

## **Electrochemistry of Pd-based nanoparticles prepared via thermal decomposition of palladium acetylacetonate**

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### **Experimental**

#### **Synthesis procedure**

Pd(acac)<sub>2</sub> (Sigma-Aldrich, 97%) was dissolved in tetrahydrofuran (THF). The THF volume was selected to ensure complete dissolution of the Pd(acac)<sub>2</sub>. Following THF dissolution, Vulcan XC-72 carbon support was added to the solution. The mixture was evaporated in an ultrasonic bath at room temperature. The obtained carbon support was placed in a programmable furnace. The required heating rate (2 K min<sup>-1</sup>) was set, and the crucible with the sample was heated. The synthesis was carried out in an air atmosphere. After reaching the final temperature 300 °C, the sample was cooled in the furnace with its door open for Pd/C materials obtaining and with its door closed for Pd-PdO/C materials obtaining. The metal loading in the materials was 14±1 wt.%.

#### **X-ray diffraction measurements**

X-ray diffraction (XRD) measurements were performed using an ARL X'TRA X-ray diffractometer (Thermo Fisher Scientific Inc., USA) with Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å). XRD patterns with  $2\theta$  ranging from 10° to 120° were collected in continuous-scanning mode with interval of 0.03 s at a speed of 3° min<sup>-1</sup>. The diffractometer resolution function was determined using NIST powder LaB<sub>6</sub> (NISTSRM660a). The Rietveld refinement of the XRD data has been done using FullProf software.

#### **Transmission electron microscopy**

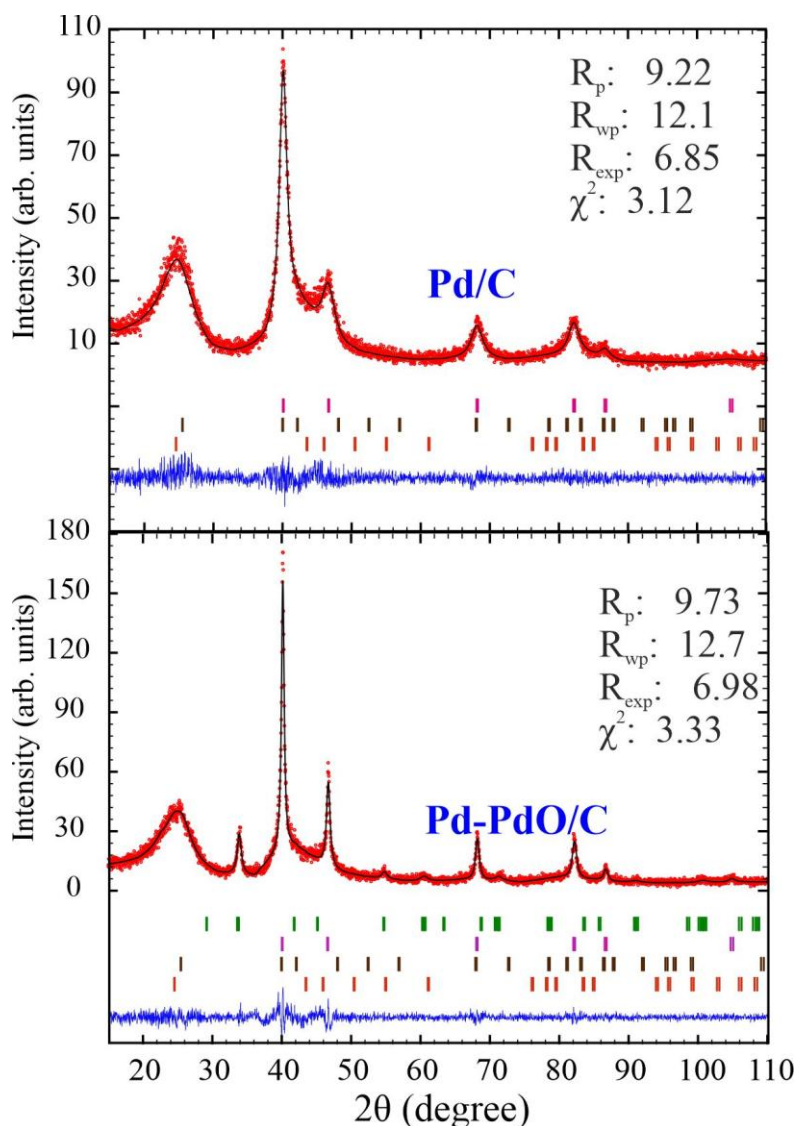
Transmission electron microscopy (TEM) was performed using a 200 kV JEOL 2100 microscope with a LaB<sub>6</sub> cathode. The particle size distribution was determined using a software package ImageJ.

## Electrochemical measurements

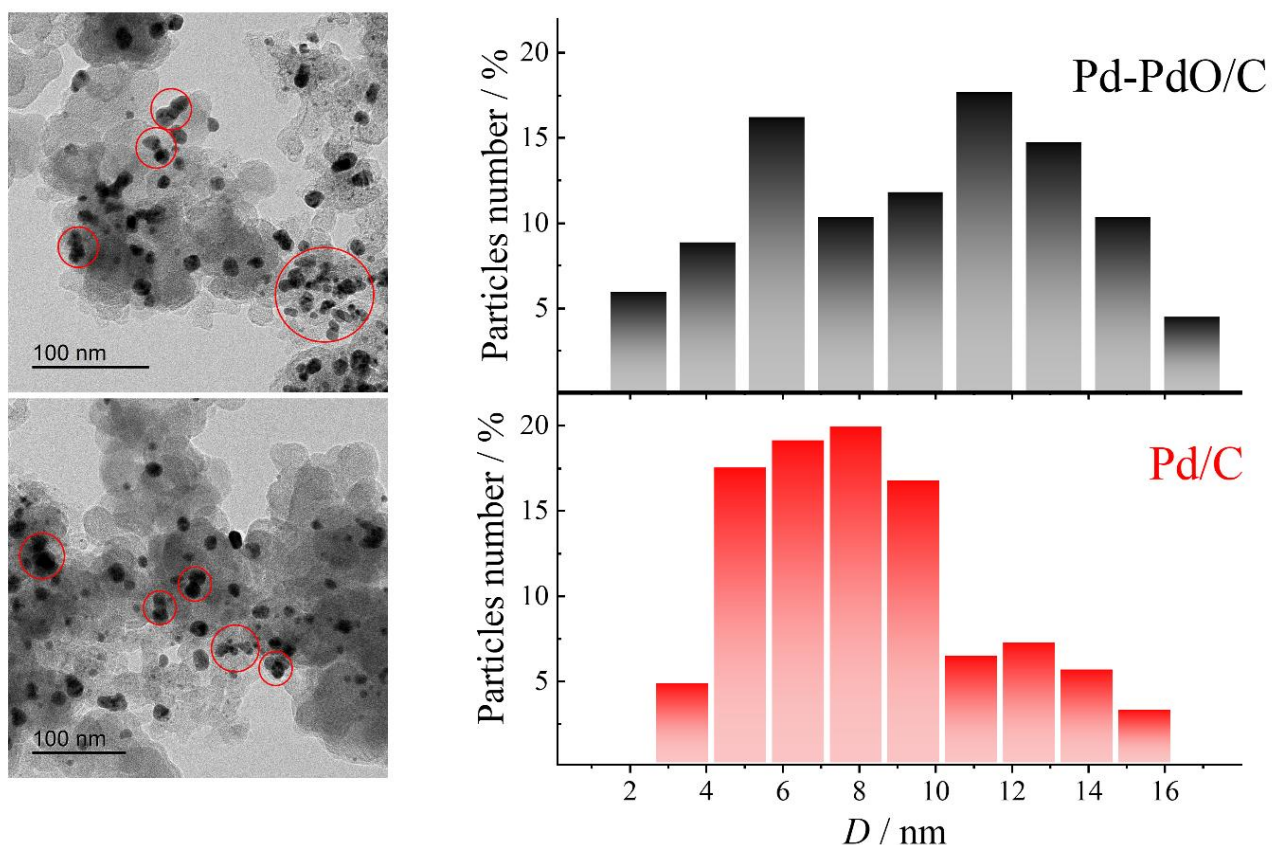
In order to perform electrochemical studies on a Pd-based samples, the preparation of "catalytic ink" was carried out as outlined below. 14 mg of Pd-based material was introduced into 0.5 ml of isopropyl alcohol, followed by the addition of a 10% aqueous suspension of the proton-conducting polymer Nafion, ensuring that the Nafion content represented 25% of the mass of carbon in the Pd-based sample. The resultant "catalytic ink" had been stirring on a magnetic stirrer for a minimum of 2 hours. For the preparation of the working electrode, 4  $\mu\text{L}$  of the "catalytic ink" was deposited onto the glassy carbon and allowed to air-dry.

All electrochemical investigations were carried out in the standard three-electrode system. A silver chloride electrode (Ag/AgCl) was utilized as the reference electrode, while a platinum wire functioned as the counter electrode. This paper presents all potentials in relation to the reversible hydrogen electrode (RHE). Prior to performing electrochemical studies, the working electrode underwent pretreatment in a 0.1M  $\text{HClO}_4$  background electrolyte. This involved cycling the potential between 50 and 1300 mV (RHE) at a scan rate of  $50 \text{ mV s}^{-1}$  for a total of 40 cycles.

The electrochemically active surface areas (ECSA) of Pd-based samples were assessed using the oxidative desorption of carbon monoxide (CO-stripping technique). The working electrode was polarised at 0.2 V (vs. RHE) in a supporting electrolyte 0.1 M  $\text{HClO}_4$  that had been bubbled with Ar for 20 minutes. Subsequently, the supporting electrolyte was purged with CO, while the working electrode was polarised at 0.2 V for 10 minutes. Then, the electrolyte was again purged with an Ar for 15 minutes. After that, two CVs curves were acquired from a potential of 0.0 V within the range of -0.05 to 1.30 V at a scan rate of  $0.02 \text{ V s}^{-1}$ . The peak of oxidative CO desorption was detected during the initial cycle. The ECSA value was based on the fact that 420  $\mu\text{C}$  are used for CO desorption from  $1 \text{ cm}^2$  of Pd when CO is oxidised. An CV investigation of the electrochemical oxidation of ethanol was conducted within a potential range of 0.05-1.05 V in 0.1 M  $\text{HClO}_4$  + 0.5 M  $\text{C}_2\text{H}_5\text{OH}$  at a scan rate of  $50 \text{ mV s}^{-1}$ . An CV investigation of the electrochemical reduction of  $\text{H}_2\text{O}_2$  was conducted within a potential range of -0.15-1.4 V in 0.1 M  $\text{KH}_2\text{PO}_4$ , utilising various concentrations of  $\text{H}_2\text{O}_2$  at a scan rate of  $50 \text{ mV s}^{-1}$ . A multi-step potential analysis of Pd-based materials was conducted in a 0.1 M  $\text{KH}_2\text{PO}_4$  supporting electrolyte, utilising a rotating working electrode at 1000 rpm in potentiostatic mode, with the addition of 2 mM  $\text{H}_2\text{O}_2$  to the supporting electrolyte approximately every 10 minutes at a stationary potential of the working electrode of 0.1 V.



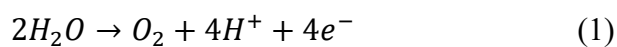
**Figure S1.** Experimental XRD powder patterns (red dots) and Rietveld refinement plots (black solid line) for the (a) Pd/C and (b) Pd-PdO/C materials. The blue line represents the difference between the experimental and calculated patterns. The vertical bars indicate the Bragg peak positions for the  $P4_2/mmc$  space group of PdO (green), the  $Fm3m$  space group of Pd (purple), and the  $P6_3/mmc$  (brown) and  $R3m$  (orange) phases of the Vulcan XC-72 carbon support. The R-factors and  $\chi^2$  (chi-squared) values, which characterize the quality of the refinement, are also presented on the figure.



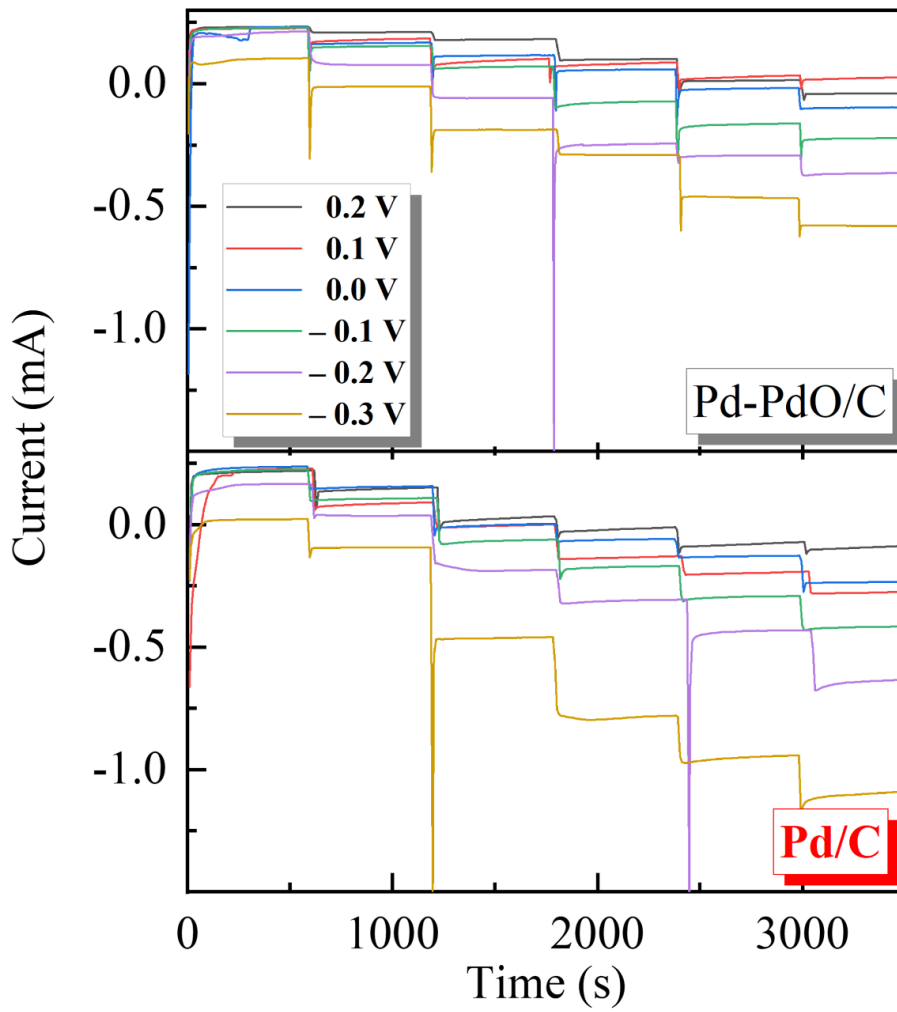
**Figure S2.** TEM images and particles size distributions of Pd-PdO/C and Pd/C materials.

### Multi-step potential analysis of H<sub>2</sub>O<sub>2</sub> reduction

The multi-step potential analysis (Figure S3) allowed us to determine that as the stationary potential values increase into the negative region beyond E=0.0 V, a more significant current response is noted in comparison to the potential range of 0.0–0.2 V. This observation may be attributed to hydrogen evolution reaction as a result of the discharge of solvent molecules [S1]:



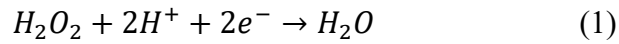
A stationary potential of E = 0.1 V (vs. RHE) was selected for further studies to mitigate the influence of these processes.



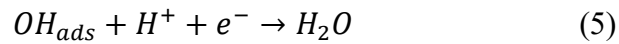
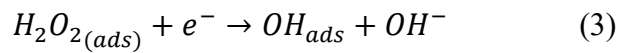
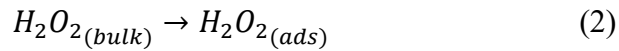
**Figure S3.** Multi-step potential analysis of Pd-PdO/C and Pd/C materials with the addition of 2 mM H<sub>2</sub>O<sub>2</sub> in 0.1 M KH<sub>2</sub>PO<sub>4</sub> supporting electrolyte.

### Electrochemical reduction of H<sub>2</sub>O<sub>2</sub> on Pd-based electrocatalysts

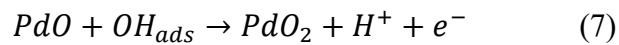
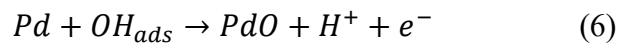
The reduction of H<sub>2</sub>O<sub>2</sub> in an acidic medium (pH (0.1 M KH<sub>2</sub>PO<sub>4</sub>) = 4.1):



can be considered a process that involves the formation of adsorbed  $OH_{ads}$  species:



Furthermore,  $OH_{ads}$  may be involved in the oxidation processes of both metallic palladium and PdO:



## References

- S1. A. J. Shih, M. C. O. Monteiro, F. Dattila, D. Pavesi, M. Philips, A. H. M. da Silva, R. E. Vos, K. Ojha, S. Park, O. van der Heijden, G. Marcandalli, A. Goyal, M. Villalba, X. Chen, G. T. K. K. Gunasooriya, I. McCrum, R. Mom, N. López and M. T. M. Koper, *Nat. Rev. Methods Primers*, 2022, **2**, 84; <https://doi.org/10.1038/s43586-022-00164-0>.