# POLITECNICO DI TORINO Repository ISTITUZIONALE

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

Original

Reply to: On the role of metal cations in CO2 electrocatalytic reduction / Dattila, Federico; Monteiro, Mariana C. O.; Koper, Marc T. M.; López, Núria. - In: NATURE CATALYSIS. - ISSN 2520-1158. - 5:11(2022), pp. 979-981. [10.1038/s41929-022-00877-1]

Availability: This version is available at: 11583/2981915 since: 2023-09-11T09:10:58Z

Publisher: NATURE PORTFOLIO

Published DOI:10.1038/s41929-022-00877-1

Terms of use:

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

Publisher copyright

(Article begins on next page)

- 1 Reply to: "On the role of metal cations in CO<sub>2</sub> electroreduction reduction"
- 2

3

Federico Dattila<sup>1</sup>, Mariana C. O. Monteiro<sup>2,3</sup>, Marc T. M. Koper<sup>3\*</sup> and Núria López<sup>4\*</sup>

<sup>1</sup> Department of Applied Science and Technology (DISAT), Politecnico di Torino, Corso Duca
degli Abruzzi 24, 10129 Turin, Italy

<sup>6</sup> <sup>2</sup> Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, 14195 Berlin, Germany

- <sup>3</sup> Leiden Institute of Chemistry, Leiden University, 2300 RA Leiden, The Netherlands
- 8 <sup>4</sup> Institute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute of Science and

9 Technology (BIST), 43007 Tarragona, Spain

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).<sup>1,2</sup> We chose the PBE density functional (ref 3) including dispersion 15 through the DFT-D2 method,<sup>4,5</sup> with our reparametrized C<sub>6</sub> coefficients.<sup>6</sup> Inner electrons were 16 represented by PAW pseudopotentials<sup>7,8</sup> and the monoelectronic 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 H<sub>2</sub>O molecules within the solvation layer. A vacuum thickness of around 8 Å vacuum was included

- beyond the outermost H<sub>2</sub>O molecule. A  $K^+$  was inserted within the solvation layer to assess the "with metal cation" case (see Fig.1a), while no cation was present in the system "without metal
- cation" (Fig. 1c). To model the case "with metal cation" but "no excess electron", we removed one
- hydrogen from one H<sub>2</sub>O molecule (Fig. 1b), leading to a charge balanced cell with one  $K^+$  and one
- OH<sup>-</sup>. To compute activation angle  $\alpha$  (Fig. 1d,e) and Bader charge q (Fig. 1f,g) of the CO<sub>2</sub> unit, we
- carried out a ionic optimization of the overall system: Au surface, H<sub>2</sub>O molecules, cation (if
- present), and a  $CO_2$  molecule initially adsorbed on the surface and let free to move. Since  $K^+$ ,  $CO_2$ ,
- and the explicit solvation layer were placed only on one side of the slab, we applied an additional  $\frac{1}{2}$
- dipole correction to remove spurious contributions arising from the asymmetric slab model.<sup>9</sup>

To assess the role of explicit electrostatic effects on CO<sub>2</sub> activation, we applied different intensities of electric field ( $\vec{E}_{EDL}$ ) through a dipole correction (refs. 6,10): -0.2 V Å<sup>-1</sup>, -0.4 V Å<sup>-1</sup>, -0.6 V Å<sup>-1</sup> 1. Considering a potential of zero charge ( $U_{PZC}$ ) for polycrystalline gold of +0.2 V vs SHE (ref. 13) and an electrical double layer thickness ( $d_{EDL}$ ) of 3 Å,<sup>11,12</sup> such electric field intensities correspond roughly to values of electric potential of -0.4 V vs. SHE, -1.0 V vs. SHE, and -1.6 V

vs. SHE respectively, Supporting Equation 1.

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

)

## 36 Supplementary References

37 38	1.	Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. <i>Phys. Rev. B</i> <b>54</b> , 11169–11186 (1996).
39 40	2.	Kresse, G. & Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. <i>Comput. Mater. Sci.</i> <b>6</b> , 15–50 (1996).
41 42	3.	Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. <i>Phys. Rev. Lett.</i> <b>77</b> , 3865–3868 (1996).
43 44	4.	Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. J. Comput. Chem. 27, 1787–1799 (2006).
45 46 47	5.	Bucko, T. <i>et al.</i> Improved description of the structure of molecular and layered crystals: Ab initio DFT calculations with van der Waals corrections. <i>J. Phys. Chem. A</i> <b>114</b> , 11814–11824 (2010).
48 49	6.	Almora-Barrios, N., Carchini, G., Błoński, P. & López, N. Costless derivation of dispersion coefficients for metal surfaces. <i>J. Chem. Theory Comput.</i> <b>10</b> , 5002–5009 (2014).
50	7.	Blöchl, P. E. Projector augmented-wave method. Phys. Rev. B 50, 17953-17979 (1994).
51 52	8.	Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. <i>Phys. Rev. B</i> <b>59</b> , 1758–1775 (1999).
53 54	9.	Makov, G. & Payne, M. C. Periodic boundary conditions in ab initio calculations. <i>Phys. Rev. B</i> <b>51</b> , 4014–4022 (1995).
55 56	10.	Feibelman, P. J. Surface-diffusion mechanism versus electric field: Pt/Pt(001). <i>Phys. Rev. B</i> - <i>Condens. Matter Mater. Phys.</i> <b>64</b> , 125403 (2001).
57 58	11.	McCrum, I. T., Bondue, C. J. & Koper, M. T. M. Hydrogen-induced step-edge roughening of platinum electrode surfaces. <i>J. Phys. Chem. Lett.</i> <b>10</b> , 6842–6849 (2019).
59 60	12.	Chen, L. D., Urushihara, M., Chan, K. & Nørskov, J. K. Electric Field Effects in Electrochemical CO <sub>2</sub> Reduction. <i>ACS Catal.</i> <b>6</b> , 7133–7139 (2016).
61 62	13.	White, R. E., Bockris, J. O. & Conway, B. E. <i>Modern aspects of electrochemistry</i> . (Kluwer Academic Publishers, 2002).

63