

Reply to: On the role of metal cations in CO₂ electrocatalytic reduction

Original

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1 Reply to: “On the role of metal cations in CO₂ electroreduction reduction”

2
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10 11 Supplementary Information

12 Supplementary Methods

13 Density functional theory (DFT) simulations were carried out through the Vienna Ab Initio
14 Simulation Package(VASP).^{1,2} We chose the PBE density functional (ref 3) including dispersion
15 through the DFT-D2 method,^{4,5} with our reparametrized C₆ coefficients.⁶ Inner electrons were
16 represented by PAW pseudopotentials^{7,8} and the mono-electronic states for the valence electrons
17 were expanded as plane waves with a kinetic energy cutoff of 450 eV. We employed a 4-layer
18 thick Au(111) (3×3) supercell, with the two innermost Au layers fixed to mimic the bulk and 3
19 H₂O molecules within the solvation layer. A vacuum thickness of around 8 Å vacuum was included
20 beyond the outermost H₂O molecule. A K⁺ was inserted within the solvation layer to assess the
21 “with metal cation” case (see Fig.1a), while no cation was present in the system “without metal
22 cation” (Fig. 1c). To model the case “with metal cation” but “no excess electron”, we removed one
23 hydrogen from one H₂O molecule (Fig. 1b), leading to a charge balanced cell with one K⁺ and one
24 OH⁻. To compute activation angle α (Fig. 1d,e) and Bader charge q (Fig. 1f,g) of the CO₂ unit, we
25 carried out a ionic optimization of the overall system: Au surface, H₂O molecules, cation (if
26 present), and a CO₂ molecule initially adsorbed on the surface and let free to move. Since K⁺, CO₂,
27 and the explicit solvation layer were placed only on one side of the slab, we applied an additional
28 dipole correction to remove spurious contributions arising from the asymmetric slab model.⁹

29 To assess the role of explicit electrostatic effects on CO₂ activation, we applied different intensities
30 of electric field (\vec{E}_{EDL}) through a dipole correction (refs. 6,10): -0.2 V \AA^{-1} , -0.4 V \AA^{-1} , -0.6 V \AA^{-1}
31 ¹. Considering a potential of zero charge (U_{PZC}) for polycrystalline gold of +0.2 V vs SHE (ref.
32 13) and an electrical double layer thickness (d_{EDL}) of 3 Å,^{11,12} such electric field intensities
33 correspond roughly to values of electric potential of -0.4 V vs. SHE , -1.0 V vs. SHE , and -1.6 V
34 vs. SHE respectively, Supporting Equation 1.

$$35 \quad U \text{ (vs. SHE)} = U_{PZC} + \vec{E}_{EDL} \cdot d_{EDL} \quad (1)$$

36 Supplementary References

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