

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

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Cigéo is the future French industrial project for the deep geological disposal of High-Level Long-Lived Radioactive Waste. The Callovo-Oxfordian clay formation (Cox) has been selected at a depth of 500 m as a natural barrier to isolate the waste from living beings and the environment. This project is supervised by the French National Agency for Radioactive Waste Management (Andra). The Cox formation is a layer of clay-rich rock approximately 130 m thick, formed around 160 million years ago. It is located at depths ranging from 400 to 600 m underground. This formation is characterized by its high water saturation, very low permeability, porosity, and hydraulic conductivity. The temperature, pH, and CO_2 partial pressure of the Cox pore-water solution remain consistent at 25°C, 7.3 (± 0.1), and $8 \cdot 10^{-3}$ atm, respectively [1].

In order to effectively monitor the near-field evolution around radioactive waste, the use of dependable all-solid-state reference electrodes and sensors is crucial for ensuring safety and reversibility. Parameters such as pH and redox potential play a significant role in physical, chemical, and electrochemical (redox) transformations, which, consequently, need to be monitored.

Due to reversible interfacial redox processes involving only protons, metal oxy-hydroxides (M_xO_y) potentiometric electrodes are considered promising for pH measurements. This is because of their inherent mechanical stability in various conditions such as temperature, pressure, and harsh environments. The development of all-solid-state pH electrodes is attracting considerable attention because such electrodes are more favorable for process monitoring where robustness and resistance to high temperature, high salinity, and high pressure are required.

This work aims to develop pH innovative all-solid-state electrodes based on molybdenum Oxide (Mo_xO_y)/molybdenum (Mo). 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.

Among the molybdenum sensors developed in the literature, one study conducted by Shuk et al., [2] focuses on pH sensors based on single crystals of molybdenum oxide bronzes for monitoring pH titrations. In this previously cited study, the pH electrodes responded reproducibly to pH changes in the range of 4 to 9, with a response time of less than 5 seconds.

In our case, the sensors were prepared by thermal oxidation at 370, 400, 500 and 600°C. The sensibility of electrodes was then evaluated by potentiometric measurements during electrode immersion in pH buffers solutions, at 25°C, under both oxidic (at atmospheric pressure) and anoxic conditions (in a glove box (GB), $p_{\text{N}_2} = 1$ atm; $p_{\text{O}_2} = 10^{-6}$ atm), in the presence and the absence of sulfides at various concentrations (ranging from 10^{-7} to 10^{-3} mol/L).

We employed various heat treatment parameters in our study because our aim is also to diversify the electrodes for pH measurements to prevent any dysfunction that may occur over time. By multiplying the electrodes dedicated to pH measurement, we indirectly enhance, firstly, the reliability of the measurements by allowing comparison of potentiometric responses

across all electrodes, and secondly, the monitoring duration, in the event of alterations to electrode surfaces caused by variations in the physical and chemical parameters within the nuclear waste repository.

Mo_xO_y films seem to be robust and exhibit a good sensitivity under oxic and anoxic conditions, and, furthermore, the absence of oxygen (in GB) leads to an increase in sensitivity and a decrease in the experimental standard potential E°_{Exp} .

The sensors were subsequently observed using a scanning electron microscope (SEM); the films appear to be adhesive. The electrodes made at 500°C seem to be more homogeneous. The immersion of the Mo_xO_y/Mo sensors in milliQ water for 70 days allows the hydration of the Mo_xO_y layer, which is responsible of an increase of sensitivity. XPS analyses were carried out before and after hydration, to determine the main redox couples responsible for electrode response to pH variations.

Finally, the performances of Mo_xO_y - pH sensors show their utility and ability for long-term pH monitoring.

Work is in progress to demonstrate the robustness of the Mo_xO_y/Mo electrodes into actual Cox pore water solution over a long period.

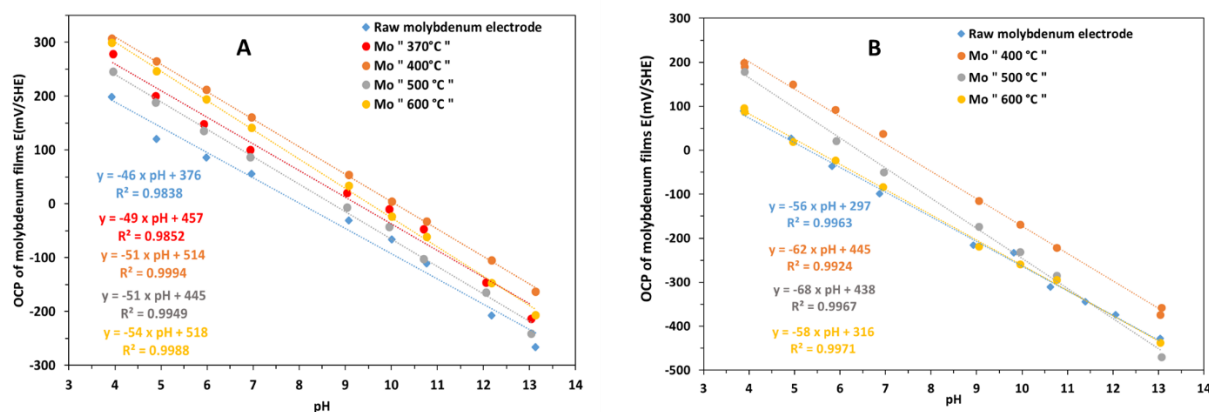


Figure 1: Open circuit potential of Mo/Mo_xO_y electrodes as a function of pH under oxic conditions (A) and anoxic conditions (B)

References

- [1] A. Lassin et al., « Equilibrium partial pressure of CO₂ in Callovian–Oxfordian argillite as a function of relative humidity: Experiments and modelling », *Geochimica et Cosmochimica Acta*, vol. 186, p. 91-104, août 2016, doi: 10.1016/j.gca.2016.04.028.
- [2] P. Shuk, K. V. Ramanujachary, et M. Greenblatt, « Molybdenum oxide bronzes as pH sensors », *Electrochimica Acta*, vol. 41, n° 13, p. 2055-2058, août 1996, doi: 10.1016/0013-4686(95)00415-7.