Supplementary Information (SI) for Physical Chemistry Chemical Physics.
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Ammonia Electro-Oxidation on Nickel Hydroxide: Phases, pH and Poisoning

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Supporting information

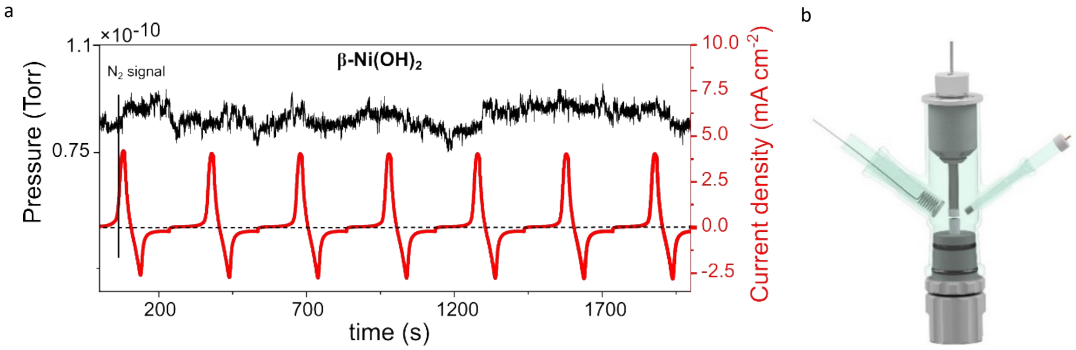

Figure S1: (a) Differential electrochemical mass spectrometry (DEMS) on the less-active β-Ni(OH)$_2$ catalyst, following the N_2 signal produced (black, top) during CV at 5 mV/s from 0.8 V to 1.55 V (red, bottom) with 1 M NH_3 added. Note that the mass loading of this electrode was twice that of the α-Ni(OH)$_2$ in Figure 3, to attempt a better signal to noise ratio, due to lower inherent current of the β-Ni(OH)$_2$ catalyst. The produced N_2 is correlated to the peak onset in the first cycle, even though the correlation becomes delayed relative to the CV peaks at later cycles, due to prolonged and belated bubble release in the thicker electrode layer. (b) Schematic figure of the custom-designed DEMS cell, portraying the MS probe above the glassy carbon electrode, inside the electrolyte.

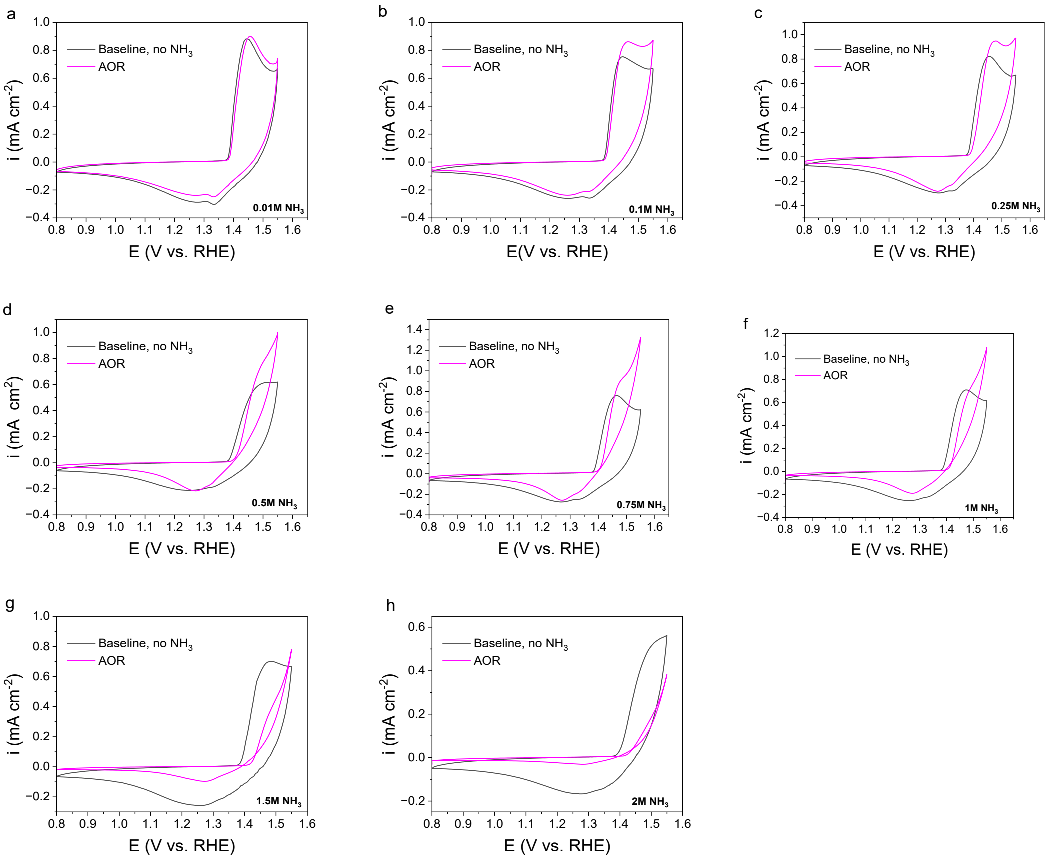

Figure S2: Cyclic voltammograms of α-Ni(OH)$_2$ at the 10th cycle in 1 M KOH + 0.5 M K_2SO_4 without ammonia (black) and the first cycle with ammonia (pink) at ammonia concentrations of: (a) 0.01 M, (b) 0.1 M, (c) 0.25 M (d) 0.5 M, (e) 0.75 M, (f) 1 M , (g) 1.5 M and (h) 2 M.

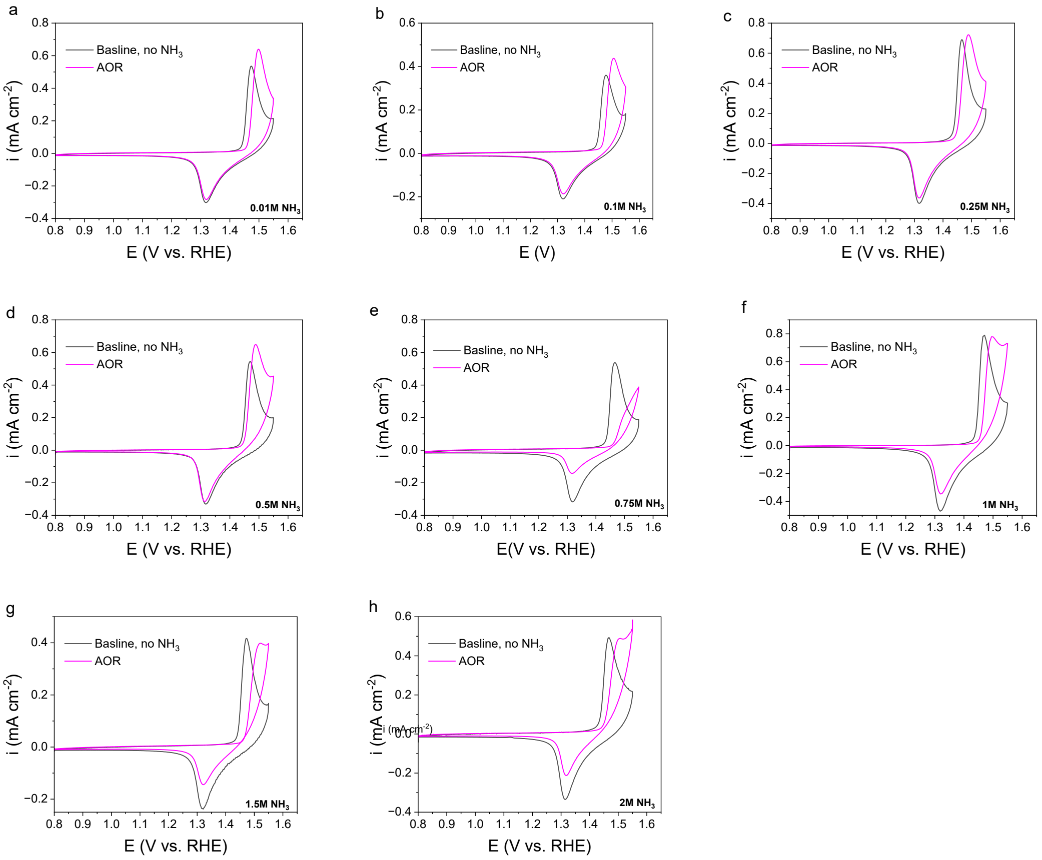

Figure S3: Cyclic voltammograms of β-Ni(OH)$_2$ at the 10th cycle in 1 M KOH + 0.5 M K$_2$SO$_4$ without ammonia (black) and the first cycle with ammonia (pink) at ammonia concentrations of: (a) 0.01 M, (b) 0.1 M, (c) 0.25 M (d) 0.5 M, (e) 0.75 M, (f) 1 M , (g) 1.5 M and (h) 2 M.

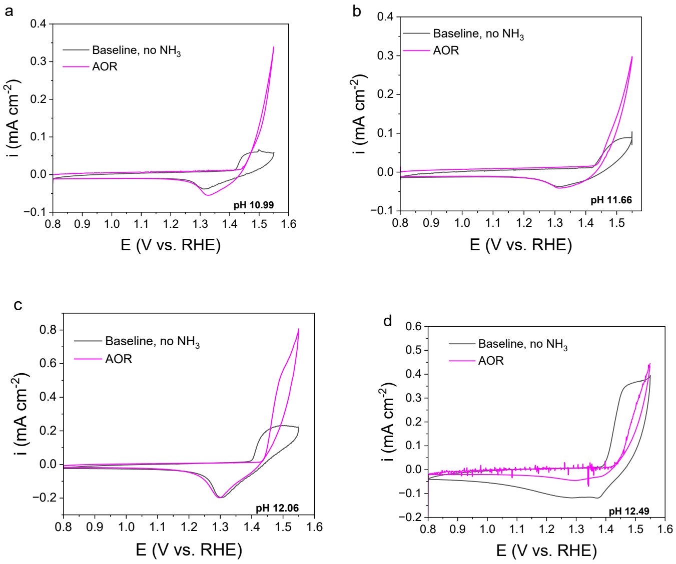

Figure S4 : Cyclic voltammograms of α-Ni(OH)$_2$ at the 10th cycle in 0.5 M K$_2$SO$_4$ without ammonia (black) and the first cycle with 0.5 M ammonia (pink), with KOH concentrations of: (a) 0.001 M, (b) 0.005 M, (c) 0.01 M (d) 0.05 M. The pH values reported are the measured ones.

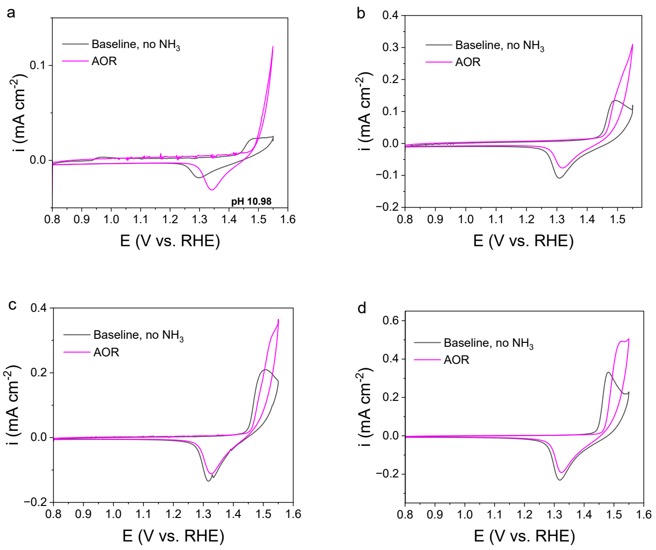

Figure S5: Cyclic voltammograms of β-$Ni(OH)_2$ at the 10th cycle in 0.5 M K_2SO_4 without ammonia (black) and the first cycle with 0.5 M ammonia (pink), with KOH concentrations of: (a) 0.001 M, (b) 0.005 M, (c) 0.01 M (d) 0.05 M. The pH values reported are the measured ones.

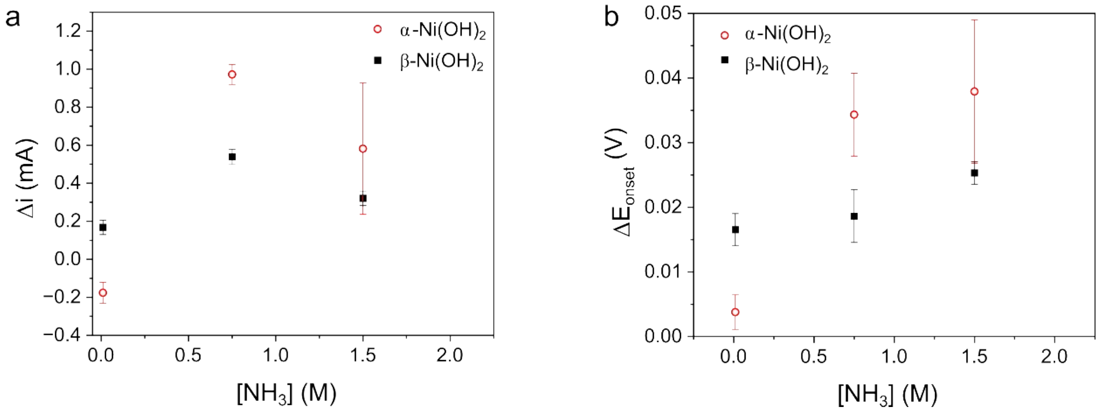

Figure S6 : Trends of AOR in Fe-free electrolyte: (a) The trend of increase/decrease in oxidation current at 1.535V (Δi) , (b) the delay in onset potential (ΔE_{onset}).

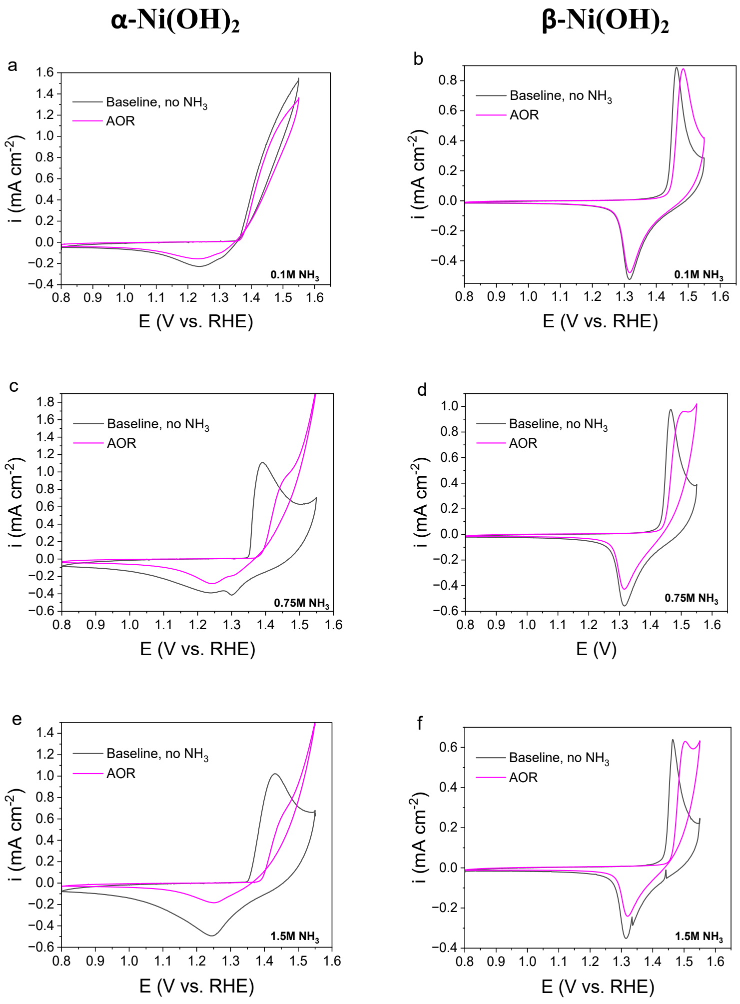

Figure S7: CVs at Fe-free 0.1 M KOH + 0.5 M K_2SO_4 electrolyte. Left: α-$Ni(OH)_2$; right: β-$Ni(OH)_2$. (a,b) 0.1 M, (c,d) 0.75 M (e,f) 1.5 M.

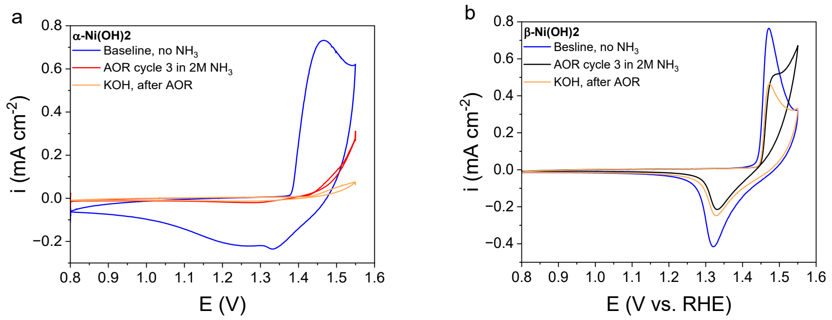

Figure S8: CV of a) α-$Ni(OH)_2$ and (b)β-$Ni(OH)_2$ in an ammonia free-electrolyte (10th cycle, blue), AOR cycling in an electrolyte containing 2M ammonia (3rd cycle) and after the AOR, back in an ammonia free-electrolyte (2nd cycle, orange).

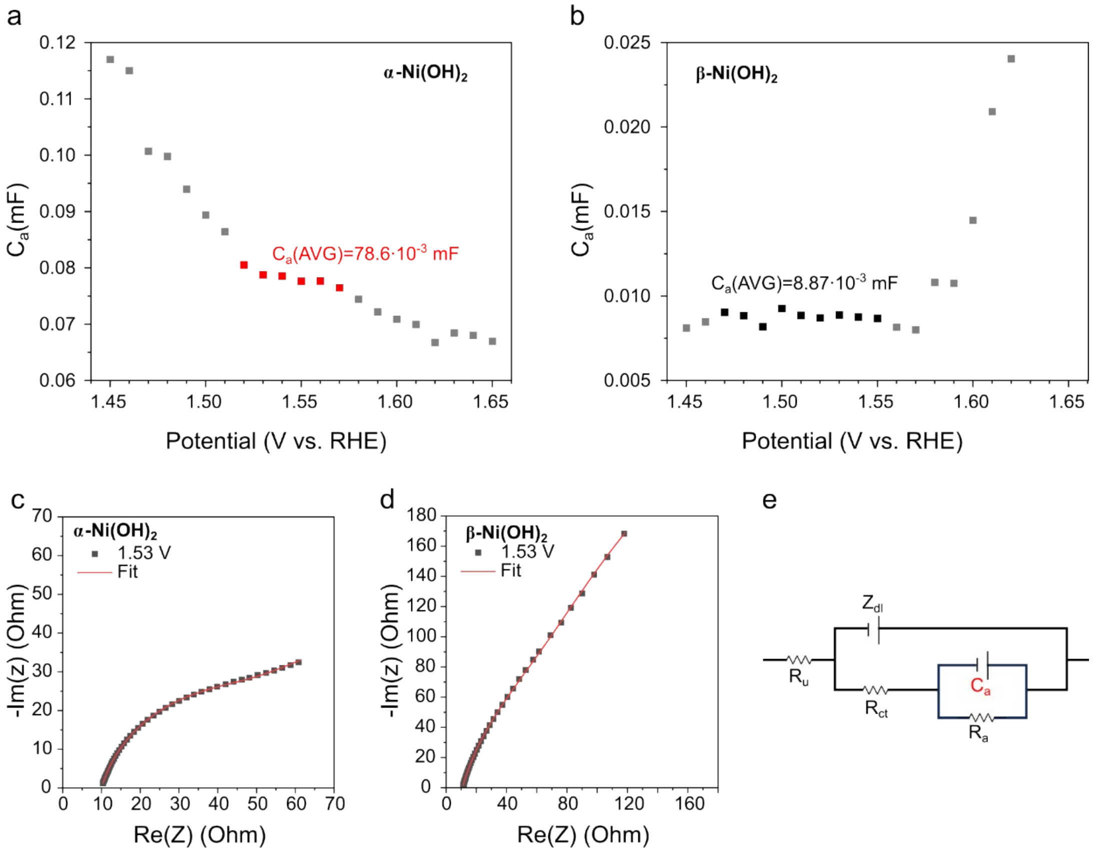

Figure S9: Capacitance of oxygen-based adsorbates (during early stages of the OER), at different potentials for (a) α-Ni(OH)$_2$ and (b) β-Ni(OH)$_2$. Values were obtained from the fitting of EIS spectra to the equivalent circuit in (e).[1] The plateau area represents the values at full cover of the surface by the adsorbates and is used to calculate the capacitance, to estimate the ECSA. EIS spectra (black) recorded at 1.53V with frequency range of 30 KHz to 10 Hz, with an amplitude of 10 mV for (c) α-Ni(OH)$_2$ (d) β-Ni(OH)$_2$ and the fitting (red line) to the equivalent circuit in (e).

References

1 S. Watzele, P. Hauenstein, Y. Liang, S. Xue, J. Fichtner, B. Garlyyev, D. Scieszka, F. Claudel, F. Maillard and A. S. Bandarenka, Determination of Electroactive Surface Area of Ni-, Co-, Fe-, and Ir-Based Oxide Electrocatalysts, *ACS Catal.*, 2019, **9**, 9222–9230.