

Zeolite-based composite membranes for high temperature direct methanol fuel cells

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Abstract

Composite Nafion membranes containing three natural zeolites (Mordenite, Chabazite and Clinoptilolite) were prepared by using a recast procedure for application in high temperature Direct Methanol Fuel Cells (DMFCs). The Nafion-zeolite membranes have shown good properties for high temperature DMFC application, due to their improved water retention characteristics. A maximum power density of 390 mW cm⁻² was achieved at 140 °C with the mordenite-based composite membranes in the presence of oxygen feed. The electrochemical behaviour of the composite membranes was interpreted in the light of surface properties and acidic characteristics of the fillers.

1. Introduction

Direct methanol fuel cells (DMFCs) have good potentialities for application in transportation, portable power sources and distributed generation of clean energy due to their low environmental impact [1–3]. The main problems that have hindered the market penetration of these systems are the slow methanol oxidation reaction rate of the anode catalyst, the cost of the polymer electrolyte membrane presently used in these devices, the membrane dehydration at temperatures higher than 100–120 °C and the methanol cross-over [4–7].

A direct methanol fuel cell based on a high temperature proton conducting membrane with suitable conductivity and stability up to 130–150 °C and characterized by low thermal and water management would become a viable system for mobile applications. In this regard, composite membranes with the filler exhibiting strong affinity towards water molecules are of particular interest. Various reports have dealt with the use of composite recast Nafion membranes containing finely dispersed ceramic oxide powders in high temperature direct methanol and H₂-air fuel cells [8–13]. In fact, the role of inorganic filler is to improve the water retention in the membrane, allowing an increase of fuel cell operation temperature in conjunction with low external humidification conditions. A further effect of the composite membrane is the reduction of methanol cross-over [14, 15]. It is well known that the physical adsorption of water by materials such as silica (one of

the most used inorganic fillers) is mainly determined by the functional groups on the surface of these oxides that act as water co-ordination centers [16]; similar considerations can be made for other hygroscopic inorganic materials such as zeolites [17, 18].

To improve the proton conductivity of Nafion at high temperature, we have selected three natural zeolites as inorganic fillers in composite membranes, due to their characteristics as proton conductors and hygroscopic materials [15, 17, 19]. Thus, in the present work, we have prepared Nafion-zeolite composite membranes using Chabazite, Clinoptilolite and Mordenite as fillers. The behaviour of the composite membranes was evaluated under high temperature DMFC operation (140 °C). A membrane/electrode assembly (MEA) based on bare recast Nafion membrane was also investigated for comparison.

2. Experimental

The zeolites were received from GSA Resources Inc, Tucson AZ. The as-received zeolite materials were ground in an agate mill until a very fine powder was obtained. The zeolites were converted from Na⁺ to H⁺-form by treatment in a 0.01 M H₂SO₄ aqueous solution. X-ray diffraction (XRD) analysis of the zeolite powders before and after the acid treatment was carried out with a Philips X-Pert X-ray diffractometer using Cu K α source operating at 40 kV and 20 mA. BET surface area measurements of the zeolite fillers were made by a

Thermoquest 1990 series Sorptomatic. The fillers were compacted into pellets at 50 MPa and degassed in a sample holder at 140 °C under vacuum before the measurement. Potentiometric titrations of the inorganic fillers were carried out as reported previously [20]; a Metrohm automated titration system equipped with an ATC compensated pH probe was used. The inorganic powder was suspended in aqueous electrolyte (KNO₃ 0.1 M) and continuously stirred in the presence of N₂ purging. A defined amount of 0.1 M KOH was added for each sample and the slurry was back-titrated with 0.1 M HNO₃. The steady-state pH value was measured after each HNO₃ addition. The acid–base surface functional groups and the adsorption density function (OH⁻ – H⁺) were determined from these measurements by a WinZPC software (Costech International).

The composite membranes were prepared using an alternative approach than that presented in our previous papers [16, 21]. Five volumes of Nafion solution (5 wt% Aldrich) were mixed with 5 volumes of ethanol and 3 volumes of N, N-dimethylformamide (DMF). The fine zeolite powder (in H⁺-form) was then added to the resulting mixture and dispersed by stirring and sonication. The suspension was cast in a Teflon dish; afterwards, it was treated at 80 °C in a vacuum oven. Composite membranes with zeolite content of 3 and 6 vol. % were thus obtained. In order to evaluate the influence of the zeolite fillers on the electrochemical behaviour of the membrane for application in high temperature DMFC, a bare recast Nafion membrane was also prepared using the same procedure. The thickness of all the membranes was about 70 μm. The catalyst employed for methanol oxidation was a 60 wt% Pt–Ru (1:1)/Vulcan (E-TEK), whereas a 30 wt% Pt/Vulcan (E-TEK) was used for oxygen reduction. The platinum loading in all the electrodes was 2 ± 0.2 mg cm⁻². For both anode and cathode, the reaction layer was prepared by directly mixing in an ultrasonic bath a suspension of Nafion ionomer in water

with the catalyst powder (catalyst/dry ionomer = 2/1); the obtained paste was spread on carbon cloth backings. Membrane & electrodes assemblies were prepared by hot pressing the electrodes onto the membrane at 130 °C and 50 kg cm⁻².

Fuel cell tests were carried out in a 5 cm² single cell (GlobeTech, Inc.) connected to a HP 6060B electronic load. Two molar aqueous solutions of methanol and oxygen, preheated at 85 °C, were fed to the cell. The methanol solution was fed into the cell at a flow rate of 2.5 ml min⁻¹ whereas for the cathode feed oxygen at a flow rate of 500 ml min⁻¹ was passed through a humidification bottle maintained at 85 °C. Different operating temperatures for the cell were in the range 90–145 °C. The anode back-pressure was varied between 1 and 3.5 atm abs. as the temperature was increased from 90 to 145 °C; the cathode compartment back-pressure was maintained constant at 3.5 atm abs.

3. Results and discussion

Figure 1 shows the X-ray diffraction patterns of the three zeolite powders converted in H⁺-form by treatment in diluted sulfuric acid. From a comparison between the diffraction patterns of the powders before (not shown) and after the treatment, no change in the crystallographic structure of the zeolites was evident. The treated materials were used as fillers in the composite membranes in order to take advantage of the proton conduction, as well as the water retention properties of these powders.

The host environment of the inorganic filler particles inside the membrane may be considered, to a first approximation, as a solution of a dilute strong acid. The conductivity of Nafion® 1100 at room temperature is almost one order of magnitude lower than a 0.5 M H₂SO₄ solution (6 × 10⁻² S cm⁻¹ vs 4 × 10⁻¹ S cm⁻¹). Accordingly, the adsorption density of OH⁻ species in

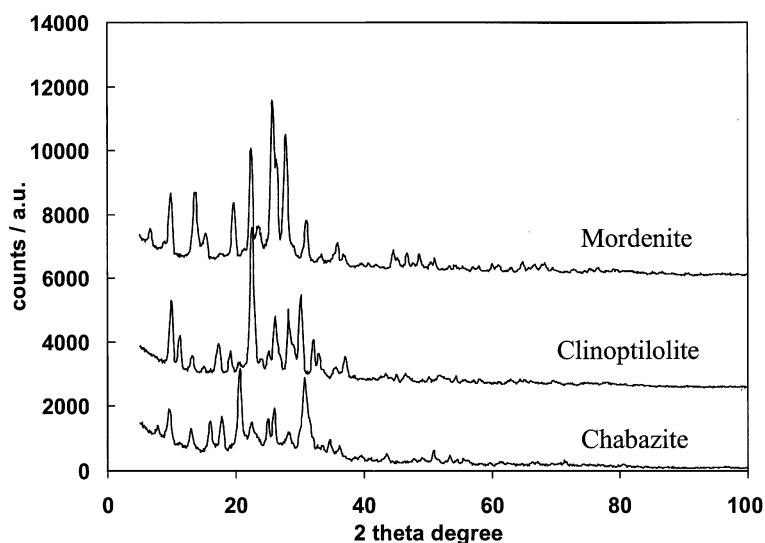


Fig. 1. X-ray diffraction patterns of the various zeolite powders after acid treatment.

the pH region around 2, as well as the zero point of charge (ZPC), may be indicative of the capability of the filler to adsorb water on the surface (Table 1). Figure 2 shows the variation of the $(\text{OH}^- - \text{H}^+)$ adsorption function versus pH for the H^+ – exchanged zeolites in powder form. It is clearly observed that the adsorption density $(\text{OH}^- - \text{H}^+)$ decreases in the low pH region according to the following series: mordenite > clinoptilolite > chabazite. The adsorption density appears to be related to the amount and strength of functional groups rather than to the BET surface area (Table 1).

The beneficial influence of the acid characteristics of the inorganic fillers on the high temperature performance of composite membranes in direct methanol fuel cells was demonstrated in a recent paper [21]. The presence of acidic groups on the particle surface facilitates the co-ordination of water, which acts as vehicle for proton migration. Furthermore, the characteristics of proton conduction of the zeolite materials enhance the conductivity of the polymeric membranes.

Figure 3 shows the variation of cell resistance with temperature for the MEAs equipped with the composite membranes compared to bare recast Nafion. MEAs based on composite membranes containing 3 vol. % inorganic filler showed similar cell resistances for the three different zeolites. This resistance did not vary significantly in the range between 90 and 145 °C. Effectively a small decrease from 90 to 130 °C was

observed, followed by a slight increase at about 140 °C. For the bare recast Nafion prepared by the same method, the cell resistance at 90 and 100 °C was lower than that of composite membranes, whereas it increased significantly with increase in temperature due to the dehydration of the membrane at high temperature. This probably indicates that the water retention effect is more significant with respect to the proton conduction behaviour of the zeolite powders.

All the MEAs equipped with the composite membranes were capable of operation at 140 °C with an increase in cell performance as the temperature was increased from 90 °C up to 140 °C. Also the cell based on bare recast Nafion membrane as electrolyte reached the operating temperature of 140 °C, but the cell performance recorded at this temperature was equal to that obtained at 120–130 °C due to the increased cell resistance caused by dehydration (not shown).

The polarization curves obtained for the fuel cells equipped with the different membranes containing 3 vol. % zeolite filler at 140 °C in the presence of oxygen feed at the cathode and 2 M methanol solution at the anode are shown in Figure 4. A similar electrochemical behaviour was observed for the various composite membranes, whereas the polarization curve of the cell equipped with bare recast Nafion was significantly affected by a larger ohmic drop. The best electrochemical performance was obtained with the mordenite-based membrane, which gave a maximum power density of

Table 1. Surface properties of zeolite fillers

Filler	BET surface area/m ² g ⁻¹	ZPC	Extra ads. function at pH 2.8 ($\Gamma_{\text{OH}^- - \text{H}^+}$) $\mu\text{mol g}^{-1}$	Basic or acidic functional group dissociation constants	Basic or acidic functional group amounts/meq g ⁻¹
Mordenite	194.07	2.10	490.05	pKa = 8.03 pKa = 3.56	1.053 0.965
Chabazite	341.25	3.43	-603.91	pKa = 8.02 pKa = 4.16	0.650 0.950
Clinoptilolite	5.87	2.90	-31.11	pKa = 7.98 pKa = 3.86	0.550 0.500

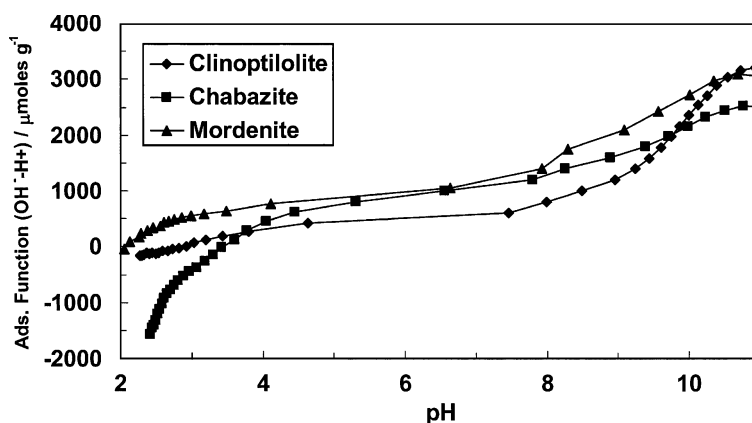


Fig. 2. Variation of the adsorption density function vs pH for the various zeolite fillers.

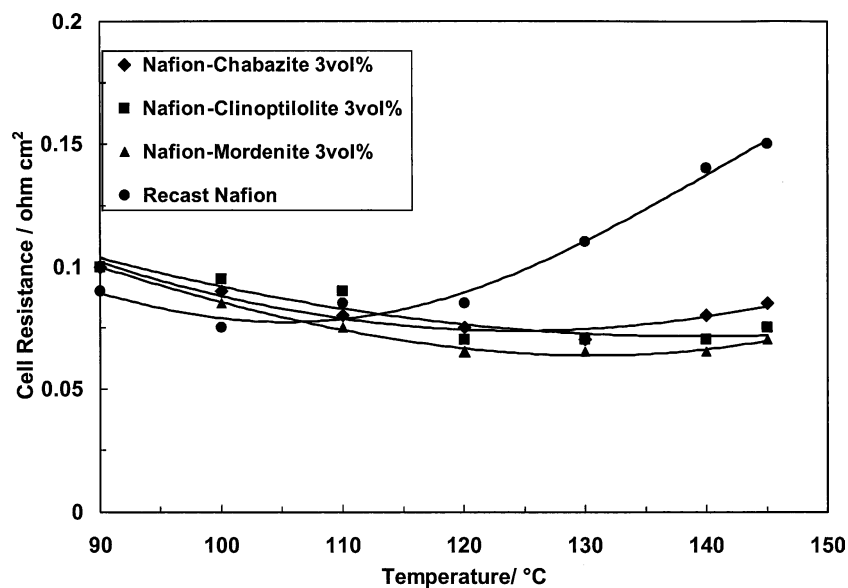


Fig. 3. Variation of cell resistance values as a function of the operating temperature for DMFCs employing the zeolite-based composite membranes compared to bare recast Nafion.

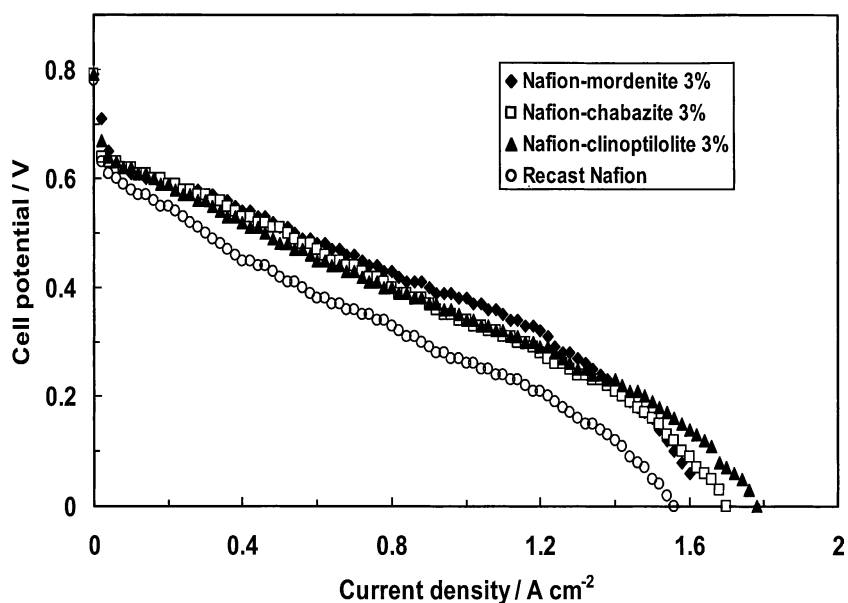


Fig. 4. DMFC polarization curves in the presence of oxygen feed at 140 °C for various MEAs equipped with the composite membranes containing 3 vol. % zeolite powders compared to bare recast Nafion.

390 mW cm⁻² at a current density of about 1.1 A cm⁻² at 140 °C under oxygen feed (Figure 5). Similar performances were recorded for the DMFCs equipped with 6 vol.% zeolite-Nafion membranes (not shown); however, at larger loadings, the occurrence of pinholes inside the membrane was observed to be more probable.

The effect of temperature on the electrochemical polarization and power density behaviour of a fuel cell equipped with the mordenite-based membrane is shown in Figure 6. The voltage loss in the activation control region decreases progressively as the temperature increases from 90 to 140 °C, indicating the strong

activation nature of the methanol electro-oxidation process.

4. Conclusions

Composite Nafion-zeolite membranes have shown good properties for high temperature DMFC operation, mainly due to their improved water retention characteristics. As observed with other inorganic fillers, the proton conduction properties [17] of the zeolite materials may also play a role in the enhanced conductivity

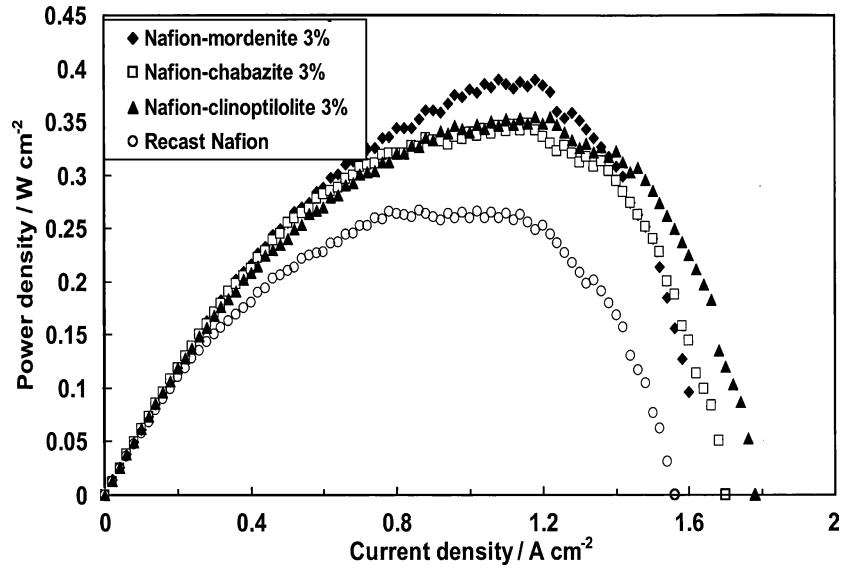


Fig. 5. DMFC power density curves in the presence of oxygen feed at 140 °C for various MEAs equipped with the composite membranes containing 3 vol. % zeolite powders compared to bare recast Nafion.

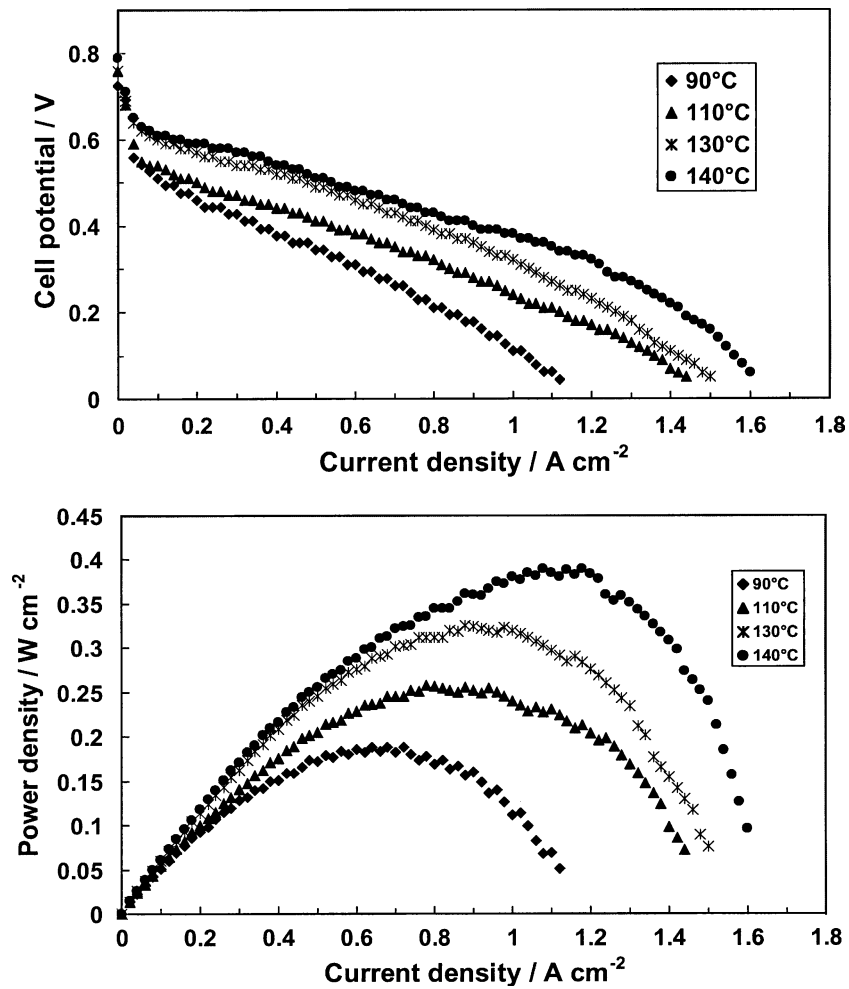


Fig. 6. Influence of operating temperature on the DMFC polarization and power density behaviour for the MEA equipped with mordenite-based membrane in the presence of oxygen and 2 M methanol feed.

of the DMFC at high temperature. However, this latter aspect requires further investigation. Maximum power densities between 350 and 390 mW cm⁻² were recorded at 140 °C under oxygen operation and 2 M MeOH with the 3 and 6 vol. % zeolite-based membranes. Such results indicate that an increase in membrane conductivity and DMFC performance can be achieved through an appropriate tailoring of the surface acid-base properties of the inorganic filler in the composite membranes.

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