

Supporting Information

Highly Selective Formate Formation via Bicarbonate Conversions

*Kohta Nomoto, Takuya Okazaki, Kosuke Beppu, Tetsuya Shishido, Fumiaki Amano**

Department of Applied Chemistry for Environment, Tokyo Metropolitan University, 1-1
Minami-Osawa, Hachioji, Tokyo 192-0397, Japan

Corresponding Author

* Fumiaki Amano

Postal: Department of Applied Chemistry for Environment, Tokyo Metropolitan University,
1-1 Minami-Osawa, Hachioji, Tokyo 192-0397, Japan

Phone: +81-42-677-2852

E-mail: f.amano@tmu.ac.jp

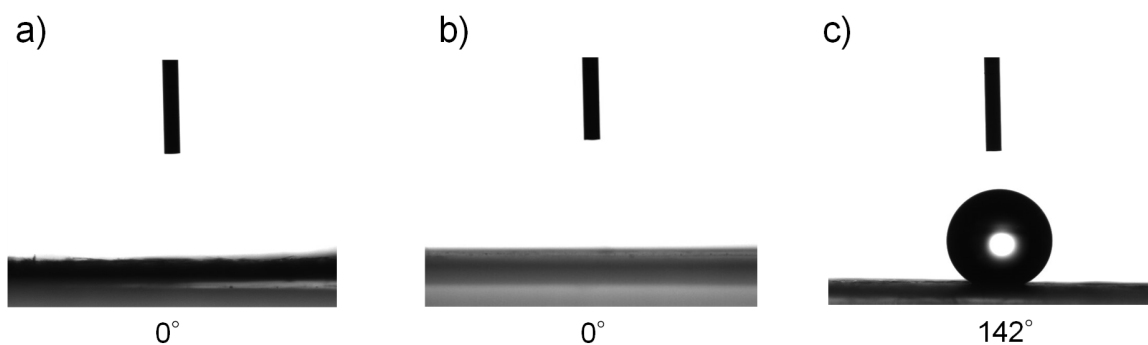


Figure S1. Contact angle measurement: (a) bismuth cathode, (b) hydrophilic porous membrane (mixed cellulose esters filter), and (c) PTFE-deposited bismuth cathode.

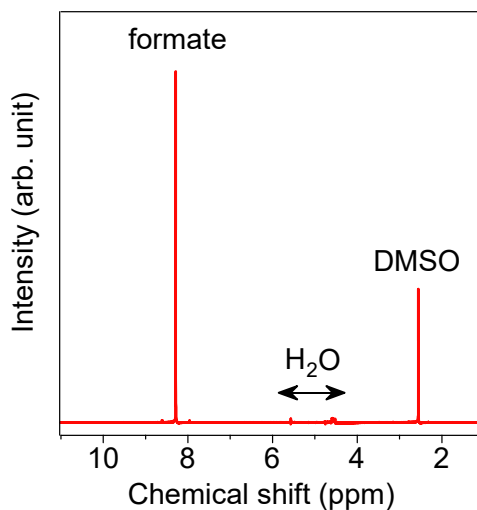


Figure S2. Proton nuclear magnetic resonance (^1H NMR) spectra of the catholyte solution after 1-h bicarbonate electrolysis at 100 mA cm^{-2} . The singlet peaks at 8.35 ppm and 2.50 ppm are attributed to formate and dimethyl sulfoxide (DMSO, internal standard). Water signals were suppressed. No peaks attributable to other CO_2 reduction products were observed.

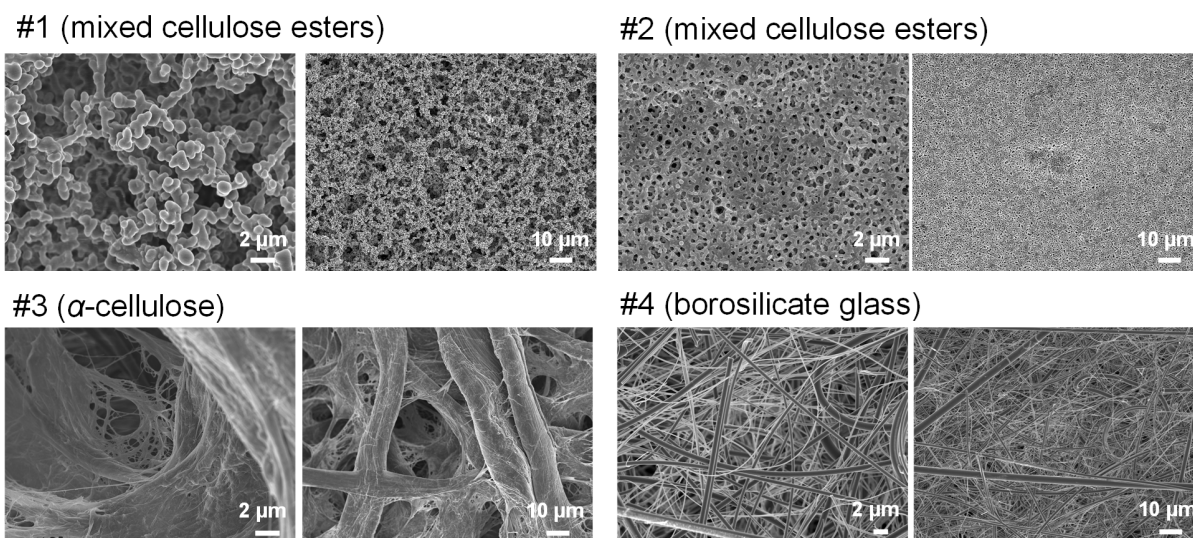


Figure S3. SEM images of porous membranes (#1–4) as an intermediate layer.

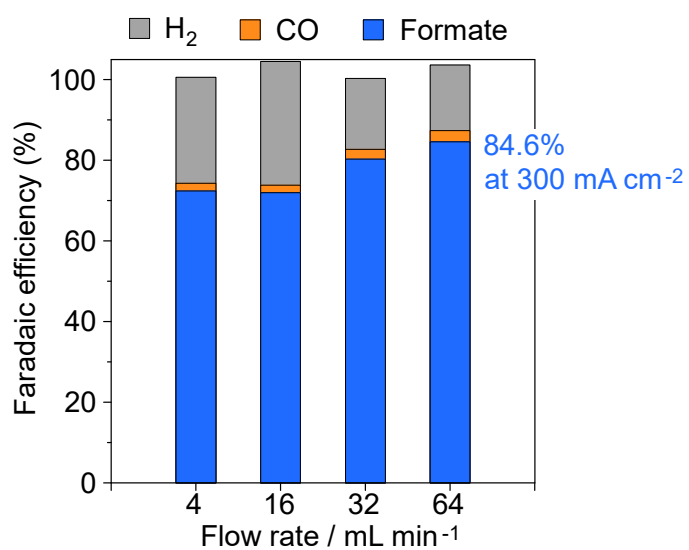


Figure S4. Effect of flow rate of 3.0 M KHCO₃ (pH 8.5) on FEs of each product at 300 mA cm⁻². The flow rate of 64 mL min⁻¹ enhanced formate FE to 84.6% even at 300 mA cm⁻².

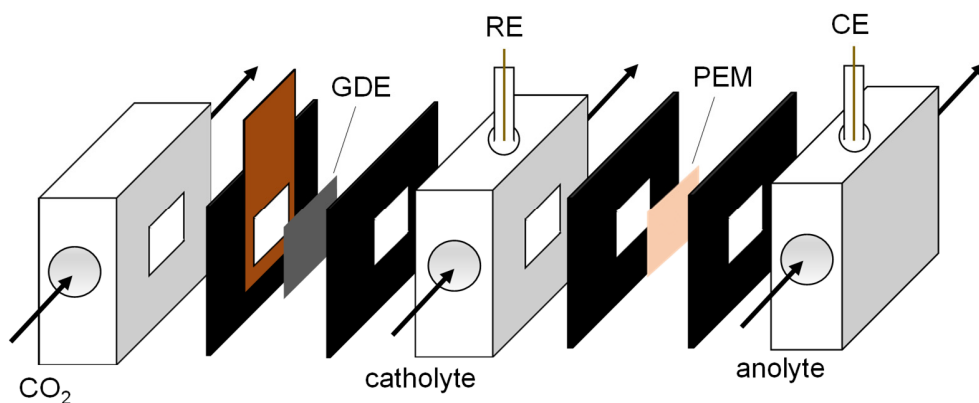


Figure S5. Schematics of gas-fed CO₂ electrolyzer. Gaseous CO₂ was supplied to the PTFE-treated Bi cathode (hydrophobic GDE) at 50 mL min⁻¹. Solutions of 3.0 M KHCO₃ were supplied at 4 mL min⁻¹ as catholyte and anolyte. The reference electrode (RE) and counter electrode (CE) were Ag/AgCl and Pt wire electrodes, respectively.

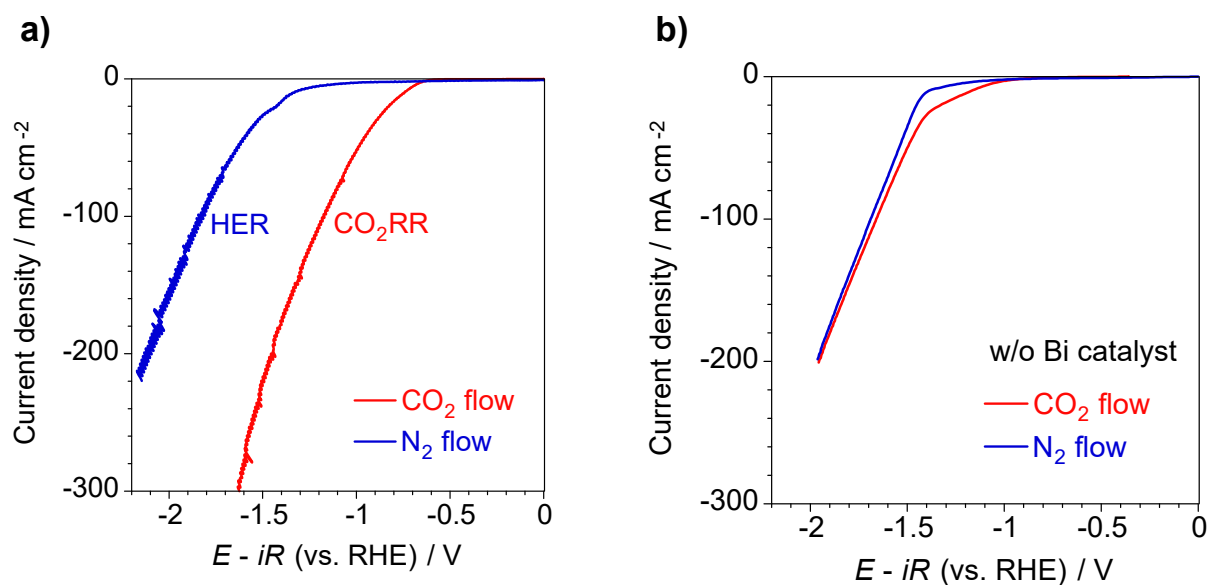


Figure S6. Linear sweep voltammetry (LSV) curves of (a) PTFE-treated Bi cathode and (b) PTFE-treated carbon paper (without Bi catalyst) in the gas-fed electrolyzer under N₂ and CO₂ flows. The cathodic current under N₂ flow is attributed to HER.

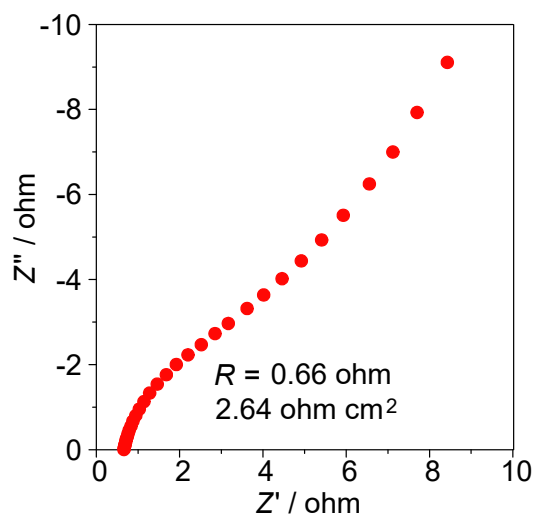


Figure S7. Nyquist plot of a bicarbonate electrolyzer at open circuit potential (frequencies from 500 kHz to 1 Hz). The x-intercept was used as the ohmic resistance (R).

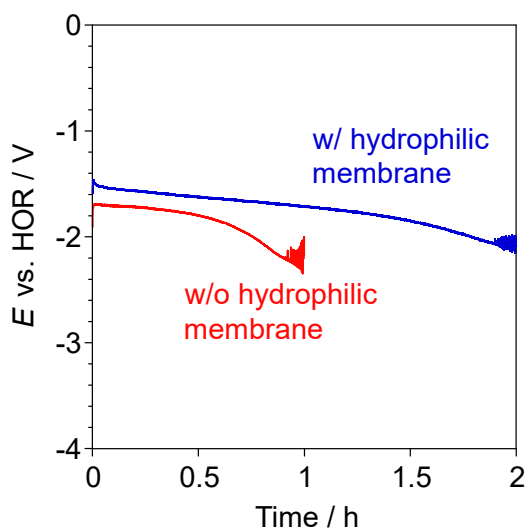


Figure S8. Chronopotentiometry at 100 mA cm^{-2} with and without intermediate hydrophilic membrane when Pt/CB anode is used for HOR. Reactions were performed under 3.0 M KHCO_3 flow at 32 mL min^{-1} using a grid flow plate. The overpotential gradually increased and became unstable in 1–2 hours when using a Pt/CB cathode.

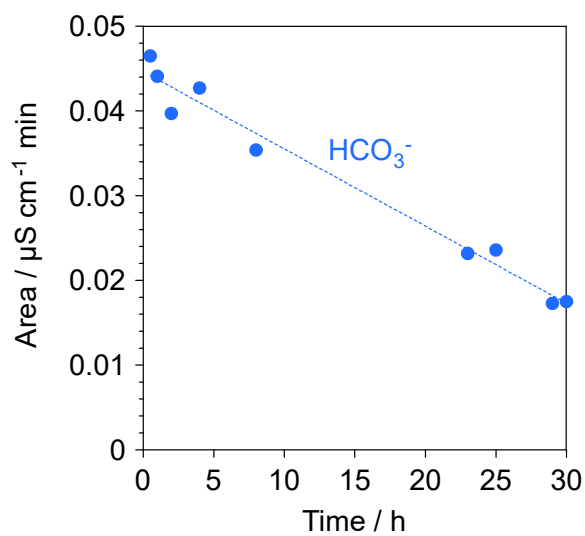


Figure S9. Time course of ion chromatography peak area of bicarbonate ion. The peak area gradually decreased from 3.0 M KHCO_3 over time during the 30-h reaction at 100 mA cm^{-2} . CO_2 gas was continuously bubbled into the circulating electrolyte during the reaction.

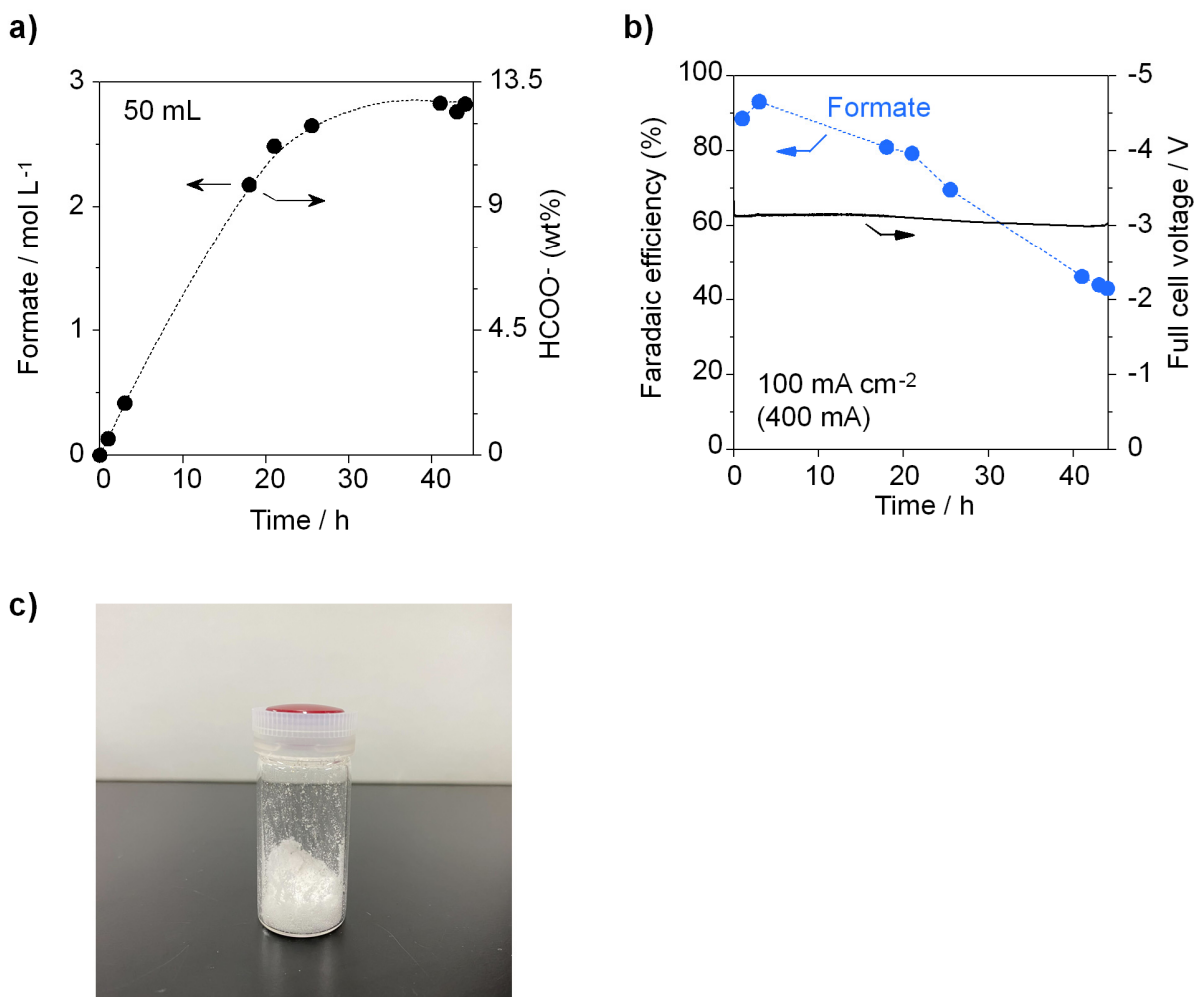


Figure S10. Electrochemical formate formation by a bicarbonate electrolyzer using IrO₂ anode for OER (OER|PEM|HCO₃⁻): (a) Concentration of formate in the circulated 50 mL catholyte (3.0 M KHCO₃) at 100 mA cm⁻². (b) Corresponding time course of formate FE and full cell voltage (without *iR* compensation). Reactions were performed under 3.0 M KHCO₃ flow at 32 mL min⁻¹ using a mixed cellulose esters membrane and a grid flow plate. The bicarbonate feedstock was continuously bubbled with 100% CO₂ gas to make up the loss. (c) Solid HCOOK electrochemically synthesized from KHCO₃ aqueous solution. The precipitate was obtained by evaporating the catholyte after the bicarbonate-fed electrolysis.