ELECTRONIC SUPPLEMENTARY INFORMATION

Selective reduction of carbon dioxide to formate through bicarbonate reduction on metal electrodes: New insights gained from substrate-generation/tip-collection mode of scanning electrochemical microscopy

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Experimental Section

Chemicals

KHCO₃ (Sigma-Aldrich), HCOONa (Merck), Na₂HPO₄ (SRL), NaH₂PO₄ (SRL), Hg₂ (NO₃)₂ (LobaChem), Ferrocenemethanol (97%, Aldrich), KCl (Merck), HNO₃ (SRL), KNO₃ (Merck), Bi(NO₃)₃.5H₂O(Aldrich), KOH (Merck), CH₃COONa (Merck) and CH₃COOH (Merck) were used as received

Disk electrodes of gold (BASi), silver (BASi), glassy carbon (BASi) and a home-fabricated Pd electrode were used as substrates. Electrodes were polished using alumina powder (1 μ m to 0.5 μ m), sonicated for 5 minutes and rinsed in ultrapure water. Gold and palladium electrodes were electrochemically cycled in 0.5M H₂SO₄ solution till a stable response was obtained. A blank voltammetric response was established for the glassy carbon electrode in sulphuric acid solution. Pt10 μ m ultramicroelectrode (CH Instruments, USA) was polished using 0.5 μ m alumina powder, sonicated and rinsed in ultrapure water and then cycled in 0.5M H₂SO₄. The RG value of Pt UME was calculated to be \approx 5 by fitting the approach curve ^{S1}.

Preparation of Mercury- and bismuth-film electrodes: Deoxygenated solutions of 10 mM $Hg_2(NO_3)_2 + 0.5\%$ HNO₃ in 0.1M KNO₃ was used for the electrodeposition of a thin film of mercury on to a glassy carbon electrode (GCE) by applying a potential of -0.1 V(vs Ag/AgCl) for 100 seconds ^{S2}. For the bismuth film deposition, 1 mM bismuth nitrate + 5% HNO₃ in 0.1 M acetate buffer solution was used for electrolysis at -1.0 V vs Ag/AgCl for 50 seconds ^{S3}.

The current values were normalized using the electrochemically active surface area (to be more precise), using methods specific to the (substrate) electrode material

For Au & Pd^[S4]: using the relationship between active surface area and the charge under the rereduction peak in the CV response characteristic of Au (Pd)'s oxidation-reduction voltammetry.

For Pt ^[S4]: using the relationship between the active surface area and the charge under the peaks corresponding to hydrogen adsorption-desorption (hydrogen underpotential deposition).

For Bi ^[S5]: Voltammetry of a reversible redox, Ru(NH3)6 2+/3+ was performed and the active surface area was calculated using the well-known Randles-Sevcik equation.

For Ag ^[S6]: using the relationship between the active surface area and the charge under the peaks corresponding to the monolayer-adsorption of Pb^{2+} on Ag surface in voltammetry (Pb-underpotential deposition).

For Hg film: As Hg's roughness factor is 1.0, the geometric surface area was used for the calculation of current density.

 CO_2 and bicarbonate reduction: Linear sweep voltammetry and cyclic voltammetry of CO₂ and bicarbonate reduction were studied in a conventional three-electrode system. Ag/AgCl was used as the reference electrode, Pt wire as the counter electrode and Hg, Bi, Pd, Au, Ag electrodes were used as working electrodes substrates and Pt UME as the tip in SECM. The electrolytes were 0.1M KHCO₃, 0.5M KOH and phosphate buffer solution (PBS) + 0.1KHCO₃.Electrolytes were purged with N₂ and the first two electrolytes were saturated with CO₂ when required. Scan rate employed for all the voltammetric experiments was 0.05Vs⁻¹.

CO oxidation reaction: CO oxidation voltammograms were obtained after passing CO for 10 minutes through the electrolyte solution keeping the Pt UME (10μ) at 0.05V, followed by N₂ purging for 20 minutes to remove excess CO. Then the CO oxidation was followed by recording the cyclic voltammogram by scanning the Pt UME (tip) potential anodically from -0.6V - 0.9V.

NMR analysis: The ¹³C NMR acquired on a Brucker 400MHz NMR instrument using CDCl₃ as the internal standared. NMR spectra has Formic acid obtained by electrolyzing 0.1 M KHCO₃ for an hour using a polished gold palate (0.5 cm x 0.5 cm) as working electrode and graphite rod as counter electrode applying -1.3 V vs. Ag/AgCl. After electrolysis the solution was acidified with dilute HClO₄ in order to remove un-reacted bicarbonate.

Scanning Electrochemical Microscopy: All the experiments were conducted by using CHI 900B SECM instrument. The Pt 10 µm UME was used as a probe for all the SECM experiments and the substrates were Au, Pd, Ag, and thin films of Hg and Bi deposited on glassy carbon surface. The Pt 10 μ m UME was kept and maintained at a constant distance of $\approx 20 \ \mu$ m from the substrate using positive feedback mode for noble metals (Au,Ag and Pd) and negative feedback mode (Bi and Hg) of SECM in ferrocenemethanol (1 mM) + 0.2 M KCl solutions. Bicarbonate reduction was followed at the substrate that is kept at a potential (called substrate potential (E_s)) and the voltammetric patterns for the oxidation of substrate-generated species were obtained at the Pt UME in a potential region of -0.6V to 0.9V. Ag/AgCl(satd KCl) reference electrode and Pt wire served as counter electrode for all the experiments. In this work, we used substrate generation-tip collection mode (SG-TC) of SECM. Freshly prepared 0.1M KHCO₃ solutions (pH = 8.34) deaerated with N₂ were used for the direct reduction of bicarbonate and CO₂-saturated 0.1M KHCO₃ solutions (pH = 6.8). A Pt UME 10 μ m immersed in the same solution opposite the substrate (at a distance of $\approx 20 \ \mu m$) served as the tip for the electro-oxidation of the products of HCO_3^{-}/CO_2 reduction at the substrate. Freshly prepared phosphate buffer solution (PBS) + 0.1 M KHCO₃ solution of pH= 6.7, Carbonate buffer of pH = 9 and 0.5 M KOH + CO_2 solution of pH = 8 were used to study bicarbonate and CO_2 reduction at different pH values. All the solutions were thoroughly deaerated with N₂.



Electrochemical reduction of CO₂ / HCO₃-on Ag surface

Figure S1: [Reduction of Bicarbonate/CO₂]: Linear sweep voltammetry of CO₂ reduction on Ag in 0.1M KHCO₃ solutions.



Figure S2: [Oxidation of Products (formate)]:(a) Cyclic voltammetric responses of Pt UME-tip probe to the products (e.g., formate/formic acid) generated at Au substrate in 0.1M KHCO₃ solution, (b) in 0.1M KHCO₃ solution saturated with CO₂. Tip scan rate: 0.05Vs⁻¹.

Electrochemical bicarbonate reduction of Pd surface



Figure S3: [Reduction of Bicarbonate]: Cyclic voltammetry of bicarbonate reduction on Pd in 0.1M KHCO₃ solution, scan rate: 0.05 Vs⁻¹.



Figure S4: [Oxidation of Products (formate)]: Cyclic voltammetric responses of Pt UME-tip probe to the products generated at Pd substrate in 0.1M KHCO₃ solution; Tip scan rate: $0.05Vs^{-1}$; Substrate Potential (E_s) values are given for each voltammetric response.

Electrochemical reduction of CO₂ / HCO₃-on Hg surface.



Figure S5: [Reduction of Bicarbonate/CO₂]: Linear sweep voltammetry of Hg in 0.1M KHCO₃ solutions of different pH: (i) 0.1M KHCO₃ solution (pH = 8.3) (black); (ii) 0.1M KHCO₃ solution saturated with $CO_2(pH = 6.8)$ (red); (iii) 0.1M KHCO₃+ PBS (pH = 6.8) (blue).Solutions de-aerated with N₂.



Figure S6: [Oxidation of Products (formate)]: Cyclic voltammetric responses of Pt UME-tip probe to the products generated at Hg substrate in 0.1M KHCO₃ solutions of different pH(i) 0.1M KHCO₃ solution+ PBS (pH = 6.8) (black); (ii) 0.1M KHCO₃ solution saturated with CO₂ (pH = 6.8) (red); Solutions de-aerated with N₂.Tip scan rate: 0.05Vs⁻¹; Substrate Potential (E₈) is fixed at -1.7V vs Ag/AgCl.

Electrochemical reduction of CO₂ / HCO₃-on Bi surface.



Figure S7: [Reduction of Bicarbonate/CO₂]: Linear sweep voltammetry of Bi in 0.1M KHCO₃ solutions of different pH: (i) 0.1M KHCO₃ solution, pH=8.3 (black); (ii) 0.1M KHCO₃ solution saturated with CO₂ (pH=6.8) (red); (iii) 0.1M KHCO₃+ PBS (pH = 6.8 (blue). Solutions dearerated with N₂.Scan rate: 0.05 Vs⁻¹



Figure S8: [Oxidation of Products (formate)]:Cyclic voltammetric responses of Pt UME-tip probe to the products generated at Bi substrate in 0.1M KHCO₃ solutions of different pH; (i) 0.1M KHCO₃ solution+ PBS (pH = 6.8) (black); (ii) 0.1M KHCO₃ solution saturated with CO₂ (pH = 6.8) (red); Solutions de-aerated with N₂.Tip scan rate: 0.05Vs⁻¹; Substrate Potential (E_s) is fixed at -1.4V vs Ag/AgCl.



Effect of tip-to-substrate distance (d) on the tip response to formate product.

Figure S9: [Oxidation of Products (formate)]: Cyclic voltammetric responses of Pt UME-tip probe to the products generated at Au substrate in 0.1M KHCO₃ solutions of different tip-substrate disatance (d) ranging from 5 to 40 μ m.

Local pH Effect



Figure S10: [Oxidation of Products (formate)]: Cyclic voltammetric responses of Pt UME-tip probe to the products generated at Au substrate in (a) 0.1M KHCO₃ and (b) 0.1M KHCO₃ + CO₂ solutions, before and after electrolysis.

Notes: According to Koper et al [Figure 1 in Ref.S7], the peak potential of formate ion oxidation at Pt electrode shifts to cathodic potentials systematically, following a catalytic proton-coupled electron transfer pathway. Based on the data reliability, we employed the cathodic shift of formate ion oxidation on Pt UME (tip-to-substrate distance ~ 20 μ m) as a probe of local pH changes at the substrate.

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Figure S11:NMR spectra of (a) potassium bicarbonate; and (b) formic acid obtained after electrolysis of 0.1 M KHCO₃ solution on gold electrode for one hour and later acidified with dilute HClO₄ to remove un-reacted bicarbonate.

References

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