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Experimental Investigation of PVC Composite Membrane for Polymer Electrolyte Membrane Fuel Cell

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Abstract: Now day Fuel cells have received a lot of attention for alternative energy compared to fossil fuel-based energy sources. On various types of composite ion-exchange membranes, the latest initiative is observed with organic and inorganic membranes to overcome the limitations. In this view, a composite membrane comprising PVC combined with titanium dioxide and zirconium oxide represents a new class of ion-exchange materials that may be prepared. It connects physic-chemical characteristics of inorganic parts within a single composite. A composite ion exchange membrane was synthesized with 1g of composite material mixed thoroughly. The ring is left for slow evaporation of THF to obtain thin film and a sheet of master membrane. The Composite membrane was tested for chemical stability in acidic, alkaline, and strongly oxidant media. The composite membrane was found to be thermally and chemically most stable. It is suggested that when swelling and porosity are examined diffusion across the membrane would occur mainly through exchange sites.

Keywords: Polyvinyl Chloride (PVC), Polymer Electrolyte Membrane (PEM), Fuel Cell, Thin Film Membrane (TFM)

I. INTRODUCTION

In the present time shortage of energy and pollution is important of the environment become more development of society. Confronting the urgent problems of environmental pollution and exhaustion an alternative to sustainable and clean energy technology is extremely necessary. The lithium- ion battery is an efficient energy storage system, that has attracted to the attention of a wide variety of new energy vehicles have a high energy density, low self-discharge rate, excellent power density, long cycle life as well as low memory effect and environmental friendliness. It is widely recognized that the lithium-ion battery is mainly composed of four parts including a cathode, anode, separator, and liquid electrolyte. And separator plays an indispensable role in immediate contact of cathode and the anode is provide the effective channels for the transmission of lithium- ions between electrodes have a significant influence of performance and cycle capability of the battery. Several membranes have been prepared using inorganic–salt. However, these inorganic membranes have sufficiently low chemical stability in the acidic and alkaline mediums due to the dissolution of inorganic phosphate into inorganic salt Although many studies have been offered on the development of TFC membranes during the last decades, there is still an ongoing need to develop technically and economically more feasible TFC membranes with a high separation performance and low energy costs for their industrial applications

II. MATERIALS AND METHODOLOGY

Materials: The polyvinyl chloride employed for the preparation of the composite membrane had a degree of polymerization of 500–1500, hydrolysis of 86.5–89 mol%, and a molecular weight of 31000 – 94000 g/ mol. Zirconium oxide (ZrO_2) and Titanium oxide (TiO_2) material powders were employed as fillers for the composite films. Characterization of polyvinyl chloride is carried out the chemical composition of the raw material is analysed and the particle size of the powder obtained by the process is found out techniques. The PVC powder was composition of stabilisers, lubricants, plasticisers and processing aids were synthesized following the method described in previous reports [2]. Oxygen (99.999% of purity) was used in permeation experiments.

Membrane preparation: A membrane was synthesized with a method similar to that of Coetzee et al. A 4% portion of composite material as prepared above was grinded to fine powder, and was mixed thoroughly with PVC, dissolved in 10 mL of tetrahydrofuran (THF) and finally 10 drops of dioctylphthalate used as a plasticizer was added and mixed

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thoroughly. The resulting solution was carefully poured into a glass-casting ring diameter 10 mm) resting on a glass plate. The ring was left for slow evaporation of THF to obtain thin film and a sheet of master membrane was obtained.

Table 1. List of Polymer Membrane used in Fuel cell

Fuel cell name	Electrolyte	Qualified Power(W)	Work temp(°C)	Efficiency		Status
				Cell	System	
Regenerative fuel cell	Polymer membrane (ionomer)		< 50			Commercial / Research
Reformed methanol fuel cell	Polymer membrane (ionomer)	5 W – 100 kW	250–300 (reformer) 125–200 (PBI)	50–60%	25–40%	Commercial / Research
Proton-exchange membrane fuel cell	Polymer membrane (ionomer)	1 W – 500 kW	50–100 (Nafion) 120–200 (PBI)	50–70%	30–50%	Commercial / Research
Microbial fuel cell	Polymer membrane or humic acid		< 40			Research
Direct-ethanol fuel cell	Polymer membrane (ionomer)	< 140 mW/cm²	> 25 90–120			Research
Direct methanol fuel cell	Polymer membrane (ionomer)	100 mW – 1 kW	90–120	20–30%	10–25%	Commercial / Research
Direct formic acid fuel cell (DFAFC)	Polymer membrane (ionomer)	< 50 W	< 40			Commercial / Research

Table 2. Experimental Plan:

Experiment No.	Sample No.	Reinforcement (%)				
		Calcium Carbonate	Plasticizer	Flow Promoter	Titanium Dioxide	Zirconium Oxide
1.	1.	10	1	0.5	4	-
2	2	10	1	0.5	-	4

Table 3. Mass Calculation of Composite Materials:

Experiment No.	Sample No.	Mass (gram)				
		PVC	Calcium Carbonate	Plasticizer	Flow Promoter	Composite Material
1.	1.	75	8	3	2	4
2	2	75	8	3	2	4

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Fig 1. Prepared on composite membrane of 4% TiO_2 and 4% ZrO_2

Instruments and techniques:

FT-IR Spectroscopy: Fourier transform infrared (FT-IR) spectra of the fillers and the composite films were recorded using attenuated total reflection method (ATR) on a Thermo Fisher Mid-Infrared FT-IR Nicolet iS5 Spectrometer. The spectra were recorded at room temperature in the range of 4000 to 400 cm^{-1} at a 4 cm^{-1} resolution. Fillers in powder form were measured using KBr pellets.

XRD Characterization: XRD results of the PVC composite membrane are shown. Diffraction pattern indicated that PVC powder possessed sharp peaks indicating a higher degree of crystallinity. At 20_, a peak with weaker intensity is observed in the XRD pattern of the final composite ion exchange membrane indicating the semi-crystalline nature of PVC. Therefore, a composite synthesized membrane exhibited the characteristic of pure PVC but with less intensity for the crystalline peak.

TGA Analysis: The thermal shrinkage property of composite membranes were examined by comparing the dimensional changes of the samples after thermal treatment at 80 °C, 120 °C, 160 °C and 200 °C for 2 h of using Thermo gravimetric analysis.

Water uptake : The physico-chemical characterization of PVC based polyvinyl alcohol zinc oxide composite membrane which involves the determination of all such parameters that affect its electro chemical properties. These parameters include membrane water uptake and swelling, etc. These were determined in accordance with the previously reported method.

$$\text{Water uptake} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \quad (1)$$

W_{wet} and W_{dry} were the mass of the membranes before and after immersing in the electrolyte for 24 h, respectively.

Porosity: The porosity of composite membranes was measured by immersing them into *n*-butanol for 2 h. The redundant n-butanol adhering on the surface of membranes was gently removed with wiped papers. The porosity (%) of samples was calculated by the equation

$$\varepsilon = \frac{Mb - Ma}{M_a} \times 100\% \quad (2)$$

where ε (%) was the electrolyte uptake. M_a and M_b were the mass of the membranes before and after immersing in the electrolyte for 24 h, respectively.

Chemical Stability: Chemical stability was evaluated on the basis of ASTM D543- m95 method. Membrane was exposed to several commonly used media, such as acidic (1 M HNO3), alkaline (1 M NaOH) and strong oxidant (KMnO4). Membrane was evaluated after 24, 48 and 168 h, analysing alteration in colour, texture, brightness, decomposition, splits, holes, bubbles, curving and stickiness.

$$\text{Chemical uptake} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \quad (3)$$

W_{wet} and W_{dry} were the mass of the membranes before and after immersing in the electrolyte for 24 h, respectively.

Thickness: The thickness of the membrane was measured by taking the average thickness of the membrane using screw gauze.

Swelling: It was calculated as the difference between the average thickness of the membrane equilibrated with 1 M NaCl for 24 h and the dry membrane.

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III. RESULTS AND DISCUSSION

Structural characterization by X-Ray diffraction

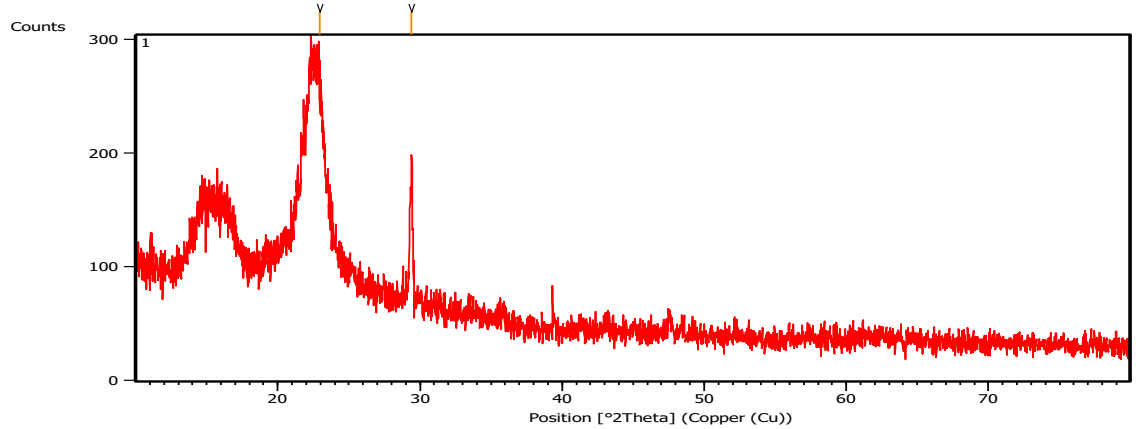

Fig.2 XRD Pattern for PVC-TiO_2 Membrane

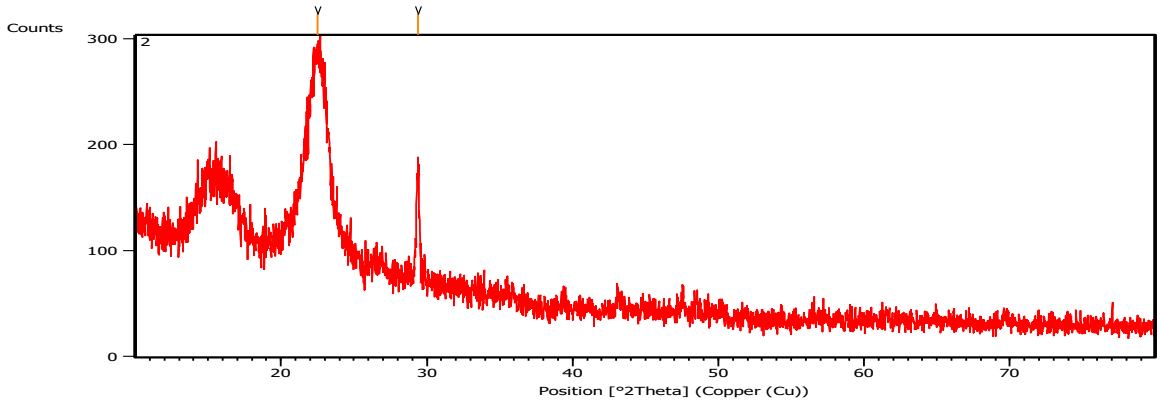

Fig.3 XRD Pattern for PVC- ZrO_2 Membrane

X-Ray powder diffractogram of the layered host matrix, is shown in Fig. 2. This reflection peak appeared at 22.54° and 29.39° corresponding to a d-value of 3.34 Å. The immobilization of the organic anions into the interlayer region by substitution of the acetate anions of the layered host matrix after the anion exchange reaction leads to an expansion of d-value from 3.94 to 3.03 Å, as can be seen in Fig. 3 for ZHA-SA. The sharp reflection in the XRD pattern of the hybrid material revealed a solid with good crystallinity.

Chemical stability: PVC composite membrane was tested for chemical stability in acidic, alkaline and strongly oxidant (KMnO4) media. In acidic (1 M H2SO4) and alkaline media (1 M NaOH) few noteworthy modifications were observed after 24, 48 and 168 h, demonstrating that the membrane was quite effective in such media. However, in strong oxidant (KMnO4) media the synthesized membrane became fragile in 48 h and broken after 168 h, losing mechanical strength. In general membranes having the same chemical composition were found to absorb same amount of water, where density ionisable groups are same throughout the membrane.

Water Uptake, Swelling and Porosity

The results of thickness, water content, porosity and swelling of PVC composite membrane are summarized. The ion exchange capacity provides information on the charge density in the membranes, which is an important factor, related to the transport properties of the membranes. The water content of a membrane depends on the vapour pressure of the surroundings.

In case of most of the transport measurements, only the membrane water content at saturation is needed, and that too mostly as a function of solute concentration. Thus, low order of water content, swelling and porosity with less thickness of membrane suggests that interstices are negligible and diffusion across the membrane would occur mainly through exchange sites.

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Table. 4 Characterization of PVC composite membrane

Characterstics	PVC-TiO_2	PVC-ZrO_2
Thickness (cm)	0.178 cm	0.180cm
Water uptake (%)	0.09 %	0.09 %
Porosity	0.24 %	0.22%
Swelling	No swell	No swell
IEC(m mol/g)	0.17 mol/g	0.174 mol/g

IV. CONCLUSION

The Polyvinyl chloride composite membranes were successfully prepared by solution casting method. The fuel cell membranes are made and the properties of PVC-TiO_2 and PVC- ZrO_2 water uptake, final thickness, porosity and IEC of PVC-TiO_2 are 0.178 cm, 9 %, 24%, 0.17 mol/g, and 0.180cm, 9%, 22%, 0.174 mol /g respectively. The work showed that for both composite's chemical stability test for acidic gives the better stability condition than the alkaline conditions. The membrane was found to be mechanically and chemically stable in all environments which are essential for practical applications. Structural (XRD) studies confirmed the formation of hybrid composite membrane. The result indicates that the behaviour of the investigated membrane is cation selective. Computational studies of also analysed. All these results suggest that the composite membrane offers great potential applications.

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