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Absence of CO<sub>2</sub> electroreduction on copper, gold and silver electrodes without metal cations in solution / Monteiro, M.C.O., Dattila, F., Hagedoorn, B., García-Muelas, R., López, N., Koper, M.T.M.. - In: NATURE CATALYSIS. - ISSN 2520-1158. - 4:8(2021), pp. 654-662. [10.1038/s41929-021-00655-5]

*Availability:*

This version is available at: 11583/2981910 since: 2024-06-03T14:48:36Z

*Publisher:*

Springer

*Published*

DOI:10.1038/s41929-021-00655-5

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# **Absence of CO<sub>2</sub> electroreduction on copper, gold and silver electrodes without metal cations in solution**

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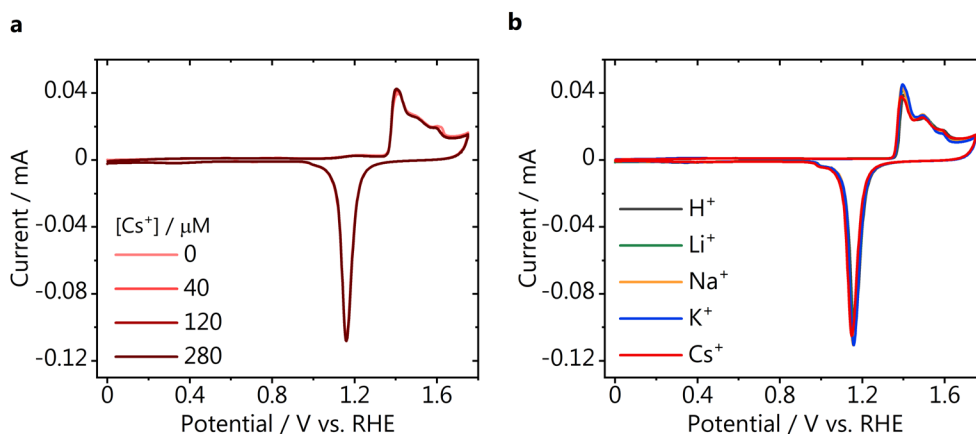
## **Supplementary Information**

## Supplementary Discussion

### Hanging meniscus experiments

#### Characterization of the polycrystalline gold electrode

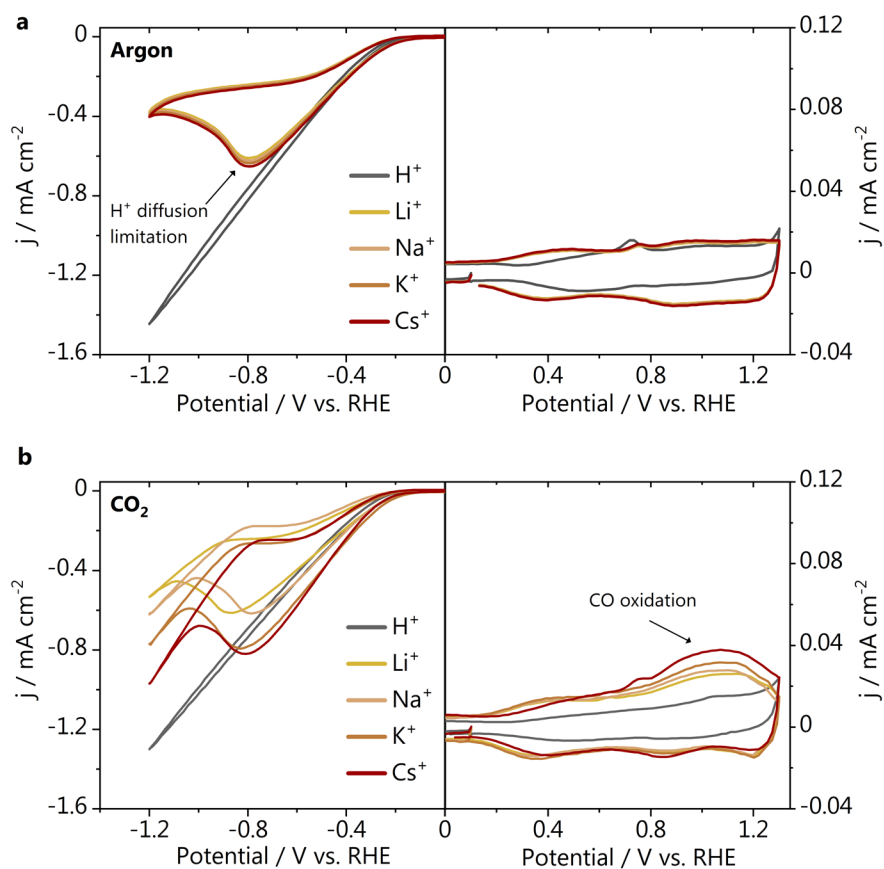
Before all the CO<sub>2</sub> reduction experiments in hanging meniscus configuration were performed, the gold electrode was flame annealed using the protocol previously described<sup>1</sup> and the electrode was characterized in 0.1 M H<sub>2</sub>SO<sub>4</sub>. The characterization by cyclic voltammetry (CV) was done in between all measurements, to assure a reproducible surface which allows for comparison of the CO<sub>2</sub> reduction results and determination of the electrochemical active surface area. The characterization CVs recorded during the hanging meniscus experiments presented in the main text can be found in Supplementary Figure 1.



**Supplementary Figure 1.** Blank voltammetry of the gold electrode used in the hanging meniscus experiments after surface preparation through polishing and flame annealing. **a**, CVs recorded before the measurements in 1 mM H<sub>2</sub>SO<sub>4</sub> with the addition of different amounts of Cs<sup>+</sup>, **b**, CVs recorded before the measurements in 1 mM M<sub>2</sub>SO<sub>4</sub> (*M* = H, Li, Na, K, Cs).

#### Hydrogen evolution and CO<sub>2</sub> reduction in 1mM M<sub>2</sub>SO<sub>4</sub> (*M* = H, Li, Na, K, Cs)

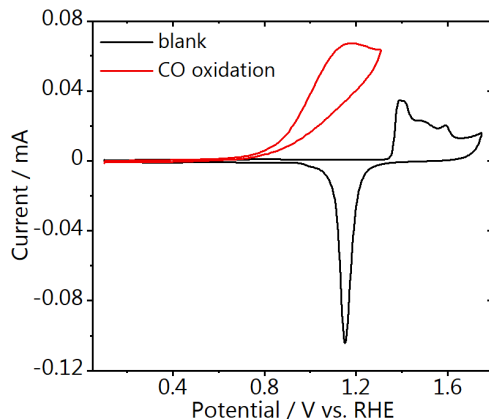
Hydrogen evolution and CO<sub>2</sub> reduction were also carried out in 1 mM sulfate solutions of different cations, all adjusted to pH = 3 when necessary. The cyclic voltammetry can be seen in the figure below, together with the results obtained in 1 mM H<sub>2</sub>SO<sub>4</sub>, for comparison. To calculate the CO oxidation charge density shown in the main text, the double layer charge recorded in Argon was subtracted from the total charge found in CO<sub>2</sub> atmosphere.



**Supplementary Figure 2.** Cyclic voltammetry recorded in **a**, argon and **b**, CO<sub>2</sub> atmosphere on gold in 1 mM M<sub>2</sub>SO<sub>4</sub> (M = H, Li, Na, K, Cs) at pH = 3 (50 mV s<sup>-1</sup>).

### CO oxidation control experiment

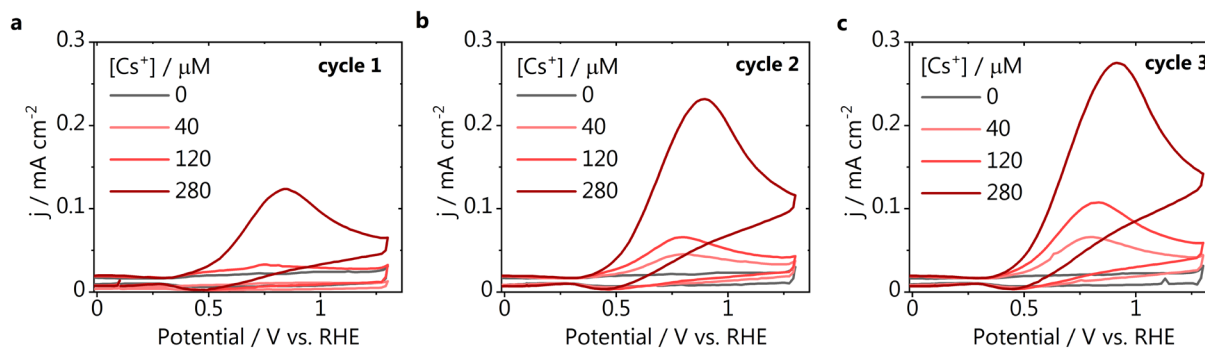
A control experiment was performed to show that CO can be oxidized on the gold electrode in the absence of a metal cation in the electrolyte. Before the measurement the gold electrode was characterized in argon saturated 0.1 M H<sub>2</sub>SO<sub>4</sub> electrolyte. The 0.1 M H<sub>2</sub>SO<sub>4</sub> electrolyte was saturated with CO for 5 minutes and subsequently a cyclic voltammogram was recorded. Supplementary Figure 3 displays both CVs, in which the large anodic current (red curve) starting at 0.8 V vs RHE shows that CO can be oxidized without a metal ion in solution.



**Supplementary Figure 3.** CO oxidation voltammetry on gold recorded in 0.1 M H<sub>2</sub>SO<sub>4</sub> after saturation the electrolyte with CO (50 mV s<sup>-1</sup>).

### CO<sub>2</sub> reduction in 1mM H<sub>2</sub>SO<sub>4</sub> + μM Cs<sup>+</sup>

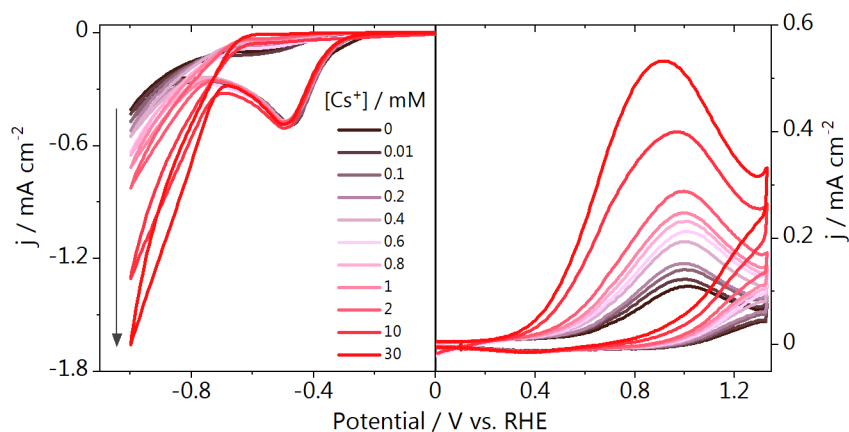
CVs were recorded directly after the CO<sub>2</sub> reduction cathodic scan from 0 to -1.2 V vs. RHE in 1 mM H<sub>2</sub>SO<sub>4</sub> in order to semi-quantitatively determine the amount of CO produced with and without the addition of different amounts of Cs<sup>+</sup>. The three subsequently cycles recorded are shown in Supplementary Figure 4a-c and the first cycles are shown in the main text. The increase in the amount of CO produced over the 3 cycles for each concentration is likely due to an accumulation of CO<sub>2</sub> near the surface after CO oxidation. Additionally, considering a direct competition between proton and CO<sub>2</sub> reduction, an increase of the interfacial pH and consequent suppression of proton reduction, could lead to more CO produced.



**Supplementary Figure 4.** a, First, b, second and c, third cycles recorded at 50 mV s<sup>-1</sup> on a gold electrode directly after a cathodic scan in CO<sub>2</sub> atmosphere when different amounts of Cs<sup>+</sup> were added to the 1 mM H<sub>2</sub>SO<sub>4</sub> electrolyte.

### CO<sub>2</sub> reduction in Li<sub>2</sub>SO<sub>4</sub> + μM Cs<sup>+</sup>

Li<sub>2</sub>SO<sub>4</sub> was used as background electrolyte to investigate the effect of the Cs<sup>+</sup> concentration in the CO production. The cathodic and subsequently anodic cyclic voltammetry recorded can be seen in Supplementary Figure 5.



**Supplementary Figure 5.** Cyclic voltammetry recorded at  $50 \text{ mV s}^{-1}$  during  $\text{CO}_2$  reduction on gold in  $\text{Li}_2\text{SO}_4$  electrolyte containing different concentrations of  $\text{Cs}^+$ . The total cation concentration in solution was kept  $0.1 \text{ M}$  and the  $\text{pH} = 3$ .

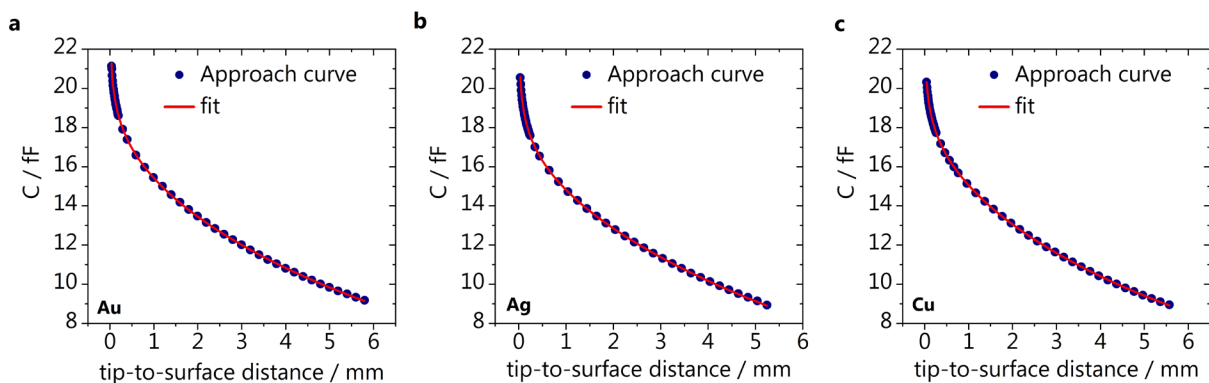
## SECM experiments

### Capacitive approach curve fitting

A capacitive approach in air is performed before the SECM measurements in order to determine the tip-to-surface distance. The approach curve is constructed by applying an AC voltage to the sample and recording the capacitive current generated at the tip as a function of position until reaching the exponential regime of the capacitance. The position is converted to distance by fitting the approach curve with Supplementary Equation 1, which provides the absolute surface position ( $d_0$ ). This fitting function is different than the one presented in our previous work<sup>2</sup>. It describes the system as a point charge in front of a plate, instead of a pure parallel plate capacitor, which we find to give a more precise estimation of  $d_0$ .<sup>3</sup>

$$C_{tot}(Z) = -A_1 * \ln(d_0 - Z) + B + \left( \frac{A_2}{L_{par} + d_0 - Z} \right) \quad (1)$$

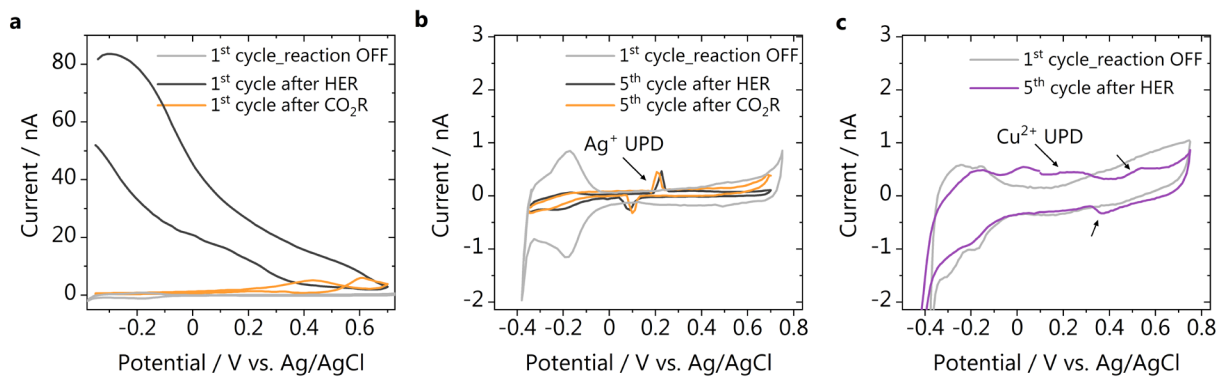
Supplementary Figure 6 shows the Pt-UME approach curves recorded before the SECM experiments performed using the gold, silver and copper samples. The fit is shown in red.



**Supplementary Figure 6.** Capacitive approach curves recorded before the SECM experiments on **a**, gold, **b**, silver and **c**, copper.

### Stability of the silver and copper electrodes

Supplementary Figure 7 shows the instability of the silver and copper electrodes when potentials more cathodic than  $-0.8$  and  $-1$  V vs. RHE are applied to the sample, respectively. It shows different cycles of the Pt-UME voltammetry recorded subsequently, either after hydrogen evolution or  $\text{CO}_2$  reduction are carried out at the sample. As can be seen in Supplementary Figure 7a when  $\text{CO}_2$  reduction is performed on silver in 1 mM  $\text{H}_2\text{SO}_4$  at  $-1$  V vs. RHE, CO is produced, at small amounts. This goes against what was observed in all the other experiments shown in the main text, in which  $\text{CO}_2$  reduction does not take place at all without a metal ion in solution. The difference here, is that under this cathodic potential  $\text{Ag}^+$  ions go into solution, enabling the  $\text{CO}_2$  reduction reaction.<sup>4</sup> This happens as due to the SECM capacitive approach, the sample is exposed to air for a relatively long period of time, which likely leads to the formation of a very small amount of oxide. The presence of  $\text{Ag}^+$  ions in the electrolyte can be confirmed looking at the 5<sup>th</sup> cycle recorded from the Pt-UME shown in Supplementary Figure 7b, which presents voltammetric features characteristic of the underpotential deposition of  $\text{Ag}^+$  on polycrystalline platinum.<sup>5</sup> The same happens with the copper sample when polarized more negatively than  $-1$  V vs. RHE. Copper deposition is observed in the Pt-UME voltammetry and can be seen in Supplementary Figure 7c.<sup>6</sup> These observations were made when either HER or  $\text{CO}_2$  reduction were performed at the sample and are crucial for the correct execution and judgment of the experimental results. In between measurements, the SECM cell was always fully disassembled and thoroughly cleaned as here we observed that trace amounts of metal ions can already lead to the production of CO.

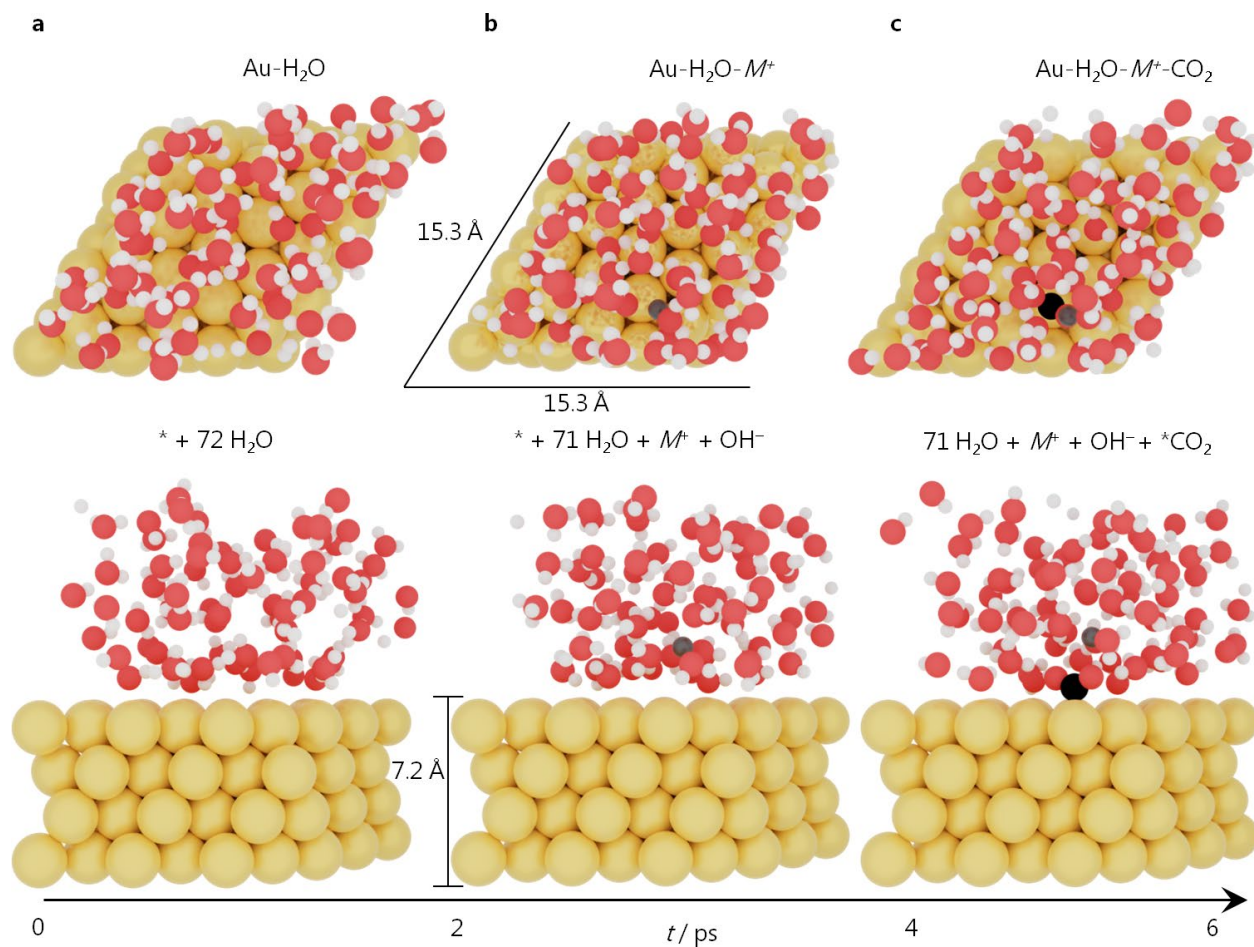


**Supplementary Figure 7.** Pt-UME voltammetry **a**, after HER or CO<sub>2</sub> reduction are performed on silver in 1 mM H<sub>2</sub>SO<sub>4</sub> and **b**, subsequent cycles from the same experiment showing the presence of Ag<sup>+</sup> ions in the electrolyte and **c**, similar observations on the copper electrode.

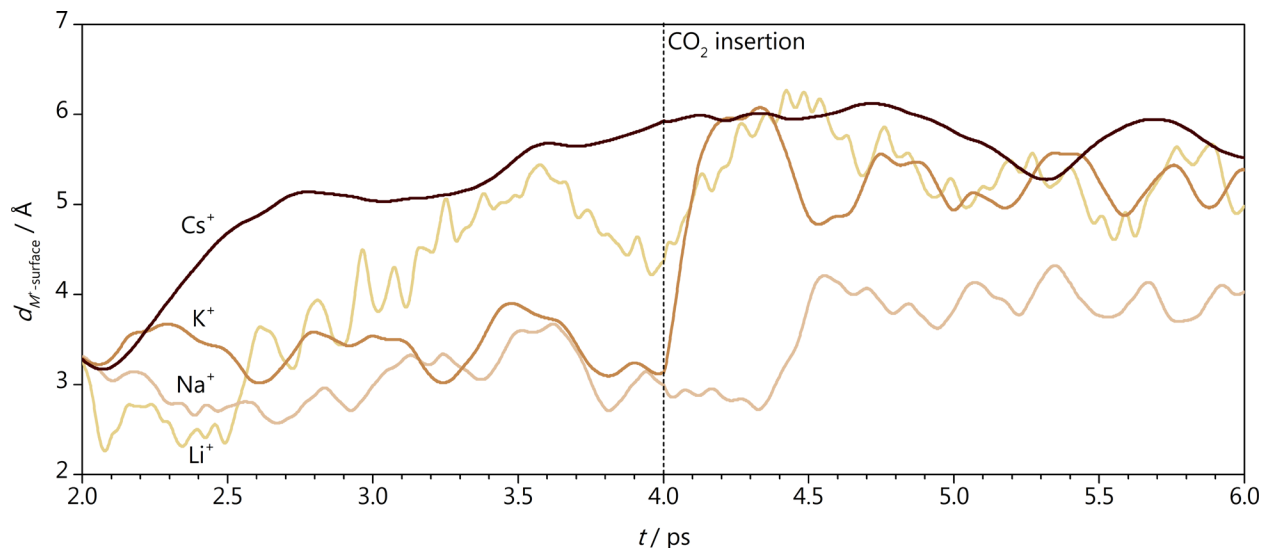
## Supplementary Methods

### Model

An accurate density functional theory (DFT) modeling of the interaction between ions and water molecules close to the catalytic surface requires *ab initio* molecular dynamics (AIMD) simulations with a suitable number of explicit solvent molecules and a proper choice of the equilibration time. Generally, at least 4 water bilayers are required, as well as at least 10 ps of equilibration time.<sup>7</sup> Since platinum and gold present similar structural properties, we inherited an explicit solvation configuration equilibrated for 11 ps of AIMD on (3√3×3√3)R30° Pt(111) at 300 K (4 water bilayers, 72 water molecules).<sup>7</sup> The pre-equilibrated water molecules were inserted on top of a (3√3×3√3) R30° Au(111) (4 layers, 15.3 Å × 15.3 Å × 30.0 Å, 8 Å vacuum thickness) and let further equilibrate for 2 ps with time steps of 1 fs at 300 K on the gold supercell (Supplementary Figure 8a). This system was named Au-H<sub>2</sub>O, since it reproduces the cation-free experimental sample. After this equilibration, an alkali atom (Li, Na, K, or Cs) was inserted in a solvation cavity close to the surface (initial  $d_{M\text{-surface}} = 3.3 \text{ \AA}$ , Supplementary Figure 9) and the four systems were equilibrated for 2 ps at 300 K (Supplementary Figure 8b). A hydrogen was removed from a water molecule in the fourth water bilayer, so that the +1 |e<sup>-</sup>| charge of the cation was balanced by the -1 |e<sup>-</sup>| charge of the resulting OH<sup>-</sup>. These systems were classified as Au-H<sub>2</sub>O-*M*<sup>+</sup> where *M*<sup>+</sup> stands for Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, and Cs<sup>+</sup>. Given the thickness of the solvation layer, around 1.4 nm, Au geometrical area, 2.0 nm<sup>2</sup>, and the number of water molecules, 72, the cation surface concentration is between 0.5 (1/*N*<sub>A</sub> mol of cation within  $V = 3.29 \text{ nm}^3$ ) and 0.8 M (1/72 of water molar concentration, 55.5 M). Finally, a CO<sub>2</sub> molecule was inserted close to the surface for both Au-H<sub>2</sub>O and Au-H<sub>2</sub>O-*M*<sup>+</sup> systems, with a surface coverage of 0.04 ML (1 molecule for 27 Au surface atoms), as shown in Supplementary Figure 8c. Upon interaction with solvation molecules and cation during 2 additional ps at 300 K, CO<sub>2</sub> adsorbed on the surface *via* a  $\eta^2_{\text{C,O}}$  conformation (bidentate through carbon and one oxygen) and the second oxygen coordinated to the alkali cation or to water molecules through H-bonds. These final systems were labelled Au-H<sub>2</sub>O-CO<sub>2</sub> and Au-H<sub>2</sub>O-*M*<sup>+</sup>-CO<sub>2</sub>.



**Supplementary Figure 8.** Input models for *ab initio* molecular dynamics simulation carried out on a (3x3x3)R30° Au(111) supercell (15.3 Å x 15.3 Å x 30.0 Å) with 72 water molecules. **a**, The Au-H<sub>2</sub>O system equilibrated for 2 ps (1 fs time step) at 300 K. **b**, Insertion of an alkali cation (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Cs<sup>+</sup>) close to the surface and equilibration for another 2 ps at 300 K. **c**, Addition of a CO<sub>2</sub> molecule to the system, that interacts with the gold surface *via* a  $\eta^2_{C,O}$  conformation with one oxygen coordinated to the alkali cation, and AIMD further carried out for 2 ps at 300 K. The portrayed cation is Li<sup>+</sup>.



**Supplementary Figure 9.** Distance between cation ( $M^+$ ) and surface calculated during equilibration of the Au-H<sub>2</sub>O- $M^+$  system (from 2 to 4 ps) and upon insertion of CO<sub>2</sub> in the vicinity of the cation (from 4 to 6 ps).

### Cation-water radial distribution functions

Cation-water radial distribution functions,  $g_{M^+-H_2O}(r)$  were obtained for the 2 ps equilibration of the Au-H<sub>2</sub>O- $M^+$  systems to account for the density of water molecules around the alkali metal center,  $M^+$ . We first calculated the distribution of distances,  $\eta(r)$ , defined as the number of H<sub>2</sub>O oxygens at a distance between  $r$  and  $r + \Delta r$  for all the molecular dynamics steps, where  $r$  is the position vector from the central cation and  $\Delta r$  is its differential. We then normalized  $\eta(r)$  for the expected surface density of cations  $\rho$  corresponding to 2D annulus formed by the solvation layer, Supplementary Equation 2:

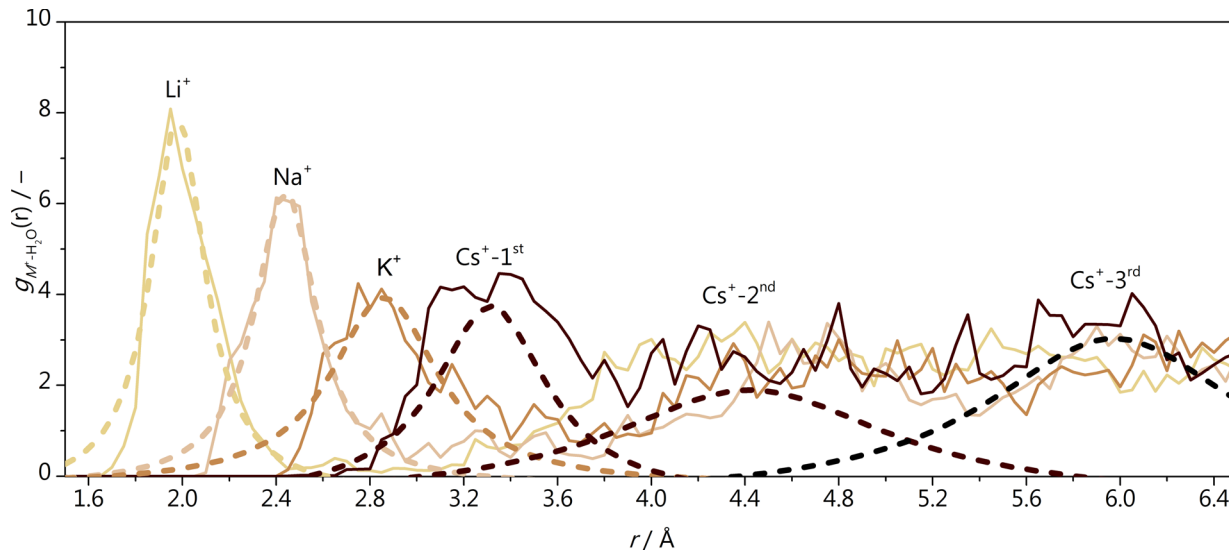
$$g(r)_{2D} = \frac{\eta(r)}{2\pi r \cdot \Delta r \cdot \rho} \quad (2)$$

where  $g(r)$  is the radial distribution function (dimensionless),  $\eta(r)$  the distribution of distances (dimensionless),  $r$  the position vector,  $\Delta r$  its differential (both in Å), and  $\rho$  the cation surface density (Å<sup>-2</sup>). Cation-water radial distribution functions are reported in Supplementary Figure 10 and the parameters of the Lorentzian fit on the first solvation shell peaks are shown in Supplementary Table 1. A Lorentzian fit was applied through Supplementary Equation 3 and it was preferred to a Gaussian fit since it was numerically more stable:

$$g(r) = g(r)_0 + \left(\frac{2A}{\pi}\right) \cdot \left(\frac{w}{4(r-d_{M^+-O})^2 + w^2}\right) \quad (3)$$

where  $g(r)$  is the radial distribution function,  $r$  the position vector (Å),  $w$  the full width at half maximum (Å),  $d_{M^+-O}$  the cation-oxygen bond length (Å), whilst  $g(r)_0$  (dimensionless) and  $A$  (Å) are fit parameters. For larger alkali cations, the first solvation shell becomes softer as indicated by the broadening of the first  $g_{M^+-H_2O}(r)$  peak and the increase of  $w$  (Supplementary Table 1). For Cs<sup>+</sup> the transition between first, second, and third solvation shell is continuous, therefore this alkali metal can easily modify its coordination. The parameters of the Lorentzian fit (dashed lines) and the consequent estimation of the cation-oxygen distances in the first solvation shell are reported in Supplementary Table 1 and agree with

previous experimental and theoretical reports.<sup>8,9</sup> The cation-oxygen bond length ( $d_{M^+-O}$ ) and its associated uncertainty are obtained from the fit parameters on the  $g(r)$  first peaks. The term  $d_{M^+-O(S.A.)}$  stands for averages of state-of-the-art values for cation-water distances.<sup>8,9</sup>



**Supplementary Figure 10.** Cation solvation shells during 2 ps equilibration of the Au-H<sub>2</sub>O- $M^+$ , described by the cation-water radial distribution functions.

**Supplementary Table 1.** Parameters of the Lorentzian fit and distances between cation and water molecules in the first solvation shell, estimated from the position of the first peak of cation-water radial distribution functions, Supplementary Figure 10.  $g(r)_0$ ,  $A$ ,  $w(\text{Å})$ ,  $\chi^2_v$  and  $d_{M^+-O}$  (Å) are fit parameters with the associated fit uncertainties. The state-of-the-art values for cation-water distances,  $d_{M^+-O(S.A.)}$  (Å), and associated uncertainties are taken from Ref.[9].

$M^+$	$g(r)_0 / -$	$A / \text{Å}$	$w / \text{Å}$	$\chi^2_v / -$	$d_{M^+-O} / \text{Å}$	$d_{M^+-O(S.A.)} / \text{Å}$
Li <sup>+</sup>	$-0.39 \pm 0.16$	$3.7 \pm 0.3$	$0.28 \pm 0.02$	0.34	$1.981 \pm 0.007$	$2.08 \pm 0.07$
Na <sup>+</sup>	$-0.22 \pm 0.08$	$3.3 \pm 0.2$	$0.32 \pm 0.02$	0.12	$2.440 \pm 0.005$	$2.36 \pm 0.06$
K <sup>+</sup>	$-0.22 \pm 0.12$	$3.6 \pm 0.4$	$0.55 \pm 0.06$	0.22	$2.86 \pm 0.02$	$2.80 \pm 0.08$
Cs <sup>+</sup> -1 <sup>st</sup>	$-0.53 \pm 0.12$	$3.9 \pm 0.6$	$0.58 \pm 0.07$	0.21	$3.32 \pm 0.02$	$3.14 \pm 0.08$
Cs <sup>+</sup> -2 <sup>nd</sup>	$-0.53 \pm 0.12$	$6 \pm 2$	$1.5 \pm 0.4$	0.21	$4.42 \pm 0.08$	–
Cs <sup>+</sup> -3 <sup>rd</sup>	$-0.53 \pm 0.12$	$7 \pm 2$	$1.3 \pm 0.4$	0.21	$5.97 \pm 0.06$	–

### Cation coordination number

To obtain the coordination number  $N_{M^+-O}$  of the alkali cations  $M^+$ , we assigned a bond value equal to one if the cation-oxygen distance  $r_{M^+-O}$  was equal or lower than the cation-oxygen bond length  $d_{M^+-O}$ , Supplementary Table 1. Otherwise, the bond value was set to zero if  $r_{M^+-O}$  was larger than a certain threshold  $th_{M^+-O}$ : 2.5, 3.0, 3.5, 4.0 Å for Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, and Cs<sup>+</sup>, respectively (Supplementary Figure 10). Between these extremes,  $N_{M^+-O}$  was calculated through Supplementary Equation 4 following a decay controlled by the error function (erf), Supplementary Equation 5.<sup>10</sup> In Supplementary Equation 4,  $N_{M^+-O}$  is the cation coordination number (dimensionless),  $r_{M^+-O}$  is the cation-oxygen distance (Å),  $d_{M^+-O}$  the cation-

oxygen bond length ( $\text{\AA}$ ),  $th_{M^+-O}$  the cation-oxygen threshold ( $\text{\AA}$ ) and avg stands for average. In Supplementary Equation 5,  $t$  (dimensionless) is the variable of integration and 0 and  $z$  represent the integration limits.

$$N_{M^+-O} = \frac{1}{2} - \frac{1}{2} \operatorname{erf}\left(\frac{r_{M^+-O} - \operatorname{avg}(d_{M^+-O}, th_{M^+-O})}{0.2 \text{\AA}}\right) \quad (4)$$

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-t^2) dt \quad (5)$$

**Supplementary Table 2.** Cation coordination numbers to oxygen atoms in water ( $N_{M^+-O(H_2O)}$ ) and  $\text{CO}_2$  ( $N_{M^+-O(\text{CO}_2)}$ ) in presence and absence of adsorbed  $\text{CO}_2$  as calculated through Supplementary Equation 4. Cation coordination to water molecules or  $\text{CO}_2$  was calculated for  $\text{Au-H}_2\text{O-M}^+$  and  $\text{Au-H}_2\text{O-M}^+-\text{CO}_2$  during 2 ps AIMD at 300 K. Coordination numbers are reported as averages with their associated standard deviation  $\sigma(N_{M^+-O})$ , median, maximum, and minimum values.

$M^+$	$N_{M^+-O(H_2O)} (\text{Au-H}_2\text{O-M}^+)$				$N_{M^+-O(H_2O)} (\text{Au-H}_2\text{O-M}^+-\text{CO}_2)$				$N_{M^+-O(\text{CO}_2)} (\text{Au-H}_2\text{O-M}^+-\text{CO}_2)$			
	Mean	Median	Max	Min	Mean	Median	Max	Min	Mean	Median	Max	Min
$\text{Li}^+$	$2.8 \pm 0.8$	2.9	3.9	0.3	$3.2 \pm 0.5$	3.3	3.9	1.8	$0.1 \pm 0.3$	0.0	1.0	0.0
$\text{Na}^+$	$3.2 \pm 0.5$	3.0	4.7	2.1	$2.3 \pm 0.4$	2.3	3.0	1.2	$0.9 \pm 0.2$	1.0	1.0	0.0
$\text{K}^+$	$3.5 \pm 0.9$	3.4	4.9	1.1	$3.6 \pm 0.6$	3.7	4.9	1.7	$0.9 \pm 0.4$	1.0	2.0	0.0
$\text{Cs}^+$	$5.8 \pm 1.2$	5.9	8.0	2.9	$5.4 \pm 0.9$	5.4	6.9	3.6	$1.3 \pm 0.5$	1.1	2.0	0.0

**Supplementary Table 3.** Average  $\text{CO}_2$  adsorption Gibbs free energy  $\Delta G^*_{\text{CO}_2}$  (eV) and cation induced stabilization,  $\Delta\Delta G^*_{\text{CO}_2}$  (eV).  $\Delta G^*_{\text{CO}_2}$  are reported with their associated standard deviations  $\sigma(\Delta G^*_{\text{CO}_2})$ . The systems under study were  $\text{Au-H}_2\text{O-CO}_2$  and  $\text{Au-H}_2\text{O-CO}_2\text{-M}^+$  equilibrated for 1 and 2 ps AIMD respectively. The explicit solvent layer includes 72  $\text{H}_2\text{O}$  molecules. Those containing cations have a water molecule replaced by  $M^+\text{OH}$ .

System	$\Delta G^*_{\text{CO}_2} / \text{eV}$	$\Delta\Delta G^*_{\text{CO}_2} / \text{eV}$
$\text{H}_2\text{O}$	$+0.80 \pm 0.18$	–
$\text{Li}^+$	$+0.16 \pm 0.24$	–0.64
$\text{Na}^+$	$+0.28 \pm 0.18$	–0.53
$\text{K}^+$	$+0.41 \pm 0.12$	–0.39
$\text{Cs}^+$	$+0.23 \pm 0.21$	–0.58

**Supplementary Table 4.** Average  $\text{CO}_2$  adsorption Gibbs free energy  $\Delta G^*_{\text{CO}_2}$  (eV),  $\text{CO}_2$  activation angle  $\alpha$  (degrees), Bader charges for  $\text{CO}_2$  intermediate and cation  $M^+$ , either coordinated to  $\text{CO}_2$  or in the reference system ( $\text{CO}_2$  removed), reported in elementary charge ( $|e^-|$ ) and net  $\text{CO}_2$  surface normal electric dipole moment  $\vec{p}$  reported in  $|e^-| \text{\AA}$ . Uncertainties are given as the standard deviation of the data. For cation Bader charges,  $\Delta q \leq 0.01 |e^-|$ .

System	$\Delta G^*_{\text{CO}_2} / \text{eV}$	$\alpha / ^\circ$	$q_{\text{CO}_2} /  e^- $	$q_{M^+(\text{CO}_2)} /  e^- $	$q_{M^+(\text{ref})} /  e^- $	$\vec{p}_{\text{CO}_2} /  e^-  \text{\AA}$
$\text{H}_2\text{O}$	$+0.80 \pm 0.18$	$137 \pm 5$	$-0.47 \pm 0.10$	–	–	$+0.40 \pm 0.09$
$\text{Li}^+$	$+0.16 \pm 0.24$	$133 \pm 5$	$-0.67 \pm 0.08$	–0.91	–0.90	$+0.66 \pm 0.11$
$\text{Na}^+$	$+0.28 \pm 0.18$	$134 \pm 5$	$-0.65 \pm 0.08$	–0.91	–0.90	$+0.54 \pm 0.08$
$\text{K}^+$	$+0.41 \pm 0.12$	$136 \pm 3$	$-0.58 \pm 0.09$	–0.91	–0.90	$+0.54 \pm 0.09$
$\text{Cs}^+$	$+0.23 \pm 0.21$	$131 \pm 4$	$-0.71 \pm 0.08$	–0.91	–0.91	$+0.65 \pm 0.13$

## Supplementary Note 1

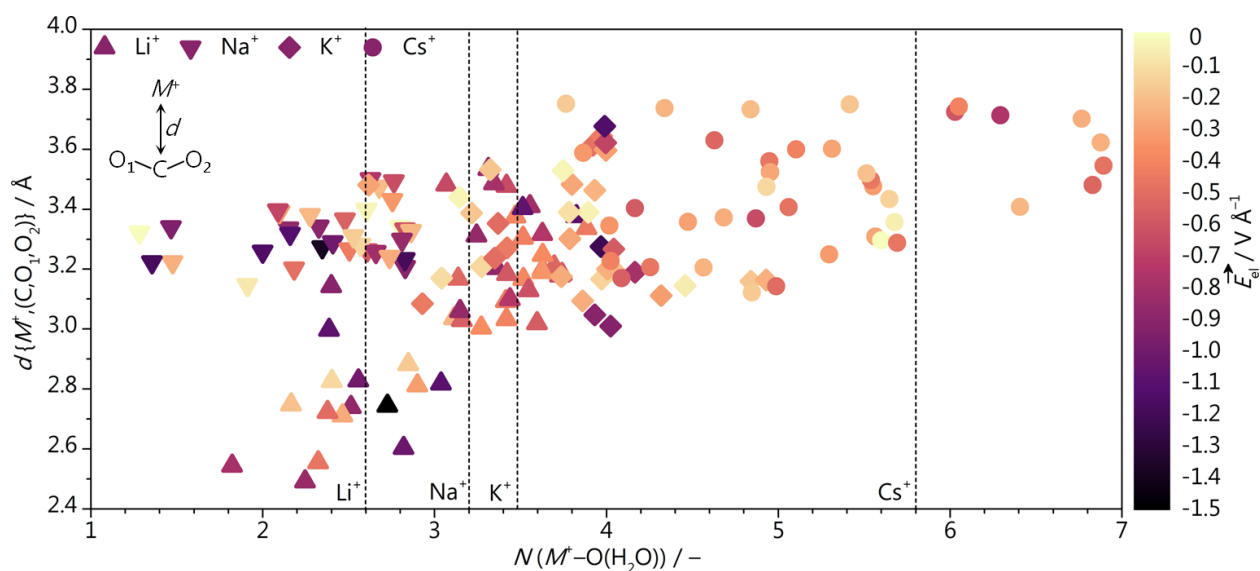
### Cation-induced electric field

We estimated the cation-induced electric field following a similar procedure as introduced by Chen *et al.*<sup>11</sup> First, we calculated the electrostatic potential induced by the cation upon removal of the CO<sub>2</sub> intermediate through Supplementary Equation 6, where  $U_{\text{surf+solv+ion}}$ ,  $U_{\text{surf+solv}}$ ,  $U_{\text{ion}}$  indicate the electrostatic potential for the overall system (surface, solvation and ion), the environment (surface and solvation), and the ion alone respectively. Then, assuming the cation as a point charge, we define the local electric field  $\vec{E}_{\text{el}}$  through Supplementary Equation 7, where  $U(\vec{r})$  is the cation-induced electrostatic potential difference at a given coordinate  $\vec{r}$ .  $\vec{r}_{\text{ads}}$  and  $\vec{r}_{M^+}$  represent the adsorbate and cation positions, respectively. The additional negative sign is introduced to assess the electric field induced on a negatively charged adsorbate, such as \*CO<sub>2</sub><sup>-</sup>.

$$U(\vec{r}) = U_{\text{surf+solv+ion}} - U_{\text{surf+solv}} - U_{\text{ion}} \quad (6)$$

$$-\vec{E}_{\text{el}} = -\left(-\frac{U(\vec{r}_{\text{ads}})-U(\vec{r}_{M^+})}{\|\vec{r}_{\text{ads}}-\vec{r}_{M^+}\|}\right)\hat{r} \quad (7)$$

We calculated the local electric field around the \*CO<sub>2</sub><sup>-</sup> adsorbate for different cation configurations over the last 1 ps of AIMD simulation. We applied Supplementary Equation 6 to estimate  $\vec{E}_{\text{el}}$  at the position of C, O<sub>1</sub>, and O<sub>2</sub> and then we plotted the averaged value versus the average between cation-(C, O<sub>1</sub>, O<sub>2</sub>) distances and cation-water coordination numbers. The electric field distribution is affected by both  $d(M^+, \{C, O_1, O_2\})$  and the instantaneous coordination number  $N(M^+-O(H_2O))$  and highest intensities are reported for low cation-water coordination numbers and short distances, in agreement with a recent theoretical characterization for electrochemical CO<sub>2</sub> reduction on gold.<sup>12</sup>



**Supplementary Figure 11.** Cation-induced electric field as a function of the cation-water coordination number,  $N(M^+-O(H_2O))$ , (horizontal axis) and the average between cation-(C,O<sub>1</sub>,O<sub>2</sub>) distances (vertical axis) for different AIMD configurations.  $\blacktriangle$ ,  $\blacktriangledown$ ,  $\blacklozenge$ , and  $\bullet$  represent Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, and Cs<sup>+</sup> respectively. Dashed lines represent average cation-water coordination numbers and are taken from Supplementary Table 2.

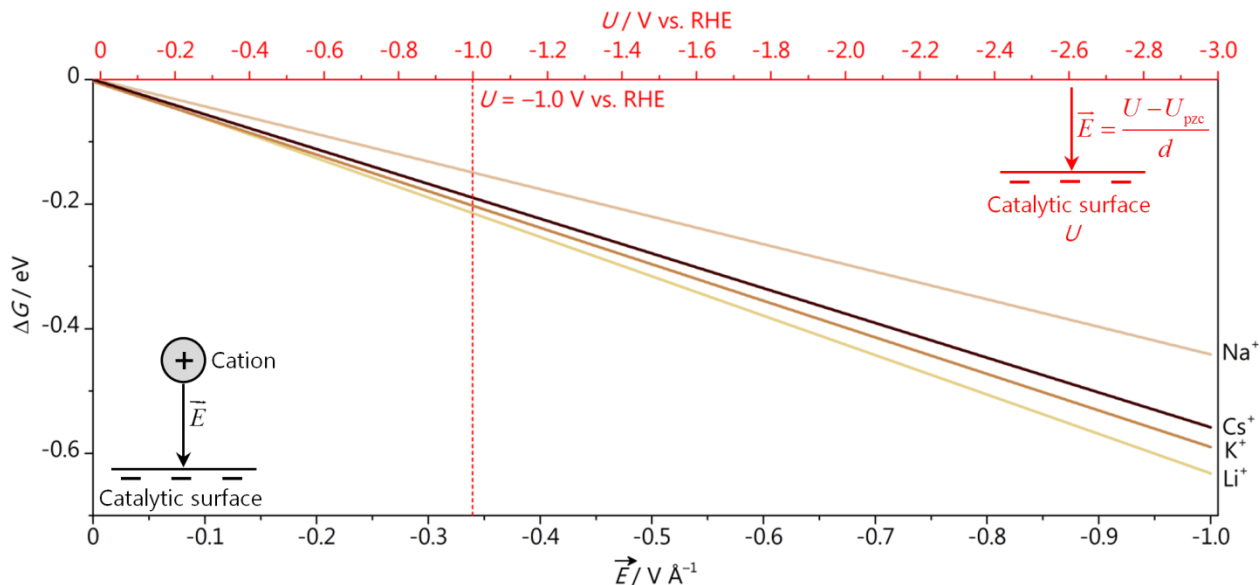
## Supplementary Note 2

### Electric dipole effects

Intermediates with large electric dipole moments are affected by electrostatic fields across the electrical double layer (EDL), and their Gibbs free energy of adsorption changes according to Supplementary Equation 8.<sup>13</sup> Thus, the stabilization (or destabilization) of adsorbates depends on their net electric dipole moment  $\vec{p}$  and their relative orientation with respect to the electric field  $\vec{E}_{\text{el}}$  within the EDL. The electric field is caused by the electric potential  $U$  applied to the electrode with respect to its potential of zero charge  $U_{\text{pzc}}$  (+0.2 V vs. SHE for polycrystalline gold<sup>14</sup>), and the contribution of neighboring ions,  $\vec{E}_{\text{el-ion}}$ , which is in the order of  $1 \text{ V } \text{\AA}^{-1}$ .<sup>11,15</sup> In Supplementary Equation 8  $d$  stands for the thickness of the EDL, which is usually assumed around  $3 \text{ \AA}$ .<sup>11,13,16</sup>

$$\Delta G = +\vec{p} \cdot \vec{E}_{\text{el}} = +\vec{p} \cdot \left( \frac{U - U_{\text{pzc}}}{d} \hat{z} + \vec{E}_{\text{el-ion}} \right) \quad (8)$$

Given the electric dipole moments calculated for adsorbed  $\text{CO}_2$  (Supplementary Table 4), we estimated that the stabilization for  $\text{CO}_2^-$  adsorption due to dipole/electric field interactions adds up to 0.6 eV in the presence of a partially desolvated neighboring cation ( $\vec{E}_{\text{el}} = 1 \text{ V } \text{\AA}^{-1}$ , Supplementary Figure 12). These values agree with the change in the Gibbs free energy of adsorption for  $\text{CO}_2^-$  due to cation- $\text{CO}_2$  interaction (Figure 7 in the Main Text). In the absence of a cation, a cathodic potential as negative as  $-3.0 \text{ V}$  vs. RHE is required to induce an equivalent electric field. Therefore, under standard  $\text{CO}_2$  reduction conditions the cation is key to open the reduction reaction pathway *via* explicit ionic bond with negatively charged intermediate and explicit, short-range dipole/cation-induced electric field effect.



**Supplementary Figure 12.** Stabilization of  $\text{CO}_2$  adsorption due to the interaction between  $\text{CO}_2$  dipole moment and local electric field generated by the cation (bottom axis, inset on the left). Top x-axis (red, inset on the right) reports the cathodic potential needed to achieve an equivalent electric field in absence of cation, according to Supplementary Equation 8 and assuming an EDL thickness,  $d$ , of  $3 \text{ \AA}$ .<sup>11,13,16</sup> Red dashed line indicates the potential applied during the study of CO production vs.  $\text{Cs}^+$  concentration on gold (Figure 2).

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