

## Fabrication and Characterisation of Nanostructured Palladium Hydride Microelectrode pH Sensors

Toru Imokawa, Guy Denuault

Department of Chemistry, University of Southampton  
Highfield, Southampton SO17 1BJ, United Kingdom

The electrochemical deposition of nanostructured metal films using a molecular template created by a hexagonal lyotropic crystalline phase has been developed and studied extensively<sup>1</sup>. Bartlett et al<sup>2</sup> deposited mesoporous Pd films on 1 mm diameter Au microelectrodes and showed that the hydrogen insertion into the palladium film is fast and the formation of palladium hydride phases is observed at potentials similar to those reported for bulk palladium.

We prepared potentiometric pH microsensors by loading nanostructured Pd microelectrodes with hydrogen. The preparation method and potentiometric response of the sensors have been investigated.

Nanostructured Pd microelectrodes were prepared by depositing mesoporous Pd films on Pt microelectrodes by the method described above. While retaining micrometer dimensions these electrodes possess huge electroactive surface areas. From the oxide stripping peak of cyclic voltammograms in dilute sulfuric acid media, electroactive surface areas were estimated to be typically 300 times greater than the original geometric surface areas.

The hydrogen absorption property of the nanostructured Pd films was then investigated as a function of the potential in 0.5 M Na<sub>2</sub>SO<sub>4</sub> solutions with various pHs (controlled by H<sub>2</sub>SO<sub>4</sub>, NaOH). It was found to be possible to obtain the  $\alpha + \beta$  phase of the palladium hydride with the desired H/Pd ratio by controlling the potential and the time of electrolysis.

Nanostructured Pd microelectrodes were loaded with hydrogen potentiostatically to the  $\alpha + \beta$  phase and their open circuit potential ( $E_{OC}$ ) versus a saturated mercury sulfate reference electrode (SMSE) was measured in the same solution. Fig.1 shows an example of the  $E_{OC}$  monitored in a deaerated solution (pH=1.85) after the loading procedure. The  $E_{OC}$  rose slowly to reach a constant value corresponding to the  $\alpha + \beta$  palladium hydride<sup>3</sup>. The  $E_{OC}$  was very stable ( $\pm 1.5$  mV) for about 3 hours. The stability, however, appeared to be considerably shorter in aerated solutions. Dissolved oxygen was thought to accelerate the desorption of absorbed hydrogen.

The potentiometric pH response of nanostructured palladium hydride electrodes was investigated in deaerated 0.5 M Na<sub>2</sub>SO<sub>4</sub> solutions with various pHs at 25 °C. An example of the  $E_{OC}$  - pH calibration curves is shown in Fig. 2. The relation between the  $E_{OC}$  and pH was found to be linear with a slope of -0.059 V / pH over a wide pH range. The response was found to be reproducible between different nanostructured palladium hydride electrodes. Excellent stability and reproducibility of the  $E_{OC}$  makes it possible to conduct pH measurements without calibration before and/or after the measurements, a procedure normally essential for potentiometric pH microsensors.

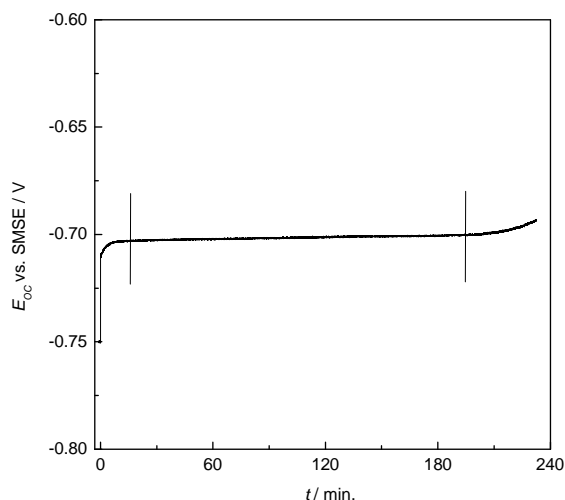


Fig. 1. Open circuit potential of a nanostructured palladium hydride microelectrode monitored in a deaerated 0.5 M Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub> solution (pH=1.85) immediately after loading hydrogen at -0.75 V.

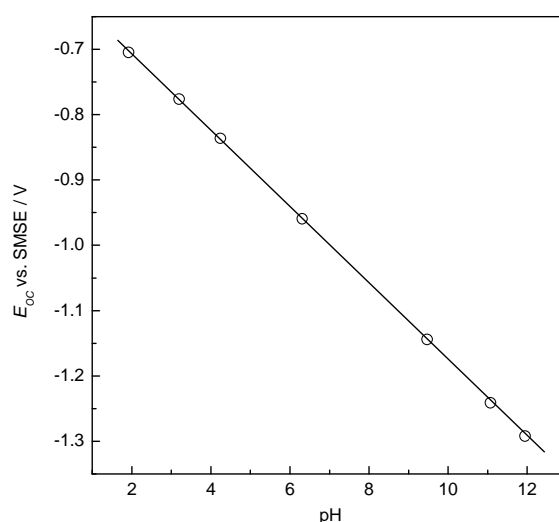


Fig. 2. Example of open circuit potential against pH calibration curves in deaerated 0.5 M Na<sub>2</sub>SO<sub>4</sub> solutions. The nanostructured Pd microelectrode was loaded with hydrogen at -0.75 V in a solution with pH=1.85.

### REFERENCES

1. See, for example, G. S. Attard, P. N. Bartlett, N. R. B. Coleman, J. M. Elliott, J. R. Owen and J. H. Wang, *Science*, **278**, 838 (1997)
2. P. N. Bartlett, B. Gollas, S. Guerin and J. Marwan, *Phys. Chem. Chem. Phys.*, **4**, 3835 (2002)
3. D. J. G. Ives and G. J. Jans, "Reference Electrodes. Theory and Practice," Academic Press, New York (1961)