Synthesis of Anion Exchange Polystyrene Membranes for the Electrolysis of Sodium Chloride

Sonny Sachdeva, Ram P. Ram, Jayant K. Singh, and Anil Kumar
Dept. of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur 208016, India

We have prepared a cross-linked polystyrene anion exchange composite membrane for the electrolysis of sodium chloride to produce sodium hydroxide by selective removal of chloride ions. The composite membrane is homogeneously modified by gas phase nitration, followed by amination using hydrazine hydrate, and further reaction with dichloroethane and triethylamine to introduce quaternary ammonium charges on it. We showed that the membrane is specific to the transport of chloride ions through its pores. The performance of the membrane has been evaluated in terms of current efficiency and power consumption, and the effect of various parameters like current density, initial salt concentration, and circulation rate is studied. The maximum current efficiency obtained is 96.5% and the corresponding power consumption is 0.1216 kWh/ mol at 5.2 N initial salt concentration and current density of 254 A/m². © 2008 American Institute of Chemical Engineers AIChE J, 54: 940–949, 2008
Keywords: anion exchange membrane, membrane electrolysis, polystyrene

Introduction

Electrodialysis is a mass separation technique, in which electrically charged membranes are used and electrical potential difference is applied to cause a reaction at the electrodes and separate ionic species.[1] Some of the applications of this process include production of caustic soda,[2–4] ultra pure water,[5] and metal ion removal from waste water.[6] Electrodialysis has been used for the separation of brine in the presence of calcium sulfate (cation and anion exchange membranes (CMV and AMV)) from Asahi Glass membranes having current efficiency of 85% and power consumption varying between 2 and 7.1 kWh/m³),[7,8] desalination of brackish water (using CMXSb and ACS by Tokuyama, Japan),[2,9] desalination of coal-mine brine (using commercial CMV, AMV membranes from Asahi Glass yielding 85% recovery and energy consumption of 7.8–14.4 kWh/m³),[10] removal of copper ions (CMV and AMV from Asahi Glass membranes,

current efficiency 94.94% and power consumption 0.4 kWh/ m³),[11] lead ions (AR204SXR412 and CR67, MK111, Ionics, USA),[12] and Cr(III) and Cr(VI) ions (using Neosepta cation exchange membranes and Tokoyuma Soda anion exchange membranes having a current efficiency of 80%)[13,14] from waste water.

Electrodialysis can be carried out either in a three-compartment cell having both cation and anion exchange membranes as reported above, or a two compartment cell that has only one type of an ion exchange membrane. Figure 1 shows a schematic picture of electrolysis of sodium chloride in a two-compartment cell having an anion exchange membrane. Anion exchange membranes in two-compartment electrodialysis have been used for various applications like recovery of chlorine from dilute hydrochloric acid (MAP-1 based on methyl vinyl pyridine, Research Institute of Plastics G. S. Petrov, Moscow, 1.740 kWh/kg of chlorine, 4000 A/m²),[15] to concentrate nitric acid beyond the azeotropic mixture (AW and ARA from Solvay, France, Raipore 5035 and Raipore 6030 from Pall, ACS and AFN7 from Tokuyama, Japan, of which Raipore 6030 gave the least power consumption of 1.41 kWh/kg and current efficiency 83% at 300 mA/cm)[16]

Reaction at the Anode: $2Cl^- \rightarrow Cl_2 + 2\underline{e}^-$

Reaction at the Cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Overall Reaction: $2NaCl + 2H_2O \rightarrow Cl_2 + H_2 + 2NaOH$
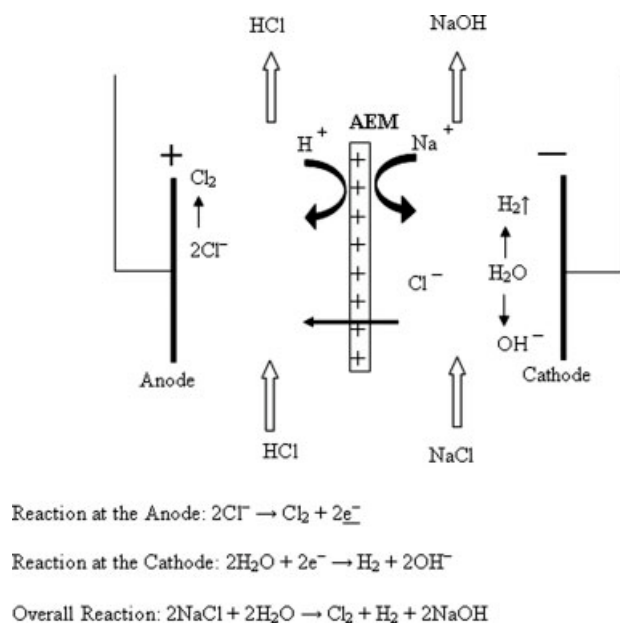
Figure 1. Schematic diagram of membrane electrolytic cell using an anion exchange membrane.

and sodium sulfate splitting to produce sodium hydroxide (Pall R1030, USA, current efficiency, 75%, 500 A/m^2).[17] Salt splitting is also performed using grafted polytetrafluoroethylene (PTFE)[18,19] anion exchange membranes that gave a current efficiency of 63–75% and energy consumption of 0.129 kWh/mol at current density of 1000 A/m^2.

The homogeneously charged membranes (the ones in which functionalized moieties are introduced on the polymer) used for electrodialysis have been copoly(vinyl alcohol)/formyl methyl peridinium,[20] sulfonated polyphasphazene,[21] poly(2, 6-dimethyl-1, 4-phenylene oxide),[22] and PTFE.[23] The commercially available ion exchange membranes Nafion (Du Pont), Aciplex, and Flemion generally suffer from the problems of fouling by metal, coion leakage, and degradation at high usage temperature. Polystyrene based on ion-exchange membranes overcome these problems, but are brittle under the application of high temperature.[24–27]

In this work, we have prepared ceramic supported crosslinked polystyrene anion exchange membrane having a high charge density of quaternary ammonium charges on its surface. The membrane has a high selectivity for the chloride ions as compared to the hydroxyl ions, and so has been used for the electrolysis of sodium chloride. Because of the vast industrial significance of the electrochemical splitting of sodium chloride into caustic soda and chlorine, we have studied this separation process using our membrane at high salt concentration at low current densities. The performance of the membrane has been studied in terms of current efficiency and power requirement by varying parameters such as current density, circulation rate, and salt (catholyte) concentration. The maximum current efficiency obtained is 96.5%, and the corresponding power consumption is 0.1216 kWh/mol at 5.2 N initial salt concentration and current density of 254 A/m^2 that is comparable to the commercially available membranes.

Experimental

Materials

Analytical grade calcium carbonate, ferrous sulfate, sulfuric acid, hydrochloric acid, oxalic acid, sodium nitrite, hydrazine, triethylamine, dimethyl aniline, benzyol peroxide (BPO), and azo-bis-isobutyronitrile (AIBN) are purchased from S. D. Fine Chemicals, (Mumbai, India). Analytical grade sodium chloride, tetra-ethoxysilane (TEOS), silver nitrate, sodium nitrate, nitric acid, toluene, methanol, 1,2 dichloroethane, ethanol, sodium hydroxide, and fused calcium chloride are obtained from Qualigens (Mumbai, India). Styrene and divinyl benzene (DVB) are procured from Merck (Philadelphia, USA).

Before polymerization, styrene and DVB are washed with 5% (by wt.) NaOH aqueous solution to remove all the inhibitors, and then further purified by vacuum distillation. AIBN and BPO are recrystallized in methanol several times before using them as initiators in the styrene–DVB polymerization reactions. All other chemicals are used in the experiments as received.

Preparation of clay supports

Microporous ceramic supports are prepared from a mixture of clays (kaolin, ball clay, pyrophallite, calcium carbonate, feldspar, and quartz) in water.[28] A paste of all these clays is made in water and cast on a gypsum surface in the form of a circular disc using an aluminum ring of 76-mm internal diameter and 4-mm thickness. These supports are dried at three different temperatures, 25, 100, and 250°C, for 24 h at each temperature to ensure the slow removal of water. The dried supports are further calcined at 900°C for 8 h to impart required hardness and porosity. Finally, the supports are polished using a silicon carbide abrasive paper (No. C-220) to get smooth and flat ceramic discs of diameter 64 mm and thickness of 2–3 mm. To increase the stability of the ion exchange membranes in oxidizing and reducing atmospheres, the polished clay supports are dipped in a polymerized solution of TEOS, which is prepared at room temperature by continuous stirring of TEOS, HCl, and H$_2$O in the molar ratio of 1:0.04:2.[29] Subsequently, the clay supports are calcined at 1000°C for 6 h.

Membrane preparation

Preparation of Composite Polystyrene Membrane. The composite polystyrene membrane is prepared by first making styrene-DVB copolymer syrup and then casting it on a wet clay support. The copolymer syrup is prepared from styrene and DVB monomers, using a dual intiator system (BPO and AIBN), and DMA as an accelerator. The DVB also acts as the cross-linking agent in the polymerization reaction. In a typical experiment, a mixture of styrene (0.048 g mol), BPO (2.78×10^{-4} g mol), AIBN (2.25×10^{-4} g mol), DMA (1.69×10^{-4} g mol), and DVB (1.15×10^{-3} g mol) is heated in N$_2$ atmosphere at 70°C for 1 h in an oil bath and then cooled to room temperature quickly by placing the mixture in a refrigerator in order to arrest the polymerization reaction. The reaction product, which is a homogeneous and viscous solution of the copolymer, is diluted with toluene to 66% by weight of copolymer before casting the membrane on the clay support.

The clay support is placed over wet polyurethane foam so that the air present inside the pores of the support is displaced by water. The copolymer solution of known weight (~2 g) is poured and uniformly spread over the wet clay support, and dried at room temperature till all the solvent (toluene) evaporates. As water is a nonsolvent for the copolymer, it does not allow the latter to penetrate inside the pores of the support, thus ensuring the formation of a distinct thin layer of copolymer on the surface. Finally, the polymer-coated clay support is further dried and cross-linked at 70°C for 24 h, and the thickness of the polymer layer is found to be 20–25 μm as determined from the scanning electron microscopy (SEM) measurements and gain in weight of the support due to the polymer film. In the following sections, we will denote the polymer-coated clay support as "composite membrane."

Modification of Composite Polystyrene Membrane. The composite membrane is nonionic and hydrophobic in nature, and therefore chemical modifications are required to make it anion-exchangeable and hydrophilic. The chemical modifications are carried out in a series of four steps. In the first step, the composite membrane is functionalized with nitro-groups ($—NO_2$) by a gas phase nitration reaction. The composite membrane is placed in a glass reactor having a stainless steel lid with a rubber septum fixed in the centre of the lid. Vacuum is created inside the reactor by sucking out air through a needle fixed in the septum using a vacuum pump. A gaseous mixture of NO and NO_2 (called NO_x) is generated in a tightly stoppered glass bottle by the reaction of sodium nitrite (0.14 mol), sulfuric acid (36 N, 25 ml), and ferrous sulfate (0.072 mol), and fed to the glass reactor. The septum allows easy injection of NO_x gases using a syringe without the loss of vacuum or gases from the reactor. The composite membrane was maintained in the NO_x gas environment at 110°C for 6 h.[30] After the nitration reaction, the membrane is kept in distilled water to remove the NO_x gas physically adsorbed by the clay support.
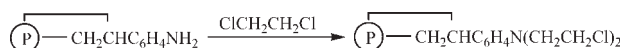
The nitration reaction can be shown as below:

$$\text{(P)CH}_2\text{CHC}_6\text{H}_5 \xrightarrow{NO_x} \text{(P)CH}_2\text{CHC}_6\text{H}_4\text{NO}_2$$
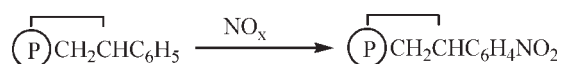
In the second step, the nitrated composite membrane is further refluxed with 50% (by vol.) hydrazine–water mixture at 50°C for 6 h in a water bath so as to reduce the NO_2 groups to amine (NH_2) groups as shown in the following scheme.

$$\text{(P)—CH}_2\text{CHC}_6\text{H}_4\text{NO}_2 \xrightarrow{NH_2NH_2} \text{(P)—CH}_2\text{CHC}_6\text{H}_4\text{NH}_2$$
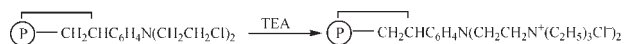
In the third step, the aminated membrane is further modified by refluxing it at 50°C with 2% (by vol.) 1,2 dichloro-ethane solution in ethanol for 4 h. The reaction occurs as follows:

$$\text{(P)—CH}_2\text{CHC}_6\text{H}_4\text{NH}_2 \xrightarrow{ClCH_2CH_2Cl} \text{(P)—CH}_2\text{CHC}_6\text{H}_4\text{N(CH}_2\text{CH}_2\text{Cl)}_2$$

In the final step, the membrane is quaternized by refluxing it at 50°C with 5% solution of triethylamine in ethanol for 4 h. This modified membrane is a strong anion exchange membrane having quaternary ammonium groups.

$$\text{(P)—CH}_2\text{CHC}_6\text{H}_4\text{N(CH}_2\text{CH}_2\text{Cl)}_2 \xrightarrow{TEA} \text{(P)—CH}_2\text{CHC}_6\text{H}_4\text{N(CH}_2\text{CH}_2\text{N}^+\text{(C}_2\text{H}_5\text{)}_3\text{Cl}^-\text{)}_2$$

Membrane characterization

Ion Exchange Capacity. The anion exchange capacity (AEC) of unsupported quaternized polystyrene films is determined by gravimetric method following the method reported in literature.[31] In this method, the membrane films are kept in a mixture of 10% NaCl and 4% HCl for 24 h to convert them to Cl^- form. These are then washed well with distilled water until they become free of the acid. Further, the above regenerated polystyrene films are kept in 0.1 N $NaNO_3$ solution (8.5 g $NaNO_3$ in 100 ml of distilled water) for another 24 h. The films are removed and 1.7 g of $AgNO_3$ with 2–3 drops of nitric acid added to the remaining water to precipitate the AgCl. The precipitate is filtered, dried, and weighed accurately to determine the AEC using the following relation

$$\text{AEC (mequiv/g)} = W/M, \tag{1}$$

where W = weight of precipitate formed, M = molecular weight of $AgNO_3$.

Current–Voltage Characteristics and Ionic Conductivity. The current–voltage curve is obtained by using a two compartment test cell as shown in Figure 2. The voltage drop across the membrane is measured using two Ag/AgCl electrodes. The clay supported composite membrane is first equilibrated in a salt solution of concentration 1 M for 24 h and the two compartments are rinsed with the salt solution. Salt solution (1 M NaCl) is circulated in the compartments with the membrane sandwiched between them for a couple of hours prior to obtaining the current–voltage data. The current–voltage curve is obtained by applying the potential difference across the cell via a DC source and allowing the current to reach a steady state.[32] We have calculated the ionic conductivity of the membrane in a similar manner following the procedure described elsewhere.[33]
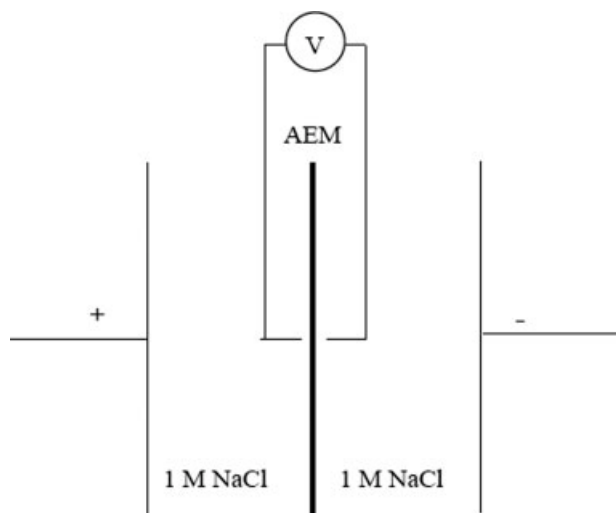

Figure 2. Cell arrangement for measuring the potential drop across the membrane.

Contact Angle Measurement. Static contact angles of water on the membrane surface are measured following the sessile drop method using a goniometer (Model 100-00-230) supplied by r′ame-hart, USA with RH1 2001 Imaging software. To confirm the effect of modification on hydrophilicity, we have measured the contact angle of water with the unmodified, nitrated, aminated, and quaternized polystyrene composite membranes. Droplets of double distilled water (~3 ml) are positioned at different places on the membrane surface, and at least 20 readings are taken to determine the average contact angle value.

Equilibrium Water Content. Water uptake of the unsupported films has been measured by calculating the difference in weight of the dry and wet membrane sample. To ensure saturation of the membranes samples, these are completely soaked in water for 24 h. The excess water is removed by gently wiping it off with a filter paper, and the wet membrane samples are weighed. These are then dried for 24 h at 75°C to completely remove the water and weighed again.

$$\text{Water Uptake } (\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100. \qquad (2)$$

Experimental set up for electrolysis

The schematic of two compartment electrolysis setup used in this work, shown in Figure 3, has been described elsewhere.[34] The anion exchange membrane, having an exposed area of 19.6 cm^2, is sandwiched between the compartments, each compartment having a capacity to hold 75 ml of electrolyte solution. The ceramic-supported anion exchange membrane always faces the cathode side of the setup. The electrodes, cathode and anode, are made of 316 stainless steel and platinum wires, respectively, and have an interelectrode distance of ~3 mm. The anolyte (HCl) and catholyte
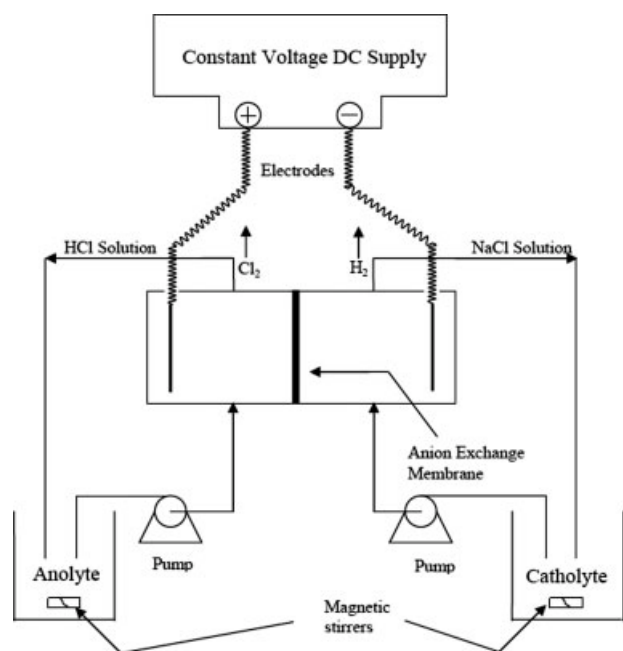

Figure 3. Schematic representation of the experimental setup for the electrolysis of sodium chloride.

(NaCl) solutions stirred with magnetic stirrers are circulated on each side of the membrane through two 1-liter glass reservoirs using peristaltic pumps. Experiments are carried out under constant DC current supplied by a DC power source (Aplab India, 0–32 V, 10 A), and the cell voltage is continuously adjusted and measured using a digital multimeter.

In this work, the electrolysis of sodium chloride has been carried out using an anion exchange membrane with an objective to produce industrially important sodium hydroxide by the selective removal of chloride ions through the membrane. To ensure that the membrane is selective to the chloride ions and has little leakage of hydroxyl ions through the anion exchange membrane; we have performed two sets of experiments. In the first experiment, we have carried out electrolysis of 0.55 M (initial concentration) HCl solution, keeping the same concentration on both sides of the membrane. In the second experiment, we have carried out electrolysis of 0.6 M (initial concentration) NaOH solution, again keeping the initial concentration same on both sides of the membrane.

The performance of the membrane has been studied by varying parameters such as current density (127, 254, and 509 A/m^2), circulation rate (33, 66, and 99 ml/min) and salt (catholyte) concentration (2.5, 4.2, and 5.2 N). When experiments are performed to determine the influence of one parameter, other parameters are kept constant at operating conditions of 4.2 N NaCl (catholyte) and 0.5 N HCl (anolyte) concentration, 254.6 A/m^2 of current density, and a circulation rate of 66 ml/min. Samples of catholyte are taken at regular intervals of 30 min and the concentration of NaOH produced is determined by volumetric titration of NaOH with oxalic acid. Each electrolysis run is typically carried out for 150 min under the chosen operating conditions. We have used the same membrane throughout the experimentation to observe the effect of current density, concentration, and circulation rate. Also, the membrane used for experimentation was supported on the ceramic support. For determination of the energy consumed, the voltage is assumed to be approximately constant between two consecutive readings. The current efficiency (η, %) and the energy consumed (E, kWh/mol NaOH produced) are calculated by the following relations:

$$\eta = \frac{\Delta C \cdot v}{(I \cdot \Delta t / F)} \times 100 \qquad (3)$$

$$E = \frac{V_{\text{Avg}} \cdot F}{\eta \cdot 1000} \quad \text{kWh/moles of NaOH produced}, \qquad (4)$$

where ΔC is the change in concentration of NaOH (mol/lit) in time Δt seconds, v is the volume of catholyte solution in litres, I is the current in Amperes, F is the Faraday constant, V_{Avg} is the average cell voltage for each electrolysis run, and t is time for which electrolysis is run.

Results and Discussion

Formation of clay supports

The clay supports are prepared in this work according to procedure given in the experimental section. In the calcination step (heating at 900°C for 6–8 h), the supports gained

the desired mechanical strength and structural stability. Because of the addition of TEOS and calcination at 1000°C the, membranes could withstand long runs of experimentation even in oxidizing and reducing environments of the anolyte and catholyte.

Membrane preparation

The copolymerization of styrene and DVB has been carried out using a dual initiator system of AIBN and BPO in the weight ratio of 1:2 in presence of DMA. The accelerator DMA forms a radical cation with BPO,[35] which has considerably high reactivity and activation energy much lower than that of the dissociation of BPO.[34] The AIBN initiator alone decomposes to its radicals at higher temperature of 50–90°C and is unaffected by the room temperature polymerization. The reaction mixture of styrene, DVB, AIBN, BPO, and DMA in the above proportion is heated at 70°C for 1 h and then cooled to the room temperature quickly. The reaction mass becomes sufficiently viscous within 1–2 h and the reaction stops. If BPO + DMA initiator system (without AIBN) is used, we find that on further heating the polymerization does not progress anymore (conversion 8%). However, on using dual initiating system of BPO and AIBN in presence of DMA, the conversion stops at 10%, but after the membrane is cast on the support this dual initiator system causes the polymerization to progress to completion. The copolymer solution mixed in toluene is spread on the polished wet ceramic supports. The unreacted monomers evaporate from the wet surface of the ceramic support and leave behind a thin polymer layer that completely adheres to the support. On heating this membrane at 70°C, we get a high molecular weight polymer membrane with thickness of ~20–30 μm. In this work, we have used low (3 wt %) divinylbenzene (DVB), because with the increase in the amount of DVB (cross-linking agent) the polymer obtained is highly cross-linked that swells very little in the solvents in which it is to be modified. As a result of this, it becomes difficult to functionalize the polymer membrane leading to a low ion exchange capacity.[23,36] Moreover, a highly cross-linked membrane offers high resistance to the flow of current and has low water content.

The composite membrane thus formed is modified by gas phase nitration. A change in the appearance of the membrane occurs as its surface becomes uniformly pale yellow on nitration. The gas phase nitration is preferred over the conventional liquid phase procedure of nitration (which uses nitric and sulfuric acid) as the gas phase reaction occurs uniformly and at lower temperatures without exposing the membrane to harsh acidic environments that can lead to polymer degradation. The nitrated membrane is further aminated using 50% hydrazine hydrate solution to reduce the nitro groups to amine groups. The polymer layer now becomes dark yellowish in appearance, and is more hydrophilic as compared to the polymeric membrane. The amination step is followed by quaternization that occurs in a series of two reactions. The first one is reaction with dichloroethane to increase the number of exchange sites on the aminated membrane and then quaternization with triethylamimne. The membrane prepared in this way has quaternary ammonium groups and is much more hydrophilic in nature as compared to the polymer film as has also been confirmed by contact angle measurements.

Membrane characterization

Scanning Electron Microscopy (SEM). The structural morphology of the top surface and the cross section of the composite membrane has been analyzed using Joel-JSM (Model 840 A) SEM at 3-keV acceleration voltage as seen in Figure 4. All the membrane samples are dipped in liquid nitrogen and sputtered with gold to a thickness of ~150 Å to create a conducting surface before the analysis. Figure 4a shows the surface of the ceramic support suggesting that it is highly porous. The white regions in this photograph are considered to be ceramic particles and the spacing between the ceramic particles represents to be probable pores. In Figure 4b, a smooth layer of unmodified membrane at 14,000 magnifications is clearly visible with lines running across the surface. These lines on higher magnifications show a cleavage due to evaporation of solvents, but since a pressure is required to cause a flow across it, it was concluded that these changes are not cracks and the membrane material is almost continuous. Most of the pores may have existed within these cleavages for separation. The SEM pictures of the quaternized membrane (Figure 4c) show that these lines have more or less disappeared and a second phase with continuous pores has appeared. The SEM picture in Figure 4d shows the cross sectional view of the membrane that clearly distinguishes the polymer layer from the clay support. This shows that the polymer layer just remains adhered to the clay support and does not penetrate inside the pores of the clay support. The thickness of the polymer layer obtained was 20–25 μm.

FTIR Analysis. To confirm the presence of amine and nitro groups on the membrane surface, FTIR spectra of the unmodified, nitrated, aminated, and quaternized membrane samples are obtained using Bruker VERTEX 22 spectrometer. Infrared spectra of fresh polymer films crushed as powder samples are obtained by using 200 mg of IR spectroscopic grade KBr pellets and 1 mg of membrane sample in the range of 500–4000 cm^{-1} as shown in Figure 5. Aromatic nitro groups absorb infrared radiation in the range of 1550 and 1372 cm^{-1}. Our membrane samples show an asymmetric ArNO$_2$ stretch at 1553 cm^{-1} and a symmetric ArNO$_2$ stretch at 1344 cm^{-1} in Figure 5b. Nitroaromatic compounds show a C—N stretching vibration near 870 cm^{-1} at 854 cm^{-1} for our nitrated membrane. Salts of primary amine groups show strong, broad absorption between 3000 and 2800 cm^{-1} arising from asymmetrical and symmetrical stretching in NH$_3^+$ group. The absorption peak of the C—N stretch of primary amines lies at 1369 cm^{-1} that has been clearly shown in the aminated membranes. It can also be seen that the peaks for the nitro groups have disappeared in the FTIR spectrum of aminated membrane. It is known that the quaternary ammonium salts do not show any absorption in the IR region, but a high AEC obtained for these membranes shows presence of quaternary ammonium ions.

Ion Exchange Capacity. Ion exchange capacity of the quaternized membrane has been determined using a procedure given by the ASTM standards[31] and is found to be 2.58 mequiv/g confirming that the membrane obtained is a strong
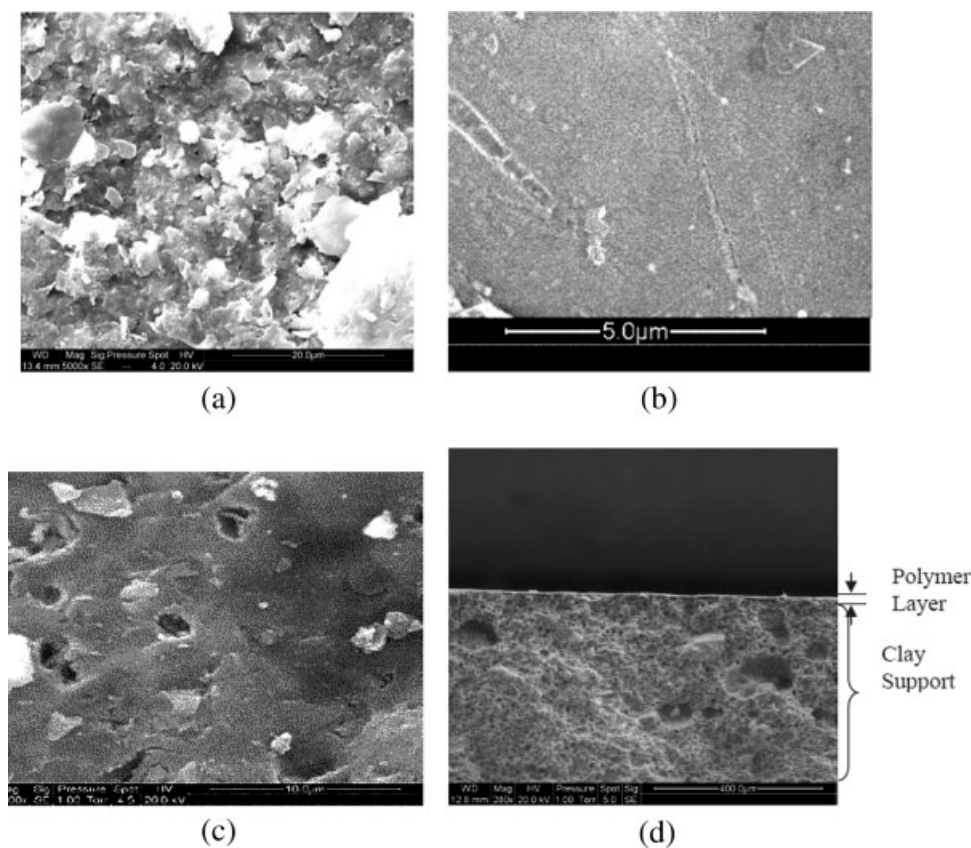
Figure 4. SEM pictures of (a) clay support (b) unmodified membrane (c) quaternized membrane (d) cross-sectional view of polymer layer on clay support.

anion exchange type and is therefore, suitable for the eletro-dialysis application.

Current Voltage Characteristic and Ionic Conductivity. The current voltage characteristics of a membrane are obtained to find the limiting current density below which the membrane could successfully operate. It is seen that within the range of voltage applied, the voltage drop increases linearly with the applied current density indicating ohmic behavior except that the straight line does not pass through the origin. The I–V curve obtained for the composite anion exchange membrane in Figure 6 shows a voltage drop of 1.15 V across the membrane at zero current density, as has been indicated by the intercept of the straight line drawn through the curve. This is the overall electrode potential drop, commonly known as the decomposition voltage. The decomposition voltage has been defined as the potential developed at the electrodes primarily due to the electrochemical reactions that are necessary for the passage of direct current through the membrane sample.[33]

We have found the conductivity of the membrane to be 1.99 mS/cm that is comparable to the results reported.[33]

Contact Angle Measurement. The contact angle of the water on the membranes (unmodified, nitrated, aminated, and quaternized) was measured using a Goniometer. The average contact angle for the unmodified membrane was found to be 77.13°, whereas it was 73.5° and 48.7° for nitrated and aminated membranes, respectively. It is evident from the contact angle measurement data that the contact angle decreased on modification confirming the increase of hydrophilicity. The contact angle for the quaternized membrane could not be measured because of the complete absorption of water that further explains the increase in hydrophilicity of the membrane on quaternization.

Equilibrium Water Content. The swelling behavior of the membranes is investigated in terms of water content, and it was determined for both unmodified and modified polystyrene membranes reported in this work. For this, the polymer film was immersed in distilled water for 24 h, and the wet film was weighed after wiping off the excess water on its surface with a filter paper. The polymer film was then dried at a fixed temperature of 75°C until a constant weight was obtained. The mass of the water lost by this procedure is termed as unbound moisture. The remaining water present in the film is called the bound moisture that is very difficult to remove. Based on the above weight taken, the water content for polymer and quaternized membrane is found to be 1% and 20.1%, respectively.

Effect of operating conditions on membrane performance

We have carried out electrolysis of sodium chloride to produce sodium hydroxide and chlorine by selective removal of chloride ions using anion exchange membranes. With anion
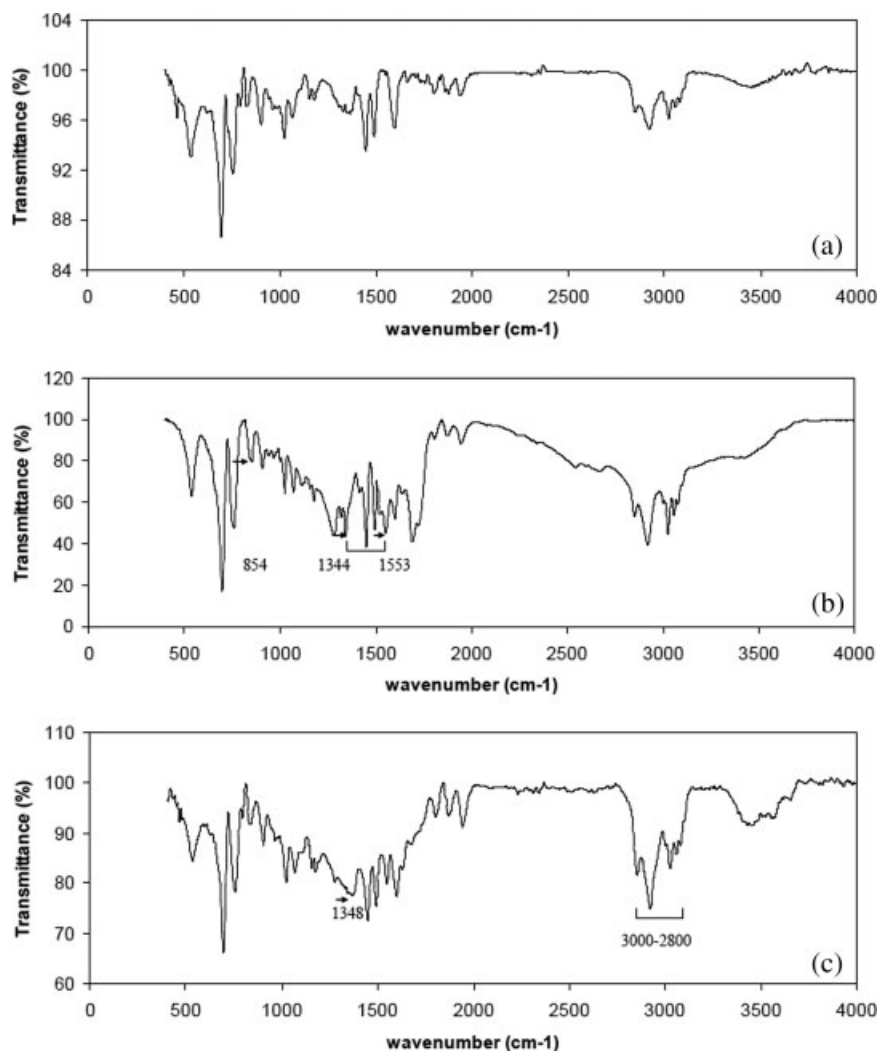
Figure 5. FTIR Spectra of (a) unmodified membrane (b) nitrated membrane (c) aminated polystyrene membrane.
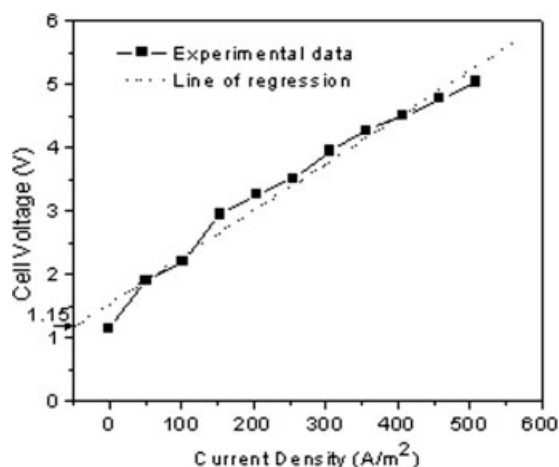

Figure 6. I–V characteristics of the anion exchange membrane (AEM).

A dotted regression line has been drawn through the data points with a slope 0.00736 and intercept of 1.15 V. The decomposition voltage of 1.15 V is indicated by the intercept at zero current density obtained by the extrapolation of this straight line drawn through the curve.

exchange membrane, the chloride ion Cl^- as well as OH^- both can be transported through the membrane capillaries. To ensure the selectivity of the membrane to chloride ions and little leakage of hydroxyl ions, we have carried out electrolysis of HCl (0.55 N, initial concentration) at 254.6 A/m^2 with same concentration on either side of the membrane. Electrolysis experiments can be represented as:

Anode | HCl (aq) (c') | Membrane | HCl (aq) (c'') | Cathode, where $c' = c'' = 0.55$ N.

The catholyte concentration was measured with time, and it was found that there was a fall in the concentration of HCl and an equivalent rise in the anolyte as shown in Figure 7. Similar experiments have been conducted with 0.6 N (initial concentration) solution of NaOH on either side of the membrane. Electrolysis experiment can be represented as:

Anode | NaOH (aq) (c') | Membrane | NaOH (aq) (c'') | Cathode, where $c' = c'' = 0.6$ N.

It was found that NaOH concentration fell initially and remained nearly constant for the rest of experimentation. This confirmed that there was little leakage of hydroxyl ion through the membrane. However, a small leakage of H^+ ions cannot be negated and may as well cause a fall in efficiency.
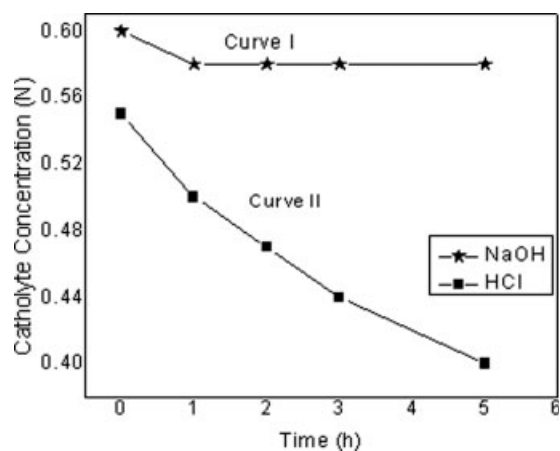
Figure 7. Curve I is for the case where both catholyte and anolyte have been filled with 0.6 N NaOH concentration, and indicates that the concentration of OH$^-$ ion remains nearly constant in the catholyte.

Curve II is when both chambers are filled with 0.55 N HCl and shows a fall in the concentration of HCl in the catholyte due to the selective movement of Cl$^-$ ions through the membrane.

Our experiments illustrate that for such a high current efficiency obtained, the dominant factor in current movement is the transport of chloride ions through the membrane.

The performance of the membrane has been evaluated in terms of current efficiency and energy consumption for the production of sodium hydroxide. The former is a measure of the fraction of current carried by chloride ions through the anion exchange membrane. The most important operating parameters that affect the current efficiency are current, flow rate of solutions, and salt (catholyte) concentration. The effect of these parameters has been studied in this work to evaluate the performance of the membrane. The same membrane has been used throughout the experiments carried out to evaluate
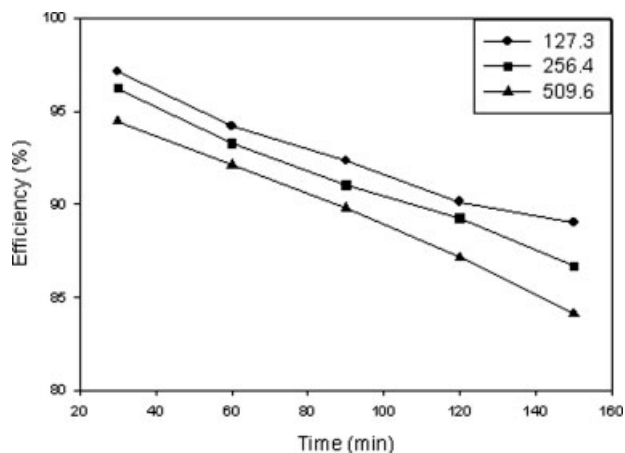

Figure 9. Variation of current efficiency for AEM with time at different salt concentrations, N (current density = 254 A/m^2, flow rate = 66 ml/min, HCl concentration 0.5 N, temperature = 25°C).

the effect of these parameters. When the experiments were performed to determine influence of one parameter, the other variables were kept constant at operating base case conditions of 4.2 N NaCl (catholyte), 0.5 N HCl (anolyte), 254.6 A/m^2 of current density, and a circulation rate of 66 ml/min.

In Figure 8, the effect of current density on the current efficiency is shown at standard conditions of circulation rate of 66 ml/min, salt (catholyte) concentration of 4.2 N NaCl, and initial (anolyte) HCl concentration of 0.5 N. From this figure, it is observed that there is a slight decrease in current efficiency at higher current densities. The fall in efficiency is more at higher current density (509 A/m^2) as reported earlier by Tzanetakis et al.,[18] where it has been indicated that the higher current densities might be close to the limiting current for the membrane though it is not evident from the I–V curve. Moreover, as we have confirmed through additional experiments (see Figure 7) that there is little leakage of the hydroxyl ion and chloride ion selectively passes.

Figure 8. Variation of current efficiency for AEM with time at different current densities, A/m^2 (salt concentration = 4.2 N, flow rate = 66 ml/min, HCl concentration 0.5 N, temperature = 25°C).
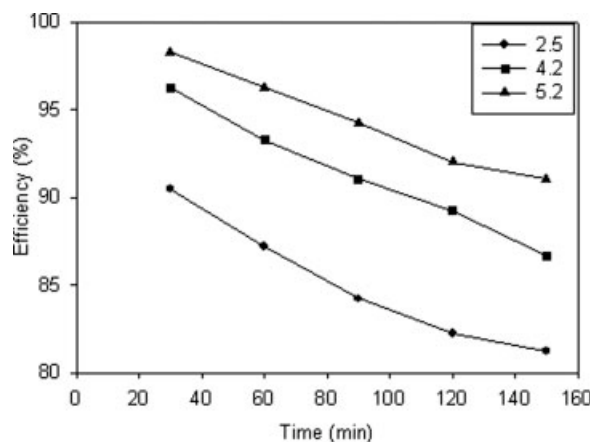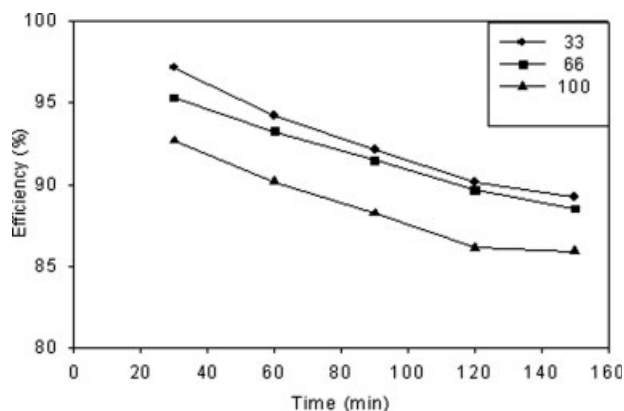

Figure 10. Variation of current efficiency for AEM with time at different circulation rates, ml/min (current density = 254 A/m^2, salt concentration = 4.2 N, HCl concentration 0.5 N, temperature = 25°C).

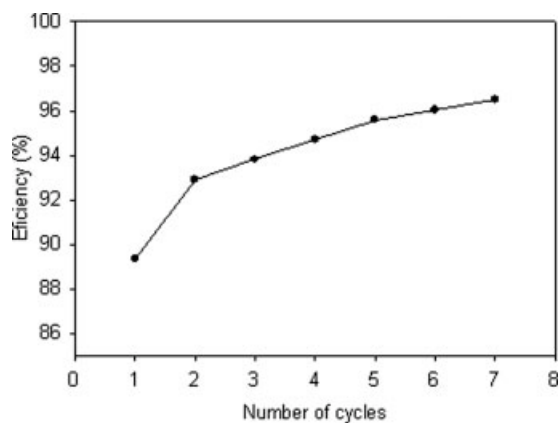**Table 1. Overall Performance of the Anion Exchange Membrane**

Run	Flow Rate (ml/min)	Current Density (A/m^2)	NaCl (N)	HCl (N)	Cell Voltage (V)	Current Efficiency (%)	Energy Consumption (kWh/mol)
1	33	254.6	4.2	0.5	4.52	92.56	0.130
2	66	254.6	4.2	0.5	4.30	91.62	0.133
3	100	254.6	4.2	0.5	4.52	88.63	0.138
4	66	254.6	2.5	0.5	4.54	85.07	0.146
5	66	254.6	5.2	0.5	4.50	96.5	0.1216
6	66	127.3	4.2	0.5	4.54	92.5	0.125
7	66	254.6	4.2	0.5	4.56	92.56	0.133
8	66	509.2	4.2	0.5	4.62	89.52	0.139

Figure 9 shows the effect of the salt concentration on the current efficiency that clearly shows that the current efficiency increases with increase in salt concentration. The prime reason for such a trend is that increase in salt concentration increases the driving force (concentration gradient) for the movement of chloride ions. Thus, the salt concentration ideally should be high[19] so as to obtain higher current efficiency and low energy consumption. The influence of flow rates on current efficiency for the anion exchange membrane (see Figure 10) shows that the current efficiencies slightly decreased at higher circulation rates. This may have been due to the transport behavior associated with gas evolution that is not the rate-determining step in the narrow cell channel at low flow rates.[19] There is a slight increase in the energy requirements due to this at low flow rates.

The maximum current efficiency is found to be 96.5% and corresponding power consumption to be 0.1216 kWh/mol at 254 A/m^2, 5.2 N, and 66 ml/min. To compare the performance of our membrane to the commercially available membranes, Nafion 117 (cation exchange membrane)[17] and Pall R 1030 (anion exchange membrane),[17] we have calculated the energy consumed by these for the electrolysis of sodium sulfate at almost similar operating conditions (500 A/m^2, 2.0 M) as ours. The current efficiency and energy consumption obtained for Nafion membrane was found to be 71.9% and 0.166 kWh/mol, respectively. For similar operating conditions (509 A/m^2, 2.5 M), we have obtained a higher current efficiency of about 87% and a lower energy consumption of about 0.143 kWh/mol as compared to the Nafion membrane.

Also, a much lower current efficiency is obtained for the Pall R 1030 membrane (80–62%) at similar operating conditions.[17] The cell voltage, 4.50 V obtained in our work is also comparable to Nafion membrane, 4.45 V. We have tabulated the data on energy consumption, current efficiency, and cell voltage for all the parameters studied here in Table 1.

The freshly prepared membrane has a lower current efficiency of around 89% as seen in Figure 11. We placed the membrane in the experimental setup and operated the cell for 2 h at room temperature with catholyte chamber having brine solution (concentration 4.2 N). It was then shutdown for 24 h and this constituted one cycle. The next day, the membrane was subjected to second cycle, and the average current efficiency over the 2 h experiment was evaluated. This was repeated till a constant efficiency was obtained. With repeated experiments, it was found that the efficiency of the membrane increased from first cycle (89%) to seventh cycle (96.5%), after which it became constant. This experiment suggests that all the charges on the membrane pores were initially not active and some ions were trapped inside the membrane. The electrolysis of NaCl under the flow of current regenerated all the inactive groups on the membrane pores and also released the trapped ions, thus increasing the membrane efficiency. This shows that the membrane requires a conditioning of about 7–8 cycles before it starts to give a constant efficiency. It is also evident that with the increase in number of cycles, the membrane retains its selectivity. We have conducted the experiments continuously for over 3 months and noticed no appreciable change in the membrane efficiency.

Conclusion

In this work, we have carried out electrolysis of sodium chloride by using a cross-linked polystyrene anion exchange composite membrane that allows selective movement of the chloride ions and little leakage of hydroxyl ions through it. This composite membrane has been prepared by first preparing polymer syrup of styrene/DVB using a dual initiator system (AIBN, BPO, and DMA) and subsequently coating it on a clay support. The membrane so prepared is homogeneously charged by nitration reaction followed by amination and quaternization. The performance of the membrane has been evaluated in terms of current efficiency and power consumption and the effect of current density, concentration of the solute, and circulation rate on these has been determined. The maximum current efficiency and the power consumption are found to be 96.5% and 0.1216 kWh/mol, respectively. The performance of the membranes has been compared to the commercially available ones (Nafion and Pall R 1030 membrane) and

Figure 11. Variation of current efficiency with number of experimental cycles.

A cycle is defined as a 2-h experimental run in 24 h.

it was found that we have obtained an average current efficiency of about 87% and a power consumption of about 0.143 kWh/mol, which are more than that of Nafion membrane (71.9%, 0.166 kWh/mol) and Pall R 1030 membrane (80–62%) at almost similar operating conditions (509 A/m^2, 2.5 M). The membrane exhibits very low power consumption indicating its viability for commercial electrodialysis applications.

Literature Cited

1. Strathmann H. Electrodialysis and related processes. In: Noble RD, Stern SA, editors. *Membrane Separation Technology-Principle and Applications*. Amsterdam: Elsevier Science, 1995:214–278.

2. Ortiz JM, Sotoca JA, Exposito E, Gallud F, Garcia VG, Montiel V, Aldaz A. Brackish water desalination by electrodialysis: batch recirculation operation modeling. *J Membr Sci*. 2005;252:65–75.

3. Rakib M, Moçotéguy PH, Viers PH, Petit E, Durand G. Behavior of Nafion 350 membrane in sodium sulfate electrochemical splitting: continuous process modeling and pilot scale tests. *J Appl Electrochem*. 1999;29:1439–1444.

4. Faverjon F, Durand G, Rakib M. Regeneration of hydrochloric acid and sodium hydroxide from purified sodium chloride by membrane electrolysis using a hydrogen diffusion anode-membrane assembly. *J Membr Sci*. 2006;284:223–330.

5. Nagarale RK, Gohil GS, Shahi VK. Recent developments on ion-exchange membranes and electro-membrane processes. *Adv Colloid Interface Sci*. 2006;119:97–130.

6. Ahmed MI, Chang HT, Selman JR, Holsen TM. Electrochemical chromic acid regeneration process: fitting of membrane transport properties. *J Membr Sci*. 2002;197:63–74.

7. Korngold E, Aronov L, Belayev N, Kock K. Electrodialysis with brine solutions oversaturated with calcium sulfate. *Desalination* 2005;172:63–75.

8. Bazinet L, Farias MA. Effect of calcium and carbonate concentrations on cationic membrane fouling during electrodialysis. *J Colloid Interface Sci*. 2005;281:188–196.

9. Quemeneur F, Schlumpf JP, Firdaous L, Stitou M, Maleriat JP, Jaouen P. Modification of ionic composition of natural salt-waters by electrodialysis. *Desalination* 2002;149:411–416.

10. Marian T. Electrodialytic desalination and concentration of coal-mine brine. *Desalination* 2004;162:355–359.

11. Mohammadi T, Moheb A, Sadrzadeh M, Razmi A. Separation of copper by electrodialysis using Taguchi experimental design. *Desalination* 2004;169:21–31.

12. Mohammadi T, Razmi A, Sadrzadeh M. Effect of operating parameters on Pb^{2+} seperation from wastewater using electrodialysis. *Desalination* 2004;167:379–385.

13. Tor A, Buyukerkek T, Cengeloglu Y, Ersoz M. Simultaneous recovery of Cr (III) and Cr(VI) from the aqueous phase with ion-exchange membranes. *Desalination* 2004;171:233–241.

14. Costa RFD, Rodrigues MAS, Ferreira JZ. Transport of trivalent and hexavalent chromium through different ion-selective membranes in acidic aqueous media. *Sep Sci Technol*. 1998;33:1135–1143.

15. Barmashenko V, Jorissen J. Recovery of chlorine from dilute hydrochloric acid by electrolysis using a chlorine resistant anion exchange membrane. *J Appl Electrochem*. 2005;35:1311–1319.

16. Leon CP, Field RW. Comparison of anionic membranes used to concentrate nitric acid to beyond the azeotropic mixture. *J Membr Sci*. 2000;171:67–77.

17. Tzanetakis N, Taama WM, Scott K. Comparative performance of ion exchange membranes for salt splitting. *Filtr Sep*. 2003;40:33–39.

18. Tzanetakis N, Varcoe J, Slade RS, Scott K. Salt splitting with radiation-grafted PVDF anion exchange membrane. *Electrochem Commun*. 2003;5:115–119.

19. Tzanetakis N, Varcoe JR, Slade RCT, Scott K. Radiation-grafted PVDF anion exchange membrane for salt splitting. *Desalination* 2005;174:257–265.

20. Choi YJ, Park JM, Yeon KH, Moon SH. Electrochemical characterization of poly (vinyl alcohol)/formyl methyl pyridinium (PVA-FP) anion-exchange membranes. *J Membr Sci*. 2005;250:295–304.

21. Wycisk R, Pintauro PN. Sulfonated polyphosphazene ion-exchange membranes. *J Membr Sci*. 1996;119:155–160.

22. Xu T, Yang W. Fundamental studies on a novel series of bipolar membranes prepared from poly (2,6-dimethyl-1,4-phenylene oxide) (PPO). I. Effect of anion exchange layers on I-V curves of bipolar membranes. *J Membr Sci*. 2004;238:123–129.

23. Shin J-P, Chang B-J, Kim J-H, Lee S-B, Suh DH. Sulfonated polystyrene/PTFE composite membranes. *J Membr Sci*. 2005;251:247–254.

24. Kreuer KD. On the development of proton conducting polymer membranes for hydrogen and methanol fuel cells. *J Membr Sci*. 2001;185:29–39.

25. Amado, Franco DR, Gondran E, Ferreira Jane Z, Rodrigues Marco AS, Ferreira Carlos A. Synthesis and characterization of high impact polystyrene/polyaniline composite membranes for electrodialysis. *J Membr Sci*. 2004;234:139–145.

26. Nasef MM, Saidi H. Preparation of crosslinked cation exchange membranes by radiation grafting of styrene/divinylbenzene mixtures onto PFA films. *J Membr Sci*. 2003;216:27–38.

27. Eto R, Tanioka A. Characteristic proton transport through composite membrane composed of quaternary-amino poly (sulfone) and sulfonated co-poly (styrene and divinylbenzene). *J Colloid Interface Sci*. 1998;200:59–65.

28. Gues ER, Exter MJ, Bekkum HV. Synthesis and characterization of zeolite (MFI) membranes on porous ceramic support. *J Chem Soc Faraday Trans*. 1992;88:3101–3109.

29. Joo J, Hyeon T, Hyeon-Lee J. Fabrication of novel mesoporous dimethylsiloxane-incorporated silicas. *Chem Commun*. 2000;21:1487–1488.

30. Sinha S, Jayaswal S, Kumar A. Preparation of high capacity weak base polymethylmethacrylate ethylene glycoldimethacrylate (PMMA-EGDM) copolymer anion exchange resin by modification using No$_x$. *J Appl Polym Sci*. 2003;89:1991–1999.

31. IS: 7330-1988, Indian Standard, Methods of sampling and test for ion-exchange resins (first revision), 1989, 1–14.

32. Barragan VM, Bauza CR. Current-voltage curves for ion-exchange membranes: a method for determining the limiting current density. *J Colloid Interface Sci*. 1998;205:365–373.

33. Wallace RA, Ampaya JP. Transport within ion-exchange membranes. *Desalination* 1974;14:121–134.

34. Kumar M, Agarwal S, Pugazhenthi G, Shukla A, Kumar A. Preparation and characterization of iron salt embedded electrodialysis Anal-cime-C zeolite clay composite membrane. *J Membr Sci*. 2006;275:110–118.

35. Elvy SB, Dennis GR, Loo-Teck NG, Catalyst-accelerator method for preparation of wood-polymer composite at ambient temperature. *J Appl Polym Sci*. 1995;56:591–595.

36. Choi YJ, Kang MS, Moon SH. A new preparation method for cation-exchange membrane using monomer sorption into reinforcing materials. *Desalination* 2002;146:287–291.