Morphology and Composition of Electrodeposited Cu+PdO/Pd Composites

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The electrodeposition of composites consisting of a Cu matrix and of PdO or Pd dispersed phases has been studied with the aim of achieving porous thin films able to catalyze the oxidation of methane and low alkanes in the gas phase. This was an attempt to extend a procedure which has become fairly common in the preparation of electrocatalysts to the preparation of metal surfaces able to catalyze the low temperature combustion of hydrocarbons. The PdO/Pd system was selected as dispersed phase since it is recognized as the most active catalyst for methane oxidation, and Cu was chosen as a matrix because CuO has also some catalytic activity[1,2]. In the present communication, the essential features of the electrodeposition process, a SEM-EDX characterization and EIS data are reported.

Cu+PdO composites were obtained using either an acid Cu sulfate bath or a basic pyrophosphate bath, in which PdO particles were suspended, typically at a concentration of 10 g L^{-1}. Most deposits were formed on Ni rotating disc electrodes, under galvanostatic control. In the former medium, PdO is not indefinitely stable towards dissolution and it is therefore possible that part of the Pd is deposited via dissolution of Pd^{2+} and its cathodic reduction. Reduction of co-deposited PdO to Pd is also likely to occur at the deposition potential.

Figure 1 shows a Cu+PdO deposit obtained from the acid Cu sulfate bath, which exhibits a highly porous structure, a desirable feature in heterogeneous catalysis. Figure 2 shows a fracture section of a Cu+PdO deposit (ca. 200 μm thick) formed on a Zn electrode, from which it was easily detached. Clearly, the deposit is porous throughout its thickness. The empty volume fraction could be estimated to be ca. 0.7, by measuring the film volume and its mass. The magnified view in Figure 3 shows that the composite consists of an assembly of microcrystals, about 1 μm in size.

The composition of the sample in Figure 2 was measured by EDX, by sampling the "inner face", i.e. the one facing the metal during the deposition, the fracture section at different positions along the film depth and the "outer face". The atomic fraction of Pd was found to be 0.005 for the inner face, 0.03 to 0.06 for the film bulk and 0.09 for the outer face.

The surface roughness of Cu+PdO and Cu+Pd composites was estimated by measuring the double layer capacity values of the porous deposits and dividing them by the double layer capacity of a polished Cu electrode. The capacities were determined by EIS in a 0.5 M Na_2SO_4 solution. Typical values of surface roughness were 140 for Cu+PdO deposits ca. 270 μm thick and 260 for Cu+Pd deposits ca. 70 μm thick. Such highly porous structures of the Cu+PdO and Cu+Pd composites are not normally achieved in the electrodeposition of Cu-Pd alloys[3].

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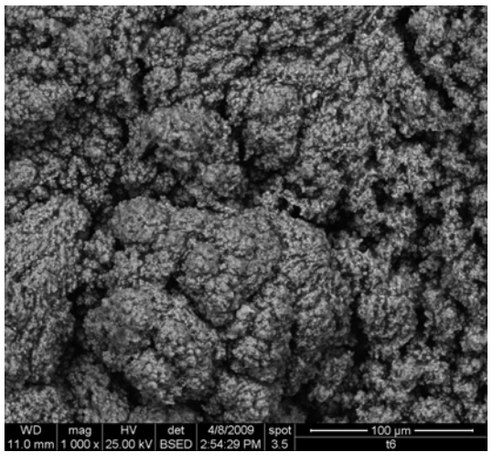

Figure 1. SEM image of a Cu+PdO deposit obtained from a suspension of PdO particles in an acid Cu sulfate bath. The deposit side facing the electrolyte is shown.

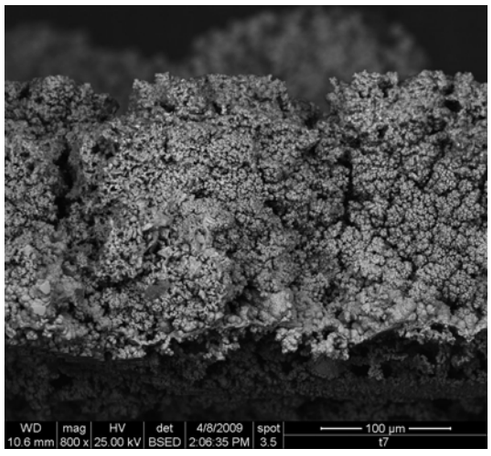

Figure 2. SEM image of the fracture section of a Cu+PdO composite.

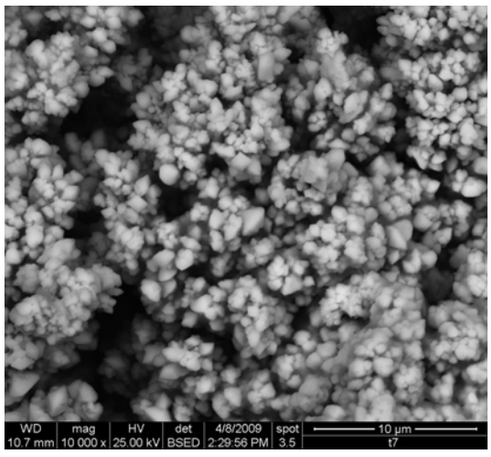

Figure 3. Magnified SEM image of the sample in Figure 2 (fracture section).