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Phosphotungstic Acid Modified Expanded PTFE based Nafion Composites

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Abstract: *Composite membranes have been prepared by impregnation of PFSI(perfluorosulphonic acid ionomer) solution (Nafion®) into the expanded polytetrafluoroethylene (EPTFE) matrix. The matrix was modified by Na/Naphthalene treatment and with phosphotungstic acid (PTA). The matrix modifications helped in reducing the contact angle thereby improving the impregnation process by reducing the hydrophobicity of the matrix. The fuel cell made with these composite membranes showed that the performance of PTA modified matrix is comparable to that of Na/ naphthalene modified matrix. Further the performances of matrix modified membranes were higher than that of the as received matrix-composites. PTA treatment offers a simple method of matrix modification to achieve high performance.*

Keywords: Polymer electrolyte membrane fuel cells, Composite ionomers, expanded PTFE, Phosphotungstic acid, surface modification

1. INTRODUCTION

Perfluorosulphonic acid ionomers (PFSI) are fast ion conductors and are widely used as an electrolyte in many electrochemical devices [1]. Recent literature reports have shown that composite membranes of PFSI offer many advantages in terms of lower cost, higher thermal stability and good mechanical strength [2], improved durability and performance [3], reduced swelling characteristics [4] etc. A composite membrane prepared using a porous framework substrate with the pores filled with a PFSI such as Nafion offers all the benefits described above [5,6]. Nafion has a hydrophobic tetrafluoroethylene backbone and hydrophilic side chains that aggregate making it difficult to fill the porous EPTFE substrates with Nafion solutions. Various methods to improve impregnation include use of solvents having solubility parameters suitable to backbone/ ionomer[2,7], use of surfactants [8], surface modification of EPTFE through etching [9,10] etc.

Heteropolyacids (HPAs) are the most attractive inorganic modifiers because these materials in crystalline form are highly conductive [11] and thermally stable. The use of heteropolyacids in preparation of composite polymer electrolytes for fuel cell offer many advantages as they improve conductivity and decrease the dependence of the membrane on humidity for optimum performance [12]. In addition, they have also been proven to improve the high temperature performance of the most commonly used perfluorosulphonic acid based polymer electrolyte in fuel cells [13,14]. Malhotra and Dutta [15] showed that incorporation of inorganic solid acids (phosphotungstic acid) in Nafion resulted in improved water retention capacity due to additional acid sites and good fuel cell performance at elevated temperatures. Kannan et al [16] have prepared modified Nafion membranes with phosphosilicate for improved water retention and proton conduction. They also found that samples with higher phosphate content exhibited high water uptake and proton conductivity.

Literature studies thus cite the advantages of using Nafion/EPTFE composite membranes and the use of heteropolyacids as additives for improvement in properties. Further surface modified EPTFE have been shown to have better wetting characteristics and improved properties due to better interactions between the substrate and Nafion. As EPTFE substrate is very stable it requires a strong radical ion (sodium Naphthalene radical) to abstract the fluoride ion from backbone. The process requires the use of a number of solvents and the localized heat generated during defluorination may damage the membrane. A simpler process for surface modification would hence be advantages. This paper suggests a non-reactive surface modification method using phosphotungstic acid. The EPTFE substrate treated with PTA solution would have a coating of PTA molecules in the pores of the sample. Due to good interactions between the PTA and Nafion all the pores of substrate would get coated and an improved membrane

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would be obtained. The results of these modifications are presented in this paper. To the best of our knowledge this is the only paper where PTA has been used first to treat the matrix to be coated with Nafion later.

2. EXPERIMENTAL

2.1. Preparation of Nafion/EPTFE composites

Porous EPTFE (Yeu Ming Tai Chemical Industrial Co., Ltd., Taiwan, thickness 25±5μm, porosity 85%) was first washed with alcohol and dried in oven. The EPTFE film was then mounted on a frame and soaked in acetone for 30 min. Nafion solution (5%) obtained from Dupont Co, with an equivalent weight of 1000 was used for impregnating the porous EPTFE film. To minimize the aggregation of Nafion in the solution it was mixed with a high boiling solvent (dimethylformamide / etylene glycol) to make the solution into 2.5% of polymer in the solvent. The Nafion loading in the porous EPTFE film was maintained constant at 2mg/cm^2 for all the membranes. Impregnation was carried out in steps to ensure that all the pores of the membrane were fully blocked to avoid gas crossover.

Membrane post treatment procedure included pressing the membranes at 30kg/cm^2 at 120°C for 3 minutes followed by annealing. The membranes were soaked in water for 24 hrs and then in dilute H_2SO_4 for 4 hrs. The membranes were washed free of acid and used for further studies. The average thickness of the membranes was 27±5μm.

For preparation of etched membranes the procedure adopted by Tang et al [9] and Jie et al [10] were used. The etched membranes were impregnated with Nafion using the procedure mentioned above. Fig 1 shows the schematic for the preparation of PTA modified membranes. The impregnation procedure and the post treatment procedures followed were the same as that for other membranes.

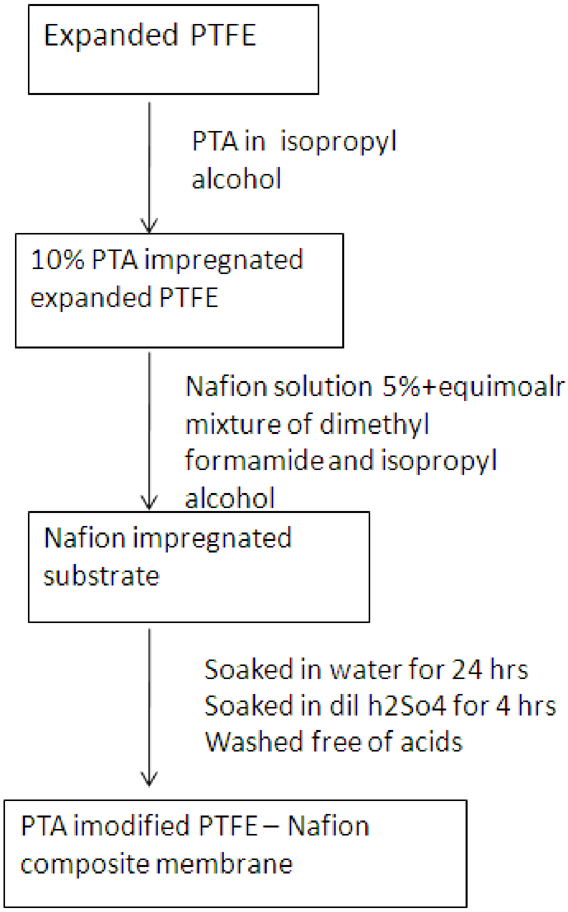

Figure 1. Schematic for the preparation of PTA modified PTFE composite

2.2. Characterization of Nafion/EPTFE composites

The morphology of the surface of the composite membranes was studied using scanning electron microscope (SEM). The surface of the sample was coated with gold before the morphology of the membranes was observed. EDAX analysis was carried out to study the various elements present on the surface. FTIR studies were carried out to study the functional groups present and the interaction between the various groups present. Thermogravimetry studies were carried out to study the thermal stability of the various membranes prepared. Contact angle measurements were carried out to study the effect of various surface modifications on the porous PTFE substrate. Conductivity measurements were carried out in the transverse direction using two probe techniques. The membrane resistance was obtained by AC impedance technique in the frequency range of 100kHz to 100 Hz.

2.3. Gas permeability and Fuel cell polarization studies

Gas permeability across the membranes were tested by assembling the membrane in a fuel cell set up and passing the gas on one side of the cell. The test consisted of applying a 1kg/cm^2 differential over pressure on one side while capping the other inlet and leading the outlet to a water reservoir[3]. If any bubble was observed in the water reservoir the membranes were not used for fabrication of the MEA.

The composite membranes prepared by the above techniques were used for the preparation of membrane electrode assemblies. The membrane electrode assemblies were made by a proprietary technique developed in our lab using 40% Pt/C(Arora Mathey, India), 5% Nafion Solution (DuPont, USA) and Carbon substrate from Ballard, USA. The catalyst layers were coated on a Gas diffusion layer by brush and the catalyst loading (total) was 1mg/sq cm. The performance data were obtained from a 6.75 cm^2 active area cell. Pure hydrogen and air were used as fuel and the oxidant. The cells were operated at ambient pressure conditions. The inlet gases were humidified to temperatures higher by 10°C and 5°C than cell temperature for hydrogen and air respectively.

3. RESULTS AND DISCUSSION

Three types of composite membranes based on Nafion/EPTFE were prepared. This included impregnation of pure EPTFE with Nafion solution, fabrication of etched EPTFE/ Nafion composite and third non-interacting PTA modified EPTFE/Nafion composite. Although etching is a good surface modification method, it requires the use of Na/naphthalene radical synthesis and many solvents. The process may also not lead to uniform etching when large area mem-

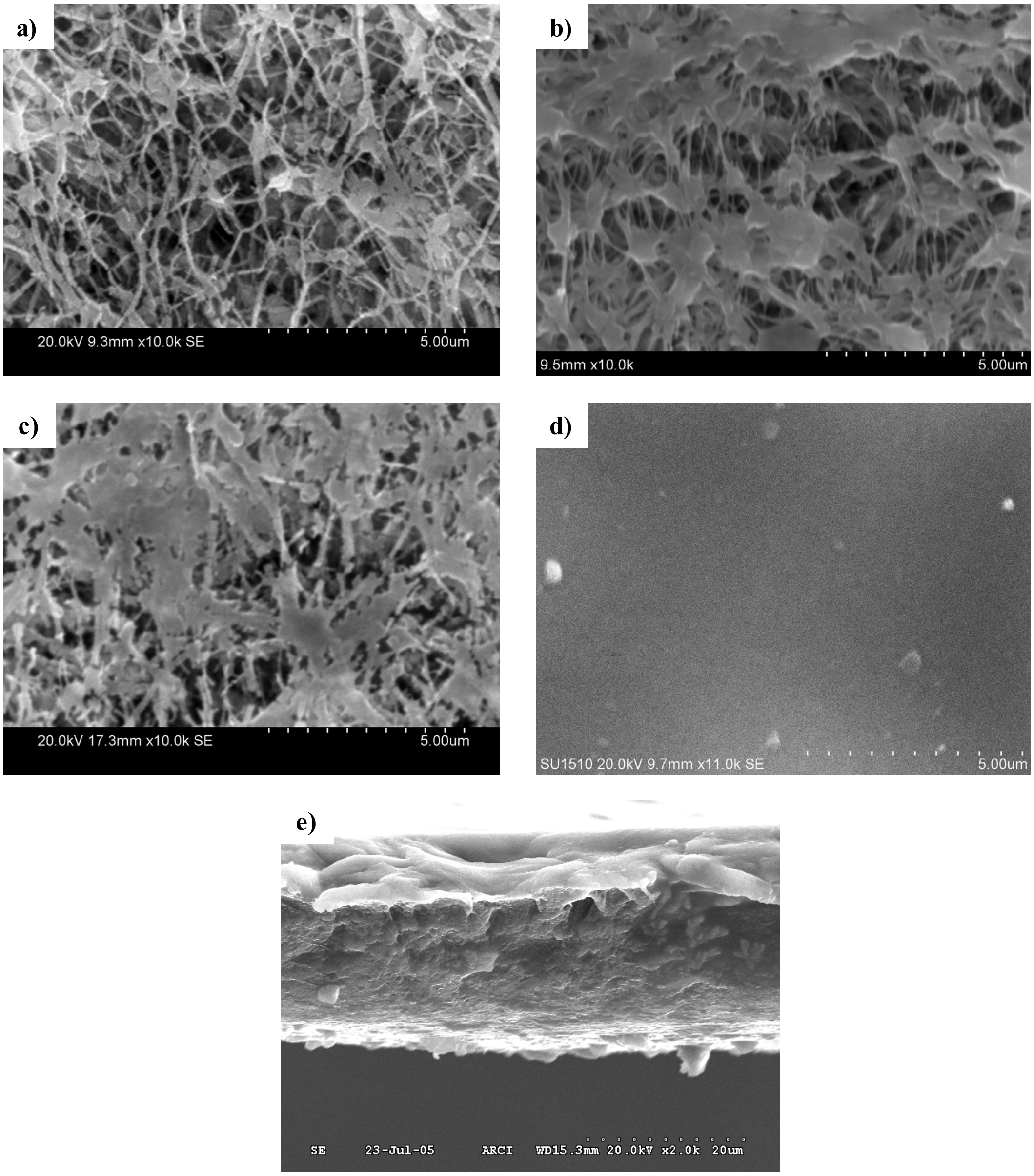

Figure 2. SEM pictures of a) Plain EPTFE, b) Etched EPTFE and c) PTA modified EPTFE d) Nafion coated EPTFE e) Transverse section of Nafion- ePTFE

branes have to be processed. A non-reactive surface modification method is suggested and the properties are compared with that obtained in other methods. The PTA modification was expected to improve coatability and reduce interfacial resistance due to decrease in contact angle as a result of PTA coating on the pores and surface of the matrix when treated with a dilute solution of PTA in a wetting liquid and due to interaction of Nafion with PTA.

3.1. SEM-EDAX analysis

Fig 2 shows the SEM picture of different types of EPTFE membrane. The surface of the pure EPTFE (Fig 2a) film shows the presence of fibers and knots and these enclose the micropores. The surface of the etched EPTFE(Fig 2b) film shows that in comparison to that of pure PTFE film the pores have become smaller. The decrease in the pore size has been reported to be due to structure and stress change as a result of Na/Naphthalene treatment [9]. The reduction in pore size was also reported to be advantageous for impregnation of the pores due to higher capillary force. The smooth surface of the etched film shows that the film has not been damaged either in the surface or in cross section due to Na/naphthalene treatment. Fig 2c shows the surface of the PTA modified EPTFE film. The pore size in this case has decreased due to the presence of PTA. As the solution of PTA has low viscosity it coats the pores with it and decreases the pore size. The PTA molecules are held within the matrix as they are entangled in the fibers and knots of the EPTFE film. The EDAX analysis confirmed the presence of

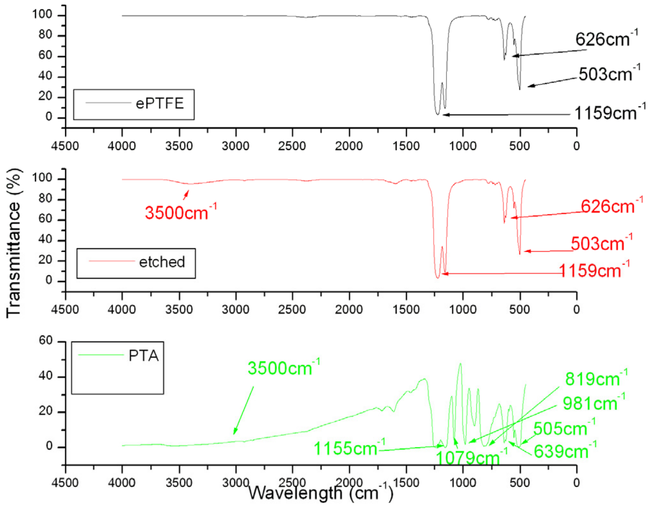

Figure 3. IR Curves for Plain, Etched and PTA modified membranes

PTA on the surface as both tungsten and phosphorous could be detected on the surface while the EDAX of pure PTFE showed only the presence of carbon and fluorine. The surface of the Nafion coated films is smooth, uniform and without any cracks(fig 2d). SEM picture of the transverse section shows that all the pores are filled (fig 2e). The EDAX of Nafion coated films shows the presence of O and S along with carbon and fluorine. The surface of the PTA modified film shows the presence of W and P even after post processing indicating that there is stabilizing interactions between Nafion and PTA. Also, PTA has not been leached out during the post treatment of the membranes (processing with acid and that with water).

3.2. FTIR analysis of EPTFE membranes

Fig 3 shows the FTIR curves for Plain EPTFE, etched EPTFE and PTA modified EPTFE. The plain EPTFE shows characteristic peaks in the region 503 cm-1 due to -CF2 rocking mode, 620-640 cm-1 due to -CF2 wagging, 1150 cm-1 due to -CF2 stretching and 1240 cm-1 due to –CF3 stretching. The surface of the etched PTFE shows peaks at 3500 cm-1 due to – OH groups, at 2950 cm-1 and 1739 cm-1 due to – CH3 and -CO groups. The presence of these groups indicate less hydrophobicity of the material and easy coatability with solvents like dimethyl formamide, dimethylacetamide , N methylpyrolidone etc. The PTA modified EPTFE shows bands due to O-H bending at 1630 cm-1, P-O stretching at 1080cm-1, W=O stretching at 987 cm-1, W-O-W stretching at 886 cm-1 and 810 cm-1. As PTA is a non- interacting material with EPTFE, no shifts in the EPTE bands are seen.

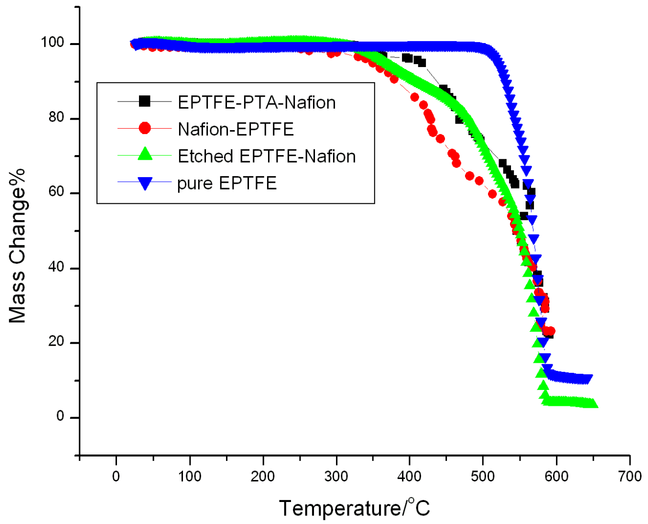

Figure 4. TGA curves for various membranes

3.3. Thermogravimetric analysis for the membranes

Fig 4 gives the TGA curves for the various EPTFE membranes prepared. Pure EPTFE film is very stable and starts decomposing above 530°C only. As these films are hydrophobic moisture loss below 100°C are also not seen. EPTFE-Nafion composite shows transitions due to sulphonic acid groups above 300°C followed by the main chain scission above 450°C. The etched EPTFE films show transition at the temperatures higher than that of Pure composite membrane with peak temperatures at 348°C for sulphonic acid groups and 569°C for the main chain. The increase in degradation temperature could be due interaction between the sulphonic acid groups of the PFSI and the hydrophilic groups introduced due to Na/ naphthalene etching. The slight changes in the transition temperature between the etched and the pure EPTFE based ionomers suggests that Na/Naphthalene treatment have been carried out only to the moderate extent and no large scale degradation in the main chain have occurred. These results also concur with the SEM and IR data. The PTA modified EPTFE shows transitions at peak temperature of above 390°C. This could be due to stabilizing bond formed between sulphonic acid groups of the PFSI and the acid functionality of PTA.

3.4. Contact angle measurement

Table 1 gives the contact angles measured for various membranes. The plain EPTFE is very hydrophobic and has a contact angle of 153°. Treatment with Na/naphthalene renders the surface of EPTFE less hydrophobic as seen by the presence of –OH, -CH$_3$ and –CO groups in the FTIR study. As a result the contact angle

Table 1. Properties of the EPTFE membranes

S. No	Membrane type	Thickness of Matrix (µM)	Contact angle(/°) of the matrix	Conductivity (mS/cm) of ionomer coated membranes
1	Plain EPTFE	25±5	153	16
2	Etched EPTFE	24±5	84	30
3	PTA modified EPTFE	27±5	132	23

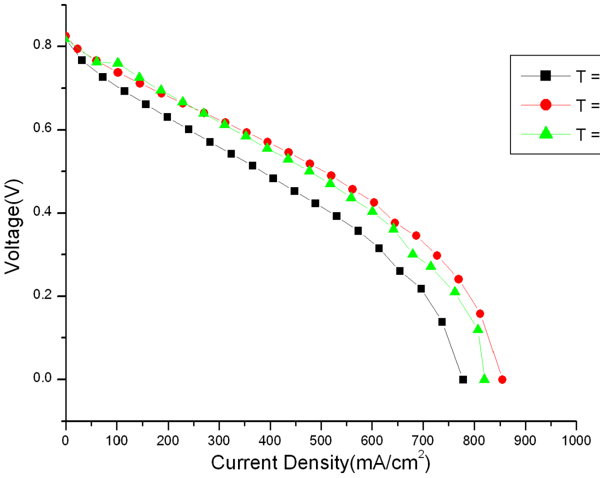

Figure 5. H_2/Air Polarization curves for Pure EPTFE

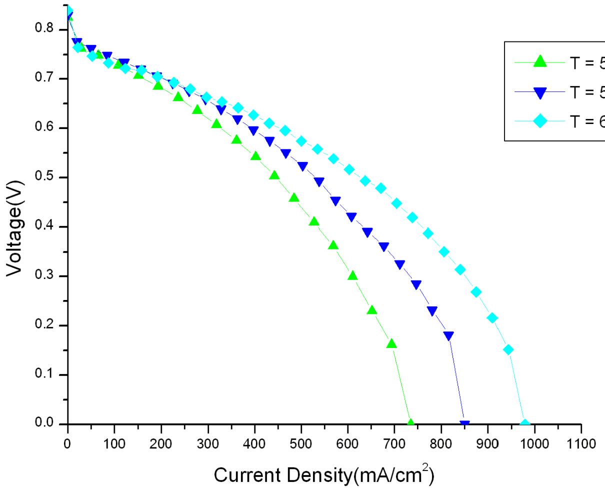

Figure 6. H_2/Air Polarization curves for Etched EPTFE

decreases and was found to be 84° for the etched sample. This improves the coatability with Perfuorosulphonic acid polymer that has hydrophobic backbone and hydrophilic pendent groups. PTA modified EPTFE has a coating of PTA on the surface of EPTFE. As a result the contact angle should decrease. The results concur with the hypothesis and the contact angle was found to be 132°. The decrease in the contact angle along with the ability to interact with Nafion(as indicated by TGA studies) is expected to provide membranes with low interfacial resistance and performance.

3.5. Conductivity analysis

Table 1 gives the through plane conductivity values for various Nafion coated membranes at 30°C. The composite membranes based on EPTFE and PFSI have an interface between the two (the matrix being non conducting). The conductivity values were found to be a function of ability to completely fill Nafion in the pores of the EPTFE matrix (to reduce the interfacial resistance). This depends on the either the interaction between the matrix and the PFSI or improved coating techniques using surface modification methods. Thus the conductivity value for etched EPTFE membranes that have the lowest contact angle (indicating better interaction between the substrate and PFSI) are the highest. PFSI coated on the plain EPTFE membranes have the lowest conductivity. The contact angle for PTA modified membrane is in between that of etched and the plain EPTFE membrane. The PTA modified membrane has higher conductivity than that of as received EPTFE coated membrane due to its better pore filling ability.

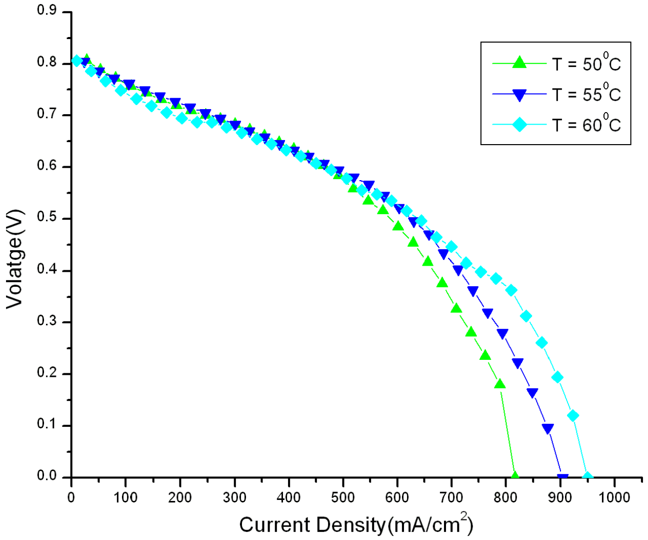

Figure 7. H_2/Air Polarization curves for PTA modified composite membrane

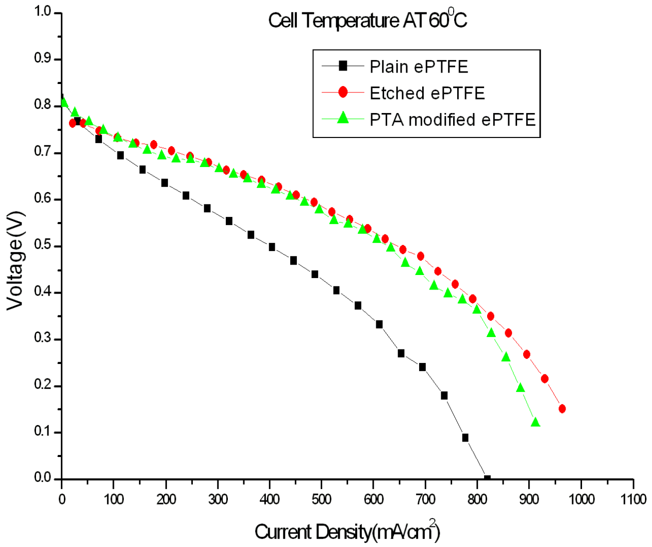

Figure 8. Comparative Polarization curves for various membranes

3.6. Fuel cell Performance of the membranes

The current-voltage (I-V) curves for single cells fabricated with various PEM's are shown in Fig 5-8. The open circuit voltage for the plain EPTFE based PEM is lower than that of etched and PTA modified PEM. This indicates that the pores of the matrix are coated better when the matrix is less hydrophobic or when it is modified. The cell performance of the plain EPTFE based PEM is lower than that of the other PEMs (Fig 5). The lower performance of the plain EPTFE composite PEM at higher temperatures may also be due increase in gas permeability at high temperatures. Fig 6 shows the performance of the etched PTFE –Nafion composite PEM. Due to higher interaction between PFSI and the matrix (as the matrix is less hydrophobic) the performance of these membranes are superior to that of the Plain EPTFE- composite PEM. The increase in performance at high temperature is also indicative of the same. PTA modified EPTFE composite PEM shows similar performance characteristics as that of etched membrane. As PTA modification improves the membrane properties, due to decrease in contact angle and its ability to interact with Nafion, comparable performance characteristics as that of the etched membrane is obtained (Fig 7). Also, PTA is known to improve high temperature performance of the membrane due to its ability to retain water molecules (11-15). Fig 8 shows the comparative performance of the different types of the membrane. It can thus be concluded that PTA modification is a simpler method and can be used for uniform preparation of large area membranes based on EPTFE.

4. CONCLUSIONS

Composite polymer electrolytes based on EPTFE and PFSI are low cost alternatives to pure PFSI membranes. Matrix modification carried out to reduce the hydrophobicity and coatability improved the membrane properties. The PTA modified membrane had PTA particles lodged between the fibers of the matrix. This also reduced the pore size. As the PFSI resin (Nafion) has favorable interactions with PTA it improves the coating characteristics. The fuel cell performance study for single cells at ambient pressure conditions showed that performance of PTA modified ionomer is similar to that of Na/naphthalene treated ionomer for the same amount resin content in the membranes. PTA modification thus offers improvements in composite membranes due to better filling of the pores by the PFSI resin. Improvements in performance are seen owing to the presence of heteropolyacid that imparts improved water retention at high temperatures.

5. ACKNOWLEDGEMENT

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