

## Electrodeposited Nickel-based Electrocatalysts for Oxygen Evolution Reaction (OER)

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Lowering the overpotential required to drive the oxygen evolution reaction (OER) is critical for the development of efficient solar fuels devices. NiO<sub>x</sub> is known as the best earth-abundant metal oxide catalyst for the OER in alkaline media.<sup>1-2</sup> The addition of transitional metals and/or rare earth elements to NiO<sub>x</sub> has been shown to enhance the catalytic activity of the OER through the formation of a spinel, e.g. NiFe<sub>2</sub>O<sub>4</sub>,<sup>3</sup> or a perovskite, e.g. LaNiO<sub>3</sub>,<sup>4</sup> structure. However, the formation of such structures, especially the perovskite-type structure, often requires high-temperature annealing, which limits the application of such catalysts, especially in the incorporation with a photocatalyst in a solar fuel device. Electrodeposition has advantages over other preparation methods, allowing for facile scaling-up, controlled film thickness, and it is accessible to all conductive substrates. Corrigan and Bendert have reported that the electrodeposition of Ni with other metal elements significantly changes the performance of oxygen evolution reaction.<sup>5</sup>

Knowledge of the structure and surface properties of electrodeposited oxide films is essential for understanding the mechanism and electrocatalysts. In alkaline solution, a layer of Ni(OH)<sub>2</sub> is formed immediately and then transformed to NiOOH when a positive potential is applied (Figure 1). Ni(OH)<sub>2</sub> and NiOOH have different structures related to the OER activity.<sup>6</sup> It's widely accepted in the literature that the β-type is the active form for catalysis of the OER.<sup>7</sup> The structural differences of these phases gives rise to the variation of the Ni-O lattice modes, which can be distinguished via Raman or IR spectroscopy at frequencies between 400 and 700 cm<sup>-1</sup> (Figure 2). It's evident in our in-situ Raman study that at the potential where the OER occurs, the β-NiOOH phase related Ni-O vibration was observed on rare earth metal-doped NiO<sub>x</sub>, while a γ-phase was seen on NiO<sub>x</sub> film.

We report here a study of electrodeposited NiO<sub>x</sub> thin films into which rare earth elements (Ce and La) have been incorporated. We find that the addition of rare earth elements enhances the OER activity of NiO<sub>x</sub> but do not require the formation of a perovskite. In situ Raman spectroscopy, X-ray photoelectron spectroscopy, and scanning electron microscopy were used together with electrochemical measurements in order determine the effects of the rare earth additives on the catalyst structure as well as its chemical and physical properties.

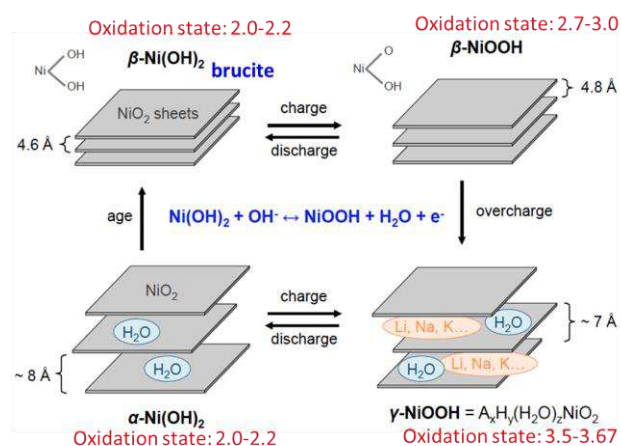


Figure 1. Bode Scheme of Ni(OH)<sub>2</sub> / NiOOH redox couple transformation. Adapted from Ref. 6.

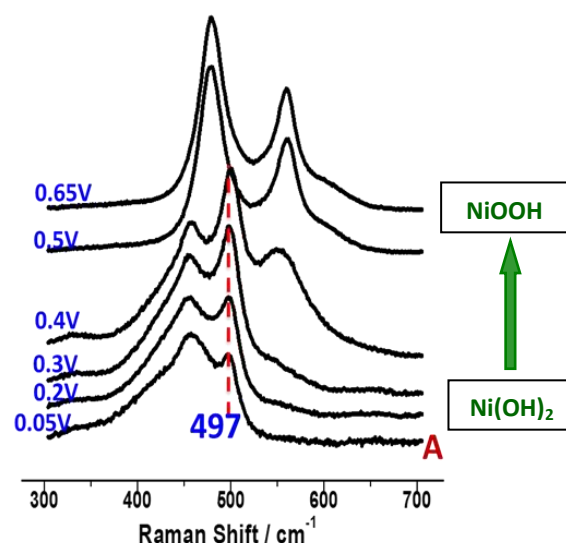


Figure 2. In-situ Raman spectra of an electrodeposited NiO<sub>x</sub> film in 1M KOH with applied electrochemical potentials.

## References

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