

Facile Fabrication of Ultra Porous Platinum Electrodes and Their Application for Energy Harvesting Glucose Fuel Cells

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We present a new method for the generation of ultra porous noble metal electrodes. The method is based on alternated alloy deposition and removal of a non-noble alloy partner during cyclic voltammetry. Performing this method in acidic H_2PtCl_6 - $CuSO_4$ electrolyte, roughness factors of fabricated electrodes exceeded 5000, higher than reported elsewhere. The novel platinum electrodes were tested for their potential use in implantable glucose fuel cells. They show competitive performance to state of the art at significantly reduced platinum consumption and substantially facilitated fabrication.

INTRODUCTION: Nanoporous platinum with high surface area is of great general interest for applications related to catalysis such as fuel cells, chemical engineering or sensors. Porous platinum films can be created by utilization of templates such as polystyrene-microspheres [1] or liquid crystal during deposition, which in general is elaborate. The fabrication from platinum alloys represents an alternative way but often requires high temperatures for alloy formation [2]. An easy to perform purely electrochemical fabrication route uses co-deposition of platinum and copper, followed by electrochemical etching of copper leading to surface roughness factors (ratio of active to geometrical area) of 700 [3]. Our objective was to obtain even increased surface area by implementation of a novel electrochemical deposition procedure.

FABRICATION: To generate platinum electrodes with higher roughness factors, we performed **multiple cycles** of the above mentioned steps **electrochemical co-deposition of a Pt-Cu alloy and etching of copper**. This was done by conducting cyclic voltammetry (1.4 to -0.6 V, 50 mV s^{-1}) in an acidic solution of H_2PtCl_6 and $CuSO_4$ (each 0.02 mmol l^{-1}) using evaporated platinum substrates. In each cycle a novel layer of alloy is deposited for cathodic potentials more negative than 0 V and subsequently copper is extracted for anodic potentials more positive than 0.1 V. The growth of the surface area with increasing cycle number can be observed by the growing peak-heights in figure 1.

CHARACTERIZATION: From table 1 it can be seen that the roughness factor (determined by hydrogen desorption charge in CVs recorded in $0.5\text{ mol l}^{-1} H_2SO_4$) increases nearly linearly with the number of deposition cycles. After 500 deposition cycles a roughness factor of 5200 is obtained with a yield of 271 cm^2 per mg deposited platinum. A further linear dependence on the number of deposition cycles was found for the layer thickness, observed with a profilometer.

Figure 2 shows electron micrographs of samples fabricated with 50, 150 and 500 deposition cycles. Besides several large free standing, porous microparticles, a base layer consisting of neighboring smaller particles can be seen. The observed average particle size in the base layer (given in table 1) also follows a linear dependence with increasing number of deposition cycles. These results suggest an increasing agglomeration of smaller particles during the deposition process.

APPLICATION: Porous platinum electrodes are of a special interest for glucose oxidation in energy harvesting glucose fuel cells, intended as power supply for medical implants [2]. In comparison to state of the art (PtZn-anodes [2]) the novel electrodes show a comparable polarization slope at approximately 100 mV less negative anode potential in load curves (figure 3).

Besides extremely high roughness factors this new deposition method provides several general advantages: facile and template-less fabrication at room temperature, on-line process monitoring (from changes in CVs), flexible choice of substrate and consumption of only low amounts of platinum.

CONCLUSION AND OUTLOOK: We demonstrated and characterized a novel and facile fabrication technique for the generation of ultra porous platinum electrodes. Roughness factors of above 5000 and a linear dependence of the roughness factor on the number of performed deposition cycles were obtained. The novel electrodes showed a competitive performance for glucose oxidation in implantable glucose fuel cells.

In our future work we will carefully optimize deposition parameters to further improve the anode potential. Moreover, the high surface areas promise further application in other fuel cell and sensor devices.

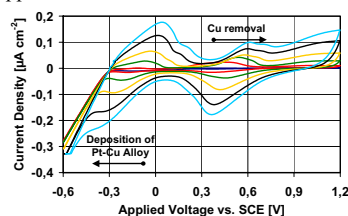


Figure 1: Evolution of cyclic voltammograms during deposition from H_2PtCl_6 and $CuSO_4$ (0.02 mol l^{-1} each) in H_2SO_4 (0.5 mol l^{-1}) shown for cycles 1, 5, 20, 50, 100, 150

Table 1: Results for electrode structure characterization

| Deposition Cycles | 0 | 50 | 150 | 500 |
|--|-----|-----|------|------|
| Roughness Factor | 4,5 | 820 | 1650 | 5200 |
| Surface Area per Mass [$\text{cm}^2\text{ mg}^{-1}$] | - | 194 | 180 | 271 |
| Layer Thickness [μm] | 0 | 3.8 | 8.5 | 27.5 |
| Average Particle Diameter [μm] | - | 1 | 3 | 7.5 |

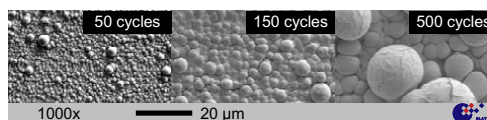


Figure 2: Electron micrographs of electrode surfaces fabricated with different numbers of deposition cycles

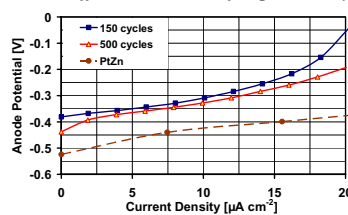


Figure 3: Characterization of anode potentials in load curves recorded under nitrogen at $37\text{ }^\circ\text{C}$ in phosphate buffered saline with 3 mmol l^{-1} glucose.

[1] P.N. Bartlett et al., Chem. Mater. 2002, 14, 2199-2208

[2] Kerzenmacher et al., Proceedings of 7th Power MEMS 2007, 31-34

[3] Liu et al., Nanotechnology 2006, 17, 2167-217