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Hydrous iridium oxide for *in situ* pH sensing electrodeposition, properties and applications

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Abstract

For heterogeneous processes, such as electrochemical reactions taking place at an electrode, the chemical conditions at the reaction interface can differ significantly from the bulk. Consumption of reactants leads to local depletion, whereas product formation results in excess concentration. For reactions involving protons and hydroxide ions, these changes can be described in terms of local pH. In this thesis, a method to measure near surface pH with rotating ring disc electrodes (RRDE) was investigated. In this method, the RRDE is not used in the classical generator collector mode with amperometric detection on the ring, but with the ring as a potentiometric pH sensor. Hydrus iridium oxide films (HIROF) were electrodeposited to serve as thin film pH sensors.

The chemistry of the deposition medium used for preparing the HIROFs was studied in detail. The existence of crystalline nanoparticles in the film was proven by transmission electron microscopy. HIROF exhibit a pH response greater than 60 mV, up to 90 mV, depending on the amount of crystalline matter and the redox buffering in the film. Variations in the pH sensitivity were related to the average oxidation state, by measuring titration curves after potential conditioning at different potentials. The pH sensitivity followed the cyclic voltammogram (CV) of HIROF, with two maxima near the two redox couples in the CV.

The films did not fully adapt to conditioning potentials more positive than the first redox couple. This phenomenon was discussed within the context of a DFT study on the binuclear mechanism for the oxygen evolution reaction. Combination of experimental observations and results from DFT calculations, revealed that the full oxidation of Ir(IV) to Ir(V) oxide is inhibited and only partial oxidation to Ir(V) is allowed before the start of oxygen evolution.

After determining the pH sensing properties of HIROFs, films were deposited on the ring of RRDEs and successfully used in *in situ* near surface pH measurements. The ocp of HIROF ring electrode was measured, during water and oxygen reduction on the disc. Next, the ocp values were correlated to pH, using calibration curves measured in standard buffer solutions, to obtain information on the near surface pH changes

Hydrogen peroxide, a redox compound, is one of the products of O₂ reduction. Redox reactions between the HIROF and such species, could hinder pH measurements. However, for low H₂O₂ concentrations, a suitable potential conditioning of the HIROF, was shown to subdue this influence. Thus, optimisation for systems under study is possible, facilitating *in situ* pH measurements even in the presence of electroactive substances in solution.

Finally, the growth of ZnO rods was studied, with focus on electrodeposition on gold. Deposition is induced by changing near surface pH with a electrochemical reaction, like oxygen reduction, to induce precipitation of ZnO onto the electrode. The current density, related to the local pH, was found to have a profound influence on coverage density and rod dimensions.

Keywords: hydrus iridium oxide, zinc oxide, electrodeposition, pH sensor, oxidation state, RDE, RRDE, SEM