

Effects of iron impurities and ferroelectrics on the activity of cobalt-based oxide catalysts for Oxygen Evolution Reaction

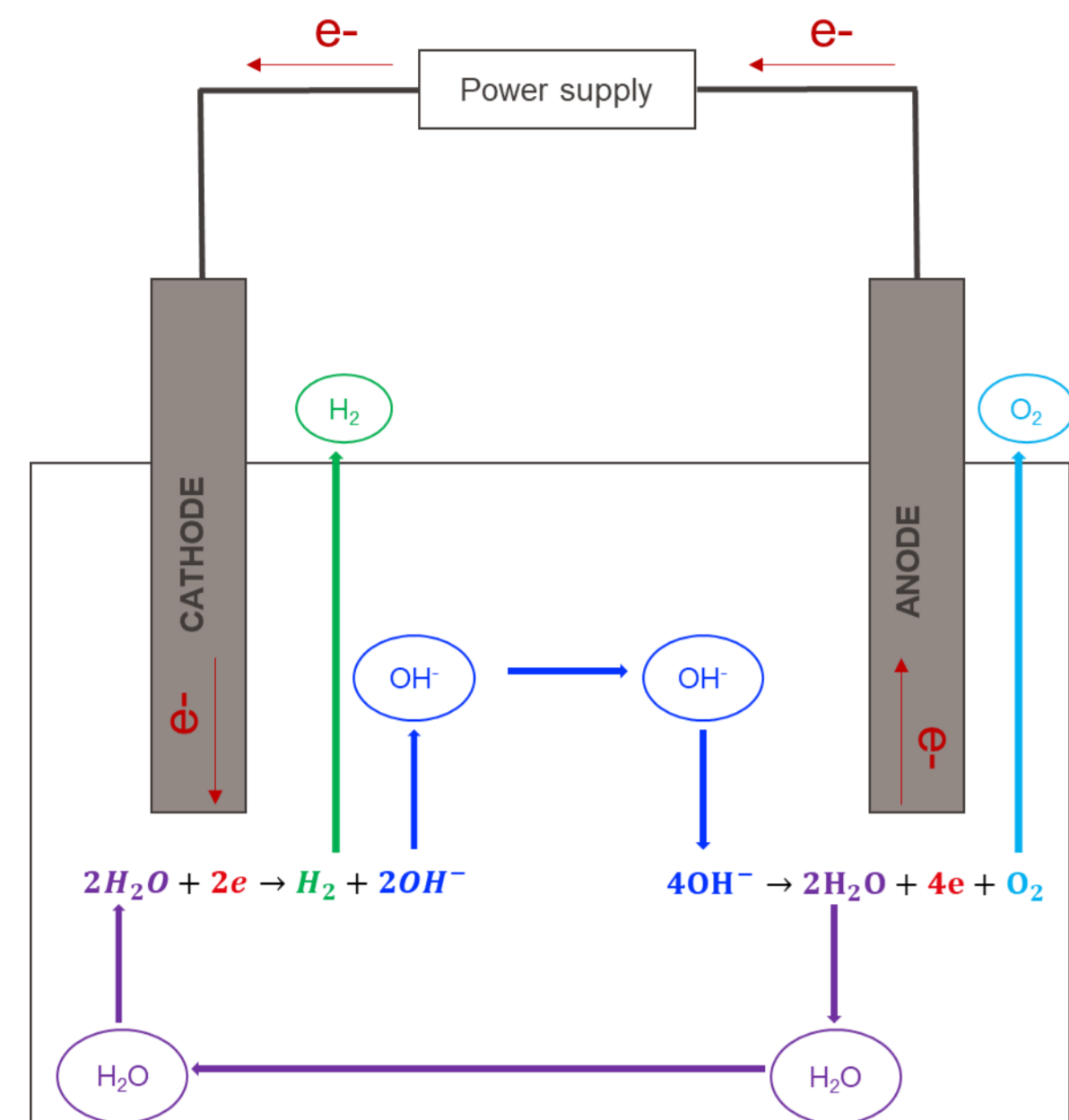
Thi Ha My Pham, Tzu-Hsien Shen and Vasiliki Tileli

Institute of Materials, École Polytechnique Fédérale de Lausanne, Switzerland

Abstract

This work focuses on the effects of iron impurities and ferroelectric materials on the activity of cobalt-based oxide catalysts for oxygen evolution reaction (OER). Cyclic voltammetry is performed on cobalt-based oxides in 0.1 M KOH and in FeSO₄-contained 0.1 M KOH solutions. The activity of Co-based oxides improves significantly with the addition of 1 mM FeSO₄ while the boost in activity decreases when the catalysts is placed back in 0.1 M KOH. The experimental results suggest that a physical mixing of the catalytic oxides and ferroelectric materials does not enhance the electrocatalytic performance of the catalysts.

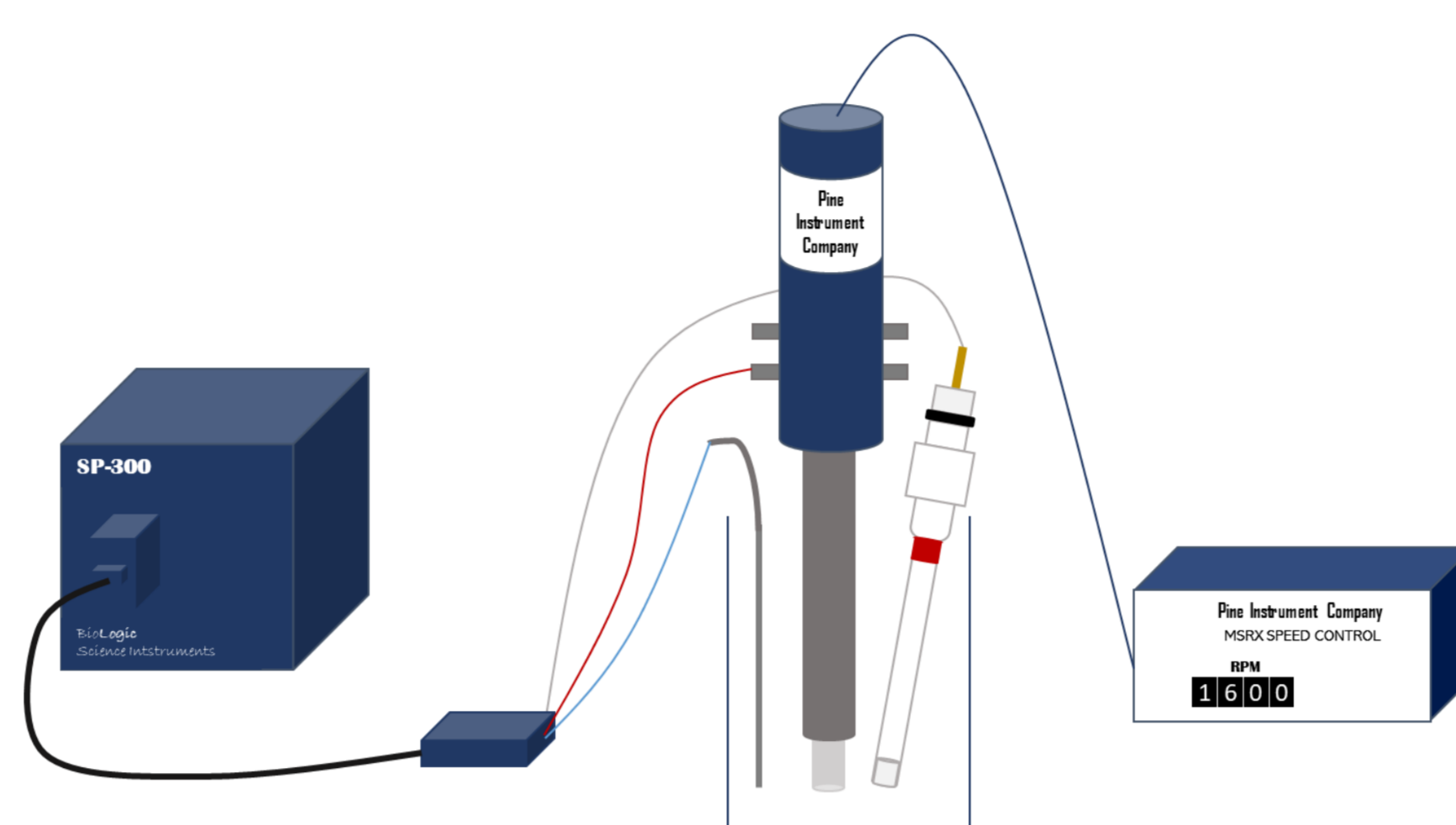
1. Motivation



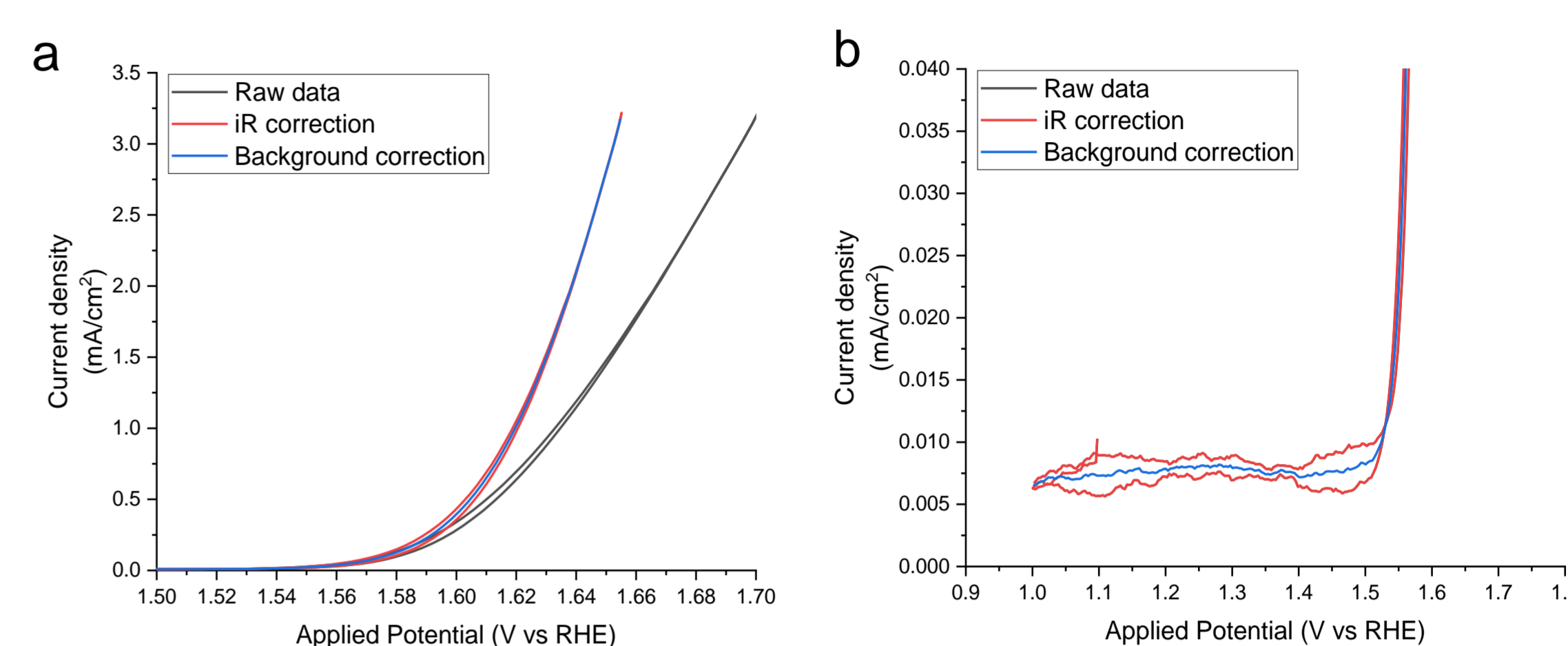
Schematic of water electrolysis in alkaline condition

- The oxygen evolution reaction (OER) at the anode is the sluggish step in water electrolysis [1]
- To improve the activity of Co-based oxide catalysts, we followed two routes:
 - Addition of Fe²⁺ in the electrolyte [2]
 - Physical mixing with ferroelectrics [3]

2. Experimental setup and data correction



Three-electrode setup for electrochemical measurements

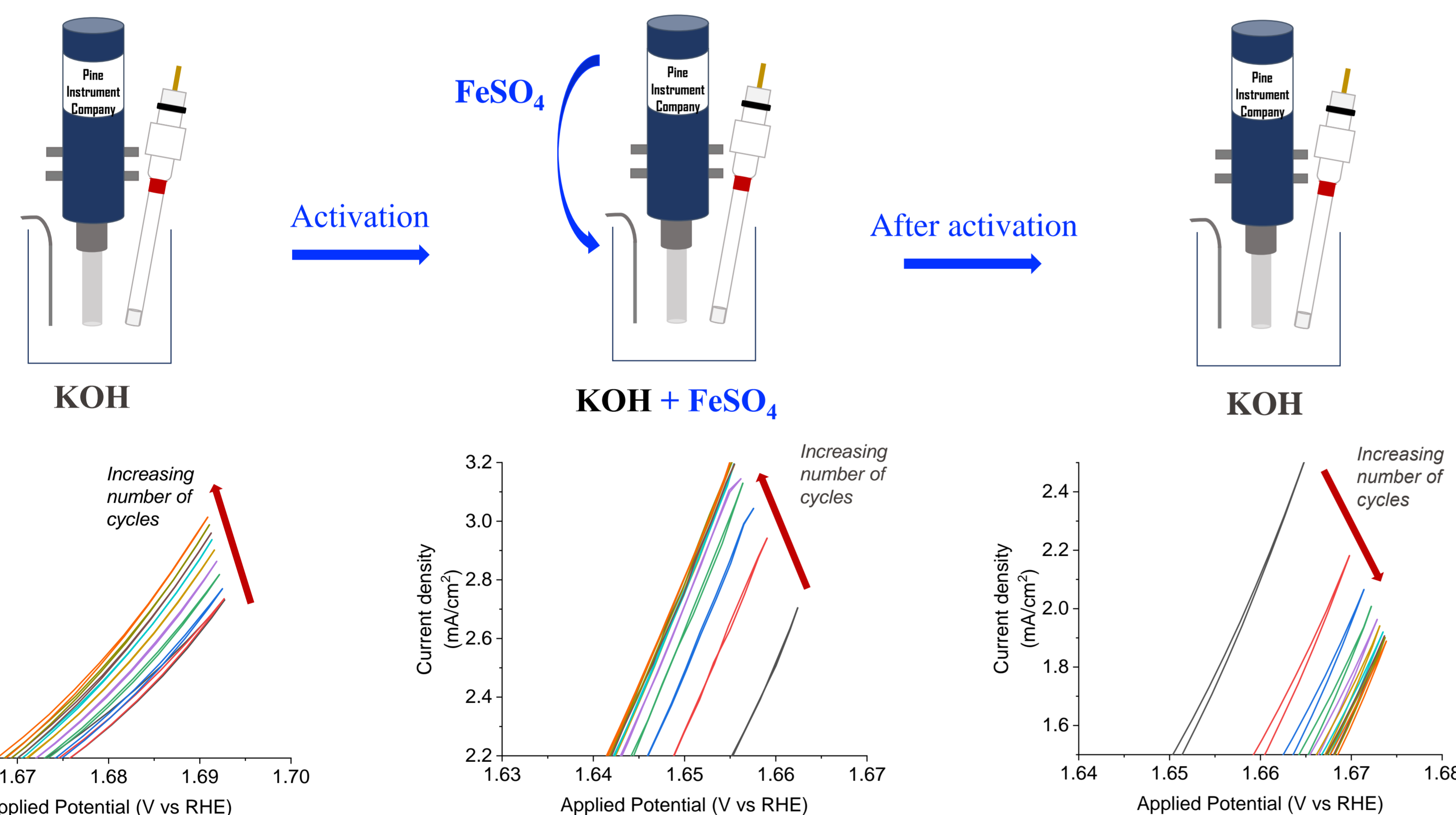


iR correction and background correction in a) OER and b) pre-OER regions

- The catalyst was deposited on working electrode by ink-casting
- Conventional three electrode setup was used for electrochemical impedance spectroscopy (EIS) and for cyclic voltammetry (CV)
- iR correction [4] was conducted to remove the ohmic drop in the electrolyte
- Background correction [4] was performed to cancel out the contribution of the double layer charging current

3. "Activation" process: CoO in KOH + Fe²⁺

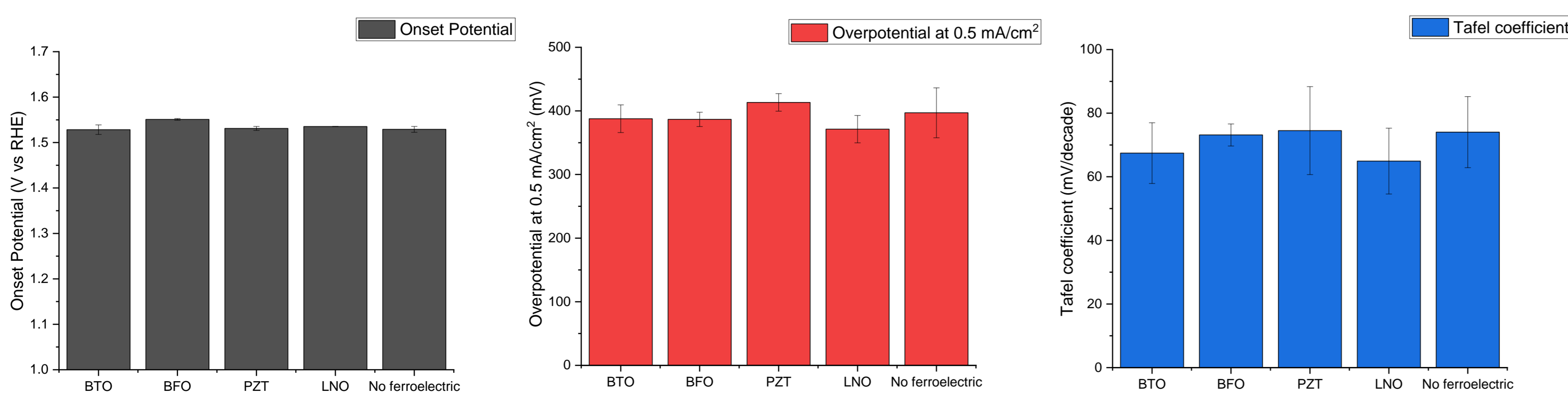
4. Effect of Fe impurities on activity of CoO



CV measurements before, during and after activation

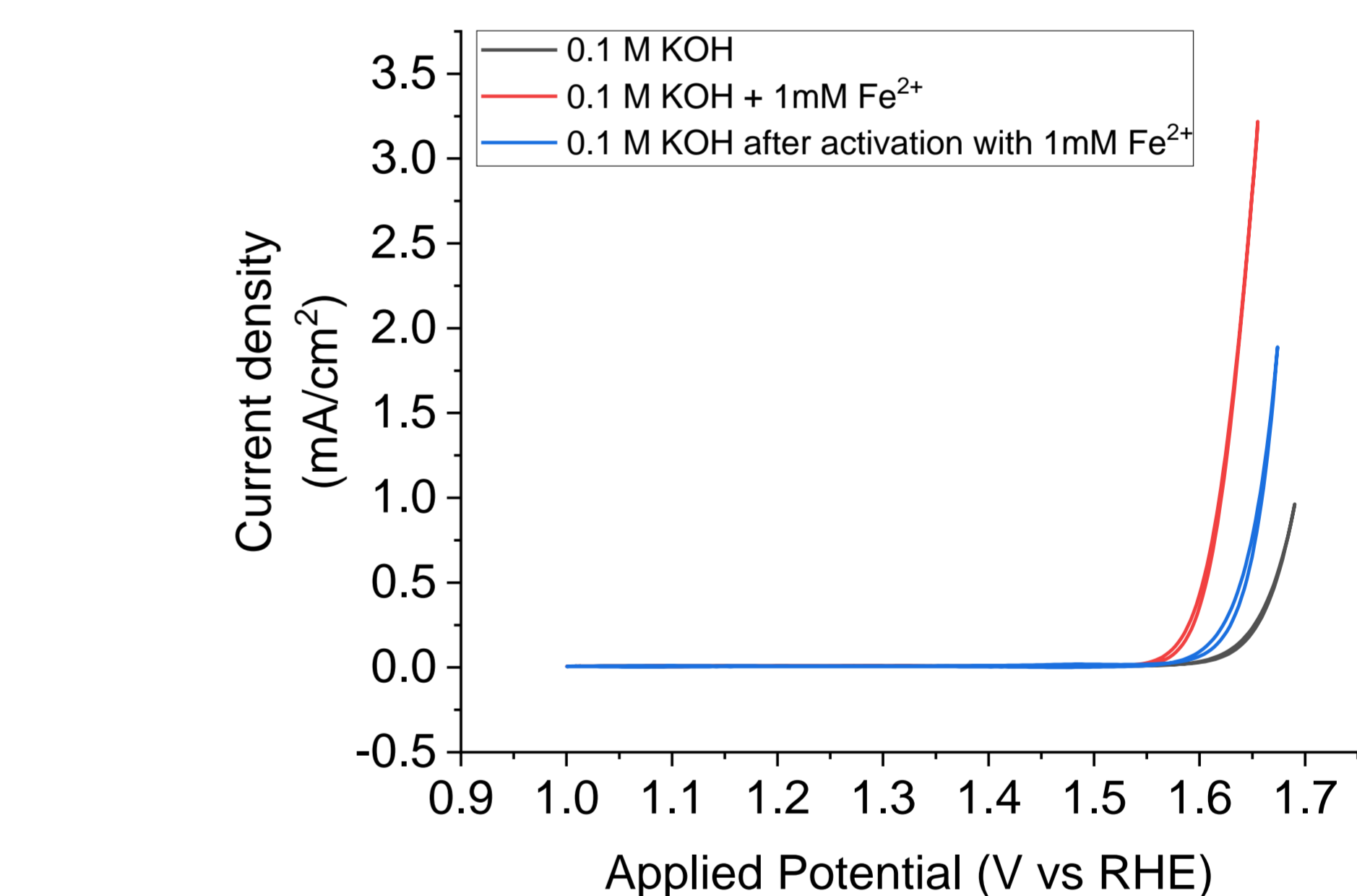
- An "activation" process was designed as following:
 - 10 cycles in KOH => 10 cycles in KOH + 1mM FeSO₄ => 10 cycles in KOH
- The results showed that the activity of CoO improved when cycling in KOH (containing Fe impurities) and when Fe was added intentionally (in KOH + 1mM FeSO₄)
- The convergence of the OER curves after 10 cycles was attributed to surface saturation in Fe

5. Effects of ferroelectrics on activity of Co₃O₄



Onset potential, overpotential at 0.5 mA/cm² and Tafel coefficient of ferroelectrics + Co₃O₄

- Physical mixing with a ratio of 1:10 of ferroelectrics to Co₃O₄ did not have any effect on the catalytic activity attributes



CV before, during and after activation (only the last cycle is plotted)

- Redox peaks in pre-OER region arise from the formation of oxyhydroxide phase just before the OER onset potential
- Addition of FeSO₄ (red curve) significantly enhances the activity but the latter reduces when the electrode is placed back in pure KOH (blue curve)
- It appears that Fe is incorporated into the surface during activation and then it partially releases after activation

6. Conclusions

- Iron impurities in the alkaline electrolyte increase the catalytic activity of Co-based oxides
- The activity can be further improved by intentional addition of iron ions into the solution, however, at a certain point, the incorporation of iron into the surface of the catalyst saturates
- A range of ferroelectric materials were investigated, however, their physical mixing with catalytic particles did not affect the electrocatalytic performance of Co₃O₄

7. References

- [1] Fabbri *et al.* (2018). *ACS Catal.*, 8(10), 9765–9774
- [2] Trotochaud *et al.* (2014). *J. Am. Chem. Soc.* 136, 6744–6753
- [3] Kushwaha *et al.* (2018). *J. Mater. Sci.* 53, 1414–1423
- [4] Wei *et al.* (2019). *Adv. Mater.*, 31(31), 1–24