

Insulating Diamond Particles as Substrate for Pd Electrocatalysts

Amy Moore,^a Verónica Celorrio,^b María Montes de Oca,^a Daniela Plana,^a Wiphada Hongthani,^a María J. Lázaro^b and David J. Fermin^{*a}

^a School of Chemistry, University of Bristol, Cantocks Close, Bristol BS8 1TS, UK. Fax: +44 1179250612; Tel: +44 117928981; E-mail: david.fermin@bristol.ac.uk

^b Instituto de Carboquímica (CSIC), Miguel Luesma Castán 4, 50018 – Zaragoza, Spain.

ELECTRONIC SUPPLEMENTARY INFORMATION

Preparation of the Pd/DP composite

As-received HPHT particles were exposed to a bath of concentrated HNO₃ and H₂SO₄ (9:1 v/v respectively) at 200°C for 30 minutes. This bath allows the removal of traces of impurities, including sp² carbon, present in the as-received material.¹ All of the reagents used in the preparation of the composites and electrochemical studies were of the highest purity and used without further purification.

The Pd electrocatalysts were prepared by an impregnation method, using sodium borohydride. Each carbon support (80 mg) was impregnated with a solution of sodium hexachloro palladate (IV) hydrate (84 mg, Sigma Aldrich), in ultrapure water (35 mL, Millipore Milli-Q system). The pH was adjusted to 5 with sodium hydroxide (Sigma Aldrich) and the metal was reduced with a solution of sodium borohydride (20 mg, Sigma Aldrich), in ultrapure water (20 mL), at 5°C, under sonication. The resulting solution was filtered and dried in an oven at 60°C.

Thermogravimetric studies of the supports and composites

Thermogravimetric analysis of the Pd/DP and Pd/vulcan composites is presented in **figure S1**, along with that of the supports without Pd present. The Pd/DP composite revealed complete stability up to 600°C, in agreement with previous work on Pt-coated BDD.² Although Pd has been shown to aggregate on diamond, at temperatures above 400°C,³ due to increased surface mobility, the stability of the diamond remains virtually unchanged by the presence of metal centres. The thermal stability of Vulcan, however, greatly decreased in the presence of the Pd nanostructures. The temperature at which degradation begins drops from close to 700°C down to less than 400°C; this type of behaviour has been previously observed for Pt/Vulcan.¹

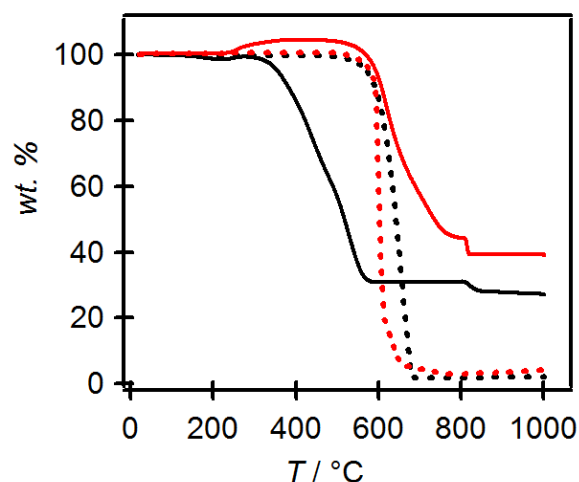


Figure S1. Thermogravimetric analysis of the DP (red) and Vulcan (black), with (solid lines) and without (dashed lines) Pd.

Voltammetric responses of the Pd/DP composite in acid solutions

A cyclic voltammogram of the Pd/DP electrode, in 0.5 mol dm⁻³ H₂SO₄, is shown in **figure S2**. The electrode surface was initially pre-treated by a series of consecutive scans, at 0.5 V s⁻¹, between -0.35 and 1 V. The characteristic signals associated with Pd oxide formation, at 0.6 V in the positive scan, and oxide reduction, at 0.5 V in the negative scan, can be clearly seen in the voltammogram. Towards negative potentials, the peaks associated with hydrogen and sulfate/bisulfate adsorption appear very well-defined. The voltammetric features do not appear distorted by uncompensated resistance between the working and reference electrode. These results provide a first set of evidence of good electronic communication between the electroactive Pd centres and the electrode surface.

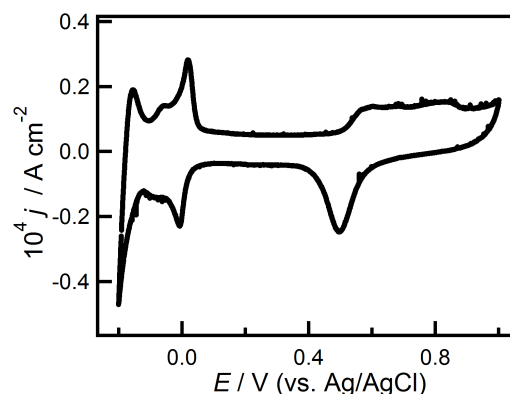


Figure S2. Cyclic voltammogram of the Pd/DP electrocatalyst drop-cast at a glassy carbon electrode in 0.5 mol dm⁻³ H₂SO₄, at 0.02 V s⁻¹.

References

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