Electronic Supplementary Material (ESI) for RSC Advances. This journal is © The Royal Society of Chemistry 2018

Supplementary Information

Pt-grown carbon nanofibers for detection of hydrogen peroxide

Noora Isoaho^a, Sami Sainio^b, Niklas Wester^b, Luis Botello^d, Leena-Sisko Johansson^c, Emilia Peltola^a, Victor Climent^d, Juan Feliu^d, Jari Koskinen^b, Tomi Laurila^{a*}

^a Department of Electrical Engineering and Automation, School of Electrical Engineering, Aalto University, PO Box 13500, 00076 Aalto, Finland

^b Department Chemistry and Materials Science, School of Chemical Technology, Aalto University, PO Box 16200, 00076 Aalto, Finland

^c Department of Bioprocess and Biosystems, School of Chemical Technology, Aalto University, PO Box 16300, 00076 Aalto, Finland

^d Instituto de Electroquímica, Universidad de Alicante, Apt. 99, 03080 Alicante, Spain

*Corresponding author: tomi.laurila@aalto.fi, +358 50 341 4375



Figure S1. Fitted Pt 4 f doublet from the XPS spectrum.

The Pt 4f spectrum recorded from the Pt-CNF sample was fitted to estimate the amount of metallic and oxidized Pt species (Figure S1). Peak positions for metallic Pt and the Pt doublet were 71.1 eV and 74.4 eV, respectively. The Pt(OH)2 and its corresponding doublet peak were fitted at 1.2 eV above the metallic and metal doublet peaks. Pt oxides were fitted at 2.4 eV above the metallic line. Based on the fit it can be estimated that at least 75% of the Pt in the samples is in its metallic form and the remaining 25% in the form of different Pt oxides, mainly as $Pt(OH)_2$. Peak positions were estimated from following publications: Hammond & Winogard¹, Aricò *et al.*² and Wagner *et al.*³.



Figure S2. ND-CNFs show (pseudo) reversible electron transfer kinetics with ΔEp increasing from 62 mV for scan rate of 10 mV/s to 69 mV for scan rate of 400 mV/s. In order to make it easier to compare with Figure 2 in the original manuscript the graph here is presented in RHE scale even though the original measurements was performed against Ag/AgCl/KCl sat'd.

Figure S2 show the characterization of nanodiamond-grown carbon nanofibers (ND-CNFs) with 1 mM hexaammineruthenium(III) chloride in 1 M KCl. The utilization of Randles-Sevcik equation for evaluation of the active surface area was justified as the ND-CNFs show nearly reversible behavior with Δ Ep increasing from 62 mV for scan rate of 10 mV/s to 69 mV for scan rate of 400 mV/s.



Figure S3. When H_2O_2 is added into the N_2 -purged PBS at high concentrations (1000 μ M) an additional peak appears at approximately -0.2 V vs. Ag/AgCl with Pt-CNFs. The concentration of H_2O_2 has to be higher in degassed than in non-degassed PBS which supports the suggestions that 1) the peak arises from O_2 generated from H_2O_2 and 2) there exist some threshold concentration of H_2O_2/O_2 for the peak to appear. Similar peak does not emerge in phosphate buffers that do not contain chlorides and thus this peak could be related to ORR.

When cycling the potential of the samples in N₂-purged PBS containing large amounts (1000 μ M) of H₂O₂, an additional peak appeared approximately at -0.2 V vs. Ag/AgCl in the voltammogram (Figure S3). In non-deaerated (initially O2-containing) PBS the peak appeared already with addition of 500 μ M H₂O₂.

Figure S4 shows the RDE experiments with Pt-CNFs without post iR correction for the phosphate buffer ($R_u = 100 \Omega$). It can be seen that the resistivity of the solution has an effect on the shape of the curve in both anodic and cathodic ends. The effect becomes more pronounced when the rotation rate is increased.



Figure S4. RDE experiments (50 mV/s) with Pt-CNFs at 400 rpm, 900 rpm, 1600 rpm and at 2500 rpm in 0.15 M H₂SO₄, PB_{Na} and mixed solution of phosphate buffer and H₂SO₄ with 5 mM H₂O₂ without post iR correction. To take the pH difference into account the graphs are presented in RHE scale even though the original measurements were performed against Ag/AgCl/KCl sat'd. Conversion was done by utilizing Nernst equation taking into account solution pH.

References

- J. S. Hammond and N. Winograd, XPS Sspectroscopic Study of Potentiostatic and Galvanostatic Oxidation of Pt Electrodes in H₂SO₄ and HClO₄, *J. Electroanal. Chem. Interfacial Electrochem.*, 1977, 78, 55–69.
- A. S. Aricò, A. K. Shukla, H. Kim, S. Park, M. Min and V. Antonucci, XPS Study on Oxidation States of Pt and Its Alloys with Co and Cr and Its Relevance to Electroreduction of Oxygen, *Appl. Surf. Sci.*, **2001**, 172, 33–40.
- 3 C. D. Wagner, W. M. Riggs, L. E. Davis and J. F. Moulder, *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer Corporation, Eden Prairie, MN, **1978**.