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Quantum chemical studies of redox properties and catalytic mechanism of a four-center iron CO₂ reduction electrocatalyst

The CO₂ reduction electrocatalyst [Fe₄N(CO)₁₂]⁻ (abbrev. **1**⁻) reduces CO₂ to HCO₂⁻ in a two-electron, one-proton catalytic cycle. Here we employ *ab initio* calculations to estimate the first two redox potentials of **1**⁻ and explore the pathway of the main catalytic mechanism and a side-reaction involving CO dissociation from the catalyst. Using the BP86 density functional approximation, the redox potentials were computed with a root mean squared error of 0.15 V with respect to experiment. High-temperature Born-Oppenheimer molecular dynamics was employed to discover the elementary steps of the catalytic mechanism and inactivation mechanism. A blind test of the predicted structure of the inactivation product, [Fe₄N(CO)₁₁]³⁻, resulted in a 0.13 Å RMSD from the experimental crystal structure, lending confidence to the predictive power of the method. Multireference CASSCF calculations are used to check the assumptions of DFT approximations used to obtain the majority of the results.