

**Electrodeposition of Pd-Cu alloys:
Evidence for the accumulative underpotential deposition
and formation of nanoporous Pd by anodic dealloying**

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The application of Pd-Cu alloys is a rapidly expanding field nowadays. Several attempts have been made to use Pd-Cu alloys for selective electrochemical reduction of nitrate and nitrite ions, selective cleavage of carbon-halogen bond, electrochemical transformation of CO, etc. Although both palladium and copper are more noble metals than hydrogen and they exhibit an unlimited solubility at high temperature, systematic studies on the Pd-Cu codeposition are very scarce.

Codeposition of palladium and copper was studied by using electrolytes made from sulfuric acid, copper(II) sulfate and palladium(II) nitrate. The halogenide-free solutions were applied in order to eliminate the formation of Cu(I) intermediate. The deposition rate is fairly low due to the weak solubility of the palladium nitrate in aqueous solutions.

The deposition was studied by using a potentiostat and a quartz crystal microbalance. Composition of the alloys was obtained by electron microprobe analysis in a scanning electron microscope.

Deposits made from electrolytes with several Pd²⁺:Cu²⁺ ratios were studied. The composition of the alloys was a monotonous function of the electrode potential. Palladium deposition starts at the potential where the surface oxide on Pd can be reduced. Codeposition of copper occurs at the potential regime where Cu is known to form a UPD layer on Pd. This potential interval is some 200 mV more positive than the onset potential of Cu deposition from Pd-free electrolyte. Hence, the codeposition process can be classified as accumulative underpotential deposition. X-ray diffractograms showed that a homogeneous alloy was formed with a face centered cubic lattice.

From the electrolyte used for the deposition, a little amount of Cu deposited can be dissolved during anodic polarization, but the oxidation of Pd was very slow. Therefore, the deposition can be taken as an irreversible process. However, it was also revealed that by changing the electrolyte to a hydrochloric acid solution, two subsequent voltammetric peaks were obtained that can be correlated by the dissolution of Cu and Pd. By stopping the anodic dissolution of the layer deposited after the dissolution of Cu, a very porous and black layer remains on the substrate. This is a porous palladium layer which was characterized to estimate the surface roughness and hydrogen adsorption/absorption properties by voltammetric methods. The structure and the morphology of the dealloyed Pd-rich residue can be illustrated by scanning electron micrographs.