

# Nanoporous palladium with sub-10 nm dendrites by electrodeposition for ethanol and ethylene glycol oxidation†

Serhiy Cherevko,\*<sup>a</sup> Nadiia Kulyk,<sup>a</sup> and Chan-Hwa Chung\*<sup>a</sup>

*Advanced Materials and Process Research Center for IT, School of Chemical Engineering, Sungkyunkwan University, Suwon 440-746, Republic of Korea.*

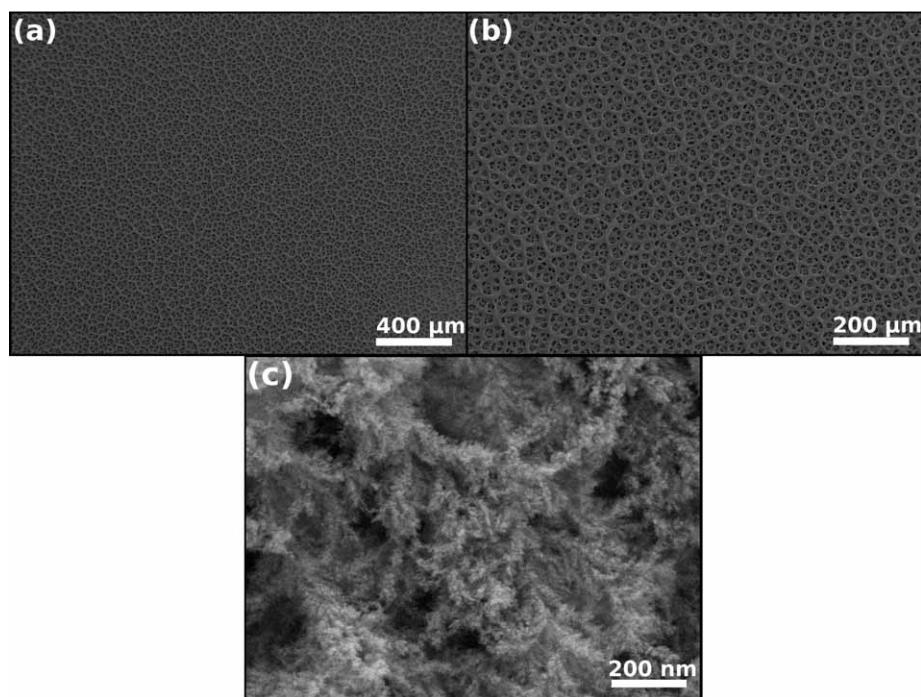
Fax: (+82) 31-290-7272; Tel: (+82) 31-290-7260;  
E-mail: [s.cherevko@gmail.com](mailto:s.cherevko@gmail.com); [chchung@skku.edu](mailto:chchung@skku.edu)

## Experimental

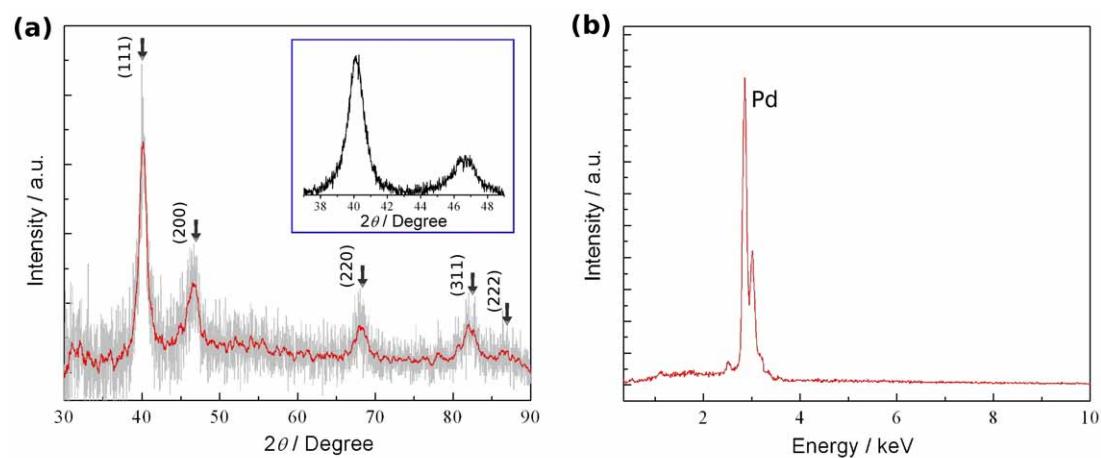
Nanoporous palladium foams were directly electrodeposited on a Pt/Ti/Si substrate. The substrate was prepared by electron beam evaporation of 10 nm thick layer of Ti followed by deposition of *ca.* 200 nm thick Pt on an Si wafer.<sup>1</sup> Strips of 15 × 5 mm<sup>2</sup> diced from the substrate and covered by an insulating material exposing area of 4 mm diameter were used as working electrodes. Ag/AgCl (3M NaCl) and a Pt plate served as reference and counter electrodes, in a three electrode configuration. The electrodeposition was carried out in a potentiostatic mode with potential controlled at E = -4 V. The deposition was performed at room temperature from an unstirred solution for 30 s. The solutions were prepared from deionized water (DI) to which 1 M of H<sub>2</sub>SO<sub>4</sub> (Duksan Reagents, Korea) and PdCl<sub>2</sub> (99.9+%, Sigma-Aldrich, USA) were added. Electrodes prepared from the solutions with different Pd amount were assigned as El1 (3.75 mM), El2 (7.5 mM), El3 (15 mM) and El4 (30 mM). After deposition the porous Pd electrodes were washed with DI water and dried in nitrogen. Prepared electrodes were than used in electrochemical studies or physical characterizations. The electrochemical study included the nanoporous palladium behavior in an acidic media (nitrogen purged 1 M H<sub>2</sub>SO<sub>4</sub> solution) and its catalytic activity. The former one was revealed by taking cyclic voltammogram (CV) (5 mV s<sup>-1</sup>) in a broad potential window where oxygen and hydrogen sorption/desorption processes take place. Roughness factor (R<sub>f</sub> - the relationship between real surface area and geometric area of an electrode) of porous Pd electrodes was estimated by using three methods; following reference values for 1 cm<sup>2</sup> real area were used: oxygen desorption charge – 424 µC cm<sup>-2</sup>, DL capacitance – 45 µF cm<sup>-2</sup>, and hydrogen desorption – 212 µC cm<sup>-2</sup> (0.69 H atom for each Pd atom).<sup>2</sup> To estimate H<sub>ads</sub> charge, the integration of anodic peaks was carried out between -0.1 and 0.15 V with subtraction of capacitive charge assuming that latter one is independent of potential. The catalytic activity was studied by recording CV (20 mV s<sup>-1</sup>) and pseudo-steady-state curves in deaerated NaOH (>98%, Samchun Chemicals, Korea) + ethanol (EtOH) (99.9%, Sigma-Aldrich, USA) or ethylene glycol (EG) (99.8%, Sigma-Aldrich, USA) solutions.

The deposition and all electrochemical measurements were performed using an electrochemical workstation (Zahner® Elektric IM6ex, Germany). Ag/AgCl (3M NaCl) (acidic solutions) or Hg/HgO (1M NaOH) (alkaline solutions) electrodes were used as the reference electrodes. The morphology and composition of the freshly prepared samples were studied using a JEOL JSM-7000F (Japan) scanning electron microscope (SEM) equipped with an Oxford energy dispersive X-ray spectrometer (EDS). Transmission electron microscopy (TEM) (JEOL JEM-2100F, Japan) was employed to evaluate the morphology on a nanometer scale. The structural properties were examined by X-ray diffractometry (XRD) (Bruker AXS D8 Discover (Germany) with Cu Kα radiation at 40 kV and 40 mA). The mass of deposited Pd was estimated by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) (Shimadzu ICPS-7500). The analyzed electrodes were immersed into a solution prepared from HCl and HNO<sub>3</sub> (volume ratio 3 to 1) for a few minutes until all Pd is dissolved. The obtained solutions, after dilution in DI water, were used in the ICP-AES investigation.

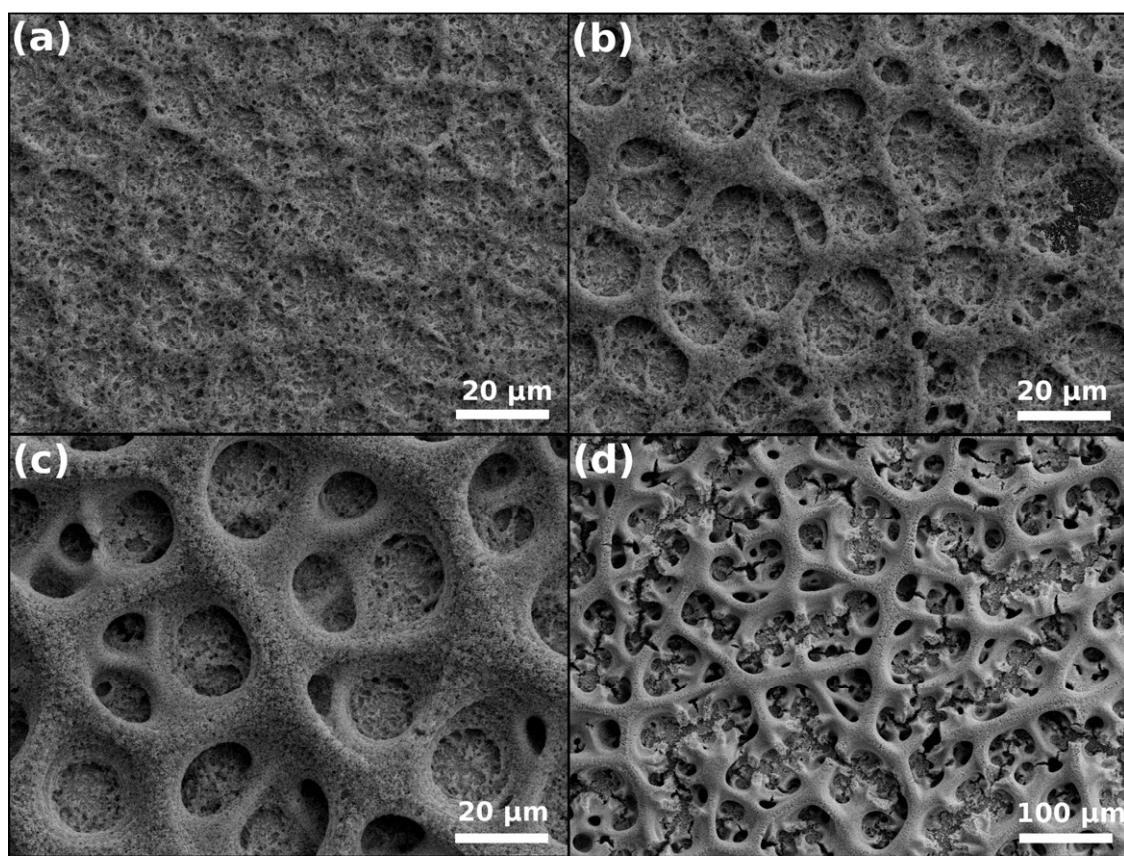
## Results



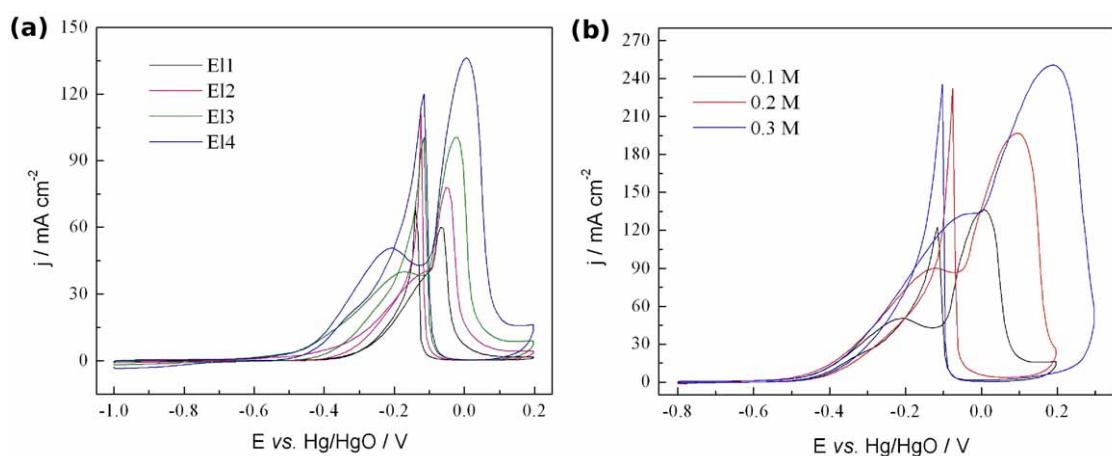
**Fig. S1.** SEM images of as-deposited porous Pd (15 mM of  $\text{Pd}^{2+}$ ) taken with different magnifications.



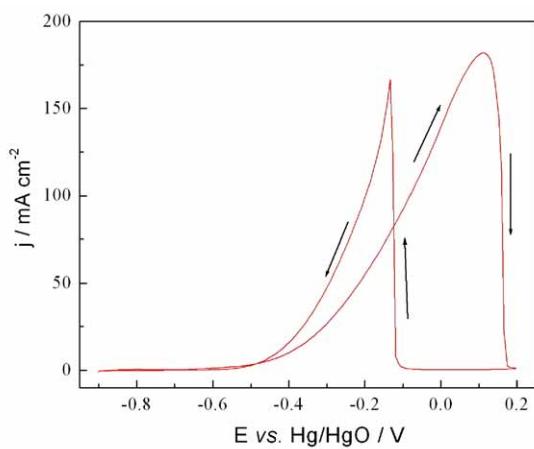
**Fig. S2.** (a) XRD pattern and (b) EDS spectrum of a nanoporous Pd. The experimentally obtained XRD pattern (grey) is shown alongside with averaged (each 20<sup>th</sup> point) one. Inset in (a) presents the XRD pattern taken in the Pd (111) and Pd (200) diffraction regions at a smaller scan rate (0.5 Deg/min.).



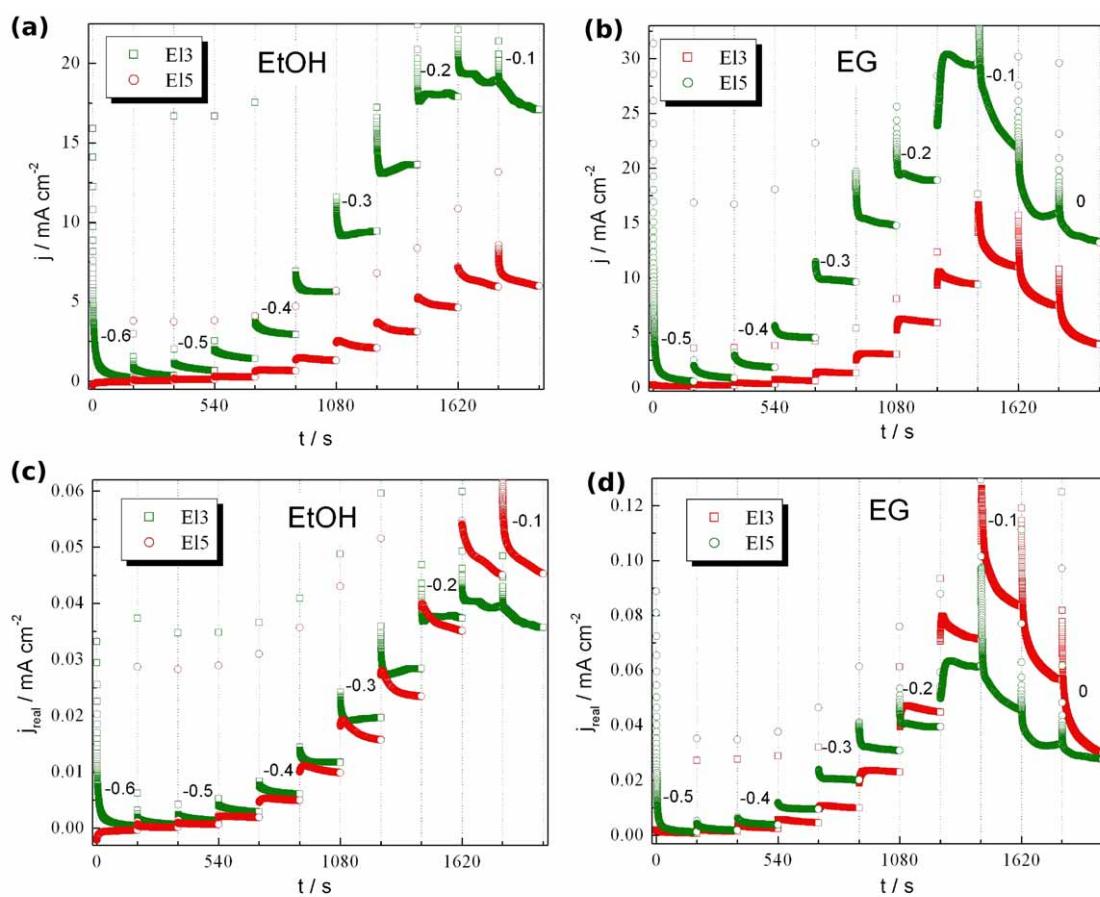
**Fig. S3.(a-d)** SEM images of El1-El4, respectively.



**Fig. S4.** (a) Cyclic voltammograms recorded with nanoporous Pd electrodes in 1 M NaOH + 0.1 M ethylene glycol. (b) CVs taken with El4 in 1 M NaOH with alcohol amount indicated. Scan rate was 20 mV s<sup>-1</sup>.



**Fig. S5.** CV recorded on E11 in 1 M NaOH + 1 M EtOH at  $5 \text{ mV s}^{-1}$ .



**Fig. S6.** Current-time curves taken in a 1 M NaOH + (a) 0.1 M ethanol or (b) 0.1 M ethylene glycol solutions on EI3. The potential was sequentially increased from (a) -0.6 to -0.1 or (b) -0.5 to 0 V, with 0.05 V steps. Each step time was 3 min. (c) and (d) are curves corresponding to (a) and (b) but normalized to the real surface area of the electrode.

**Table S1.** Dependence of the roughness factor ( $R_f$ ), weight (m), specific surface area (A), and normalized by the Pd weight Ethanol ( $I_{p,EtOH}$ ) and Ethylene Glycol ( $I_{p,EG}$ ) peak currents on the amount of  $Pd^{2+}$  in the employed electrolyte.

Electrode	$Pd^{2+}$ , mM	$R_f^*$	m , mg	$A, m^2 g^{-1}$	$I_{p,EtOH}, A g^{-1}**$	$I_{p,EG}, A g^{-1}**$
EI1	3.75	78	0.018	53.3	221	413
EI2	7.5	209	0.049	53.5	99	201
EI3	15	479	0.104	57.6	57	121
EI4	30	1133	0.211	67.5	39	81
EI5	13.6	132	0.392	4.2	12.5	21

\* $R_f$  is measured in the oxygen region.

\*\*The highest peaks on anodic curves (forward going scans) of 0.1 M EtOH or 0.1 M EG oxidation (Fig. 3a,b in the main text) were used.

## References

1. (a) S. Cherevko and C.-H. Chung, *Electrochim. Commun.*, 2011, **13**, 16-19; (b) S. Cherevko, X. Xing and C.-H. Chung, *Electrochim. Commun.*, 2010, **12**, 467-470; (c) S. Cherevko and C.-H. Chung, *Electrochim. Acta*, 2010, **55**, 6383-6390; (d) S. Cherevko and C.-H. Chung, *Talanta*, 2010, **80**, 1371-1377; (e) X. Xing, S. Cherevko and C.-H. Chung, *Mater. Chem. Phys.*, 2011, **126**, 36-40.
2. R. Woods, in *Electroanalytical chemistry*, ed. A. J. Bard, Marcel Dekker, INC., New York, 1976, vol. 9.