Electro-Tuned Catalysts: Voltage-Controlled Activity Selection of Bimetallic Exsolution Particles

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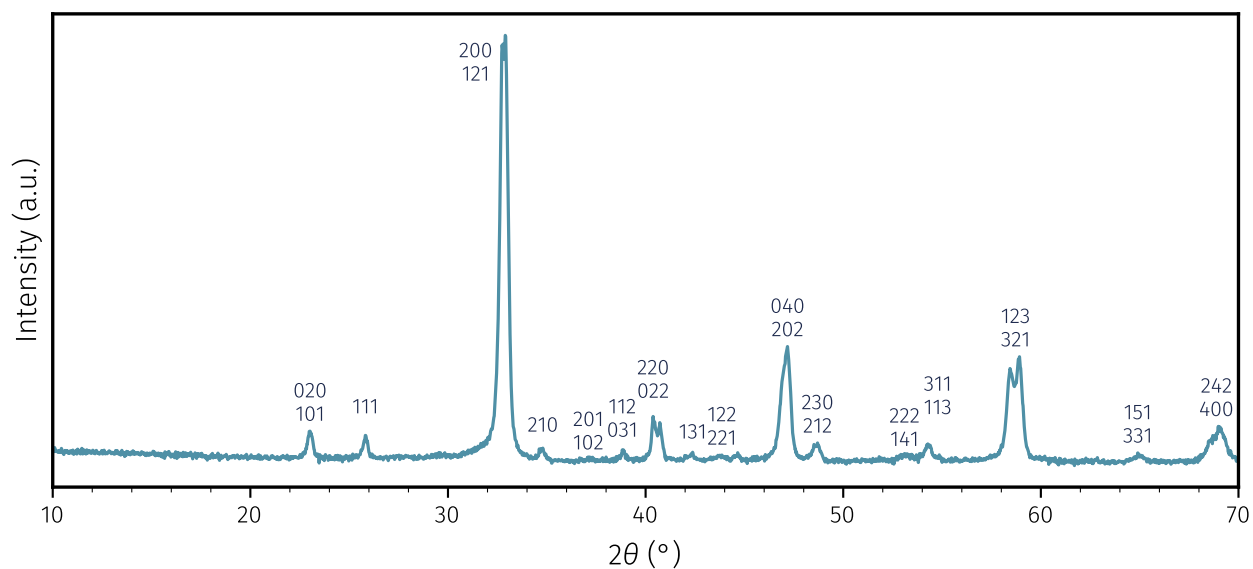
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Supporting Information

Figure S1: XRD pattern of the NCFNi target with (hkl) indices corresponding to orthorhombic, Pnma, space group # 62
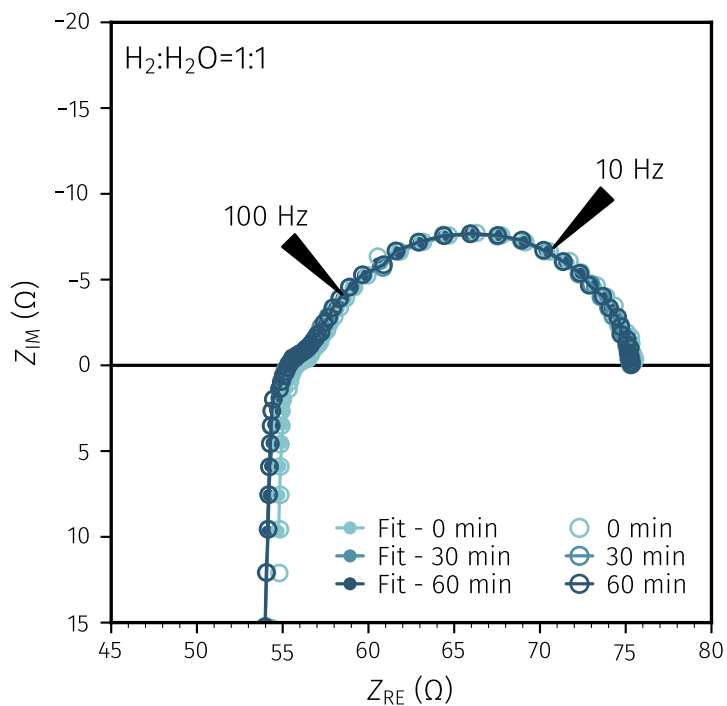

Figure S2: Exemplary impedance spectra of NCFNi at 600 °C in H_2:H_2O 1:1 right after heating (0 min), in between (30 min) and at the end 60 min of the 1 h long equilibration period before the start of the DC measurements.
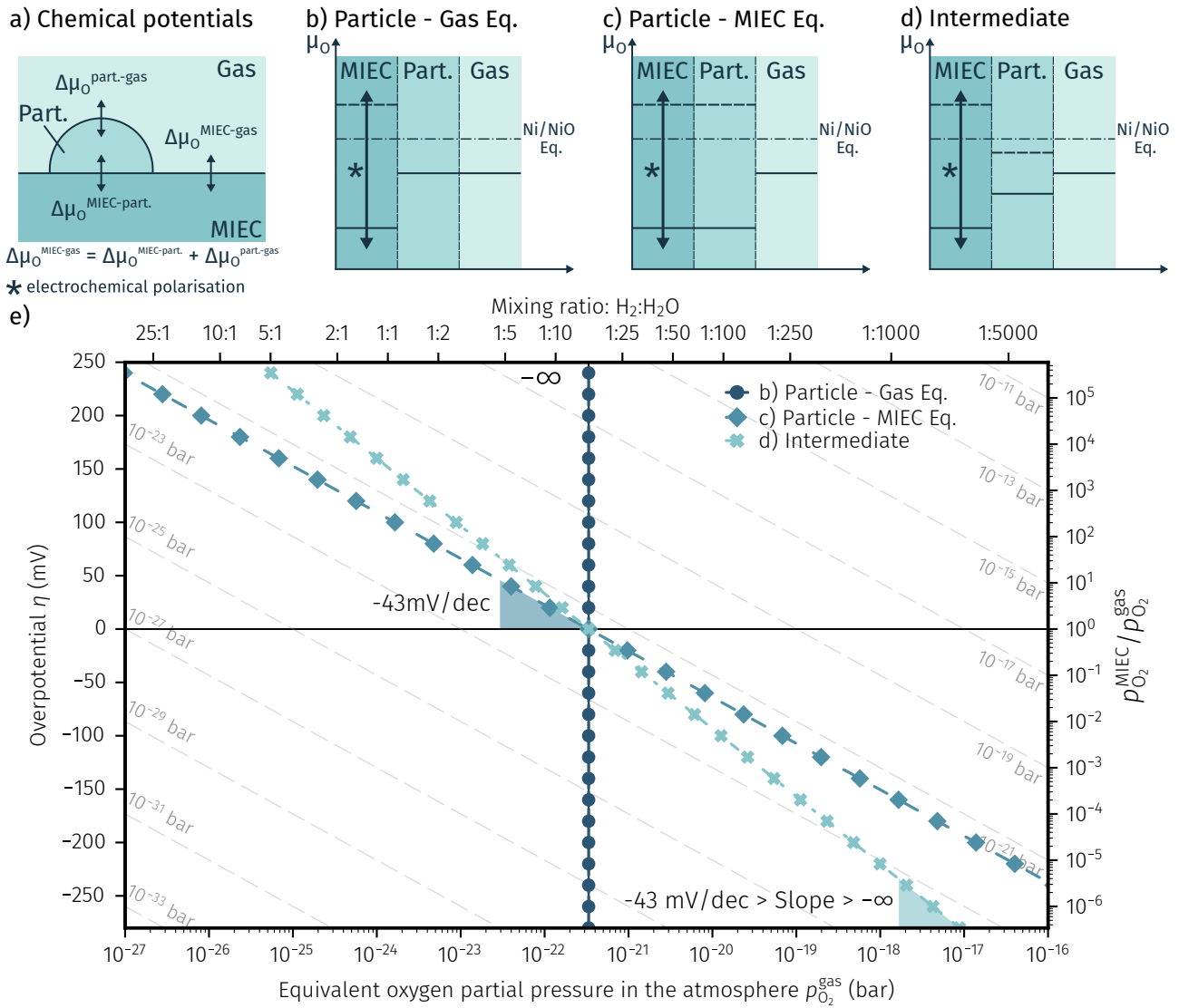
FIGURE S3: Adapted to Ni^0/NiO from our previous study for Fe^0/FeO^1: a) Sketch of all gradients in the oxygen chemical potential $\Delta\mu_O$ of the involved phases. b-d) Three different possibilities for the switching behaviour where either b) $\Delta\mu_O^{MIEC-gas} \approx \Delta\mu_O^{MIEC-part.}$ or c) $\Delta\mu_O^{MIEC-gas} \approx \Delta\mu_O^{part.-gas}$ applies as well as an d) intermediate one with both, MIEC and gas, affecting the particle. e) Resulting Ni/NiO equilibria for all three cases shown in a semilogarithmic plot of the overpotential η at the working electrode versus the equivalent oxygen partial pressure $p_{O_2}^{gas}$ in the atmosphere. The dashed lines represent the isobars of $p_{O_2}^{MIEC}$.
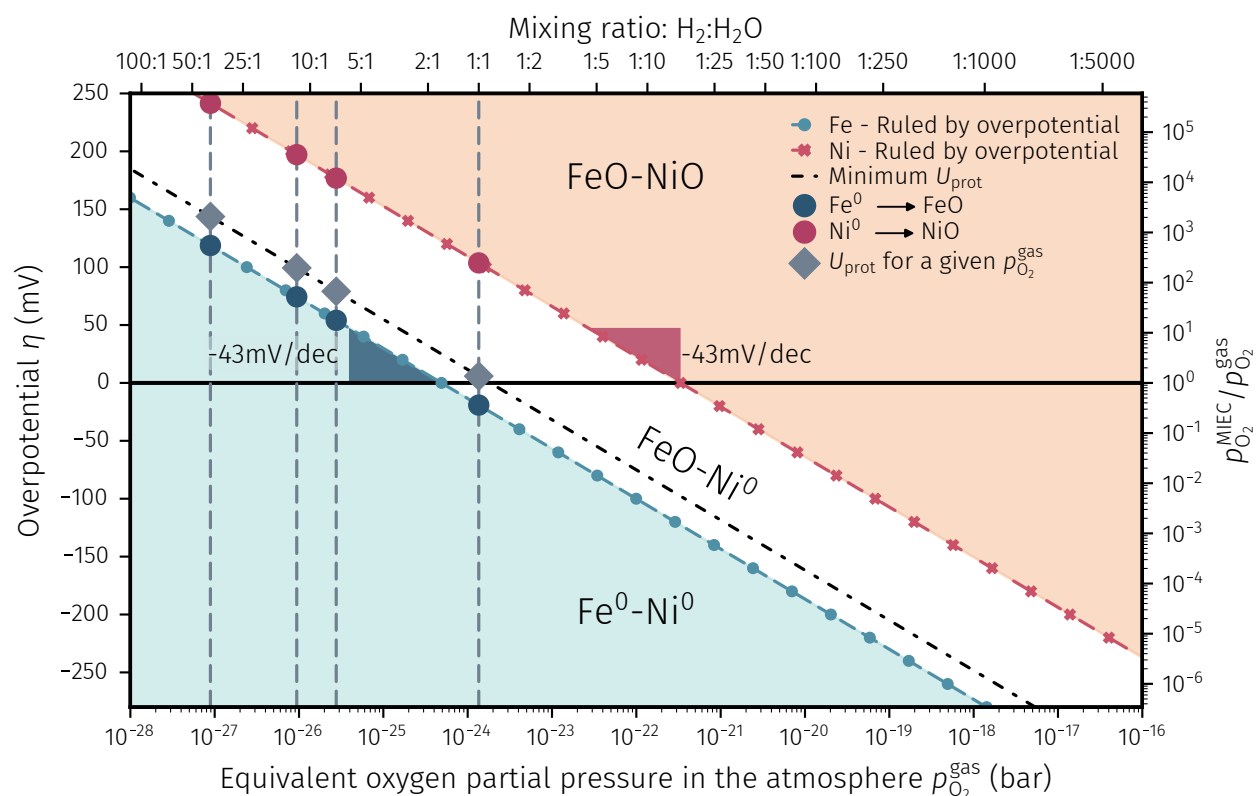
FIGURE S4: Semilogarithmic of the overpotential η at the working electrode versus the equivalent oxygen partial pressure $p_{O_2}^{gas}$ in the atmosphere. If the oxidation state of exsolved iron and nickel particles is mainly governed by the electrochemical reaction, it is possible to distinguish between three distinct segments: Fe^0-Ni^0 (light teal), $FeO-Ni^0$ (white) and $FeO-NiO$ (orange). The corresponding working atmospheres in Fig. 4 are depicted as grey dashed lines and the dark teal/red dots mark the overpotential values where iron/nickel metal transition to their respective oxides. The protection voltage U_{prot} for a given atmosphere (grey diamonds) was chosen by shifting the Fe^0-FeO equilibrium line 25 mV up (dot-dashed black line) and thus preventing Fe^0 from ever being the more stable surface state.
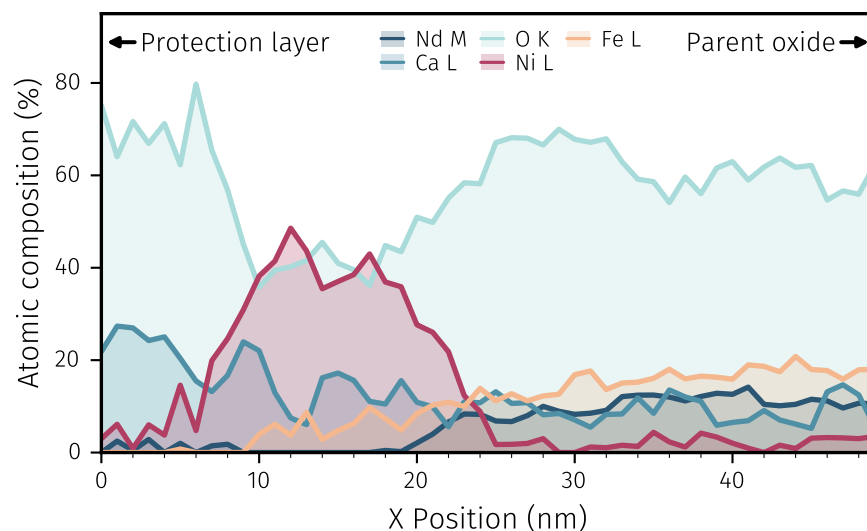

FIGURE S5: Atomic compositions of all main components (Nd, O, Ca, Ni, Fe) as determined by an EELS line scan of a pristine *in situ* sample ranging from the protective layer through the surface particle to the parent oxide. A clear accumulation of Ni between 6 nm and 24 nm is recognisable.

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References

(1) H. Summerer, A. Nenning, C. Rameshan and A. K. Opitz, *EES Catalysis*, 2023, **1**, 274–289.