

Title: Atomically dispersed Fe³⁺ sites catalyze efficient CO₂ electroreduction to CO

Abstract: Currently the most active electrocatalysts for the conversion of CO₂ to CO are gold-based nanomaterials, whereas non-precious metal catalysts have shown low to modest activity. Here we report a catalyst of dispersed single-atom iron sites that produces CO at an overpotential as low as 80 mV. Partial current density reaches 94 mA·cm⁻² at an overpotential of 340 mV. Operando x-ray absorption spectroscopy revealed the active sites to be discrete Fe³⁺ ions, coordinated to pyrrolic N atoms of the N-doped carbon support, that maintain their +3 oxidation state during electrocatalysis, probably through electronic coupling to the conductive carbon support. Electrochemical data suggest the Fe³⁺ sites derive their superior activity from faster CO₂ adsorption and weaker CO adsorption than conventional Fe²⁺ sites.

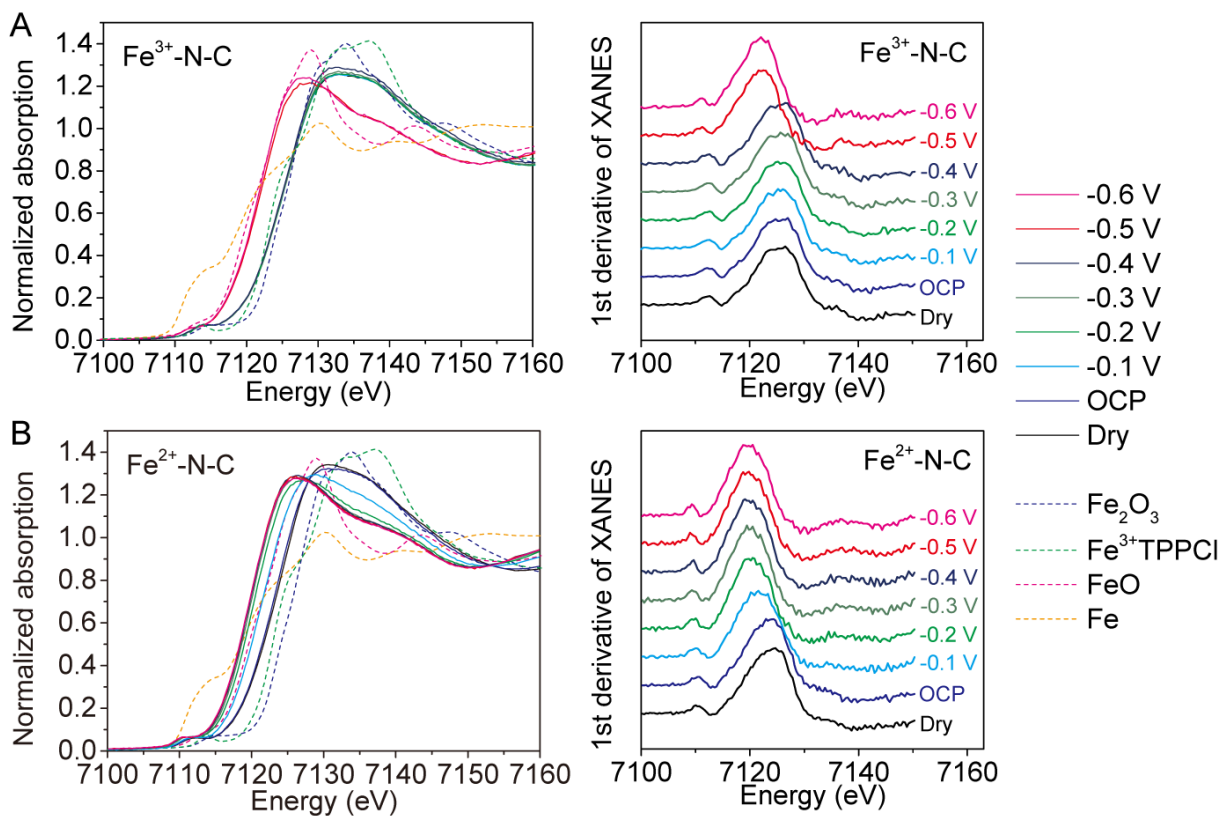


Figure . Operando XAS characterization. Fe K-edge XANES spectra (left) and the 1st derivative of the spectra (right) of (A) Fe³⁺-N-C and (B) Fe²⁺-N-C as dry powder (black), and loaded on glassy carbon electrodes at open circuit potential (OCP, blue), -0.1 V (light blue), -0.2 V (green), -0.3 V (dark green), -0.4 V (dark blue), -0.5 V (red) and -0.6 V (pink) vs RHE, with the spectra of Fe₂O₃ (blue dashed), Fe³⁺TPPCL (green dashed), FeO (pink dashed) and Fe foil (orange dashed) as references.