

Anomalous Responses of Gold Sensor Electrodes due to the Presence of Metastable Surface States

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Metals in high energy, metastable states are a well known item of commerce, the market value for such materials in the US in the early 1990's was quoted¹ at ca. 0.3 billion dollars p.a. It is thus quite surprising that such materials, especially in the case of the noble metals, has received very little attention in electrochemistry. A basic property of a metastable state is that it is unstable; however, the state in question is usually trapped or frozen-in. Nanoparticle materials, i.e. compacted metal nanoparticles, and rapidly quenched metals are typical examples of metastable systems.

Storage of excess energy in the metastable state may be explained in a number of ways, all of which, in the case of bulk metals, involve the presence of extended defects or disorder, e.g. low co-ordination metal atoms, dislocations, grain boundaries, or the existence of quantum confinement effects in extremely small particles or grains. In the case of a bulk activated metal the state in question may be produced by a variety of techniques¹, e.g. rapid thermal quenching, high energy ball milling, evaporation followed by condensation. The principle involved is the same in all cases; the metal is taken through a pretreatment cycle involving a considerable input of energy, at the end of which an appreciable percentage of the energy remains semipermanently trapped in disordered states within the metal. In many cases the activation of the metal is carried out inadvertently, e.g. a sample may be subjected to thermal pretreatment with a view to cleaning its surface or a metal film may be produced² by screen printing a metal ink which is then annealed; in such cases the possibility of generating a superactive state is usually ignored.

The ability to generate high levels of superactive states at metal electrode surfaces was discussed in a recent publication from this laboratory³. Various pretreatments, e.g. rapid thermal quenching, cathodization, abrasion and electrodeposition, may be employed to produce such surface states. A characteristic feature of the latter is that the metal atoms involved undergo oxidation in aqueous media at anomalously low potentials. The metastable nature of active site atoms at surfaces was highlighted by Taylor⁴ in his active site theory of heterogeneous catalysis: basically, low coverage superactivity or disorder often plays a vital role in catalysis at surfaces and interfaces.

With regard to microsensors the metal of choice is often gold and this is usually used in thin film form. The deposits in question are often produced by unusual techniques, e.g. evaporation, sputtering or screen printing followed by thermal annealing², which evidently lead to surfaces with an unusual coverage of active gold atoms. Several reports have been published^{2,5} where thin film gold microelectrodes in aqueous media (in the absence of an analyte) exhibit major redox transitions within the double layer region. Such behaviour, which complicates the analytical applications of amperometric sensors, are due to the presence of superactive gold atoms, rather than impurities. The effect, which should be avoidable by the use of appropriate annealing of the film, will be described for gold electrodes in both neutral and acid solution.

References

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