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

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Introduction

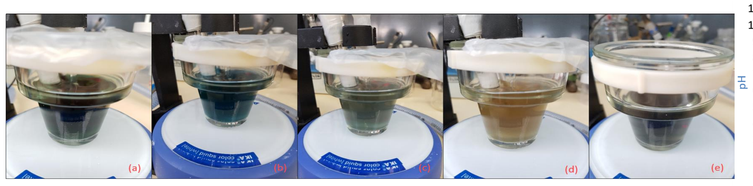
The development of robust **all-solid pH sensors**, which do not necessitate any maintenance, is required for the **long-term monitoring** of the **pore water** of clay-based disposal systems.
Due to their high stability, corrosion resistance and reversible redox properties, **iridium oxy-hydroxides (IrOx)** are widely investigated for pH sensing and can be regarded for pH monitoring of underground components of nuclear repositories.
This work aims at **investigating** and **optimizing** the **IrOx electrodeposition process** for **accurate pH measurements** with the specific constraints related to on-site conditions.

Materials and methods

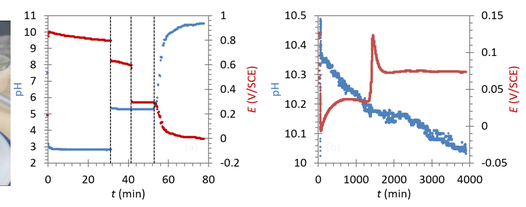
I. Preparation of $Ir^{IV/III}$-based solutions

Based on the protocol proposed first by Yamanaka [1]

75 mg of $IrCl_4$ in 50 mL milli-Q water → + 375 mg of $K_2C_2O_4$ (oxalate) → + 0.5 mL H_2O_2 30% w/v → + K_2CO_3 (up to pH = 10.5) → After three days (pH = 10)



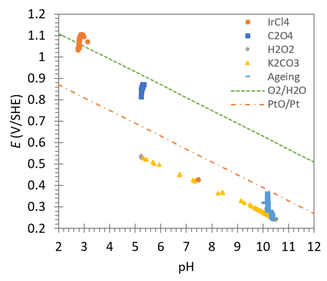
E_h/pH monitoring

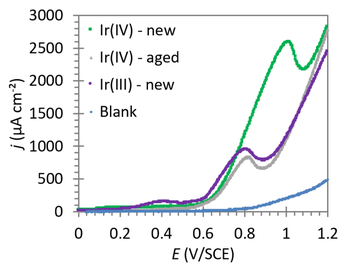


II. Investigation of the electrodeposition mechanism

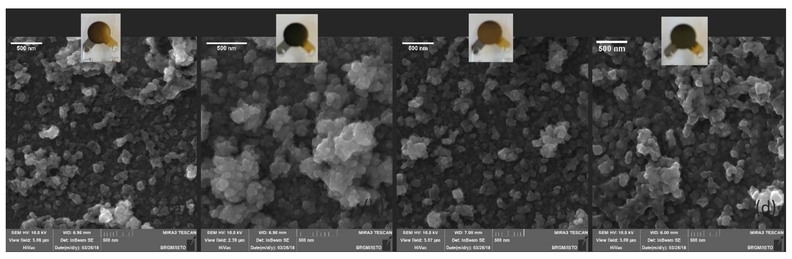
Use of electrochemical quartz crystal microbalance (EQCM) to determine the variation in mass during experiments

- Characterization of the blank solution
- Characterization of the $IrCl_x$ solutions





- **Galvanostatic** electrodeposition ($I_{constant}$)
- **Potentiostatic** electrodeposition ($E_{constant}$)
- Electrodeposition by **cyclic voltammetry**
- Characterization of the IrOx films



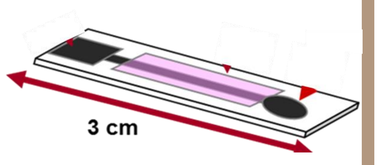
Electrochemistry: PARSTAT 4000A + QCM922
WE: gold-coated quartz (0.198 cm²)
RE: saturated calomel electrode (SCE)
CE: platinum wire

Sauerbrey equation:

$$\Delta m = \frac{-A\sqrt{\mu_q \rho_q}}{2 f_q^2}\Delta f = -k\Delta f$$

III. Determination of the sensitivity of IrOx films

Electrodeposition of IrOx films on Carbon-based Screen-Printed Electrodes (SPEs), as already performed in [2] for Sb-based SPEs

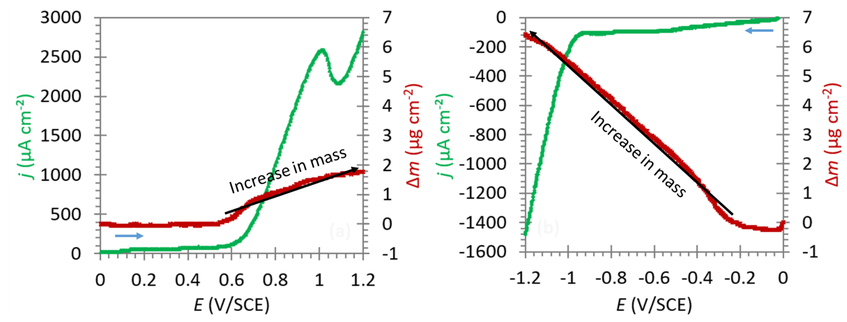


- Same electrodeposition methods as described above
- Potentiometric measurements in **pH buffers 4-12 at 25 °C, under atmosphere and in glove box** (GB, $pO_2 = 10^{-6}$ atm)

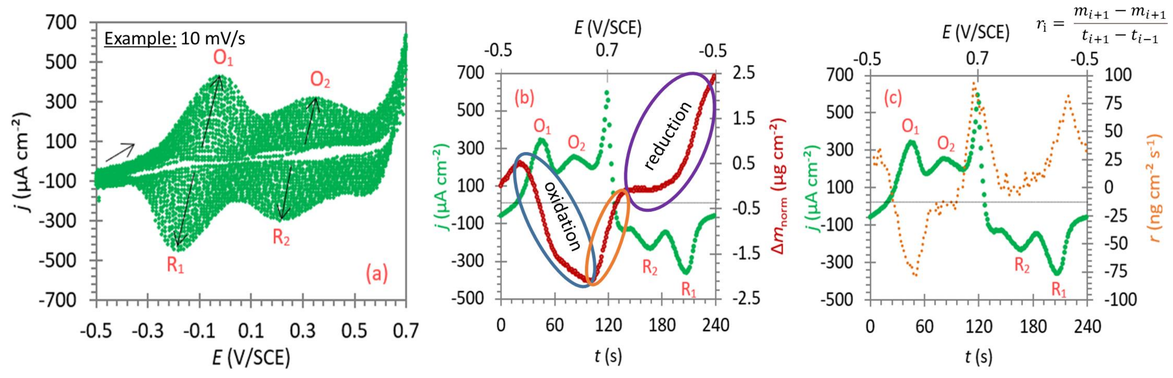
Results

I. Electrodeposition mechanism

- Presence of **many electroactive species** in the solutions
- Electrodeposition mainly observed in parallel to **water oxidation** (E > 0.6 V/SCE)/**oxygen reduction** (E < 0 V/SCE)



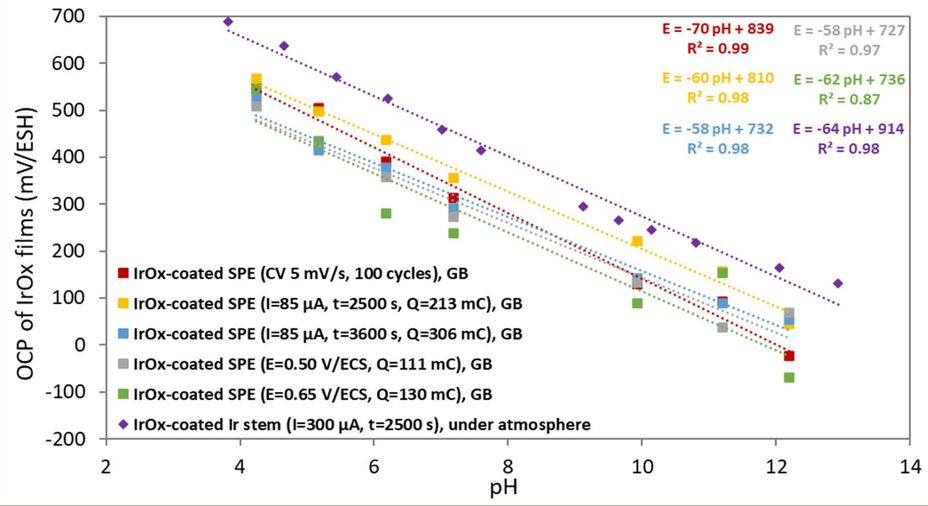
- Identification of **$Ir^{(III)}/Ir^{(IV)}$** (O_1/R_1) and **$Ir^{(IV)}/Ir^{(V)}$** (O_2/R_2) redox couples on IrOx films during cyclic voltammetry



- **Loss in mass during their oxidation** (O_1 and O_2), and **gain in mass during their reduction** (R_1 and R_2)

II. Sensitivity of IrOx films for pH monitoring

- **Higher sensitivity** with **galvanostatic** electrodeposition or **cyclic voltammetry** (slopes between -60 and -70 mV/pH)
- Low corrosion rates (EIS measurements) → **good stability**



Conclusions and perspectives

1. Electrodeposition by cyclic voltammetry involves several electroactive Ir^{III} and Ir^{IV} species. Mass variations occurs mainly in parallel to water oxidation and oxygen reduction reactions.
2. Variation during cyclic voltammetry suggests deprotonation during oxidation of IrOx films and (re-)protonation or hydroxylation during their reduction
3. IrOx films properties (hydration, oxidation state) can be tuned after electrodeposition, irrespective of the method of electrodeposition
4. IrOx films appear stable and can exhibit a high sensitivity (60-70 mV/pH), showing their interest and ability for long-term pH monitoring

Further work is in progress to demonstrate the robustness of IrOx-based sensors *in situ* over a long period

References/Acknowledgments

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[2] J. Daoudi, S. Betelu, T. Tzedakis, J. Bertrand, I. Ignatiadis. Sensors 17 (2017) 1372.
[3] R. Rodrigues, J. Bertrand, I. Ignatiadis, S. Betelu. Article on the electrodeposition mechanism in preparation

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