Supporting Information

Electrolyte Buffering Species as Oxygen Donor Shuttles in CO Electrooxidation

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Electrochemical Characterization



Figure S1: Cyclic voltammetry of the (A) Au and (B) Pt RDE electrode in 0.1 M H_2SO_4 at $50mVs^{-1}$.

Derivation Diffusion Coefficient

The diffusion coefficients in the different electrolytes were obtained correcting the experimentally limiting current (j_{lim}) for the contribution of OH⁻ to the total COOR diffusion limiting current, according to:

$$j_{lim} = j_{lim,A^-} + j_{lim,OH^-}; \tag{S1}$$

where j_{lim,A^-} is the COOR diffusion limiting current due to A^- and j_{lim,OH^-} is the COOR diffusion limiting current due to OH⁻. Using Levich equation (Eq. 4), we calculated j_{lim,OH^-} using a concentration of OH⁻ derived from the experimentally measured pH and D equals to $4.51*10^{-5}$ cm² s⁻¹ (i.e. the diffusion coefficient value obtained for OH⁻.). Then, we derived the diffusion coefficients by doing the linear fitting of j_{lim,A^-} :

• vs. the square root of the rotation (see Fig. 3 A), as:

$$D = \left(\frac{slope_{\omega}}{0.62nF\nu^{-1/6}c}\right)^{3/2}; (S2)$$

where *n* the number of electron transferred is 2, F the Faraday constant is 96485 (C mol⁻¹), ν the kinematic viscosity of water is 0.01 (cm²s⁻¹) and *c* is the bulk concentration of A⁻ (mol cm⁻³);

• vs. the concentration (see Fig. 3 B), as:

$$D = \left(\frac{slope_c}{0.62nF\nu^{-1/6}\omega^{1/2}}\right)^{3/2}; (S3)$$

where ω the rotation rate is 167.55 (rads⁻¹).

The reported value of the diffusion coefficient in Fig. 3 are the average over the value obtained by Eq. S2 and Eq. S2.

Table S1: Diffusion coefficients (cm² s⁻¹) as calculated from the obtained slope for 1st and 2nd plateaus (D_{peak1} and D_{peak2}), and tabulated values for the different species (D_{tabulated}).^{28,32}

	D_{peak}	$\mathbf{D}_{tabulated}$	
СО	(1.19 ± 00) *10 ⁻⁵	$2.03*10^{-5}$	
OH^-	$(4.51 \pm 0.86) * 10^{-5}$	5.27^*10^{-5}	
HCO_{3}^{-}	-	0.95^*10^{-5}	
CO_3^{2-}	$(1.79 \pm 0.27) * 10^{-6}$	1.19^*10^{-5}	
$H_2PO_4^-$	-	0.96^*10^{-5}	
HPO_4^{2-}	$(1.14 \pm 0.66)^* 10^{-6}$	$0.76^{*}10^{-5}$	
PO_4^{3-}	-	$0.82^{*}10^{-5}$	
$B(OH)_4^-$	$(1.28 \pm 0.39) * 10^{-6}$	1.64^*10^{-5}	



Figure S2: Voltammetry of the Au RDE electrode in CO-saturated (A) 0.1 M KClO₄, (B) 0.1 M KClO₄ + 0.1 mM OH⁻, (C) 0.1 M KClO₄ + 0.5 mM OH⁻, (D) 0.1 M KClO₄ + 1 mM OH⁻ and (E) 0.1 M KClO₄ + 2 mM OH⁻ at 50mVs⁻¹ and different rotation rates (100, 400, 900,1600 and 2500 RPM).



Figure S3: Voltammetry of the Au RDE electrode in CO-saturated 0.1 M KClO₄ with the addition of 1 mM equimolar solutions of (A) phosphate buffer KH_2PO_4/K_2HPO_4 , (B) borate buffer $B(OH)_3/KB(OH)_4$, (C) bicarbonate buffer $KHCO_3/K_2CO_3$ and (D) phosphate buffer K_2HPO_4/K_3PO_4 at 50mVs⁻¹ and different rotation rates (100, 400, 900,1600 and 2500 RPM).



Figure S4: Voltammetry of the Au RDE electrode in CO-saturated 0.1 M KClO₄ with the addition of (A) 0.5 mM KHCO₃ and (B) 0.5 mM K₂CO₃ at 50mVs^{-1} and different rotation rates (100, 400, 900, 1200, 1600 and 2500 RPM).

Gold Oxide



Figure S5: Cyclic voltammetry of the Au RDE electrode in CO-saturated (A) 0.1 M KClO₄, (B) 0.1 M KClO₄ + 0.1 mM OH⁻, (C) 0.1 M KClO₄ + 0.5 mM OH⁻, (D) 0.1 M KClO₄ + 1 mM OH⁻ and (E) 0.1 M KClO₄ + 2 mM OH⁻ at 50mVs⁻¹ and 1600 RPM.

Online Electrochemical Mass Spectrometry

The online electrochemical mass spectrometry measurements (OLEMS) was carried out in the configuration described in³³ using a gold polycrystalline electrode. We detected that the product of COOR correspond to CO₂, as measured by the signal of mass fragment (m/z) 44. The value of the ratio between the 1st and 2nd peak obtained from the CO₂ OLEMS signal and from the current from voltammetry is comparable. The latter observation suggests that both 1st and 2nd peak corresponds to COOR to CO₂.



Figure S6: (A) OLEMS mass fragment measured during COOR corresponding to the formation of CO_2 during (B) voltammetry at 1 mVs⁻¹ in 0.1 M KClO₄ + 2 mM B(OH)₃/KB(OH)₄. In (B) it is also shown the voltammetry at 50 mVs⁻¹ measured in the hanging meniscus configuration in the OLEMS cell to verify the correctness of the voltammetry.

Additional Infrared Spectroscopy Data



Figure S7: Cyclic voltammetry of the Au thin film used in the ATR-FTIR measurements in CO-saturated 0.1 M KClO₄, 0.1 M KClO₄ + 4 mM KH₂PO₄/K₂HPO₄, 0.1 M KClO₄ + 4 mM KHCO₃/K₂CO₃ and 0.1 M KClO₄ + 2 mM KOH at 100 mVs⁻¹.



Figure S8: Transmission spectra recorded on a ZnSe hemispherical prism of (A) 0.2 M $\rm KH_2PO_4/K_2HPO_4$, 0.1 M $\rm KH_2PO_4$, 0.1 M $\rm K_2HPO_4$ and (B) 0.2 M $\rm KHCO_3/K_2CO_3$, 0.1 M $\rm KHCO_3$, 0.1 M $\rm K_2CO_3$. The background spectra was measured in water.



Figure S9: (A) ATR spectra of adsorbed CO species on a Au thin film during COOR in CO-saturated 0.1 M KHCO₃ (pH ca. 9). Starting from $E_{ref} = 0.1$ V, the potential was increased in 0.1 V step. (B) The calculated Stark tuning effect for adsorbed CO on top and on bridge site, as measured in (A).



Figure S10: ATR spectra of a Au thin film in CO-saturated (A) 0.1 M KClO₄, (B) 0.1 M KClO₄ + 2 mM KOH, (C) 0.1 M KClO₄ + 8 mM KH₂PO₄/K₂HPO₄ and (D) 0.1 M KClO₄+ 8 mM KHCO₃/K₂CO₃ with $E_{ref} = 0.0$ V.

COOR on Au in the Ammonium Buffer



Figure S11: Voltammetry of the Au RDE electrode in CO-saturated 0.1 M KClO₄ with the addition of equimolar solution of ammonium buffer (NH_4ClO_4/NH_3) at 1600 RPM and different scan rates (5, 50 and 1000 mVs⁻¹).



Figure S12: Voltammetry of the Pt RDE electrode in CO-saturated 0.1 M KClO₄ with the addition of equimolar solutions (1,2 and 4 mM) of (A) phosphate buffer KH_2PO_4/K_2HPO_4 , (B) borate buffer $B(OH)_3/KB(OH)_4$ and (C) bicarbonate buffer $KHCO_3/K_2CO_3$ at $50mVs^{-1}$ and 1600 RPM.



Figure S13: Voltammetry of the Pt RDE electrode in CO-saturated 0.1 M KClO₄ with the addition of equimolar 1 mM solution of (A) phosphate buffer $\rm KH_2PO_4/K_2HPO_4$, (B) borate buffer B(OH)₃/KB(OH)₄ and (C) bicarbonate buffer KHCO₃/K₂CO₃ at 50mVs⁻¹ and different rotation rates (100, 400, 900, 1600 and 2500 RPM).

Microkinetic Modelling

The following parameters were used in the microkinetic modelling.

Table S2: Diffusion coefficients.

Species	$D_i(m^2 \ s^{-1})$
OH-	5.27^*10^{-9}
H^+	$9.3^{*}10^{-9}$
HCO_{3}^{-}	0.95^*10^{-9}
$\mathrm{CO}_3^{\ 2-}$	1.19^*10^{-9}

Table S3: Kinetic rates for the homogeneous reactions.³⁴

Equation	$ \mathbf{k}_{f} $	k _b	Κ
6	$1.4^{*}10^{-3} \mathrm{Ms}^{-1}$	$\mathrm{k}_{6,f}/\mathrm{K}_{6}$	10^{-14}
7	$k_{7,b}/(K_6/K_8)$	$6.0^*10^9 (Ms)^{-1}$	$10^{-3.67}$
8	$k_{8,b}$ *K ₈	$5^*10^{10} \mathrm{Ms}^{-1}$	$10^{-10.3}$

From Koutecky-Levich analysis (see Fig. S14 A), we extrapolated the kinetic current (j_k) at different potentials. Hence, in Fig. S14 B we built a Tafel plot of the j_k . From j_k at the standard equilibrium potential of CO₂/CO ($E^0=0.1$ V vs. RHE at pH 10.6), we extracted the standard rate constant $k^0 = 1.67^*10^{-7}$ m s⁻¹. From a Tafel Slope of ca. 120 mVdec⁻¹, indicating the first electron transfer to be rate limiting, we assume a charge transfer coefficient $\alpha=0.5$.



Figure S14: (A) Koutecky-Levich analysis at 0.25, 0.3, 0.35 and 0.4 V of the COOR current measured by voltammetry in CO-saturated 0.1 M KClO₄+ 1 mM KOH as in Fig. S2 D. (B) Tafel plot of the kinetic current (j_k) extrapolated at infinite rotation in (B).



Figure S15: The Tafel slope extracted from the voltammetry of the Au RDE electrode in CO-saturated 0.1 M KClO₄, 0.1 M KClO₄ + 0.5 mM OH⁻ and (C) 0.1 M KClO₄ + 2 mM OH⁻ at 50 mVs⁻¹ and 1600 RPM.



Figure S16: (A) Levich plot of the simulated diffusion limiting current for the 1st COOR plateau in 2 mM HCO₃⁻/CO₃²⁻ at pH 10.33. (B) Concentration profiles of OH⁻ for different bulk bicarbonate concentration (0, 2 and 4 mM) under diffusion limitation (E=0.4 V) at 1600 RPM. Vertical line represents the theoretical diffusion layer thickness (δ) for OH⁻. The linear fitting of the concentration profile between 0-5 μ m (grey triangles) and between 5-12 μ m (red triangles).(C) Dependence of the simulated diffusion layer thickness on the CO₃²⁻ concentration, as obtained by linear fitting of the simulations in the first region (0-5 μ m, grey) and second region (5-12 μ m, red) of the diffusion layer.



Figure S17: (A) Simulated surface concentration of OH^- at different rotation rates in 2 mM HCO_3^{-}/CO_3^{-2-} at pH 10.33 at 50 mVs⁻¹. (B) Corresponding simulated voltammograms for j_{COOR} according to Eq. 10.



Figure S18: (A) Simulated surface pK_b for reaction (7) in 2 mM $HCO_3^{-}/CO_3^{2^-}$. (B) Concentration profiles of $CO_3^{2^-}$ under diffusion limitation (E=0.4 V) for different bulk bicarbonate concentration at pH 10.33 and 1600 RPM. Vertical line represents the theoretical diffusion layer thickness (δ) for $CO_3^{2^-}$, (dotted line) linear fitting of the concentration profile between $0-5\mu$ m. (C) Comparison of the simulated COOR current calculated using the Butler-Volmer or as the flux of each species in 2 mM $HCO_3^{-}/CO_3^{2^-}$. (C) Simulated pK_b for reaction (7) across the diffusion layer.