

Assessing Electrocatalytic Mechanisms on Ni-based Hydroxides by *In Situ* UV-Vis Spectroscopy

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Nickel-based hydroxides are extensively utilized in electrochemical applications, including electrocatalysis, energy storage, and electrochromic devices.¹ Interestingly, the Ni^{2+} to Ni^{3+} transition can be modulated by doping with additional transition metals. Incorporating Co reduces the potential required for Ni^{2+} oxidation, whereas Fe increases this potential. Here, we compare the electrocatalytic activity of Ni, NiCo, and NiFe hydroxides for oxygen evolution reaction (OER) and ethanol oxidation (EO), employing *in situ* UV-Vis spectroelectrochemistry to indirectly monitor changes in the Ni oxidation state. Transmittance measurements at 456 nm indicate electrode surface darkening concurrent with Ni^{2+} oxidation during both OER and EO (Fig. 1A-C). The onset potential for Ni^{2+} oxidation is correlated with catalytic activity for ethanol oxidation, supporting the proposed mechanism involving ethanol-driven reduction of NiOOH to $\text{Ni}(\text{OH})_2$ (Fig. 1D).^{2,3} Additionally, open-circuit potential (OCP) transient experiments further substantiate this indirect oxidation mechanism, as evidenced by the accelerated OCP decay and increased transmittance in ethanol-containing electrolyte compared to the blank electrolyte (Fig. 1E). These results underscore the effectiveness of *in situ* UV-Vis spectroscopy for elucidating electrocatalytic mechanisms and monitoring catalyst surface oxidation states.

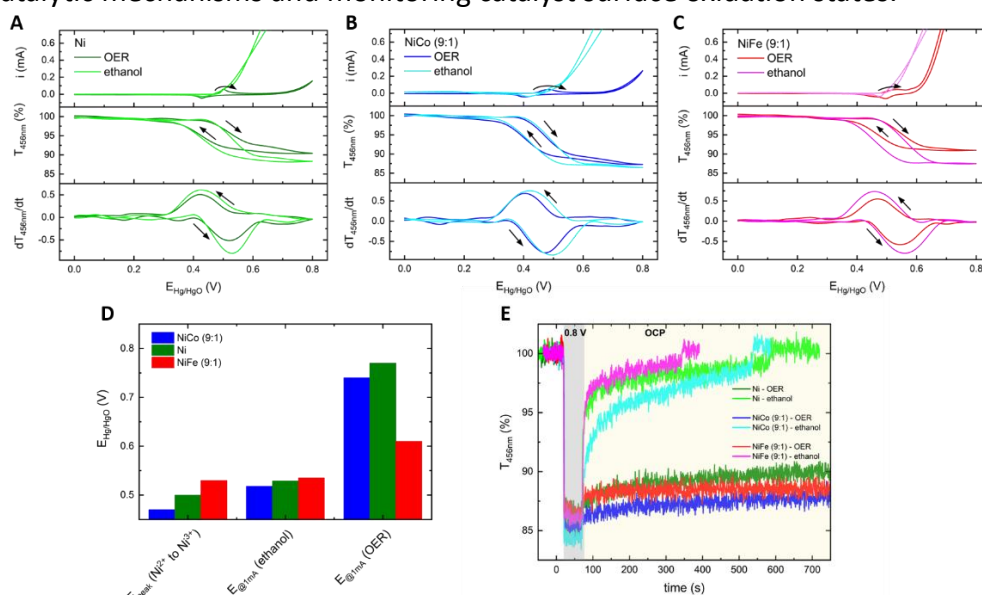


Figure 1. (A–C) UV-Vis transmittance signals at 456 nm coupled with electrochemical characterization of Ni, NiCo, and NiFe during oxygen evolution reaction (OER) and ethanol oxidation (EO) in alkaline medium. (D) Comparison of characteristic potentials highlighting differences in electroactivity among the studied electrocatalysts. (E) Time-resolved transmittance profiles at 456 nm recorded during potential-step experiments (from 0.8 V to open-circuit potential, OCP), illustrating the transient behavior of each electrocatalyst in pure electrolyte (OER conditions) and with ethanol present.

1) *Quim. Nova*, **2010**, 33(10), 2176-2186

2) *J. Am. Chem. Soc.* **2025**, 147, 3925-3930

3) *J. Chem. Soc., Perkin Trans.*, **1972**, 2, 1396-1403