

# Electroreforming of Glucose and Xylose in Alkaline Medium at Carbon Supported Alloyed Pd<sub>3</sub>Au<sub>7</sub> Nanocatalysts: Effect of Aldose Concentration and Electrolysis Cell Voltage

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## S1. Synthesis of Catalysts by the Water in Oil Microemulsion Method

Appropriate amounts of metal salts (tetrachloroplatinic acid H<sub>2</sub>PtCl<sub>6</sub>, tetrachloropalladate K<sub>2</sub>PdCl<sub>4</sub> and tetrachloroauric acid trihydrate H<sub>3</sub>AuCl<sub>4</sub>·3H<sub>2</sub>O, 99.99% purity, Alfa Aesar) are dissolved in ultra-high purity water (Milli-Q, 18.2 MΩ cm, Millipore) to reach a total metal concentration of 0.10 mol L<sup>-1</sup>. For the PdAu bimetallic catalyst, the Pd/Au molar ratio in aqueous solution of K<sub>2</sub>PdCl<sub>4</sub> and H<sub>3</sub>AuCl<sub>4</sub>·3H<sub>2</sub>O is fixed to 3/7. A 1.6 mL aliquot of aqueous solution containing metal salts is added to a homogeneous solution of 37.0 g n-heptane (99% purity, Acros Organics) and 16.1 g polyethylene glycol dodecyl ether (Brij®L4, Sigma Aldrich). The mixture is stirred until a translucent and stable microemulsion is obtained. Then, 100 mg of sodium borohydride are added as reducing agent. After reduction of metal salts, a given amount of carbon powder (Vulcan XC72, Cabot Corp.) is added to the colloidal solution in order to reach a metal loading of 40 wt%. The mixture is then filtered and washed several times with acetone and ultrapure water. The catalytic powder is dried overnight in an oven at 343 K before undergoing a thermal treatment for 2 h at 573 K under air to eliminate remaining surfactant.

## S2. Formulation of the Catalytic Ink and Preparation of the Working Electrode for Cyclic Voltammetry Experiments

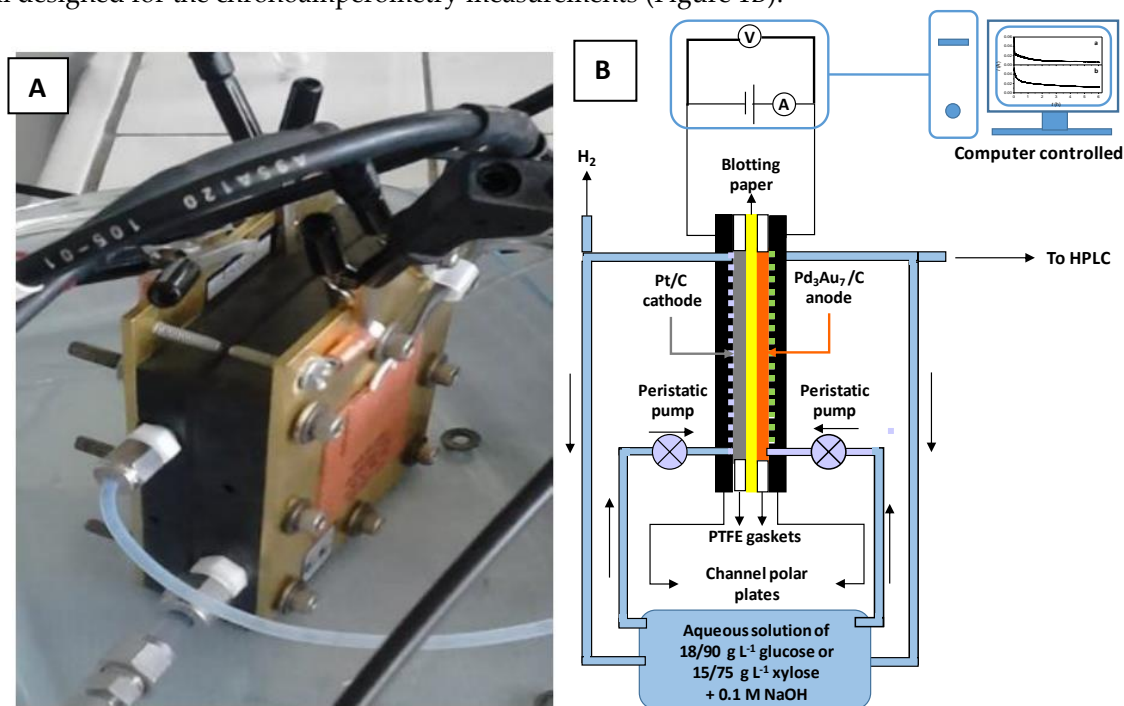
The working electrodes are prepared by dispensing onto the glassy carbon disk 3 μL of a catalytic ink prepared as follows: first, 17.7 mg of Pd/C, Au/C or Pd<sub>3</sub>Au<sub>7</sub>/C catalytic powder are added to 2.646 mL of ultra-high purity water and the suspension is homogenized using an ultrasonic bath for about 15 min, then, 354 μL of commercial solution of Nafion dissolved in aliphatic alcohols (5 wt%, Sigma Aldrich) are added to the above-described suspension and the mixture is homogenized in an ultrasonic bath for about 30 s. The metal loading on the electrode is 100 μg cm<sup>-2</sup>.

## S3. Chronoamperometry Measurements

Chronoamperometry measurements are carried out at 293 K in a 25 cm<sup>2</sup> single filter press type electrolysis cell (from Electrochem Inc.).

Carbon gas diffusion electrodes are homemade by using a carbon cloth from Electrochem, onto which an ink made of Vulcan XC 72 carbon powder and PTFE dissolved in isopropanol is brushed. The gas diffusion electrodes are loaded with a mixture of carbon powder and 20 wt% PTFE (4 mg cm<sup>-2</sup>). Electrodes for the electrolysis cell are prepared from inks that consists in a mixture of Nafion (5 wt% from Aldrich) solution, water, and catalytic powder dried on the carbon gas diffusion electrodes. The metal loading of the electrodes is 0.5 mg cm<sup>-2</sup> and the Nafion loading of the electrode is ca. 0.8 mg cm<sup>-2</sup>.

Both electrodes are separated by a blotting paper and mechanically pressed in the cell. The anodic and cathodic compartments of the cell are fed in recirculation at 25 mL min<sup>-1</sup> with 30 mL solution of 0.10 mol L<sup>-1</sup> or 0.50 mol L<sup>-1</sup> aldose in 0.10 mol L<sup>-1</sup> NaOH using a Masterflex L/S peristaltic pump fitted with Norpren tubes (Masterflex precision tubing L/S 14), and rotated at 50 rpm. The  $I_{\text{cell}}(t)$  curves are recorded with an interfaced Voltalab PGZ402 potentiostat (Radiometer analytical). Figure S1 displays a picture of the electrochemical cell (Figure 1A) and a schematic representation of the filter press type electrolysis cell designed for the chronoamperometry measurements (Figure 1B).

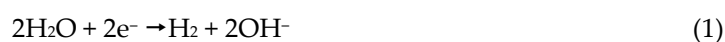


**Figure S3.** Picture of the electrochemical cell for chronoamperometry measurements and schematic representation of the electrolysis system designed for the chronoamperometry measurements.

Aliquot of 0.6 mL is taken every hour and analyzed by HPLC (Varian Prostar HPLC equipped with a Transgenomic ICsep ICE-COREGEL 107H column for the separation of organic acids, aldehydes, alcohols and ketone molecules). All standards corresponding to the compounds expected are prepared from sodium gluconate, lithium xylonate, tartronic acid, 2-ketogluconic acid, 5-ketogluconic acid, glucuronic acid, oxalic acid, formic acid, tartaric acid, glycolic acid and glyoxylic acid from Sigma-Aldrich (purity  $\geq 97\%$  except for lithium xylonate,  $\geq 95\%$ ). The chromatography is performed with 0.007 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> aqueous solution as eluent at 0.6 mL min<sup>-1</sup> flow rate with UV detector set at = 210 nm.

#### S4. Calculation of the Energetic Consumption to Produce Xylonate and Hydrogen

The counter reaction in the electrolysis cell is the hydrogen evolution reaction occurring according to the following electrochemical reaction:



This equation shows that the production of one molecule of hydrogen consumes two electrons. Therefore, the number of moles of hydrogen ( $n_{\text{H}_2}$ ) produced can be calculated using the following equation:

$$n_{\text{H}_2} = Q/nF \quad (2)$$

where  $Q$  is the charge involved in the electrolysis process ( $Q = 1,603,843.3\text{ C}$ ),  $n$  is the number of Faraday per molecule of H<sub>2</sub> produced ( $n = 2$ ) and  $F$  is the Faraday constant ( $F = 96,485\text{ C}$ ) [1].

The standard equilibrium voltage of a H<sub>2</sub>/O<sub>2</sub> cell being 1.23 V, the electrical energy needed to produce 1 kg of H<sub>2</sub> from water electrolysis (H<sub>2</sub>O → H<sub>2</sub> + ½O<sub>2</sub>) is 33 kWh [2]. The electric energy (W<sub>e</sub>) consumed to produce hydrogen can be expressed as follows [3]:

$$W_e = \frac{nF}{3600V_m \times 10^3} U_{\text{cell}}(I) \quad (3)$$

where V<sub>m</sub> is the molar volume of an ideal gas at a temperature of 25 °C under a pressure of 101.325 kPa (V<sub>m</sub> = 24.465 × 10<sup>-3</sup> m<sup>3</sup> mol<sup>-1</sup>) and U<sub>cell</sub>(I) is the electrolysis cell voltage at a current I.

Equation (3) indicates that the electric energy consumed to produce 1 kg of H<sub>2</sub> is only dependent on the cell voltage. Therefore, the electro-reforming of saccharides at +0.4 V, +0.6 V and +0.8 V provides high purity hydrogen for 10.73, 16.10 and 21.46 kWh kg<sub>H<sub>2</sub></sub><sup>-1</sup>, i.e. for 32.5%, 48.8% and 65% of the theoretical energy required from water electrolysis.

The formation of 0.0820 mol L<sup>-1</sup> xylonate from the electro-reforming of 0.10 mol L<sup>-1</sup> xylose at +0.8 V of 30 mL xylose solution, as an example, corresponds to 0.00246 moles of sodium xylonate produced. The production of 0.00246 moles of xylonate has involved the consumption of 651 C (Table 3). The formation of 1 kg of xylonate (ca. 6 moles) will then need (651/(0.00246 × 0.165)) = 1,603,843.3 C, which correspond to the concomitant production of ca. 16.6 g of hydrogen, i.e. 16.6 kg H<sub>2</sub> produced per ton of xylonate (8,300 mol, 186.5 m<sup>2</sup>). Therefore, the electric energy consumed to produce 1 ton of xylonate at +0.8 V from 0.10 mol L<sup>-1</sup> xylose solution is 16.6 × 21.46 = 356.78 kWh. The same calculation can be done for all configurations in Table 2 and Table 3 of the main manuscript.

Now, considering the mean electricity cost in Europe (ca. 0.15 € / kWh) [68], the energy cost to produce 1 ton of xylonate and 16.6 kg of H<sub>2</sub> under these conditions will be ca. 53.5 €. This cost represents only between 8 and 10% of the global cost of gluconic acid or sodium gluconate industrially produced using biotechnological processes, which ranges between ca. 600 to ca. 750 US \$ (520 to 650 €) per ton (Dezhou Huiyang Biotechnology Co., Ltd, Wuxi Fengmin Environmental Technology Development Co., Ltd, etc.).

## References

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