

AN EXPERIMENTAL PREPARATION OF FUEL CELL QUATERNARY POLYVINYL BENZYL CHLORIDE (QPVBCL) ALKALINE ANION EXCHANGE MEMBRANE AND INVESTIGATION OF ITS CONDUCTIVITY CHARACTERISTICS

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Abstract:-

There are different methods of preparing Quaternary polyvinyl benzyl chloride (qPVBCl) alkaline anion exchange membrane. The method which was chosen in this project is simple, relatively cheap and less time-consuming compared to the other methods. This membrane was prepared from a new polymer compound; polyvinyl benzyl chloride (PVBCl). The final membrane is a pale yellow and transparent solid, odourless, flat and smooth with the absence of air bubbles. Through-plane conductivity measurement was performed on qPVBCl alkaline anion exchange membrane and the result showed that the membrane's conductivity rose from 1.35×10^{-2} S/cm to 1.57×10^{-2} S/cm as temperature increased from 21°C to 61°C. It also showed that the conductivity of the membrane was virtually constant at different periods of time at 61°C. The conductivity was found to be excellent in the fully hydrated condition at optimum temperature 61°C. These results give evidence that the ultimate qPVBCl Alkaline Anion Exchange membrane has enormous potentials for use in alkaline fuel cell.

Key-words:- *qPVBCl alkaline anion exchange membrane; Conductivity; Conductivity measurement; Alkaline fuel cell.*

1. INTRODUCTION

1.1 Fuel Cells

In this present century, climate change, energy insecurity, the ongoing demand of energy and the wide range utilization of carbon dioxide (CO₂) from fossil fuels have been a great challenge to several countries in the world. The incorporation of renewable energy sources would help in curtailing these issues because they are very abundant, sustainable with few or zero CO₂ emissions [1]. Highly sufficient investment in these freshly advanced energy sources is necessary in order to reinforce the energy security and minimize the overdependence of fossil fuel energy sources in a few years' time [2]. Fuel cells, as a result of their unique benefits in effectively converting energy with minimum or without CO₂ emissions, fulfill all the recipes for applications in stationary and mobile devices. They possess distinct excellent efficiency over thermal engines and batteries and they lack restrictions to the heat engine thermodynamic limitations e.g. the Carnot efficiency because the generation of heat energy and mechanical work from intermediate reactions which usually takes place in ordinary methods of power supply are prevented. In the future, fuel cells are among the forthcoming renewable energy source technologies for the generation of clean energy. Their configurations are simple with few components and their operations are quieter and more environmentally benign. Therefore, due to its special characteristics and attributes, fuel cells are identified as a novel energy generating source with utmost attention [3].

There are different types of fuel cells which include alkaline fuel cells, polymer electrolyte membrane fuel cells, phosphoric acid fuel cells, molten carbonate fuel cells, solid oxide fuel cells, direct methanol fuel cells etc.

1.2 Alkaline Anion Exchange Membrane Fuel Cells

Among alkaline fuel cell types, alkaline anion exchange membrane fuel cells are one of the most efficient fuel cells. They enable the use of non-precious metal catalysts thereby minimizing cost. Alkaline anion exchange membranes are developed in order to curtail the challenges observed in the use of polymer exchange membrane fuel cells. Alkaline anion exchange membranes eradicate the issues of alkaline electrolyte (electrolyte leakage) and they are effective in separating fuels and oxidant. They also enhance the kinetics of the reduction reaction of oxygen [4 - 8]. Despite the alkaline anion exchange membranes advantages, they experience some challenges which limit their further development. For example, the Hoffman elimination and direct displacement reaction which occurs when there is a degradation of quaternary ammonium groups [9]. However, novel techniques for developing alkaline anion exchange membranes in fuel cells are enhancing the chemical strength of the cationic groups present in the membrane by the application of quaternary ammonium groups which prevents the allowance of β - hydrogen and raising the alkaline spacer distance amid the ammonium group nitrogen atom and the aromatic polymer backbone [10]. The use of cross linkers help in boosting the chemical and thermal stability of alkaline anion exchange membranes e.g. N, N, N', N' - tetramethylhexane - 1, 6 - diamine [11 - 14].

Y. Cao et al [15] prepared a qPVBCl alkaline anion exchange membrane from methylated melamine grafted polyvinyl benzyl chloride. The membrane has considerable ion conductivity (1.3×10^{-2} – 1.7×10^{-2} S/cm) and high mechanical properties. However, this preparation method is expensive and involves several chains of experimental processes.

To assess the suitability of a membrane for fuel cells, it is necessary to test its properties. One of the issues membrane developers experience is their testing procedures. Using metal - electrode assembly as a testing procedure is costly and time consuming [16]. Thus, simpler methods of testing membranes, through plane conductivity measurement technologies, are necessary and desirable.

The objective of this work is to prepare the qPVBCl alkaline anion exchange membrane and investigate its conductivity characteristics as a function of temperature and time in order to assess its suitability in the construction of fuel cells.

2 Materials and Methods

The main equipment and accessories used in the experiment include a Frequency response analyzer (Voltech TF2000, UK), Conductivity cell, Cell thermometer, Drying oven, Micrometer screw gauge, Voltmeter, Ammeter, Timer Clock and Glass petri dish, Beaker, Glass bottle, Scissors, Knife, Plastic pan while the reagents used for preparation of membrane include Polyvinyl benzyl chloride (PVBCl), Tetrahydrofuran (THF) and Potassium hydroxide (KOH) solutions and Distilled water.

2.1 Preparation of qPVBCl Alkaline Anion Exchange Membrane

As mentioned earlier, there are different methods of preparing qPVBCl alkaline anion exchange membrane. The method which was chosen in this project is simple, relatively cheap and less time-consuming compared to the other methods. Thus, 10 mL of PVBCl solution was placed inside a small glass petri dish after which 5 mL of THF solution was added and stirred thoroughly for 5 minutes to ensure proper mixing and to prevent the formation of air bubbles on the surface of the membrane after drying. After stirring the solution mixture, the petri dish containing the ionomer solution was then placed inside the oven as shown in Figs. 1a and 1b and heated at a temperature of 120 °C and for a period of 1 hour. This result is a membrane with a flat, smooth and bubble-free surface.



Fig. 1a: An Oven



Fig.1b: Theoven containing a qPVBCl Alkaline Anion Exchange Membrane

Next a solution of 11 mL of 1 M Potassium hydroxide (KOH) was added into the petri dish containing the membrane and covered with a small pan so as to prevent the solution from being exposed to carbon dioxide in the air. This was left for 1 hour to ensure proper mixing of the KOH solution with the solid membrane and the complete conversion of the chloride ion in the membrane to hydroxide ion. The pan was then removed and the solid membrane was peeled off from the petri dish using a small knife. The membrane was cut into 4 cm x 4 cm square pieces as shown in Fig. 2. The cutting process was executed very quickly (about 10 minutes) so as to prevent the membrane from excessive exposure to carbon dioxide in the air. The pieces of membrane were placed in a beaker and washed thoroughly with distilled water to remove small amount of carbon dioxide and other impurities that may be present. They were finally immersed and sealed in a small glass bottle containing distilled water.

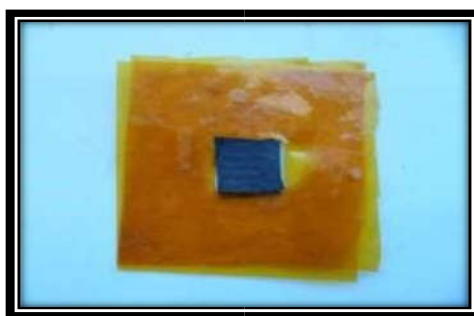


Fig. 2: A qPVBCl Alkaline Anion Exchange Membrane

2.2 Testing the variation of membrane conductivity with temperature

The synthesized membrane shown in Fig. 2 was washed with distilled water to remove excess KOH solution. It was cut into strips of surface dimension 4cm x 1cm. The thickness was measured at four different sections on the membrane using a micrometer screw gauge and values of 0.1100mm, 0.1103mm, 0.1107mm and 0.1110mm were obtained. This resulted in an average thickness value of 0.1105mm (0.01105cm).

The membrane ionic conductivity test was carried out by placing the 4 cm x 1 cm membrane strip across four foils in the conductivity cell (Fig. 3) made of platinum and having equivalent spacing of 0.5cm.



Fig. 3: A Conductivity Cell

The temperature in the cell was first set at room temperature of 21°C and, after adjusting the frequency on the frequency response analyzer (Fig. 4) to 20 KHz, the AC voltage and current displayed on the analyzer were recorded. Keeping the

temperature constant, the voltage and current for successively lower frequencies down to 1 KHz were also recorded. The temperature was again increased successively by 20 °C up to a maximum of 102 °C and, in each case, the corresponding voltage and current values as described for the 21°C temperature were recorded over the same range of frequencies of 20 KHz to 1 KHz.



Fig. 4: A Frequency Response Analyzer

The electrical resistances (R in Ohms) for every pair of voltage (V in Volts) and current (I in Amps) values were calculated from Ohm's law as in Eqn. 1;

$$R = \frac{V}{I} \quad (1)$$

At each specific temperature, the resistance values were plotted against frequency as shown in **Fig. 5**.

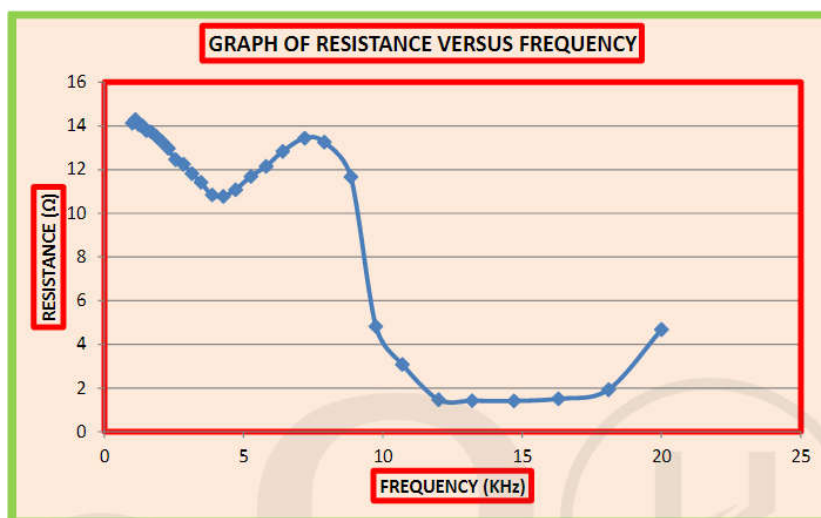


Fig. 5: Graph showing variation of Resistance with Frequency of analyzer at a constant temperature of 61°C

The general pattern especially after about 7 KHz is a sudden decrease in resistance as frequency increase to about 14 KHz followed by a gradual increase in resistance as frequency increased to 20 KHz, the maximum used in the experiment. From this graph, it was possible to identify the smallest resistance R_{MIN} for a given temperature. This smallest resistance (R_{MIN} in ohms (Ω)), the membrane thickness (L in cm) and the surface area (A in cm^2) were used to calculate the conductivity (σ in S/cm^2) of the membrane using the equation;

$$\sigma = \frac{L}{R_{\text{MIN}} \times A} \quad (2)$$

The conductivities calculated from Eqn. 2 were plotted against temperature values between 21°C and 102°C as shown in Fig. 6 to show the variation of membrane conductivity with temperature.

2.3 Test of the Variation of Membrane Conductivity with Time

To investigate the behavior of the membrane conductivity as a function of time, the observation of the existence of a minimum resistance in the region of 14 KHz was taken into consideration. The experiment was performed over a period of 1440 min. Thus, starting at time $t = 0$, the AC voltage and AC current values were recorded when the frequency on the analyzer registered 14 KHz. This was repeated after time intervals of 30 min and terminating at $t = 1440$ min. Temperature was kept constant at 61°C because it was the temperature that gave the highest (peak) conductivity value in the graph of conductivity versus temperature in Fig. 6. A graph of conductivity versus time was generated from these values as shown in Fig. 7.

3 Results and Discussion

3.1 Result of Preparation of qPVBCl Alkaline Anion Exchange Membrane

The results of the qPVBCl alkaline anion exchange membrane preparation experiment are reported in Table 1 with regard to the physical state, colour and odour.

Table 1: Properties of qPVBCl Alkaline Anion Exchange Membrane

	PROPERTY	
1.	Physical state	Solid
2.	Colour	Pale Yellow
3.	Odour	Odourless

The result shows that the membrane is a pale yellow and transparent solid, odourless, flat and smooth without the presence of air bubbles.

3.2 Result of Test of Variation of Membrane Conductivity with Temperature

The measurements were conducted to determine the conductivity of the anions within the alkaline anion exchange membrane at different values of temperature and at a relative humidity of 100%. As shown in Fig. 5, the membrane conductivity increased from 1.35×10^{-2} S/cm at 21°C reaching a maximum value of 1.57×10^{-2} S/cm at a temperature of 61°C after which it decreased approximately linearly to a value of 1.34×10^{-2} S/cm at 102 °C. Thus, within the range of temperatures investigated, the 61°C temperature is regarded as the desired temperature for which the membrane conductivity is highest. At 102 °C, the conductivity of the membrane dropped due to very low relative humidity and reactivity between the quaternary cations $R^1 R^2 R^3 R^4 N^+$ (present in the membrane) and mobile hydroxyl anions OH^- (from water molecules) in the dehydrating environment [15]

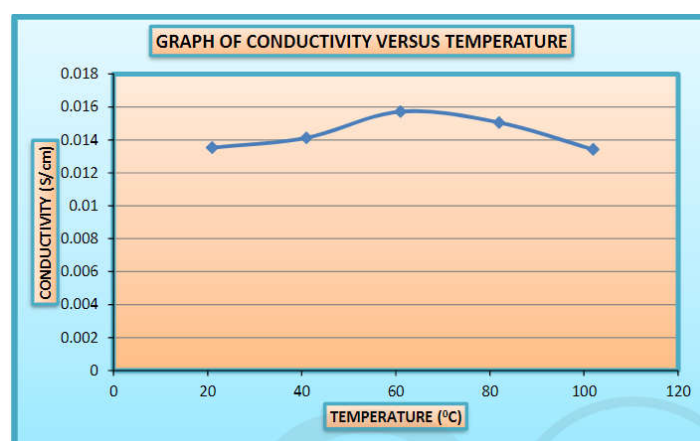


Fig. 6: Graph of variation of conductivity of ion exchanged qPVBCl membrane with temperature

3.3 Result of Test of Variation of Membrane Conductivity with Time

Besides the behavior of the membrane conductivity with temperature, it was also necessary to investigate how the conductivity of the anions within the alkaline anion exchange membrane, at constant temperature of 61°C and at relative humidity of 100%, behaved with time. As stated earlier, the temperature of 61°C was used because the membrane displayed the highest conductivity at that temperature.

The membrane conductivity was nearly constant at different periods of time at 61°C as shown in Fig. 7.

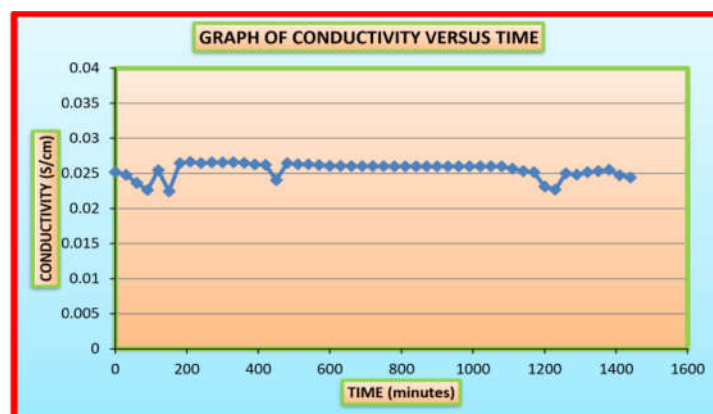


Fig. 7: Graph of variation of conductivity of ion exchanged qPVBCl membrane with time

4 Conclusions

A modern alkaline anion exchange membrane was progressively prepared from polyvinyl benzyl chloride solution. The resulting membrane is a pale yellow, transparent and odourless solid, with a flat and smooth surface devoid of air bubbles. The membrane exhibited a conductivity variation from 1.35×10^{-2} S/cm at 21°C to 1.57×10^{-2} S/cm at a temperature of 61°C. The conductivity test showed that the optimum operational temperature of the membrane was 61°C and its degradation temperature was 102°C. The other test on conductivity variation with time showed that, at a temperature of 61°C the conductivity of the membrane remained almost constant and hence operationally stable over a long periods of time.

This alkaline anion exchange membrane is simple and economic and its preparation is easy and less time-consuming. The quality of this membrane is appreciably similar to the standard membranes reported in literature.

From the experimental results, it is clear that the membrane will find wide use in fuel cells for the generation of sustainable electrical and heat energy for domestic and industrial applications.

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