Supporting Information

Enhanced Electroreduction of CO₂ by Ni–N–C Catalysts from the Interplay Between Valency and Local Coordination Symmetry

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Fig. S1 DFT-calculated geometry of the CO$_2$ adsorption step on the Ni$^{2+}$ sites. Each simulation cell had an excess charge corresponding to -2.0 e, and the potentials versus SHE ($V_{SHE}$) corresponding to the excess charge were specified.
**Fig. S2** Change of partial charges on the Ni center (blue) and C atom of the CO$_2$ (grey) depending on the applied potential $U_{\text{appl}}$. No charge transfer is observed between Ni$^{2+}$ and CO$_2$. 
Fig. S3 Grand-canonical energy profiles versus SHE (first row) and RHE (second row, at pH = 6.8) of the CO$_2$, COOH, and CO intermediates adsorbed on the Ni–N$_4$ system.
**Fig. S4** Grand-canonical energy profiles versus SHE (first row) and RHE (second row, at pH = 6.8) of the CO$_2$, COOH, and CO intermediates adsorbed on the Ni–N$_3$O system.
Fig. S5 Grand-canonical energy profiles versus SHE (first row) and RHE (second row, at pH = 6.8) of the CO$_2$, COOH, and CO intermediates adsorbed on the Ni–N$_3$V system.
Fig. S6 Grand-canonical energy profiles versus RHE (pH = 6.8) of Ni–N₄, Ni–N₃O, and Ni–N₃V systems with two different Ni oxidation states (Ni²⁺ and Ni¹⁺).
Fig. S7 Change of local spin ($S$) at the Ni$^{1+}$ center for Ni–N$_4$ (blue), Ni–N$_3$O (coral), and Ni–N$_3$V (green) systems with RHE (pH = 6.8).
The grey, blue, red, light-green and cyan spheres represent carbon, nitrogen, oxygen, nickel and hydrogen atoms, respectively. The adsorption energy ($\Delta E_{ads}$) of each adsorbate are computed as the following steps: $\Delta E_{ads,H} = E(H-Ni-Ni_3V) - E(Ni-Ni_3V) - \frac{1}{2}E(H_2)$, $\Delta E_{ads,OH} = E(OH-Ni-Ni_3V) - E(Ni-Ni_3V) - E(H_2O) + \frac{1}{2}E(H_2)$, and $\Delta E_{ads,H_2O} = E(H_2O-Ni-Ni_3V) - E(Ni-Ni_3V) - E(H_2O)$. Note that the $\Delta E_{ads}$ does not include an entropic contribution. For example, a dramatic entropic cost is expected for the binding of liquid water ($S_{wat(liq.)} = 69.9 \text{ J K}^{-1} \text{ mol}^{-1}$, converting into the free energy cost of 0.22 eV at 300 K).