

Assessing Speech Model Performance: A Subgroup Perspective

Original

Assessing Speech Model Performance: A Subgroup Perspective / Koudounas, Alkis; Pastor, Eliana; Baralis, Elena. - 3741:(2024), pp. 101-111. (Intervento presentato al convegno SEBD 2024: 32nd Symposium on Advanced Database System tenutosi a Villasimius, Sardinia (IT) nel 23-26 June, 2024).

Availability:

This version is available at: 11583/2992889 since: 2024-09-29T16:49:00Z

Publisher:

CEUR Workshop Proceedings

Published

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Origin of the Selective Electroreduction of Carbon Dioxide to Formate by Chalcogen Modified Copper

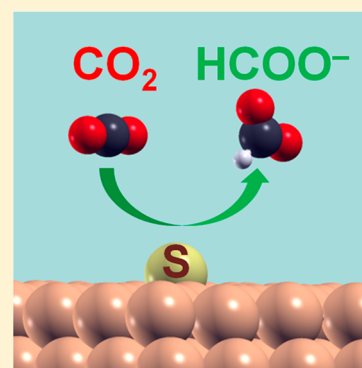
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Supporting Information

ABSTRACT: The electrochemical reduction of atmospheric CO₂ by renewable electricity opens new routes to synthesize fuels and chemicals, but more selective and efficient catalysts are needed. Herein, by combining experimental and first-principles studies, we explain why chalcogen modified copper catalysts are selective toward formate as the only carbon product. On the unmodified copper, adsorbed CO₂ is the key intermediate, yielding carbon monoxide and formate as carbon products. On sulfur, selenium, or tellurium modified copper, chalcogen atoms are present on the surface and actively participate in the reaction, either by transferring a hydride or by tethering CO₂ thus suppressing the formation of CO. These results highlight the active role of chalcogen centers via chemical steps and point toward basicity as the key descriptor for the stability and selectivity of these catalysts.



The electrochemical CO₂ reduction reaction (eCO₂RR) driven by renewable electricity can mimic the natural photosynthetic cycle and thus is a key element to meet climate targets.^{1,2} In spite of the populated catalogue of catalysts identified, with carbon monoxide, hydrocarbons, and formate as more frequently reported products,^{3–5} this technology remains at an incipient stage as existing materials are suboptimal regarding activity, selectivity, stability, and scalability for practical purposes.⁶ These complications are related to the lack of robust structure-performance relationships, limited by (i) the complexity of the reaction network, (ii) the challenging application of *in situ* studies in electrochemical environments,⁷ and (iii) the simplifications in the models representing electrochemical processes at the molecular scale.

Theoretical attempts to explain the eCO₂RR over well-defined transition metal surfaces^{8–11} combine Density Functional Theory (DFT) and the computational hydrogen electrode (CHE) approach.^{10,12,13} This strategy allows for solvent contributions to be introduced through approximate models,^{14–16} while electric potential and pH effects can be added as linear corrections.^{16,17} Neither the effect of the applied potential on adsorption nor the impact of pH on selectivity (known to control methane and ethylene formation^{18–22}) are fully included in the simulations, although significant advances have been made lately (see ref 23 and references therein). On clean metals, the reaction starts with the adsorption of CO₂, followed by a succession of proton-coupled electron transfers (PCETs),¹⁷ although decoupled

steps have also been proposed;^{17,24,25} see Scheme 1. The DFT-CHE model predicts medium-to-high overpotentials for eCO₂RR and describes selectivity trends observed for C₁ and C₂ products on different metals and surface orientations.^{8,10,17,23} Carbon monoxide is the key intermediate for most eCO₂RR products, with the exception of formate. The linear scaling relationships (LSRs) between the binding energies of different intermediates on transition metals²⁶ impose constraints, limiting the optimization of metallic catalysts or alloys.^{8,9,27} As we show in the present letter, surface modifiers can break LSRs by adding chemical (potential-independent) steps, thus improving the selectivity control.

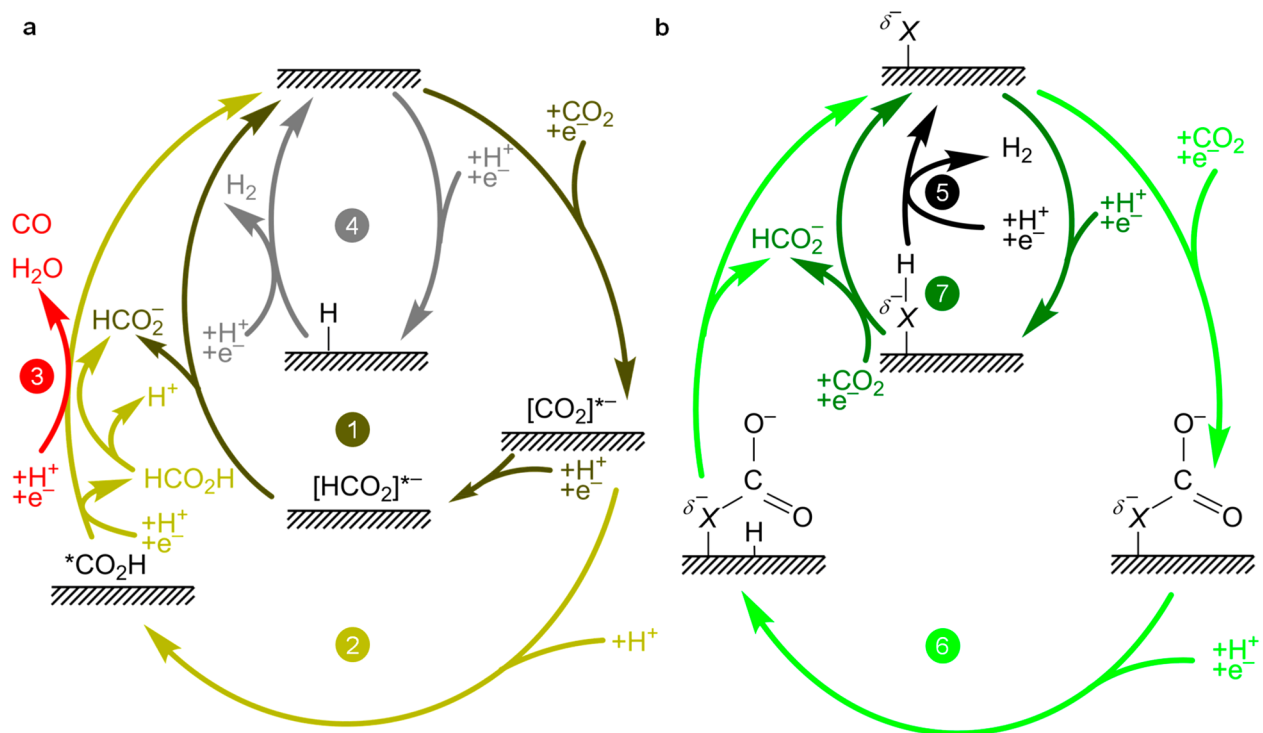
Copper is unique in that it reduces CO₂ to compounds demanding more than two electron transfer steps with reasonable selectivity.^{2,4} Recent studies have pointed out that p-block elements^{5,24,29–34} can act as modifiers and that tiny amounts of sulfur^{29,30} and selenium²⁹ switch the eCO₂RR selectivity toward formate, otherwise a minor product, while largely inhibiting the undesired hydrogen evolution reaction (HER). The aim of our work is to unravel the mechanistic origin of the selectivity switch reported for the sulfur-modified copper catalyst, Cu–S, and illustrate if the effect persists for other chalcogenides. To this end, we have performed DFT

Received: October 21, 2018

Accepted: December 11, 2018

Published: December 11, 2018

Scheme 1. (a) Simplified Reaction Mechanisms for the eCO₂RR toward Formate/Formic Acid (Paths 1–2, in Olive and Yellow) and CO (Path 3, Red), and for the Parasitic HER (Path 4, Gray) on Clean Cu;^{28, a} (b) Reactions Mechanisms in Which the Chalcogens Act as Active Centers: CO₂ Tethering (Path 6, Light Green), Heyrovsky-like Hydride Shuttle (Path 7, Dark Green), and the HER (Path 5, Black).^b



^aThe full mechanism is presented in Scheme S1. ^bThe charge of an adsorbed chalcogen, δ^- , depends on the external potential U .

simulations for the systems including O, S, Se, and Te as dopants and compared them to the experimental systems. The true state of O-containing samples is difficult to assess (see below).

We synthesized three copper catalysts from its oxidic Cu₂O phase, modified by sulfur (Cu–S), selenium (Cu–Se), or tellurium (Cu–Te) via a solvothermal route.³⁰ The fresh samples exhibited micro-sized aggregates containing nano-metric particles (Figures S1–S4) with a chalcogen content of 1–3 at. % relative to copper (Table 1). The chalcogens were uniformly distributed, as shown by energy dispersive X-ray spectroscopy coupled to scanning electron microscopy (EDX-SEM, Figure 1a). As for the crystalline structures, Cu–S, Cu–Se, and Cu–Te exhibited X-ray diffraction patterns assigned to Cu₂O accompanied by traces of the metallic Cu phase (Figure S2), likely due to the rapid formation of a native oxide layer

Table 1. Double-Layer Capacitance, C_{DL} in mF cm⁻², and XPS- or EDX-Measured Chalcogen Elemental Content, before and after Electrocatalytic Testing, in Atomic Percentage Relative to Cu^a

	C_{DL}	relative content			
		XPS _{fresh}	XPS _{used}	EDX _{fresh}	EDX _{used}
Cu– \emptyset	2.9	78.2 ± 0.1	77.9 ± 0.1	45.8	48.7
Cu–S	1.4	3.4 ± 1.0	1.1 ± 1.1	0.6	0.6
Cu–Se	2.3	2.3 ± 2.2	1.5 ± 1.4	0.2	n.q. ^b
Cu–Te	2.8	n.q. ^b	10.0 ± 8.2	1.1	0.7

^aFor the Cu₂O-derived Cu catalyst (Cu– \emptyset), the percentages refer to oxygen. ^bn.q. nonquantifiable.

over the metallic copper particles when exposed to air.³³ The introduction of the chalcogen modifiers did not alter the crystallite size. In addition, as chalcogens are present at low concentrations they likely prevented the identification of any related bulk chalcogen reflections. The presence of chalcogen species on the topmost surface (approximately 1 nm) of the synthesized catalysts was clearly indicated by the time-of-flight secondary ion mass spectroscopy (ToF-SIMS) analysis (Figure S5). X-ray photoelectron spectroscopy (XPS) analysis suggested a very limited presence of surface chalcogenide phases in the as-synthesized materials, as shown for measurements before eCO₂RR testing (Figure 1b; see signal at binding energies of ca. 162, 54, and 573 eV for Cu_xS, Cu_xSe, and Cu_xTe, respectively). The chalcogen-free catalyst (Cu– \emptyset) was prepared by skipping the addition of chalcogen species^{29,30} (see Experimental Procedures in Section S1), resulting in unmodified Cu₂O particles (see Figure S3).

Cu–Se and Cu–Te exhibit slightly better catalytic performance than Cu with a mild preference for HCOO⁻ among the eCO₂RR products measured with chronoamperometry (CA) at –0.6 V vs Reversible Hydrogen Electrode (RHE), Figure 1c. In contrast, over Cu–S, HCOO⁻ is the main carbon product, being in equal proportion with H₂ whereas only trace amounts of CO were detected. The Cu–S becomes more selective toward formate at higher overpotentials until the presence of CO and more complex products, typically associated with clean copper, becomes detectable at –0.9 V vs RHE (Figures S6–S7).³⁵ At –0.8 V, the incipient volcano-like behavior in terms of selectivity observed at –0.6 V manifests now clearly (Figure 1c), suggesting the presence of a general effect modulated by the nature of the chalcogen. Comparison of our

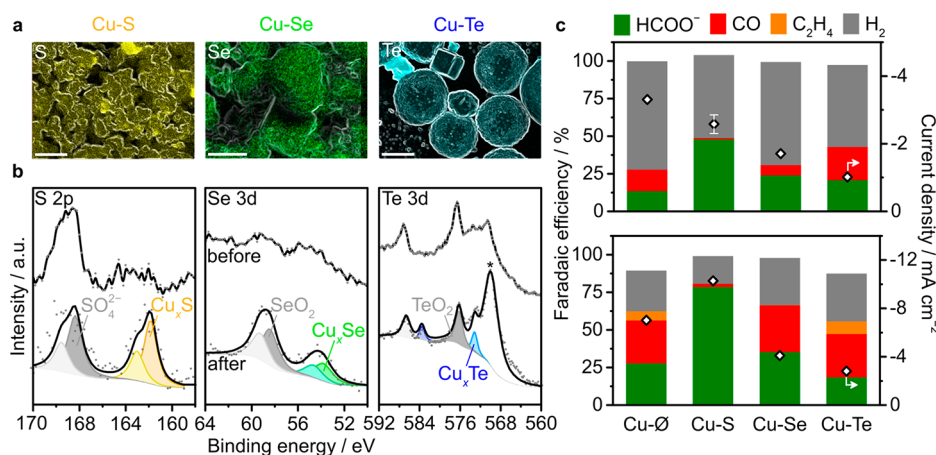


Figure 1. (a) EDX elemental maps of chalcogen elements for the corresponding fresh catalysts. White contours indicating the particle borders are added as a visual aid (see Figure S4). Scale bars: 2 μm . (b) Chalcogen XPS spectra before and after the eCO₂RR testing at -0.6 V vs RHE showing their presence after reaction. The peak indicated by asterisk (*) originates from the Auger emission in the Cu LMM region. (c) Product distribution over the copper-chalcogen catalysts, obtained by chronoamperometry at -0.6 (top) and -0.8 V (bottom) vs RHE for 1.5 h in 0.1 M KHCO₃ saturated with CO₂ (pH 6.7). Polycrystalline copper¹⁰ yields around 10% of both HCOO⁻ and CO at -0.6 V, and 20%/30%, respectively, at -0.8 V. Further tests regarding the electric potential dependence and the role of alkaline cations are presented in Figures S6–S8 and Section S3.

pure Cu (Cu- \emptyset) with polycrystalline, oxide-derived Cu reveals close similarities in product distribution,¹⁰ suggesting the removal of oxygen atoms from the copper surface under reaction conditions. *In situ* studies on oxide-derived copper catalysts have hinted at the presence of oxygen near the surface.^{32,36,37} Nevertheless, the absence of such an oxidic phase has also been suggested³³ and the promotion of carbon products formation was associated with grain boundaries.^{33,34,38} Under the eCO₂RR conditions, the surface of the electrocatalysts reconstructs (Figure S1) and the chalcogen content seems to decrease within the limited accuracy at such low concentrations (Table 1). Accordingly, XPS excitations around the Cu 2p peak showed the presence of Cu₂O and Cu²⁺ (Figure S9), whereas peaks compatible with the copper chalcogenide phases built up (Figure 1b; Tables 1, S1).³⁹ The broad peaks at higher binding energies in Figure 1b are ascribable to oxidic phases,⁴⁰ presumably formed upon exposure of the chalcogenides samples to air during characterization.⁴¹ Further ToF-SIMS analysis confirmed the increase in the relative abundance of chalcogen on the topmost layer upon the reaction (Figure S5). Upon the restructuring process, the surface remains populated by chalcogen atoms, although some leaching occurs.³⁰ We remark that the presence of copper chalcogenide phases after the eCO₂RR testing is not expected from a thermodynamic point of view, because Pourbaix diagrams predict metallic copper as the most stable phase under operation conditions (Figure S10); however, small domains cannot be fully discarded. In summary, the unmodified catalyst (Cu- \emptyset) can be identified as polycrystalline Cu under operation conditions, since (i) the removal of oxygen atoms or hydroxyl groups is largely favored (Tables S2 and S3) and (ii) the product distribution of Cu- \emptyset follows that of polycrystalline Cu (Figure 1c). Therefore, the selectivity patterns observed for Cu-S, Cu-Se, and Cu-Te can be ascribed to the chalcogen modifier.

To unravel the origin of the selectivity patterns, polycrystalline Cu was modeled by the lowest energy Cu(111) surface. Our calculations show that the results of the Cu(211), (110), and (100) facets yield qualitatively the same results, Figure S11. In the model, the chalcogens ($X = \text{O}, \text{S}, \text{Se}, \text{Te}$) are added

as adatoms sitting on surface fcc sites (Table S2) leading to a relative composition of 2.7 at. % ($X = 1, \text{Cu} = 36$) mimicking the experimental content, Table 1. Other structural models were tested but found less stable (Table S2). The removal of S, Se, and Te as H₂S, HSe⁻, and H₂CO₂Te occurs at more negative potentials than $U = -0.92, -1.06,$ and -0.87 V vs RHE, respectively (Table 2), explaining why all Cu- X systems

Table 2. Computed Properties of the Chalcogen Modified Cu(111) Surface^a

system	$\Delta G_{\text{H}_2\text{X}}$	ΔG_{HX^-}	$\Delta G_{\text{XCO}_2\text{H}_2}$	q_{X^*}	$\epsilon_{\text{p}} - \epsilon_{\text{F}}$	$\Delta(\epsilon_{\text{d}} - \epsilon_{\text{F}})$
Cu-O	-1.28	-0.84	+1.86	-0.93	-2.50	-0.16
Cu-OH	-0.60	-0.16	-	-0.59	-4.22	-0.11
Cu-S	+0.92	+0.94	+2.95	-0.59	-1.61	-0.07
Cu-Se	+1.22	+1.06	+3.74	-0.43	-1.28	-0.05
Cu-Te	+1.71	+1.48	+0.87	-0.21	-0.88	-0.07

^a $\Delta G_{\text{H}_2\text{X}}, \Delta G_{\text{HX}^-}, \Delta G_{\text{XCO}_2\text{H}_2}$: desorption energies for the chalcogens to produce H₂X, HX⁻, and XCO₂H₂ ($X = \text{O}, \text{S}, \text{Se}, \text{Te}$), in eV. q_{X^*} : Bader charges of the adsorbed chalcogen, in $|\text{e}^-|$. $\epsilon_{\text{p}} - \epsilon_{\text{F}}$: center of the chalcogen p-band with respect to the Fermi level of the system, in eV. $\Delta(\epsilon_{\text{d}} - \epsilon_{\text{F}})$: d-band center shift for the adjacent Cu atoms upon anchoring of the chalcogen, in eV.

were stable at the working potentials from -0.6 to -0.8 V vs RHE.³⁰ At more cathodic potentials than -0.90 vs RHE, the Cu-S performance starts resembling that of polycrystalline copper,¹⁰ Table 2 and Figures S6. The stability of the Cu-S system was further tested, Figures S12–S13, suggesting the progressive loss of sulfur from the surface at deeper cathodic potentials.

To understand the mechanistic implications of the eCO₂RR on Cu, we start by analyzing the reactions listed in Scheme 1a where the parasitic hydrogen evolution reaction is also presented. In the reaction network, either coupled or sequential proton and electron transfers appear, and their relative contributions are given by their different dependence on the potential and the interface pH. To elucidate the origin of the selectivity switch imposed by the chalcogen modifier, we modeled CO₂ adsorption as an electron transfer process and

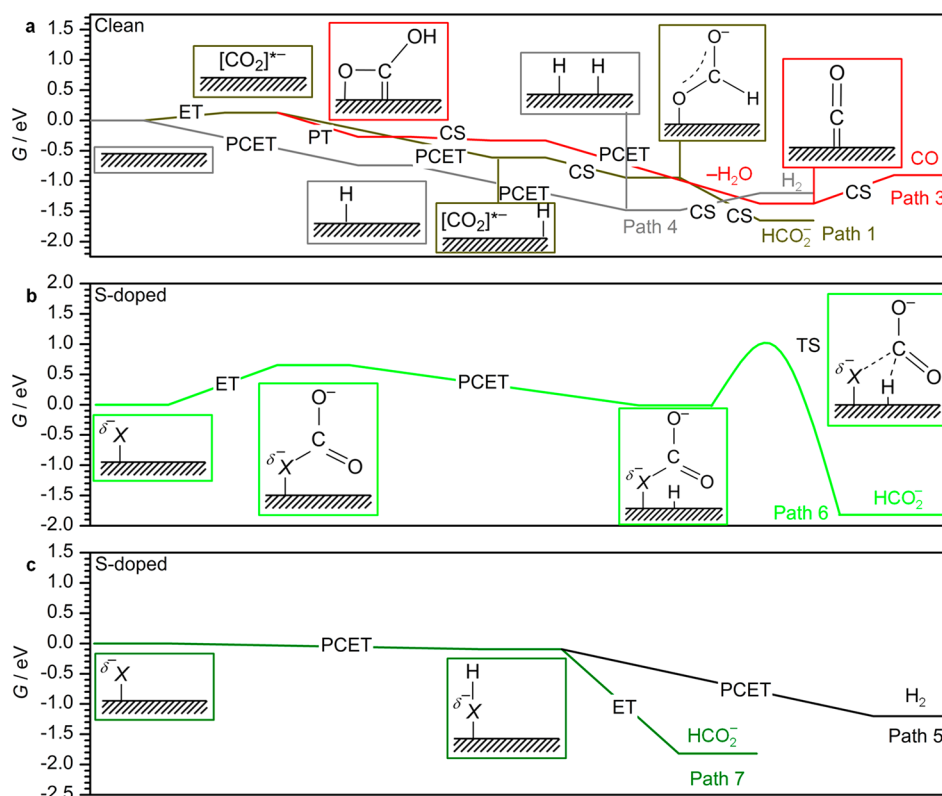


Figure 2. Gibbs free energy profiles on clean and chalcogen modified Cu(111) surfaces at $U = -0.6$ V vs RHE. (a) Electrochemical CO_2 reduction toward formate (path 1, olive), CO (path 3, red), and hydrogen evolution reaction (path 4, gray) on clean Cu(111). Path 2 is also downhill from CO_2^{*-} and is omitted for simplicity. For S-modified surfaces (b) presents path 6 starting from tethered CO_2^{*-} toward formate and (c) the S-mediated formate path 7 and HER. PCET: proton-coupled electron transfer. ET: electron transfer. PT: proton transfer. CS: chemical step. TS: transition state in CS. The profiles for $U = 0.0$ and -0.8 V vs RHE are shown in Figure S16, and those for other chalcogens, in Figure S17.

decoupled all the other steps along the whole reaction network when possible.^{17,42} The rate-determining step in the eCO_2RR process is the difficult CO_2 adsorption both on pure metal electrodes and in molecular catalysts.^{3,17,24} Raman spectroscopy has recently evidenced that the resulting carboxylate species is the first intermediate in the CO_2 conversion to formate on copper.^{43,44} From a mechanistic perspective, successful CO_2 adsorption and activation imply the endothermic bending of the O–C–O bond, which requires 3.05 eV for the neutral molecule but only 1.23 eV for the negatively charged species, Figure S14. Therefore, its activation implies the electron transfer to its high lying LUMO.⁴⁵ On the surface, CO_2^{*-} can adopt four possible conformations,¹⁷ depending on the surface potential, Figure S15a. The most stable adsorbed structure at $U = -0.6$ V is $\eta_{2(\text{C},\text{O})}$, where both C and O are bonded to the surface.

Then a proton can be adsorbed onto the copper surface as H^* through a PCET step, path 1 in Scheme 1a, reacting with the carboxylate via a chemical step yielding monodentate HCOO^{*-} , which desorbs as formate, Figure S15b,⁴⁶ similar to CO_2 reduction on PdH_x .¹⁷ A proton from solution is transferred to a terminal oxygen of CO_2^{*-} , giving rise to a carboxyl intermediate (path 2) that reacts with H^* to produce formic acid. Formic acid desorbs spontaneously and converts to formate due to the solution's pH (buffered at 6.7). Alternatively, the COOH^* intermediate decomposes to CO^* and water through either decoupled or concerted proton–electron transfer, path 3. The desorption of CO from Cu is endergonic,⁹ Figure 2a, thus allowing further reduction toward methanol and hydrocarbons.¹⁰ More cathodic potentials can

stabilize the CO_2^{*-} intermediate, thus simultaneously increasing the Faradaic efficiency or production of HCOO^- and CO, until mild overpotentials are reached.¹⁰ The parasitic HER, by contrast, occurs through either a classical Volmer–Tafel mechanism, path 4, or a Volmer–Heyrovsky mechanism, omitted here for simplicity. As both eCO_2RR and HER have H^* as a common intermediate, a mild metal–hydrogen bonding strength promotes both reactions.⁴⁷ Applied to other transition metals, the reaction network in Scheme 1a predicts that they are poor formate-producing catalysts.^{23,48,49}

The energy profile for Cu shown in Figure 2a at $U = -0.6$ V can be explained as follows: the markedly endergonic CO_2 adsorption, Table S4, requires considerable overpotentials to trigger its reduction. The HER largely predominates at potentials more anodic than -0.8 V. As CO_2 adsorption becomes more exergonic, paths 1 and 2 start competing with the HER (path 4). At higher overpotentials, the increasingly larger CO_2^{*-} coverage enhances the production of formate and CO,⁵⁰ accounting for the concomitant HER decrease. In our energy profiles, Figure 2a, the HER is preferable over the CO_2 reduction. The larger Faradaic efficiency toward formate could come from mass-transport phenomena^{19,51,52} (local pH at the interface, local CO_2 concentration) not included in our model.

Modification of the copper surface with chalcogen (X) adatoms leads to stable configurations with a polarized X–metal bond ($X^{\delta-}$) according to the Bader charges of $\delta = -0.93$, -0.59 , -0.43 , and -0.21 |e⁻| for O, S, Se, and Te respectively, Table S3. Along the series, the bond is more covalent as the partially empty p-states of the chalcogens lie

closer to the highest, unperturbed Cu bands (the d-band is invariant; see Tables 2 and S3). At more negative potentials,⁵³ the partial charge of the chalcogens, $X^{\delta-}(U)$, increases to $\delta = -0.98, -0.76, -0.66,$ and -0.53 e⁻. The $X^{\delta-}$ surface site acts as a nucleophile to trap CO₂ concomitant with an electron transfer, producing a chalcocarbonate $X^{\delta-}\text{CO}_2^{*-}$, path 6 in Scheme 1b. The computed free energies for S-decorated Cu (new paths 5, 6, and 7) are shown in Figure 2. Due to its geometry, $X^{\delta-}\text{CO}_2^{*-}$ cannot form CO, as it would imply breaking the C–X and C–O bonds simultaneously. In parallel, a proton can adsorb on the neighboring Cu from the solution with an electron from Cu to form H*.⁴² The reaction proceeds with H* attacking the carbon atom in $X^{\delta-}\text{CO}_2^{*-}$ to produce formate, as indicated by the inset labeled TS in Figure 2b. This potential-independent chemical step presents an activation energy of 1.02 eV. The $X^{\delta-}$ site can also attract protons to produce $X^{\delta-}\text{H}$, paths 5 and 7 in Scheme 1b. This species can attack either a proton or a CO₂ in the solution, to produce hydrogen (HER path 5) or formate (path 7) respectively in Heyrovsky-like mechanisms. Paths 6 and 7 agree with the Tafel plot in Figure S7, which indicates that the rate-determining step for the reaction involves a single electron transfer (slope 120 mV dec⁻¹). Finally, the presence of the chalcogen prevents the adsorption of CO₂ on its neighborhood (destabilizing adsorption by 0.53, 0.27, and 0.12 eV for first, second, and third nearest Cu sites, respectively), blocking unselective paths occurring on Cu-only sites, Figure 2.

The energy profiles in Figure 2 enable the rationalization of the experimental catalytic trends over Cu–S, Cu–Se, and Cu–Te in Figure 1c. Since all steps in path 7 become exergonic from $U = -0.6$ V vs RHE toward more cathodic potentials and the chalcogen atom destabilizes path 2, the chalcogen centers become highly selective for the eCO₂RR toward formate. As the formation of XH* becomes more endergonic for heavier chalcogens, the activity of paths 5 and 7 is reduced along the chalcogen series (Table S4). As already noted, the blocking effect of Se and Te in neighboring Cu atoms is milder than that of S, Table S4, in line with the experimental trends observed in Figure 1.

The differences in activity and selectivity can be traced back to an intrinsic property of the adsorbed chalcogenides as both the tethering of CO₂ (Figure 3a) and the formation of XH* (Figure 3b) depend on the donor ability of X. Figure 3c–d compile the key energy figures in paths 6 and 7 as a function of the basicity obtained as the p-band center of the chalcogen.⁵⁴ In Figure 3c (path 6) the low basicity enhances the stability of the $X\text{CO}_2^{*-}$ adsorbate, while higher basicity makes HCOO⁻ formation more exergonic. In Figure 3d (path 7), the limiting factors are the formation of XH* and formate, where the former becomes more endergonic at larger basicities. In turn the HER is controlled by H adsorption on Cu (gray) and does not depend on the nature of the adatom. The optimal crossing point between the stability of the key intermediate and formate appears at -2.5 (path 6) and -2.2 eV (path 7), respectively. Thus, in both cases the chalcogen that shows the closest value is sulfur, which is in agreement with its unique catalytic performance among the family of chalcogen modifiers identified in Figure 1. It is also significant that the stability of the chalcogens on the surface correlates with the basicity, Figure S18.

In summary, the selective production of formate upon chalcogen modified copper is due to (i) the presence of basic sites where CO₂ is tethered blocking its dissociation toward

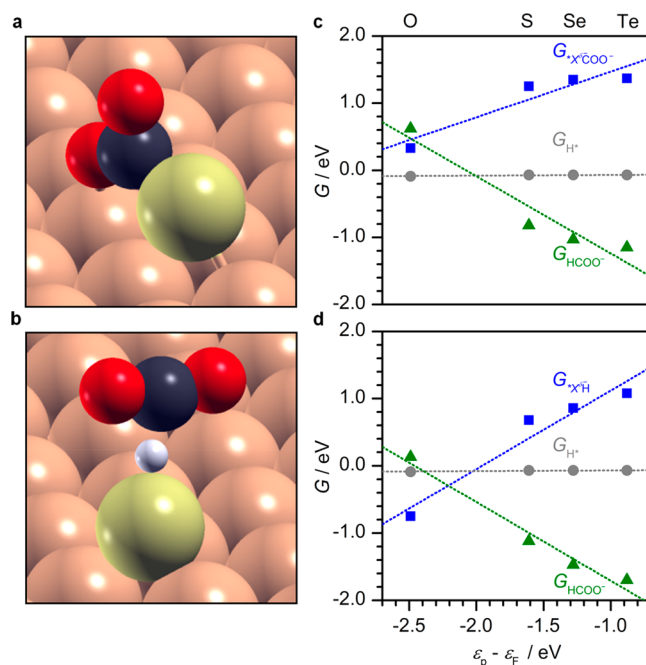


Figure 3. Most important intermediates for formate production (a) via CO₂ tethering on the chalcogen adatom or (b) via the Heyrovsky mechanism (path 6 and 7 in Scheme 1, respectively). (c–d) Gibbs energies ($U = 0.0$ V vs RHE) of the crucial intermediates as a function of the basicity of the chalcogen, computed as the center of the chalcogen p-band. Blue dots correspond to the energy of the precursors $X^{\delta-}\text{CO}_2^{*-}$ and $X^{\delta-}\text{H}$, respectively shown in the (a–b) panels, while the energy of HCOO⁻ is shown in green. The largest activity is expected when the green and blue lines cross as the process will be isoenergetic. Gray dots represent the adsorption energy of hydrogen on copper atoms in the vicinity of X. Lines were added as a guide to the eye.

CO, (ii) the ability of chalcogens to directly transfer hydrides to CO₂, and (iii) the effective blocking of unselective paths on the surrounding Cu atoms. Our results point out the role of chemical steps in electrochemical processes.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcllett.8b03212.

Experimental procedures, computational details, cation effect, supplementary schemes, figures, tables, and references (PDF)

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Notes

The authors declare no competing financial interest.

The DFT data that support the findings of this study are available in ioChem-BD⁵⁵ at DOI 10.19061/iochem-bd-1-92.

ACKNOWLEDGMENTS

We are thankful for the financial support from MINECO (Grant Number CTQ2015-68770-R), ETH Zurich, and the European Union under Projects A-LEAF (732840-A-LEAF) and ELCoREL (721624-ELCOREL). The ScopeM of ETH Zurich and the Barcelona Supercomputing Centre (BSC-RES) are thanked for access to their facilities and generous computational resources.

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