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On the role of metal cations in CO_2 electrocatalytic reduction

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Metal cations are widely considered to influence the electrocatalytic reduction of CO_2, however, their roles are still being identified. Recently, Monteiro et al.[1] proposed a mechanism in which the main effect of the cations is to stabilize CO_2 adsorption on the electrode surface based on evidence from experiments and ab initio molecular dynamics (AIMD) simulations. This Matters Arising points to an essential constraint applied in the AIMD simulations, which calls into question the conclusions that are drawn and suggests the need for unrestricted AIMD simulations for electrocatalytic reactions.

In their investigation of CO_2 electroreduction on copper, gold and silver electrodes, Monteiro et al.[1] demonstrate that CO is produced only if a metal cation such as Li^+, K^+, Na^+ or Cs^+ is added to the electrolyte. Aided by results of AIMD simulations of CO_2 adsorption on the Au(111) surface with and without metal cations, they conclude that among the models proposed to explain the effect of cations only that with electrostatic interactions between metal cations and key intermediates explains their observations. Their proposed mechanism begins with the adsorption of CO_2 on the electrode surface to form CO_2* species, followed by its stabilization by a solvated metal cation. Such stabilization is necessary for further reaction with H_2O to form COOH*, followed by CO* and OH* species. Furthermore, Monteiro et al.[1] show that the larger the size of the cation, the higher the production of CO.

The above mechanism was partially derived from results of AIMD simulations that tracked the M^+–O bond length. These simulations also show CO_2 to be adsorbed on the Au(111) surface both with and without the metal cation. This chemisorption of CO_2 in a bent configuration on Au(111) is intriguing, since conventional wisdom from the gas/solid interface points to a weak adsorption on Au(111) (refs. [2,3]). Could the solvent make the difference? On turning to the movies provided in the supplementary information[1] and computational data[4] we, however, realized that the simulations were performed by freezing Au atoms of the Au(111) slab and the C atom of the CO_2 molecule (this information was not disclosed in the publication[1]). While freezing Au atoms may not have a significant effect on the dynamics of the electrolyte, or CO_2, or the metal cation, freezing C atom does. In the simulation of CO_2 on Au(111) (Supplementary Video 1 in ref. [1]), C atoms were held at a distance of 2.16 Å above the Au surface to restrict desorption of CO_2 from the surface. Similarly, in the simulation of CO_2 on Au(111) in the presence of metal cations (Supplementary Videos 2–5 in ref. [1]), C atoms were not allowed to move to prevent them from diffusing away and from desorbing from the Au(111) surface.

While such a constraint may have been necessary for providing evidence for the proposed mechanism, it leads to a false impression that the CO_2 molecules bind to the Au(111) surface in a bent configuration with and without the metal cation. To further examine the CO_2 adsorption characteristics, we have carried out AIMD simulations of CO_2 on Au(111) with and without K^+, that is Au-H_2O-CO_2 and Au-H_2O-K^+-CO_2 systems following the recipe provided by Monteiro et al.[1], starting from their equilibrated configurations[4] and unfreezing the C and Au atoms in the top two layers of the Au(111) slab. Our simulations reveal that within a short simulation time (less than 100 fs), CO_2 molecules desorb from the Au(111) surface and the $\widehat{OCO}$ angle returns to ~180° regardless of the presence of K^+ (Fig. 1). In addition to the desorption of CO_2, we also find that the distance between K^+ and CO_2 increases as the simulation proceeds (Fig. 1b), indicating their decoupling. Results of the simulations are shown in Supplementary Videos 1 and 2.

Realizing that the provided structures may not have the optimal configuration of CO_2 on the Au(111) surface, we performed ionic relaxation of the Au-H_2O-CO_2 structure (without H_2O molecules), using the same parameters for the density functional theory (DFT) calculations as in ref. [1], but were unable to reproduce the bidentate configuration of CO_2 on Au(111) described by Monteiro et al.[1].

The results above neither provide direct evidence for the mechanism proposed by Monteiro et al.[1], nor do they invalidate the mechanism. In fact a couple of reasons could validate the proposed mechanism. Polycrystalline gold used as electrode in the experiments may have several surface terminations and the ones that activate CO_2 reduction may not be the (111) facet. Earlier work[5] points to the Au(110) surface as the most active low Miller index surface for CO_2 reduction. It also shows that the CO_2 reduction happens at around −0.8 V vs standard hydrogen electrode (or −0.4 V vs reversible hydrogen electrode, close to the value reported in ref. [1]).

We also noticed in a recent AIMD simulation on Au(110) (ref. [6]) that two K^+ ions are required for activation of CO_2 on the electrode. According to the authors, such activation is possible because the K atoms donate electrons to charge the electrode surface. This explanation

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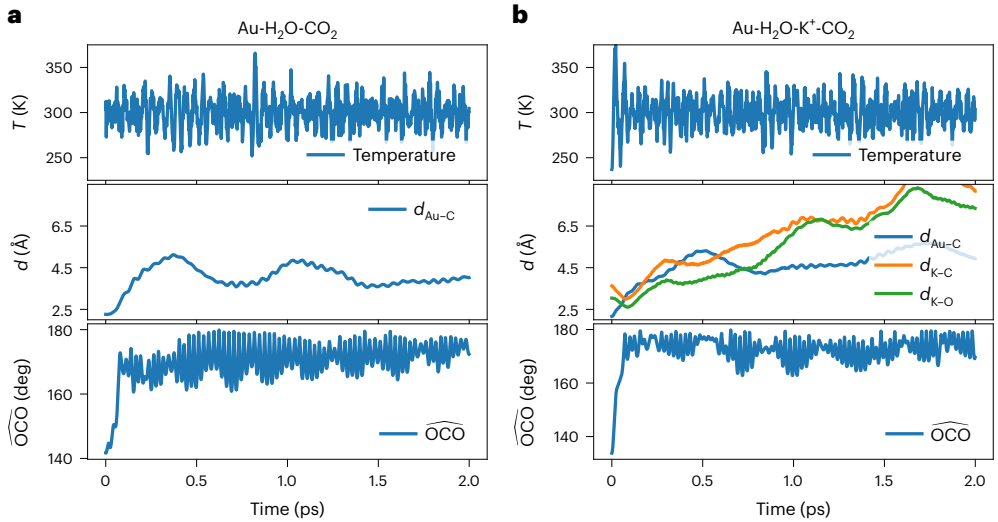

Fig. 1 | AIMD simulations of CO_2 desorption from the Au(111) surface. **a**,**b**, Results of AIMD simulations for Au-H_2O-CO_2 **(a)** and Au-H_2O-K^+-CO_2 **(b)** at temperature $T = 300$ K: $d_{Au\text{-}C}$ measures the distance between C and the Au surface atom on which the molecule binds; $d_{K\text{-}C}$ measures the distance between K^+ and C; $d_{K\text{-}O}$ is the distance between K^+ and its nearest O atom of the CO_2 molecule; $\widehat{OCO}$ is the bending angle of the CO_2 molecule.

seems plausible; however, it requires a high potassium concentration (~2.6 M) at the electrode surface, which is many orders of magnitude higher than the μM or mM used by Monteiro et al.[1]. It should be also noted that surface charge is controlled by the electrode potential and thus the role of K^+ should not be that of charging the electrode.

Although revealing the true effects of metal cations and the mechanism of CO_2 electroreduction are of our interest, they are not the focus of this Matters Arising since doing so requires significant effort and deserves a separate publication. Our purpose here is to raise the awareness that appropriate AIMD simulations are needed to address this challenging issue and that the Au(111) surface may not be a good choice. Such simulations should include the potential on the electrode, that is AIMD should be performed with a target potential (grand-canonical DFT[7,8]) to mimic experimental conditions, appropriate cation concentration and realistic electrode models.

Data availability

The dataset generated and analysed in the current study are available at https://doi.org/10.5281/zenodo.7122467.

References

1. Monteiro, M. C. O. et al. Absence of CO_2 electroreduction on copper, gold and silver electrodes without metal cations in solution. *Nat. Catal.* **4**, 654–662 (2021).
2. Farkas, A. P. & Solymosi, F. Activation and Reactions of CO_2 on a K-Promoted Au(111) Surface. *J. Phys. Chem. C* **113**, 19930–19936 (2009).
3. Farkas, A. P. & Solymosi, F. Photolysis of the CO_2 + K/Au(111) System. *J. Phys. Chem. C* **114**, 16979–16982 (2010).
4. Dattila, F. Cation-effect-CO2-reduction. *ioChem-BD* https://doi.org/10.19061/iochem-bd-1-194 (2021).
5. Marcandalli, G., Villalba, M. & Koper, M. T. M. The importance of acid–base equilibria in bicarbonate electrolytes for CO_2 electrochemical reduction and CO reoxidation studied on Au(hkl) electrodes. *Langmuir* **37**, 5707–5716 (2021).
6. Qin, X., Vegge, T. & Hansen, H. A. CO_2 activation at Au(110)–water interfaces: An ab initio molecular dynamics study. *J. Chem. Phys.* **155**, 134703 (2021).
7. Sundararaman, R., Goddard, W. A. & Arias, T. A. Grand canonical electronic density-functional theory: Algorithms and applications to electrochemistry. *J. Chem. Phys.* **146**, 114104 (2017).
8. Sundararaman, R. & Arias, T. A. In *Atomic-Scale Modelling of Electrochemical Systems* (eds M. M. Melander et al.) 139–172 (John Wiley & Sons, 2021).

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Author contributions

D.L. carried out the simulations. D.L. and T.S.R. wrote and edited the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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