Formic acid microfluidic fuel cell based on well-defined Pd nanocubes

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Abstract. Microfluidic fuel cells (µFFC) are emerging as a promising solution for small-scale power demands. The T-shaped architecture of the µFFC promotes a laminar flow regimen between the catholyte and anolyte streams excluding the use of a membrane, this property allows a simplest design and the use of several micromachining techniques based on a lab-on-chip technologies. This work presents a combination of new materials and low cost fabrication processes to develop a light, small, flexible and environmental friendly device able to supply the energy demand of some portable devices. Well-defined and homogeneous Pd nanocubes which exhibited the (100) preferential crystallographic plane were supported on Vulcan carbon and used as anodic electrocatalyst in a novel and compact design of a SU-8 µFFC feded with formic acid as fuel. The SU-8 photoresist properties and the organic microelectronic technology were important factors to reduce the dimensions of the µFFC structure. The results obtained from polarization and power density curves exhibited the highest power density (8.3 mW cm⁻²) reported in literature for direct formic acid µFFCs.

1. Introduction

A special kind of miniaturized fuel cells is emerging: the microfluidic fuel cells (µFFC); their operation mode is based in the liquid-liquid (fuel and oxidant) interface under laminar flow regimen, this particular property, is precisely the main advantage over static membrane fuel cells [1- 4], since their operation requires a smaller number of components and sporadic maintenance events[1, 5-8]. The aim of the µFFCs is and has been to supply the energy demand of portable devices such as cell phones, sensors and medical transplants [1, 9, 10]. The main problem of µFFCs is the long-times durability and their performance. In this work we attacked the performance problem using Pd nanocubes which is known that exhibit high current densities due to the presence of (100) crystallographic planes using formic acid as fuel due to its high theoretical energy density (2.086 kW L⁻¹) and low cross-over effect compared with methanol [11].
2. Methodology

2.1 Fabrication process

The use of polymeric materials like polymethyl methacrylate (PMMA) and poly-dimethylsiloxane (PDMS) has recently been proposed to produce micro-fuel cell components [3, 6, 7, 13]. However UV-sensitive resists such as SU-8 have demonstrated to be excellent candidates to build microfluidic fuel cells since they present some important advantages like flexibility and the capability to be sealed each other by a hot-pressing technique [12, 14]. The µFFC assembly used a silicone polymer microchannel sandwiched between two SU-8 current collectors. The SU-8 fabrication process was previously detailed by Esquivel et al. [12]; where three main sections (fig. 1) were assembled to build the µFFC: the silicone polymer microchannel (section 1) sandwiched between two SU-8 current collectors (sections 2 and 3). The SU-8 microfabrication process was based on photolithography. Ti-Au-Ni layers (50nm each) were used as current collectors using metal sputtering deposition. To assure homogeneity of the catalyst deposition, this was performed by a numerical control spray system.

3. Experimental

3.1. Synthesis of Pd nanocubes

The synthesis of homogeneous and well-ordered cubic-shaped Pd nanoparticles (namely Pd nanocubes for simplification purposes) was carried out by typical chemical reduction in aqueous medium [14]. In a usual synthesis two solution are made, in a first solution the surfactant (0.105 g polyvinylpyrrolidone, Sigma-Aldrich, average mol wt 44,000 g mol\(^{-1}\)) and the reductive agent (0.023 g L-ascorbic acid, Sigma-Aldrich, BioXtra, ≥99.0%) were mixed in 8 mL of water and the temperature was raised at 80°C. The second solution was prepared mixing the Pd source (0.056 g Na\(_2\)PdCl\(_4\), Aldrich, 98%) and the additive (0.2496 g of the NaBr, Sigma-Aldrich, SigmaUltra, >99.0%) in 3 mL of water and added to the first solution when the desire temperature of the first solution was reached. The final solution was then magnetically stirred for 3 hours at 80°C. After that, Vulcan carbon was added and the solution was stirred for 30 minutes, washed with isopropyl alcohol (1:5 v/v solution and alcohol), centrifuged at 10,000 rpm and dried at 60°C.

3.2. Physicochemical characterization

Pd nanocubes were characterized by X-ray diffraction using a Bruker D8 Advanced diffractometer operated at 30 kV and 30 mA. HR-TEM images and EDX analysis were acquired through a Phillips Model CM200 transmission electron microscope.
3.3. Electrochemical characterization

The electrocatalytic activity of Pd nanocubes/C and commercial Pd/C was determined by half-cell experiments using a PGSTAT AutoLab 302 Potentiostat/Galvanostat (Metrohm®). The experiments were carried out in a typical three electrodes electrochemical cell employing 0.5 M H$_2$SO$_4$ (99.7 %, J. T. Baker) as the electrolytic solution to determine the Pd nanocubes/C and commercial Pd/C behavior in acidic media. The Hg/Hg$_2$SO$_4$ saturated in K$_2$SO$_4$ electrode was used as the reference electrode, a Pt wire as the counter electrode and the anode current collector as working electrode.

3.4. Evaluation of the SU-8 microfluidic fuel cell performance

The deposition of the catalyst was performed by spraying a catalyst ink over the current collectors. The catalytic ink was composed of 7 µL Nafion® 5% (Sigma–Aldrich), 73 µL isopropyl alcohol (J.T. Baker) and 1 mg electrocatalyst materials, mixed in ultrasonic bath for 20 min. Two micro-fuel cells were constructed in order to compare our synthesized Pd nanocubes against the Pd/C XC-72 material. The cathode electrode was maintained in both cells with a loading of 1 mg cm$^{-2}$ using Pt/C (30 wt. % E-TEK). Anode electrodes were constructed using Pd/C XC-72 (20 wt. %, E-TEK) and Pd nanocubes/C (40 wt. %) with a Pd loading of 1 mg cm$^{-2}$ respectively.

0.5 M formic acid in 0.5 M H$_2$SO$_4$ and oxygen (4.3 U.A.P. Praxair) dissolved in 0.5 M H$_2$SO$_4$ were used as fuel and oxidant solutions, respectively. The anolyte and catholyte streams were fed to the corresponding inlets in laminar flows with a Pressure-driven fluid flow of 600 µL min$^{-1}$ using syringe pump (NE-4000, New Era Pump Systems Inc.). All tests were performed at 25 °C. Voltage and current measurements were performed using an Epsilon potentiostat, version 1.40.67 from Bioanalytical Systems.

4. Results and discussion

4.1. Physicochemical characterization

XRD diffraction pattern for Pd nanocubes/C and TEM images are presented in Figure 2. The typical face-centered cubic Pd structure was found (Fig. 2-I). The (111), (200), (220) and (311) crystallographic planes were located at 40.04, 46.5, 68.04 and 82.19 degrees, respectively. A (200) preferential plane was found, which was expected due to the cubic-shape. The crystal size was calculated through (111) and (220) planes using the Scherrer’s equation. Also, the lattice parameter using the (220) planes was calculated and showed in Table 1. HR-TEM images (Fig. 2-II) confirmed the presence of Pd nanocubes, where other geometries were not observed. Furthermore, the particle size and the interplanar distance were calculated through HR-TEM images and are also presented in Table 1. The interplanar distance 1.93 Å is in agreement with the (100) plane families.

![Figure 2. I) X-ray Diffraction patterns for Pd nanocubes and II) TEM images of Pd nanocubes](image-url)
Table 1. Particle size, lattice parameter and interplanar distances for Pd nanocubes.

| Parameter               | XRD | TEM |
|-------------------------|-----|-----|
| Particle size           | 11.5 nm | 10.6 nm |
| Lattice parameter (XRD) | 3.8802 Å | |
| Interplanar distance    | 1.93 Å | |

4.2. Electrochemical characterization
The electrochemical behavior in acidic media is illustrated in Fig. 3. Three well-known zones were observed, the hydrogen adsorption/desorption zone (marked in dashed rectangle), the double layer zone and the Pd oxides formation and their reduction zone. Also, the characteristic peak attributed to the (100) plane is observed at 0.28 V vs. NHE [15]. The electrochemical surface area (ECSA) was calculated through the Pd oxides reduction peak using the theoretical value of 424 µC cm\(^{-2}\) [16] resulting in an area of 10.60 cm\(^2\). The electrocatalytic activity of Pd nanocubes was evaluated for the formic acid electrooxidation reaction at 0.5 M formic acid concentration using sulfuric acid as electrolyte (Fig. 3). The electrocatalyst showed good catalytic properties with a high current density.

**Figure 3.** a) Cyclic voltammogram in acidic media (0.5 M H\(_2\)SO\(_4\)) and b) Cyclic voltammogram for the formic acid electrooxidation (0.5 M formic acid in 0.5 M H\(_2\)SO\(_4\) as electrolyte) using Pd nanocubes as electrocatalyst.

4.3. SU-8 Microfluidic Fuel Cell Performance.
The polarization curves recorded for these SU-8 microfluidic fuel cells have the same characteristic shape of typical fuel cells, with kinetically, ohmic, and mass transport limited regions. Fig. 4 shows the polarization and power density curves for Pd nanocubes/C and Pd/C. At 0.5 M formic acid concentration is interesting to note that the open circuit potential (OCP) is similar for both microfluidic fuel cells. However, the current density values show an increase for the fuel cell using Pd nanocubes/ C than Pd/C, as a consequence of mass transport limitations (15.4 and 19.57 mW cm\(^{-2}\) respectively). Besides, the same figure shows power density values divided by Pd loading, following the same performance when is used both catalyst.
5. Conclusions
A small, light and flexible direct formic acid µFFC was developed by using photosensitive SU-8 platform as current collectors and thin films of silicone where the “T” shape microchannel is delineated. Two configurations of the µFFC were compared, the first one employed commercial Pd/C as anode electrocatalyst, the second one used well-defined and homogeneous Pd nanocubes with (100) preferential crystallographic plane supported on Vulcan; both µFFC presented excellent performance (around 8.3 mW cm\(^{-2}\)); compared against similar works, this is the highest value reported so far, however the µFFC Pd-cubes based showed a slightly improvement in current density. In this way, there is an indicative of the importance of the mass activity of Pd-cubes and is expected depurate it to improve the µFFC performance.

6. Acknowledgements
The authors gratefully acknowledge the financial support from the Mexican Council of Science and Technology through FOMIX-QUERETARO (grant 193148) and ANR-CONACYT (grant 163114).

7. References
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