Nafion–TiO$_2$ composite DMFC membranes: physico-chemical properties of the filler versus electrochemical performance

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Abstract

TiO$_2$ nanometric powders were prepared via a sol–gel procedure and calcined at various temperatures to obtain different surface and bulk properties. The calcined powders were used as fillers in composite Nafion membranes for application in high temperature direct methanol fuel cells (DMFCs). The powder physico-chemical properties were investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and pH measurements. The observed characteristics were correlated to the DMFC electrochemical behaviour. Analysis of the high temperature conductivity and DMFC performance reveals a significant influence of the surface characteristics of the ceramic oxide, such as oxygen functional groups and surface area, on the membrane electrochemical behaviour. A maximum DMFC power density of 350 mW cm^{-2} was achieved under oxygen feed at 145 °C in a pressurized DMFC (2.5 bar, anode and cathode) equipped with TiO$_2$ nano-particles based composite membranes.
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1. Introduction

Liquid-fuelled solid-polymer-electrolyte fuel cells are very promising as electrochemical power sources for application in portable devices and transportation, due to their simple design and low environmental impact [1–3]. Yet, despite the practical system benefits, the power density and the efficiency of direct methanol fuel cells (DMFCs) are low compared to polymer electrolyte fuel cells (PEFCs) operating with hydrogen because of the slow methanol oxidation kinetics and the fuel cross-over through the membrane [1–9].

In a pioneering work of Watanabe et al., composite membranes containing Pt-modified inorganic fillers have been shown to facilitate the electrolyte self-humidification by the recombination of H$_2$ and O$_2$ on the filler surface in PEMFC, at moderate temperatures (80 °C) [5]. Whereas, great efforts have been addressed to the development of polymeric membranes for high temperature DMFCs [10–14]. Operation temperatures above 120 °C are needed to reduce catalyst poisoning by adsorbed CO and enhance methanol oxidation rate. Composite membranes containing finely dispersed hygroscopic inorganic oxides [10,15] or heteropolyacids [16,17] effectively show large water retention properties and, consequently, suitable proton conductivity at high temperatures. Similar evidences have been observed when inorganic proton conductors, such as zirconium phosphate, have been used as fillers in DMFC membranes [11]. In particular DMFC operation at temperatures close to 150 °C has been demonstrated with composite Nafion membranes [10,11,15,17]. The adsorption and retention of water on inorganic oxides depends on their surface properties; in particular, the amount of

co-ordinated water depends on the nature and relative concentration of the surface functional groups [15,18,19].

As a progress of our activity in the development of innovative composite membranes for FCs application, this work deals with an investigation of the influence of morphological and chemical characteristics of TiO_2 as filler for Nafion-based composite membranes. TiO_2 nanometric powders were in-house prepared via a sol–gel procedure. Thermal treatments at different temperatures were performed to tailor the oxide powder properties. The electrochemical behaviour of DM-FCs equipped with the composite membranes based on TiO_2 fillers with different characteristics was investigated.

2. Experimental

Nanosized titanium oxide was synthesized by sol–gel hydrolysing an alcoholic solution of $Ti(OiPr)_4$ (Aldrich) according to a previously reported procedure [20]. TG analysis of the obtained titania precursor was carried out in a Netzsch TG/DSC/DTA analyser. The precursor was then thermally treated at different temperatures (500, 650 and 800 °C) for 2 h. X-ray diffraction (XRD) analysis was performed with a Philips X-Pert diffractometer using Cu Kα source operating at 40 kV and 20 mA. Transmission electron microscopy (TEM) of the powders was carried out using a Philips CM12 microscope equipped with LaB_6 filament. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Physical Electronics (PHI) 5800-01 spectrometer equipped with a monochromatic Al source operating at 350 W. Element spectra were acquired with pass energy of 11.75 eV. The pH of slurry was measured at room temperature by an ATC compensated pH probe (Orion). The slurry was composed by 0.5 g of powder suspended in 0.1 L of bi-distilled water and stirred for 24 h in the presence of a stream of nitrogen. A steady pH value was typically obtained after a few tens of minutes and no significant pH drift was recorded after 24 h (<0.05 pH units). The pH of slurry was sampled in any case after 24 h.

All the composite membranes were prepared by using the recast procedure. The Nafion ionomer was mixed with dimethyl-sulfoxide (DMSO) and TiO_2 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. This latter was detached from the glass substrate by addition of distilled water and hot pressed between two PTFE foils at 160 °C for 10 min. Membrane thickness was about $100 \pm 5\,\mu m$. The methanol oxidation catalyst was a 60% Pt–Ru (1:1)/Vulcan (E-TEK), whereas a 30% Pt/Vulcan (E-TEK) was used for oxygen reduction. The catalyst layers, including 33 wt.% Nafion ionomer, were supported on a carbon cloth support coated with a diffusion layer. The platinum loading for all the electrodes used in the experiments was $2 \pm 0.1\,mg\,cm^{-2}$. MEAs were prepared by hot pressing the electrodes onto the membrane at 130 °C and 50 bar. Fuel cell tests were performed
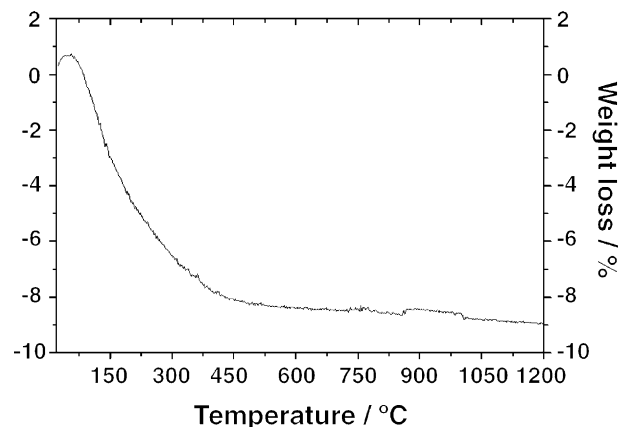

Fig. 1. TG analysis of the titania precursor obtained from the sol–gel procedure.

in a $5\,cm^2$ single cell (GlobeTech, Inc.) connected to a HP 6060B electronic load. A 2 M aqueous solution of methanol and an oxygen stream were preheated at 85 °C and fed to the cell. The methanol solution was fed into the cell at a flow rate of 2.5 mL/min whereas the cathode feed was passed through a humidification bottle with a flow rate of 500 mL/min. The anode and the cathode back pressure was 2.5 bar at 145 °C. The cell resistance was determined at the various temperatures by the current interrupter method during cell operation at $400\,mA\,cm^{-2}$.

3. Results and discussion

The TG scan of the precursor obtained by sol–gel shows that only a very slight weight loss (1% wt.) occurs above 450 °C (Fig. 1). The powders were then calcined at 500, 650 and 800 °C to obtain crystalline TiO_2. Fig. 2 shows the X-ray diffraction patterns of the TiO_2 samples after thermal treatments at the three selected temperatures. The presence
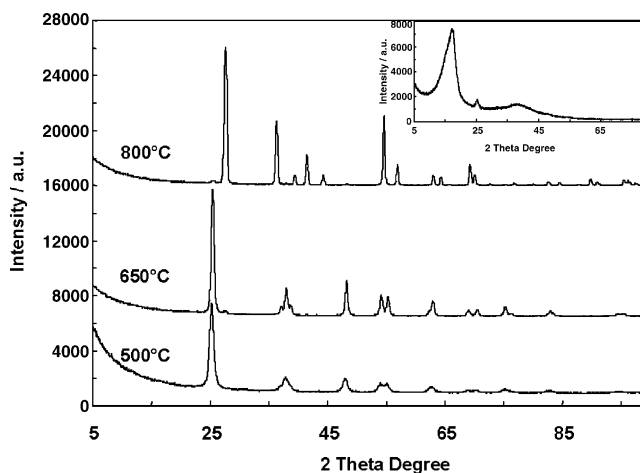

Fig. 2. X-ray diffraction patterns of TiO_2 powders calcined at different temperatures; inset: 5 wt.% TiO_2 (calcined at 500 °C) based recast Nafion membrane.

of the crystallographic structure of anatase was observed for the powders calcined at 500 and 650 °C while the crystallographic structure of rutile was observed for the sample calcined at 800 °C [20]. The crystallite size for the three samples, determined using the Scherrer's equation, was 12, 22 and 39 nm, respectively. The inset of Fig. 2 shows the XRD pattern of the composite Nafion membrane containing 5 wt.% TiO_2 calcined at 500 °C. This composite membrane shows the typical diffraction pattern of Nafion and small reflections due to TiO_2 in the anatase phase.

Fig. 3 shows the TEM micrographs of the various TiO_2 samples. The particle size is in agreement with the XRD measurements for the powder calcined at the lowest temperature (500 °C), although proper determination of the primary particle dimension was not possible because of the presence of agglomerates. Larger particles were observed in the TEM images of the samples fired at 650 and 800 °C; as expected, the particle size increases progressively with the thermal treatment temperature.

The surface chemistry of the TiO_2 powders was investigated by X-ray photoelectron spectroscopy (Figs. 4 and 5). The Ti $2p_{3/2}$ and Ti $2p_{1/2}$ photo-electron lines (Fig. 4) occurred at the same binding energies for the three samples

Fig. 4. Comparison of the Ti 2p X-ray photoelectron peaks for the TiO_2 powder calcined at different temperatures.
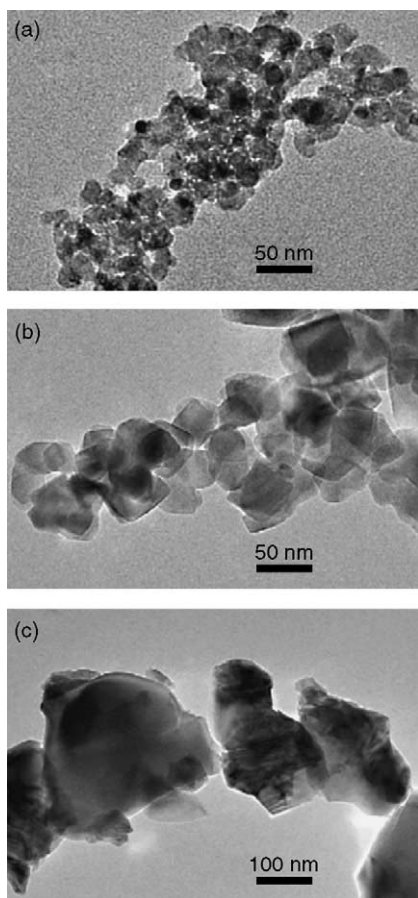
Fig. 3. Transmission electron micrographs of the TiO_2 powders calcined at 500 °C (a), 650 °C (b) and 800 °C (c) employed in the preparation of the composite membranes.
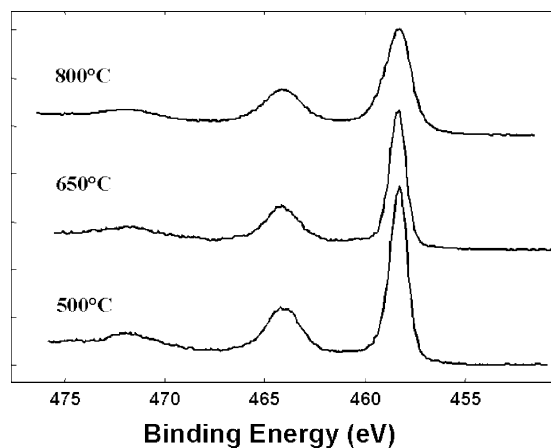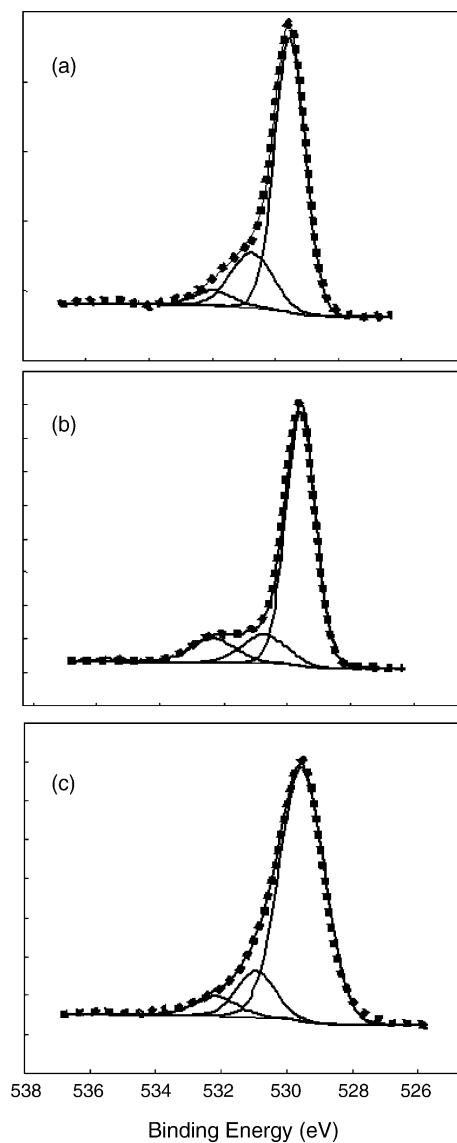
Fig. 5. Curve fitting of O 1s X-ray photoelectron peaks for the TiO_2 powder calcined at 500 °C (a), 650 °C (b) and 800 °C (c).

Table 1
B.E. and relative peak areas of O 1s species from curve-fitted XPS spectra
for the various TiO_2 powders

Species	B.E. (eV)	Relative peak area (%)
TiO_2 calcined at 500 °C	O 1s	
	529.54	72.91
	530.76	21.08
	531.98	5.01
TiO_2 calcined at 650 °C	O 1s	
	529.56	75.52
	530.71	12.61
	532.33	11.87
TiO_2 calcined at 800 °C	O 1s	
	529.53	84.23
	530.93	11.20
	532.17	4.57

(458.4 ± 0.2 eV and 463.94 ± 0.2 eV, respectively). This
B.E. is typical of TiO_2 compounds; accordingly, the photo-
electron peaks are mainly associated to the main Ti sites from
the titania framework with small influence from surface de-
fects. The O 1s region of the XPS spectra (Fig. 5) showed sim-
ilar values of B.E. for the main peak (Table 1) of the various
TiO_2 samples (529.6 eV). However, the TiO_2 powders treated
at 500 and 650 °C and characterized by the anatase structure
showed a larger content of oxygen species at higher binding
energies. These peaks, centered at about 530.8 eV (Fig. 5),
are associated with the presence of surface OH groups. Their
intensity is not very high with respect to the main O 1s peak
deriving from crystalline TiO_2 framework. However, the oc-
currence of Ti–OH groups on the surface imparts a slight
acidic behaviour to the fillers [19]. This finding was con-
firmed by the measurements of the pH of slurry for the titania
powders; the higher the temperature of the powder calcina-
tions, the higher the measured values of the pH of slurry, up
to basic value for the powder heated to 800 °C (Table 2). The
XPS analysis showed that the ratio between the intensities of
the acidic Ti–OH surface species and the neutral –O–Ti–O–
species from the framework was slightly larger for the sample
treated at the lowest temperature (500 °C). The more acidic
behaviour of this sample with respect to the powder heated
to 650 °C can be also ascribed to its smaller particle size, and
thus its larger surface area (Fig. 5a and b). The concentration
of surface OH groups was lower for the sample calcined at
800 °C and having the rutile structure, because of the wa-
ter elimination reactions induced by the thermal treatment
(Fig. 5c). Yet, a small peak was still present in the higher
binding energies region of the O 1s spectrum.

Table 2
Physico-chemical properties of TiO_2 powders

Filler	Crystallographic structure	Mean particle size[a] (nm)	pH of slurry
TiO_2 calcined at 500 °C	Anatase	12	5.3
TiO_2 calcined at 650 °C	Anatase	22	6.2
TiO_2 calcined at 800 °C	Rutile	39	9.0

[a] From XRD; (1 0 1) reflection for anatase and (1 1 1) reflection for rutile.

These surface oxygen species are believed to be respon-
sible of the water co-ordination on the filler surface during
membrane operation above 100 °C, probably assisting at dif-
ferent extents the proton conduction [18,19]. The XPS O 1s
peak component at higher B.E.s (at about 532 eV) could be
associated with the presence of surface oxygen containing
carbonaceous species adsorbed from the atmosphere.

To evaluate the influence of physico-chemical properties
of the inorganic filler on the electrochemical behaviour, com-
posite recast Nafion membranes containing 5 wt.% TiO_2
powder calcined at the three different temperatures (500, 650,
800 °C) were prepared and tested in fuel cell devices. Fig. 6
shows the polarization curves recorded at 145 °C for the var-
ious MEAs equipped with the composite Nafion membranes
containing 5 wt.% TiO_2 calcined at different temperatures.
The inset of Fig. 6 shows the variation of cell resistance as a
function of the operating temperature for DMFCs employing
these composite membranes. Since the nature of the surface
functional groups is essentially the same for the three inor-
ganic fillers, the variation in performance and conductivity
can be mainly attributed to the different particle size, and thus
to the different specific surface areas (SSA). A powder with a
large specific surface area is characterized by a large number
of adsorbing sites. Accordingly, a significant number of water
molecules will be coordinated by the OH groups present on
the surface of TiO_2 particles, promoting the proton transport
through the membrane at high temperatures.

No specific role appeared to be played by the bulk struc-
ture. The membranes treated at 650 and 800 °C, contain-
ing fillers with the anatase and rutile structure, respectively,
showed similar electrochemical properties. In agreement, the
XPS analysis showed for these samples essentially simi-
lar surface functionalities independently from the crystal-
lographic structure. The main differences among these two
powders consisted in the relative concentration of the func-
tional groups capable of water coordination [15,18,19], as
determined by XPS. The specific surface area can be roughly
evaluated from particle size [21], by assuming an approx-
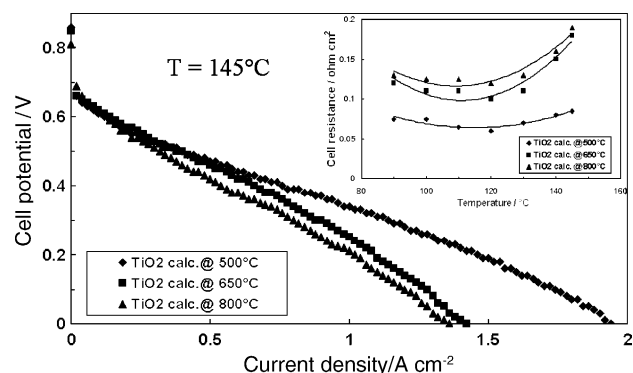imately spherical shape for the primary particles; applying

Fig. 6. Variation of cell resistance (inset) as a function of the operating tem-
perature and polarization curves at 145 °C for the various MEAs equipped
with the composite Nafion membranes containing 5 wt.% TiO_2 calcined at
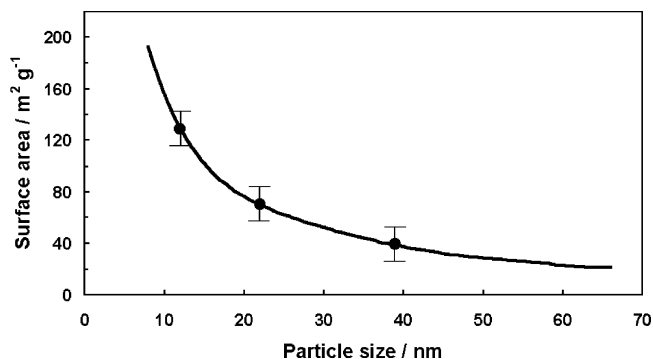different temperatures. 2 M Methanol feed, 2.5 bar; oxygen feed, 2.5 bar.

Fig. 7. Variation surface area as a function of particle size for the various TiO$_2$ powders.

Fig. 9. Variation of DMFC current density for the MEA based on composite recast Nafion membrane containing TiO$_2$ calcined at 500 °C as a function of time during a day operation under potentiostatic control. Cell voltage 0.4 V, temperature 145 °C, 2 M methanol feed, 2.5 at. rel., oxygen feed, 2.5 at. rel.

such model a sudden increase in SSA (m^2/g) would occur for particle sizes smaller than about 20 nm (Fig. 7); this may explain the improvement in performance and conductivity of the membranes based on TiO$_2$ powder with an average particle size close to 11 nm (Fig. 6).

A maximum power density of 350 mW cm^{-2} was obtained at 145 °C with the cell equipped with the composite membrane containing TiO$_2$ calcined at 500 °C (Fig. 8). The cells equipped with the membranes with larger TiO$_2$ particles were also operated up to 145 °C, but, the performance did not increase significantly going from 130 to 145 °C (not shown) because of a significant increase in cell resistance (Fig. 6, inset).

A considerable aspect for a successful application of a composite polymer electrolyte in fuel cell devices is the performance stability. Accordingly, the DMFC equipped with Nafion membrane containing TiO$_2$ calcined at 500 °C was subjected to 1 month operation with daily-cycles of start up and shut down. The recorded cell current density, at a cell potential of 0.4 V, for a typical day of operation is reported in Fig. 9. A similar behaviour was recorded during all the days of operation. The slight decrease of performance with time was probably due to a poisoning effect by methanolic residues at the anode as well as the formation of oxide species on the cathode surface [22]. After discharging the cell by feeding
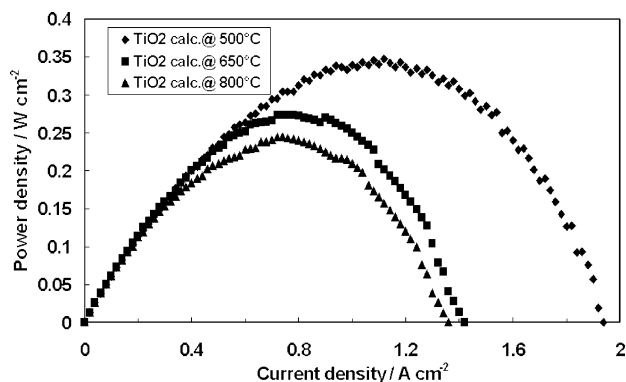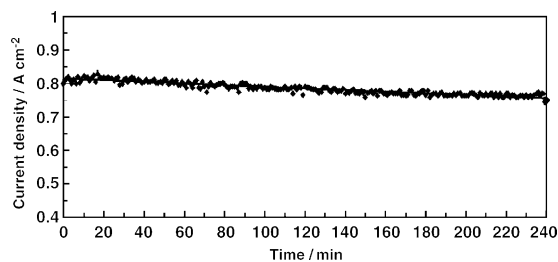
water at the anode, the day after the cell regained the initial performance.

4. Conclusions

The influence of physico-chemical properties of TiO$_2$ inorganic filler on the electrochemical behaviour of a DMFC based on composite membranes was investigated. It clearly appears that, for materials characterized by similar surface functional groups, the effect of the filler surface area becomes prevailing in determining the water retention properties of the composite membranes at high temperature. This effect appears to be associated to the larger number of water-adsorbing acidic sites on the filler surface. As expected, the surface properties play a role more important than the crystalline structure of the filler, since the water molecules acting as promoters towards the proton migration are effectively coordinated by the surface groups. A further increase of the electrochemical performance may thus be achieved by appropriate tailoring of the surface characteristics of the inorganic filler.

Fig. 8. Power density curves at 145 °C for the various MEAs equipped with the composite Nafion membranes containing 5 wt.% TiO$_2$ calcined at different temperatures. 2 M Methanol feed, 2.5 bar; oxygen feed, 2.5 bar.

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