

Research Article

Performance of a 1 kW Class Nafion-PTFE Composite Membrane Fuel Cell Stack

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Composite membranes have been prepared by impregnation of Nafion into the expanded polytetrafluoroethylene (EPTFE) matrix. Nafion loading in the composite membranes was kept constant at 2 mg/cm². The lower amount of electrolyte per unit area in the composite membranes offers cost advantages compared to conventional membrane of 50 μ m thickness with an electrolyte loading of \sim 9 mg/cm². Composite membranes (30 μ m thickness) were found to have higher thermal stability and mechanical strength compared to the conventional membranes (50 μ m thickness). The performance of the membrane electrode assembly made with these composite membranes was comparable to that of the conventional membranes. Single cells fabricated from these MEAs were tested for their performance and durability before scaling them up for large area. The performance of a 20-cell stack of active area 330 cm² fabricated using these membranes is reported.

1. Introduction

Polymer electrolyte membrane fuel cell (PEMFC) presents an attractive alternative to traditional power sources, due to high efficiency and low pollution. The efficiency of the fuel cell vehicle using direct hydrogen fuel cells has been reported to be twice that of the gasoline vehicles [1, 2]. Fuel cell efficiency is high even at partial loads compared to the internal combustion engines, which operate at high efficiency only at full loads. The only emissions in vehicles operating on hydrogen as fuel is water and is hence non-polluting. Fuel cell stacks of sub-kW and 1 kW level find applications as power sources in electronic equipments and as power source in portable applications. A 3 kW fuel cell stack has been projected for applications in the telecommunication sectors as highly reliable and durable on-site power generation technology is required for these applications. Stacks of 5 kW and above are used as power sources in various stationary and vehicular applications. Combined heat and power generation using fuel cells is especially attractive for stationary power generation. Further, these short stacks hybridized with electrical storage devices

(batteries and/or ultra-capacitors) can have several benefits, including capturing regenerative braking energy, enhancing fuel economy, providing a more flexible operating strategy, overcoming fuel cell cold-start and transient shortfalls, and lowering the cost per unit power. In a PEMFC, the proton-conducting membrane is located between the cathode and anode and transports protons from anode to cathode. The membranes for high performance PEM fuel cells have to meet the requirements of low cost, high proton conductivity, good water uptake, low gas permeability (<1 mA/cm² at 60°C) [3], and so forth. Nafion, the widely used polymer electrolyte membrane, is a fast proton-conducting separator and shows excellent performance at low temperatures and high humidities. However, the cost of the membrane is high thus limiting its applications in commercial systems. Other disadvantages include the loss of conductivity at high temperature, decrease in strength in thin sections of the membrane and significant dimensional change on hydration [4, 5]. Composite membranes based on substrate and ionomer offer advantages in terms of cost and strength while retaining similar conductivities. Gore Tex materials are made of porous inert polytetrafluoroethylene filled with ion

exchange polymer (usually Nafion) [6]. The same approach was adopted by another company (Johnson Matthey) using a nonwoven silica substrate [7]. Very thin membranes could be made due to better mechanical properties compensating for the higher intrinsic resistance. The concept of using porous substrate-based composite membranes has been used to prepare a low proton resistance PBI/PTFE composite membrane [8]. Nafion composite membranes with porous Teflon, polypropylene, nylon, and Celgard substrates have been studied and their properties are reported in the literature [9, 10]. The composite membranes based on expanded PTFE has been the subject of study of many researchers and studies on methods to reduce the resistance of the membranes through surface modification of EPTFE [11–13], changes in the solvent solubility parameter [14], addition of additives during membrane fabrication [15] have been investigated.

Present PEMFC fuel cell stacks use conventional commercially available materials. As bipolar plates, membranes and catalysts form the major cost component in a fuel cell, most of the research is carried out on alternative substitutes for these materials. PEMFC stacks are being developed with alternate materials to meet the cost targets set for various transport and stationary applications. PEMFC stacks have been designed, assembled, and tested at the 1 kWe, 5 kWe, and 10 kWe size from a range of materials including uncoated stainless steel (type 904) coated stainless steel (type 316) and coated titanium [16, 17]. Performance of a 1 kW-class PEMFC stack using TiN-coated 316 stainless steel bipolar plates have been reported by Cho et al. [16]. The authors have concluded that TiN-coated stainless steel performed better than bare stainless steel. LF11 Al alloy bipolar plates with gold plating (coated by surface plasma technique) were used to develop 1 kW fuel cell stack [17] to study its properties as these bipolar plates had preferable properties compared to graphite- and gold-coated stainless steel plates. Nafion/SiO₂ composite membrane stack have been developed using sol-gel technique to control the SiO₂ particle size in Nafion NRE 212 membrane [18]. A ten cell stack developed using the composite membrane could be operated at 110°C using 90% glycol solution as the coolant and pure hydrogen and oxygen as the reactant. Bandlamudi et al. [19] have studied the properties of 150 W PBI/H₃PO₄ Gel-Based Polymer Electrolyte Membrane Fuel Cells under the Influence of Reformates. Stacks based on Celtec-P commercial high temperature membranes are also being tested [20]. Bonville et al. [21] have studied the effect of scaling up (from 25 cm² to 300 cm²) on the cell performance and properties using Ionomem corporations composite membrane based on PTFE, Nafion and phosphotungstic acid at 120°C and 35% RH. Based on the performance, the process of scaling up was verified.

Although a number of papers based on composite membranes are available in the literature, papers on fuel cell stack are mainly based on commercial membranes. Composite-membrane-based stack are being developed only by the manufacturers of these membranes. The present paper illustrates a simple method to prepare composite membranes with comparable performance to those reported in the

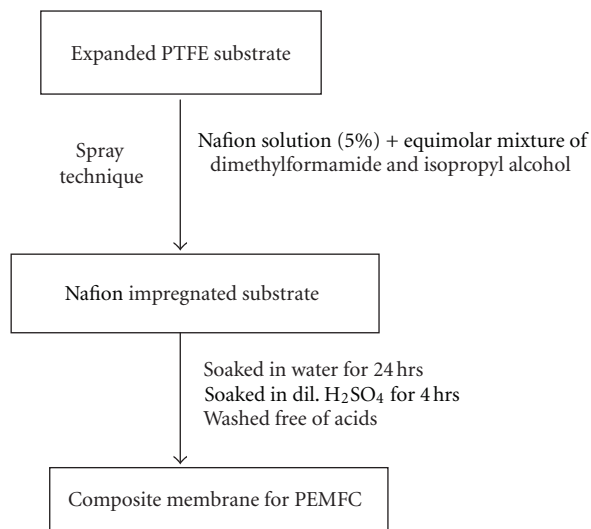


FIGURE 1: Fabrication procedure for composite membranes.

literature that can be easily scaled up to fabricate membranes of large size for development of fuel cell stacks for various applications. The results of the properties of the composite membrane developed using a PTFE matrix and Nafion ionomer and that of the 1 kW stack fabricated using them are presented in the current paper.

2. Experimental

2.1. Preparation of Nafion/EPTFE Composites. Figure 1 gives the general procedure for preparation of the composite membrane. Porous EPTFE was first washed with alcohol and dried in oven and mounted on a frame. The film was soaked in acetone for 30 min before impregnating with ionomer. Nafion solution (5%) obtained from Dupont Co, with an equivalent weight of 1000, was used for impregnating the porous EPTFE film. Nafion solution was mixed with dimethylformamide to make the solution into 2.5% of polymer in the solvent. The Nafion loading in the porous EPTFE film was maintained constant at 2 mg/cm² 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 by spray method. Membranes were pressed at 30 kg/cm² (using a Carver, USA hot press) at 120°C for 3 minutes followed by annealing. The membranes were soaked in water for 24 hrs and then in dilute H₂SO₄ for 4 hrs and washed free of acid before use.

2.2. Characterization of the Composite Membranes. The composite membranes were characterized by IR spectroscopy (Perkin Elmer FTIR), thermogravimetric analysis (Netzsch thermal analyzer model no. STA 449 F1, Germany), dynamic mechanical analysis (Dynamic mechanical analyzer model Q800 by TA instruments, USA.), and conductivity measurement (by Impedance analysis using Solatron Analytical frequency analyzer model 1400 Test system) before fuel cell testing. Gas permeability across the membranes were tested

TABLE 1: Properties of the composite membrane.

S. No	Property	
1	Substrate	Expanded PTFE
2	Substrate pore size	5 μm
3	Substrate porosity	85%
4	Substrate thickness	25 $\mu\text{m} \pm 5$
5	Composite membrane thickness	28 ± 5 μm
6	Composite membrane conductivity	16 mS/cm

by assembling the membrane in a fuel cell set up and passing the gas on one side of the cell. The other inlet is capped and the outlet is dipped into a water reservoir after applying a differential pressure of 1 Kg/cm² on one side. Membranes that did not show any permeability were only used for making MEA. The maximum pressure up to which these membranes were tested was 3 Kg/cm².

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 1 mg/sq cm. Pure hydrogen and air were used as fuel and the oxidant. The cells were operated at ambient pressure conditions. Preliminary performance comparison, durability studies (by cycling between two different potentials) were carried out in 30 cm² active area MEA before scaling up the membrane production to prepare MEAs with an active area of 330 cm². The MEAs were tested using an Arbin Fuel cell test station, USA. A 1 kW stack was built using 20 MEAs of 330 cm² active area. The stack was operated at the cell temperature of 50°C using water as the coolant.

3. Results and Discussion

Composite membranes based on expanded PTFE substrate were prepared by spray method as described in Figure 1. The properties of the substrate used and the membrane are given in Table 1. The SEM images of the substrate and the composite membrane have been discussed in detail earlier [14]. Conductivity measurements were made by sandwiching the membrane between conducting plates and measuring the impedance. The composite membranes have good conductivity due to their reduced thickness even though a substrate of high resistance is used.

3.1. Composite Membrane Characterization. Figure 2 shows the IR spectrum of the substrate and Nafion impregnated EPTFE membrane. 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. As the plain EPTFE does not absorb any moisture, no characteristic peak is seen in the region 3000–4000 cm⁻¹. In the composite Nafion membrane, the finger print region due to the PTFE background is still retained and no significant shift is observed due to any interactions in this region. Additional peaks due to -C-O-C-stretching band (970 cm⁻¹), weak

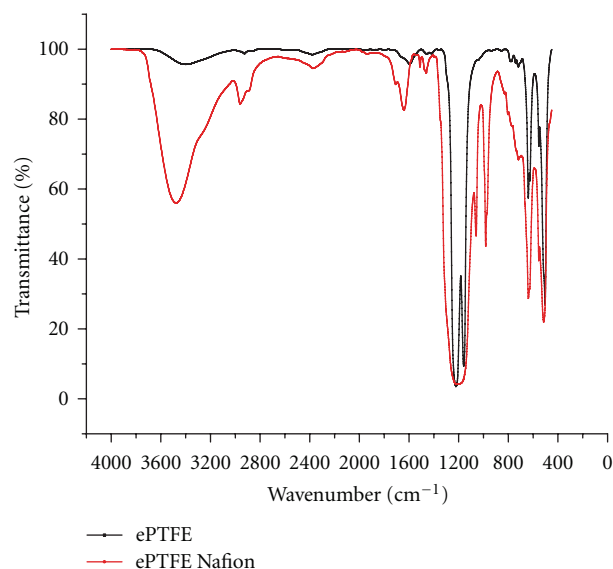


FIGURE 2: IR curves for the substrate and the composite membrane.

band at 805 cm⁻¹ due to -C-S-stretching, a band in the 1100–1200 cm⁻¹ region due to highly polar sulphonic acid groups, -OH bending vibration in the 1600–1800 cm⁻¹ region, and band in the 3200–3800 cm⁻¹ region due to water fundamental vibrations, are seen. These results confirm the impregnation of Nafion in PTFE and correspond with the Nafion and the PTFE bands observed in the literature [23].

Figure 3 shows the TGA curves obtained for the substrate PTFE and that of Nafion impregnated PTFE. It was found that pure PTFE is very stable and shows no transitions below 500°C. The composite Nafion membrane due to the presence of the ionomer shows transition around 300°C and 450°C due to degradation of the sulphonic acid groups and the main chain scission of Nafion ionomer. Nafion 112 membranes have been shown to have 3–5°C lower initial thermal decomposition temperature than the composite membranes by Huang et al. [22]. Figure 4 shows the stress-strain curves of Nafion and Composite membrane at 30°C. The composite membrane shows low-dimensional changes to applied stress compared to pure Nafion membrane. This property would be advantageous while operating a fuel cell. The membrane electrode assembly in a fuel cell undergoes stress due to tensile/compressive forces, hydration of the membrane due to water present in the vapor and liquid phase, cycling temperatures, and dynamic load cycles. Such stresses can lead to changes in the performance of the MEA. As these stresses are related more to the membrane than the other components of the MEA, the composite membrane that shows low variations in the stress is more advantageous. Further, it can also be seen that the composite membranes have higher modulus even though they are thinner than the pure Nafion membrane. Table 2 shows the comparison in properties between the developed composite membranes and Nafion 112 membranes.

3.2. Fuel Cell Characterization. Figure 5 compares the performance of the MEAs fabricated using the composite membrane and Nafion 212 membrane tested using a 30 cm²

TABLE 2: Comparison of the properties of the composite membrane with Nafion 112 membranes.

S. No	Property	Composite membrane	Nafion 112
1	Thickness	$28 \pm 5 \mu\text{m}$	$50 \mu\text{m}$
2	Water uptake	16	30
3	Thermal stability	$>300^\circ\text{C}$	$<300^\circ\text{C}^*$
4	Youngs modulus (Mpa)	241	117.7
5	Ionomer content (mg/cm^2)	2	9

* [22]

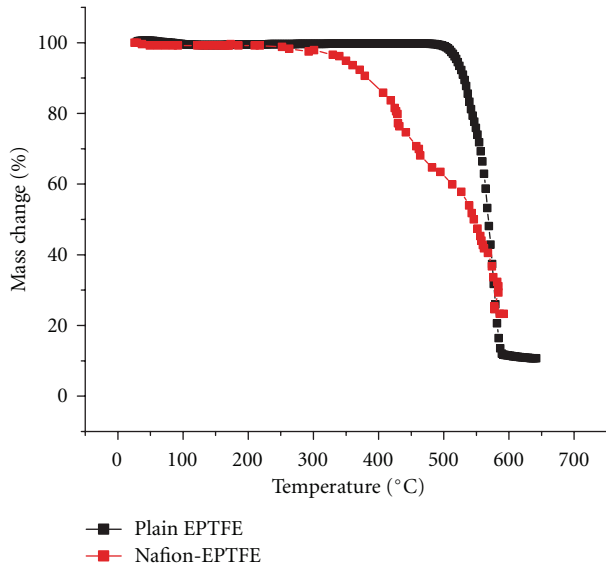


FIGURE 3: TGA curves for the substrate and the composite membrane.

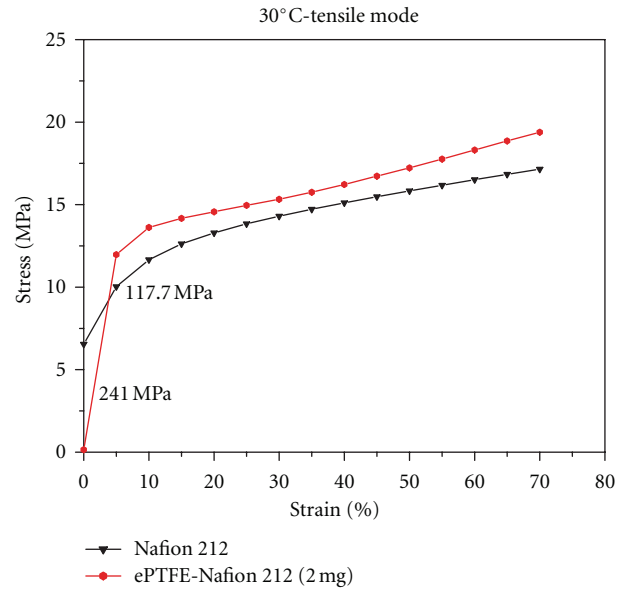
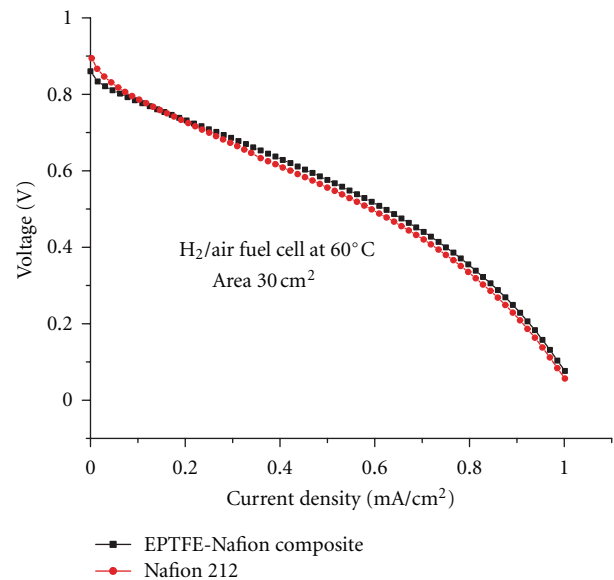


FIGURE 4: Stress-strain curves for the composite membrane and Nafion 212 membrane.

active area MEA with hydrogen and air as fuel and oxidant, respectively, at 60°C . The open circuit voltage for the composite PTFE-Nafion membrane is lower than that of pure Nafion membrane. This could be attributed to higher permeability of the composite membranes to reactant gases. Higher gas permeability for the composite membranes has been reported in the literature [24] in comparison to recast Nafion membranes and commercial Nafion 212 membranes. Polarization curves obtained for composite Nafion membrane and pure Nafion membranes show comparable performance at 60°C under humidified reactant conditions. The reactant gases were humidified at 10°C and 5°C higher than the cell temperature for hydrogen gas and air, respectively. As the polarization curves are a complex function of kinetic and mass transport-related parameters in addition to the ohmic resistance, similar performances indicate the applicability of these membranes for fuel cell applications.

3.3. Durability Testing of the MEAs. Cost and lifetime of the cells are two interrelated parameters, which have to be considered while development of new materials. As a lower

FIGURE 5: Comparison in performance between composite membrane and Nafion 112 at 60°C and ambient pressure conditions.

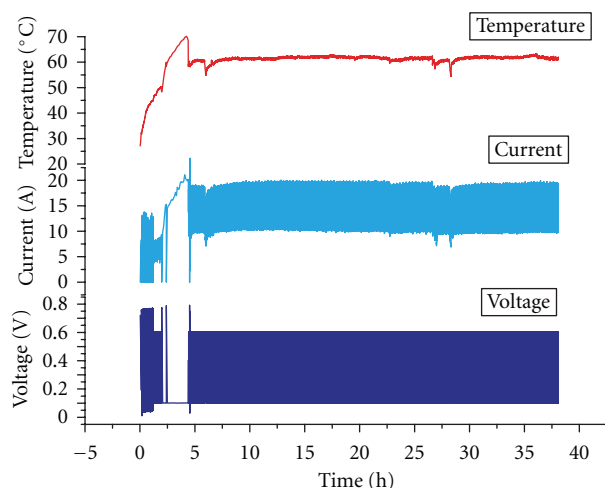


FIGURE 6: Durability of the composite membrane performance to repeated cycling.

cost, thinner alternative material is currently being considered, lifetime studies have to be carried out to study its applicability. Lifetime of the cell is dependent on many parameters like platinum particle dissolution and sintering, carbon corrosion, membrane thinning, operating parameters like voltage and current, cell temperature, pressure of the reactants, transient or continuous operation, number of startups and shut down, and so forth. As it is important to test durability under various conditions, one of the parameters, that is, cycling between operating voltage and very low voltage was carried out to study the membrane durability. Such extreme voltage parameters ensure that the cell is operated between high current density and nominal current density leading to differences in the water contents in the cell and induce enough stress to test the membrane properties and their durability. Figure 6 shows the results of the cycling studies carried out on the composite MEA. The MEA was held at a potential of 0.6 V for a period 30 s and 0.1 V for a period of 30 s. The entire cycle was thus completed in 1 min. It can be seen that the characteristics of the cell are constant for more than 2000 cycles studied. Further, during the long-term operation, ac impedance was also measured as shown in Figure 7. Ohmic and charge transfer resistance of the single cells employed using these composite membranes changed only marginally during cycling (after 2000 cycles). It has been reported that Nafion 112 membrane [25, 26] shows higher degradation at low humidity and high temperature of operation due to water-dependent glass transition temperature of Nafion and the humidity and temperature-dependent peroxide formation rates. Studies by Janssen et al. [27] on PEMFC durability by load on/off cycling with near saturated H_2 and air at ambient pressure concluded that membrane degradation did not contribute significantly to losses and that losses were mainly due to decrease in kinetic parameters and transport losses due to change in hydrophilicity of the electrodes. As the present study has been carried using fully saturated gases and optimal temperatures, it can be concluded that membrane degradation is not taking place.

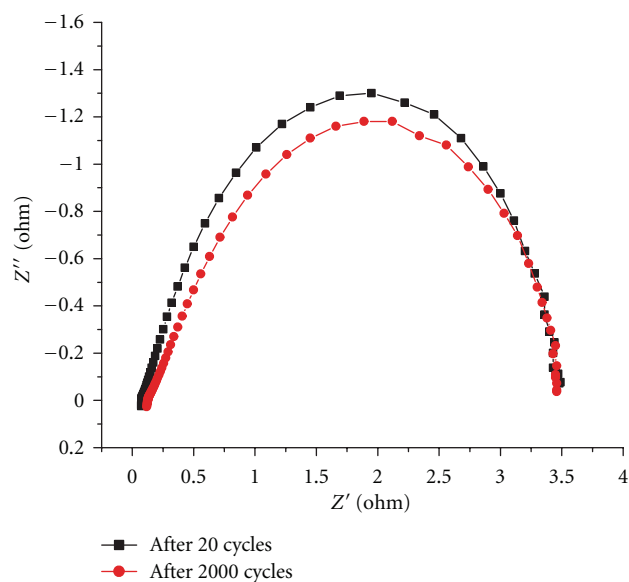


FIGURE 7: Comparison of impedance curves during cycling.

3.4. Fuel Cell Stack Characterization. Based on the results obtained from single cell studies, membrane fabrication was scaled up to form MEAs with an active area of 330 cm^2 . The major challenges to be faced during the scaling up process include nonuniformity in coating and incomplete coverage of the pores of ePTFE substrate. The spray method used for coating of the membrane included repetitive spraying in the longitudinal and transverse directions on the entire surface of the membrane to ensure complete coverage. Also the solution viscosity was maintained at constant level and evaporation losses were minimized by addition of high boiling solvents so as to have a uniform coating. The process developed produced membranes with less than 10% wastage. A fuel cell stack with 20 cells was fabricated from these membranes after testing individual membranes for permeability characteristics as mentioned in Section 2.1. Figure 8 shows the composite membrane of 30 cm^2 active area and a 330 cm^2 active area membrane along with the 20 cell stack assembled with these membranes. The stack design selected had the following configuration: number of cells—20, Active area 330 cm^2 , commercial supported catalyst (40%) for both anode and cathode, Serpentine flow field channels, water cooling channels after 2 cells, and internal fuel and oxidant manifold. After assembly of the stack, it was tested for electrical short circuits, internal or external leakage of gases, coolants, and so forth. The stack was operated using hydrogen and air as reactants at ambient pressure conditions and 50°C. The performance data for the stack is shown in Figure 9. The open circuit voltage for the stack was 16.04 V with the average individual cell open circuit voltage of ~810 mV. The voltage lowered to 15.28 V, 14.48 V, and 14.01 V as the current increased from 10 A to 20 A and 30 A, respectively. A peak power of 1.01 kW was obtained at the voltage of 11.22 V and 90 A current. In a fuel cell stack, uniform performance of each unit cell is preferable. The performances of the individual cells at

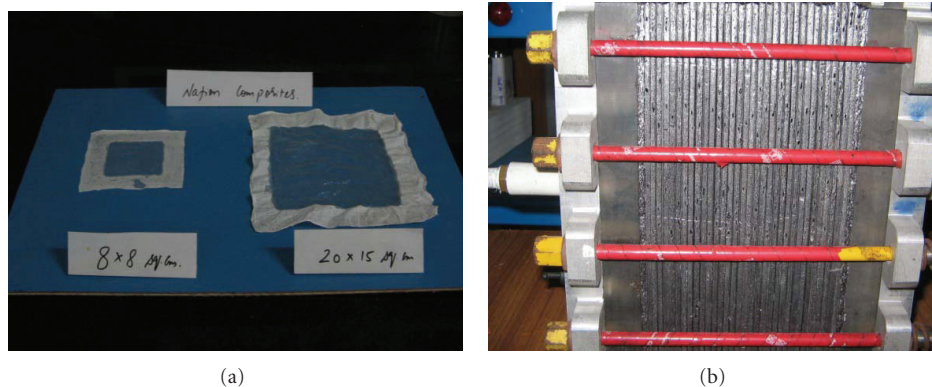


FIGURE 8: Composite membranes fabricated and the 20 cell PEMFC stack.

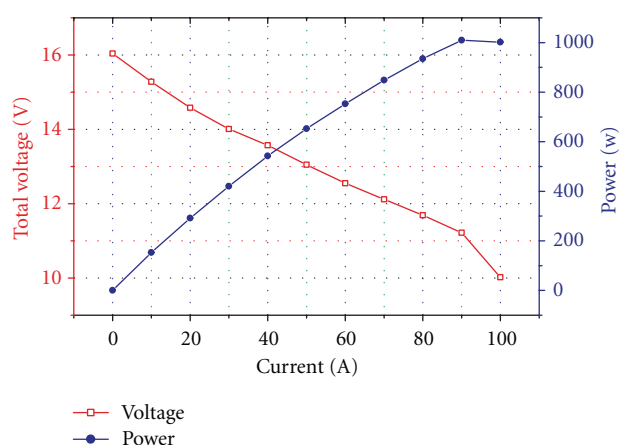


FIGURE 9: Performance of 20 cell fuel cell stack using the composite membrane.

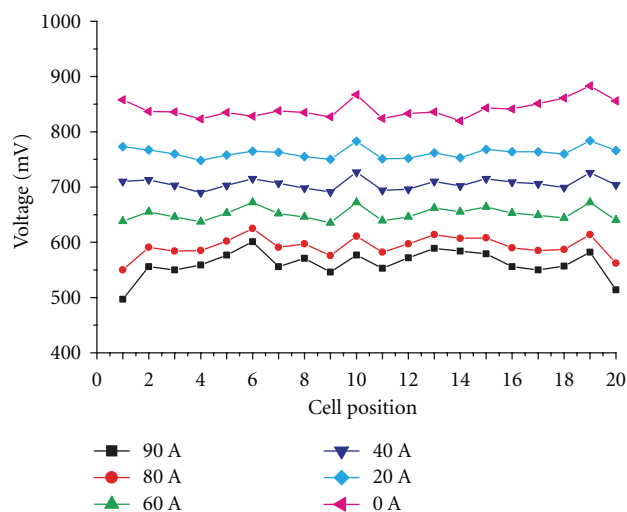


FIGURE 10: Performance of the individual cells at various current.

various currents are shown in Figure 10. The results show that the voltage distribution is fairly uniform. The deviation from the mean voltage at current densities up to 200 mA/cm^2 was less than 6% and increasing to 12% at a current density of 250 mA/cm^2 . These results suggest that the membranes

of comparable uniformity and quality have been prepared using the spray method, and the slight differences in the voltages of the various cells could be the result of slight differences in the internal resistance of the cells, nonuniform distribution of the reactant gases from the gas inlet to the outlet, and differences in the activation polarization of the electrodes, and so forth. With respect to endurance testing, the stack was not continuously tested at any particular power for long duration. The stack has been tested for more than 300 hrs at various conditions. The research and development program thus resulted in the development of 1 kW stack demonstrated using a composite membrane prepared in the lab. The process can be scaled up further to produce large stacks.

4. Conclusions

Composite Nafion membranes were fabricated by impregnating expanded PTFE substrate with the ionomer solution. Composite membranes with ionomer loading of 2 mg/cm^2 and thickness of $30 \mu\text{m}$ were found to have higher thermal stability and mechanical strength than conventional membranes with ionomer loading of $\sim 9 \text{ mg/cm}^2$ and $50 \mu\text{m}$ thickness. The composite membranes also offered cost advantages due to lower active material loading compared to the conventional membranes besides having comparable performance. Durability of the MEAs was tested by carrying out cycling studies between two voltages of 0.6 V and 0.1 V. The MEAs were cycled to ~ 2000 cycles, and it was found to give stable performance. Impedance analysis of the MEAs before and after cycling showed that the differences in the solution and the charge transfer resistances were almost the same indicating negligible membrane degradation. Based on the results, the membrane fabrication was scaled up and a 20 cell stack with an active area of 330 cm^2 were fabricated. A peak power of 1.01 kW was obtained with fairly uniform performance of the individual cells.

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