

PEMFC electrode preparation: Influence of the solvent composition and evaporation rate on the catalytic layer microstructure

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Abstract

A series of parameters affecting the catalytic layer microstructure in polymer exchange fuel cell electrodes have been evaluated. The deposition of the catalytic layer in the gas diffusion support is shown to depend not only on the ink deposition method but also on the characteristics of the solvent used to disperse both the catalyst and the Nafion ionomer. The solvent viscosity and its dielectric constant are two important factors to control for the catalytic ink preparation. In particular, the solvent dielectric constant is shown to be directly related to the electrode performance in single cell tests.

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1. Introduction

Several recent studies on the preparation of electrodes for polymer exchange membrane fuel cells (PEMFC) reveal the importance of maintaining a suitable equilibrium between electronic and protonic conductivity in the electrodes for improving the rate of the reduction–oxidation processes and decreasing the system resistance to the electric current and to the mass transport phenomena. Nafion[®] ionomer is commonly used in PEMFC electrodes to enhance proton conduction from the electrocatalytic metallic surface towards the polymer electrolyte. The ionomer content variation in the catalytic layer has been one of the most analysed parameters. Different studies have concluded that the optimum Nafion[®] amount in the electrode catalytic layer ranges from 30 to 36 wt.% of the catalyst weight [1–3], but it has been recently proved to depend on factors such as the Pt metallic loading in the catalyst [4,5]. Sasikumar et al. [6] have found optimum values of Nafion[®] content in the electrodes which can

reach up to 50 wt.% of catalyst for Pt loadings as low as of 0.1 mg cm⁻² using a catalyst with 20 wt.% of Pt.

In the same way that not only the platinum loading but also its dispersion are key factors in the design of catalysts for electrodes to maximise their active surface area, not only the ionomer content but also its distribution, microstructure, porosity and interconnection are also essential for providing a good proton transfer rate from the anode to the cathode without increasing the mass transfer resistance and obtaining high efficiency in the electrochemical conversion [7–10].

From this standpoint, conditions for Nafion[®] ionomer incorporation into the catalytic layer must be controlled in order to achieve high performance components and minimising ohmic and mass transport overpotentials. The Nafion[®] network structure and its interconnection throughout the electrode determine the three-dimensional zone of the catalytic layer, the triple-phase boundary and the porosity. The solvents used for inks preparation play a key role in the formation process of the proton conduction network, since the dielectric constant of the solvent influences the degree of aggregation of the Nafion[®] ionomers [11,12]. When Nafion[®] is mixed with organic solvents, the mixture may become a so-

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lution, a colloid or a precipitate, depending on the interaction between the solvent molecules and the ionomer molecule. This paper examines the effect of the inks composition in the electrodes texture and microstructure, which will be shown to be intimately related to the performance of the single cell.

2. Experimental

2.1. Electrodes preparation and characterisation

The inks for the catalytic layers were prepared by dispersing a commercial Pt/Vulcan XC72 catalyst (20 wt.% Pt from E-TEK) and Nafion 117 solution (5 wt.%, from Fluka) in a mixture of solvents. Five pure solvents were used to prepare the dispersing medium: i.e. distilled water, ethanol, isopropyl-alcohol, butyl-acetate and glycerine. The suspensions obtained by mixing the catalyst, the Nafion ionomer and the solvents were submitted to an ultrasonic bath in order to improve their stability with time.

The dielectric constants and viscosity of the solvents and the mixtures of solvents used in the tests were experimentally determined at 298 K using a liquid dielectric constant meter (Brookhaven Instruments Corp.) and a viscometer (ST Digit).

The prepared inks were sprayed over water-proof carbon cloth supplied by E-TEK. The ink deposition over the gas diffusion support was carried out by means of an automated device which allowed obtaining a constant rate of ink dosing while a programmed movement of the electrode support on both the x - y axes was performed to cover the required surface (3 cm \times 3 cm). This device was equipped with an infrared radiation source to evaporate instantaneously the solvents when the ink reached the cloth surface. The Nafion 117 stability in the dry inks was verified by FTIR spectroscopy as a function of the heating temperature. A Nicolet 5ZDX spectrometer was used for the experiments. For FTIR analysis, the inks or the Nafion solutions were sprayed in KBr wafers and submitted to a heating treatment in air.

Both inks and electrodes have been characterised by combining electron microscopy and energy dispersive X-ray analysis (EDAX). A mapping of the composition of selected zones of the surface was carried out in order to analyse the uniformity of the impregnation process.

2.2. Membrane–electrode assembly (MEA) preparation and characterisation

Nafion 117 (Aldrich) was used as the polymer electrolyte membrane. Prior to use, it was boiled successively in H₂O₂, H₂O, H₂SO₄ 0.5 M and H₂O for twice. The membrane–electrode assemblies (MEAs) have been prepared by facing two identical electrodes at both sides of a Nafion 117 membrane and hot pressing at 200 bar and 100 °C for 1 min. The hot pressing parameters and procedure were optimised in order to avoid deformation of the MEA and to obtain

good adherence between electrode and membrane and good reproducibility.

MEAs obtained from different inks were tested in single cell experiments. Polarisation curves were obtained in a test station equipped with mass flow controllers, humidifiers and temperature indicators. Tests were carried out using hydrogen and oxygen reactants at 1 atm and 298 K. The reactants streams were saturated with water at 298 K.

3. Results and discussion

In order to determine the effect of the catalytic ink composition on the electroactive layer microstructure, a series of solvent mixtures composed of up to three compounds were tested. For the preparation of a solvent of suitable characteristics to disperse the catalyst, a number of single compounds were selected according to their physicochemical properties, which are compiled in Table 1.

Liquids with high dielectric constants, above 10, are known to form a perfect Nafion solution, while solvents with dielectric constants below 3 lead to the formation of precipitates [2]. Ideally, it would be preferable using solvents with intermediate values for obtaining a Nafion colloidal solution, which provides a porous and uniform network without large polymer aggregates. The different texture adopted by Nafion depending on the solvent used becomes clear from the analysis of SEM micrographs of gas diffusion supports that were impregnated with solutions of the ionomer dispersed in different organic compounds. Fig. 1 presents these images in comparison with the carbon cloth support before its impregnation with Nafion. The physical properties of the used solvent not only influence the degree of dissolution of the ionomer, but also the porosity, distribution, coverage and adherence of the Nafion layer over the carbon cloth support. High dielectric constant alcohols (such as ethanol) lead to the formation of a high density Nafion film, which mainly covers the upper fibres of the carbon support without penetrating in the cloth (Fig. 1b). On the contrary, impregnation of the ionomer with a low dielectric constant solvent, such as butyl-acetate [5], results in a porous and less uniform structure, which is better distributed among the gas diffuser (Fig. 1c).

However, the deposition process of the ink requires a compromise between the dielectric constant and other physical

Table 1
Physical properties of the single solvents used for inks preparation

Solvent	Dielectric constant	Viscosity ^a (cP)	Boiling point (K)
Water	78.0	0.89	373
Ethanol	24.3	1.22	352
Isopropyl-alcohol	18.3	2.27	356
Butyl-acetate	5.0	0.69	400
Glycerine	42.5	1400	563 ^b

^a Measurements at 298 K.

^b Glycerine boils with decomposition.

properties, such as the viscosity, the boiling point and the carbon wet capacity of the solvent. Butyl-acetate has been selected as one of the candidates for the composition of these mixtures because of its low dielectric constant. However, its high volatility and low viscosity make necessary to use other compounds to improve the properties of the ink solvent. Glycerine has been also selected as component for solvent mix-

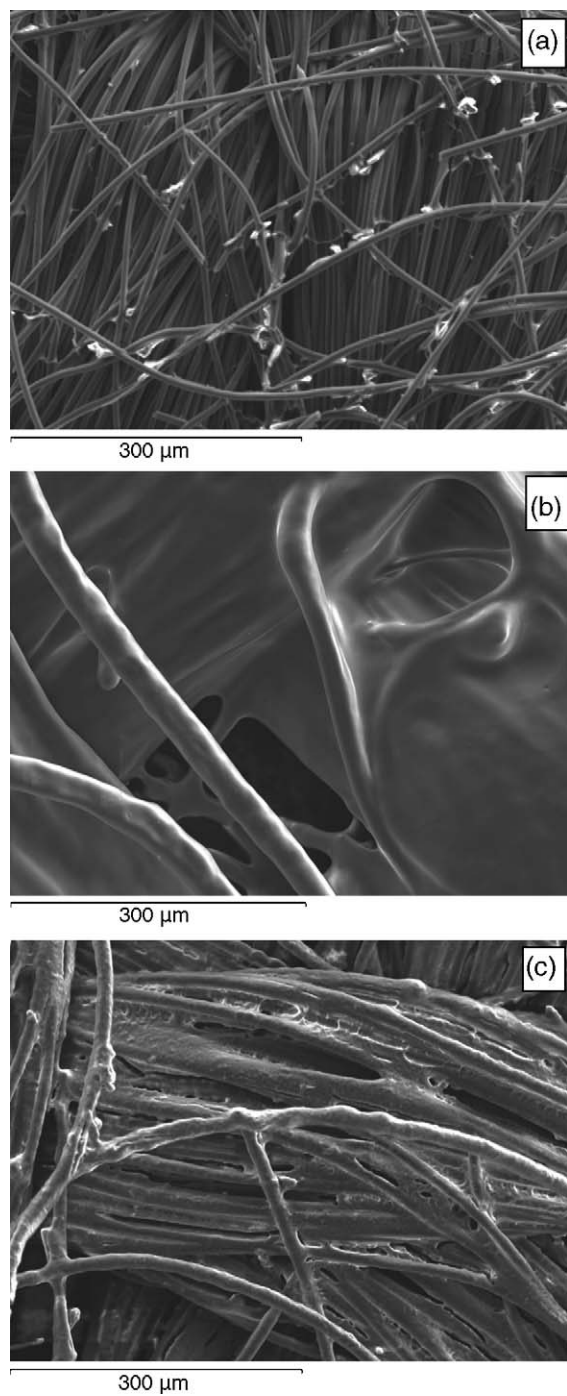


Fig. 1. SEM micrographs of the gas diffusion support: (a) without treatment; (b) impregnated with a solution of Nafion in ethanol; (c) impregnated with a solution of Nafion in butyl-acetate.

Table 2

Experimental values of dielectric constants and viscosity obtained for binary and ternary mixtures of solvents with glycerine

Solvent	Dielectric constant	Viscosity ^a (cP)
Butyl-acetate:glycerine (85:15) ^b	–	–
Ethanol:glycerine (85:15)	25.9	2.02
Isopropyl-alcohol:glycerine (85:15)	20.0	3.75
Water:glycerine (85:15)	74.9	1.40
Ethanol:butyl-acetate:glycerine (45:40:15)	16.5	2.80

^a Measurements at 298 K.

^b Not determined, unstable solution.

tures because of its high viscosity, which allows maintaining a stable suspension during the ink deposition process. The added amount has been reduced to a minimum in the mixtures to avoid increasing too much the dielectric constant value and the boiling temperature for solvent removal. It must be taken into account that the catalyst density influences the solvent viscosity requirements. The higher the catalyst metal loading for a given support, the higher the glycerine content required to maintain the catalyst in suspension. By considering the use of carbon blacks, the minimum amount of glycerine in the ethanol solvent to prepare a stable suspension of a bare Vulcan XC72 support was determined to be 5 wt.%. However, this percentage must be progressively increased for catalytic inks in order to maintain an acceptable stability. Minimum concentrations of glycerine of up to a 15 wt.% are required when preparing inks with 20 wt.% Pt/Vulcan XC72 catalyst. On the other hand, both ethanol and isopropyl-alcohol could be also considered in principle suitable media for the suspension as main components of the solvent mixture and in contrast with water, which has an extremely high dielectric constant.

Table 2 presents the composition of some representative binary mixtures of solvents and their physico-chemical properties, such as their dielectric constant value and viscosity. The dielectric constants of the prepared binary mixtures ranged from 20 to 75, with viscosity values between 1.4 and 3.8 cP (Table 2). It must be noted the low miscibility between butyl-acetate and glycerine, which did not allow obtaining a single phase as required for suitable ink impregnation.

The other above mentioned solvents were used for the preparation of inks, which were sprayed on the carbon cloth. The ink deposition process and the morphology of the catalytic layers formed were observed to be greatly influenced by the solvents evaporation rate. SEM micrographs of electrodes prepared using these binary mixtures are presented in Fig. 2. Electrodes prepared from the water:glycerine mixture (Fig. 2a) were constituted by a highly dense catalytic layer of low porosity, which contrasts with that formed from the ethanol:glycerine mixture (Fig. 2b). This latter electrode showed a thinner and more uniformly distributed catalytic

layer that covered completely and individually the carbon fibres. The electrode prepared from the ink dispersed in the isopropyl-alcohol:glycerine mixture is the result of an intermediate situation (Fig. 2c). According to their physical properties, both isopropyl-alcohol and ethanol were considered initially good candidates as base components of the solvent mixtures. Furthermore, the higher viscosity and the slightly lower dielectric constant of the isopropyl-alcohol:glycerine mixture are even more favourable for the catalytic layer properties. However, the observation of the deposited catalytic

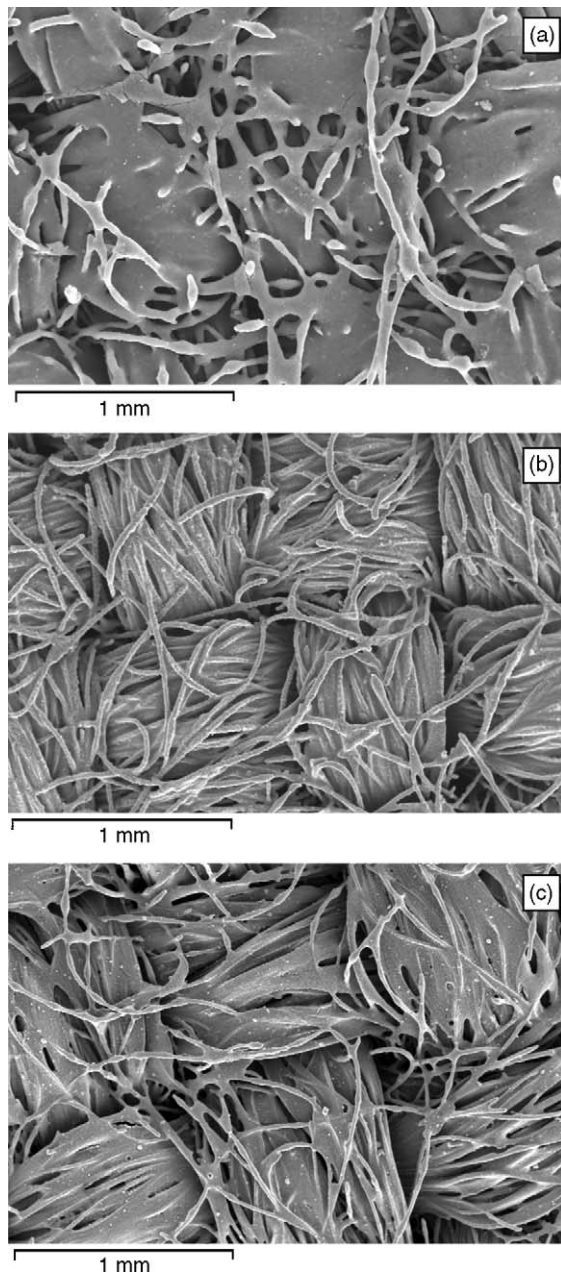


Fig. 2. SEM micrographs of electrodes prepared from inks dispersed in binary mixtures of (a) water:glycerine (85:15); (b) ethanol:glycerine (85:15) and (c) isopropyl-alcohol:glycerine (85:15) (impregnation has been performed with simultaneous evaporation of solvents).

layer reveals a better wetting ability of the fibres in the case of the ethanol–glycerine mixture.

Typically water–glycerine solutions have been applied for thin film methods of deposition of the electrode catalytic layer as in the procedure in the Wilson's patent in 1993 [13]. However, this kind of solvents yields highly dense films, which do not allow an effective dispersion of the catalyst. The effect of glycerine content in the catalytic ink was studied by Chun et al. [14], who found that high glycerine contents (above 25%) resulted in a high significant drop of performance, specially at high current densities, which the attributed to a contact area reduction between catalyst and Nafion.

In order to reduce more the dielectric constant value of the ink solvent, ternary mixtures based in ethanol, butyl-acetate and glycerine were tested. The best results were obtained for a mixture whose percentages in weight of the single components were 45:40:15, respectively (Table 2). The dielectric constant measured for this solvent was 16.5, with a viscosity of 2.80 cP at 298 K. The structure of the Nafion film deposited over a carbon cloth using this mixture is presented in Fig. 3. A comparison among the Nafion coverage obtained with this ternary mixture and those resulting from its solution in single component solvents (Fig. 1b and c) shows a large improvement in the distribution and homogeneity of the ionomer film.

It must be stressed the importance of the ink drying process throughout the deposition, which is evidenced in Fig. 4. This figure compares the morphology of two electrodes prepared from a ternary ethanol:butyl-acetate:glycerine ink with and without instantaneous evaporation of the solvents. During the airbrushing period, the accumulation of ink on the surface of the gas diffuser support at room temperature gives place to a thick and continuous catalyst layer that remains in the space among fibres when it is finally dried to remove the solvents (Fig. 4a). Although the catalyst is uniformly distributed in the layer formed without heating, this structure increases the mass transfer resistance, makes more difficult the gas diffu-

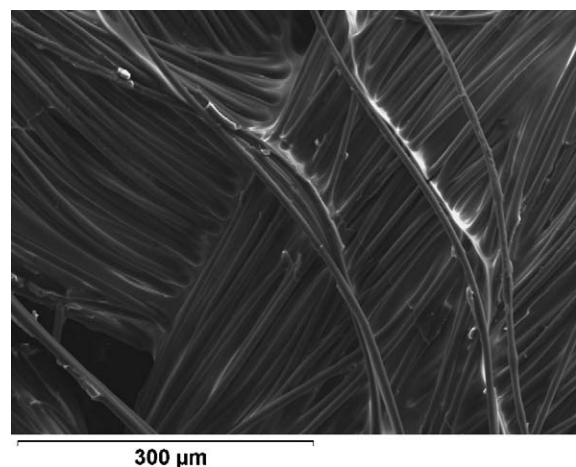


Fig. 3. SEM micrographs of the gas diffusion support impregnated with a solution of Nafion in a mixture of ethanol:butyl-acetate:glycerine in proportions 45:40:15.

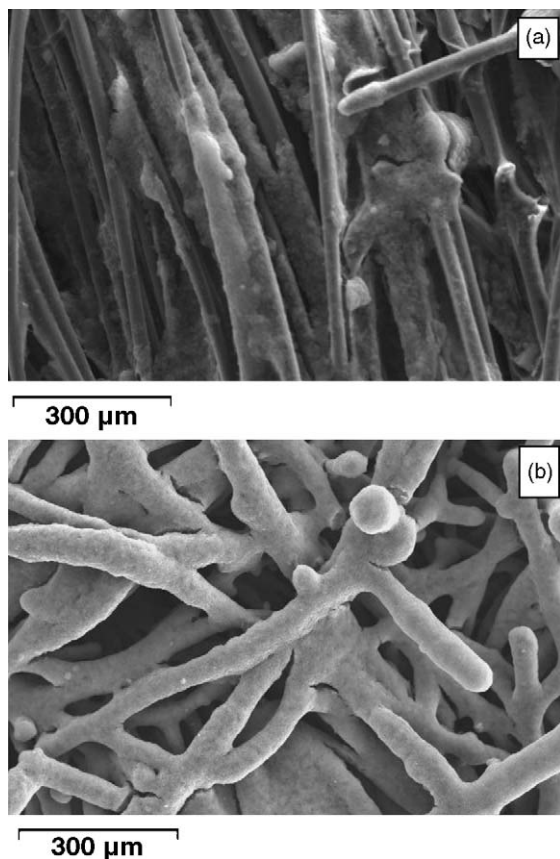


Fig. 4. Surface structure of two electrodes prepared with an ink dispersed in a mixture of ethanol:butyl-acetate:glycerine (45:40:15) by air-brushing: (a) dried in an oven after the ink deposition and (b) heated in situ for simultaneous solvent removal during the air-brushing process.

sion through the electrode and reduces the contact between the catalytic layer and the carbon cloth support. This problem is even aggravated when high boiling point components are present in the ink. The structure of the formed catalytic layer and its distribution can be largely improved by the instantaneous removal of solvents during the airbrushing process as shown in Fig. 4b. An infrared source coupled to the airbrushing automatized device is responsible of the heating over the gas diffusion support at temperatures close to 473 K. This fast drying produces a uniform coverage of the single fibres with the ink leaving a free space among them that improves the gas diffusion throughout the electrode. A detail of the covered fibres and their granular and porous microstructure is shown in Fig. 5. Granules of about $0.1 \mu\text{m}$ size and a regular porous structure can be differentiated in the catalytic layer.

The distribution of catalyst and ionomer at the nanometric scale was verified by TEM. Apparently, Nafion structures could not be differentiated from catalyst particles, although energy dispersive X-ray analysis revealed the presence of the ionomer throughout the overall examined zone.

The Pt/F and Pt/S ratios were obtained from EDAX analysis of the catalytic layer at different magnifications in the SEM, which yielded averaged values of 0.08 and 1.80, respectively. The theoretical ratios calculated from the nominal

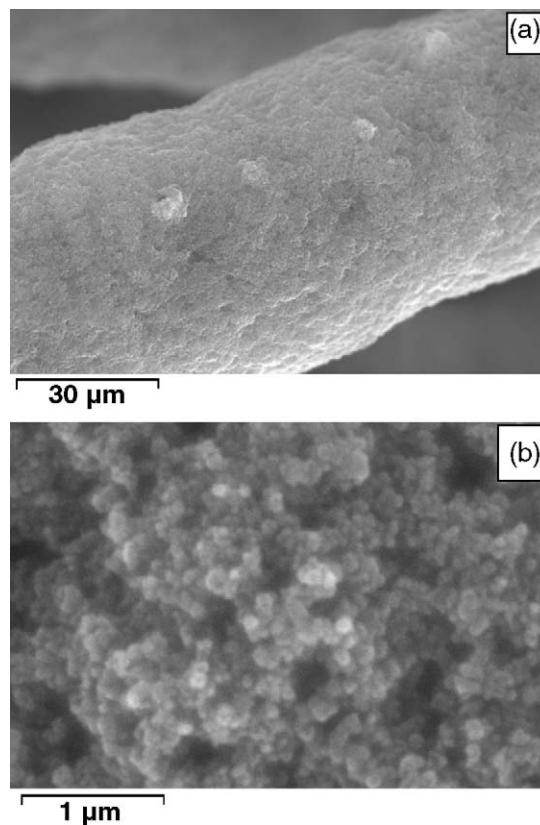


Fig. 5. SEM micrographs of an electrode prepared by air brushing with simultaneous removal of the solvent ethanol:butyl-acetate:glycerine (45:40:15): (a) detail of an impregnated carbon cloth fibre; (b) microstructure of the catalyst-Nafion composite.

content of Pt and ionomer in the catalytic layer were determined to be: Pt/F=0.10 and Pt/S=1.54. The good agreement between experimental and theoretical values indicates a good dispersion of ionomer and catalyst throughout the electrode. The deviation of the Pt/F ratio to a lower value as compared to the theoretical one, and in contrast to that of Pt/S (slightly higher than the theoretical ratio), can be attributed to the water-proof treatment of the carbon cloth support with PTFE. A mapping of the samples in the scanning electron microscope revealed in them a highly homogeneous distribution of Nafion and catalyst in the cloth fibres according to the quantitative analysis of the elements F, S and Pt.

With the aim of verifying the complete removal of solvents from the inks and confirming the stability of the Nafion ionomer, the ink was analysed by FTIR in transmission mode after heating at different temperatures. The FTIR spectrum of the Nafion ionomer heated at 493 K was identical to that obtained after drying at ambient temperature, which indicates no alteration of its molecular structure. Four main features at 1220, 1155, 1057 and 980 cm^{-1} were detected in the region from 1350 to 850 cm^{-1} , corresponding to the asymmetric and symmetric vibration of CF_2 , symmetric stretch of HSO_3^- and C–F symmetric stretch in the $\text{CF}_2\text{--CF--CF}_3$ group respectively (Fig. 6e). A series of spectra was also obtained from the ink prepared from the ternary mixture of solvents

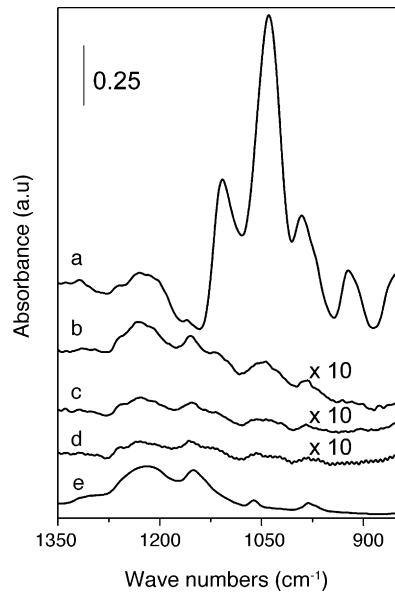


Fig. 6. FTIR spectra of the ink dispersed in the ethanol:butyl-acetate:glycerine (45:40:15) mixture after drying at: (a) 298 K; (b) 383 K; (c) 438 K; and (d) 493 K. A spectrum obtained from the Nafion ionomer dried at 493 K is presented for comparison (e).

in order to check the removal of each one of them from the catalytic layer (Fig. 6a–d). Butyl-acetate was easily removed at ambient temperature and no IR features corresponding to this compound were found in the spectra. Ethanol was detected in the ink at temperatures up to 353 K showing the main absorption bands in the region near ca. 3478 cm^{-1} due to the OH group stretch vibration and at 2953 , 2918 , 2867 and 2844 cm^{-1} corresponding to the asymmetric and symmetric stretch of the CH_3 and CH_2 groups respectively. Somewhat higher temperatures were needed to eliminate glycerine residues from the ink. The glycerine characteristic bands at wave numbers between 1300 and 850 cm^{-1} (peaks at ca. 1108 , 1040 , 991 , 922 and 852 cm^{-1}) decreased drastically at temperatures around 383 K indicating practically complete glycerine removal from the catalytic layer as shown in Fig. 6. Infrared absorption bands remaining in the ink spectrum after heating at 438 K are mainly due to Nafion (Fig. 6b–d) [15].

The performance of the electrodes prepared from inks dispersed in binary mixtures of solvents were also compared with that obtained from the ternary mixture of solvents (ethanol:butyl-acetate:glycerine). The polarisation curves obtained from the different MEAs (Fig. 7) reveal a perfect correlation between the electrodes microstructure and the performance of the single cells. For identical Nafion content and Pt loading in the electrode, the efficiency of the cell increases as the solvent constant dielectric constant becomes reduced: water:glycerine < ethanol:glycerine < isopropyl-alcohol:glycerine < ethanol:butyl-acetate:glycerine. The better performance of the electrodes prepared from inks of lower dielectric constant solvents is evidenced in terms of higher voltage and power density for a given current density. This variation is represented as a function of the solvent

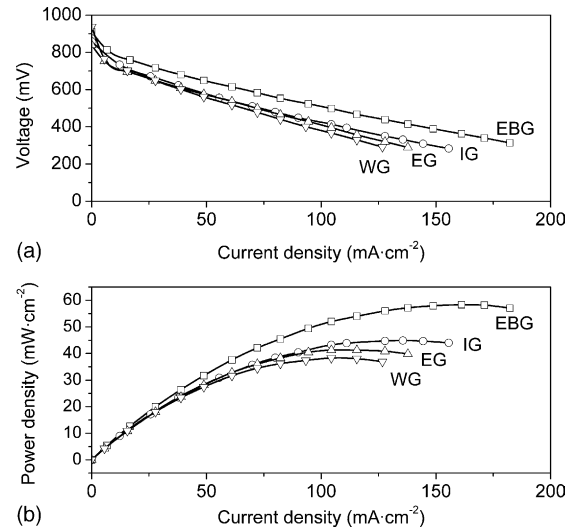


Fig. 7. (a) Current–voltage characteristic curves of the MEAs prepared from inks dispersed in ethanol:butyl-acetate:glycerine (45:40:15) (EBG), isopropyl-alcohol:glycerine (85:15) (IG), ethanol:glycerine (85:15) (EG) and water:glycerine (85:15) (WG). Test conditions: water saturated H_2 and O_2 streams at 1 atm and 298 K. Cell temperature: 298 K.

dielectric constant in Fig. 8. The observed trend indicates the close correlation between the ink physico-chemical properties and the microstructure of the electrodes, which is finally manifested in terms of performance. The effect of the preparation method of the inks on the performance of PEMFC electrodes was recently pointed out by Shin et al. [12] using as solvents butyl-acetate and isopropyl-alcohol. Ink solvents with suitable properties for the formation of fine colloidal dispersions of Nafion favour the deposition of catalytic layers of porous structure for reducing mass transfer resistance and providing good ionomer dispersion for enhanced proton conductivity. These two characteristics are key issues for the preparation of high-performance electrodes.

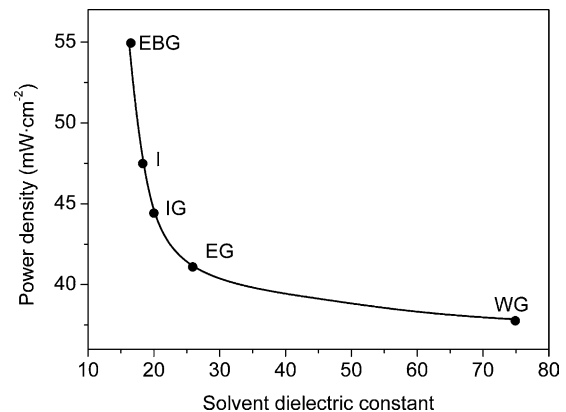


Fig. 8. Variation of the MEAs power density as a function of the dielectric constant of the ink solvent (EBG: ethanol:butyl-acetate:glycerine (45:40:15); I: isopropyl-alcohol (100); IG: isopropyl-alcohol:glycerine (85:15); EG: ethanol:glycerine (85:15); WG: water:glycerine (85:15)). Current density: 120 mA cm^{-2} . Test conditions: water saturated H_2 and O_2 streams at 1 atm and 298 K. Cell temperature: 298 K.

4. Conclusions

A series of electrodes have been prepared from catalytic inks of different properties. It has been shown that the deposition process of the ink requires a compromise between the dielectric constant and other physical properties, such as the viscosity, the boiling point and the carbon wet capacity of the solvent. Furthermore, a fast solvent removal during the ink deposition process largely improves the distribution and adherence of the catalytic layer to the gas diffusion support and reduces the mass transfer resistance. The catalytic layer microstructure is closely related to the ability of the solvent for dispersing the Nafion ionomer and forming fine colloidal solutions. For a given Pt and Nafion loading in the catalytic layer, the electrode performance has been shown to be intimately related to its microstructure, which is finally defined by the solvent dielectric constant.

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