Supporting Information:
Electrolyte Effects on the Faradaic Efficiency of CO$_2$ reduction to CO on a Gold Electrode

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Electrochemical Characterization

Figure S1: Electrochemical characterization of the gold disk (A) and of the gold ring (B) in 0.1 M H$_2$SO$_4$ at 20mVs$^{-1}$ after the dopamine coating was removed by electrooxidation.
Processing RRDE Data

The experimental collection efficiency \( N \) was calculated using:

\[
N = \left| \frac{i_{\text{ring}}}{i_{\text{disk}}} \right|
\]  \hspace{1cm} (S1)

where \( i_{\text{ring}} \) and \( i_{\text{disk}} \) are the current measured at the ring and at disk in 0.1 M KNO\(_3\)/0.01 M K\(_3\)Fe(CN)\(_6\). The deposition of dopamine does not affect the collection efficiency, which we measured to be comparable to the one provided for the commercial RRDE tip (\( N \) ca. 0.24). We did not measure the thickness of the as-deposited polydopamine film, but for similar experimental condition a thickness between 10 and 20 nm was reported.\(^{S1}\)

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Figure S2: CVs in 0.1 M KNO\(_3\)/0.01 M K\(_3\)Fe(CN)\(_6\) recorded with the RRDE at 20 mVs\(^{-1}\) for 400 and 2500 RPM. Inset: collection efficiency calculated as the ratio between the ring and the disk current between 0.0 and -0.2 V vs. AgAgCl(sat).
Design of the Electrochemical Cell

Figure S3: Schematics of the configuration of the three-electrode cell used.
The RRDE Measurements

The exploitation of RRDE, as a technique to quantify the products evolved at the disk by the ring current, is limited by the attachment of bubbles on the PEEK spacer. The gas bubbles (especially CO bubbles) evolved at the disk during cathodic scan tend to stick on the PEEK spacer leading to a lower collection efficiency at the ring. As illustrated in our previous work, coating the PEEK spacer with dopamine increases the hydrophilicity resulting in a lower bubbles attachment. Still, a way to confirm the quality of the coating is given by the hysteresis of the ring cyclic voltammogram (CV), as well as the level of noise in the CV caused by bubbles evolution. The CV hysteresis (i.e., the overlapping between forward and backward scan) indicates whether there is bubble accumulation. In other words, bubble accumulation during the forward scan leads to a decrease in the collection efficiency, hence, to a lower ring current in the backward scan. Fig. S4 and Fig. S5 show the cyclic voltammetry as measured by RRDE at 400 and 2500 RPM in 0.01 and 0.5 M HCO$_3^-$, respectively. The ring CVs exhibit negligible hysteresis, validating the quality of the measurements. Nonetheless, this kind of RRDE measurements is limited to a current range in the order of 10 mA cm$^{-2}$. Larger currents result in a large amount of bubbles leading to disruption of the dopamine coating. Larger rotation speeds help to prevent bubble accumulation by quickly transporting away the gas evolved at the cathode compared to lower rotation rates. For this reason, we could scan the CVs to more negative potential at larger (2500 RPM) than at lower (400 RPM) rotation rates (see Fig. S17, Fig. S16, Fig. S19 and Fig. S18 in Supporting Information).
Figure S4: The total (A), the CO2RR (B) and the HER (C) currents in CO$_2$-saturated 0.01 M NaHCO$_3$ and 0.5 M Na$^+$ as measured by RRDE cyclic voltammetry at 20 mVs$^{-1}$ at 2500 (solid line) and 400 (dashed line) RPM. The inset in (B) presents the measured ring current used to derive the CO2RR current.

Figure S5: The total (A), the CO2RR (B) and the HER (C) currents in CO$_2$-saturated 0.5 M NaHCO$_3$ as measured by RRDE cyclic voltammetry at 20 mVs$^{-1}$ at 2500 (solid line) and 400 (dashed line) RPM. The inset in (B) presents the measured ring current used to derive the CO2RR current.
The Scan Rate Dependence

For scan rate lower than 20 mVs$^{-1}$, a total current in the order of 10 mA cm$^{-2}$ (due to CO2RR and/or HER) leads to the critical accumulation of bubbles on the PEEK spacer of the RRDE. In the study of oxygen evolution reaction (OER) catalysts by RRDE, scan rate in the order of 1 to 5 mVs$^{-1}$ have been used. The difference in the choice of scan rate can mainly be attributed to a lower disk current as well as a minor amount of evolved gas. In fact, the number of electrons needed to form one CO (or H$_2$) molecule is 2, while it is 4 for one molecule of O$_2$, thus, at the same current value, the amount of CO (or H$_2$) evolved is double the amount of O$_2$.

Figure S6: The CO2RR (A) and HER (B) current at different scan rates in CO$_2$-saturated 0.1 M NaHCO$_3$ as measured by RRDE voltammetry at 2500 RPM.

Figure S7: The CO2RR (A) and HER (B) current at different scan rates in CO$_2$-saturated 0.5 M NaHCO$_3$ as measured by RRDE voltammetry at 2500 RPM.
Bicarbonate and Cation Dependence at 400 RPM

Figure S8: The CO2RR (A) and HER (B) current in CO2-saturated bicarbonate electrolytes of different concentration of NaHCO3 and constant concentration of Na+ (0.5 M) as measured by RRDE voltammetry at 20 mVs⁻¹ and 400 RPM.

Figure S9: The CO2RR (A) and HER (B) current in CO2-saturated bicarbonate electrolytes of different concentration of Na⁺ (0.1, 0.2, 0.3 and 0.5 M) and constant concentration of NaHCO3 (0.1 M) as measured by RRDE voltammetry at 20 mVs⁻¹ and 400 RPM.
Bicarbonate Concentration Dependence: SHE vs. RHE Scale

Figure S10: The CO2RR (A) and HER (B) currents in CO₂-saturated bicarbonate electrolytes of different concentration of NaHCO₃ and constant concentration of Na⁺ (0.5 M) as measured by RRDE voltammetry at 20 mVs⁻¹ and 2500 RPM.

Figure S11: The extracted reaction order in bicarbonate for CO2RR at constant potential on the SHE (A) and on the RHE (B) scale in CO₂-saturated bicarbonate electrolytes of different concentration of NaHCO₃ and constant concentration of Na⁺ (0.5 M) as measured by RRDE voltammetry at 20 mVs⁻¹ and 2500 RPM.
Bicarbonate and Cation Concentration Dependence in Ar-saturated Electrolytes

Figure S12: The HER current in Ar-saturated bicarbonate electrolytes of different concentration of NaHCO$_3$ and constant concentration of Na$^+$ (0.5 M) as measured by RDE voltammetry at 20 mVs$^{-1}$ and 2500 RPM.

Figure S13: (A) The extracted reaction order in bicarbonate for HER in Ar-saturated electrolytes. (B) The rotation dependence expressed as the ratio of the current at 2500 RPM to the current at 400 RPM for HER as a function of bicarbonate concentration.
Figure S14: The HER current in Ar-saturated bicarbonate electrolytes of different concentration of Na\textsuperscript{+} and constant concentration of HCO\textsubscript{3}\textsuperscript{-} (0.1 M) as measured by RDE voltammetry at 20 mVs\textsuperscript{-1} and 2500 RPM.

Figure S15: (A) The extracted reaction order in cation for HER in Ar-saturated electrolytes. (B) The rotation dependence expressed as the ratio of the current at 2500 RPM to the current at 400 RPM for HER as a function of cation concentration.
CO2RR and HER in a given Electrolyte

To better compare CO2RR and HER rates for the same electrolyte condition, we plotted $j_{tot}$, $j_{CO}$ and $j_{H2}$. Fig. S16 and Fig. S17 show voltammetry measurements for the different bicarbonate concentrations at 400 and 2500 RPM, respectively. Fig. S18 and Fig. S19 show voltammetry measurements for the different sodium cation concentrations at 400 and 2500 RPM, respectively. The FE(CO) plots reported in Fig.1 and Fig.3 were obtained from the data presented here according to Eq.7.

Figure S16: The total (solid line), CO2RR (dotted line) and HER (dashed line) current in CO$_2$-saturated bicarbonate electrolytes of different concentration of NaHCO$_3$ and constant concentration of Na$^+$ (0.5 M) as measured by RRDE voltammetry at 20 mVs$^{-1}$ and 400 RPM.

Figure S17: The total (solid line), CO2RR (dotted line) and HER (dashed line) current in CO$_2$-saturated bicarbonate electrolytes of different concentration of NaHCO$_3$ and constant concentration of Na$^+$ (0.5 M) as measured by RRDE voltammetry at 20 mVs$^{-1}$ and 2500 RPM.
Figure S18: The total (solid line), CO2RR (dotted line) and HER (dashed line) current in CO2-saturated bicarbonate electrolytes of different concentration of Na+ and constant concentration of NaHCO3 (0.1 M) as measured by RRDE voltammetry at 20 mVs−1 and 400 RPM.

Figure S19: The total (solid line), CO2RR (dotted line) and HER (dashed line) current in CO2-saturated bicarbonate electrolytes of different concentration of Na+ and constant concentration of NaHCO3 (0.1 M) as measured by RRDE voltammetry at 20 mVs−1 and 2500 RPM.
The Cation Concentration Dependence in the Presence of a Chelating Agent

Figure S20: The CO₂RR (A) and HER (B) currents in CO₂-saturated bicarbonate electrolytes of different concentration of Na⁺ and constant concentration of NaHCO₃ (0.1 M) as measured by RRDE voltammetry at 20 mV s⁻¹ and 2500 RPM. Prior to use, the electrolytes were treated by adding Chelex 100 to remove possible traces of metal impurities.
The Nature of the Proton Donor for HER

Figure S21: Tafel slope for HER in CO$_2$-saturated 0.5 M NaHCO$_3$ derived from chronoamperometry (120 s) measurements at 2500 RPM.

Figure S22: The HER currents at low applied negative potential measured in CO$_2$-saturated 0.01 M NaHCO$_3$ and 0.5 M Na$^+$ as measured by RRDE for different rotation rates (A) and scan rates (B).
Calculations of the Limiting Current for HER

We calculated the limiting currents density for HER (\(j_{\text{lim}}\)) according to the Levich equation:

\[
j_{\text{lim}} = -0.62 \times n \times F \times D^{2/3} \times \omega^{1/2} \times \nu^{-1/6} \times C_{PD}
\]

where \(n\) is the number of electron transferred, \(F\) is the Faraday constant (C mol\(^{-1}\)), \(D\) is the diffusion coefficient (cm\(^2\) s\(^{-1}\)), \(\omega\) is the angular rotation rate (rad s\(^{-1}\)), \(\nu\) is the kinematic viscosity (cm\(^2\) s\(^{-1}\)) and \(C\) is the bulk concentration of the proton donor (mol cm\(^{-3}\)). For HER \(n\) is equal to 2. The diffusion coefficient \(D\) is 1.0\times10^{-5} cm\(^2\) s\(^{-1}\) for H\(_2\)CO\(_3\) and 1.2\times10^{-5} cm\(^2\) s\(^{-1}\) for HCO\(_3^-\). The kinematic viscosity of water is 0.009132 cm\(^2\) s\(^{-1}\). The angular rotation rate of 2500 RPM corresponds to 261.8 rad s\(^{-1}\). The bulk concentrations of H\(_2\)CO\(_3\) and HCO\(_3^-\) were calculated using the method described in \(S2\) and they are reported in Table 3.

References

(S1) Ball, V.; Del Frari, D.; Michel, M.; Buehler, M. J.; Toniazzo, V.; Singh, M. K.; Grace, J.; Ruch, D. Deposition Mechanism and Properties of Thin Polydopamine Films for High Added Value Applications in Surface Science at the Nanoscale. BioNanoScience 2012, 2, 16-34.

(S2) Zhong, H.; Fujii, K.; Nakano, Y.; Jin, F. Effect of CO2 Bubbling into Aqueous Solutions Used for Electrochemical Reduction of CO2 for Energy Conversion and Storage. The Journal of Physical Chemistry C 2015, 119, 55-61.