



Effect of the solvent in the catalyst ink preparation on the properties and performance of unsupported PtRu catalyst layers in direct methanol fuel cells



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ARTICLE INFO

Article history:

Received 27 July 2016

Received in revised form 21 February 2017

Accepted 21 February 2017

Available online 24 February 2017

Keywords:

direct methanol fuel cell
catalyst ink
PtRu black
catalyst layer
Nafion[®] ionomer

ABSTRACT

The effect of the organic solvent polarity on the properties of unsupported PtRu catalyst inks and on the performance of the catalyst layers prepared with them for the methanol electrooxidation, has been studied. The light scattering results indicate that the PtRu-Nafion[®] aggregates in the inks prepared with n-butyl acetate (NBA) are larger than those prepared with 2-propanol (IPA). The lower polarity of the former favours the aggregation of Nafion[®] and nanoparticles. The electron microscopy images and porosimetry measurements of the catalyst layers show that the secondary pore volume between the agglomerates is larger for NBA. The linear sweep voltammetry and *eis* results for the methanol electrooxidation in the three-electrode cell denote the higher active surface area for NBA and comparable specific oxidation rates of the intermediates in both catalysts layers. The current densities for PtRu anode catalyst layers in single DMFC are higher when the solvent is NBA, the mass transport limitations being much more apparent with IPA. The adapted transmission line equivalent circuit to interpret the impedance results in single DMFC indicates that the proton resistance for NBA is significantly lower than for IPA, thus suggesting that the greater number of accessible active sites for methanol oxidation in the former are well connected to the Nafion[®] ionomers and easier transported to the membrane.

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1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are nowadays receiving much attention due to their attractive properties as a power source for both, stationary and mobile applications. Some of their main advantages are the absence of electrolyte leakage, low corrosion and simple stack design [1]. Liquid-feed direct methanol fuel cells (DMFCs) based on a Nafion[®] proton exchange membrane (PEM) appear to be the most promising for portable and low-power applications, because of their simple and compact design, lightweight, no need for hydrogen storage or a fuel reformer, no need of the hydrogen and air humidification, easy recharging and easy storage, distribution and management of the liquid alcohol [2].

It is known that the power output of a PEMFC is related to the electrode catalyst layers. In fact, one of the main challenges in this research field is the optimization of the electrode composition and morphology in order to improve the fuel cell performance and durability. Many attempts to improve the electrode manufacturing of H₂-fuelled PEMFCs have been made [1,3–12], whereas those performed on DMFCs are comparatively smaller [2,13–18]. Thus, in H₂-fuelled PEMFCs more attention has been paid in the literature to supported catalysts for increasing the active surface area and to obtain better cell performance [1,3–12,18,19]. In contrast, the use of unsupported catalysts is more extended in DMFCs. Unsupported catalysts or metal blacks are mainly utilized in systems operating in passive mode, that is, without any air blowers or fuel circulating pumps, such as in portable electronic applications [20–24] and related miniaturized systems [25–27]. In this sense, it has been reported that the best compromise between power density (21 mW cm⁻²) and fuel efficiency (63%) for a passive single DMFC containing PtRu and Pt blacks is achieved with a methanol feed concentration of 2 mol dm⁻³ operating at room temperature [28].

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With regard to DMFC systems operating in active mode, the performance depends largely on the experimental operating conditions. For an active DMFC 30-cell stack containing PtRu and Pt blacks fed with 0.48 mol dm^{-3} methanol solution and dry air at 7.35 slpm (standard litre per minute) and 0.76 atm, a power density of 63 mW cm^{-2} (0.467 V/cell) and fuel efficiency of 89% was reported operating at 60°C [29]. More recently, for single DMFC with PtRu and Pt blacks, after discharging the cell at constant current density of 0.200 A cm^{-2} for 1450 h, a maximum power density of 37 mW cm^{-2} (0.306 V) was reported at 70°C , decreasing from an initial value of 100 mW cm^{-2} (0.346 V), feeding the anode and cathode with 1 mol dm^{-3} methanol and air, respectively (both at stoichiometry $\lambda = 6$) [30]. Furthermore, an active single DMFC using supported catalysts was described showing a maximum power density of 180 mW cm^{-2} (0.300 V), at 80°C and optimum operating conditions [31].

The technical interest in unsupported PtRu alloy catalysts is based on the fact that, in practical applications, it is expected that catalyst layers with reduced thickness show better performance, due to the improved mass transport and the decrease of the inner electrical resistance [32]. In these catalysts, Ru forms oxygenated species at lower potentials than platinum and promotes the oxidation of adsorbed CO molecules on platinum to CO_2 , thus increasing the CO tolerance of the catalyst. At high concentrations, CO_2 can remain trapped inside the catalyst layer and therefore, mass transport limitations can appear. The use of unsupported catalysts facilitates the CO_2 transport because thinner active layers can be obtained in comparison to supported catalysts with similar catalysts loadings [33,34]. Furthermore, regarding durability issues, the use of unsupported catalysts avoids the problem of carbon corrosion [30,35].

As previously mentioned, the morphology and composition of the electrode plays an important role in the fuel cell performance. This issue is closely related to the dispersion techniques [3] and solvents [1,5,8–10,14] used in the catalyst inks for preparation of the electrode active layers in the MEAs (membrane electrode assemblies). It is known that the performance of a catalyst layer depends on the catalyst ink composition, the ink preparation procedure, and the application method onto a substrate to fabricate the MEA. Uchida and col. [5] reported the changes of the Nafion[®] layout in various kinds of organic media, depending on their dielectric constant. Thus, in organic solvents with $\epsilon > 10$, a solution is formed; when $3 < \epsilon < 10$, a colloidal solution results; and with $\epsilon < 3$, precipitation occurs [1,5,14]. In the first case, it is considered that the ionomer can cover the surface of the carbon and, as the ionomer is an electron insulator, the Pt utilization decreases and the conduction of electrons is blocked. This possibility leads to low fuel cell performance. In the second case, the ionomer colloids adsorb the catalyst powder and the size of the agglomerates of catalyst powder increases. Then, the electrode porosity increases, and the mass transfer is facilitated. A continuous network of ionomer throughout the catalytic layer can be built up, thus improving the proton conduction from the electrode to the membrane and resulting in a better fuel cell performance [1,14]. It has been reported that the electrode prepared by colloid formation shows an increase of about 30% in the electrochemical reaction area and therefore, the cell performance is significantly improved when compared to the cell using electrodes prepared by the solution method. Another point is that when the colloid is formed, the ionomers can easily penetrate into the large pores and the small pores below $0.07 \mu\text{m}$ are not blocked. Conversely, all pores below $0.07 \mu\text{m}$ are blocked by ionomers in the case of the solution method [1].

An additional condition for producing a stable cast ionomer is related to the higher boiling point of the solvent with respect to water [14]. Even if ϵ of an organic solvent is larger than 10 and the

perfluorosulfonated ionomer dissolves into the catalyst ink solution, a different type of organic solvent could form a different catalyst layer structure. This is because the pores in the catalyst layer are formed during the evaporation process of the catalyst ink, and the process depends on the physical and thermodynamic properties of the organic solvent [8]. Thus, it has been shown that the porosity of the catalyst layer can be tuned even when using solvents with $\epsilon > 10$, although the difference in their viscosity and boiling points are essential in this case [8–10]. It is worth mentioning that, in the best of the authors' knowledge, the influence of the ink composition on the catalytic layer properties for PEMFCs has only been studied when using carbon supported catalysts. The study of the effect of the catalyst ink composition for unsupported catalysts would be also of interest since they are frequently used in DMFCs.

This work deals with the study of the solvent influence on the catalyst inks for active layer manufacturing in DMFC applications, to show whether the aforementioned considerations also apply for the unsupported catalysts. Two types of solvents, leading to the solution and to the colloidal methods discussed above, 2-propanol (IPA) and n-butyl acetate (NBA), respectively, have been used. The corresponding catalysts, characterized using physical methods, have been applied to single electrodes to study the methanol oxidation reaction using electrochemical techniques in a three-electrode configuration cell. In addition, MEAs have also been manufactured using the prepared catalysts layers to test their performance in single liquid-feed DMFCs.

2. Experimental

2.1. Porous diffusion electrodes

Porous diffusion anodes consist of a gas diffusion layer (GDL) and a catalyst layer (CL). The GDL was a thin layer made of Vulcan XC-72 (Cabot Corp.) carbon black and polytetrafluoroethylene deposited on the top of hydrofobized Toray carbon paper (TGPH-090, 20% wet proofing, E-TEK Inc.) [36]. A catalyst ink was prepared using the following procedure based on the "dropping process" reported by Uchida et al. for PEMFC electrodes [3]. First, the PtRu black catalyst (Pt:Ru; 50:50 at. %, HISPEC[™] 6000, Alfa Aesar[®]) was wetted with ultrapure water ($\kappa \leq 0.054 \mu\text{S cm}^{-1}$, obtained from a Millipore System), and mixed with an organic solvent (see Table 1 for more details) under ultrasonic stirring for 30 min. Next, an appropriate amount of Nafion[®] dispersion (5% wt., Aldrich) was dropped into the catalyst solution while stirring to achieve a dry ionomer composition of 15 wt. % in the CL [37–40]. Ultrasonic stirring was applied for another 2 h at room temperature to obtain a uniform dispersion. Afterwards, the catalyst ink was sprayed onto the GDL by an air-gun feed with pure nitrogen (99.999%, Praxair) and dried at 60°C in an oven. The PtRu black loading was adjusted to 4.0 mg cm^{-2} .

The gas diffusion cathode consists of an ELAT[®] V2.1 (E-TEK, Inc.) gas diffusion layer and a catalyst layer made of Pt black (HSA, Premetek Co.) at a loading of 4.0 mg cm^{-2} and Nafion[®] ionomer with a 10 wt. % by dry weight content. The CL was prepared

Table 1

Selected physical properties of the organic solvents used to prepare the catalyst inks.

Solvent	ϵ^a	P_v^b/hPa	$T_b^c/^\circ\text{C}$
n-butyl acetate (NBA)	5.01	13.0	126.5
2-propanol (IPA)	18.0	43.0	82.4

^a Dielectric constant at 25°C .

^b Vapour pressure at 20°C .

^c Boiling temperature.

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