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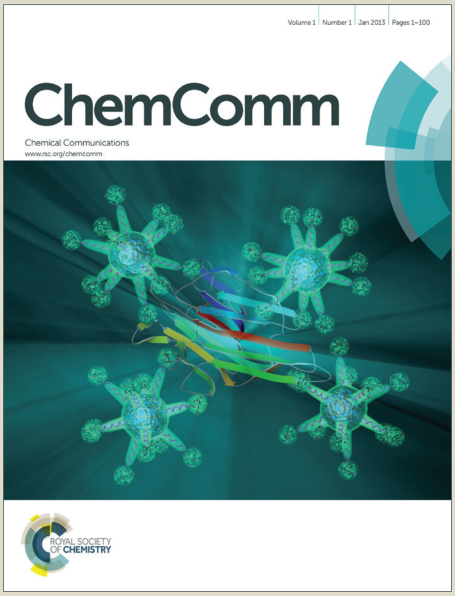

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AuPd/Polyaniline as anode in an ethylene glycol microfluidic fuel cell operated at room temperature

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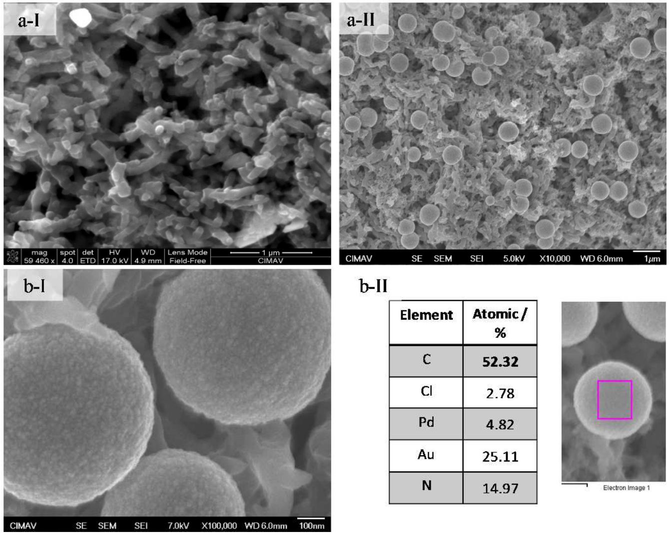
AuPd/Polyaniline was used for first time, for ethylene glycol (EG) electrooxidation in a novel microfluidic fuel cell (MFC) operated at room temperature. The device exhibits high electrocatalytic performance and stability for the conversion of cheap and fully available EG as fuel.

Microfluidic fuel cells (MFCs) are electrochemical devices for conversion of chemical to electrical energy where at least one dimension is on the micrometric order (1-1000 μm).[1]The microfluidic area for energy conversion is relatively new; since 2008, the number of groups focused on MFCs has been increasing. Kjeang, et al.[2] published a nice review on this topic, which shows that the most typical fuels for MFCs are vanadium, formic acid, methanol, ethanol, hydrogen and glucose. In energetic terms, ethanol, glucose and methanol exhibit the theoretical energy densities 8000, 4430 and 6100 Wh/kg, respectively.[3] Methanol is widely employed for energy conversion because it is a small molecule that can be easily oxidized to carbon dioxide. Despite such use, methanol is highly toxic and exhibits a large problem with fuel crossover from the anode to cathode, which inhibits cell performance.[4]

Ethylene glycol is an interesting fuel because it is widely used in the automobile industry, it is highly available to the renewable energy field, and its theoretical energy density is 17% higher than methanol.[4] Pt-based materials have been used for the EGEOR (Ethylene glycol electrooxidation reaction). At room temperature this reaction yields incomplete EG oxidation, which forms glycolaldehyde, glyoxal, glycolic acid and other by-products[5] that could decrease fuel cell performance. Thus, all articles related to proton-exchange membrane ethylene glycol fuel cells (PEM-EGFCs) in acidic or basic media are focused on cell performance in the range 60 to 130°C.[6,7]

Metal mixtures, such as Pt-M alloys, have been developed to increase the performance and reduce the undesirable by-products at ambient temperature.[8] Thus, we synthesized a novel AuPd as a metal mixture through chemical deposition on polyaniline films, which was synthesized through electro-deposition in a Vulcan carbon compact layer electrode to increase the surface area (the concentration ratio for AuPd was 1:20 due to the polyaniline affinity for the Au^{3+} reduction).[9]The AuPd metal mixture was obtained submerged the polyaniline/Vulcan electrode in the AuPd solution (Pd 10 mM, Na_2PdCl_4, Sigma-Aldrich and Au 0.5 mM, $HAuCl_4$, Sigma-Aldrich) for 24 h to ensure complete reduction. Polyaniline was used as support and as reducing agent (Fig. 1a-I).



Element	Atomic / %
C	**52.32**
Cl	2.78
Pd	4.82
Au	25.11
N	14.97

Figure 1 SEM micrographs for a-I) electrodeposited polyaniline, a-II)AuPd/Polyaniline at high and b-I) low magnification. b-II) EDX analysis.

The polyaniline film was uniform and presents fibber morphology (Fig. 1 a-I). Semispherical particles with homogeneous size of AuPd were obtained by the chemical reduction procedure (Fig. 1 a-II). These particles were in the order of micrometres, nevertheless are composed of small nanoparticles (Fig. 1 b-I). EDX analysis was performed for a single microstructure (Fig. 1b-II), which yielded an atomic percentage 4.5-fold higher for Au compared with Pd; this was expected due to the polyaniline's high affinity for Au reduction. The X-ray pattern for AuPd/Polyaniline generated on a graphite substrate is shown in Fig. 2. (111) and (311) crystallographic planes that belong to a typical face-centred cubic fcc structure were observed and located at 39.75 and 80.83°, respectively[10]. Typically, the (111) plane for Au is located at 38.1°(JCPDS File #4-0784) and 40.2° for Pd materials (JCPDS File #87-0638); however, the AuPd (111) plane was located at 39.75°; this peak, which is between Au and Pd, is similar than the peak for bulk AuPd alloy.[11]Meanwhile (311) broader plane corresponds to fcc of Pd (JCPDS File # 5-681). The graphite peaks were labelled in grey colour and correspond to the following peaks: (100), (101), (102), (004), (103), (110) and (112).

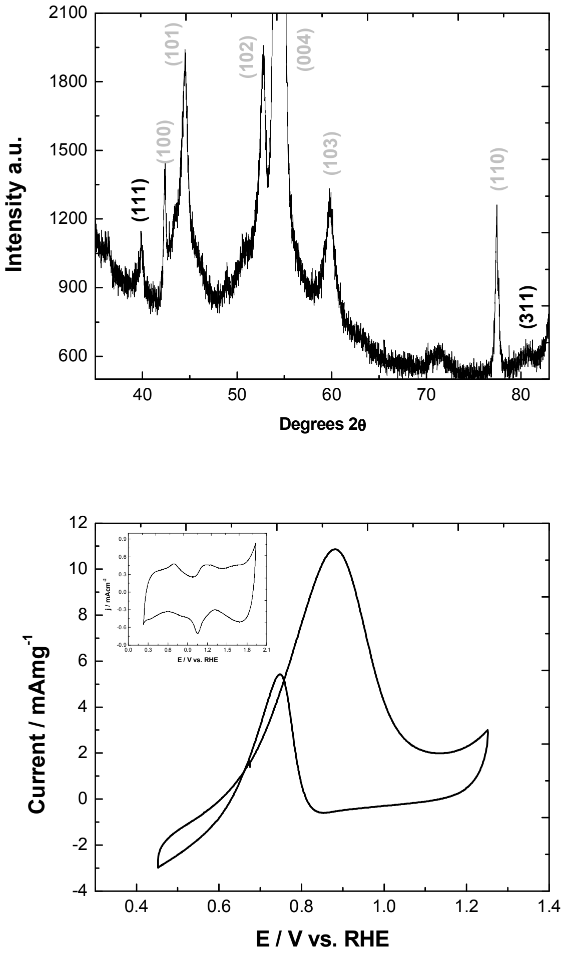


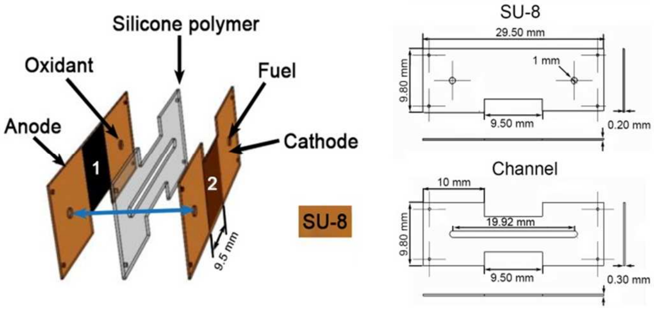
Figure 2X-ray diffraction pattern for AuPd/Polyaniline. Cyclic voltammogram of AuPd/Polyaniline for 0.1 M EG electrooxidation reaction in 0.3 M KOH as electrolyte. Inset: the electrochemical response of AuPd/Polyaniline in 0.3 M KOH

The electrochemical response of AuPd/polyaniline in basic medium (0.3 M KOH, 87%, J. T. Baker) and an evaluation of electrocatalytic activity toward electrooxidation 0.1 M EG, normalized by the Au loading, is shown in Figure 2. The electrochemical response of AuPd/polyaniline in 0.3 M KOH (Figure 2 inset) shows the typical behaviour of Pd-based materials. The peak potential attributed to EG electrooxidation was 0.88 V vs. RHE. A low poisoning effect from CO formation was observed because the reverse scan charge is lower than the forward scan charge.[12] This behaviour is attributed to the presence of Pd and the interaction of the bimetallic mixture-support.[15-18]On the other hand, Au has a significant effect on EG electrooxidation because EG hydroxyl groups can be activated to form oxalates with a high Faradic efficiency.[13] Furthermore, formation of formate as a principal by-product is possible due to the C-C bond cleavage.[14]

The value of potential obtained for EGEOR on Au and on Pd nanoparticles is1.2 V and 0.92 V vs. RHE (See supplementary Information) respectively; meanwhile with the use of AuPd/polyaniline as anode, the value of potential for EGEOR is 0.88 V vs. RHE, which presents a negative shift compared with bare Au and Pd. We consider that the electronic and chemical properties of polyaniline[18,19] as well as the specific interaction between Au and Pd are important for enhancing the electrocatalytic activity toward EG electrooxidation due to a synergic effect with the AuPd/polyaniline composite.[20]

A schematic representation of the MFCs is shown in Scheme 1. The MFC is composed of four principal sections. The first section is a polymer channel (10×1-mm length and width, 500 micrometers thick), where the fuel and oxidant are driven. It was fabricated from a silicon polymer using a Silhouette® cutting plotter. The second and the principal parts are the current collectors, which were constructed using SU-8 material and the UV-lithography technique (the fabrication procedure was described previously).[21] The Vulcan carbon compact layer on SU-8 as anode and cathode were made through the spray method using an ink prepared with 10 mg Vulcan, 75 µL and 15 µL aqueous Nafion® per Vulcan milligram. The fourth section corresponds to poly-methyl methacrylate (PMMA) plates, which were used to seal the other components. Because the second and fourth parts are flat surfaces, the fluids could pass between the SU-8 collectors and PMMA plates. Thus, a silicone elastomer (Silastic®, Dow Corning) was used as the third section to obtain a good seal for the MFC. The final area, where the electrodes contacted the oxidant and fuel solutions, was 0.07 cm^2.

Scheme 1: Microfluidic fuel cell design.



Ethylene glycol (J.T. Baker, 99.9%) at the three concentrations: 0.5, 1 and 2 M was prepared in 0.3 M KOH as electrolyte and de-aerated using nitrogen as an inert gas (99.999%, Infra). Oxygen as an oxidant was also prepared in 0.3 M KOH and bubbled for 30 min (4.3 U. A. P. Praxair).The anodic and cathodic flows were varied at a low EG concentration (0.5 M) to determine the optimal stoichiometry for the co-laminar flow[22] (see supplementary information)As a result, the fuel and oxidant solutions entered the systems at low flow rates, 11 and 3 mL per h, respectively, using syringe-infusion pumps (Cole-Parmer 78-0100C) to maintain a laminar regime. The flow rate was higher for the fuel than the oxidant due to the influence of the EG viscosity and density on the pumping force.[23] Despite such conditions, at a low EG concentration (0.5 M), the open circuit potential (OCP) is low (almost 0. 4 V), as shown in Figure 3A. The anode potential depends on the interfacial concentration of EG and OH$^-$ ions on the active surface; this value (0.4 V) could be related to a non-fully activate surface, which dominates for hydroxide ion adsorption. Further, in Figure 3A, when the EG concentration is increased, the OCP is enhanced until it reaches the maximum value 0.53 V for the 2 M EG concentration. This value is similar for 1 M EG and is comparable than those OCPs founded in the literature for high-temperature proton-exchange membrane ethylene glycol fuel cells.[6,7,24,25]

For current densities, the difference between 0.5 and 1 M is almost two-fold. For solutions between 1 and 2 M, the variance is smaller. Thus, the use of higher EG concentrations did not result in further improved performance, which could be related with several factors as the oxygen availability or active surface-site saturation. However, a comparison at 0.25 V for three EG concentrations was done, resulting in 1.2, 5 and 6.3 mA cm^{-2}for 0.5, 1 and 2 M EG respectively. Consistent with the open circuit potential and current density values, the 2 M EG solution shows the highest performance for this type of devices with the value 1.6 mW cm^{-2}.

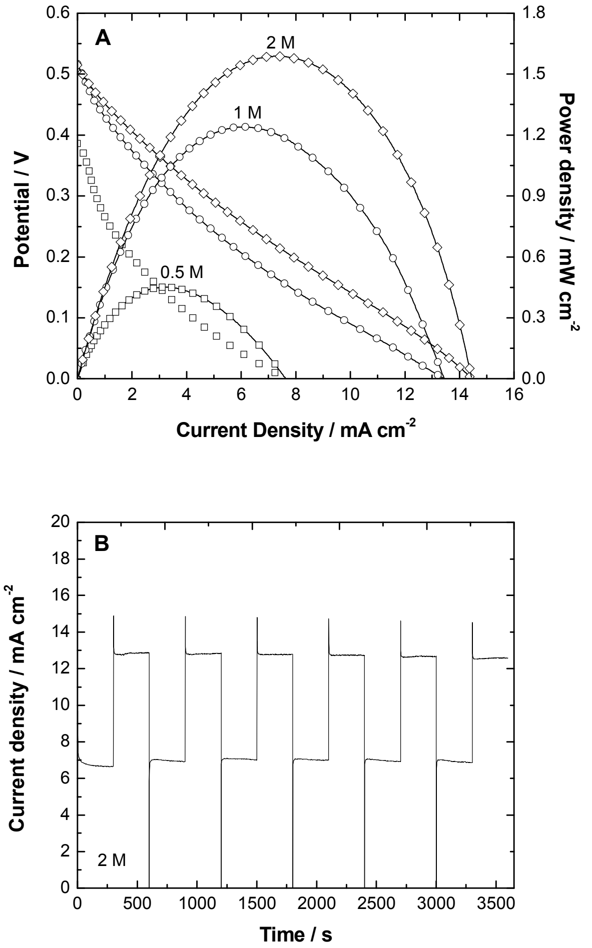


Figure 3. A) Polarisation and performance curves for the three ethylene glycol concentrations 0.5, 1 and 2 M. B) Stability curve at 0.21 V and 0.02 V for 2 M ethylene glycol.

Device performance cannot be compared with other micro-fluidic fuel cells because the literature does not report results for similar microfluidic devices operates at room temperature, that employ EG as the fuel. Finally, the MFC stability was tested for the 2 M EG solution through polarisation curves using the potential close to the maximum current density (0.02 V) and the potential at maximum power density (0.21 V) for 1 h with the pulse potential duration 300 s (Fig. 3B). The current density associated with each potential remained constant after several cycles, which indicates high catalyst and device stabilities.

In summary, AuPd supported on polyaniline with a homogeneous semi-spherical shape was synthesized through a chemical/electrochemical method and used for the first time in the ethylene glycol electrooxidation reaction. Its activity was evaluated in a novel microfluidic fuel cell, and it was successfully operated at room temperature. With this contribution, we demonstrate that, even at the micro-scale, cheap and fully available ethylene glycol can be used.

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Notes and references

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