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Optimization of iridium oxy-hydroxide films for pH monitoring of underground components of nuclear repositories

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For the long-term monitoring of the pore water of clay-based disposal systems, the development of robust all-solid pH sensors, which do not necessitate any maintenance, is required. Due to their high stability, corrosion resistance and reversible redox properties, iridium oxyhydroxides (IrOx) are widely investigated for pH sensing and can be regarded among the promising technologies to be devoted to the observation and monitoring of pH of underground components of nuclear repositories.

This work aimed at in depth investigating and optimizing the IrOx coating process for pH measurements in agreement with the specific constraints related to on-site conditions. Electrochemically assisted synthesis was selected in order to control the oxidation states of IrOx redox active species in the coating.

The first objective was to give insights into the mechanism of electrodeposition of IrOx film on gold- or platinum-coated electrodes ($S=0.198 \text{ cm}^2$) by coupling electrochemistry with quartz crystal microbalance (QCM) measurements and scanning electronic microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS). Electro-assisted syntheses were performed using an $\text{Ir}^{(\text{IV})}$ -based salt solution which was prepared according to [1]. Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) identified both $\text{Ir}^{(\text{III})}/\text{Ir}^{(\text{IV})}$ and $\text{Ir}^{(\text{IV})}/\text{Ir}^{(\text{V})}$ as well as $\text{O}_2/\text{H}_2\text{O}$ and OH/O_2 redox couples involved at the electrode interface during the electro-assisted synthesis (Fig. 1a). The coupling of QCM with LSV, CV, chronopotentiometry (CP) or chronoamperometry (CA) provided results clarifying the different physical and chemical processes associated to redox reactions occurring at the electrode (Fig. 1b).

The second objective of this study was to determine the sensitivity and stability of the IrOx-based sensor depending on the electrochemically assisted synthesis technique and methodology. Electro-generation of IrOx-coatings were performed on carbon-based screen-printed electrodes (SPEs), which allow quick generation of reliable data [2]. Measurements were conducted by potentiometric measurements at several pH in the range 4-12 at 25 °C, under atmosphere and in a glove box (GB, $p\text{O}_2 = 10^{-6} \text{ atm}$). These conditions were selected in agreement with those encountered in the environment of the nuclear repositories. Irrespective of the selected electrodeposition technique, IrOx films can exhibit a super-Nernstian response ($> 59.2 \text{ mV/pH}$), depending on the electrodeposition time or sweep rate (Fig. 2). Among the different techniques tested, the more suitable to improve the sensitivity in the entire pH range are CP and CV, with slopes between -60 and -70 mV/pH ($R^2 \geq 0.98$). Electrochemical impedance spectroscopy measurements showed low corrosion rates, indicating the stability of IrOx films. They appear thus appropriate for the long-term monitoring of the pore water of nuclear waste repositories. Work is in progress to demonstrate the robustness of IrOx-based sensors in situ over a long period.

References:

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- [2] J. Daoudi, S. Betelu, T. Tzedakis, J. Bertrand, I. Ignatiadis, A Multi-Parametric Device with Innovative Solid Electrodes for Long-Term Monitoring of pH, Redox-Potential and Conductivity in a Nuclear Waste Repository, *Sensors* 17 (2017) 1372.

Figure 1:

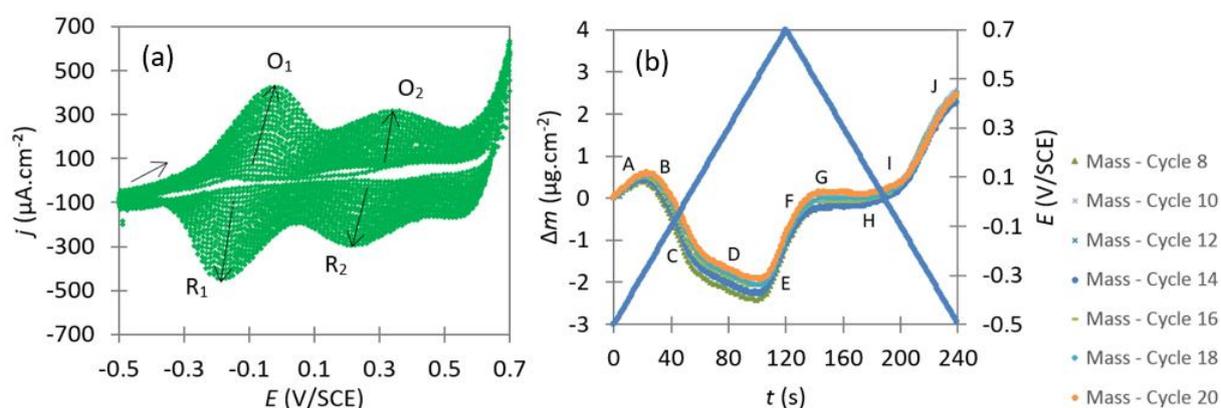


Figure 2:

