenolic and phosphoric acid groups), inorganic substances (such as sodium meta silicate, ruthenium tri-chloride, titanium oxide, manganese oxide, zeolite, chromic nitrate and indium sulphate), metallic compounds/heavy metal ions (such as Fe^{2+}, Fe^{3+}, Ti^{4+}, Sn^{2+}, Pd^{2+} and Ru^{3+}), macromolecules (like polystyrene, polycarbonate, polyvinyl alcohol (PVA), polyethylene glycol (PEG), bovine serum albumin (BSA) and polyamidoamine dendrimer (PAMAM)) and noble metal ions (like silver and platinum).

In the present work, we have prepared monopolar (cation exchange and anion exchange) and bipolar (with PVP as IL) ion exchange membranes with resin and glass fiber reinforcements using polystyrene ethylene butylene polystyrene (PSEBS) polymer. The prepared IEMs were characterized using FTIR, SEM, TGA, contact angle and some laboratory techniques. Water dissociation capacity of the prepared BPM with PVP intermediate was tested in a two compartment electrodialytic cell. The membranes were evaluated for their desalination efficiency on real sample brine solution of approximately 10,000 ppm up to 8 h. The stack performance using the synthesized membranes was compared with that of the commercial polystyrene divinylbenzene based (PSDVB) ion exchange membranes under similar experimental conditions. In addition, the decrease in sodium-chloride ion concentration, salinity and electrical conductivity of the feed water were observed.

II. MATERIALS AND METHODS

A. Preparation of reinforced IEMs

Cationic and anionic functionalized ionomer membranes of sulfonated polystyrene ethylene butylene polystyrene (SPSEBS) and quaternized polystyrene ethylene butylene polystyrene (QPSEBS) was carried out as per the procedure reported [4]. To enhance IEC, firmness and strength of the membranes, the membranes were reinforced with resin and glass fiber. Weighed amount of ion exchange resin (IER) was dried in an oven at 60 ˚C for 24 h before use. Reinforced cationic or anionic exchange membrane (RCEM/RAEM) was prepared by first dispersing a specific quantity of dried and crushed CER/AER (cationic/anionic exchange resin of various percentages of loading ranging from 10 % to 70 %) in SPSEBS/QPSEBS-tetra hydrofuran (THF) solution for 12 h using magnetic stirrer at room temperature. In order to break the aggregates and to obtain a uniform dispersion, the solution was sonicated for 30 min. Then, the solution was cast on a clean glass petridish and the glass fiber matrix was placed to get immersed in the solution before drying in the oven for 24 hours at 45 ˚C. The conductivity of the membranes increased with increase in IER loading up to 50%, beyond which the membranes became brittle. Hence, the resin loading was optimized at 40 % for both resins [5].

The prepared RCEM and RAEM were cut into pieces of 10 cm x 12 cm and washed alternatively with 1M NaOH and 1M HCl for at least 3 times in each bath. Then, they were equilibrated with 2 M NaCl solution, further washed with distilled water and dried at room temperature. The obtained RCEM acts as CEL and RAEM as AEL for preparing the reinforced BPM (RBPM). Then on one side of both CEL and AEL layers, a solution containing approximately 0.12 g of PVP in 6 mL ethanol was coated to form the IL. Finally the IL coated side of both layers (CEL and AEL) were sandwiched and subjected to hot press for 5 min at a temperature and pressure of about 64 ˚C and 3 ton respectively to finally obtain RBPM represented as RBPM-PVP.

B. Characterization of Reinforced IEMs

The incorporation of resin into functionalized PSEBS membrane was confirmed with Perkin Elmer RX I FTIR spectrophotometer. The thermal stability of the prepared membranes were studied using SDT Q 600 US analyzer (ASTM E1131) under nitrogen atmosphere with a heating rate of 20 ºC/minute from room temperature to 700 °C. The morphology of the membranes was studied using field emission HITACHI S-3400 SEM instrument. The hydrophilic and hydrophobic nature of the membranes was determined using Goniometer-sessile drop meter GBX–Digi-drop wetting and spreading studies. The conductivity of the membranes was determined using impedance spectroscopy. Water absorption and ion exchange capacity (IEC) for the prepared membranes were measured as discussed earlier [6]. The chemical stability of membranes was analyzed by accelerating the degradation process using a solution containing 4 ppm of ammonium iron (II) sulfate hexahydrate and 15 mL of H_2O_2 (3 %) (Fenton's reagent) in 500 mL distilled water at 60 °C for about an hour.

C. Brine desalination using electrodialysis stack

The BPMED unit and the commercial PSDVB BPM used in the present study were supplied by Arun Electrochemical, Chennai. The instrument used for determination of BPM efficiency was a two compartment based laboratory scale electrodialytic cell (Fig. 1(a)) and the one used for brine desalination was a five compartment based electrodialytic cell (Fig. 1(b)). The total volume of each compartment was about 160 cm^3 and was connected to a tank of 1 L capacity, which allows batch-wise recirculation mode operation. The effective membrane area of each IEM was about 120 cm^2. The configuration of the membrane arrangement in the five compartment stack was BPM-AEM-CEM-BPM, placed in between the stainless steel cathode and Ti-Ru-Pd oxides coated Ti anode. The five compartments of the BPMED unit were EC-AC-FC-BC-EC (where, EC stands for electrolyte compartment placed at the two extremes, adjacent to the electrodes; FC stands for feed compartment; AC and BC

stands for acid and base compartments respectively, placed adjacent to the feed compartment on either side). The commercial monopolar membranes (CMI – 7000S and AMI – 7001S) used for comparison was purchased from International INC, New Jersey, USA. In order to minimize the initially created cell voltage, dilute HCl (0.01 N) and dilute NaOH (0.01 N) solutions were used in AC and BC respectively. And 0.05 mol/L of NaCl solution was taken in each EC. During the performance, at every 15 minutes time interval, process parameters such as membrane stack potential, conductivity, pH and acid-base concentration of the solutions in various compartments were determined. In addition, other parameters such as energy consumption, current efficiency (CE), Transport number (T. No.) of ions, water dissociation efficiency (WDE) and water dissociation flux were determined using the same set of equations as reported earlier [7,8]. Finally, after 8 hours of treatment, the feed sample was analyzed for their salinity and electrical conductivity using WTW LF 197-S EC meter. The concentrations of chloride and sodium ions of the samples were measured by argentometric method and flame photometry respectively.

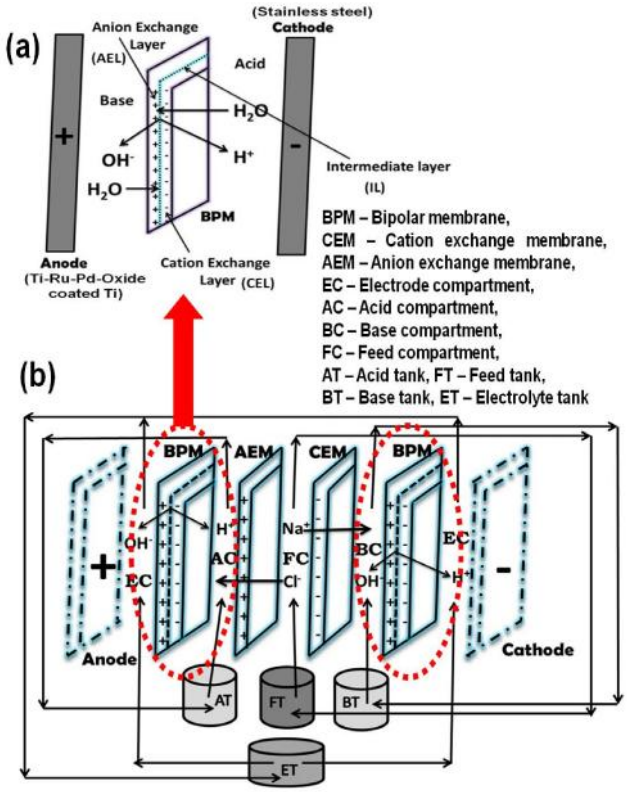

Fig. 1 Schematic representation of (a) Two compartments electrodialytic cell for BPM efficiency (b) Five compartments electrodialytic cell for brine desalination

III. RESULTS AND DISCUSSION

A. *FTIR characterization*

Pristine PSEBS, RCEM (RSPSEBS) and RAEM (RQPSEBS) membranes were characterized using FTIR (Fig. 2) to confirm their structure and the incorporation of reinforced resin. In Fig. 2 (a), the presence of bands at 3026 cm^{-1} and 758 cm^{-1} was due to the ν_s (C-H) and δ (C-H) vibration bond of aromatic hydrocarbons respectively. Appearance of transmission peaks at 2933 cm^{-1} and 2865 cm^{-1} were assigned to the aliphatic ν_{as} (C-H) and ν_s (C-H) vibrations respectively. The peaks at 1363 cm^{-1} and 1430 cm^{-1} were due to the aromatic ν_s (C=C) vibration. The appearance of these peaks confirmed the structure of PSEBS.

The appearance of a broad envelope in Fig. 2 (b) around 3000-3600 cm^{-1} was assigned to –OH stretch of sulfonic acid group present in both resin and membrane matrix. The appearance of peaks around 1118 cm^{-1}, 1049 cm^{-1} and 1161 cm^{-1} due to the O=S=O (asymmetric stretch) and the disappearance of peaks at the frequency of 730 cm^{-1} and 675 cm^{-1} confirmed that sulfonic acid group was substituted in the aromatic ring of PSEBS. The appearance of a peak at around 840 cm^{-1} showed that the sulfonic acid group was substituted at para position. The broad peaks at 3385 cm^{-1} and 1425 cm^{-1} in Fig. 2 (c) were assigned to the characteristic peak of ν_{as} (NR_3^+) and δ_{as} (NR_3^+) respectively. The appearance of a peak around 1282 cm^{-1} was assigned to C-N stretching vibration. In addition, functionalization due to sulfonation and quaternization reactions in aromatic ring of PSEBS polymer was confirmed by the shift of IR bands of aromatic ring backbone –CH– bending vibration from 1408 cm^{-1} to a lower frequency of around 1389 cm^{-1} and 1397 cm^{-1} respectively.

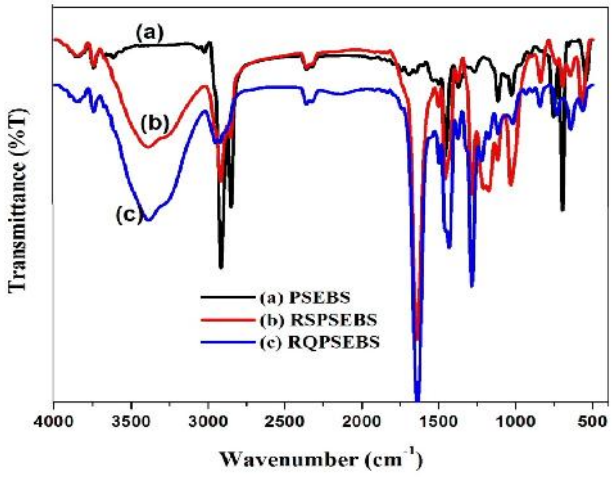

Fig. 2 FTIR spectra of (a) PSEBS, (b) RSPSEBS and (c) RQPSEBS membranes

B. *Thermo Gravimetric Analysis*

The TGA curves of the reinforced monopolar and bipolar membranes are shown in Fig. 3. The reason for the various degradation steps observed at certain temperatures are represented in Table 1. The TGA curve of pristine PSEBS, as observed in Fig. 3 (a), exhibited single stage degradation around 424 ˚C due to the degradation of polymer main chain.

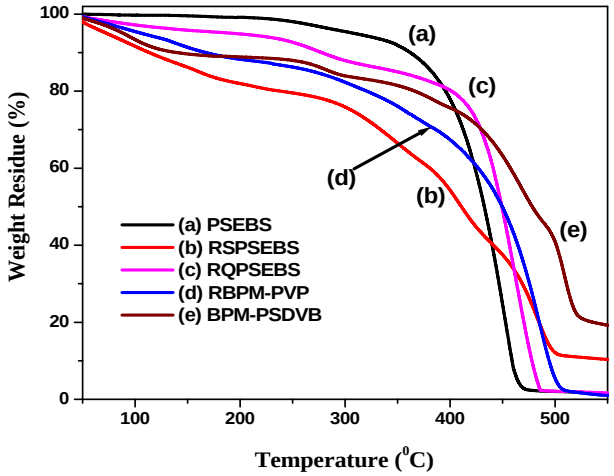

Fig. 3 TGA curves of (a) PSEBS, (b) RSPSEBS, (c) RQPSEBS, (d) RBPM and (e) PSDVB BPM

Table 1 Degradation temperatures and their reasons

Membrane code & degradation temperature / **Reason for degradation**	**RSPSEBS** (3 steps as from Fig. 3 (b))	**RQPSEBS** (3 steps as from Fig. 3 (c))	**RBPM-PVP** (3 steps as from Fig. 3 (d))	**BPM-PSDVB** (3 steps as from Fig. 3 (e))
Removal of physically & chemically bonded water + trace amounts of solvent	up to 165 ˚C	up to 190 ˚C	up to 129 ˚C	up to 129 ˚C
Degradation of functional groups (sulfonic acid group and / or quaternary ammonium group)	beyond 182 ˚C ($-SO_3H$)	227 ˚C – 326 ˚C ($-NR_3$)	138 ˚C – 236 ˚C (both)	249 ˚C – 311 ˚C (both)
Removal of loosely bound IER particles present on the surface			beyond 282 ˚C	--
Intermediate molecule degradation	--	--		
Removal of IER from the membrane	up to 492 ˚C	410 ˚C – 480 ˚C		
Removal of reinforced fiber from the membrane				beyond 336 ˚C
Polymer main chain degradation				

C. SEM Analysis

The morphology of various IEMs such as RSPSEBS, RQPSEBS and RPSEBS-BPM are shown in Fig. 4. A uniform distribution of resin particles throughout the reinforced membrane surface was observed in the surface SEM images of RSPSEBS and RQPSEBS membranes. On the other hand, cross sectional view of reinforced PSEBS-PVP based BPM i.e. RPSEBS-BPM clearly showed three distinct regions. The top layer was anion exchange layer (AEL) or RQPSEBS while the thin middle one represented the PVP – IL and the third layer correspond to the cation exchange layer (CEL) or RSPSEBS. The appearance of small spheres on both top and bottom surfaces of RPSEBS-BPM shows the presence of IER particles.

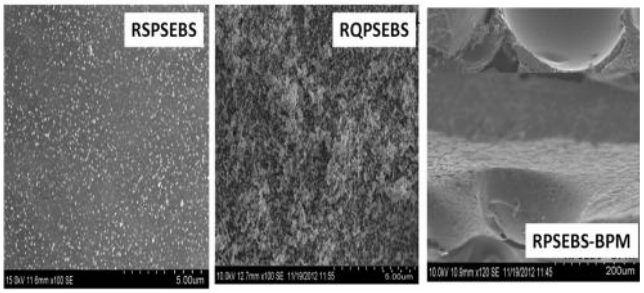

Fig. 4 SEM images of surface views of RSPSEBS and RQPSEBS membranes; and cross-sectional view of RPSEBS-BPM membrane

D. Contact Angle Measurement

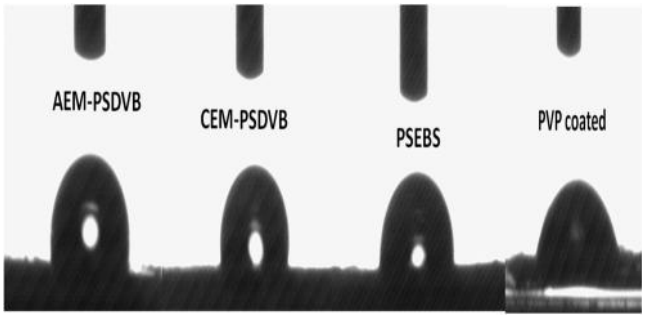

Fig. 5 Contact angles of water droplets on various membrane surfaces

From Fig. 5, it was identified that the introduction of functional group converts the hydrophobic polymer (84.39°) into hydrophilic polymer with a smaller contact angle as studied by Dias & de Pinho and Guan et al [9,10]. The contact angles of the commercial monopolar membranes such as CEM-PSDVB and AEM-PSDVB were measured to be 86.70° and 93.09° respectively. Contact angle value for the reinforced functionalized membranes such as RSPSEBS and RQPSEBS could not be measured due to complete absorption of water. This infers that the increased hydrophilicity of these membranes than the pristine membrane was due to the presence of functional groups, resins and fiber reinforcements [11]. In order to determine the nature of PVP intermediate in BPM, one face of the membrane was coated with PVP solution and its contact angle was measured and was found to be 56.39°.

E. Chemical stability

To determine the suitability of the prepared reinforced IEMs and commercial IEMs in BPMED unit, all the membranes were subjected to chemical stability test using

Fenton's reagent. The generated peroxides attacked the polymer chains to undergo faster degradation. All the subjected samples were then checked for their water absorption, IEC and conductivity values as per the standard procedures [6] and the values are tabulated in Table 2. Although the reinforced fibers held the IEMs strongly, due to enhanced degrading mechanism, the incorporated hydrophilic resins and functional groups that were present on the surface leached out from the membranes due to loosening of the fibers upon swelling which resulted in lower IEC, water absorption and conductivity values [12].

Table 2 Chemical stability test

Membrane Code	IEC (meq/g)		Water absorption (%)		Conductivity (10^{-3} S cm^{-1})	
	Initial	Final	Initial	Final	Initial	Final
RSPSEBS	4.23	3.87	118	95	5.40	5.29
RQPSEBS	3.86	3.45	4.8	3.8	4.91	4.56
RBPM-PVP	-------		96	69	7.57	7.05
CEM-PSDVB	1.6	1.5	6.5	5.4	4.86	4.64
AEM-PSDVB	1.3	1.2	3.7	3.1	4.68	4.27
BPM-PSDVB	-------		9	8.2	4.75	4.4

F. Characterization of RPSEBS-PVP and PSDVB BPMs

pH variation with time

Since BPM consisted of RCEM and RAEM as CEL and AEL layers respectively which were joined together using a catalytic PVP as IL, when it was placed in between the electrodes due to large electric field appearing at the membrane interface, an excess OH^- and H^+ ions were produced by the enhanced chemical reaction. This then migrated through the ion exchange layers into the distilled water filled compartments resulting in the formation of acid and base. This acid and base yield was analyzed using change in pH measurements. From Fig. 6 it was obvious that with increase in time, pH of the solutions in the two compartments changed from its initial distilled water value. The compartment closer to the anode side was found to be basic in nature and the one closer to the cathode side was acidic in nature. The increasing trend in pH change with time confirmed that some ions were produced newly during the performance due to certain in-situ reactions. These ions probably were protons and hydroxyl ions and formed on either side of the BPM as a result of water splitting into its ions under the electrical driving force between the electrodes. This conclusion was arrived at ease as there was no possibility of any other ions formed since only distilled water was taken in both the compartments.

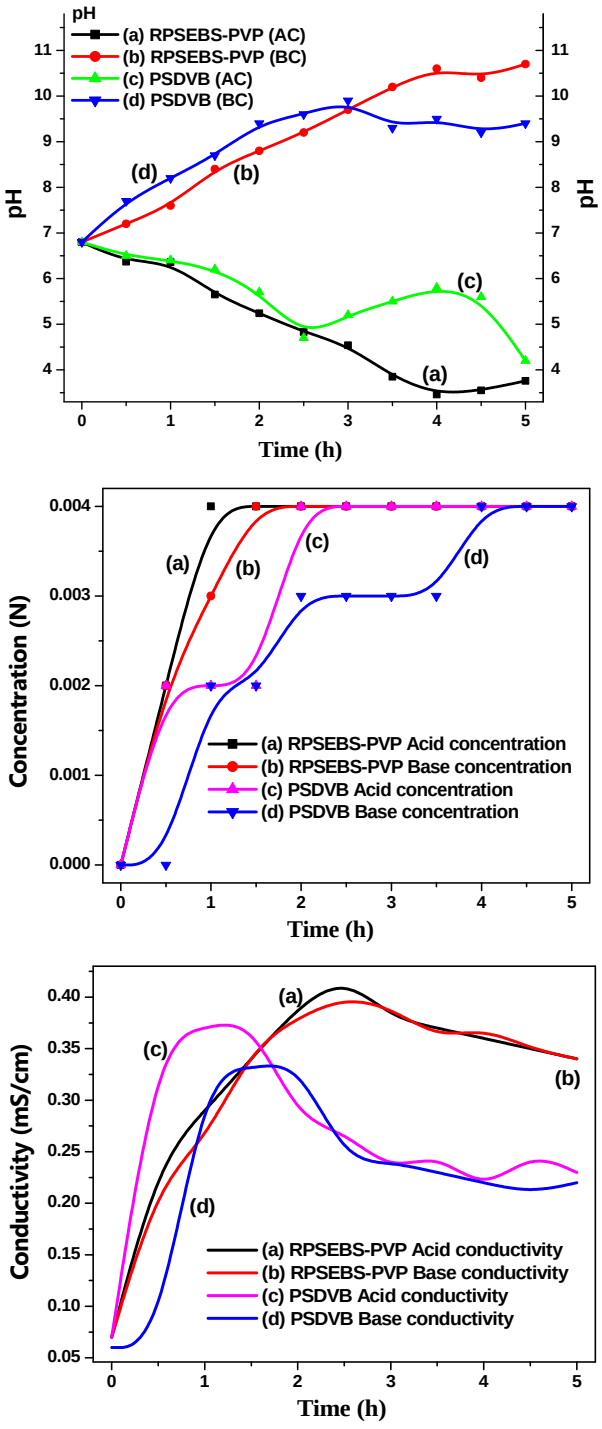

Fig. 6 pH, concentration and conductivity change with time in both AC and BC

Concentration and conductivity changes with time

The conductivity meter was optimized before taking readings using the distilled water. Fig. 6 shows the change in conductivity of the acid and base solutions with time for both RPSEBS-PVP and commercial PSDVB BPMs. Initially, the acid conductivity rose from an initial value of 0.07 mS/cm to a maximum of 0.42 mS/cm and 0.38 mS/cm and then decreased to 0.34 mS/cm and 0.23 mS/cm for synthesized and commercial membranes respectively. Similarly, the base

conductivity also rose from 0.07 mS/cm to a maximum of 0.40 mS/cm and 0.34 mS/cm and then decreased to 0.34 mS/cm and 0.22 mS/cm for synthesized and commercial membranes respectively. The sudden decrease in conductivity values after 2 h in case of PSDVB BPM was suggestive of greater leakage of ions via membranes to the neighboring compartments. Whereas, a gradual decrease in the case of RPSEBS-PVP BPM, revealed a lower level of leakage of ions. However, between the two BPMs, PSDVB showed lower values of acidic and basic conductivities when compared to RPSEBS-PVP.

Additionally, the maximum concentration of 0.004 N for both acid and base was achieved in about an hour in the case of RPSEBS-PVP when compared to PSDVB BPM (beyond 2 hours). In both BPMs, once higher concentration was reached in both AC and BC; decrease in concentration was observed for BPM which exhibited a higher leakage and was observed to get leveled off without further rise or decrease if the leakage was not much favored in BPM. Hence, from the above discussion and from Fig. 6, it was confirmed that RPSEBS-PVP showed a better performance than PSDVB.

Current-Voltage relationship

Fig. 7 (a) and (b) represents the typical steady state I-V curves as reported [5]. It was clear from the figures that no rectification was observed since current was measured under the applied voltage. The increase in current with increasing voltage proved the occurrence of water splitting in both the BPMs [13]. On comparing the potential applied during the performance of both BPMs, RPSEBS-PVP showed a higher value of up to 13 V than PSDVB (11 V) for the same duration; while the increase in current was observed to be lower for RPSEBS-PVP (44 mA) than PSDVB (52 mA). In Fig. 7 (a) the variation in current due to ionic transportation was smaller when compared with Fig. 7 (b). This magnitude is a measure of BPM selectivity towards co-ion leakage, and used to predict its efficiency. Hence, it could be concluded that RPSEBS-PVP BPM was expected to have better process efficiency when compared to PSDVB BPM. Beyond this potential, water dissociation occurs and the water splitting products (OH^-/H^+) also participated in the current transport which resulted in a steep increase in current. From this region, it could be clearly understood that the onset of water dissociation reaction occurred earlier in the case of RPSEBS-PVP BPM than PSDVB BPM. The only reason for the better performance of the RPSEBS-PVP system was due to the presence of the PVP IL along with fiber and resin reinforcements in the case of RPSEBS-PVP when compared to the PSDVB system. On introduction of the IL and resin, the region between the ion exchange layers became hydrophilic and attracted more water to the space charge region resulting in lower resistance. Whereas, in the case of commercial BPM which was without catalyst, the water dissociation resistance increased with increase in current, due to slower water dissociation rate than the ion transfer rate. The above results confirmed that the introduced PVP intermediate in RPSEBS-PVP BPM functioned as an effective water dissociation catalyst.

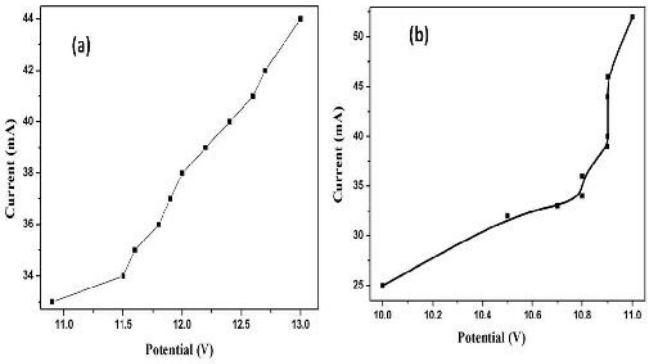

Fig. 7 Current-voltage curves for (a) RPSEBS-PVP and (b) PSDVB BPMs

G. BPMED stack performance for brine desalination

Determination of pH and conductivity changes with time

Fig. 8 represents the pH and conductivity changes with time for both RSPSEBS-PVP and PSDVB systems. The pH of the solutions in FC, EC, AC and BC was observed regularly at every 15 min interval up to 8 h. In the case of RPSEBS-PVP system, the pH in FC was observed to increase towards basicity then decrease and finally become slightly acidic in nature which was similar to the results observed in literature [14]. This is because with increase in time, higher quantities of acid were produced due to water dissociated products and thereby resulting in proton leakage through IEMs depending upon the capacity of protons to undergo back diffusion. Due to its intrinsic mobility in the presence of water, FC remained slightly acidic in nature. On the other hand, in the case of PSDVB system, the feed solution finally became basic in nature. The difference in pH observed between the two different systems was mainly attributed to the leakage of ions occurring through the membranes between the compartments in a stack. PSDVB based cell experienced a greater leakage of ions from BC to FC and thus it remained basic in nature. It was also reported that the proton leakage through PSDVB IEM was lower due to lower concentrations of acid that was produced during BPMED process [14]. In the case of EC, due to the initial addition of 0.05M NaCl solution, the pH was observed to be slightly basic during the initial stages, which was then observed to be decreasing with time. Though both the IEM systems showed the final solution to be acidic, the acidity was greater in the case of PSDVB IEM system than that observed with RPSEBS-PVP IEM system. The reason for this was attributed to the higher leakage of ions through commercial membrane than the synthesized membrane.

From Fig. 8, it was clear that the initial pH in AC and BC was found to be in the range of ~ 2.45 and ~ 10.74 respectively due to the addition of 0.01N acid and 0.01 N base solutions into their respective compartments. Moreover, the pH in both AC and BC was found to rise marginally during the initial stage and was not uniform because of the leakage of certain ions into the neighboring compartments. Later, due to higher acid production, higher acidic pH and hence greater acid leakage was observed in

case of RPSEBS-PVP IEM system when compared to PSDVB IEM system. Whereas, in the case of basic pH, both the systems showed more or less the same pH during the initial period of performance and later RPSEBS-PVP IEM system showed a little lower basic pH when compared to PSDVB IEM system. Such a pH change in AC and BC confirmed the acid-base production in their respective compartments which can also be confirmed by their conductivity and concentration measurements. This pH variation in various compartments clearly suggested that both systems possessed adequate capacity to split water into its co-ions under electric field.

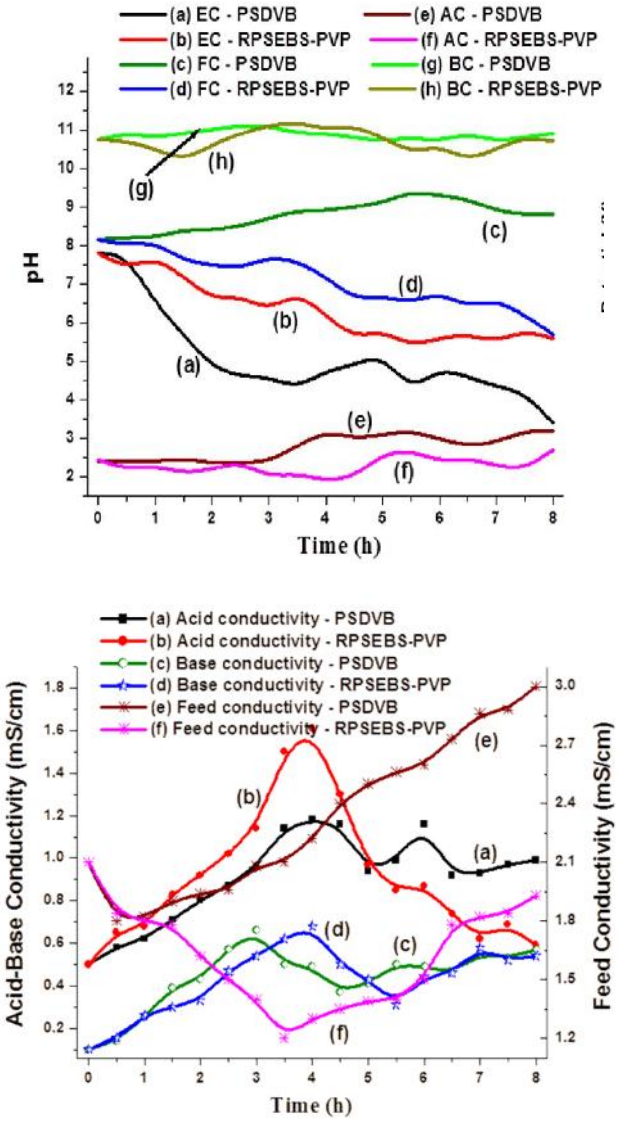

Fig. 8 Change in pH and conductivity in various compartments with time

Similar to the pH observations, in the case of conductivity too, AC and BC showed some initial conductivity. Since the ionic mobility of protons was higher than that of hydroxyl ions, the conductivity was found to be higher in the case of AC when compared to BC. The initial decrease in FC conductivity from 2.1 mS/cm to 1.2 mS/cm and 1.8 mS/cm was finally increased to 1.96 mS/cm and 3.0 mS/cm for RPSEBS-PVP and PSDVB respectively. In the case of AC, the increase in acidic conductivity reached a maximum (from an initial 0.5 mS/cm) of 1.6 mS/cm and 1.18 mS/cm for RPSEBS-PVP and PSDVB systems respectively. Similarly for BC, the basic conductivity increased from 0.10 mS/cm to a maximum of 0.68 mS/cm and 0.66 mS/cm for RPSEBS-PVP and PSDVB systems respectively. After reaching the maximum in both AC and BC, the conductivity slightly decreased or increased due to the loss of ions from this compartment or transfer of other ions from the neighboring compartment. Hence, the higher conductivity value was mainly due to the co-ions of water rather than the salt ions. This not only clearly confirmed the membrane's capacity to migrate ions from FC to the opposite electrodes but also proved the BPM's water dissociation capacity under electric field.

Determination of acid-base concentration and current-voltage measurement

When the entire ED cell was under an electric field, the Na^+ and Cl^- ions were continuously transported from FC into BC and AC respectively. In addition to this, an excess OH^- and H^+ ions produced at the AEL-CEL interface due to the field enhanced chemical reaction also permeated through the IELs resulting in the acid-base formation. From the pH and conductivity studies, it was evident that acid and base of certain concentrations were produced in the AC and BC respectively for both the systems. From Fig. 9, it was noted that a maximum acid concentration of 0.012 N and 0.008 N was achieved for RPSEBS-PVP and PSDVB systems respectively. Similarly, a maximum base concentration of 0.006 N and 0.004 N was achieved for RPSEBS-PVP and PSDVB systems respectively.

The commercial PSDVB IEM cell was meant for base production rather than acid production because of higher specific permselectivity of CEM for H^+ ions as reported in the literature [14]. However, in our study, from Fig. 9, the alkalinity concentration was observed to be lower in case of PSDVB system. This can be due to the higher intrinsic mobility of H^+ ions than the OH^- ions and hence resulting in higher leakage of H^+ ions. The T. No. of protons through AEM increased with acid concentration which would also lead to their lower concentration in AC. The maximum concentration remained constant until certain duration of time after which it decreased with increase in process time for both types of IEM system. This suggested that the mass transfer of Na^+ and Cl^- ions through the IEM diminished due to the decrease in NaCl concentration in the feed solution. Together with the increase in the concentration of Na^+ and Cl^- ions in BC and AC, the molecular back diffusion through IEM which was caused by the high concentration gradient might also hinder the transport of Na^+ and Cl^- ions. Furthermore, the dissociation of water molecules was also enhanced due to the Second Wien effect.

From Fig. 9, the current and voltage were observed to be directly proportional to each other thereby proving the water splitting at the BPM junction. In order to avoid high resistance, the membrane thickness was as thin as possible [15]. In the present work, the thickness of the membranes such as AEM, CEM and BPM used in the case of synthesized system was 0.30±0.05 mm, 0.28±0.05 mm and 0.57±0.05 mm respectively. While in the case of commercial system, the same was observed to be 0.45±0.025 mm, 0.45±0.025 mm and 0.85±0.025mm respectively. The maximum potential observed was 11.5 V and 22.5 V and the maximum current observed was 67 mA and 89 mA for RPSEBS-PVP and PSDVB systems respectively. The observed lower voltage for RPSEBS-PVP system could be explained theoretically using protonation and de-protonation reactions model and the hydrophilicity change in the interface. The presence of hydrogen bonding and polar interactions between the intermediate PVP and the water molecules speeds up the water dissociation into hydrogen and hydroxyl ions, which causes the voltage across the membrane to fall. On the other hand, PVP is a strong hydrophilic substance and when used as an intermediate the number of hydrophilic sites in the interfacial region increases, which in turn increases the efficiency of water splitting.

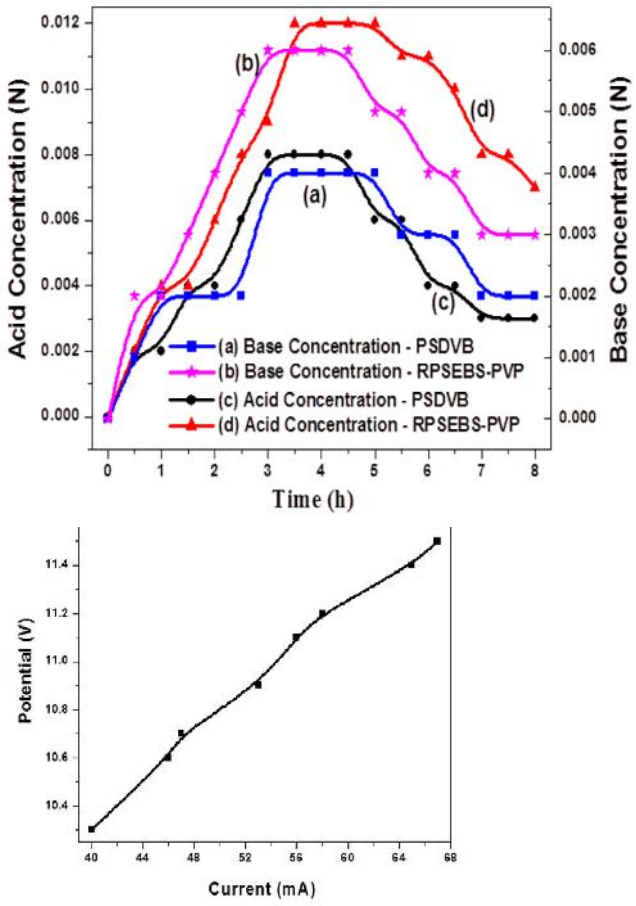

Fig. 9 I-V curves and acid-base yield with time

Determination of WDE and T. No. of ions

The BPMED process efficiency is strongly affected by the transport properties of ions present in the solution and WDE. Under an electric field, at the beginning of the BPMED process, there was a competition between the ions such as Na^+, Cl^-, H^+ and OH^- for transport, and the transfer of a large amount of Na^+ and Cl^- ions through the IEM resulted in a slow transfer of H^+ and OH^- ions. This was because of the maximum availability of initial salt concentration in FC when compared with the water dissociated ions. As the operation time passed, the dissociation of large amounts of water molecules resulted in the large accumulation of H^+ and OH^-. It should be noted that once all the Na^+ and Cl^- ions were transported from the FC, the accumulated H^+ and OH^- were also transported very efficiently resulting in the higher WDE after the first half performance time. This also explained the reason for the observed higher T. No. of ions with time during the first half part of the performance and a decrease in its value during the later stages of performance for the same membrane [14].

Ion transport number indicates the contribution of ions towards acid-base production, depending upon its electrical mobility under electric current. Fig. 10 represents the T. No. properties of both sodium and chloride ions for RPSEBS-PVP and PSDVB systems. It was from the figure that the T. No. of both Na^+ ion and Cl^- ions decreased with increase in time for both the systems. This was because NaCl concentration that was available for migration started to decrease with increase in time as discussed above. However, the performance was running steadily due to the current carried by the dissociated water products of H^+ and OH^- ions. In both IEM systems the chloride ion T. No. was observed to be greater than the sodium ion T. No. as reported in literature. The initially observed higher values of T. No. of sodium (0.21) and chloride (0.43) ions decreased to 0.05 and 0.09 respectively for RPSEBS-PVP system. Whereas, in the case of PSDVB based system, the T. No. of sodium and chloride ions decreased from their initial values of 0.4 and 0.5 to 0.37 and 0.42 respectively in brine desalination performance.

Based on feed concentration, membrane capacity and pH variation in AC and BC during the stack performance, the occurrence of water dissociation at BPM interface was confirmed. From Fig. 10, it was clear that WDE increased with increase in time. The reason for this variation of WDE with time is the same as discussed for T. No. of ions. A higher WDE of 0.86 was obtained for RPSEBS-PVP and it was 0.21 for PSDVB IEM system. The higher T. No. and steady increase in WDE with time observed for RPSEBS-PVP IEM system was due to (i) the increase in electric field, (ii) the pre-polarization of water molecules at the membrane-solution interface and (iii) the presence of a hydrophilic catalytic PVP intermediate in between the two monopolar layers of BPM. It was also noted from Fig. 10 that in both cases (acidic or basic), the water dissociation fluxes decreased with time. The main reason for the decrease in acid and base fluxes was due to (i) the depletion of Na^+ in anode compartment and Cl^- ion in cathode compartment and (ii) the availability of NaCl in FC

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for the conversion into the acid and base. The highest acidic and basic fluxes observed in the present study was 9.4 mol m^{-2} s^{-1} and 7.4 mol m^{-2} s^{-1} for PSDVB and 14.8 mol m^{-2} s^{-1} and 4.71 mol m^{-2} s^{-1} for RPSEBS-PVP systems respectively. According to Ren et al [16] the reduction in the ionic transport rate during later stages of the performance was often correlated with an increased membrane resistance due to the presence of a mixture of organic matter and inorganic salts. As a consequence, during performance of brine desalination, a slight membrane fouling was observed for both RPSEBS-PVP and PSDVB IEM systems.

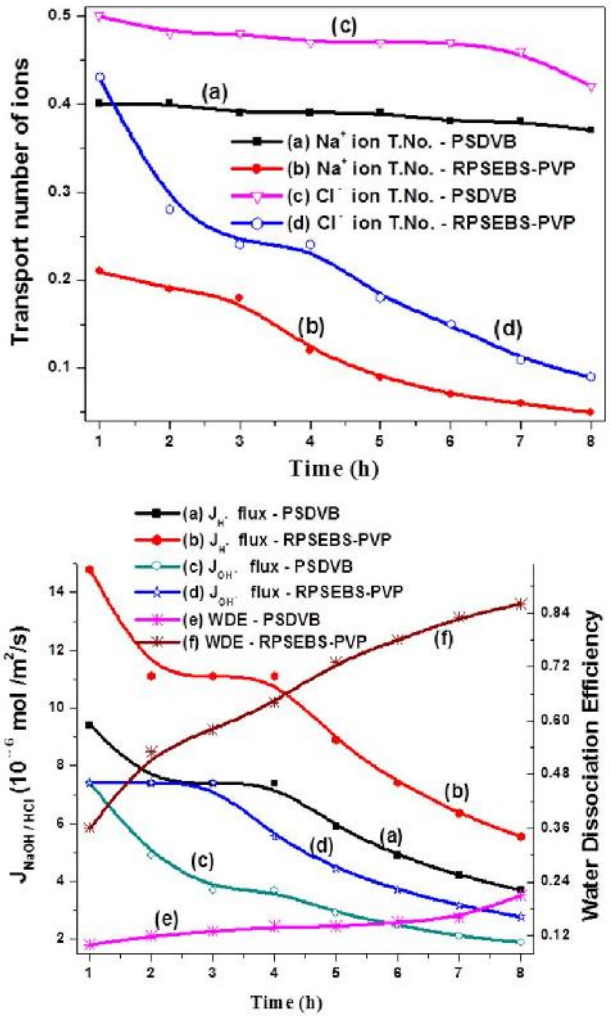

Fig. 10 Change in T. No. of ions, WDE, acidic and basic water dissociation fluxes with time

Determination of process efficiency parameters and I-V measurement

For any system, higher CE with lower energy consumption is one of the factors which determine the feasibility of electrochemical process towards higher process efficiency. It is clear from Fig. 11 that CE of BPMED stack decreased with operation time for both systems. This can be explained by invoking the concept of ion leakage through IEM as discussed in T. No. of ions. CE was observed to decrease with time from 38 % for PSDVB system and from 43 % for RPSEBS-PVP system. On the other hand, the energy consumption increased with time as shown in Fig. 11. The increase in the energy consumption was mainly attributed to the fact that a large part of the total electrical energy was consumed to overcome the electrical resistance. The decline in the applied voltage at the start of the BPMED procedure was due to either the increase in conductivity of HCl/NaOH solution in AC/BC or due to the exhaustion of NaCl in the feed solution. The increase in resistance of FC, resulted from the exhaustion of NaCl in the solution, was offset by the decrease in electrical resistance of AC and BC caused by the increase in HCl and NaOH concentrations as a consequence of transfer of Cl^- and Na^+ ions from the feed solution. Since the transformation of NaCl into acid and base solution was fully realized, the electrical resistance of feed solution increased, resulting in a sharp increase in the voltage drop. Thus, the energy consumption was observed to increase with time and reached a maximum of 6.2 Wh for PSDVB and 6.1 Wh for RPSEBS-PVP systems.

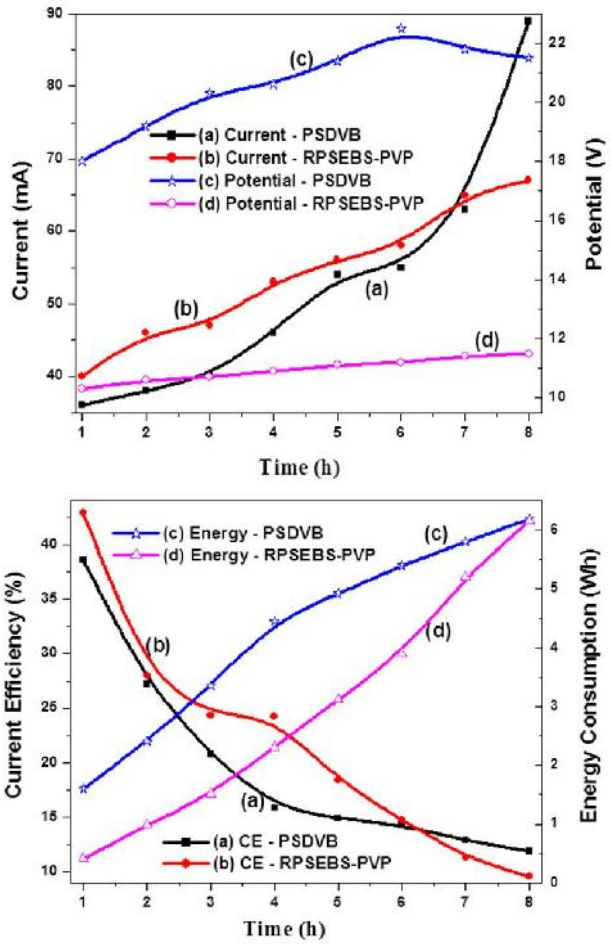

Fig. 11 Change in current, potential, CE and energy consumption with time

The current variation was observed to increase with time for both RPSEBS-PVP and PSDVB systems as shown in Fig. 11 due to the production of OH^-/H^+ by water dissociation. In FC, the decrease in salt concentration due to continuous ion transport resulted in higher resistance. The higher resistance observed initially in AC and BC because of lower

concentrations of acid and alkali decreased due to increase in acid and base concentration with increase in time. The net effect of this was the overall decrease in stack resistance with time. The difference in stack resistance and concentration polarization observed between two systems inferred a lower current of 67 mA for RPSEBS-PVP when compared to 89 mA for PSDVB system. In case of voltage versus time curve, a line parallel to X-axis indicated that both PSDVB and RPSEBS-PVP systems were chemically stable as described by Xue et al [17]. The purity of acid and alkali increased with increase in voltage to some extent, after which further increase in voltage caused heating of stack which resulted in the deterioration of membrane properties.

Determination of Electrical conductivity, Salinity and Sodium-Chloride ion Concentration

To evaluate the purity of the generated acid and base and to confirm the BPM's capacity to dissociate water, certain important parameters such as electrical conductivity, salinity, sodium ion and chloride ion concentrations were analyzed. Table 3 represents the initial and final values of electrical conductivity, salinity and sodium-chloride ion concentrations of 100 mL FC solution for both RPSEBS-PVP and PSDVB systems.

Table 3 Electrical conductivity, salinity and sodium-chloride ion concentration values for RPSEBS-PVP and PSDVB systems

Parameters		RPSEBS-PVP system	PSDVB system
Electrical conductivity (mS/cm)	Initial	17.17	17.17
	Final	8.34	12.02
Salinity (%)	Initial	11.5	11.5
	Final	5.3	7.9
Chloride ion concentration (mg/100 mL)	Initial	10.3	10.3
	Final	7.65	8.6
Sodium ion concentration (ppm)	Initial	9.0	9.0
	Final	5.1	8.0

Though the removal of NaCl ions from the FC was confirmed by its electrical conductivity measurements; the effectiveness of this process was confirmed by its salinity measurements. The observance of lower salinity and lower electrical conductivity than their initial values was mainly because of the migration of the salt ions from the FC towards the neighboring compartments. Thus, this result suggested that the water obtained after the BPMED desalination process was of better quality than the initial sample. The final FC solution showed lower sodium and chloride ion concentrations than their initial salt sample solution for both the systems. This once again, confirmed the migration of ions under the electric field from FC to the neighboring compartments. The higher difference between the initial and final values indicated the process effectiveness in removal of NaCl and higher acid-base production.

IV. CONCLUSION

Resin-glass fiber reinforced and functionalized PSEBS IEMs were prepared and characterized using FTIR, TGA, SEM and contact angle measurements. The chemical stability of the prepared IEMs was evaluated by means of ionic conductivity, water absorption and IEC. The BPM efficiency of RPSEBS-PVP and PSDVB based systems were evaluated using pH, conductivity and concentration measurements. Brine desalination performance was analyzed for both RPSEBS-PVP and PSDVB based systems and compared. Based on the results obtained for current efficiency (43 % for RPSEBS-PVP and 38 % for PSDVB), energy consumption (0.41 Wh for RPSEBS-PVP and 1.60 Wh for PSDVB), acid-base production (0.012 N acid & 0.006 N base for RPSEBS-PVP and 0.008 N acid & 0.004 N base for PSDVB) and WDE (0.87 for RPSEBS-PVP and 0.21 for PSDVB), it was concluded that RPSEBS-PVP based IEM system showed a better performance than that of the commercial PSDVB based IEM system.

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Personal Profile

First Author - Krishnaveni Venugopal

I have completed my B. Sc chemistry from Thiruvalluvar University and received my M. Sc and M. Phil degree in chemistry from University of Madras. My area of expertise includes polymer science, desalination, environmental chemistry and analytical chemistry. I have published 6 research papers in international journals so far. I have 13 international and national conference presentations and participated in 10 conferences/workshops. Methods to functionalize polymer for the preparation of ion exchange membrane, data analysis and interpretation of the obtained characterization technique results are some of my technical skills. I have received "Wilson Endowment Prize" for outstanding student in M.Sc. Chemistry and merit certificate for full attendance in S.S.L.C and Higher Secondary level. I have worked as project follower (JRF & SRF) in BRNS sponsored project for 3 years. I have visited Kathmandu, Nepal (March 20-24, 2011) for Polychar19 International Conference - World Forum on Advanced Materials. I am one of the annual members in Research Journal of Chemistry and Environment.

Second Author - Sangeetha Dharmalingam
(Corresponding Author)

I have completed my 5 Year Integrated M. Sc Course in Polymer Science from University of Madras. I have received my Ph.D from University of Madras and MBA from Anna University. Some of my areas of expertise are polymer science, biomaterials, fuel cells and desalination. I have

published more than 100 research articles in international journals, about 16 articles in national journals and 7 books. I am a type of solution oriented person, good at making right decision, building relationship, planning and managing things. I have guided about 32 M. Sc and M. Tech project students in chemistry and about 16 students in interdisciplinary subjects. I have also guided students from other colleges. So far I have filed 6 patents for approval. I have successfully completed some projects from various funding organizations like CSIR, DST, ICMR, BRNS, AICTE, MNRE with an approximate value of 2.0cr. I was awarded "Active Faculty Researcher Award" for the year 2012 in Science & Humanities for Polymer Science organized by CTDT, Anna University. Also selected as one of the top 10 finalists as the Best Chemistry Teacher by Tata Chemicals in collaboration with Association of Chemistry Teachers (ACT) for the year 2011 and as one of the top 50 innovators in India by the DST-Lockheed Martin Innovators Growth Programme 2012.

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