

Unraveling the effect of Fe in the electrocatalytic oxidation of glucose on Ni(OH)₂ in alkaline media

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Glucose oxidation reaction (GOR) in alkaline media has been intensively studied for its application in biosensors, fuel cells and electrosynthesis of high value products, with Ni being one of the most extensively explored catalysts. It was generally accepted that the GOR on Ni electrodes proceeds through an EC' mechanism in which first, in an electrochemical step, Ni(OH)₂ is oxidized to NiOOH, the latter reacting with glucose in a chemical step to ultimately form gluconate. We have recently challenged this hypothesis by studying GOR on Ni(OH)₂ electrodes by electrochemical techniques, kinetic modeling, *in situ* FTIRS, DEMS and HPLC^{1,2}. We suggest that glucose adsorbs on Ni(OH)₂ sites via C-O bond formation between negatively charged Ni-O⁻ surface species and positively charged carbon atoms of glucose, which causes dissociative glucose adsorption through C1-C2 bond cleavage, and results in the formation of formate and arabinose. Despite this, it remains unclear why the GOR 'onset' potential lies ~0.2 V below the Ni(OH)₂/NiOOH transition. In the urge to understand this, we performed studies of the GOR on Ni(OH)₂ and Ni_{1-x}Fe_x(OH)₂ electrodes through cyclic voltammetry (CV, Figure 1a) and *in situ* FTIRS (Figure 1b-c). Notably, through the incorporation of a second metal, it is possible to observe that not only the GOR 'onset' potential displaces to positive values (along with the shift in Ni(OH)₂/NiOOH transition) but, at a high Fe fraction, the reaction starts at the same potential as the Ni(OH)₂/NiOOH transition. This is further confirmed by the *in situ* FTIRS (Figure 1b-c) study, which reveals that for both Ni(OH)₂ and Ni_{0.85}Fe_{0.15}(OH)₂ the main product detected is formate (with bands at 1350, 1385 and 1580 cm⁻¹). However, gluconate detected at high potentials on Ni(OH)₂ (corresponding band at 1410 cm⁻¹) is not observed on Ni_{0.85}Fe_{0.15}(OH)₂, on which oxalate (a band at 1310 cm⁻¹) instead appears. This leads to the conclusion that the incorporation of Fe in the Ni(OH)₂ structure influences the 'onset' potential and the mechanism of the GOR, possibly due to a decrease in the number of neighboring Ni sites, as will be discussed in the presentation. Moreover, our results suggest that optimizing the Fe/Ni ratio could allow one to selectively produce formate, which is considered a high value-added product.

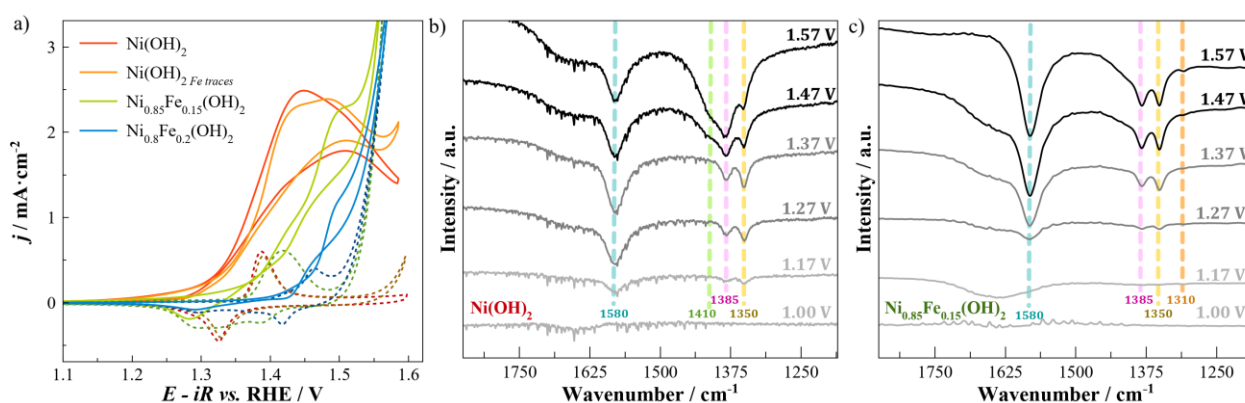


Figure 1: (a) CVs of Ni_{ED}/GC in purified and Fe-containing 0.1 M NaOH under N₂ atmosphere at 25 °C with (solid curves) and without (dashed curves) 5 mM glucose, and FTIR spectra recorded at different potentials applied to (b) Ni(OH)₂ and (c) Ni_{0.85}Fe_{0.15}(OH)₂ electrode in a deaerated 0.1 M NaOH and 5 mM glucose electrolyte.

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References

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2. A. Medrano-Banda, T. Faverge, E. Ginoux, *et al.*, *Electrochimica Acta*, submitted.