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S. Seetharaman^a, S. Ravichandran^a, D. J. Davidson^a, S. Vasudevan^a & G. Sozhan^a

^a Electro-Inorganic Chemicals Division, Central Electro Chemical Research Institute, Karaikudi, India

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Polyvinyl Alcohol Based Membrane as Separator for Alkaline Water Electrolyzer

S. Seetharaman, S. Ravichandran, D. J. Davidson, S. Vasudevan, and G. Sozhan

Electro-Inorganic Chemicals Division, Central Electro Chemical Research Institute, Karaikudi, India

Alkaline water electrolyzer employs nickel based electrodes and asbestos cloth diaphragm. Asbestos is considered as carcinogenic. In order to limit the usage of an asbestos diaphragm, a separator membrane was synthesized from polyvinyl alcohol, glutaraldehyde, *N,N,N',N'*-Tetramethyl hexane-1,6 diamine, and titanium dioxide. The role of *N,N,N',N'*-Tetramethyl hexane-1,6 diamine is to improve the dimensional stability of the membrane. The fabricated membranes were characterized by FT-IR, TGA, DSC, and SEM techniques. These fabricated membranes effectively improved the production of hydrogen, more so than the conventional asbestos diaphragm. A current density of 0.38 A/cm² was achieved when operating the cell with 5 wt% KOH at 30°C at 2 V. Polyvinyl alcohol composite membranes, besides being cheap, showed good electrochemical performance at ambient temperature and pressure than most commercial separator membranes. This comparison gives some insight as to future separator membrane design objectives.

Keywords alkaline electrolyzer; PVA; separator membrane; zero gap electrolyzer

INTRODUCTION

Hydrogen production by electrolysis in alkaline electrolyzer is a well-established technology; small commercial units cost roughly 5,000 € kW⁻¹ (1). Due to economic consideration, hydrogen production plants are typically medium sized (0.5–5 MW). The power consumption level for small advanced alkaline membrane electrolyzer (100 kW) is comparable to both energy consumption and investment cost of commercial plants. The limited market of 100 kW units is the disadvantage. Some of the strategic advantages of the alkaline electrolyzer include use of platinum free electrodes, and operating capability at low current densities less than 0.4 A/cm². One major disadvantage is the presence of atmospheric CO that should be scrubbed before air is pumped into the cathode: note that the oxygen in the air is needed to support the current at the cathode (2). In an alkaline electrolyzer, the diaphragm is made of asbestos, but this material is hazardous for

health, causing cancer, and in some countries its use is even banned.

During the last 50 years, anion exchange membranes have evolved from laboratory tool to industrial product with significant technical and commercial impacts. Soon after the early days of the development of polymer membranes, several limitations were recognized. For example, Sata et al., reported (3–5) a copolymer synthesized from chloromethylstyrene and divinylbenzene. That turned out to be a carcinogen. Similarly, chloromethyl methyl ether, also a potent carcinogen, has been restricted since 1970 (6). Asbestos separators made using naturally occurring mineral, failed due to mechanical stresses induced by the formation of gas pockets within the separator (7). Polyanionic acid (PAM) is based on an inorganic cationic ion-exchange material (8). This group, preferred over zirconium phosphate, zirconium oxide, tin oxide, bismuth oxide, and lead sulfate (9) is chemically unstable in alkaline medium, therefore, its survivability in an alkaline electrolyzer is questionable.

Polybenzimidazoles (PBI) are complex polymers, and most imidazole derivatives are not readily attacked by oxidizing agents and have high melting points and excellent stabilities at elevated temperatures (10); however, they do not withstand electrolysis conditions in alkaline medium. Furthermore, diaphragms of porous sinter material for alkaline water electrolysis have been developed, but great disadvantage exists due to its electron conducting property, and high manufacturing cost (11). Porous sheets of Teflon have been made hydrophilic through in situ impregnation with potassium titanate fibers (12), but this could not be formed into matrices without a binder. The latter matrices proved to be stable over 2300 hours at 120°C. Nafion membranes of two different equivalent weights were evaluated as a separator in an alkaline electrolyzer with nickel screen electrodes in both KOH and NaOH electrolytes over the concentration range of 10–30 wt%, and it showed maximum ionic conductance only under certain restricted conditions, and were quite expensive (13).

Polysulfones are organic polymers with excellent thermal, oxidative, and hydrolytic stability. When prepared

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Address correspondence to S. Seetharaman, Electro-Inorganic Chemicals Division, Central Electro Chemical Research Institute, Karaikudi – 630 006, India. E-mail: sram69@gmail.com

as fibers, their maximum service temperatures in water electrolyzer were less than expected. The hydrophobicity of the material was a serious problem (14,15) Gulzow (16) has hypothesized that some research groups stopped working on Alkaline Fuel cell (AFC) electrodes and stopped the development of the falling film cell. Hall (17) has studied nickel anodes in alkaline water electrolysis and concluded that nickel could be used more efficiently, primarily by increasing its electrochemically-active surface areas, particularly those based on mixed metal oxides showed great promise. Stojic et al. (18) compared alkaline and proton exchange membrane (PEM) electrolyzer and concluded that the alkaline electrolyzer had higher Faraday efficiency than the PEM electrolyzer, while less energy was required for the PEM electrolyzer compared to the alkaline one.

Varcoe et al. (19) prepared the Alkaline Anion Exchange Membrane (AAEM) –Membrane Electrode Assembly that did not contain any metal cation M^{n+} (K^+ , Na^+) ions to avoid the carbonate precipitation problem and to improve the long-term operation stability. They (20–22) developed and characterized the quaternary ammonium, the counter ions bound to the polymer backbone radiation grafted ETFC, (20), PVDF, and FEP (21) alkaline anion exchange membrane (AAEM). The addition of a ceramic filler into polymer matrix was attempted to reduce the glass transition temperature (T_g) and the crystallinity of the polymer, and also allow to increase the amorphous phases of polymer matrix and increasing the ionic conductivity. Various ceramic filler such as Al_2O_3 (23), TiO_2 (24), SiO_2 (25), ZrO_2 (26) improved the ionic conductivity.

In this work we report the performance of synthesized PVA-based composite membranes which showed better thermal and electrochemical characteristics. They contributed to hydroxyl ion conduction in alkaline electrolyzer. The impetus for this attempt has been the design of a newer class of membranes that show better conductivity; besides non-precious metals can be used as catalyst. They are also durable in a basic medium, and may not demand carcinogenic conditions.

EXPERIMENTAL

Materials

PVA-Molecular weight = 85,000/146,000, glutaraldehyde (Glu; 25 wt% water solution) and titanium oxide were obtained from Merck. *N,N,N',N'*-tetramethyl hexane 1,6 diamine was obtained from SRL Chemicals. They were used as received without further purification.

Preparation of Polyvinyl Alcohol (PVA) Based Membranes

The plain PVA membranes were prepared by a simple casting procedure. A 10% solution of PVA in Glutaraldehyde

(Glu), a cross linking agent, was made by constant stirring to obtain a clear viscous solution. About 10 wt% v/v of *N,N,N',N'*-Tetramethyl hexane 1, 6 diamine, and Titanium oxide (10 wt%) were then added and the solution was mixed for 6 h at 40°C to achieve gelification. It was observed that the rate of gelification plays a critical role in the cross-linking process (26). The film was cast on a clean glass plate with the desired thickness using the Doctor Blade technique and dried at 30°C. The thickness of the wet composite polymer membrane was between 0.20 and 0.40 mm. Once formed, the membranes were activated by immersing them in a 30 wt% KOH solution for 24 h. The resulting cross-linked membranes were finally washed with water for several times. The cross linking agent is to provide increased stability in aqueous solutions and the amination provides exchange sites.

Conductivity and Transport Property Measurements

Conductivity measurements were made for the alkaline composite membrane by the impedance technique using a two-probe method, under potentiostatic conditions using 5-mV/sec in the 1-Hz to 1-MHz frequency range. The alkaline membranes (5 cm × 5 cm) were sandwiched between stainless steel, ion blocking electrodes, each of the surface area of the electrode being 1.0 cm². The conductivity (σ) of the samples in the transverse direction was calculated from the impedance data, using the relationship $\sigma = L/RA$, where A is the area of the electrodes, L and R are the thickness and bulk resistance of the films respectively, and R was derived from the low intersection of the high frequency semi-circle on a complex impedance plane with the $Re(Z)$ axis, where Re refers to “Real” in the complex impedance plane. Prior to the conductivity measurements, membranes were immersed in deionized water for 24 h to attain hydration equilibrium. The ionic transport numbers of the alkaline anion exchange membrane were examined using a dynamic Hittorf’s method (27) at 30°C.

Swelling

The membrane swelling characteristics were determined by measuring the change of the membrane geometrical area upon equilibrating the membranes in water at room temperature for 4 h. The swelling ratio was calculated by the following equation:

$$\text{Swelling (\%)} = \frac{S_{\text{Wet}} - S_{\text{Dry}}}{S_{\text{Dry}}} \times 100$$

where, S_{dry} and S_{wet} are the area of dry and wet samples of the plain area, respectively.

Water Uptake

Water uptake (W_{wd}) was determined as the difference in weight (W) between the dried and the swollen membranes. The mass of the dried membrane was measured (W_{dry}) and then the membrane was immersed in deionized water for 4 h. Next, the membrane was removed from water, wiped with blotting paper, and weighed again to obtain the wet mass (W_{wet}). W_{wd} was calculated using formula:

$$W_{wd} (\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100$$

Electrolysis

Experiments were performed using two compartment arrangements as shown in Fig. 1 with a sintered, porous nickel as the electrode materials and synthesized membrane as separator. Electrolysis was performed at various temperatures from 30°C to 80°C at 5, 10, and 30% KOH concentrations. The resulting current density versus voltage was recorded. The experiments were repeated thrice to check for reproducibility. The membrane was in a single cell fixture for the electrolysis test. To optimize energy consumption due to reduced electrode interfacial distance we carried out in the experiment zero gap electrolyzer. The gap between the electrodes is the distance that the ions have to travel in the electrolyte. A smaller gap has the advantage of less resistance for ionic transportation. The electrolyte flow determines the mass transport in the electrolyte. To enhance mass transfer, the electrolyte was circulated.

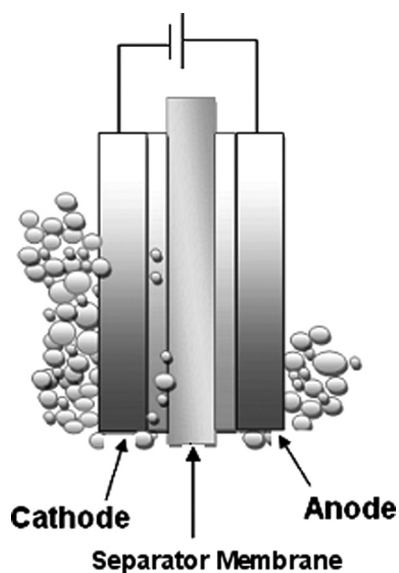


FIG. 1. Schematic of alkaline electrolyzer.

Characterization

Scanning electron microscopy (SEM) images were obtained with a Hitachi S-3000H electron microscope. The Fourier transform infrared (FTIR) spectra were recorded on a Thermo electron Corporation Nexus 670 System FTIR spectrophotometer that ranged 4,000–400 cm^{-1} . Thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) were obtained with TA Instruments SDT Q600 V8.3 operated at a heating rate of 10°C in presence of nitrogen atmosphere.

RESULTS AND DISCUSSION

FT-IR Spectroscopy

The FT-IR Spectra obtained for the membrane are shown in Fig. 2. The spectrum of a typical membrane suggests the characteristic bands of PVA, Glu, aminated membrane, and TiO_2 . The FT-IR spectrum of hybrid membranes showed bands around 3430 and 2930 cm^{-1} represent O-H stretching and $-\text{CH}_2$ stretching; the band around 1420 cm^{-1} was for $-\text{CH}_3$ bending; all these bands are characteristics of PVA. The bands around 1040 cm^{-1} are due to the formation of acetal (C-O-C) group. The positions of vibration modes of all types of M-O bonds were strongly influenced by the interaction of TiO_2 with the polymer and quaternary amine. In PVA–Water spectra, the band around 3440 cm^{-1} was very broad and this may be due to water molecule bound with the terminal alcohol group. In subsequent spectra this broad peak decreased to a sharp peak due to the removal of the water molecule. The bands around 650 cm^{-1} and 2350 cm^{-1} were due to Ti-O asymmetric stretching and amine stretching. The Ti-O bond of the aminated membrane was red shifted from 1460 to 1410 cm^{-1} . This was due to the columbic

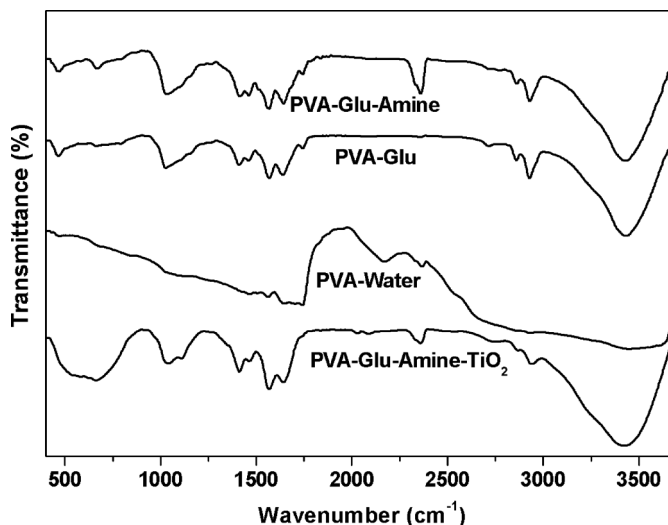


FIG. 2. FT-IR Spectra of composite membrane and its components.

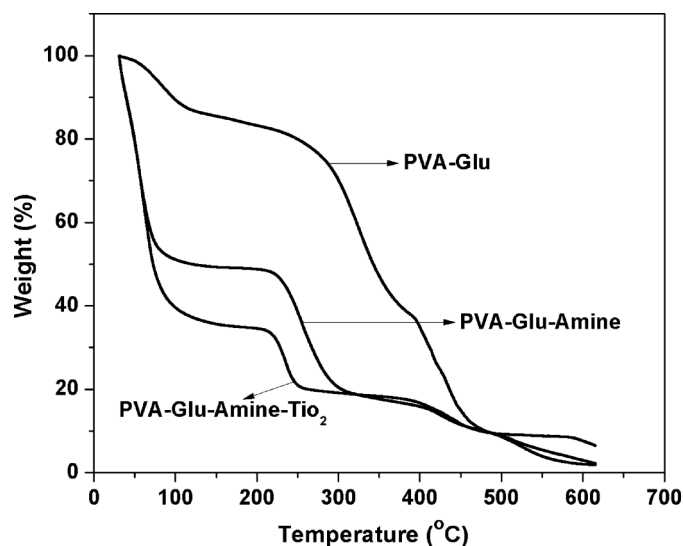


FIG. 3. TGA analysis of composite membranes in a temperature range from 0 to 700°C.

interaction between the hydroxyl group of the polyvinyl alcohol and amination.

Thermal Analysis

The data in Fig. 3 illustrates the TGA obtained for the membranes. They show three stages of degradation. The first weight loss occurred around 112°C, due to loss of the absorbed water molecule. The second weight loss in the temperature region 210–310°C was due to decomposition of polyvinyl alcohol. The third weight loss was due to decomposition of the polymer matrix. The DSC responses of the PVA membranes were presented in Fig. 4. The addition of TiO₂ into the polymer matrix

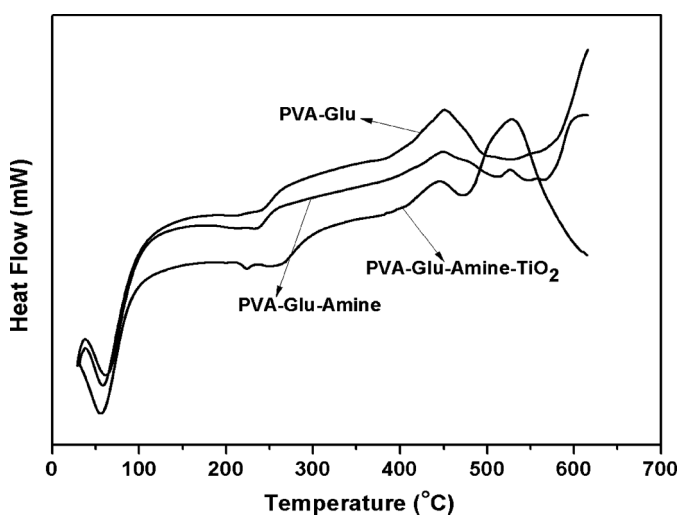


FIG. 4. DSC thermograms of composite membranes with different casting.

reduced the glass transition temperature (T_g). However, PVA is partially crystalline, exhibiting both the glass transition temperature (T_g) and melting isotherm (T_m). For pure PVA the glass transition temperature was around 90°C and melting temperature around 120°C (28). T_g of composite membranes were around 100°C which was slightly higher than that of the pure PVA. The reason for the increase in thermal stability of this membrane is due to the formation of hydrogen bonds in the polymer matrix. It was found that the degree of crystallinity is decreased as the TiO₂ was added to PVA polymer matrix. The function of the ceramic filler was to retard or inhibit the recrystallization of PVA polymer and to increase the domain of the amorphous phase and create more free volume for the mobility of the ion.

SEM

Surface morphology of the dried membrane was investigated using SEM. The results are shown in Figs. 5 and 6 for PVA-Glu-Amine-10% TiO₂ and PVA-Glu-Amine membranes. The addition of TiO₂ resulted in a modification of the composite membranes; the surface homogeneity was reduced and an extended porosity was clearly revealed. The distribution of inorganic fillers was relatively uniform in the organic matrix.

Water Uptake, Swelling, and Current Density

The water uptake and thickness plays a vital role in membrane conductivity. By increasing the thickness, the resistance increases thereby decreasing the membrane conductivity. The data, on water uptake, extent of swelling, conductivity data, and current densities for the membranes are given as Table 1. It is observed that the asbestos material exhibits lower current density due to its high

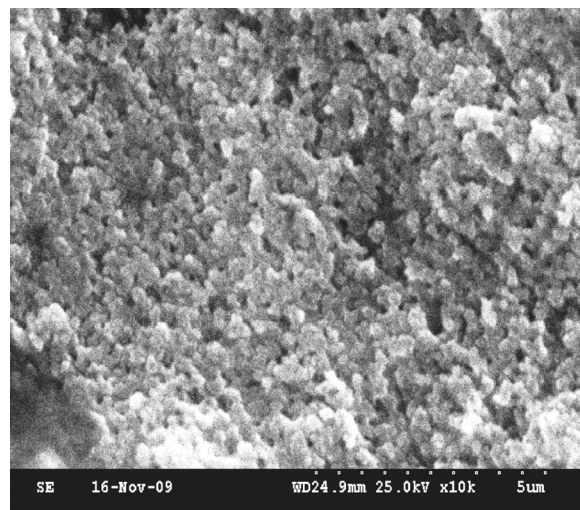


FIG. 5. SEM picture of a PVA-Glu-Amine-10 wt% TiO₂ membrane.

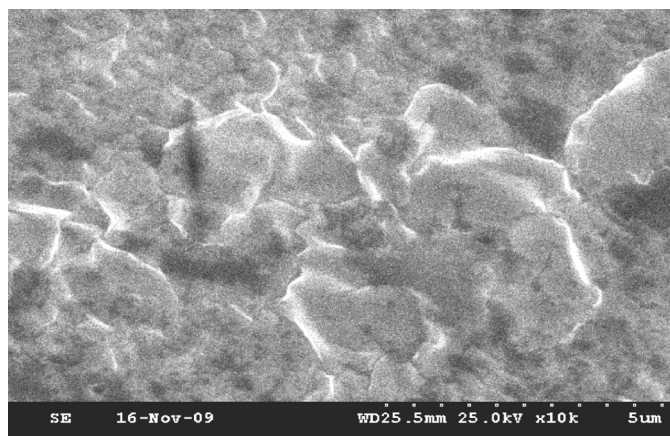


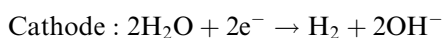
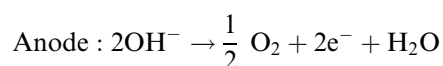
FIG. 6. SEM photographs for PVA-Glu-Amine membrane.

resistance when compared to other membranes. The current densities in Table 1 were determined at a voltage of 2 V.

Excessively high levels of water uptake can result in membrane dimensional change leading to failures in mechanical properties (29), hence the relationship between the thickness of the membrane and water uptake (%) plays a crucial role in membrane morphology.

Alkaline Water Electrolysis

Production of hydrogen by alkaline water electrolysis is a simple process with no moving parts and can be designed as a portable unit. With alkaline medium, corrosion is more easily controlled and cheaper construction medium can be used than in acidic medium. In alkaline electrolyzer, the alkaline electrolyte of approximately 30 wt% KOH was used as electrolyte (30). The following electrolytic reactions that occur on each electrode are given by:



Applying a small voltage could not set off an electrolysis current, because the applied voltage must be at least as

large as the theoretical cell voltage in order for a current to be able to flow, which could lead to the release of hydrogen at the cathode and oxygen at the anode. The differences of theoretical and experimental efficiencies are due to three main types of losses that take place and affect the hydrogen production. Activation loss that occurs at low currents, ohmic loss that takes place throughout the process, and concentration loss that is significant at high currents. The more the voltage is increased, the electrode surface are absorbing more gas until it reaches a certain saturation point where the gas pressure at the electrodes reaches the level of external air pressure and gas bubbles begin to rise at the electrodes.

It is proposed that the current density determines the rate of bubble growth and hence influences bubble coalescence on the electrode surface. Due to the very high dissolved hydrogen gas super saturation at the dense bubble growing sites, all dissolved gas is assumed to be transferred to the growing bubbles. Steady state condition is required. Next, the contour component, the electrolyte flow determines the mass transport in the electrolyte. Movement in the form of convection to circulate the electrolyte forces the sort. In general, electrochemical reactions are governed by mass transfer limitations which occur only at higher operating current densities.

Commercial membranes like PCA-70 and PCA-100 are difficult to process in alkaline water electrolysis since they cannot endure severe conditions, although they are useful in desalination applications by electrodialysis. Therefore, it was necessary at this stage to reflect on the possible utility of these composite membranes in comparison to the conventional Nafion membrane (13) and the commercial membranes PCA-70, PCA-100, and the asbestos material.

Hydrogen Production

Electrolysis was performed at various current densities from 0.1 to 0.6 A/cm² in 5 wt% KOH, since in 5 wt% the electrodes initially absorb the gases, the resultant voltage is shown in Fig. 7. The membrane had a water uptake of 44%, a thickness of 0.210 mm, and an ionic conductivity of $7.2 \times 10^{-3} \text{ Scm}^{-1}$. The effect of concentration on the cell

TABLE 1
Thickness, water uptake, swelling, conductivity, and current density values for different membranes

Membranes	Thickness [mm]	Water uptake [%]	Swelling [%]	Conductivity [S/cm]	Current density [A/cm ²] at 2 V
Asbestos	0.552	124	—	—	0.14
PCA-100	0.162	85	51	7.74×10^{-5}	0.21
PCA-70	0.134	82	44	7.29×10^{-5}	0.26
PVA-Glu- amine-Tio ₂	0.210	44	28	7.11×10^{-3}	0.38
Nafion	0.200	40	23	6.2×10^{-2}	0.40

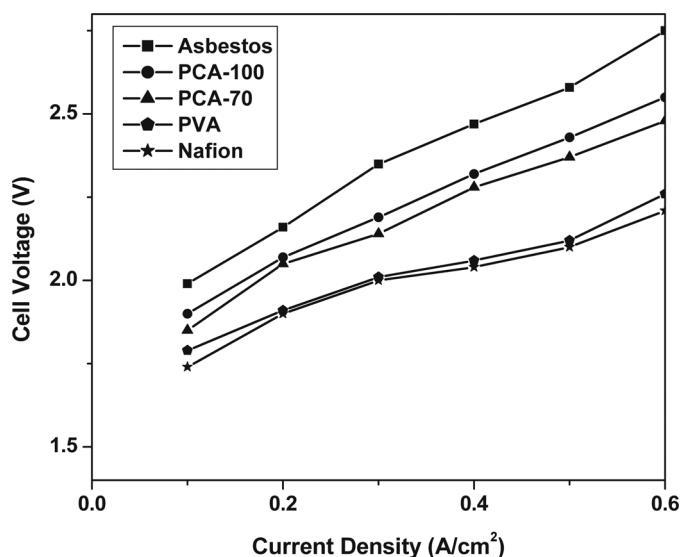


FIG. 7. Alkaline water electrolysis with 5% KOH solution for all membranes.

performance was studied by varying the KOH concentration from 5 wt% to 30 wt% is shown in Fig. 8. The effect of temperature on cell voltage with current density of 0.2 A/cm^2 in 5 wt% KOH is shown in Fig. 9.

Figure 7 shows the effect of current density on the cell performance at 2 V. It is noted that the increase in the current density is linear with the cell voltage. The error range for these measurements goes up to 4%. Initially for asbestos it is observed as 0.14 A/cm^2 , whereas PCA-100, PCA-70 shows 0.21 A/cm^2 , and 0.26 A/cm^2 respectively. In the case of the PVA membrane, it shows good response

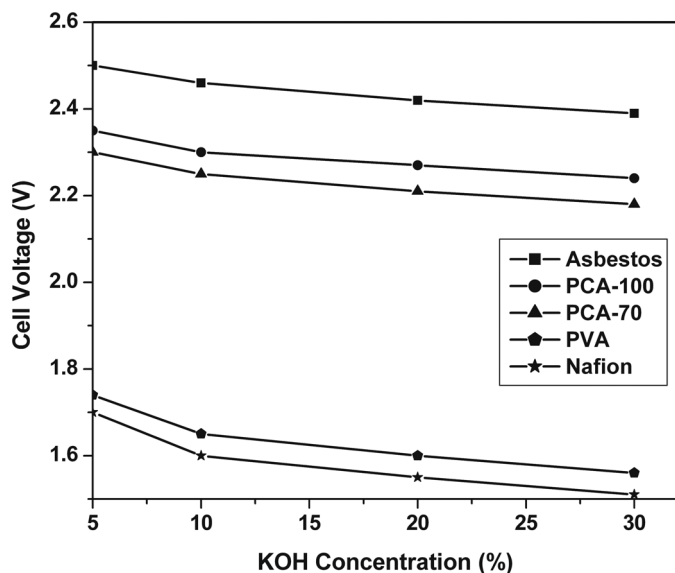


FIG. 8. Effect of KOH concentration for the all the membranes.

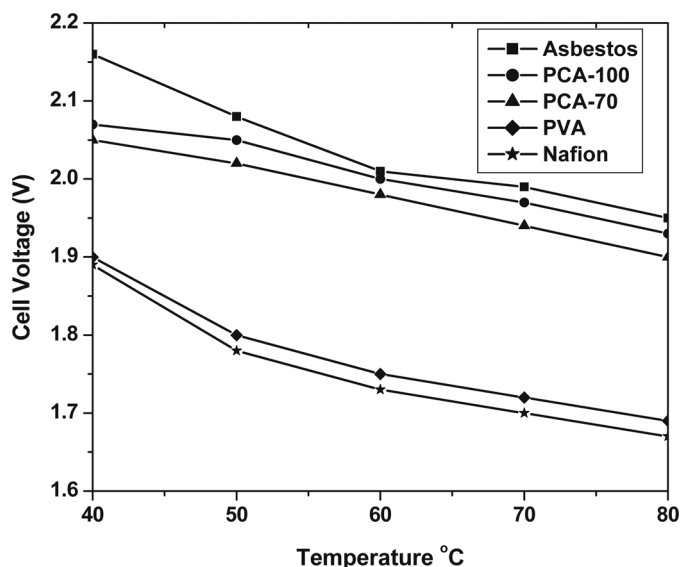


FIG. 9. Effect of temperature at 0.2 A/cm^2 for all the membranes.

of 0.38 A/cm^2 and for Nafion-117 it is observed as 0.40 A/cm^2 . In all the cases, the current density increased with voltage. The current density depends upon the membrane thickness, water uptake (%), cell hardware, conductivity, inter-electrodes distance, volume, and size of the gas bubble between the electrodes, membrane resistance electrode conductivity, and contact resistance between the current carrying components.

Figure 8 shows the effect of concentration on the cell performance from 5 – 30 wt% KOH solution. The cell voltage reached a minimum at 30 wt% KOH solution. The cell performance improved in the 30 wt% KOH than 5 wt% KOH. In all the cases, the cell voltage decreases with increase in KOH concentration. It is due to the conductivity maximum of KOH in aqueous solution at 30 wt% and at 80°C . This article aims at a composite membrane as separator, so the membrane conductivity is important. For comparison of the membrane materials, a high electrolyte concentration should be used (14).

Figure 9 presents the effect of temperature on the cell performance at 0.2 A/cm^2 and in 10 wt% KOH. The cell voltage reached a minimum at 80°C . It is also observed that the cell voltage is lower at increased temperatures. In all the cases, the cell voltage decreases with increase in temperature. This may be due to increase in reaction kinetics with temperature.

It is noted that the current consumed by the electrochemical cell increases with time for a particular voltage and this increase is due to the increase in the cell temperature. It is also found that there is a higher increase in the cell current at increased inlet temperatures. Once the cell is stabilized, that is, an appreciable amount of current density is observed, the current density is noted as a function

of voltage at constant time intervals and for the various different temperature ranges from 30°C to 80°C for the five different materials.

Asbestos materials have excessively high resistance (7), which leads to poor conductivity in the alkaline water electrolysis. In the case of PCA-100 and PCA-70, excessively high levels of water uptake, it is observed that results in membrane dimensional change leading to failures in mechanical properties.

PVA separator membrane showed similar performance comparable to Nafion 117 due to its lower thickness as well as on water uptake values. Furthermore, the addition of titanium oxide in the PVA polymer organic matrix enabled the preparation of separation membranes with a wide range of enhanced properties concerning thickness, water uptake, and current density values. Therefore, these membranes can be used in the future to make a critical evaluation of the relationship between the separator membrane properties and the alkaline water electrolysis performance.

Moreover, it was found that the ionic conductivity value exhibit a plateau when the content of the TiO₂ filler is over 10 wt%. It can be concluded that the optimum content of the TiO₂ ceramic filler for the separator membrane is about 10 wt%. However, the PVA-Glu-aminated-TiO₂ membrane indicates that the charge carriers OH⁻ ions are easy to transport in the alkaline water electrolysis.

The result of this series of the tests was that by TiO₂ addition to the casting solution a strong decrease in membrane resistance was achieved. Regarding this separator membrane, we inferred that the effect of the thermal stability dominated by the strong interaction of cross linking becomes less than by the strong interaction between ammonium groups and hydrated OH⁻ ions. On the basis of the above key developments, a prototype separator membrane completely free from noble metal catalyst is preferable to make the separator membrane for alkaline water electrolysis operations.

CONCLUSIONS

A new route for preparing a separation membrane was presented in this paper. The membranes were prepared by a straightforward casting method from polyvinyl alcohol as organic matrix and Titanium oxide as inorganic filler. In addition, electrochemical and mechanical properties were studied and found to improve with the addition of TiO₂. The resulting membrane showed good mechanical but poor thermal properties when they were swollen at 100°C. The thermal stability of the membranes were improved by cross linking using glutaraldehyde as the cross linking agent. Alkaline water electrolysis with the cross linked PVA-Glu-Amine-TiO₂ composite membranes showed appreciable improvement in the electrochemical performances at 40°C. A high current density of 0.38 A/cm² was achieved when operating the cell at 40°C. From

the economic and application point of view, the cross linked PVA-Glu-Amine-TiO₂ composite membranes can be easily mass produced without using highly carcinogenic materials. Moreover PVA is a cheap polymer material.

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