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Operando UV-Vis and Raman Spectroscopy Studies of Water Oxidation Catalysis by Nickel Hydroxide and Silk Fibroin

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The combination of electrochemical and spectroscopic studies to investigate electrocatalytic processes allows a deeper understanding of the reaction mechanisms involved. *Operando* Raman and UV-Vis spectroelectrochemical experiments were applied to study the water oxidation, specifically the oxygen evolution reaction (OER), catalyzed by nickel hydroxide and silk fibroin, a protein capable of improving $Ni(OH)_2$ electrochemical activity.[1] Partial charge-transfer in the presence of other metals play an important role in the OER activity of $Ni(OH)_2$, but it's direct observation is limited to electrochemical results.[2] We were able to identify intermediate states on Ni oxidation and correlate it to the charge transfer between Au and Ni. These results represent the first spectral evidence of this effect. Our results also revealed that OER involves a two-step mechanism, where OOH^- formation is the potential-limited step and its conversion to O^-_2 is the rate-determining step. Furthermore, we observed that the charge-transfer effect is directly related to the adsorption forces involved on Ni oxidation and OER, therefore influencing both steps of reaction. Based on these results we propose the mechanism illustrated on Figure 1. that takes in to consideration the effects of charge transfer on adsorption forces of intermediate species. Reproducing the methodology previously proposed[3] we were able to obtain the material's intrinsic turn over frequencies (TOF) and observe the Sabatier behavior. More interestingly, samples in the presence of fibroin exhibited the highest O_2 TOF, with maximum activity of 0.7 s^{-1} in comparison to 0.4 s^{-1} of pure $Ni(OH)_2$, suggesting that the protein modulates the oxygen intermediate species binding strength.

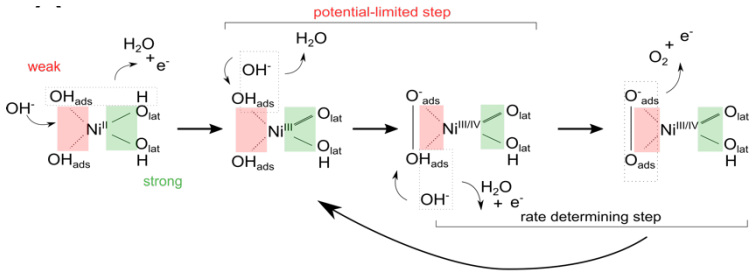

Figure 1 - Schematic representation of the proposed OER mechanism steps and the influence of charge transfer.

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References

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