

# Supporting Information

## Isolated Pd Sites as Selective Catalysts for Electrochemical and Direct Hydrogen Peroxide Synthesis

Marc Ledendecker<sup>a,b</sup>, Enrico Pizzutilo<sup>a</sup>, Grazia Malta<sup>c</sup>, Guilherme V. Fortunato<sup>a,d</sup>, Karl J. J. Mayrhofer<sup>a,e,f</sup>, Graham J. Hutchings<sup>c</sup> and Simon J. Freakley<sup>g\*</sup>

<sup>a</sup> Department of Interface Chemistry and Surface Engineering, Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Strasse 1, 40237 Düsseldorf, Germany.

<sup>b</sup> Department of Technical Chemistry, Technical University Darmstadt, Alarich-Weiss Straße 8, 64287 Darmstadt, Germany

<sup>c</sup> Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT, UK.

<sup>d</sup> Institute of Chemistry, Universidade Federal de Mato Grosso do Sul; Av. Senador Filinto Muller, 1555; Campo Grande, MS 79074-460, Brazil.

<sup>e</sup> Helmholtz-Institute Erlangen-Nürnberg for Renewable Energy (IEK-11), Forschungszentrum Jülich, Egerlandstr. 3, 91058 Erlangen, Germany.

<sup>f</sup> Department of Chemical and Biological Engineering, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany.

<sup>g</sup> Department of Chemistry, University of Bath, Claverton Down, Bath, BA2 7AY, UK.

[\\*s.freakley@bath.ac.uk](mailto:s.freakley@bath.ac.uk)

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**Table S1 – Surface Composition of 1% PdCl<sub>2</sub>/C determined by XPS survey scan**

Element (Orbital)	Atomic %	Weight %
O (1s)	6.6	8.1
C (1s)	90.2	82.8
Cl (2p)	2.5	6.7
Na (1s)	0.1	0.2
Si (2p)	0.4	0.9
Pd (3d)	0.2	1.3

**Table S2 – Comparison with state-of-the-art catalysts under identical conditions for direct H<sub>2</sub>O<sub>2</sub> synthesis.**

Catalyst	Preparation Method	Nanostructure	H <sub>2</sub> O <sub>2</sub> Productivity <sup>d</sup> (mol / kg / h)	H <sub>2</sub> O <sub>2</sub> Degradation <sup>e</sup> (mol / kg / h)
5% Pd/C <sup>a</sup>	Wet impregnation	PdO nanoparticles (2-20 nm)	52	255*
2.5% Au 2.5% Pd / C <sup>a</sup>	Wet impregnation	Homogeneous AuPd alloys (2-10 nm)	160	0
3% Pd 2% Sn / TiO <sub>2</sub> <sup>b</sup>	Wet impregnation	Sn-Pd nanoparticles (isolated species to 10 nm particles)	60	0
1% Pd/C <sup>c</sup>	Aqua regia	Isolated Pd(II) sites	30	52
Bare Carbon	Aqua regia	-	0	45
1% Pd/C <sup>c</sup>	Sol Immobilisation	Metallic Pd nanoparticles (2-6 nm)	120	360

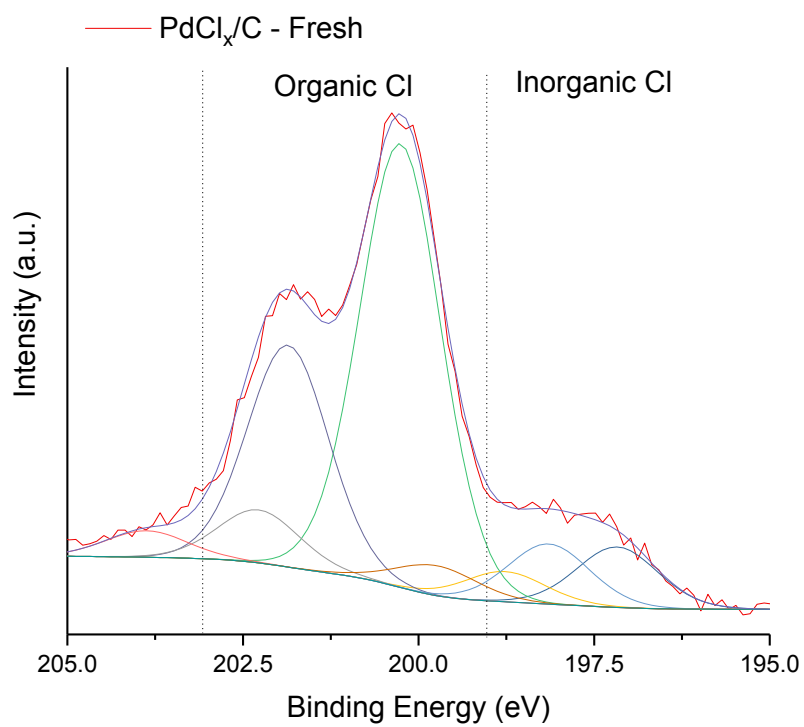
<sup>a</sup> J. K. Edwards *et al. Science*, **2009**, 323, 1037-1041 <sup>b</sup> S. J. Freakley *et al. Science*, **2016**, 351, 965-968.

<sup>c</sup> this work \*estimated from figure 1

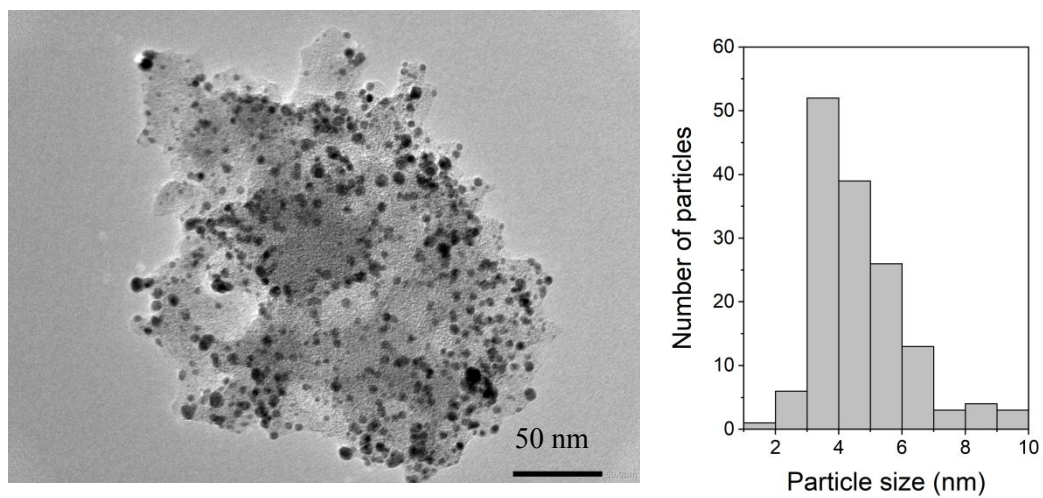
<sup>d</sup> 2 °C, 10 mg catalyst, 29 bar 5% H<sub>2</sub>/CO<sub>2</sub>, 11 bar 25% O<sub>2</sub>/CO<sub>2</sub>, 8.5 g solvent (5.6 g CH<sub>3</sub>OH + 2.9 g H<sub>2</sub>O) 1200 rpm, 30 mins.

<sup>e</sup> 2 °C, 10 mg catalyst, 29 bar 5% H<sub>2</sub>/CO<sub>2</sub>, 8.5 g solvent (5.6 g CH<sub>3</sub>OH + 2.22 g H<sub>2</sub>O + 0.68 g 50% H<sub>2</sub>O<sub>2</sub> (10 mmol)) 1200 rpm, 30 mins.

**Figure S1** - Cl (1s) X-ray photoemission spectroscopy of the 1% Pd / C carbon catalyst prepared by wet impregnation from aqua regia and dried under N<sub>2</sub> at 140 °C showing organic (~200 eV) and inorganic Cl (~198 eV) species.

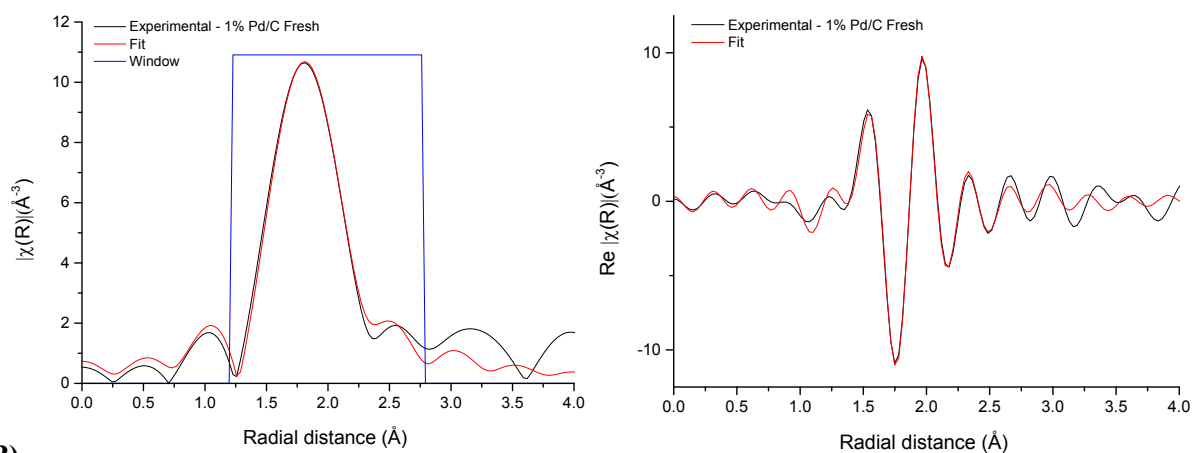


**Figure S2** – Representative TEM image and particle size distribution of a 1% Pd/C prepared by sol immobilization as a comparative catalyst containing metallic nanoparticles.



**Figure S3 – XAFS fitting parameters of fresh (a) and used (direct synthesis) (b) PdCl<sub>x</sub>/C to determine Pd-Cl first shell co-ordination using Demeter software package.**

**(A)**



**(B)**

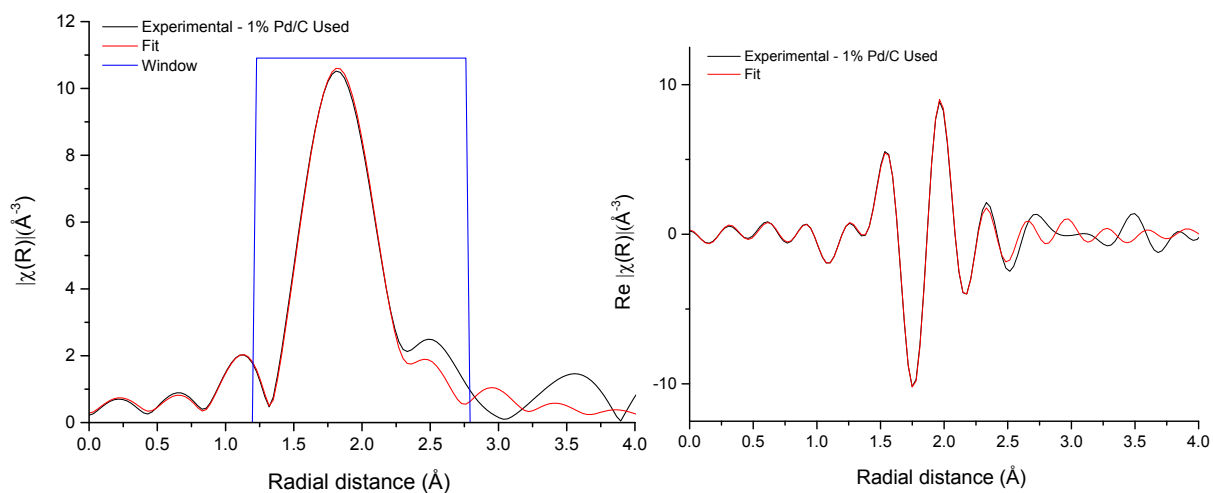


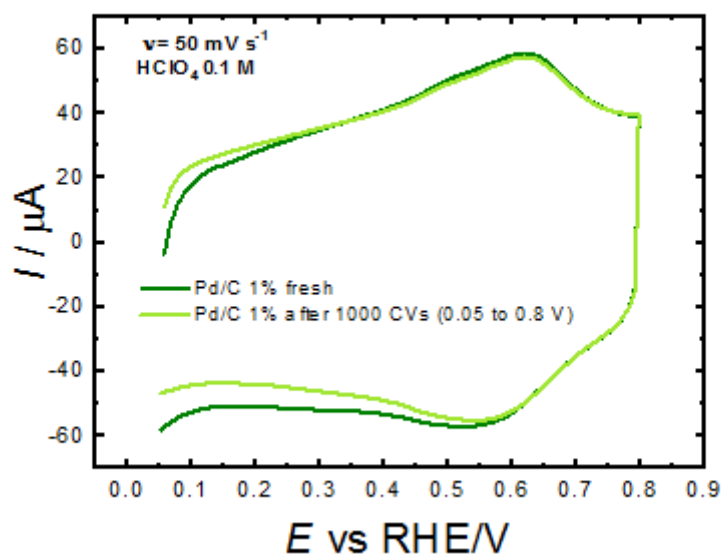
Table S3 - EXAFS distances and fitting parameters for the Pd/C catalyst, fresh and used.

Sample	Absorber-Scatterer	R (X) Å	CN	2σ <sup>2</sup> (X)	ΔE <sub>0</sub> (eV)	R <sub>factor</sub>
Pd/C - Fresh	Pd-Cl	2.308 ± 0.008	3.99 ± 0.4	0.0016 ± 0.0012	4.5 ± 1.05	0.005
Pd/C - Used	Pd-Cl	2.305 ± 0.01	3.85 ± 0.5	0.002 ± 0.0016	4.7 ± 1.41	0.01

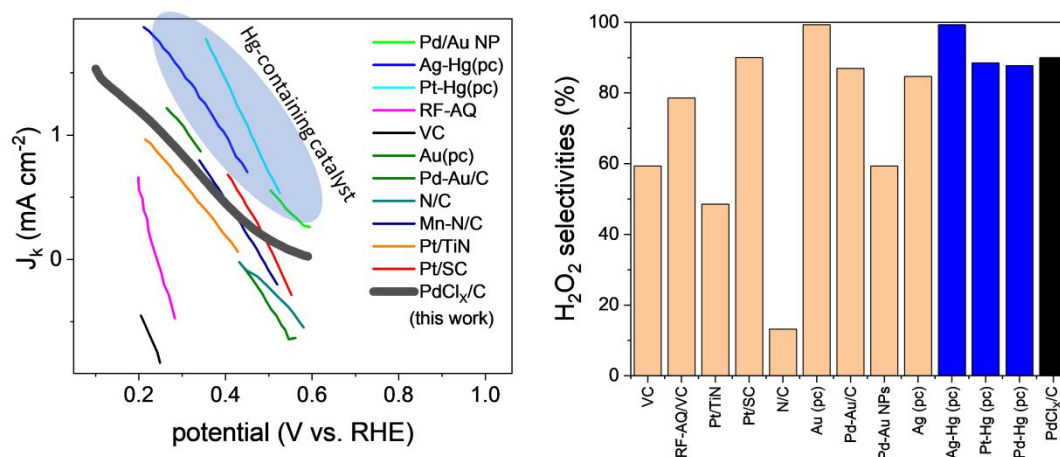
R (X) = radial distance, 2σ<sup>2</sup> (X) = Debye-Waller factor, CN = Coordination number

Fitting parameters: S<sub>0</sub><sup>2</sup> = 0.8 as deduced by Pd foil reference; fit range 3 < k < 9.5, 1.2 < R < 2.8.

**Figure S4** – Cyclic voltammetry of PdCl<sub>x</sub>/C in 0.1M HClO<sub>4</sub>, Ar<sub>sat.</sub> before and after 1000 potential cycles between 0.05 – 0.8V.



**Figure S5** – Comparison of various catalysts towards the electrochemical reduction of oxygen towards  $\text{H}_2\text{O}_2$ . Adapted from Reference <sup>1</sup>. The original references are Pt-Hg(pc)<sup>2</sup>, Pd-Hg(pc)<sup>3</sup>, Pt/SC<sup>4</sup>, Pt/TiN<sup>5</sup>, RF-AQ/VC, VC, Vulcan XC72,<sup>6</sup> N/C<sup>7</sup>; Pd-Au/C<sup>8</sup>, Au<sup>9</sup>; Au-Pd/NP<sup>10</sup>; Ag-Hg (pc), Ag<sup>2</sup>.



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