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Corrosion control of ruthenium oxy-hydroxide coating for the development of robust pH sensors: observation and monitoring of the near field of a nuclear waste disposal site.

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In Europe, nuclear waste repositories are being installed in deep excavated rock formations to store and isolate radioactive waste. The deep geological disposal (Callovo-Oxfordian formation (COx)) has been chosen in France to manage long-lived high and middle activity nuclear waste, ANDRA - French national radioactive waste management agency supervises this project. As part of the Cigéo project, ANDRA has built an underground laboratory dedicated to host-rock properties characterization at approximately -490m depth in the Callovo-Oxfordian geological formation (COx), to perform the necessary experiments. In order to monitor the evolution of the nearby field around radioactive waste, the implementation of sensors turns out to be essential for several reasons related to safety and reversibility of storage.

This study aims to develop the metal (Mo/Mox) electrodes that are regarded among the promising technologies to be innovative all-solid-state electrodes made of ruthenium (Ru) for pH measurement by the electrodeposition method. Based upon the reversible interfacial redox processes involving H⁺, metal/ oxy-hydroxide devoted to the observation and monitoring of pH into the underground components of nuclear repositories due to their physical and chemical stability, regardless temperatures, pressures and aggressive environments.

Among the metal-metal oxy-hydroxides, Ru-RuOx are one of the promising systems for pH measurements. Depending on the method of preparation and deposition, the electrical conductivity of RuO₂ is between $0,035 \cdot 10^6$ and $2 \cdot 10^6$ S.m⁻¹. The most stable oxidized species of ruthenium considered potentially responsible for the pH response of the material are Ru^(III) and Ru^(IV). Understanding the electrochemical behavior of this material thus is a key point of our research, as provides the basis for constructing the abacuses needed for developing robust and reliable field sensors.

This work aimed to calibrate ruthenium oxy-hydroxide electrode for pH measurements into the underground components of nuclear repositories. The electrode presented the advantage of being strong in the conception: it presented an important reserve of material.

The electrodeposition of RuO_x was performed on screen-printed carbon electrodes (SPE) using cyclic voltammetry (CV) at different scan rates from a soluble metal salt RuCl₃·3H₂O. The influence of pH from 4 to 13, on the potentiometric responses of the several electrodes was investigated by means of pH buffers solutions, under both oxidic (exposed at air) and anoxic conditions (in glove box: pN₂=1 atm; pO₂=10⁻⁶ atm, 25°C).

Ruthenium oxy-hydroxide electrodes showed a higher sensitivity (figure 1) using cyclic voltammetry (slopes between -63 and -67 mV/pH) under oxidic conditions and furthermore, the absence of oxygen (GB) causes sensitivity expansion (figure 2).

Immersion in milliQ water allows hydration of the RuO_x oxide layer, which is responsible for an increase in E^o_{Exp} without affecting the electrodes sensitivity. We observe the stabilisation of E^o_{Exp} stabilizes at 1000 ± 6 mV/ESH after 30 days of immersion in milliQ water.

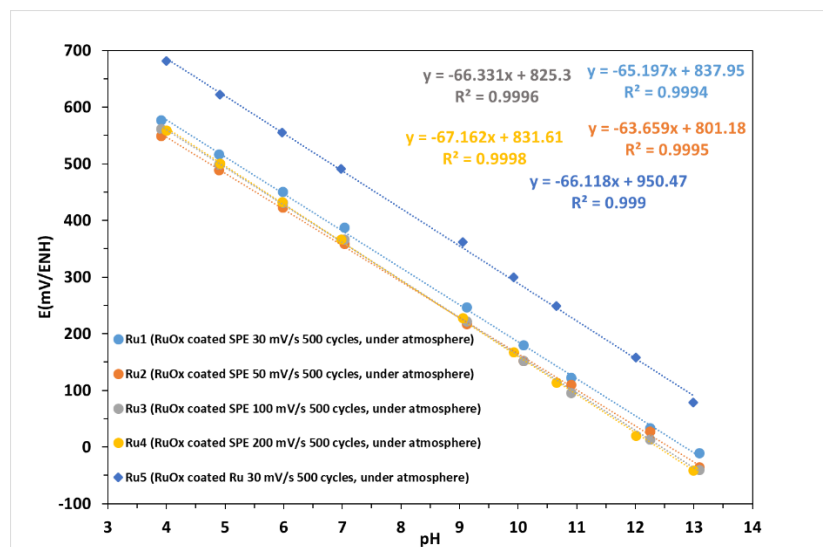


Figure 1: Open circuit potential of the RuO_x electrode as a function of pH under oxidic conditions.

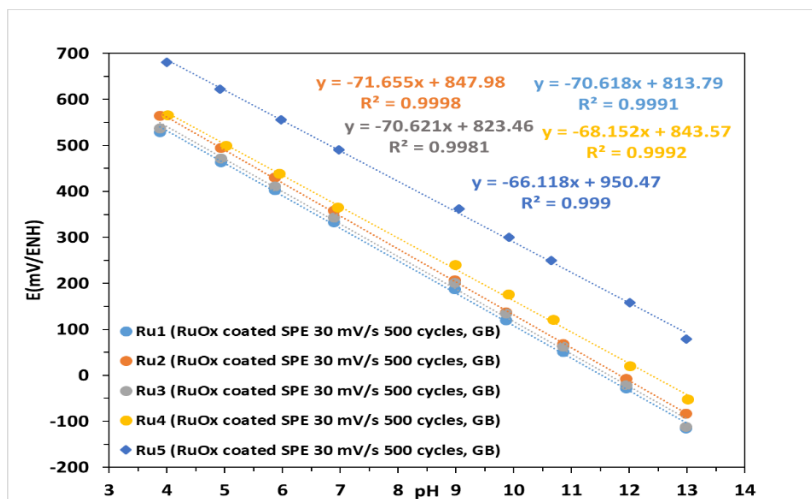


Figure 2: Open circuit potential of the RuOx electrode as a function of pH under anoxic conditions.