RSC Advances

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical quidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

www.rsc.org/advances

Page 1 of 31 RSC Advances

Evaluation of efficiency of brackish desalination ion exchange membranes using electrodialysis process

Krishnaveni Venugopal and Sangeetha Dharmalingam*

Department of Mechanical Engineering, Anna University, Guindy Chennai 600025, Tamil Nadu, India Tel: +91 044 22357763, Fax: +91 044 22357744.

***Corresponding Author: sangeetha@annauniv.edu**

Abstract

In this study, polysulfone (PSu) was functionalized and modified using resin and fiber reinforcements for the preparation of mono and bipolar ion exchange membranes. In the case of bipolar membrane, platinum was used as the intermediate layer. Solution of NaCl in the brackish water concentration ranging from 5 g/L to 25 g/L was used as the feed solution for the desalting technique using electrodialysis process. A commercially procured ion exchange membrane made of polystyrene divinyl benzene was also evaluated for the purpose of comparison. The BPMED performance reached a highest current efficiency of 82.5 % and 53.6 % with the energy consumption of 0.52 Wh and 1.39 Wh for the synthesized and commercial membranes respectively. Also the performance of the fabricated unit was assessed in terms of electrical conductivity, salinity and ion (sodium and chloride) concentrations for the feed solution after 8 hour duration. The reproducibility performance of the membranes was also analyzed for the synthetic salt solution.

Keywords

Desalination; Platinum intermediate; Current efficiency; Energy consumption; Acid-base recovery.

1 Introduction

 To satisfy the more reliable high quality water supply demand and other basics needs because of increased population and pressure for both consumptive and non-consumptive uses, desalination technique was focused in all countries. But desalination technique alone cannot deliver the promise amount of improved water supply. The ability to make the best use of desalination is a subject at present, to a series of wider water related researcher. The most common desalination processes used were distillation and membrane processes. Historically, though distillation technologies have dominated the seawater desalination market, due to its disadvantages the most new desalination plants uses membrane technologies instead of distillation technique. The quality of feed water is one of the determining factors to decide the type of membrane process to use¹. In membrane based desalination technology the utilized electric energy consumption is almost the same or lower than distillation and it does not need any thermal energy.

The new membrane based electrodialysis (ED) process was commonly used for the production of quality water through desalination technique. The energy consumption utilized for the process is directly related to the salinity of the feed water. Membrane based ED processes have considerable advantages in desalting brackish water and are used over a wide range of salinity concentration level from brackish to sea water². Many types of membranes exist due to classification under various criteria. Generally ion exchange membranes (IEMs) can be defined as a thin layer of electrolytic barrier which can separate two phases and restrict the transport of various chemical species through it and were subdivided into cation exchange membrane (CEM), anion exchange membrane (AEM) and bipolar membrane $(BPM)^3$.

Monopolar membranes (CEM & AEM) were prepared by functionalization methodologies whereas BPM can be prepared by simply laminating conventional CEM and AEM⁴. But laminated BPMs prepared with anion and cation exchange layers (CEL/AEL) alone, often do not perform efficient water dissociation⁵. But the presence of heterogeneous materials like ion-exchange resin (IER) particles in a non-conducting polymer matrix layers of a BPM and presence of catalytic intermediates like quaternary⁶, non-quaternary amine group⁷, weak acid such as phenolic, carboxylic acid or phosphoric acid groups⁸ and its corresponding base, inorganic substances such as Mg, Ni, Co, Mn, Cu, Fe and $Al⁹$, metallic compounds such as ruthenium tri-chloride, chromic nitrate, indium sulfate, hydrated zirconium oxide, etc. ^{10,11},

Page 3 of 31 RSC Advances

heavy/noble metal ions like Cr^{3+} , Fe^{2+} , Ag, Au, Pt, Pd, Os, Rh, Ti, Sn, Zr, Pa, Ru etc. 12,13 , macromolecules such as polyethylene glycol $(PEG)^{14}$, polyvinyl alcohol $(PVA)^{15}$ and bovine serum albumin (BSA) containing both carboxylic and amino groups¹⁶, starburst dendrimer polyamidoamine (PAMAM)¹⁷ etc.^{4,5} in between the CEL and AEL as intermediate layer (IL) usually results in BPM with higher mechanical stability^{18,19} with improved water dissociation effects (the rate was found to be 50 million times faster than the ordinary water dissociation in the presence of catalyst). Hence in the present study, all the IEMs were prepared with resin and glass fiber reinforcements.

Managing high salinity concentrates generated during membrane water desalination processes was a primary need to be addressed due to its potential threat to the receiving ecosystems regarding brine discharge. Depending on the desired application bipolar membrane electrodialysis (BPMED) processes can be performed with different stack configurations. Tongwen & Weihua²⁰ evaluated the effect of cell configurations such as A–C (type I), C–BP–C (type II) and BP–A–C–BP (type III) on production of citric acid using BPMED. From the results, magnitudes of cell voltage, CE and energy consumption followed the analogous order as type II \leq type I \leq type III, while the potential drop across a BPM followed the order type II \geq type I \approx type III suggesting that type II seemed to be a favorable cell configuration for the production of citric acid. Nagasawa et al^{21} used both conventional ED and five compartmental BPMED techniques separately to remove boron from sodium tetra borate solution containing 100 mg/L of boron. The results confirmed that with use of BPMED, more than 90 % of the boron was removed under both acidic (pH 2.3) and basic (pH 9.1) conditions, whereas only 35-45 % of the boron was removed using conventional ED. Nataraj et al studied the ED pilot plant unit coupled with a membrane stack containing 11 cation-exchange and 10 anion-exchange membranes for the removal of nitrates and hardness from simulated aqueous mixtures containing salts that are usually encountered in brackish water. More than 94% of the nitrates, 89% of the chlorides, and 86% of the TDS were successfully removed after 150 min of operation of the ED^{22} . Using the same membrane stack configuration waste water effluent from the paper industry could be treated. The obtained results show that 80% of wastewater could be recovered by the use of MF/ED hybrid process, while the remaining 20% of flow (concentrate) can be used as a biomass^{23} .

RSC Advances Page 4 of 31

The present study highlights the work designed to evaluate the desalination efficiency of prepared monopolar (CEM and AEM) and bipolar (with Platinum as IL) IEM with resin and glass fiber reinforcements using polysulfone (PSu). Use of platinum has been given the greatest economic importance in various applicatory fields such as automobiles, oil refining, glassmaking, medical instruments, electronics, dentistry, jewellery, computers, fertilizers, plastics, fuel cells, etc. which has also urged its use in the water treatment applications. In addition, its certain properties such as superior conductivity, resistance to oxidation and strong catalytic property compared to other types of intermediates have showed the platinum as one of the best choice to be used as intermediate for BPM in the present study. The study was conducted for five different synthetic salt water concentrations ranging from 5 g/L to 25 g/L of NaCl solution (used in feed compartment (FC)) in terms of conductivity, solution pH, transport number of ions (T. No.), feed concentration, current efficiency (CE), energy consumption, water dissociation efficiency (WDE), water dissociation flux and acid-alkali production in the acid compartment (AC) and base compartment (BC) up to 8 h. The stack performance using the synthesized membranes was compared with that of the commercial polystyrene divinylbenzene based (PSDVB) IEM under similar experimental conditions. In addition, the decrease in sodiumchloride ion concentration, salinity and electrical conductivity of the feed water were observed and the reproducibility test for the membrane system with highest CE was conducted.

2 Materials and methods

Commercial strong acid cation exchange membrane (CMI – 7000S) and commercial strong base anion exchange membrane (AMI - 7001S) were procured from Membranes International INC, New Jersey, USA. While, BPM made up of PSDVB were procured from Arun Electro chemicals, Chennai. Glass fiber was purchased from Meena glass fiber industry. Seralite (Cation Exchange resin (CER) - equivalent to Amberlite IRC - 120, 20-50 mesh standard grade) and Seralite (Anionic exchange resin (AER) - equivalent to Amberlite IRA - 400, 20-50 mesh standard grade) were obtained from Sisco Research Laboratory Pvt. Ltd. (SRL). Platinum chloride (Pt) and Polysulfone (PSu) $[M_n=16,000 \ (MO), M_w=35,000 \ (LS)]$ was purchased from Aldrich (USA).

2.1 Reinforced IEM preparation

Anionic and cationic functionalized ionomer membranes of sulfonated polysulfone (SPSu) and quaternized polysulfone (QPSu) was carried out as per the procedure reported earlier²⁴. To introduce additional functions like higher ion exchange capacity (IEC) with firmness and durability for a polymer separation membrane, its surface was modified²⁵. Reinforced cationic exchange membrane (RCEM) and reinforced anionic exchange membrane (RAEM) based on PSu polymer was prepared by first dispersing a specific quantity²⁶ (from 10 %) to 70 %) of dried (60 °C for 24 h in an oven) and crushed cationic/anionic exchange resin (CER/AER) in either SPSu- N, N′- dimethylformamide (DMF) or QPSu-DMF solution respectively for 12 h using a 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 80 °C. The IEC value for the prepared SPSu and QPSu were found to be 1.47 and 1.57 meq/g respectively. Also as expected the reinforced synthesized monopolar membrane had higher IEC value of 4.75 meq/g for RSPSu and 4.35 meq/g for RQPSu respectively.

The obtained membranes with various resin content were subjected to conductivity studies as described in the supporting information S1 and from table 1, it was observed that the conductivity of the prepared membranes increased with increase in IER loadings. And it was optimized at 40 % for both resins²⁶ because beyond 50 %, the nature of the membranes changed to brittle from its soft nature. Reinforced bipolar membrane (RBPM i.e. RPSu-Pt) was prepared using RCEM (RSPSu) and RAEM (RQPSu) as CEL and AEL respectively. Then on one side of both CEL and AEL layers, a solution containing approximately 6 mL of 0.12 g of Pt contained solution was coated to form the IL. Finally the IL coated side of both layers (CEL and AEL) were sandwiched and subjected to hot press to finally obtain RBPM represented as RBPM-Pt as shown in Fig. 1.

Table 1 Optimization of resin loadings in PSu polymer using its conductivity Fig. 1 Diagrammatic representation of methodology used in BPM preparation

2.2 Design and working principle of BPMED unit

BPMED unit used in the study for determination of desalination process efficiency was supplied by Arun Electrochemical, Chennai²⁷. The BPMED unit consisted of a DC power supply and membranes ED stack. The construction and description of the used BPMED unit is shown in Fig. 2. The cathode and anode electrodes used were stainless steel and Ti coated with Ti-Ru-Pd oxides, respectively. The active membrane area of each membrane and volume of each chamber was about 120 cm² and 160 cm³ respectively. Each compartment was connected to a tank of 1 L capacity, allowing for batch mode recirculation of external solutions by submersible pumps. The experiments were carried out at the initial voltage of 10 V and same electric field was applied for different range of feed concentration solution. In order to minimize the cell voltage generated during the initial stages of the performance, 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 used in each EC. Because at lower concentrations, higher resistances between membranes resulted and at higher concentrations, the selectivity nature of the IEMs became lower NaCl solution of concentrations ranging from 5 g/L to 25 g/L was taken in the FC in order to avoid higher rate of salt ion leakage across BPM and formation of undesired salt impurities in products during BPMED performance. During the performance, at every 15 min time interval, various process parameters were evaluated using the same set of equations as reported earlier²⁷. After 8h treatment the final solutions of various synthetic feed concentrations and reproducibility test sample were analyzed for their sodium-chloride ion concentration, salinity and electrical conductivity.

Fig. 2 Schematic representation of BPMED stack setup

3 Results and Discussion

3.1 pH change in various compartments with time

Figures 3 and 4 represent the variation of solution pH in FC, EC, AC and BC with time for brackish water feed concentration range including its reproducibility for both laboratory synthesized RPSu-Pt IEM and commercially procured PSDVB IEM systems. It was clear from these figures that with increase in salt or feed concentration, the initial pH value of the corresponding solution was also found to be higher in FC for both IEM systems. In the case of

Page 7 of 31 RSC Advances

RPSu-Pt IEM system (Fig. 3), pH in FC showed acidic nature at their final stages after an increase in its pH towards basicity at the initial stages of the performance. This is because with increasing time, higher quantities of acid were produced due to water dissociated products thereby resulting in proton leakage through IEMs depending on the capacity of protons to undergo back diffusion²⁸. On the other hand, as per Fig. 4 in case of PSDVB IEM system, the feed solution finally became basic in nature for all feed concentrations. PSDVB based cell experienced greater leakage of ions from BC to FC and thus it remained basic in nature. Moreover, proton leakage through IEM was low due to low acid concentration that was produced during BPMED process using PSDVB IEM systems 29 .

 Whereas in the case of EC, since 0.05M NaCl was taken as electrolyte solution each time, the initial pH remained constant for all performances. Though both systems showed the final solution to be acidic in nature, the acidity was greater for the PSDVB IEM system than the RPSu-Pt IEM system. The difference in pH observed between the two types of IEM systems in FC and EC was mainly attributed to the leakage of ions occurring through membranes arranged between the compartments in a stack. Similarly in case of AC and BC the solution pH was found to be approximately around 2.45 and 10.74 respectively for all performances because of dilute acid and base solutions that were taken initially.

From Figures 3 and 4, it was additionally observed that, irrespective of whether it was AC or BC, the acidity or basicity was found to get increased during the first half stage of a performance and the increase was not uniform because of the leakage of some ions into the neighboring compartments. The nature of pH change reflected their acid and base production for both PSDVB and RPSu-Pt IEM systems. This pH change in various compartments clearly suggested that both IEM systems possessed adequate capacity to split water into its co-ions under the influence of electric field. Also it should be observed that for reproducibility test, more or less the same result as that of its original feed concentration was noticed.

Fig. 3 pH changes in FC, EC, AC and BC with time for various feed concentrations of RPSu-Pt IEM system

Fig. 4 pH changes in FC, EC, AC and BC with time for various feed concentrations of PSDVB IEM system

3.2 Variation of Acid, Base and Feed Conductivities with Time

The changes in pH values are justified using its respective conductivity values. Since the ionic mobility of protons was higher than that of the hydroxyl ions, correspondingly, the conductivity value was found to be higher in the case of AC when compared with BC. For RPSu-Pt IEM system, from Fig. 5 the highest acid and base conductivity observed was 1.31 mS/cm and 0.84 mS/cm respectively. After reaching the highest conductivity, either a decrease or an increase was expected mainly due to the loss of ions from acid-base compartments or introduction of other ions from the neighboring compartments. In case of FC, a wide range in decrease of conductivity^{30,31} was observed which was then followed by an increase that did not exceed the initial conductivity of that particular feed concentration.

For PSDVB IEM system from Fig. 6, the highest acid and base conductivity values were found to be 1.29 mS/cm and 0.7 mS/cm, respectively. In addition, the lower acid and base conductivity values for 5 g/L among other feed concentrations indirectly proved its lower acid and base pH change. In case of FC the conductivity initially decreased depending upon the feed concentration, which then increased slightly and finally remained constant with time. This increased conductivity was observed to be little higher than its initial value of that particular feed concentration mainly because of leakage of ions that occurred from the neighboring compartments through the IEM into FC. It should also be noticed that the reproducibility test in both these cases showed more or less the same results as that of its original feed concentration.

Fig. 5 Conductivity changes in AC, BC and FC for different feed concentrations with time for RPSu-Pt IEM system

Fig. 6 Conductivity changes in AC, BC and FC for different feed concentrations with time for PSDVB IEM system

3.3 Effect of BPMED Process on Acid-Base Production

When the entire BPMED cell was kept under an electric field using electrodes, due to the large electric field appearing at the membrane interface, an excess of OH $⁻$ and H $⁺$ ions was</sup></sup> produced due to the field enhanced chemical reaction as per Second Wien effect. Along with

Page 9 of 31 RSC Advances

this, Na⁺ and Cl[−] ions were also continuously transported through IEMs from FC into BC and AC respectively resulting in the formation of acid and base of certain concentrations 32 which was evidently proved by pH and conductivity studies. The maximum concentration of both NaOH and HCl depended on feed concentration, time, IEC and functional group nature of that membrane.

However, Fig. 7 (a) clearly shows that RPSu-Pt IEM system produced higher acid and base concentrations of about 0.014 N and 0.006 N for the same feed concentration. It has to be noted that once the higher concentration of acid/base was reached in a particular feed concentration, it remained constant until certain duration of time after which it decreased with increase in process time due to decrease of NaCl concentration or diminished mass transfer of Na⁺ and Cl[−] ions in the feed solution.

It was observed from Fig. 7 (b) that PSDVB IEM system showed higher acid and base concentrations of about 0.009 N and 0.006 N respectively for various feed concentrations. Though PSDVB based IEM cell is meant for base production rather acid production because of higher specific permselectivity of CEM for H^+ ions as per reported in the literature²⁶, in the present study from Fig. 7 (b) it was observed that the alkalinity concentration was lower in case of PSDVB IEM system. Furthermore, H^+ ions in the presence of water have a higher intrinsic mobility than OH[−] ions thereby resulting in more leakage of H⁺ ions through AEM which led to decrease in concentration of acid in AC^{27} . Similar decreasing trend was also observed in case of BC for various feed concentrations.

In addition it should be noted that irrespective of the type of systems used (either RPSu-Pt IEM or PSDVB IEM system) , the produced acid and base values purely represent the acid and base generated during the process because the concentration value obtained from the titration procedure was subtracted from its initial concentration value (0.01 N). Thus the final value is solely due to the produced acid and base. Again, it should be noticed that the reproducibility test in both types of IEM systems showed more or less the same results as that of its original feed concentration.

Fig. 7 Changes in acid-base yield with time for various feed concentrations for (a) RPSu-Pt IEM system and (b) PSDVB IEM system

RSC Advances Page 10 of 31

3.4 Ion Transport Number and WDE Changes with Time

Since CE depends upon the ion transport and ionic mobility, for a better process efficiency it was expected that system should have both higher T. No. of ion and better WDE. Figures 8 and 9 represent T. No. properties of both sodium and chloride ions and WDE for RPSu-Pt and PSDVB IEM systems. From these figures it was clear that depending upon the membrane capacity, time and feed concentration, T. No. of both $Na⁺$ ion and Cl⁻ ions was observed to have higher value at its initial stage and then started decreasing with time for both types of IEM systems. In case of WDE, both systems showed the lowest value initially which then increased with time and then remained constant. This is because at the beginning of the BPMED process, since NaCl concentration was higher in FC, a transfer of large amount of Na⁺ and Cl[−] ions through IEM was observed. But with increasing time due to decrease of NaCl concentration, the current was carried by water dissociated products such as H^+ and OH ions.

Fig. 8 Changes in T. No. of ions and WDE for various feed concentrations with time for RPSu-Pt IEM system

Fig. 9 Changes in T. No. of ions and WDE for various feed concentrations with time for PSDVB IEM system

From Fig. 8, RPSu-Pt IEM system showed the highest T. No. of 0.57 and 0.33 for chloride and sodium ions respectively for 15 g/L feed concentration. Similarly from Fig. 9, PSDVB IEM system showed a greater T. No. of 0.16 and 0.08 of chloride and sodium ions respectively, for the same feed concentration³³. While in the case of WDE, as per Fig. 8 RPSu-Pt IEM system showed results of about 0.87 finally for different feed concentrations. The reason for this difference was mainly due to the salt concentration in FC and hence, when the feed concentration was lower it was better opportunity for the transport of water dissociated ions. But when the feed concentration was higher, the competition between these ions would be higher and more preferably the salt ion transport occurred initially followed by the water dissociated ions³⁴. Whereas as per Fig. 9 the highest WDE value observed for PSDVB IEM system was about 0.07. The highest T. No. and steady increase in WDE with time observed for RPSu-Pt IEM system was mainly due to the increase in electric field, pre-polarization of water molecules at the

Page 11 of 31 RSC Advances

membrane-solution interface and the presence of a catalytic Pt intermediate in between the two monopolar layers of BPM^{35} . In the reproducibility test for RPSu-Pt IEM systems, a little lesser value was obtained for T. No. of both ions whereas WDE showed a little higher performance when compared with that of its original feed concentration performance. For the PSDVB IEM system, T. No. of both chloride and sodium ions was observed to be little lesser and the WDE showed a more or less same performance.

3.5 Determination of Process Efficiency Parameters with Time

For any system, higher CE with lower energy consumption is one of the factors which determine the feasibility of any electrochemical process towards higher process efficiency. Fig. 10 represents the variation of CE and energy consumption of both RPSu-Pt and PSDVB IEM system with time for various feed concentrations. It was observed that both CE and energy consumption increased with increase in feed concentration due to the same reason as discussed for T. No. of ions and WDE. With increase in time CE was observed to decrease for each feed concentration mainly due to leaching out of resin particles from the functionalized polymer because of ballooning, flexible and higher elongation nature of the polymer when placed in water for a longer duration of time. The reason for the increase in energy consumption with time was mainly due to the electrical resistance in various compartments. The increase of resistance in FC resulted from the exhaustion of NaCl in the solution can be offset by the decrease of electrical resistance in AC and BC caused by the increase of acid-base concentrations as a consequence of transfer of CI^- and Na⁺ ions from the feed solution.

In the case of RPSu-Pt IEM system as per Fig. 10 (a), the highest CE and energy consumption values observed was about 82.5 % and 0.52 Wh respectively for 15 g/L feed concentration. In case of PSDVB IEM system the same was observed to be 53 % and 1.39 Wh respectively for 10 g/L feed concentration from Fig. 10 (b). From Fig. 10 (a) RPSu-Pt IEM system showed a uniform increase in energy consumption with time until final stages of experiment without any observation of oscillations with respect to various feed concentrations. This was mainly because of the presence of IER in addition to the fiber reinforcements during the membrane preparation which created an increased electrical resistance. So to overcome this additional resistance, RPSu-Pt IEM system consumed a little additional energy till the final stage of a performance resulting in the steady increase in value. Whereas from Fig. 10 (b), the PSDVB

IEM system though displayed oscillations at initial stages, its increase in energy consumption with time finally depended upon its feed concentration. In terms of reproducibility test, CE was observed to be lower and energy consumption was observed to be higher than its original feed concentration for both types of IEM system because the membrane loses some of its IEC and functional groups depending on its usage time.

Fig. 10 Variation of CE and energy consumption for various feed concentrations with time for (a) RPSu-Pt IEM system and (b) PSDVB IEM system

3.6 Variation of Current, Potential and Water Dissociation Fluxes with Time

Figures 11 and 12 reveal the relationship between current, potential and water dissociation flux of protons and hydroxyl ions with time for various feed concentrations of both RPSu-Pt and PSDVB IEM systems. Similar to the results of Michael Rajesh et $al³⁵$ from figures 11 and 12, it was clear that the current increased with time for both systems depending upon the feed concentration. The reason was mainly because of the production of OH /H⁺ during water dissociation and overall decrease of stack resistance due to resistance difference in various compartments caused by IEM. The maximum current observed finally for lowest and highest feed concentrations was about 86 mA and 89 mA respectively for RPSu-Pt and it was about 105 mA and 89 mA respectively for PSDVB IEM system.

The voltage variation slightly increased with time and attained a maximum value, depending upon feed concentration which then decreased. This is because the production of acid and alkali increased with increase in voltage to some extent, after which further increase in voltage deteriorated the membrane properties as discussed by Trivedi et al^{36} . The highest volt reached by RPSu-Pt IEM system among various feed concentrations was about 11.5 V as per Fig. 11 and it was about 23.1 V for PSDVB IEM system from Fig. 12. The reason for the observed lower voltage for RPSu-Pt IEM system can be explained theoretically using protonation and de-protonation reactions model and the hydrophilicity change in the interface¹⁴.

From figures 11 and 12, it was clear that for both IEM systems whether acidic or basic, the water dissociation flux was observed to decrease with time for the various feed concentrations mainly due to the depletion of $Na⁺$ ions in the anode compartment and Cl⁻ ions in the cathode compartment. As per Fig. 11, the higher acid and basic fluxes observed was about 37

Page 13 of 31 RSC Advances

x 10^{-6} mol m⁻² s⁻¹ and 14.8 x 10^{-6} mol m⁻² s⁻¹ in AC and BC respectively for RPSu-Pt IEM system. And for PSDVB IEM system the same was about 14.8 x 10^{-6} mol m⁻² s⁻¹ and 3.7 x 10^{-6} mol m^{-2} s⁻¹ respectively. The greater flux values for RPSu-Pt IEM system confirmed the catalytic activity of Pt intermediate layer at the BPM interface by means of hydrogen bonding and polar interaction between Pt and water molecules.

 In the reproducibility test in case of RPSu-Pt IEM system, both acidic and basic fluxes were observed to be lower than its original feed concentration. Whereas the current change was higher value and the potential change was also higher at their initial time and then fluctuated around its original feed concentration during the later stage of the performance. In case of PSDVB IEM system, the reproducibility test revealed that the dissociation fluxes were lower than the original feed concentration; while both potential and current values were observed to be higher.

Fig. 11 Variation of current, potential, protons and hydroxyl ions water dissociation fluxes with time for RPSu-Pt IEM system

- **Fig. 12 Variation of current, potential, protons and hydroxyl ions water dissociation fluxes with time for PSDVB IEM system**
- **3.7 Determination of Electrical Conductivity, Salinity and Sodium-Chloride ion Concentration.**
- **Table 2 Electrical conductivity, salinity and sodium-chloride ion concentration values for various final feed solutions using RPSu-Pt IEM system**

Table 3 Electrical conductivity, salinity and sodium-chloride ion concentration values for various final feed solutions using PSDVB IEM system

Tables 2 and 3 represent the electrical conductivity, salinity and sodium-chloride ion concentrations in 100 mL of various feed sample solutions for both RPSu-Pt and PSDVB IEM systems. It should be noted that all these parameters increased with increase in feed

RSC Advances Page 14 of 31

concentration mainly because of two reasons: (i) increased NaCl concentration in the feed solution and (ii) restricted transport of sodium and chloride ions through IEMs because of decreased membrane capacity due to the adhesion of the salt ions on the surface of the membrane, especially during higher feed concentration and at longer duration of time. Though the transfer of Na⁺ and Cl⁻ ions from FC to neighboring compartments under the electric field was confirmed by lower electrical conductivity, sodium and chloride ion concentrations of final feed solutions, the effectiveness of the process for both types of IEM systems was confirmed through salinity measurements (Tables 2 and 3). The higher difference between the initial and final values for all these parameters represents the process effectiveness in removal of NaCl and higher acid-base production. The reproducibility test results can also be discussed in a similar way.

4 Conclusion

Functionalized PSu based resin-glass fiber reinforced monopolar and bipolar (with Pt intermediate) IEMs were prepared and compared with commercial PSDVB IEM in order to evaluate their desalination efficiency for various feed concentrations using BPMED technology. Based on the results obtained for various process parameters such as current efficiency (82.5 %) for RPSu-Pt and 53.61 % for PSDVB), energy consumption (0.52 Wh for RPSu-Pt and 1.39 Wh for PSDVB), acid-base production (0.014 N acid & 0.006 N base for RPSu-Pt and 0.009 N acid & 0.006 N base for PSDVB) and WDE (0.87 for RPSu-Pt and 0.07 for PSDVB), it can be concluded that RPSu-Pt IEM system showed a better performance than that of the commercial PSDVB IEM system. Also electrical conductivity, salinity and sodium-chloride ion concentration results were observed to be better for RPSu-Pt IEM system than with PSDVB IEM system due to the presence of a catalytic intermediate region in RPSu-Pt based IEM system.

Acknowledgement

Financial support from the Board of Research in Nuclear Science (BRNS), Mumbai, India (Letter No. 2010/37C/1/BRNS/826, Dated: 28-06-2010) is gratefully acknowledged.

References

- 1. V. A. Shaposhnik, V. I. Vasileva, R. B. Ugryumov, M. S. Kozhevnikov, *Russian Journal of Electrochemistry,* 2006, **42**, 531-537.
- 2. T. Younos, K. E. Tulou, *Journal of Contemporary Water Research & Education*, 2005, **132**, 3-10.
- 3. H. Strathmann, Electrodialysis and related processes, Nobe, RD & Stern SA (eds.), in: Membrane Separation Technology - Principles and Applications, Elesevier Science B.V., 1995.
- 4. V. J. Frilette, *J. Phys. Chem.* 1956, **60**, 435-439.
- 5. A. Tanioka, K. Shimizu, K. Miyasaka, H. J. Zimmer, N. Minoura, *Polymer,*1996, **37**, 1883.
- 6. R. Simons, *Electrochimica Acta*, 1984, **29**, 151-158.
- 7. R. Simons, *Electrochimica Acta*, 1985, **30**, 275-282.
- 8. N. V. Sheldeshov, N. P. Gnusin, V. I. Zabolotskii, N. D. Pis'menskaya, *Soviet Electrochemistry*, 1987, **22**, 742.
- 9. Y. Tanaka, S. Matsuda, Y. Sato, M. Seno, *Journal of Electrochemistry Society Japan*, 1982, **50**, 667-672.
- 10. M. S. Kang, Y. J. Choi, H. J. Lee, S. H. Moon, *Journal of Colloid and Interface Science*, 2004, **273**, 523-532.
- 11. M. S. Kang, Y. J. Choi, S. H. Moon, *Journal of Colloid and Interface Science*, 2004, **273**, 533-539.
- 12. F. Hanada, K. Hirayama, S. Tanaka, N. Ohmura, Bipolar membrane and method for its production, JP Patent 2524012, 1996.
- 13. F. G. Wilhelm, N. F. A. vander vegt, M. Wessling, H. Strathmann, Bipolar membrane preparation, Kemperman, AJB (ed.), in: Bipolar membrane Handbook, Twente University Press, Enschede, The Netherlands, pp. 79-108, 2000.
- 14. R.Q. Fu, T.W. Xu, G. Wang, W.H. Yang, Z.X. Pan, *Journal of Colloid and Interface Science*, 2003, **263**, 386-390.
- 15. R.Q. Fu, Y. H. Xue, T. W. Xu, W. H. Yang, *Journal of Colloid and Interface Science*, 2005, **285**, 281-287.
- 16. R. Q. Fu, T. W. Xu, W. H. Yang, Z. X. Pan, *Journal of Colloid and Interface Science*, 2004, **278**, 318-324.
- 17. R. Q. Fu, T. W. Xu, Y. Y. Cheng, W. H. Yang, Z. X. Pan, *Journal of Membrane Science*, 2004, **240**, 141-147.
- 18. B. Bauer, F. J. Gerner, H. Strathmann, *Desalination,* 1988, **68**, 279.
- 19. O. Kedem, A. Warshawsky, A supported, mechanically stable bipolar membrane for electrodialysis. Patent to Yeda Research and development company, Ltd., Israel, EP 0,504,904 A2; 1992.
- 20. X. Tongwen, Y. Weihua, *Journal of Membrane Science*, 2002, **203**, 145-153.
- 21. H. Nagasawa, A. Iizuka, A. Yamasaki, Y. Yanagisawa, *Industrial and Engineering Chemistry Research*, 2011, **50**, 6325-6330.
- 22. S. K. Nataraj, K. M. Hosamani, T. M. Aminabhavi, *Journal of Applied Polymer Science*, 2006, **99**, 1788-1794.
- 23. S. K. Nataraj, S. Sridhar, I. N. Shaikha, D. S. Reddy, T. M. Aminabhavi, *Separation and Purification Technology*, 2007, **57**, 185-192.
- 24. V. Krishnaveni, D. Sangeetha, *Desalination*, 2012, **296**, 37.
- 25. M. Ulbricht, *Polymer*, 2006, **47**, 2217-2262.
- 26. M. Kumar, V. K. Shahi, *Journal of Membrane Science,* 2010, **349**, 130-137.
- 27. K. Venugopal, S. Dharmalingam, *Desalination*, 2014, **344**, 189–197.
- 28. Y. Wang, X. Zhang, C. Huang, T. Xu, *Journal of Membrane Science,* 2011, **385**, 226- 233.
- 29. H. Strathmann, G.H. Koop, Process economics of the electrodialytic water dissociation for the production of acid and base, in: Kemperman, A.J.B. (EdS.), Handbook on Bipolar Membrane Technology, Twente University Press, Enschede, The Netherlands, 2000, pp. 193-218.
- 30. S. Shi, Y. H. Lee, S. H. Yun, V. Phan, X. Hung, S. H. Moon, *Journal of Food Engineering*, 2010, **101**, 417-423.
- 31. M. Badruzzaman, J. Oppenheimer, S. Adham, M. Kumar, *Journal of Membrane Science*, 2009, **326**, 392-399.
- 32. Y. Wang, X. Zhang, T. Xu, *Journal of Membrane Science*, 2010, **365**, 294-301.
- 33. M. Nishapriya, K. Palanivelu, *Indian Journal of Chemical Technology*, 2006, **13**, 262-268.

Page 17 of 31 RSC Advances

- 34. J. Shen, J. Huang, L. Liu, W. Ye, J. Lin, B. V. Bruggen, *Journal of Hazardous Materials*, 2013, **260**, 660–667.
- 35. A. Michael Rajesh, M. Kumar, V. K. Shahi, *Journal of Membrane Science*, 2011, **372**, 249-257.
- 36. G. S. Trivedi, B. G. Shah, S. K. Adhikary, V. K. Indusekhar, R. Rangarajan, *Reactive Functional Polymers*, 1996, **28**, 243- 251.

Fig. 1 Diagrammatic representation of methodology used in BPM preparation

BPM - Bipolar Membrane; CEM - Cationic Exchange Membrane; AEM - Anionic Exchange Membrane; EC - Electrode Compartment; AC - Acid Compartment; BC - Base Compartment; FC - Feed Compartment; AT - Acid Tank; FT - Feed Tank; BT - Base Tank; ET - Electrolyte Tank.

Fig. 2 Schematic representation of BPMED stack setup

Fig. 3 pH changes in FC, EC, AC and BC with time for various feed concentrations of RPSu-Pt IEM system

Fig. 4 pH changes in FC, EC, AC and BC with time for various feed concentrations of PSDVB IEM system

Fig. 5 Conductivity changes in AC, BC and FC for different feed concentrations with time for RPSu-Pt IEM system

Fig. 6 Conductivity changes in AC, BC and FC for different feed concentrations with time for PSDVB IEM system

Fig. 7 Changes in acid-base yield with time for various feed concentrations for (a) RPSu-Pt IEM system and (b) PSDVB IEM system

Fig. 8 Changes in T. No. of ions and WDE for various feed concentrations with time for RPSu-Pt IEM system

Fig. 9 Changes in T. No. of ions and WDE for various feed concentrations with time for PSDVB IEM system

Fig. 10 Variation of CE and energy consumption for various feed concentrations with time for (a) RPSu-Pt IEM system and (b) PSDVB IEM system

Fig. 11 Variation of current, potential, protons and hydroxyl ions water dissociation fluxes with time for RPSu-Pt IEM system

Fig. 12 Variation of current, potential, protons and hydroxyl ions water dissociation fluxes with time for PSDVB IEM system

Table 1. Optimization of resin loadings in PSu polymer using its conductivity

Table 2. Electrical conductivity, salinity and sodium-chloride ion concentration values for various final feed solutions using RPSu-Pt IEM systems

Final feed sample solution	Electrical conductivity (mS/cm)		Salinity $(\%)$		Chloride ion concentration $(mg/100$ mL)		Sodium ion concentration (ppm)	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
5 g/L	12.53	6.84	8.2	4.2	35.96	17.55	42.9	11.7
10 g/L	20.90	8.2	14.3	5.2	39.12	22.5	44.4	15.5
15 g/L	30.40	10.69	21.3	7.0	46.69	26.1	46.2	17.4
20 g/L	37.7	12.55	26.9	8.3	54.26	26.4	48.0	17.6
25 g/L	44.9	15.34	33.1	10.2	58.68	31.95	49.1	21.3
Reproducibility test (15 g/L)	30.40	10.68	21.3	7.1	46.69	24.3	46.2	16.2

Final feed	Electrical conductivity		Salinity		Chloride ion concentration		Sodium ion concentration	
sample solution	(mS/cm)		$(\%)$		$(mg/100$ mL)		(ppm)	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
5 g/L	12.53	11.30	8.2	7.3	35.96	20.8	42.9	24.5
10 g/L	20.90	19.4	14.3	13.9	39.12	27.3	44.4	38.9
15 g/L	30.40	27.5	21.3	19.1	46.69	30.4	46.2	44.3
20 g/L	37.7	31.3	26.9	22.1	54.26	37.6	48.0	45.3
25 g/L	44.9	36.9	33.1	26.6	58.68	43.4	49.1	46.5
Reproducibility test (10 g/L)	20.90	20.4	14.3	14.0	39.12	28.7	44.4	40.0

Table 3. Electrical conductivity, salinity and sodium-chloride ion concentration values for various final feed solutions using PSDVB IEM systems

265x150mm (150 x 150 DPI)