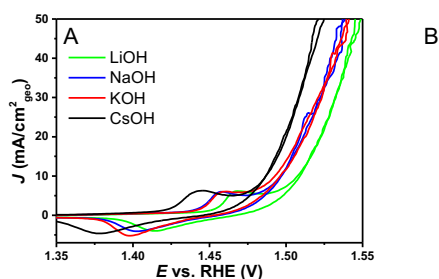


Li⁺ Cations Activate NiFeOOH for Oxygen Evolution in Sodium and Potassium Hydroxide

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Green hydrogen produced by water splitting can replace grey hydrogen produced from natural gas, which is responsible for large amounts of CO₂ emissions. However, the oxygen evolution reaction (OER) is limiting the efficiency of water splitting, as it requires a high overpotential. To reduce the overpotential an active catalyst is required, e.g., NiFeOOH in base. In addition to the optimal catalyst properties, the electrocatalytic activity also depends on the electrolyte composition. Here, we first confirmed the cation-dependent activity trend reported in the literature in the order of CsOH > KOH/NaOH > LiOH (Figure 1A)[1]. However, when small amounts of the least active LiOH are mixed with NaOH (or KOH), at constant pH, it activates NiFeOOH for the OER compared to single-cation electrolytes (Figure 1B)[2]. Figure 1C shows that the origin of activation by Li cations is primarily non-kinetic in nature, as the OER onset for the mixed electrolyte does not change and the Tafel slope at low current density is ~30 mV/dec in both electrolytes[3]. However, the increase of apparent Tafel slope is lower with Li⁺ in the electrolyte, which indicates less non-kinetic limitations at increasing current density. Moreover, the Li activation effect was maintained when the solution was returned to pure NaOH. Based on in-situ X-Ray absorption spectroscopy (XAS) measurements, we show that this reduction of non-kinetic effects is due to increased electrolyte penetration with increased intercalation of (Figure 1D) sodium, (Figure 1E) water and possibly hydroxide with Li⁺ mixed into the electrolyte. This increased intercalation is also maintained when the electrolyte was changed to pure NaOH again. So, in mixed electrolytes distinct cations can have different roles where we postulate that lithium acts as a pore-opener for NiFeOOH LDH, but sodium (or potassium) ions are still required to achieve high OER activity. Therefore, our work shows that different electrolyte ions cooperating to achieve optimal performance can provide a simple and promising strategy towards improved electrocatalytic rates.



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Figure 1. (A) CVs of NiFeOOH in 0.1 M LiOH, NaOH, KOH and CsOH, (B) CVs of NiFeOOH in 0.1 M NaOH and 0.1 M Na₉₀Li₁₀OH, (C) Tafel slope plot in NaOH and Na₉₀Li₁₀OH with less non-kinetic effects in Na₉₀Li₁₀OH compared to NaOH, (D) XAS Na K-edge spectrum of NaOH, Na₉₀Li₁₀OH and NaOH again showing increased intercalation of sodium ions, (E) XAS O K-edge spectrum showing an increased amount of intercalated water and possibly hydroxide.

[1]. A. C. Garcia, et al., *Angew. Chem. Int. ed.*, (2019), 37, 12999. [2]. O. van der Heijden, et al., *Angew. Chem. Int. ed.*, (2024), accepted. [3]. O. van der Heijden, et al., *Angew. Chem. Int. ed.*, (2023), 62, e202216477.