



Ten-fold reduction from the state-of-the-art platinum loading of electrodes prepared by electro spraying for high temperature proton exchange membrane fuel cells

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ABSTRACT

The electro spraying deposition technique was used to prepare electrodes with a Pt loading of only $0.1 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ and make membrane electrode assemblies (MEAs) for High Temperature-Proton Exchange Membrane Fuel Cells (HT-PEMFCs) based in H_3PO_4 -doped polybenzimidazole membranes. An MEA prepared from binderless electrodes yielded a maximum performance of 420 mW cm^{-2} (i.e. a cathode specific power of $4.2 \text{ kW g}_{\text{Pt}}^{-1}$) when tested with H_2/Air at ambient pressure, that is, to the best of our knowledge, the highest performance ever reported at such a low Pt loading in HT-PEMFCs. The durability of this MEA was not affected by both, the absence of binder or the low Pt loading of the catalytic layer, since it worked continuously for $> 3000 \text{ h}$ at 0.2 A cm^{-2} with a performance loss of 4% and a voltage decay of $5 \mu\text{V h}^{-1}$ in the last 1500 h.

1. Introduction

High temperature PEMFCs based in phosphoric acid- (PA-) doped polybenzimidazole (PBI) membranes have gained much of attention due to some advantages over the low-temperature (LT-) PEMFCs [1, 2]. However, among the main drawbacks is the high Pt content of the electrodes that, according to the most recent reviews [3–5], is approximately $1 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$, comparatively much higher than $0.1\text{--}0.4 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ of LT-PEMFCs. The low permeability of oxygen in the PA electrolyte and the anion phosphate adsorption in the Pt catalytic site are pointed as the main causes for the lower performance of HT-PEMFCs [2, 6]. The state-of-the-art Pt loading of HT-PEMFCs is far from the target of $0.125 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ per MEA stated in the Hydrogen and Fuel Cells Program for the year 2020 [7]. Until now, there have been only a few studies in which the Pt loading of the HT-PEMFC electrodes has been lowered down to around $0.1 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ but the performance was rather low [8–13]. Most of them have in common a binder-added catalytic layer and spraying methods for the catalyst deposition. The presence of the binder becomes crucial at low Pt loadings since a significant fraction of the current Pt sites may be blocked by the binder. The resulting performance loss adds to the phosphate anion adsorption on Pt and to the low oxygen permeability in PA making even more difficult to lower the Pt loading while keeping the adequate performance. On the other hand, the structure and the distribution of components (Pt/C and binder) in the catalytic layer rely, to a great

extent, on the catalyst deposition method which may be the key to achieve a good performance at low Pt loadings. In the present work, the catalyst deposition method was electro spray, which has been extensively used by our research group to achieve ultra-low Pt loadings for LT-PEMFCs electrodes [14, 15]. Unlike other spraying-based methods which provide catalytic layers with simple porous structures, the electro spraying method allows to tune the structure of the catalytic layer by a proper selection of the control parameters (mainly the voltage drop between the ejector needle and the collecting substrate). Thus, the ensuing electric field can be strengthened to favor ballistic trajectories of the electro sprayed droplets to get compact deposits (approaching the purely sprayed deposits) or weakened enough to promote pseudo-diffusive random trajectories of the charged droplets due to repulsive coulombic interactions that lead to highly porous fractal-like deposits with a large dispersion of the components [16, 17]. This technique was used here to prepare catalytic layers with $0.1 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$.

2. Experimental

Catalytic inks for the binderless electrodes were based in the catalyst (10 wt% Pt/C, Johnson Matthew) and ethanol. Polytetrafluoroethylene- (PTFE-) added electrodes were prepared by including the corresponding amount of PTFE to get catalytic deposits with 5–30 wt% PTFE (in solids). The catalytic inks were sonicated for

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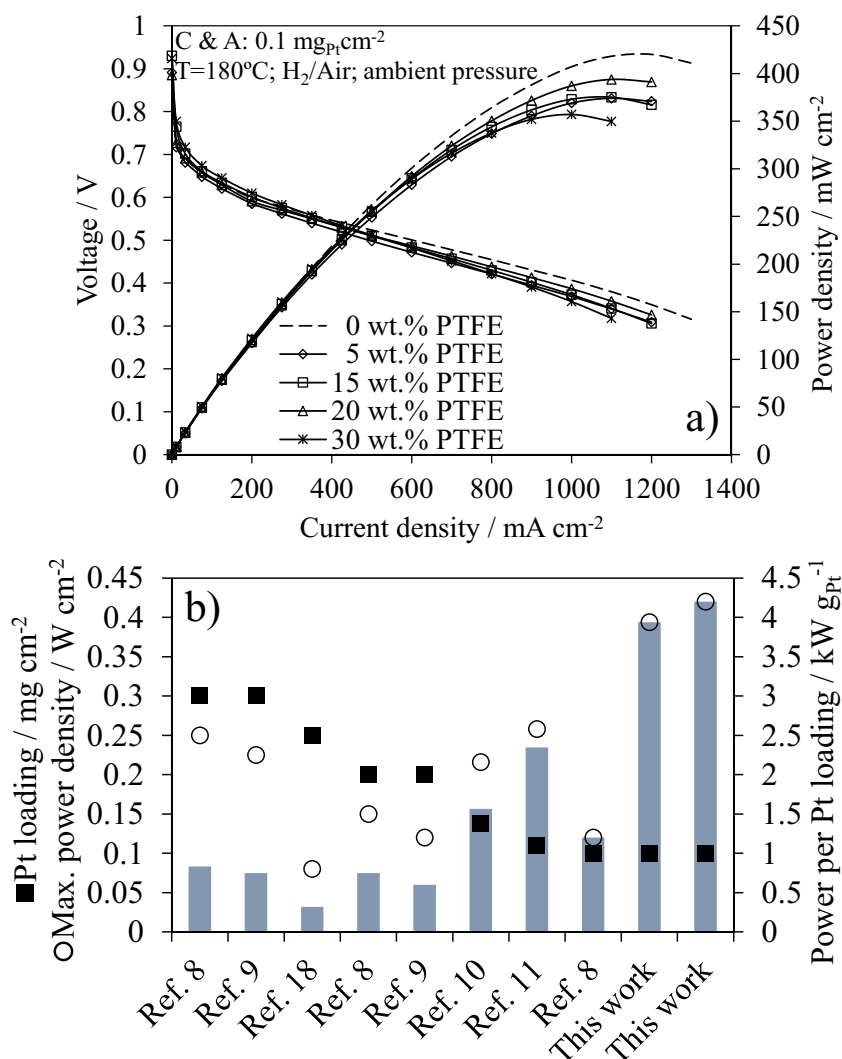


Fig. 1. a) Polarization and power density curves of MEAs with equal electrospayed electrodes, $0.1 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ each, and different PTFE content. b) Performance comparison with data collected from literature. Performance was evaluated at a temperature of 150°C in Ref. 18 and 160°C in the rest of Refs. MEA size: 49 cm^2 (Ref. 18), 5 cm^2 (Refs. 8–10) and 25 cm^2 (Ref. 11).

1 h prior electrospaying. Electrodes with $0.1 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ and active area of 4 cm^2 were prepared by electrospaying the catalytic ink on the GDL (Freudenberg H24C3). The electrospaying was performed at a flow rate of 1 ml h^{-1} , a needle-substrate distance of 5 cm and a voltage drop of $\sim 9000 \text{ V}$.

MEAs were formed by a PA-doped PBI membrane with an acid doping level of ~ 9 (Dapozol®, Danish Power Systems) inserted between the electrodes and clamped in the fuel cell hardware (FC05-01SP, Electrochem) at 2 N m. Galvanostatic polarization curves at 180°C and ambient pressure were obtained with an electronic load (Hoher & Hackl ZS506) and the voltage was recorded after 2 min at each current density. Dry H₂/Air were supplied at constant stoichiometry ($\lambda_{\text{H}_2} = 1.5$, $\lambda_{\text{Air}} = 2$) for current densities $\geq 0.2 \text{ A cm}^{-2}$. The flow rate corresponding to 0.2 A cm^{-2} was kept constant for lower current densities. Electrochemical impedance spectroscopy (EIS) was performed with a potentiostat/galvanostat (Autolab PGSTAT302N) by applying a sinusoidal voltage (amplitude: 10 mV) in the frequency range: 10^5 – 0.01 Hz . Porosimetry analysis was done with a mercury porosimeter (Autopore IV 9500). A scanning electron microscope (SEM, Hitachi S-3000 N) was used to obtain micrographs of the catalytic layers.

3. Results and discussion

In order to demonstrate the capability of the electrospaying deposition method to produce efficient electrodes at different compositions of the catalytic layer, electrodes were prepared with several concentrations of the most common binder used in HT-PEMFCs (PTFE) as well as without any binder or ionomer (binderless electrodes). Fig. 1 a) shows the polarization curves corresponding to MEAs of equal electrospayed electrodes with only $0.1 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$. The polarization curves were measured once the MEAs attained a steady-state voltage after a break-in period of about 200–300 h at 0.2 A cm^{-2} . As noted, regardless of the PTFE content in the catalytic layer, a high performance is exhibited by all the PTFE-added MEAs with maximum power densities in the interval 360 – 394 mW cm^{-2} (and voltages between 584 and 610 mV at 0.2 A cm^{-2}). Even more, the performance of the MEA with binderless electrodes is the largest at medium and high current densities. This MEA, with the simplest electrode composition, i.e. only the Pt/C catalyst particles, attains a peak power density of 420 mW cm^{-2} . However, note that at low current densities the PTFE binder seems to exert a positive effect on the performance. Thus, at 0.2 A cm^{-2} the 30 wt% PTFE MEA exhibits a greater voltage than the binderless MEA (0.61 V vs. 0.60 V, respectively) and the size of the

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