

Performance of IrO_x pH sensor prepared by thermal oxidation for the long term monitoring of nuclear waste disposals

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“Cigeo” is the name of a future deep geological disposal facility for high-level and intermediate-level long-lived radioactive waste, to be built in France, at 500 m depth within the Callovo-Oxfordian formation (Cox). The Cox is a 130 m thick clay-rich rock, dating back to 160 million years ago and lying at a depth of 400 to 600 m. It is a water-saturated environment with extremely low permeability, porosity and hydraulic conductivity.

In order to monitor the evolution of the near-field around radioactive waste, the implementation of reliable sensors turn out to be useful to support storage safety and reversibility. pH is one of the important parameters characterizing physical, chemical, and electrochemical transformations to be monitored.

This study aims to develop pH innovative all-solid-state electrodes based on Iridium Oxide (IrO_x)/Iridium (Ir). Understanding the electrochemical behavior of such metallic coatings is the key point of our research, as provides the tools for constructing and exploiting the Potential-pH abacuses, which are necessary for developing robust and reliable pH sensors.

The sensors were prepared by thermal oxidation of Iridium Ir(0) at 700°C. The sensibility of electrodes was then evaluated by potentiometric measurements during electrode immersion in pH buffers solutions, at 25°C, under both oxic (at atmospheric pressure) and anoxic conditions (in a glove box, pN₂ = 1 atm; pO₂ = 10⁻⁶ atm) and in the presence and the absence of sulfides. IrO_x films seem to be robust and steady on adherence and exhibit a good sensitivity, under oxic conditions (- 51 mV/pH), anoxic conditions without sulfides (- 56 mV/pH) and anoxic in the presence of sulfides (- 44 mV/pH). After thermal oxidation, the immersion of the electrodes in milliQ water for 100 days allows the hydration of the IrO_x layer, which is responsible for a decrease in E^o_{exp} and its stabilization at 780 mV/SHE without affecting either the sensitivity or the response time of the electrodes. XPS analyses were carried out after hydration, were shown that the Ir^{III}/Ir^{IV} redox couples are responsible for the robust pH response. Finally, the performance of IrO_x - pH sensors show their utility and ability for long-term pH monitoring.