

Nanostructured gold sponges prepared and characterized by electrochemical techniques

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Dealloying is a process leading to gradual loss of the original material properties and may represent a degradation process in technological applications, e.g. by reducing the corrosion resistance. However, the same phenomenon may be turned into a useful synthetic route of metal nanostructures by selectively leaching out the less noble component from a suitable precursor alloy. Unlike many other metals, that are pyrophoric upon exposure to ambient oxygen in the nanoporous state, gold sponges are stable and resistant to oxidation. Considering the value as a model system¹ and the numerous potential applications (catalysis, biosensing electrodes, supercapacitors and actuators²), nanoporous gold has recently received an upsurge of interest.

We present an investigation of the anodic leaching of silver from Ag₇₅Au₂₅ alloy sheets in 1 mol L⁻¹ HClO₄ (typically at 0.95 V vs SCE), discussing the role of kinetics and transport as dissolution digs progressively into the bulk of samples. The resulting gold sponge is rather brittle. SEM of fractured samples reveals a network of branched nanowires with diameters d dispersed in a rather narrow range, different for structures forming in the bulk of the sample ($d = 25$ -50 nm) or in proximity of the surface ($d = 10$ -20 nm). The observed difference in size must originate from the effect of different surrounding (bulk vs. phase boundary) on the mechanism of rearrangement leading to gold structures.¹

The characterization of the resulting nanoporous gold sample is largely based on impedance investigations, performed at different stages of the dissolution process, both during dissolution at 0.95 V and under blocking conditions at low potential (-0.1 to 0.6 V vs SCE). In both cases, a straight line forming with the real axis an angle between 45° and 60° is seen at high frequency, as expected for porous electrodes with pores of various shapes.³ At lower frequencies, the shape of the Nyquist plots recorded during dissolution is close to a semicircle, while those recorded under blocking conditions, i.e. at low potentials show a vertical straight line. In contrast to a previous report⁴ no high frequency loop is observed. The measured low frequency capacity appears to depend in a roughly linear way on Ag dissolution charge, and additionally on potential and aging. The low frequency capacity estimated after exhaustive silver dissolution is in the order of 2.6-3.0 Fg⁻¹, corresponding to a specific gold surface area of 7-10 m² g⁻¹ calculated by assuming a double layer capacity of 30-40 μF cm⁻².

Aging causes slow changes – a sample previously submitted to exhaustive dissolution shows a capacity decrease of 10-20% upon residence at open circuit in HClO₄ for a few days - probably evidence of residual coarsening processes. The early coarsening occurring during and immediately after silver dissolution is less easy to characterize.

Results are compared with previous literature investigations of porous gold samples prepared by several other methods including thermal decomposition of precursors and chemical leaching of amalgams.⁵ A discussion is proposed comparing direct SEM evidence and conclusions inferred from theoretical considerations on the relation between shape of the Nyquist plots and average or prevalent pore structure.³

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