

Electrodeposited Mesoporous Pt for Direct Ethanol Fuel Cells Anodes

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In this study mesoporous Pt was electrodeposited from liquid crystal templates with different amount of Pt (0.60 mg/cm², 1.0 mg/cm² and 1.5 mg/cm²) directly on a carbon cloth using a potentiostatic method. These mesoporous Pt electrocatalysts were used as anodes for a direct ethanol fuel cell and the activity of ethanol oxidation reaction was studied. The electrochemical active surface area of the electrodes was measured using cyclic voltammetry under fuel cell conditions. Polarization and power curves for both commercial Pt and electrodeposited mesoporous Pt at different temperatures (30 °C, 50 °C and 70 °C) were studied, showing an increase of the performance with the temperature as expected. Despite lower Pt loading, all the mesoporous samples showed similar or better performances in the direct ethanol fuel cell when compared with the commercial Pt sample (4.0 mg/cm²). These results show that this catalyst preparation method can be a new route for the development of more efficient Pt based materials for direct alcohol fuel cells applications.

Keywords: mesoporous Pt, electrodeposition, catalysts, direct ethanol fuel cell

1. INTRODUCTION

Interest in fuel cells utilising liquid fuels for mobile applications has grown in recent years. Although methanol has been the most studied fuel for this type of fuel cells, ethanol presents many advantages as a fuel such as high energy density (8.00 kWh/kg as compared to 6.09 kWh/kg for methanol) and low toxicity [1]. In addition, ethanol can be produced through agricultural bioprocesses and thus it is considered as a renewable energy source [2]. The complete electro-oxidation of ethanol to CO₂ involves a 12-electron process as follows:



However, this reaction involves a dual path mechanism where the incomplete oxidation of ethanol to acetic acid (involving transfer of only 4 electrons) can take place reducing notably the energy obtained from the process. Thus effectiveness of anode catalysts is crucial for the practical application of this direct ethanol fuel cell (DEFC) and Pt is known as the most active material for ethanol electro-oxidation inducing C-C bond breaking [3]. However, oxidation of ethanol depends on the Pt surface structure and it has been shown that Pt nanoparticles with a high amount of (111) sites are active at low potentials favouring incomplete ethanol oxidation to acetic acid [4]. Pt (100) sites promote cleavage of the C-C bond yielding adsorbed CO, which eventually is oxidized to CO₂, and show the highest catalytic activity at high potentials. Therefore, controlling surface structure formation during the synthesis of Pt particles is one approach to enhance slow ethanol electro-oxidation reaction.

Recently, electrodeposition methods have been used for preparing membrane electrode assemblies (MEA) for fuel cells because this method is simple and inexpensive. Taylor et al. [5] have developed an electrochemical catalyzation (ECC) technique to improve the utilization of Pt catalysts. In this process a gas diffusion electrode is prepared from catalyst free carbon attached on a Nafion® membrane and Pt particles are electrodeposited from a commercial plating bath through the Nafion® into the electrodes. Electrodeposited Pt using cyclic voltammetry and pulse deposition on carbon black has also been described for fuel cell applications. [6] A new approach to prepare MEAs based on pulse electrodeposition has been studied by Kim et al. [7, 8]. They have reported that with this pulse plating technique, the Pt/C ratio is increased up to 75 wt. % near the surface of the electrode increasing the efficiency.

Our previous study in an electrochemical cell have shown that mesoporous Pt enhance the ethanol oxidation reaction in comparison to commercially available materials [9]. Therefore, in this work we have used the potentiostatic electrodeposition method to synthesize mesoporous Pt directly onto a carbon cloth, which was used as an anode in a direct ethanol fuel cell. These electrodes were characterized using scanning electron microscopy, energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). The performance of the catalysts was studied in a fuel cell at different temperatures and with different metal loadings on the anode. To our knowledge, this electrode preparation method, using Pt mesoporous catalysts directly electrodeposited onto the carbon cloths has not been used in fuel cell earlier.

2. EXPERIMENTAL

2.1 Chemicals

Surfactant Brij®C10 (Aldrich), hexachloroplatinic acid hydrate (HCPA, 99.9%, Aldrich), ethanol (94 %, Altia), H₂SO₄ (Merck), 2-propanol (Merck), Carbon Cloth (GDL, FuelCellsetc), 5 wt-% Nafion® dispersion in low molecular weight alcohols (Aldrich) were used. The gases (H₂, O₂) were all produced by AGA with at least 99.99 % purity. Ion-exchanged Millipore Milli-Q water was used for solutions and cleaning of the electrodes.

2.2 Electrodeposition of Pt structures

The substrate was a carbon cloth gas diffusion layer (GDL). First the substrates were soaked in 0.05 M H₂SO₄ for at least 20 min and washed with Milli-Q water to increase the hydrophilicity of the surface.

The plating mixture contained 29 wt-% HCPA, 45 wt-% Brij®C10 and 26 wt-% water. The mixture was stirred with a plastic spatula and heated in a sealed vial to 40 °C for 30 min, this process was repeated twice, and a bright orange color was obtained. The platinum plating mixture was added onto the carbon cloth electrodes using a PTFE mould with a hole matching the electrode area of 5.29 cm². The electrode system was put into a sealed box to improve the stability of the mixture and then placed into an oven at 40 °C for two hours. The mixture was slowly cooled down with an approximate rate of 4 °C/h for at least 2 h, to make sure that liquid crystal phase was well organized.

Electrodeposition was performed on the carbon cloth surface with a deposition potential of 200 mV varying the used charges (1.23 C/cm², 2.00 C/cm² and 3.00 C/cm²) with Pt gauze as a counter electrode and a Dri-Ref (World Precision Instruments, Inc.) as a reference electrode. After electrodeposition, the surfactant template and reactants were removed by immersing the working electrode in ethanol to ensure solving out of the surfactants. The carbon cloths with the deposited electrodes were then dried in a vacuum oven at 80 °C for 2 h.

2.3 Fuel cell experimental

After the electrodeposition of mesoporous Pt on the carbon cloth, the Nafion ionomer dispersion (~425 mg) in 2-propanol (600 µl) was sprayed on its surface followed by drying in a vacuum oven. The membrane electrode assembly (MEA) was prepared using the electrodeposited mesoporous Pt (A: 0.60 mg/cm², B: 1.0 mg/cm² and C: 1.5 mg/cm²) on a carbon cloth as an anode and a commercial carbon cloth electrode (4 mg/cm² of Pt covered by Nafion from FuelCellsetc) as a cathode. For comparison, one MEA with the commercial carbon cloth electrode with 4 mg Pt/cm² as an anode was prepared. For MEA preparation, the carbon cloth electrodes (anode and cathode) were placed on each side of a Nafion 115 (Dupont) membrane and heat pressed at 120°C, with 18 kN pressure for 120 s. The fuel cell was assembled with PTFE gaskets, and the MEA, closed and tightened evenly with 10 kN force.

The fuel cell experiments were performed in a single cell direct ethanol fuel cell (DEFC) with a surface area of 5.29 cm². 1 M ethanol fuel was fed to the anode with 2.0 ml/min rate and humidified oxygen gas to the cathode at 200 ml/min. The cell was stabilized over night with the studied fuel (0.2 ml/min) and normalized 1 h prior to the polarization experiments with higher flow rates (2.0 ml/min). For measuring at different temperatures (30 °C, 50 °C and 70 °C) the whole cell set-up was allowed to stabilize for 2 h with the studied fuel prior to the experiments to obtain reproducible results. The same MEA was used for the different temperatures. Polarization curves were measured with a scan rate of 50 mV/s. An Autolab PGSTAT 20 instrument equipped with an Autolab BSTR10A booster controlled by a GPES software (version 4.9 by Eco Chemie B.V) was used for the electrochemical measurements.

The cyclic voltammograms were measured before and after the polarization curves. For the cyclic voltammetry performed in the fuel cell humidified nitrogen was fed to the anode compartment serving as a working electrode to ensure the mass transport through the electrode layer and the membrane. The cathode compartment, used as a reference electrode, was fed with humidified hydrogen flow.

2.4 Characterization of mesoporous Pt

The mesoporous Pt samples were examined using scanning electron microscopy (SEM JSM-7500F) coupled with energy-dispersive X-ray spectroscopy (EDS) and an X-ray diffraction device (XRD, Pan Analytical X'PertPro).

3. RESULTS AND DISCUSSION

3.1 Electrodepositions

We have earlier shown [9] that the potentiometric deposition of mesoporous Pt on carbon black results in high mass activities for ethanol electro-oxidation and consequently, selected this method for this further study in a fuel cell. Electrodeposition was performed on the carbon cloth surface with a deposition potential of 200 mV varying the used charges (A: 1.23 C/cm², B: 2.00 C/cm² and C: 3.00 C/cm²) in order to obtain different Pt loadings. Electrodeposition charge and the calculated theoretic mass of platinum on the electrodeposition surface of 5.29 cm² are shown in Table 1.

Table 1. Electrodeposition parameters for three mesoporous samples.

Anode	Q (C)	Q _s (C/cm ²)	m Pt (mg)	m _s Pt (mg/cm ²)
A	6.53	1.23	3.30	0.62
B	10.61	2.00	5.35	1.00
C	15.85	3.00	8.00	1.51

3.2 SEM and XRD characterization

The morphology and the size of the particles of both the commercial carbon cloth electrode and the electrodeposited mesoporous Pt on the carbon cloth were investigated by SEM (Figures 1 and 2). The commercial Pt particles were spherical in shape and packed very densely on the surface. The anodes with different mesoporous Pt loadings are shown in Figure 2 a) 0.6 mg/cm², b) 1.0 mg/cm² and c) 1.5 mg/cm². These images show that an increase in the metal loading results in more dense, compact and aggregated structures. The particle size obtained from Figure 2 increases as Pt loading increases due to the agglomeration.

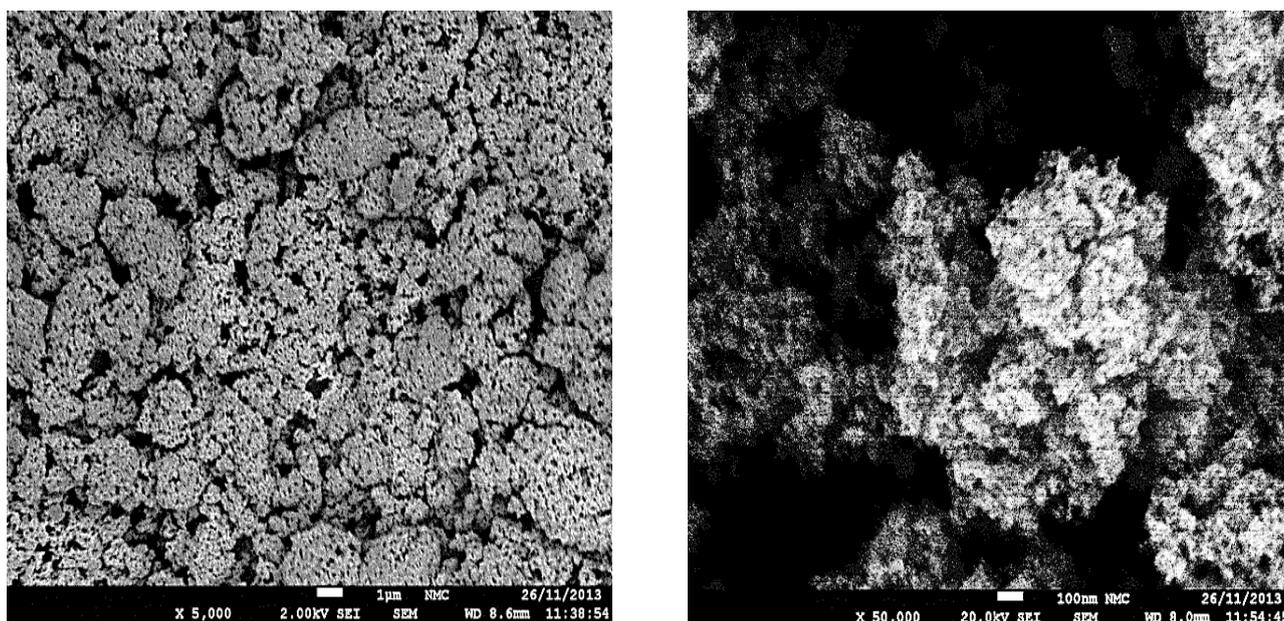


Figure 1. SEM images of the commercial carbon cloth electrodes (4 mg/cm^2 of Pt covered by Nafion ionomer), scale bar $1 \mu\text{m}$ (left) and 100 nm (right).

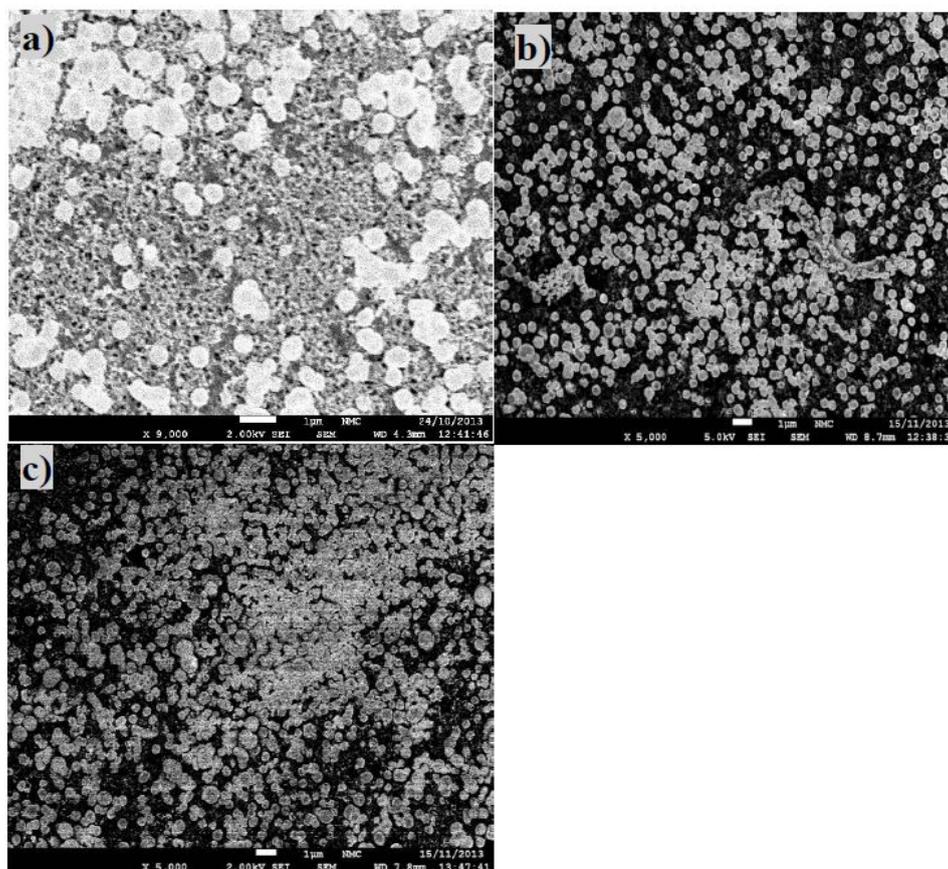


Figure 2. SEM images of the electrodeposited mesoporous Pt on the carbon cloth with a) 0.6 mg/cm^2 (scale bar $1 \mu\text{m}$), b) 1.0 mg/cm^2 (scale bar $1 \mu\text{m}$) and c) 1.5 mg/cm^2 (scale bar $1 \mu\text{m}$).

It is plausible that with a higher Pt loading new particles are formed in between and on top of the old Pt particles and these structures are observed as agglomerates as suggested in our earlier research investigating the growth mechanism [9].

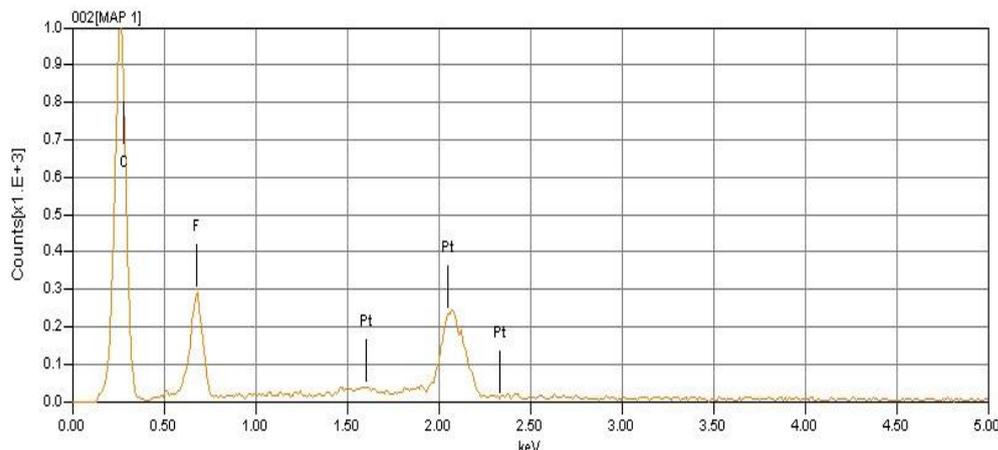


Figure 3. EDS spectrum of electrodeposited mesoporous Pt with 1.0 mg/cm² loading.

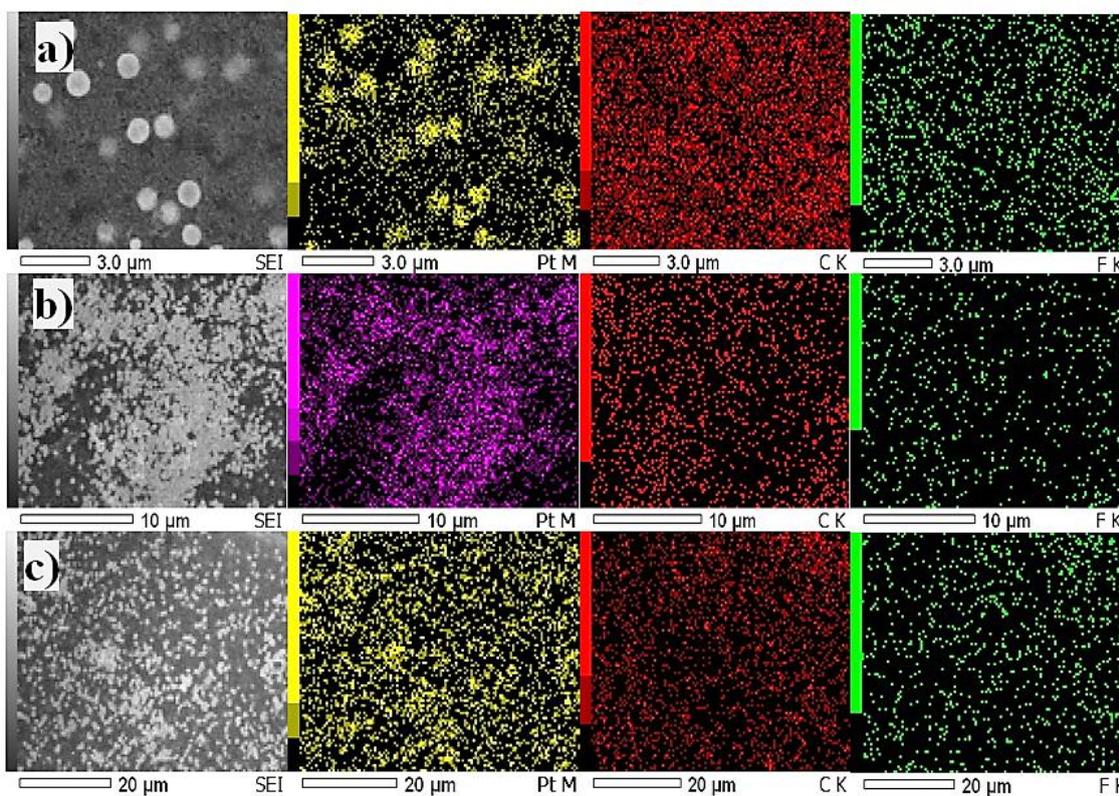


Figure 4. SEM images of elemental (Pt, C and F) distribution on the GDL surfaces with: a) 0.6 mg/cm², b) 1.0 mg/cm² and c) 1.5 mg/cm² of mesoporous Pt.

In that study, TEM results showed that in these mesoporous Pt structures the size of the particles varies from 50-400 nm with very small (approximately 3-5 nm) pores. The SEM images reported here resemble our previously reported ones on mesoporous Pt on glassy carbon substrate [9]

with a particle size range around 300-900 nm. The elemental analysis of the mesoporous Pt samples on the carbon cloth was also done by EDS, and the spectrum for the anode with 1 mg/cm² Pt is shown in Figure 3. The observed F and C peaks originate from the Nafion ionomer and the carbon cloth. The mapping of the anode surface for the 3 elements detected in the EDS spectrum and the respective SEM images for the investigated carbon cloths with the different Pt mesoporous loadings is shown in Figure 4. It is clearly observed that a good distribution of the Pt catalyst on the surface is obtained with this electrodeposition method.

The XRD patterns of the studied mesoporous and commercial Pt catalyst samples with different amount of Pt are shown in Figure 5. The characteristic peaks assigned to the face-centered cubic (fcc) crystal of Pt can be observed in the diffractograms for all the samples. The 2θ values of 39.60, 47.5, 67.60 and 81.5 corresponding to the (111), (200), (220) and (311) faces, respectively, can be identified (JCPDS card 01-087-0647). Other features on the diffractograms origin from the carbon cloth and the ionomer as can be seen from the spectrum for the bare carbon cloth. The spacing and lattice parameters of mesoporous Pt can be calculated from the width of the peaks using the Bragg's law:

$$d = \frac{n\lambda}{2 \sin \theta} \quad (2)$$

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (3)$$

where λ is the X-ray wavelength (Cu target 1.540 Å), θ is the Bragg angle in radians and a is the lattice parameter. The calculated d and a values for the (111) and (220) peaks of all the samples are shown in Table 2.

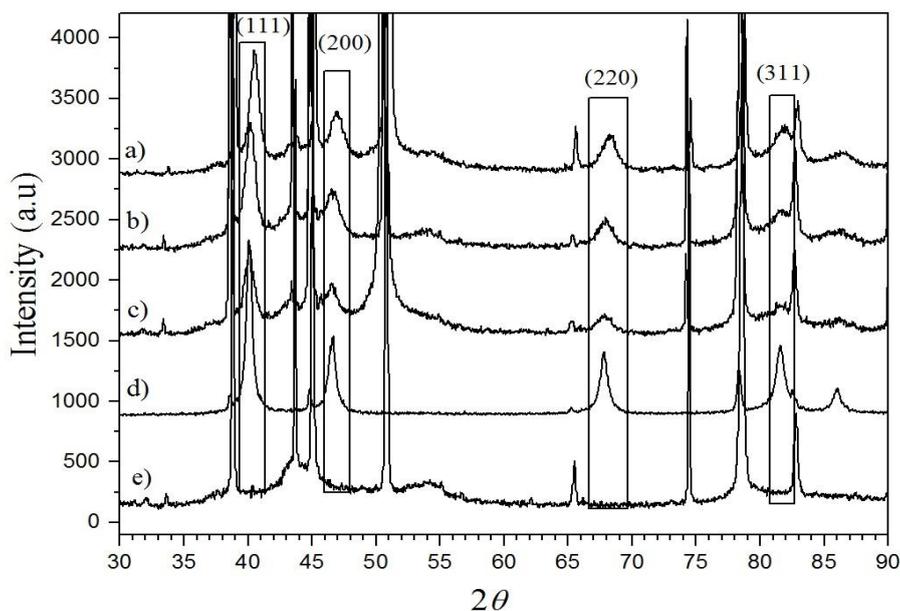


Figure 5. XRD spectrum of a) mesoporous Pt 0.6 mg/cm² b) mesoporous Pt 1.0 mg/cm² c) mesoporous Pt 1.5 mg/cm², d) commercial Pt 4.0 mg/cm² and e) bare carbon cloth

Broader peaks observed in the XRD spectra (Figure 5) for the mesoporous Pt samples indicate smaller crystallite sizes in comparison to the commercial Pt. The lattice parameters for all the measured samples show lower values than bulk Pt (3.9236) [10] which can be explained by the sizes effect. The lattice parameter of the commercial Pt electrode is slightly bigger than that of the mesoporous Pt samples indicating that the former one has bigger crystallites. However, the sample with the lowest Pt loading (0.6 mg/cm²) has the highest lattice parameter which favours complete ethanol oxidation reaction by the C-C bond breaking [3].

Table 2. Particle d spacing and lattice parameters for the commercial reference and the Pt mesoporous samples with different loadings obtained from equations 1 and 2.

Anode with Pt mass (mg/cm ²)	Plane	2 θ	d spacing (Å)	a (lattice parameter) (Å)
4.0*	111	40.08	2.25	3.90
	220	67.79	1.38	3.92
A: 0.6	111	40.09	2.25	3.90
	220	67.86	1.38	3.91
B: 1.0	111	40.17	2.25	3.89
	220	67.9	1.38	3.91
C: 1.5	111	40.5	2.23	3.86
	220	68.22	1.38	3.89

*Commercial reference sample

3.3 Electrochemical Measurements: Cyclic voltammogram

Cyclic voltammograms recorded at 50 mV/s for MEAs with different platinum loadings are shown in Figure 6. The current densities are presented both normalized to the surface active area (a) and to the Pt loading (b). Hydrogen adsorption and desorption peaks on the Pt nanoparticles and mesoporous Pt catalysts can be observed at ~0.14 V and ~0.28 V followed by the double layer region, as expected for polycrystalline Pt electrodes. In Figure 6B, it can be observed that with the lowest loading Pt sample (0.6 mg/cm²) the double layer is broader due to an effect of carbon indicating that there are some Pt free areas on the surface and the mesoporous particles are not as agglomerated as in other samples (1.0 mg/cm² and 1.5 mg/cm²). The electrochemical active surface area (EASA) was determined using the charge involved in the hydrogen adsorption/desorption reactions, corrected for the double layer region [11] using the following equation

$$EASA = \frac{Q_H}{0.21} \quad (4)$$

where Q_H is the integral charge for hydrogen desorption (mC/cm^2), and 0.21 is the charge required to oxidize a monolayer of H on Pt surface (mC/cm^2). The obtained results are reported in Table 3. As expected, the EASA values increase with the Pt loading due to the increase of the number of mesoporous Pt particles. However, the increase is not proportional to the Pt loading as can be observed by the mass specific area values. This can be explained by particle size effect (i.e. changes in the volume to surface area ratio) and increasing agglomeration of the particles with increasing Pt loading, as is observed in the SEM images in Figures 3 and 4 resulting in a decrease in the relative number of active surface sites. The macroscopic size of the particles observed here varied in the range 300-900 nm.

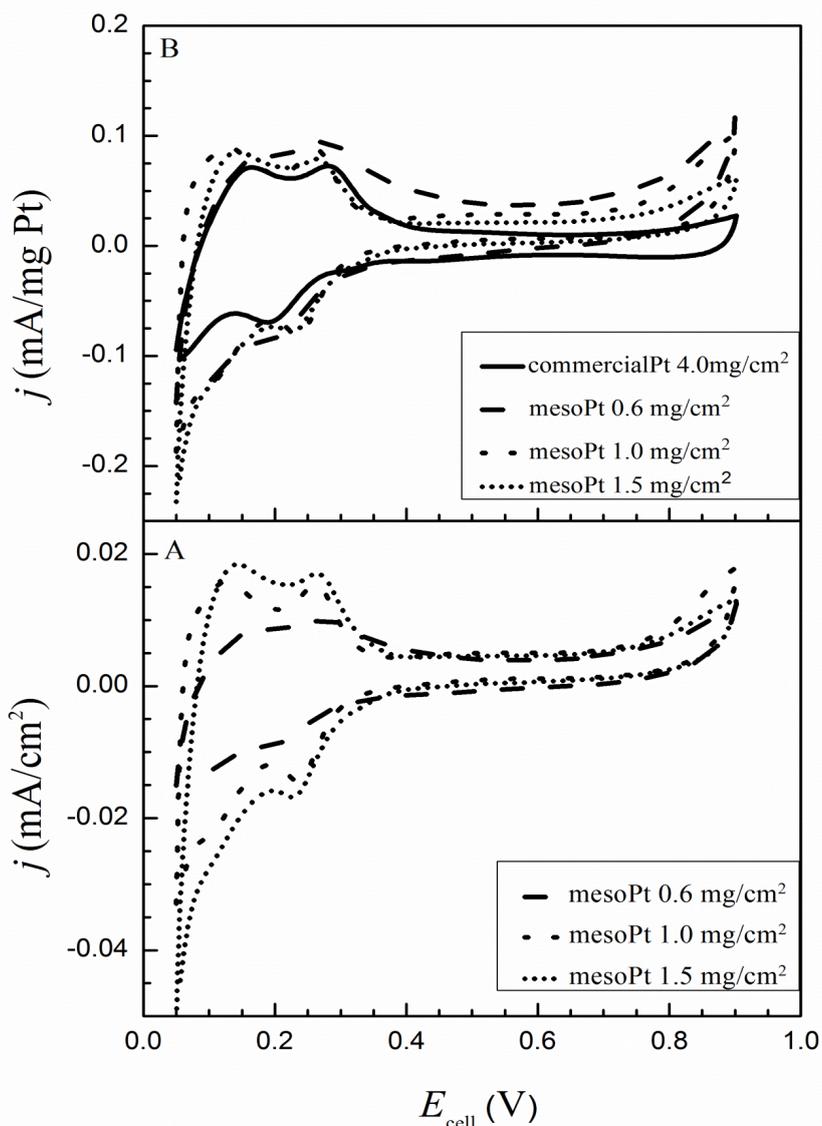


Figure 6. Cyclic voltammograms for anodes MEA with different amount of platinum loadings at 50 mV/s: current densities normalized for a) the electrochemical active surface area (EASA) and b) and for the Pt loading.

Table 3. The EASA values.

Andoe with Pt mass (mg/cm ²)	EASA (cm ²)	Mass of the Pt on the electrode (mg)	Mass specific area (m ² /g _{Pt})
4.0*	2380	29	8.2
A: 0.6	106	3.7	2.9
B: 1.0	176	7.3	2.4
C: 1.5	216	11	2.0

*Commercial sample

3.4 Performance of the direct ethanol fuel cell

The polarization and power curves for the commercial Pt and electrodeposited mesoporous Pt electrodes with the different platinum loadings operating in a temperature range from 30 °C to 70 °C are shown in Figure 7 (normalized against total platinum mass) and Figure 8 (normalized against EASA). For all the samples, the current density increases with the temperature as expected. The results in Figure 7 show good performance for the electrodeposited mesoporous anodes for all the measured temperatures. At 70°C higher performance was observed for the commercial sample with the highest amount of platinum (4.0 mg/cm²). The open circuit potential (OCP) for the commercial Pt anode is approximately 0.46 V whereas the OCP values for mesoporous Pt are slightly lower, (0.37-0.42 V). These results are very interesting as they show almost the same mass activity for all the samples, independently of the physical structure of the Pt catalyst (commercial nanoparticles and mesoporous).

The peak power density normalized with the geometrical area of the cell for the commercial sample with 4.0 mg/cm² is 5.1 mW/cm². This value is slightly higher than ~3 mW/cm² reported by Rousseau *et al.* [12] and 3.33 mW/cm² by Figueredo *et al.* [13] with Pt/C loadings of 3 and 2.3 mg/cm², respectively. It is well known that the fuel cell performance increases with increasing catalyst loading as more active sites are available for the electrocatalytic reactions explaining the higher power density measured in this study. As the loadings, and morphology, of the electrodeposited mesoporous Pt differ notably from that of the commercial reference using geometric area is not good basis for comparing the performance but values normalized with the mass loading or active Pt area are used instead.

A summary of the performances of the direct ethanol fuel cell with the four studied samples is presented in Table 4. The results showed that at the low temperature of 30 °C the anode with 0.6 mg/cm² Pt loading has the highest power density of 0.213 mW/mg_{Pt} while the commercial sample with the loading of 4.0 mg/cm² Pt (the sample with the highest Pt loading) has a lower power density 0.201 mW/mg_{Pt}. It is also observed that the temperature dependency changes with the loading. The higher the Pt loading the higher the increase in the power density, for example the power densities for the commercial sample (4.0 mg/cm² Pt loading) are 0.649 mW/mg_{Pt} at 50 °C and 1.213 mW/mg_{Pt} at 70 °C and for mesoporous Pt (0.6 mg/cm² loading) are 0.433 mW/mg_{Pt} at 50 °C and 0.866 mW/mg_{Pt} at 70 °C.

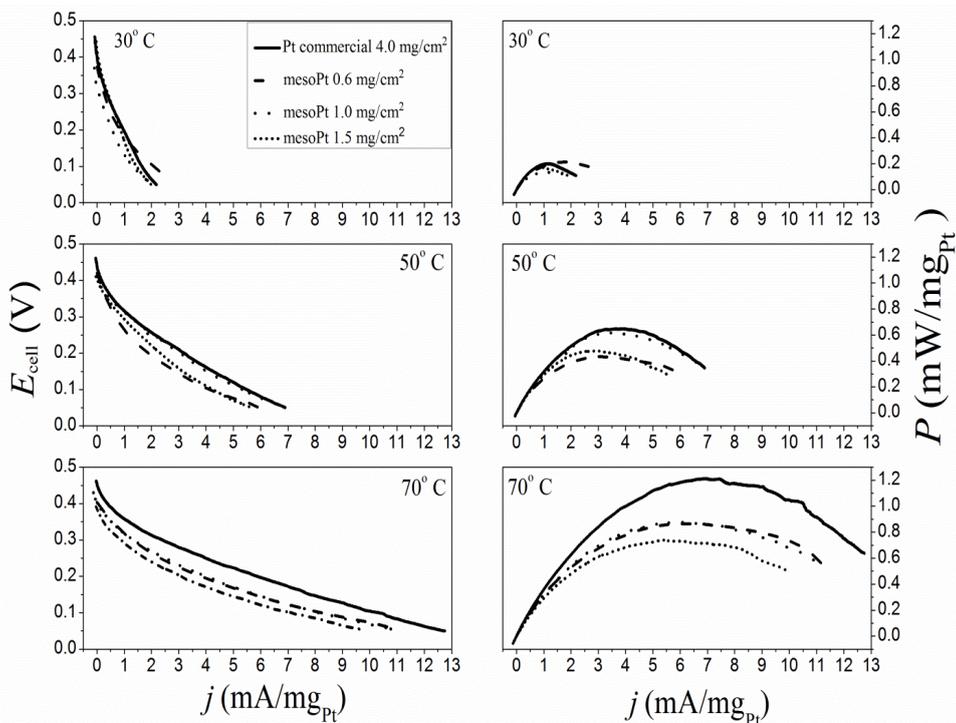


Figure 7. The polarization and power curves for commercial Pt and electrodeposited mesoporous Pt with the different platinum loadings operating in temperatures 30 °C, 50 °C and 70 °C in a direct ethanol fuel cell. The results are normalized against the total platinum mass.

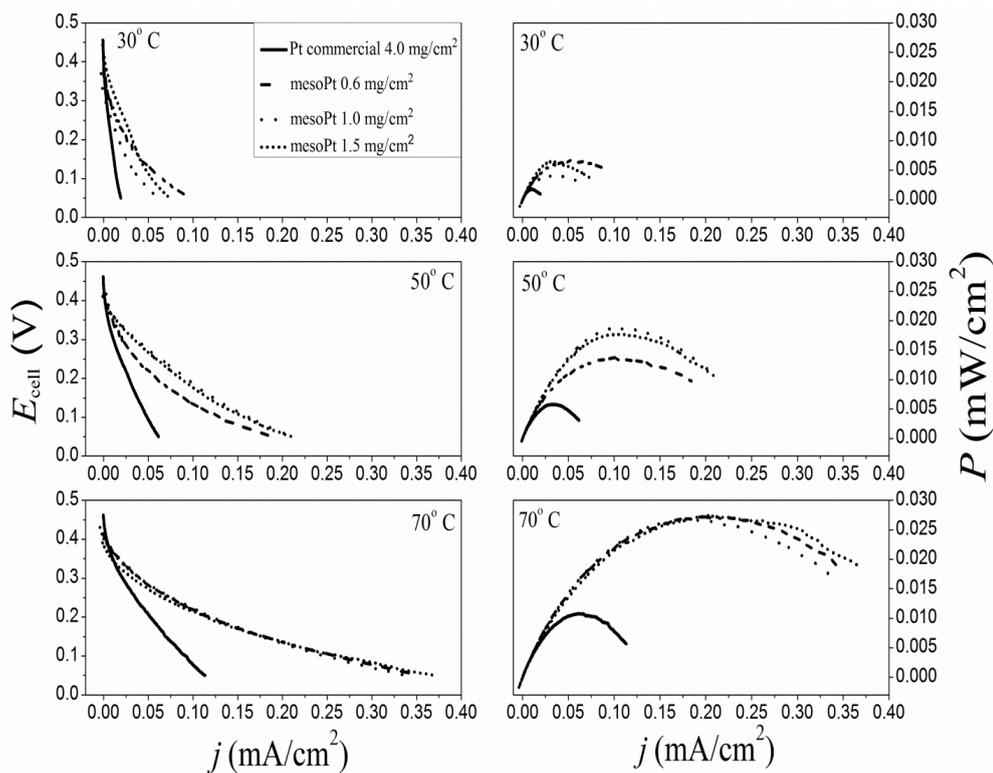


Figure 8. The polarization and power curves for commercial Pt and electrodeposited mesoporous Pt with the different platinum loadings operating in temperatures 30 °C, 50 °C and 70 °C in a direct ethanol fuel cell. The results are normalized against EASA.

It is worth noticing that when normalized with respect to the Pt mass even the Pt mesoporous anode with only 0.6 mg/cm^2 of metal has similar performance to the commercial sample with 4 mg/cm^2 . On the other hand, when the polarization and power curves are normalized for the EASA, the relative performance of the Pt mesoporous anodes increases significantly in comparison with the commercial and high loading Pt sample, for example the mesoporous anode with 0.60 mg/cm^2 Pt loading has the highest power density 0.007 mW/cm^2 at 0.055 mA/cm^2 at $30 \text{ }^\circ\text{C}$ (see Table 4).

However, when comparing the Pt loadings on the electrodeposited mesoporous samples, it can be observed that the fuel cell performance is not proportional to the Pt loading on the anode, as expected on the basis of the similar mass specific areas (Table 3). A possible explanation for this behaviour is the lower agglomeration of the particles for low loadings as observed from the SEM images (Figure 4) facilitating mass transfer. In addition, the low Pt content anode (0.6 mg/cm^2) has particles with the higher lattice parameter (XRD results in Table 2) favouring ethanol oxidation reaction by the C-C bond breaking [3]. The same behaviour, higher ethanol oxidation currents for lower Pt loadings in the mesoporous electrodes was observed in our previous work [9]. These results show that the structure of the Pt catalyst has a crucial influence on the fuel cell performance and mesoporous structures seem to favour ethanol oxidation at low temperatures.

Table 4. Summary of performances of direct ethanol fuel cells using the commercial Pt and electrodeposited mesoporous Pt (0.6 mg/cm^2 , 1.0 mg/cm^2 and 1.5 mg/cm^2) as an anode catalyst at different temperatures.

Catalyst (mg/cm^2)	OCP V	Current density (mA/mg_{Pt})		Max. power density (mW/mg_{Pt})	Current density (mA/cm^2)		Max. Power density (mW/cm^2)
		0.30 V	0.05 V		0.30 V	0.05 V	
30 °C							
Commercial Pt 4.0	0.456	0.363	2.180	0.201	0.003	0.019	0.002
A: mesoPt 0.6	0.390	0.247	3.056	0.213	0.009	0.095	0.007
B: mesoPt 1.0	0.370	0.071	2.007	0.133	0.002	0.061	0.004
C: mesoPt 1.5	0.443	0.395	1.987	0.174	0.015	0.074	0.006
50 °C							
Commercial Pt 4.0	0.461	1.245	6.899	0.649	0.011	0.061	0.006
A: mesoPt 0.6	0.419	0.669	6.019	0.434	0.020	0.188	0.014
B: mesoPt 1.0	0.415	1.209	6.910	0.616	0.037	0.210	0.019
C: mesoPt 1.5	0.411	0.926	5.655	0.477	0.034	0.210	0.018
70 °C							
Commercial Pt 4.0	0.462	2.399	12.754	1.213	0.021	0.113	0.011
A: mesoPt 0.6	0.414	1.255	11.298	0.866	0.040	0.353	0.027
B: mesoPt 1.0	0.430	1.331	11.182	0.877	0.040	0.340	0.018
C: mesoPt 1.5	0.391	0.872	9.950	0.740	0.032	0.369	0.027

4. CONCLUSIONS

In this preliminary work, we have shown that mesoporous Pt is a promising anode catalyst for ethanol oxidation in DEFCs especially at low operation temperatures. Mesoporous Pt samples were electrodeposited using a potentiostatic method from liquid crystal templates. SEM characterization showed that the structures are porous with a particle size range around 300-900 nm and the sizes of pores are around 3-5 nm [9]. Polarization and power curves for both the commercial Pt and the electrodeposited mesoporous Pt at different temperatures (30 °C, 50 °C and 70 °C) were studied, showing an increase in the performance with the temperature. All the mesoporous samples show better or similar performance in the direct ethanol fuel cell when compared with the commercial Pt sample (4.0 mg/cm²).

In this study we have shown that this electrodeposition method is easy and fast when comparing to the power/ink method for preparing MEAs for fuel cell electrodes. Moreover, with this electrodeposition method a separate carbon support is not needed as the catalyst is directly electrodeposited onto the carbon cloth diffusion layer and a good activity is achieved with a low Pt loading. Thus this kind of electrodeposition method can be a new route for the development of more efficient catalysts for direct alcohol fuel cells.

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