

Influence of TiO₂ Nanometric Filler on the Behaviour of a Composite Membrane for Applications in Direct Methanol Fuel Cells.

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Abstract: Composite Nafion membranes containing various amounts of TiO₂ (3 wt%, 5 wt% and 10 wt%) were investigated for operation in high temperature Direct Methanol Fuel Cells (DMFCs). Maximum power density of 350 mW cm⁻² was achieved in the presence of oxygen feed at 145°C for the composite membranes containing 3-5 wt% TiO₂; whereas, the maximum power density with air feed was about 210 mW cm⁻². Moreover, an investigation of the influence of titanium oxide particle size on the electrochemical behaviour of the composite membranes for high temperature operation has been carried out. The DMFC performance increases as the mean particle size of the TiO₂ filler decreases. This indicates an influence of the filler morphology on the electrochemical properties of the composite membranes.

Key words : Composite Nafion membranes, titanium oxide, direct methanol fuel cell, particle size.

1. INTRODUCTION

Direct Methanol Fuel Cells (DMFCs) are promising candidates as electric power generators for application in vehicles in place of conventional internal combustion engines, due to their low polluting emissions [1-4]. At present, much attention is received by Direct Methanol Fuel Cells operating at temperatures close to 150°C and employing composite polymer electrolyte membranes [5-9]. The relatively high protonic conductivities that perfluorosulfonic polymeric membranes exhibit at low temperatures (below 100°C), in addition to their chemical and mechanical stability, allow the use of these materials as electrolytes in Polymer Electrolyte Fuel Cells (PEFCs). In DMFCs, an increase in operation temperature up to 150°C is highly desirable to enhance the kinetics of methanol oxidation and to reduce the poisoning of the anode electrocatalyst due to the ad-

sorbed methanolic residues. Accordingly, in the last years, significant efforts have been addressed to the development of high temperature polymer electrolyte membranes for DMFCs [10-14]. Recently, the use of Nafion membranes containing finely dispersed nanocrystalline ceramic oxide powders has been proposed [5, 7]. The role of the oxide powders is to improve the water retention characteristics of the membrane [15], allowing fuel cell operation at 145°C with low external humidification conditions. Yet, limited attention has been devoted to the investigation of structural and morphological properties of these oxides in relation to their use in composite membranes.

In the present work, the electrochemical behaviour of composite TiO₂-Nafion membranes has been studied to understand the influence of the inorganic filler content on the performance of a DMFC. An investigation of the influence of particle size and TiO₂ crystallographic phase transition (from anatase to rutile) on the electrochemical behaviour of a composite membrane for high temperature operation has also been carried out.

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2. EXPERIMENTAL

TiO₂ nanometric powder was synthesized via a sol-gel procedure, starting from a Ti(OiPr)₄ (Aldrich) [16]. The obtained xerogel, after thermal analysis, was calcined at various temperatures to vary the powder particle size and crystalline phase. X-ray diffraction (XRD) patterns were obtained using a Philips X-Pert X-ray diffractometer using Cu K α source operating at 40 kV and 20 mA. The average crystallite size of the powders was determined using Scherrer's equation. Scanning electron microscopy (SEM) of the powders was carried out using a Cambridge Stereoscan 360 instrument equipped with LaB₆ filament and operating at an acceleration voltage of 20 kV.

The following membranes were prepared: 1) Recast Nafion, 2) Recast Nafion + 3 wt% TiO₂ calcined at 500°C, 3) Recast Nafion + 5 wt% TiO₂ calcined at 500°C, 4) Recast Nafion + 10 wt% TiO₂ calcined at 500°C, 5) Recast Nafion + 5 wt% TiO₂ calcined at 650°C, 6) Recast Nafion + 5 wt% TiO₂ calcined at 800°C. All the membranes were prepared by a recast procedure [6,7]. The Nafion ionomer was mixed with dimethyl-sulfoxide (DMSO) and TiO₂ powder in an ultrasonic bath. The slurry was cast over a glass substrate. The solution was slowly evaporated at 80°C under vacuum to achieve a dense polymeric film. The thickness of all the membranes was about 100 μ m. The catalyst used 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 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 wt.); the obtained paste was spread on carbon cloth backings. MEAs were prepared by hot pressing the electrodes onto the membrane at 130°C and 50 atm.

Fuel cell tests were carried out in a 5 cm² single cell (GlobeTech, Inc.) connected to a HP 6060B electronic load. Aqueous solutions of methanol of varying concentrations (0.5, 1 and 2 M) and oxidant (oxygen or air), 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. For the cathode feed, oxygen or air at a flow rate of 500 ml/min was passed through a humidification bottle maintained at 85°C. Different operating temperatures for the cell were settled in the range from 90° to 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 TiO₂ powders heated at the various temperatures. For the powders calcined at 500°C and 650°C, XRD analysis showed the crystallographic structure of anatase with a crystallite size of 12 and

22 nm, respectively. The presence of rutile with a crystallite size of about 51 nm was observed for the powder calcined at 800°C.

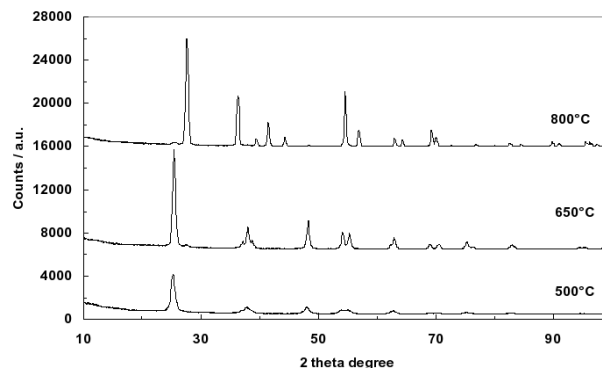


Figure 1: X-ray diffraction patterns of TiO₂ powders calcined at different temperatures employed in the preparation of the composite membranes.

Scanning electron microscopy (SEM) analysis of the nanocrystalline powders evidenced a similar morphology for the oxides with the same crystallographic structure, whereas significantly larger particles and a different morphology were observed for TiO₂ calcined at 800°C (Figure 2).

At first, the electrochemical behaviour of the various composite TiO₂-Nafion membranes was investigated to understand the influence of the inorganic filler content on the performance of a DMFC.

All the MEAs equipped with the composite membranes containing TiO₂ calcined at 500°C were capable of operation at 145°C, whereas the cell using bare recast Nafion membrane reached the maximum performance at 120°C. This behaviour is due to the higher conductivity of the cell using TiO₂-containing membranes, as confirmed by cell resistance measurements. Figure 3 shows the variation of the cell resistance as a function of the temperature for the assemblies equipped with composite membranes compared to bare recast Nafion. The cell resistance in the presence of composite membranes containing different amounts of titanium oxide did not vary in the range 90°-145°C, and it was lower than the resistance of the cell equipped with bare recast Nafion membrane. The cell resistance of the DMFC equipped with the bare recast Nafion membrane was not determined at 145°C since the cell showed very low current densities and an unstable behaviour at this temperature.

Figure 4a shows the polarization curves obtained for the fuel cell equipped with the different membranes in the presence of oxygen feed and 2 M methanol solution at 120°C. The best electrochemical performances were obtained with membranes con-

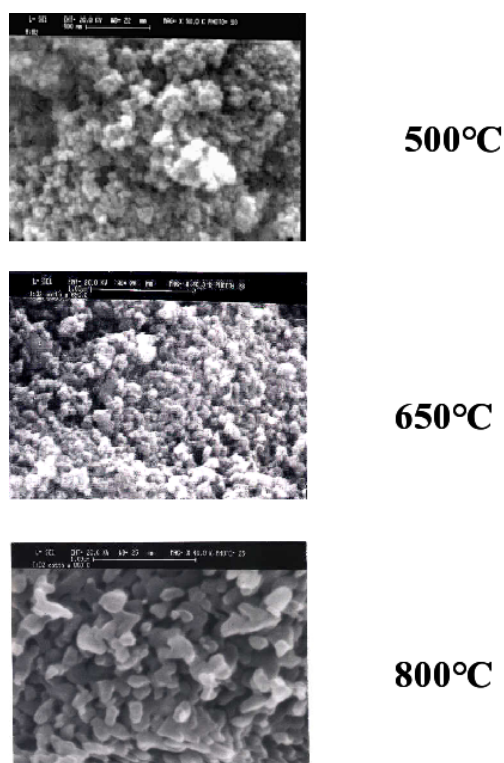


Figure 2: Scanning electron micrographs of the TiO₂ powders calcined at different temperatures employed in the preparation of the composite membranes.

taining 3-5 wt% TiO₂ loading. The maximum power density recorded at 120°C was around 280 mW cm⁻². The composite membranes showed superior power densities at 120°C with respect to the recast Nafion membrane (Fig. 4b).

It is well known that a high operating temperature, approaching 150°C, increases the catalyst tolerance towards adsorbed poisoning residues and reduces water and heat management. Figure 5 shows the polarization and power density curves for the fuel cell equipped with the composite membranes containing the various amounts of titania, in the presence of oxygen feed and 2 M methanol solution at 145°C. The DMFC performance for the composite membranes further improved up to 145°C whereas the bare membrane did not show any capability to operate under such conditions, as already stated (not shown). This was due to a strong decrease in conductivity of the bare membrane. On the contrary, the cells equipped with composite membranes reached the operation temperature of 145°C (Figure 5a).

A maximum power density of 350 mW cm⁻² was reached at a current density of about 1.1 A cm⁻² with oxygen at 145°C (Figure 5b). The performance of the composite membranes decreased with increasing the titanium oxide content up to 10 wt%, probably due to a unsuitable powder dispersion in the

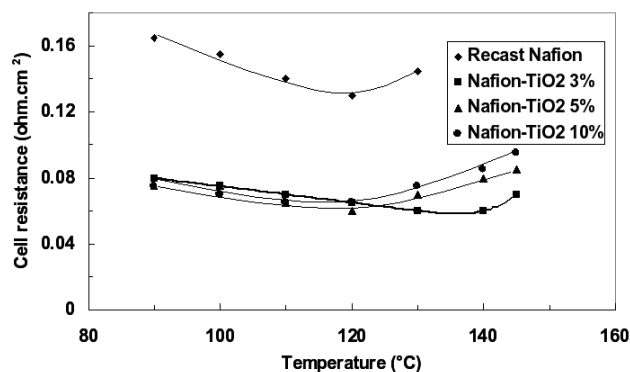


Figure 3: Variation of cell resistance values as a function of the operating temperature for DMFCs employing the composite membranes containing different amounts of TiO₂ calcined at 500°C compared to bare recast Nafion.

membrane; in this regard, the cell resistance also plays a considerable role.

Figure 6 shows the comparison between the polarization and power density curves for the fuel cell equipped with the composite membrane containing 5 wt% TiO₂, at 145°C in the presence of air or oxygen feed. The best electrochemical performances were obtained, for all the membranes, with 2 M methanol solution feed at the anode when oxygen was used as oxidant; when air was fed to the cathode compartment, the best fuel cell performances were obtained with 1M MeOH solution. This can be attributed to the effect of methanol cross-over on cathode polarization, which is more significant in the presence of air as oxidant. The maximum power density obtained in air with the recast Nafion + 5 wt% TiO₂ (calcined at 500°C) was 210 mW cm⁻² at 145°C; passing from oxygen to air the performance loss, in terms of maximum power density, was about 40%. Oxygen operation is useful to understand the fundamental properties of the membranes in absence of side effects such as mass transfer polarization constraints; air feed is important under practical operating conditions.

The 5 wt% TiO₂ loading was selected to investigate the influence of the ceramic oxide surface area on the electrochemical behaviour of DMFCs equipped with the composite membranes. Figure 7 shows the polarization and power density curves for the fuel cells equipped with recast Nafion membranes containing 5 wt% TiO₂ calcined at different temperatures. The best electrochemical performances, in terms of both power density and short circuit current density, were obtained with the cell equipped with the composite membrane including the smaller TiO₂ particles. The membranes with powder calcined at the highest temperature, having large crystallite dimensions, can also operate at 145°C but showed a poorer electrochemical be-

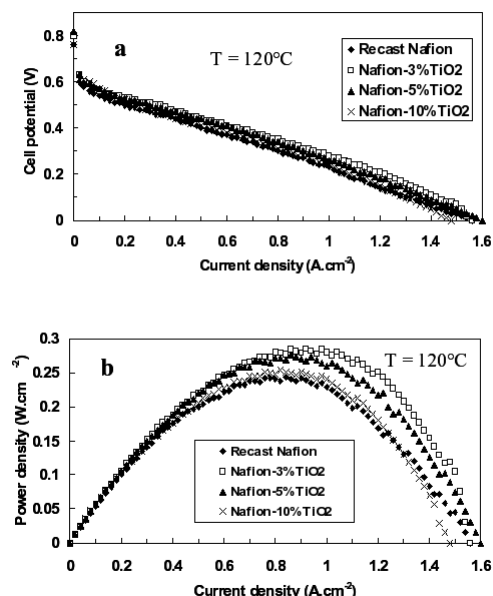


Figure 4: DMFC polarization (a) and power density (b) curves at 120°C for various MEAs equipped with the composite membranes containing different amounts of TiO₂ calcined at 500°C compared to bare recast Nafion. 2M methanol feed, 1.5 atm rel.; oxygen feed, 2.5 atm rel.

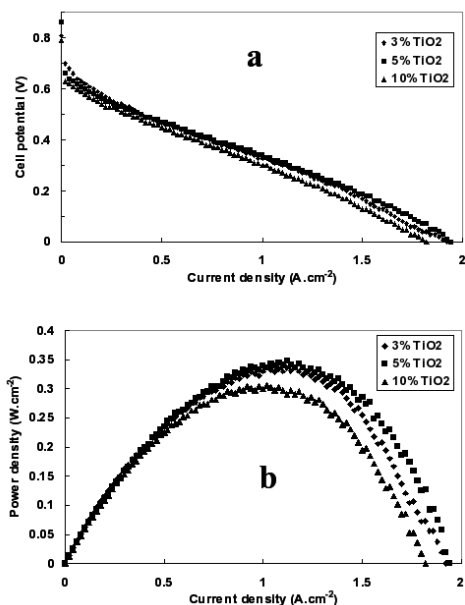


Figure 5: DMFC polarization (a) and power density (b) curves at 145°C for various MEAs equipped the composite TiO₂-Nafion membranes. 2M methanol feed, 2.5 atm rel.; oxygen feed, 2.5 atm rel.

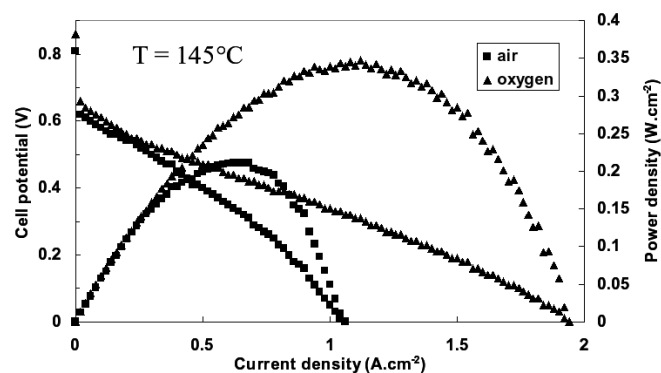


Figure 6: Comparison of the polarization and power density curves in the presence of air and oxygen feed for the MEA equipped with recast Nafion + 5 wt% TiO₂ (calcined at 500°C) at 145°C. Operating conditions: oxygen feed, 2M methanol; air feed, 1M methanol.

haviour, due to the higher cell resistance (Figure 8). This indicates that the water retention properties of the composite membranes [15] are strictly related to the number of adsorbing sites. Nothing can be said about the influence of the different crystallographic structure of titanium oxide, because different particle sizes are associated with different crystalline phases. Most likely, the differences in cell resistance and, consequently, in performance are only due to the different surface areas. The high temperature operation capability of the composite membrane relies in the water adsorption properties of the hygroscopic inorganic filler. The nature of the interaction between water molecules and the adsorbing sites on the filler surface has been previously investigated [17, 18]. The main difference between TiO₂ and other hygroscopic fillers, such as silica, is due to the nature and electronic environment of the surface functional groups. The present performances obtained with the TiO₂-composite membranes do not significantly differ from those recently reported for the Nafion-SiO₂ electrolytes [15]. It should be pointed out, however, that, in the case of the Nafion-SiO₂ membranes, amorphous silica has been mainly used. The TiO₂ powders offer the further advantage of tailoring the crystallographic structure allowing to modulate the physico-chemical characteristics and thus the water adsorption properties.

A considerable aspect for a successful application of a composite polymer electrolyte in fuel cell devices is the performance stability. In general, cycled operation is interesting for application in automotive systems where discontinuous operation is required. Accordingly, the DMFC equipped with Nafion membrane + 5 wt% TiO₂ (calcined at 500°C) was subjected to one month cycled operation. The cell was operated around 6 hours per day, including the start up and shut down procedures. Figure 9 reports the recorded cell current density, at a cell potential

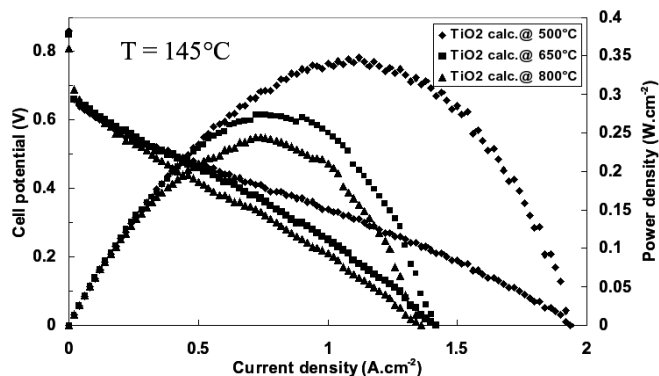


Figure 7: Polarization and power density curves at 145°C for the various MEAs equipped with the composite Nafion membranes containing 5 wt% TiO₂ calcined at different temperatures. 2M methanol feed, 2.5 atm rel.; oxygen feed, 2.5 atm rel.

of 0.4 V. A similar behaviour was recorded during all the days of operation. The slight decrease of performance with time is due to the strongly adsorbed methanolic residues poisoning the anode catalyst. When the cell is discharged by feeding water at anode, the initial performance is regained the following day.

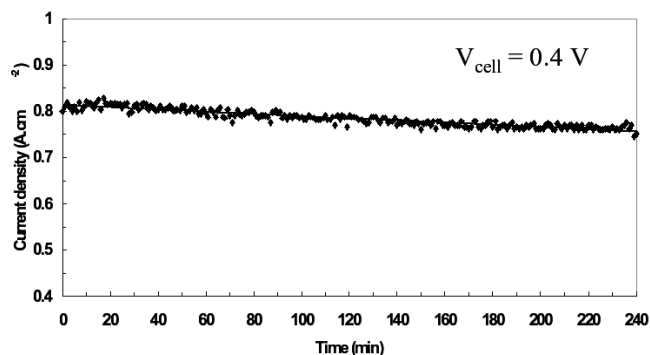


Figure 9: Variation of DMFC current density for the MEA based on composite recast Nafion membrane + 5 wt% TiO₂ calcined at 500°C as a function of time during a day operation under potentiostatic control. Cell voltage 0.4 V, temperature 145°C, 2M methanol feed, 2.5 atm rel., oxygen feed, 2.5 atm rel.

4. CONCLUSIONS

Composite Nafion-TiO₂ membranes have shown good properties for operation at 145°C in a Direct Methanol Fuel Cell, as a consequence of their improved water retention characteristics. DMFC investigation of these membranes reveals a significant influence of the ceramic oxide particle size and surface area on the electrochemical behaviour. This indicates that the water retention properties are related to the number of adsorbing sites. Further enhancement of such properties may be achieved through a proper tailoring of the filler morphology and structure.

5. ACKNOWLEDGMENTS

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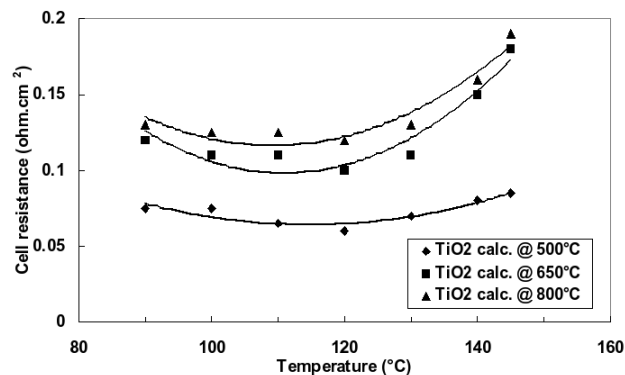


Figure 8: Variation of cell resistance values as a function of the operating temperature for DMFCs employing the composite membranes containing 5 wt% TiO₂ calcined at different temperatures.

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