Surface properties of inorganic fillers for application in composite membranes-direct methanol fuel cells

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Abstract

The surface properties of inorganic fillers employed in composite membranes have been investigated by X-ray photoelectron spectroscopy (XPS), BET surface area and acid–base characterisations. The adsorption density of hydroxyl–hydrogen ions and the pH of slurry varied with the amount and strength of acid–base surface functionalities. A shift towards higher binding energies was observed for the O 1s photoelectron peak as a function of the increase of the filler acidic behaviour. The conductivity of the membranes and the maximum power density at 145 °C for direct methanol fuel cells (DMFCs) increased with the filler surface acidity.
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1. Introduction

Composite recast Nafion® membranes containing inorganic fillers have been employed in high temperature (~150 °C) direct alcohol [1–6] and H₂–air fuel cells [7,8]. These composite membranes were originally developed for reduced humidification operation in polymer electrolyte fuel cells [9] due to the enhanced water retention inside the membrane by the effect of the inorganic filler [1,9]. A further advantage of composite membranes resides in the barrier effect given by the inorganic filler for methanol cross-over [10,11] which is of particular relevance at high temperature [12–14]. 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 their surface properties [15]; similar considerations can be made for other hygroscopic inorganic oxides such as alumina [16]. Functional groups on the surface of these oxides are believed to act as water co-ordination centres [15,16]. FTIR analysis of various silica materials suggests that oxygen surface functionalities play a prevailing role in the adsorption of water [15,16]. The surface characteristics of an inorganic oxide can be modified by thermal treatments in inert or oxidising atmosphere [15] through reactions with strong inorganic acids [17]. Most of the previous works on

composite membranes have mainly addressed the technical aspects related to the use of these materials as electrolytes in high temperature fuel cells. Accordingly, performance, conductivity and stability characteristics have been in depth investigated, but limited attention has been devoted to the surface properties of the fillers and their influence on the electrochemical behaviour at high temperature. In the present work, an attempt to correlate some of the surface properties of inorganic fillers to the electrochemical characteristics of direct methanol fuel cells (DMFCs) equipped with such membranes has been made. Accordingly, surface area analysis, X-ray photoelectron spectroscopy measurements and surface acid–base investigations of the fillers have been carried out and the derived information has been used as a basis to interpret the observed variation in membrane conductivity and DMFC performance.

2. Experimental

SiO₂, basic alumina (b-Al₂O₃) and neutral alumina (n-Al₂O₃) ceramic oxide fillers have been purchased from Cabot, Aldrich and Baker, respectively. ZrO₂ was synthesised at Rome Tor Vergata University and SiO₂–phosphotungstic acid (PWA) was prepared as described previously [2]. The SiO₂–PWA filler was composed of 70 wt.% SiO₂ and 30 wt.% H₃PW₁₂O₄₀. X-ray diffraction analysis (XRD) of the fillers was carried out with a Philips X'Pert

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diffractometer equipped with a Cu Kα X-ray source. XRF analysis was carried out by a Bruker S4 Explorer instrument. BET surface area measurements of the inorganic fillers were made by a Thermoquest 1990 Series Sorptomatic. The pH of slurry was measured at room temperature by an ATC compensated pH probe (Orion). The slurry was composed by 0.5 g powder per 0.1 l of bi-distilled water. The slurry was stirred for about 24 h. in the presence of nitrogen bubbling to obtain a steady-state pH value. Potentiometric titrations of the inorganic fillers were carried out as reported previously [18]; a Metrohm automated titration system equipped with an ATC compensated pH probe was used. The inorganic powder was suspended in aqueous electrolyte (KNO$_3$, 0.1 M) and continuously stirred in presence of N$_2$ purging. A defined amount of 0.1N KOH was added for each sample and the slurry was back-titrated with 0.1N HNO$_3$. The steady-state pH value was measured after each HNO$_3$ addition. The acid–base surface functional groups and the adsorption density function (OH$^-$–H$^+$) were determined from these measurements by WinZPC software (Costech International). X-ray photoelectron spectroscopy (XPS) measurements were performed by using a Physical Electronics (PHI) 5800-01 spectrometer. A monochromatic Al Kα X-ray source was used at a power of 350 W. Spectra were obtained with pass energy of 11.75 eV. The Ag 3d$_{5/2}$ peak of an Ag foil was taken, after argon sputtering, for checking the calibration of the binding energy (BE) scale.

The membranes were prepared by using a recast procedure previously described [1]. The membrane thickness was about 100 μm, whereas the content of inorganic filler was 3 wt.% MEAs were prepared following a procedure previously described [19]. Two molar aqueous solution of methanol and oxygen were preheated at 85 °C and fed to the cell. The catalyst employed for methanol oxidation was 60% Pt–Ru (1:1)/Vulcan XC (E-TEK), whereas a 30% Pt/Vulcan XC (E-TEK) was used for oxygen reduction. The platinum loading for all the electrodes was 2 ± 0.1 mg/cm^2. Cell resistance measurements under fuel cell operation have been carried out by the current interrupter method; methanol cross-over was determined at a fixed current by the CO$_2$ sensor method [13,14].

3. Results and discussion

Some relevant surface properties of the inorganic fillers are reported in Table 1. Two inorganic fillers used in the present study are characterised by an amorphous structure, i.e. SiO$_2$ and SiO$_2$–PWA, whereas Al$_2$O$_3$ and ZrO$_2$ have the structure of γ-alumina and cubic–monoclinic phases (ZrO$_2$), respectively. All the inorganic fillers have large surface area, ranging between 96 and 324 m^2/g. After adsorption of phosphotungstic acid on the silica surface, the surface area of the SiO$_2$ decreases from 324 to 166 m^2/g; however, it still retains an amorphous structure [2] as the raw silica. No evidence of the crystalline PWA Keggin structure [20,21] is found. This suggests that PWA is dispersed at the molecular level thus loosing its own crystal structure and long-range order. Amorphous silica powders are characterised by the presence of acidic silanolic (Si–OH) or basic siloxanic (Si–O–Si) groups on the surface [15]. Potentiometric titration results indicate a prevailing presence of silanolic functionalities on the surface of the Cabosil powder used in the present study (Table 1). Two prerequisites are essential for a proper uptake of PWA on the surface of an inorganic oxide, i.e. a strong chemical interaction and a large surface area for the oxide. As previously observed [17], impregnation of PWA on the SiO$_2$ surface involves a strong acid–base interaction where the silanolic groups behave as a Lewis base with respect to phosphotungstic acid. This acid possesses three acidic constants; at least one of these groups chemically interacts with the silica surface. Potentiometric titration analysis shows the absence of acidic groups associated to Si–OH functionalities (Table 1) as a consequence of their chemical interaction with PWA. Concurrently, the presence of two new acidic groups is detected; resulting in stronger acid properties of the surface with respect to bare silica. Neutral alumina is characterised by an amphoteric behaviour due to a comparable amount

Table 1
Surface properties of inorganic fillers

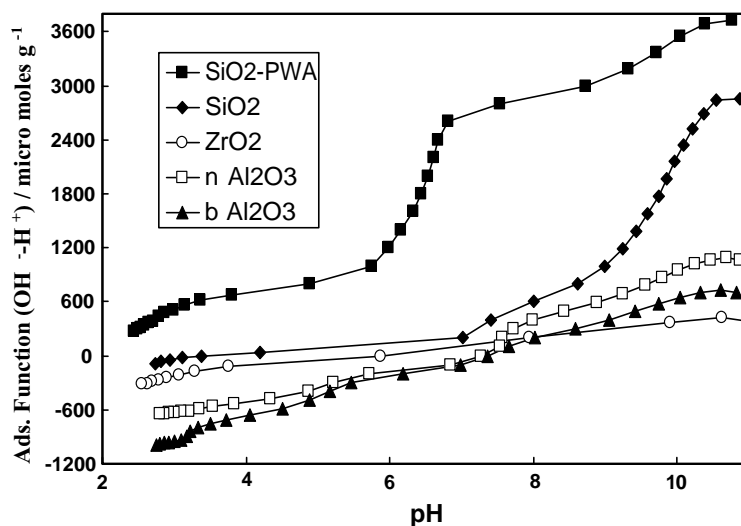| Filler	BET surface area (m^2/g)	pH of slurry	Extra adsorption function at pH 2.8 (OH$^-$–H$^+$) (μmol/g)	Basic or acidic functional group dissociation constants	Basic or acidic functional group amounts (meq./g)
SiO$_2$	324.11	4.75	−61	pK_a = 4.76	0.086
SiO$_2$–PWA	166.28	2.54	436	pK_a = 6.59	1.480
				pK_a = 3.34	0.760
ZrO$_2$	96.03	5.35	−270	pK_a = 6.24	0.067
n-Al$_2$O$_3$	109.1	7.5	−649	pK_a = 7.65	0.525
				pK_b = 6.98	0.150
				pK_b = 8.86	0.350
b-Al$_2$O$_3$	152.17	8.2	−975	pK_a = 7.78	0.275
				pK_b = 7.02	0.200
				pK_b = 8.87	0.425

Fig. 1. Variation of the adsorption density function vs. pH for various inorganic fillers.

of acidic and basic functional groups with similar strength (Table 1). The same surface groups are detected in the basic alumina but the number of basic sites is in this case prevailing. By analysing the overall acid–base behaviour (Table 1) it is observed that the pH of slurry reflects both the amount and strength of the surface functionalities, as well as the adsorption density behaviour in the acidic range; accordingly, this parameter represents a quantitative estimation of the surface acid–base behaviour for the inorganic filler and its determination is much simpler and faster than other surface parameters, such as the zero point of charge. The pH of slurry for the various fillers varies according to the following series: SiO_2–PWA < SiO_2 < ZrO_2 < n-Al_2O_3 < b-Al_2O_3.

The recast Nafion® acts as a host structure for the inorganic filler. It may be reasonably hypothesised that no filler particles may be entrapped in the crystalline region of the polymer; whereas, accessible regions are the amorphous domain and the water channels. The amount of filler entering the water channels or the amorphous region cannot be easily quantified; however, SAXS and WAXS analyses have shown only a little influence on the membrane morphology when the filler concentration is not higher than 3 wt.% [22]; however, the ceramic oxides have particle size comparable to the diameter of the water channels when the membrane is in the swollen form [22]. The host environment of the inorganic filler particles may be considered, in a first approximation, as a solution of a diluted strong acid. The conductivity of Nafion® 1100 is at room temperature almost one order of magnitude lower than a 0.5 M H_2SO_4 solution (6×10^{-2} S/cm versus 4×10^{-1} S/cm) [23]. Accordingly, the adsorption density of OH^- species in the pH range around 2 may be indicative of the capability of the filler to adsorb water on the surface. It is clearly observed in Fig. 1 that the adsorption density (OH^-–H^+) varies in the low pH range according to the following series: SiO_2–PWA > SiO_2 > ZrO_2 > n-Al_2O_3 > b-Al_2O_3. The adsorption den-

sity appears much more related to the amount and strength of functional groups than to the BET surface area (see, as an example, the SiO_2–PWA versus SiO_2). With the exception of ZrO_2, the adsorption density series for OH^- species in the basic range (Fig. 1) is similar to that of the acid range (SiO_2–PWA > SiO_2 > n-Al_2O_3 > b-Al_2O_3 > ZrO_2).

As reported in literature, the surface groups of silica, alumina and zirconia are mainly constituted by oxygen functionalities; the same holds for phosphotungstic acid whose crystallographic structure is well known [21]. Fig. 2 shows the O 1s XPS spectra for the various inorganic fillers; the O 1s peak position shifts towards higher BE values for the materials with stronger acidic character. The series of O 1s BE (SiO_2–PWA > SiO_2 > ZrO_2 > n-Al_2O_3 >
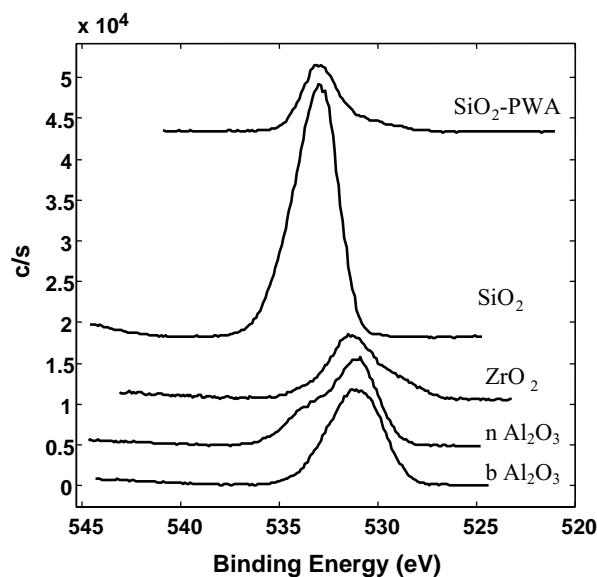

Fig. 2. Comparison of the O 1s X-ray photoelectron peak for various inorganic fillers.

b-Al$_2$O$_3$) is essentially the same to that observed for the pH of slurry and adsorption density at low pH values. The shift towards higher binding energy of more than 2 eV for the O 1s orbital passing from b-Al$_2$O$_3$ to SiO$_2$–PWA is associated to a strong electronegative effect of the chemical species bonded to the acidic surface oxygen sites which, attracting the electron clouds of these latter, increase the bond polarisation with the terminal hydrogen atoms. Thus, the O 1s peak shift towards high BE is indicative of a more acidic behaviour.

Two specific aspects concerning the XPS analysis should be discussed in detail. The analysis depth in the present investigation (about 50 Å) is larger than a few surface monolayers; accordingly, the information reflects in part the chemistry of the layers underlying the surface which are not responsible for the water adsorption during operation. The peak broadening for the O 1s signal in the various samples indicates the presence of more than one oxygenated functional group in each material; however, only in the case of neutral Al$_2$O$_3$ two distinct contributions to the XPS signal are clearly observed, since these oxides possess groups with significantly different acid–base behaviour. For the other fillers, the XPS signals associated to each group tend to overlap. Appropriate deconvolution of such peaks is not straightforward since it would require appropriate calibration of the BE for each functionality. In this regard, it may be stated that the potentiometric titration technique is more surface selective than XPS since it detects only the top layers, allowing a proper separation of the surface groups on the basis of their different acid–base behaviour. The difference in O 1s BE between SiO$_2$–PWA and SiO$_2$ is not very significant (0.2 eV) as one would expect from the acid–base properties. A significant contribution of the Si 2p 2s signals beside the W 4f signal is observed in the XP survey spectrum of SiO$_2$–PWA powder (not shown), indicating that either the analysis depth is very large (SiO$_2$ and SiO$_2$–PWA particles range between 7 and 20 nm, as indicated by TEM observation) or the coverage of the silica particles by PWA is not complete. The second hypothesis seems to be ruled out by the potentiometric titration results which do not give evidence of a significant number of functional groups with surface acid constant similar to that for the functionalities present in the bare silica. Nevertheless, the XPS results corroborate the findings of the acid–base potentiometric and pH of slurry analyses.

The electrochemical results for the MEAs based on the composite membranes are shown in Fig. 3. The comparison of the polarisation curves in the activation region shows a peculiar difference between the acidic (SiO$_2$–PWA, SiO$_2$, ZrO$_2$) and neutral–basic (n-Al$_2$O$_3$, b-Al$_2$O$_3$) fillers in the MEAs. The results point out to a possible inhibition of the electrochemical reactions at the interface caused by neutral or basic Al$_2$O$_3$ functionalities. It is also evidenced that the MEAs based on membranes containing acidic fillers do not show any significant difference in the activation controlled region. Accordingly, the in-

creased level of acidity in these latter membranes should not affect the kinetics of the reactions taking place at the electrode–electroyte interface. All MEAs include the same electrodes and the measured methanol cross-over values are similar ((4 ± 1) $\times 10^{-6}$ mol/(min cm^2)) at 145 °C and at 0.5 A/cm^2) [1]. A significantly different behaviour of the membranes, mainly reflected in the maximum power density values (see inset), is detected in the ohmic-controlled region at high currents. The observed series for the power density and conductivity (∼reciprocal of cell resistance) in the various composite membranes (SiO$_2$–PWA > SiO$_2$ > ZrO$_2$ > n-Al$_2$O$_3$ > b-Al$_2$O$_3$) is the same observed for the pH of slurry, O 1s photoelectron peak BE and adsorption density at low pH values (Fig. 3b). A well defined correlation between the electrochemical properties (power density, cell resistance) and the pH of slurry is derived. This behaviour is interpreted by considering that an increase in the acidic character of the filler increases the physical adsorption of water on the particle surface, enhancing the water retention properties in the composite membranes at high temperature as indicated by thermo-gravimetric analysis [22]. An increase of water uptake and conductance has also been found at 90 °C for recast Nafion membrane filled with silica with respect to commercial membranes [24]. Thus, the enhanced physical adsorption of water on the surface of the acidic fillers may be explained with a stronger electrostatic interaction by the water dipoles and the highly polarised surface O–H groups (Fig. 2) at the same extent as it occurs with the adsorption density of OH$^-$ ions on the filler surface at low pH values (Fig. 1). This increased water retention is associated with a lower cell resistance and a larger power density at 145 °C. Accordingly, the conductivity of the composite membranes at high temperature may be enhanced by increasing the surface acidity in the inorganic filler.

Since the aim of the present work was to investigate the relationship between the surface properties of the inorganic fillers and the electrochemical behaviour, the electrochemical measurements shown in Fig. 3 have been carried out under ideal conditions, i.e. high pressure (2.5 bar) and oxygen feed at the cathode; however, membranes based on acidic fillers also allow high temperature operation under reduced pressure. As an example, the resistance of the DMFC equipped with the SiO$_2$–PWA membrane increases from 0.05 to 0.095 Ω cm^2 as both the anode and cathode pressures are reduced from 2.5 to 0.5 bar. Accordingly, the power density obtained at 0.5 bar and 0.6 A/cm^2 should be 16 mW/cm^2 lower than that recorded at 2.5 bar by effect of the increased ohmic drop. Fig. 4 shows a loss of power density at 0.6 A/cm^2 of about 100 mW/cm^2 passing from 2.5 to 0.5 bar. Thus, it can be rationalised that the decrease of operating pressure contributes more significantly to increase both activation and diffusion control limitations than the ohmic resistance. Such effects can be explained by the evidence that a high partial pressure promotes the electrochemical reactions at high temperatures and significantly
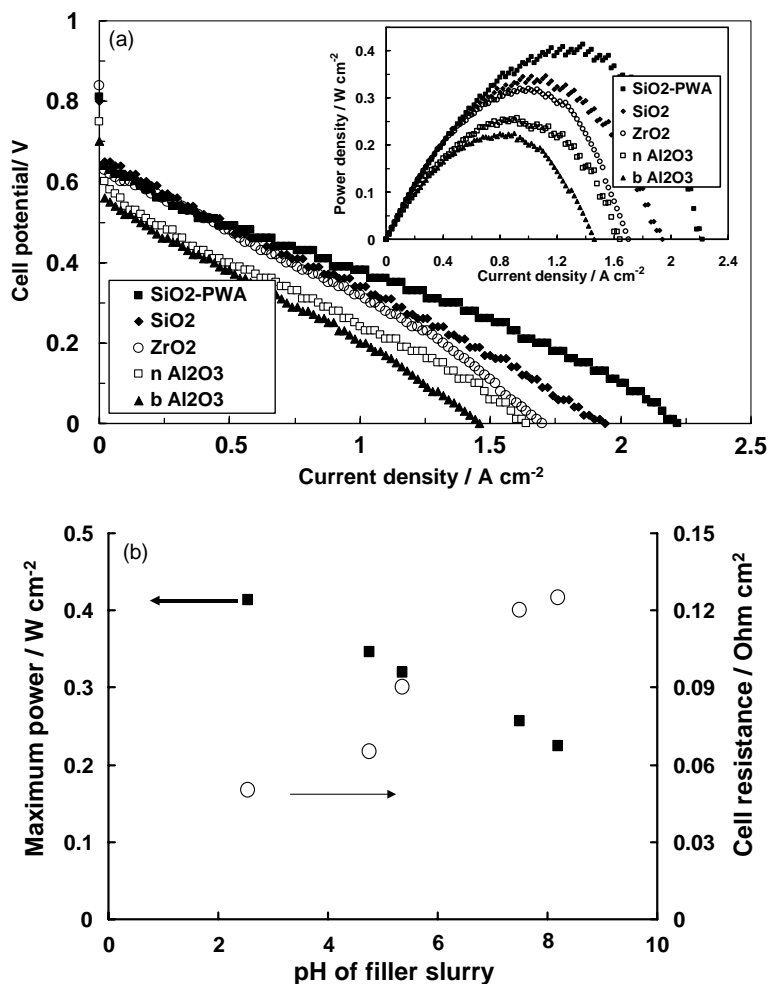
Fig. 3. (a) Polarisation and power density (inset) curves at 145 °C for various DMFC MEAs based on composite membranes containing different inorganic fillers; methanol feed, 2 M; oxygen feed, 2.5 bar; Pt loading, 2 mg/cm². (b) Relationships between the DMFC maximum power density–cell resistance values and the pH of slurry of the inorganic filler contained inside the membrane.
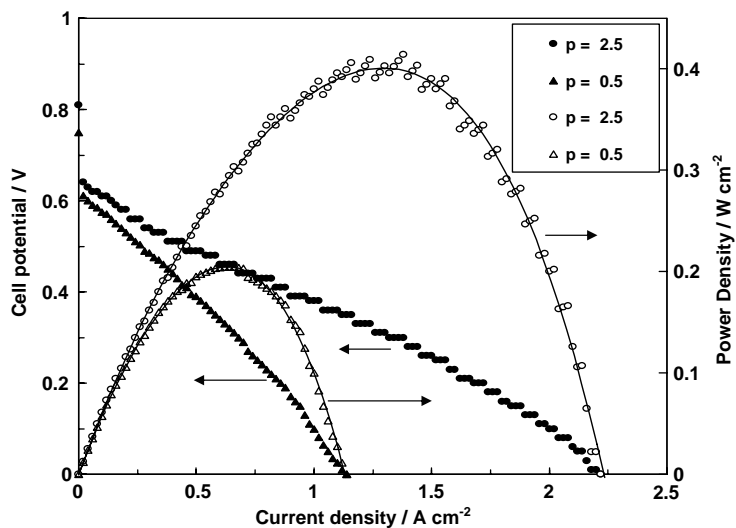

Fig. 4. DMFC polarisation curves at 145 °C for the PWA–SiO₂ based composite membrane at two different pressures (*P*, bar). Methanol feed, 2 M; oxygen feed; Pt loading, 2 mg/cm².

enhances mass transport [19,25] at the electrode–electrolyte interface. For what concerns the membrane behaviour it is derived that, although the conductivity is strongly dependent on the liquid water content inside the electrolyte, even in the presence of water vapour (0.5 bar anode and cathode pressure, 145 °C), the cell resistance is confined in a suitable range for practical operation.

4. Conclusions

A proper tailoring of the surface acid–base properties of the inorganic filler in composite Nafion membranes allows appropriate DMFC operation at high temperatures and with reduced pressures. An increase in both strength and amount of acidic surface functional groups in the fillers would enhance the water retention inside the composite membranes through an electrostatic interaction, in the presence of humidification constraints, in the same way as it occurs for the adsorption of hydroxyl ions in solution. The present results may be of potential interest to optimise the properties of composite perfluorosulphonic membranes also in relation to their use in H_2–air fuel cells. The recent development of electrolytes alternative to Nafion® indicate that perfluorosulphonic membranes are not the only choice for high temperature operation [26–34]. However, for most of these electrolytes, a suitable water content is essential for practical operation; in such cases, the present approach may be adopted to enhance the high temperature performance.

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