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SUPPLEMENTARY INFORMATION

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Continuous production of pure liquid fuel solutions via electrocatalytic CO_2 reduction using solid-electrolyte devices

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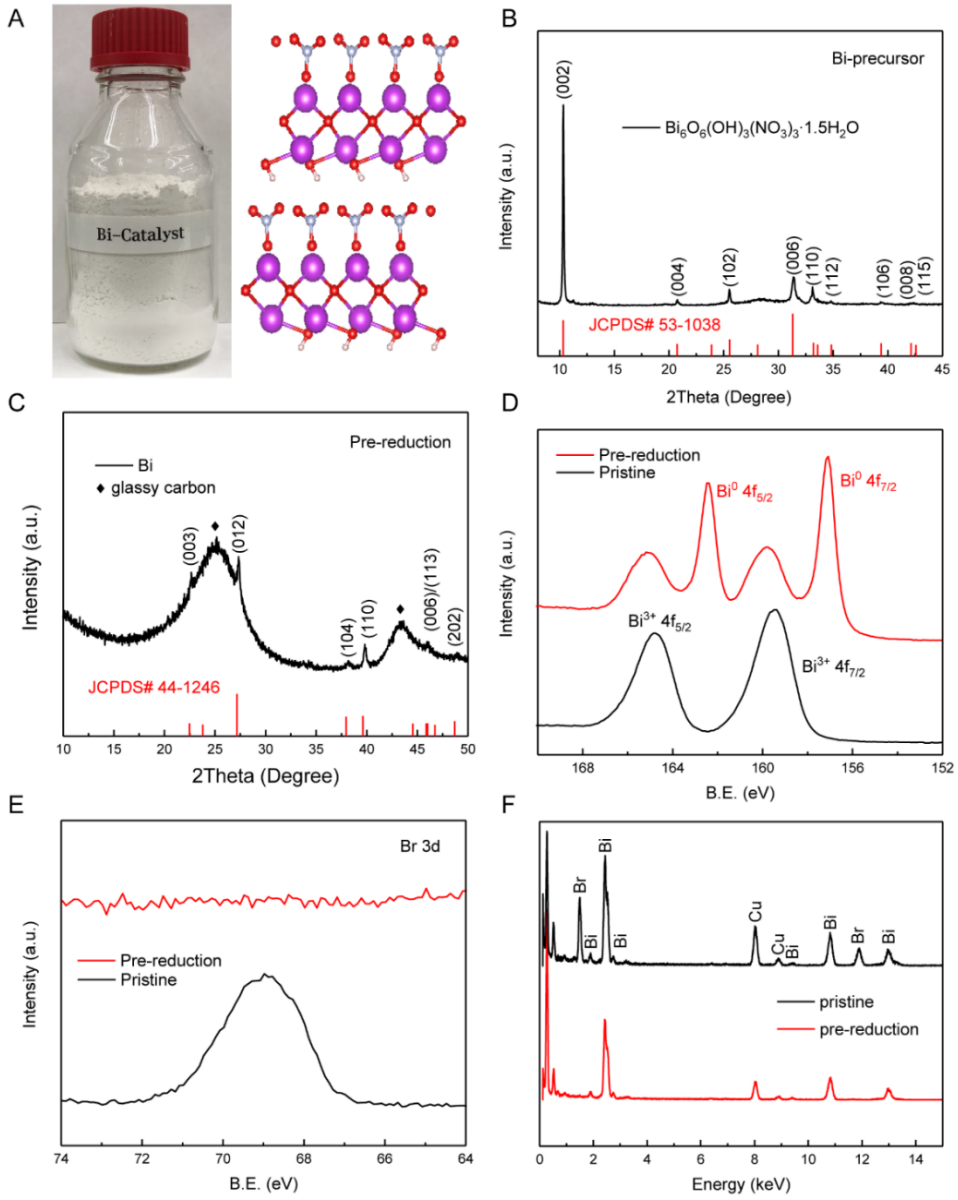
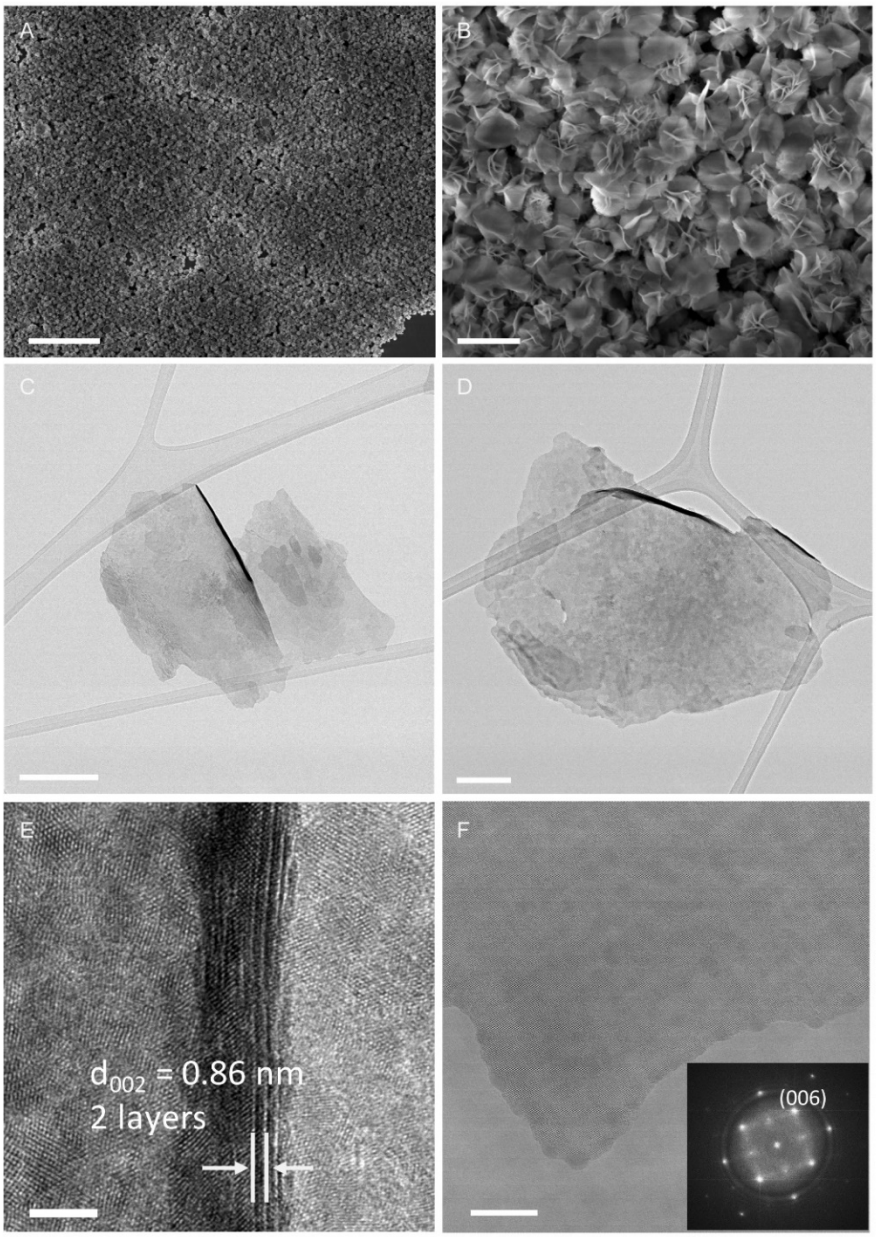
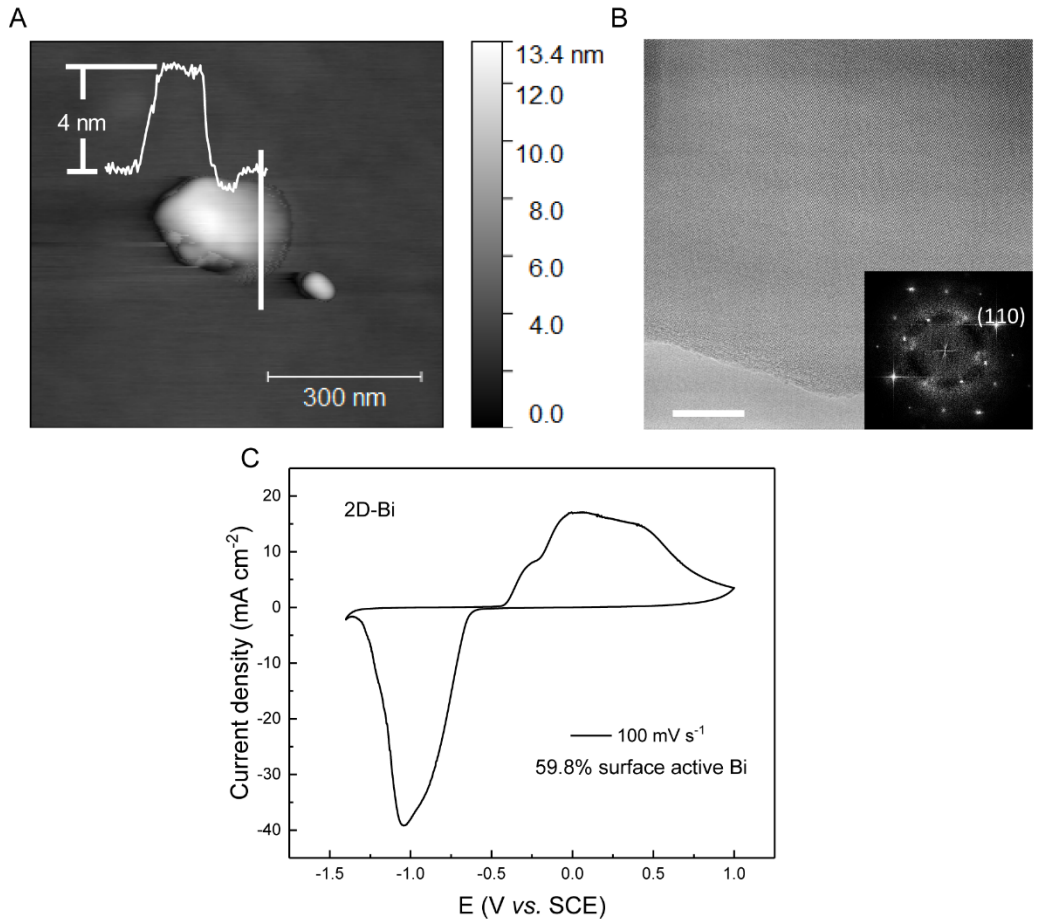


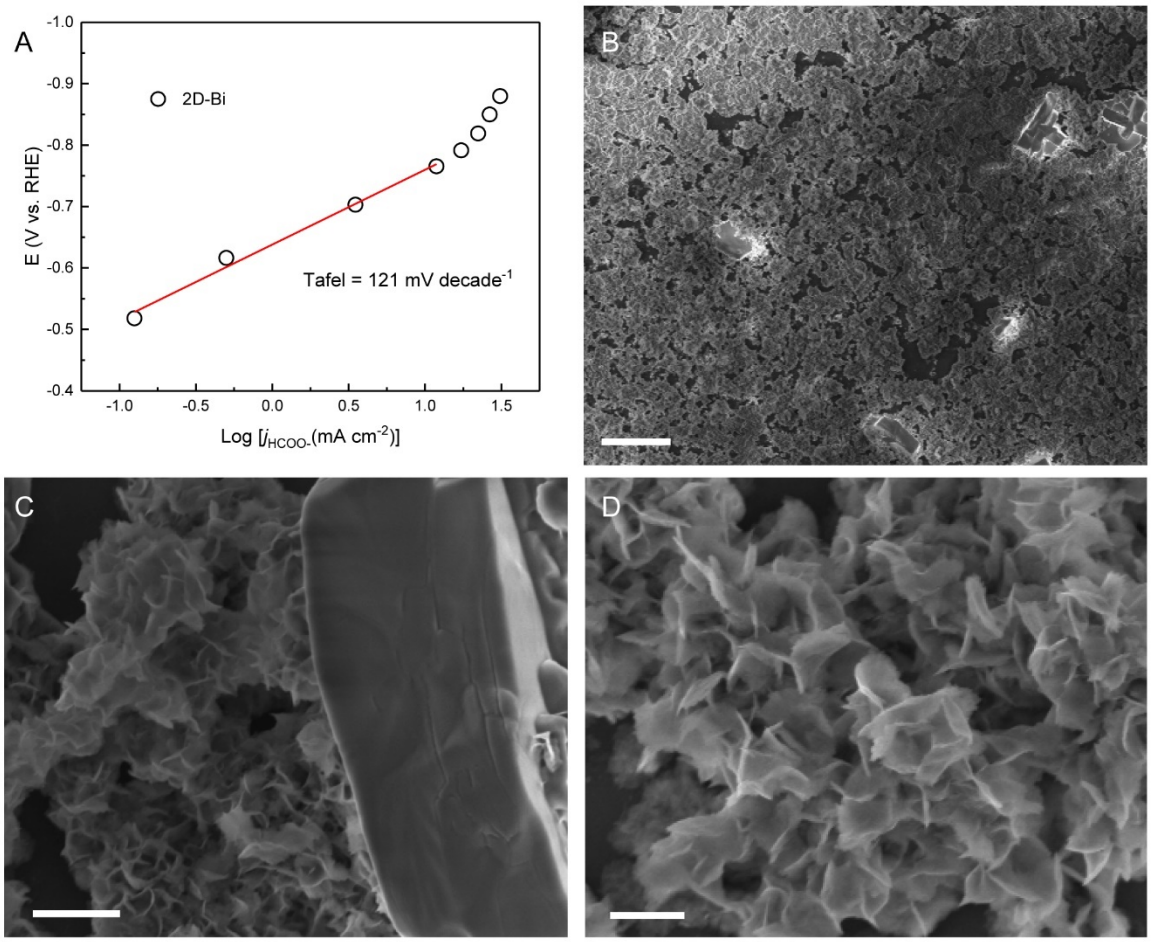
Supplementary Figure 1. Characterization of BOON and 2D-Bi. (**A**) Digital image of the synthesized 1 kilogram Bi-catalyst and its crystal structure, demonstrating that our synthesis strategy can be easily scaled up. Purple atom: Bi; red atom: O; grey atom: N; pink atom: H. (**B**) XRD pattern of as-prepared BOON nanosheets. (**C**) XRD pattern of 2D-Bi obtained from *in-situ* reduction of BOON, referred to as pre-reduction sample. (**D**) *Ex-situ* high-resolution Bi 4*f* spectra for BOON and 2D-Bi, showing that the oxidized Bi ($4f_{7/2}$ at 159.5 eV) in BOON was almost reduced into metallic Bi ($4f_{7/2}$ at 157 eV) in 2D-Bi. Note that the residual Bi oxides in 2D-Bi is due to the oxidation of active Bi when 2D-Bi catalyst was exposed to air during the XPS test. (**E**) *Ex-situ* high-resolution Br 3*d* spectra for BOON and 2D-Bi, demonstrating that the 2D-Bi surface was free of Br. (**F**) EDS analysis reveals that Br element has been completely removed from the catalyst after *in-situ* reduction, which is good agreement with XPS measurement.



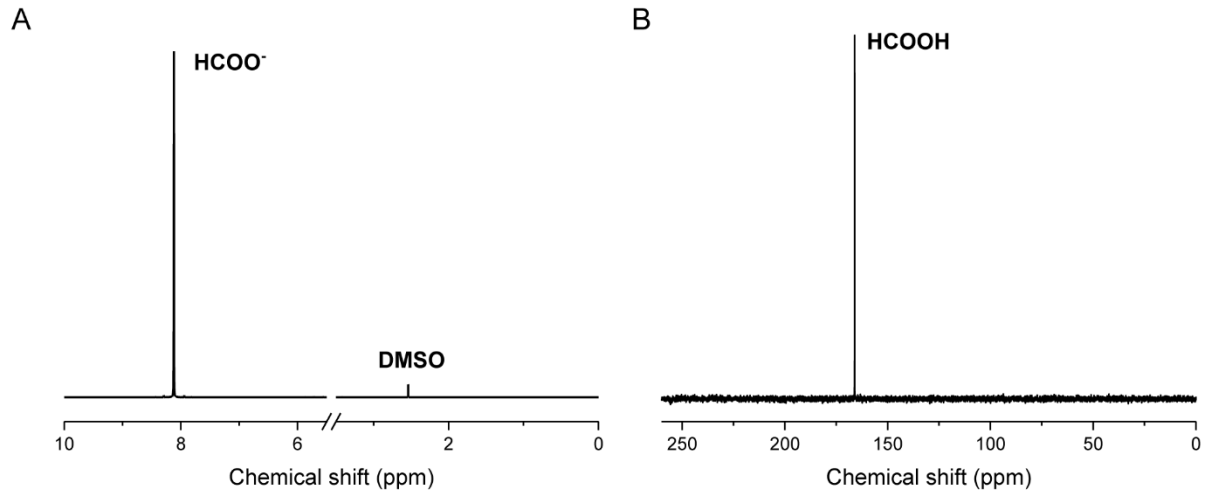
Supplementary Figure 2. Morphology characterization of BOON nanosheet. (**A-B**) SEM and (**C-D**) TEM images of as-prepared BOON nanosheet. (**E**) High-resolution TEM image of the edge of an individual BOON nanosheet displays a spacing of *ca*. 0.86 nm, which matches the *d*-spacing of the (002) planes. It shows that the BOON nanosheet only 2-layer-thick. (**F**) FFT analysis of an individual BOON nanosheet indicates its quasi-single-crystalline nature. Scale bars: **A** 20 μm; **B** 2 μm; **C** 200 nm; **D** 200 nm; **E** 2 nm; **F** 10 nm.



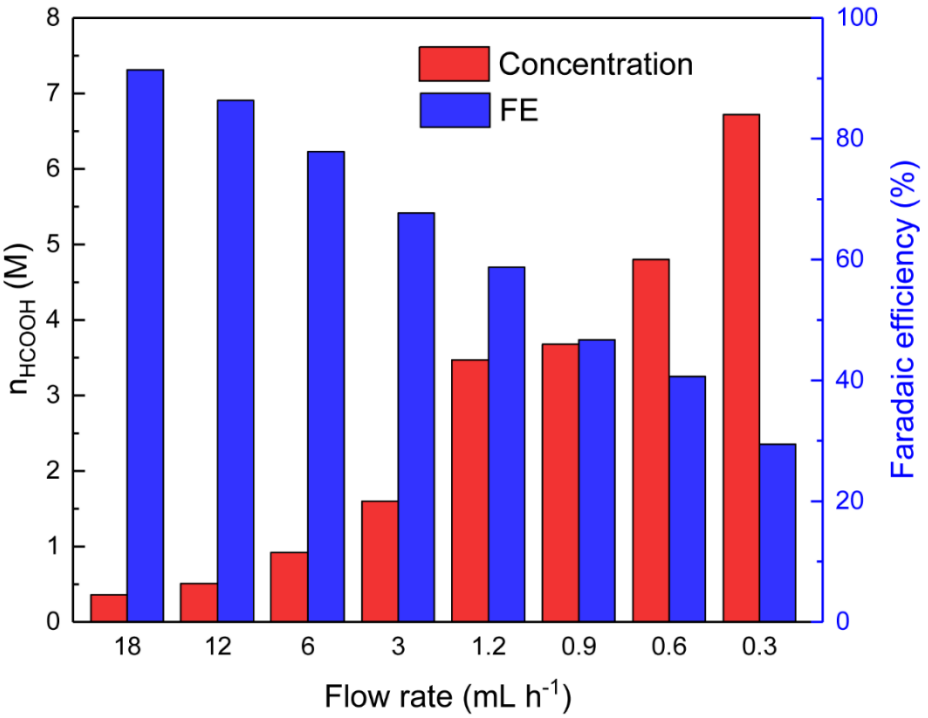
Supplementary Figure 3. Characterization of 2D-Bi nanosheet. (**A**) AFM image of individual 2D-Bi nanosheet and the corresponding height profile. (**B**) High-resolution TEM image of 2D-Bi nanosheet and the corresponding FFT image, suggesting its quasi-single-crystalline nature. (**C**) Cyclic voltammetry curve of 2D-Bi in CO_2-saturated 0.5 M $KHCO_3$ solution under the scan rate of 100 mV s^{-1}, which shows the reversible interconversion between Bi^{3+} and metallic Bi.



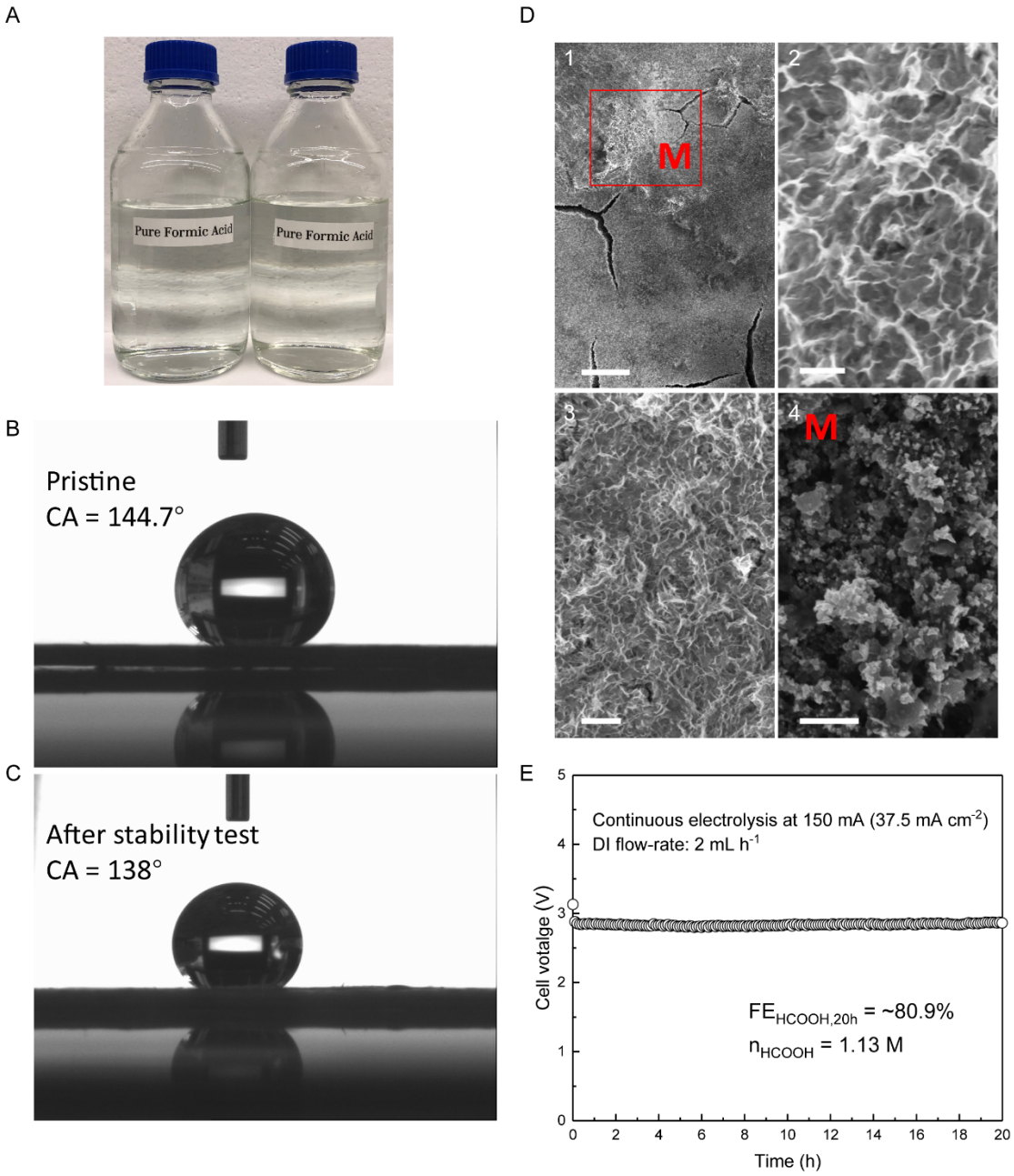
Supplementary Figure 4. Electrochemical analysis and post-characterization of 2D-Bi electrocatalyst. (**A**) Tafel plots for 2D-Bi. (**B-D**) Post-catalysis SEM images of 2D-Bi on glassy carbon, which electrolyzed in CO_2-saturated $KHCO_3$ electrolyte. Scale bars: **B** 20 μm; **C** 2 μm; **D** 2 μm.



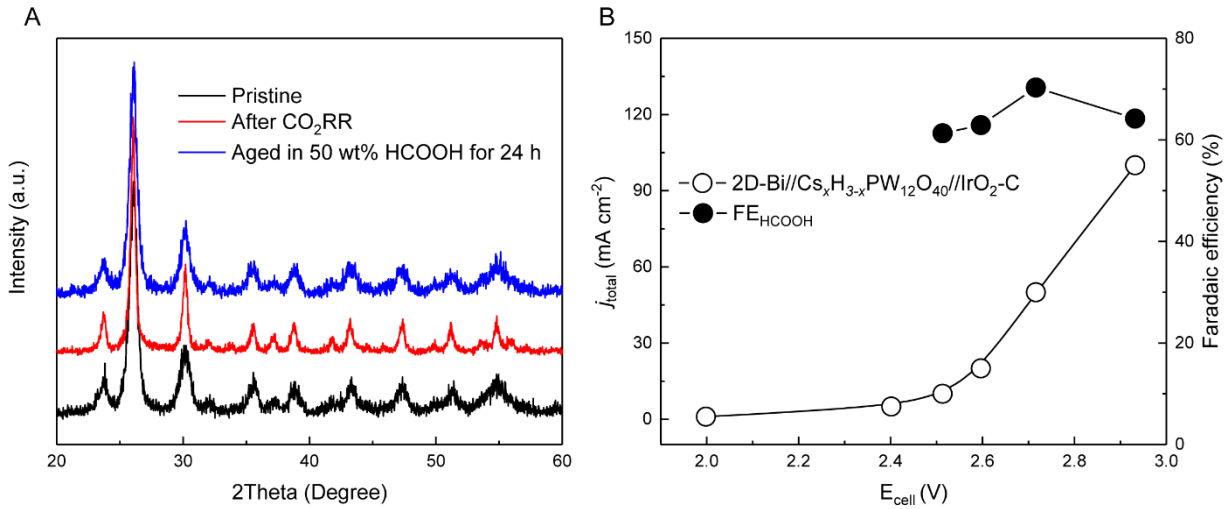
Supplementary Figure 5. NMR spectra. Typical (**A**) ^{1}H and (**B**) ^{13}C NMR spectra for as-prepared pure HCOOH solution from electrocatalytic CO_2 reduction, demonstrating that no other liquid products are formed. Note that the break region in (**A**) shows only the water peak.



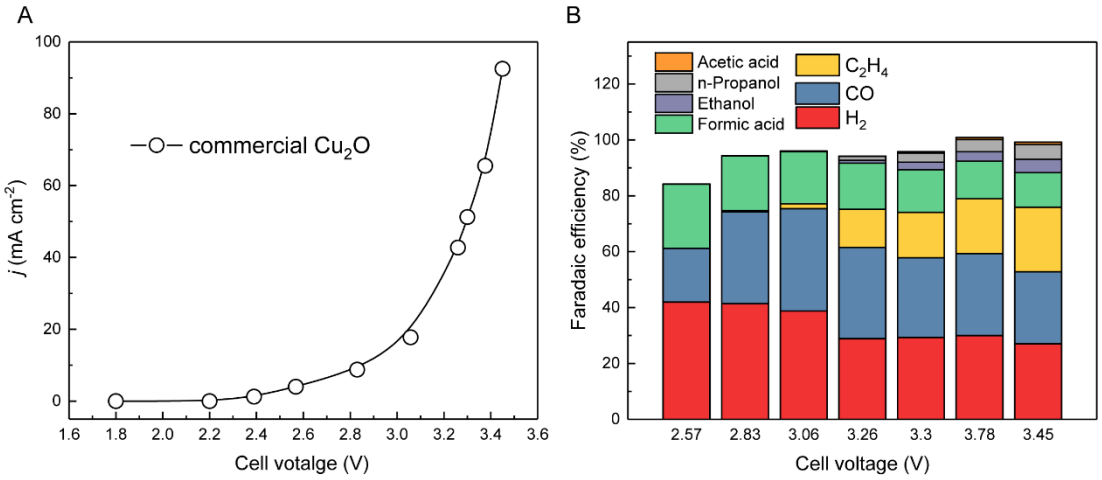
Supplementary Figure 6. CO_2RR performance of 2D-Bi//H^+-conductor//IrO_2-C cell. HCOOH concentration and corresponding Faradaic efficiency as a function of deionized water flow rate.



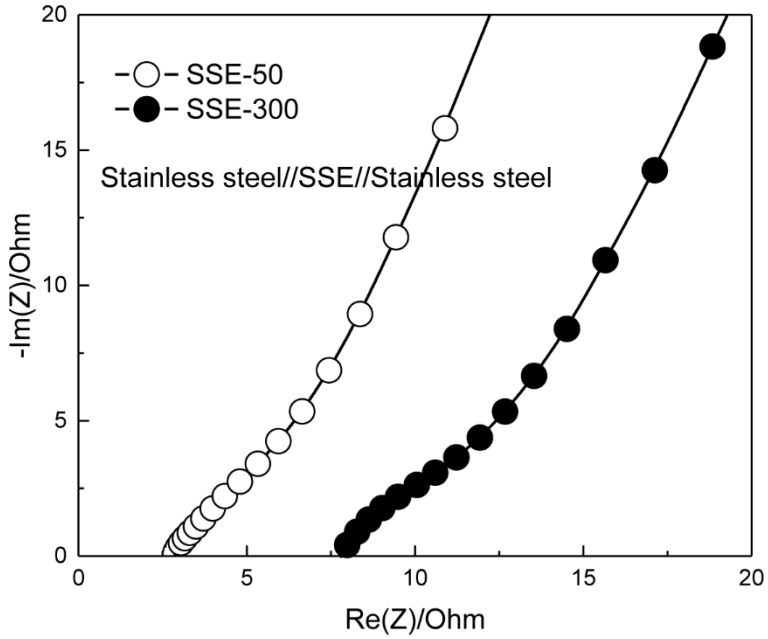
Supplementary Figure 7. Evaluation of 2D-Bi//H⁺-conductor//IrO_2-C cell. (**A**) Digital photo of continuously produced *ca*. 0.11 M pure HCOOH, showing that our strategy is very promising for large-scale application. Contact angle test of (**B**) pristine and (**C**) long-term aged GDL electrode, demonstrating its super-hydrophobic nature. (**D**) SEM images of 2D-Bi catalyst after 80 hours stability test. The SEM analysis reveals that the 2D-Bi catalyst still maintains the nanosheet morphology. Meanwhile, while some nanoparticles are also formed due to the pulverization of some ultrathin 2D-Bi, no micro-scale Bi agglomerates can be observed. (**E**) Stability test of 2D-Bi//H⁺-conductor//IrO_2-C cell at the current density of 37.5 mA cm^{-2}. After 20 hours continuous electrolysis, a *ca*. 1.13 M HCOOH solution was obtained, revealing an average HCOOH FE of 80.9%. Scale bars: **D1** 100 μm; **D2** 200 nm; **D3** 400 nm; **D4** 1 μm.



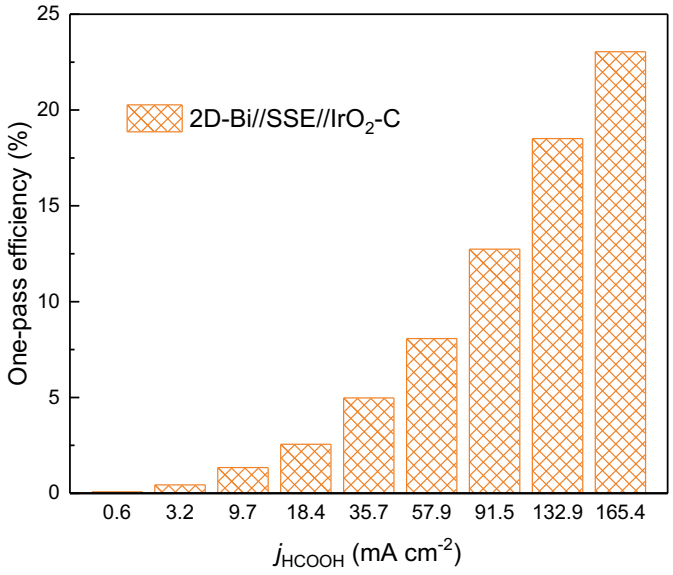
Supplementary Figure 8. Production of pure HCOOH solution using inorganic solid electrolyte. (**A**) The XRD of insoluble $Cs_xH_{3-x}PW_{12}O_{40}$ solid-electrolyte. It shows that the $Cs_xH_{3-x}PW_{12}O_{40}$ solid-electrolyte is very stable during HCOOH production. Even when aged in 50 wt% HCOOH for 24 h, we did not observe only structure evolution for $Cs_xH_{3-x}PW_{12}O_{40}$ electrolyte. (**B**) The current densities over cell voltages on 2D-Bi catalyst using our CO_2 reduction system with inorganic solid-electrolyte and the corresponding FEs for the reduction products under different cell voltages.



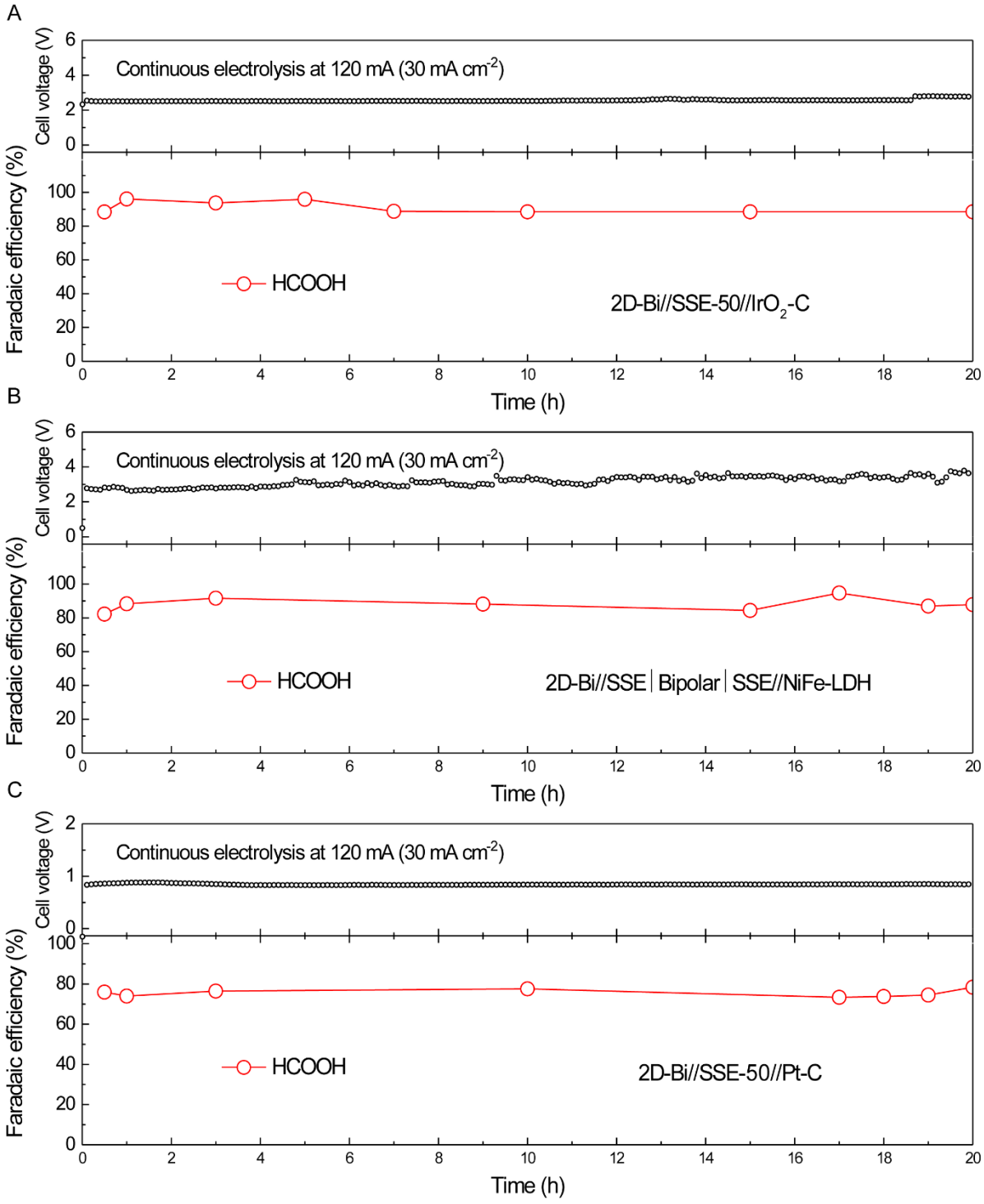
Supplementary Figure 9. CO_2 electroreduction performance of Cu_2O//H^+-conductor//IrO_2-C cell. (**A**) The overall current density at different voltage, and (**B**) the corresponding Faradaic efficiencies of all resultant products.



Supplementary Figure 10. Electrochemical impedance spectra for the solid state proton conductors. The impedance measurement of SSE-50 (BET surface area: 2.5 $m^2\ g^{-1}$) and SSE-300 (BET surface area: 0.1 $m^2\ g^{-1}$) solid proton ion conductors using a symmetric cell with two stainless steel electrodes [1]. The ionic conductivity of the solid electrolyte can be estimated from the resistivity (R) measured using the following equation: $R = \rho \frac{l}{A}$; where R represents the resistance of the electrolyte, ρ is resistivity, l is the distance between two electrodes, and A equals the cross-sectional area. The ionic conductivity κ of the electrolyte is therefore the reciprocal of the resistivity (ρ). The calculated ionic conductivity of the highly porous SSE-50 electrolyte is *ca.* 0.018 S cm^{-1} whereas that of porous SSE-300 solid electrolyte is *ca.* 0.0064 S cm^{-1}. The estimated charge transfer resistivity of SSE-50 and SSE-300 solid proton conductor is 12.5 and 24.5 Ω cm^2, respectively.



Supplementary Figure 11. Calculated one-pass efficiency of CO_2 conversion at different HCOOH partial current.



Supplementary Figure 12. Stability test of HCOOH production cell. (**A**) 20-hour operation test of electrosynthesis of pure HCOOH solution at 30 mA cm^{-2} using a 2D-Bi//IrO_2-C cell with SSE-50 solid electrolyte. (**B**) Stability test on 4-compartment cell at the current density 30 mA cm^{-2}. (**C**) Continuous electrocatalytic CO_2 hydrogenation using 2D-Bi//SSE-50//Pt-C cell.

Supplementary Note 1

Techno-economic analysis

We did a quantitatively techno-economic analysis of our strategy for HCOOH production according to previous method [2].

We reported the electrochemical CO_2 reduction to formic acid at a total current of ~ 200 mA cm^{-2} with HCOOH FE of 80%. The concentration of the final product is 1.852 M, which is collected using 100 sccm humified N_2 gas. Then, the volume percent of formic acid in the exiting electrolyte is (neglect volume change of the mixture):

$$The\ \ volume\ percent\ of\ HCOOH\ = 1L * 1.852\frac{mol}{L} * \frac{46.025g}{mol} * \frac{L}{1221g} * \frac{1}{1L\ electrolyte}$$

$$= 0.07$$

Assuming a production rate of 100,000 kg per day, the HCOOH partial current needed is:

$$100000\frac{kg}{day} * \frac{day}{86400s} * \frac{1000g}{kg} * \frac{mol}{46.025g} * 2e^- * 96485\frac{C}{mol} = 4852686.7\ A$$

The total current needed is then given by diving by the Faradaic efficiency:

$$total\ current = \frac{4852686.7\ A}{0.8} = 6065858.4\ A$$

The electrolyzer area needed is the total current divided by the current density:

$$total\ electrolyzer\ area = \frac{6065858.4\ A}{0.2\ \frac{A}{cm^2}} * \frac{m^2}{10^4 cm^2} = 3032.9\ m^2$$

The power needed is given from *P=UI*:

$$power = 2.75V * 6065858.4\ \ A * \frac{W}{10^6 MW} = 16.7\ MW$$

The CO_2 flow rate needed is:

$$CO_2\ flow = 4852686.7\ \ A * \frac{1}{2\frac{e^-}{mol\ CO_2} * 96485\frac{C}{mol}} * 0.044\frac{kg}{mol} * \frac{86400\ s}{day} = 95600.2\ \frac{kg}{day}$$

The single pass conversion is estimated as *ca.* 20% at this condition, so the inlet flow rate and outlet flow rate are:

$$CO_2\ inlet\ flow = 95600.2\ \frac{kg}{day} * \frac{day}{24\ hr} \div 0.2 = 19916.7\ \frac{kg}{hr}$$

$$CO_2\ oulet\ flow = 19916.7 * (1 - 0.2) = 15933.4\frac{kg}{hr} = 8047.2\frac{m^3}{hr}$$

Since formic acid is the dominated product, the gas product flow rate is supposed to be zero. The liquid product flow rate is:

$$Liquid\ product\ flow = 100000\frac{kg}{day} * \frac{m^3}{1221kg} * \frac{day}{24\ hr} = 3.4\ \frac{m^3}{hr} = 56.9\ \frac{L}{min}$$

Considering the final product concentration of HCOOH is 1.85 M, and we have calculated the steady-state volume concentration is 7%. Then, the continuous exit electrolyte (DI vapor) flow rate is:

$$DI\ vapor\ flow\ rate = 56.9\ \frac{L}{min} \div 0.07 = 812.5\ \frac{L}{min}$$

It is assumed the byproduct is hydrogen, so the flow rate is:

$$H_2\ flow\ rate = 6065858.4\ \ A * (1 - 0.8) * \frac{1}{2e^- * 96485\frac{C}{mol}} = 6.3\ \frac{mol}{s} = 542.6\ \frac{m^3}{hr}$$

The water flow rate for the anodic OER reaction is:

$$H_2O\ flow\ rate = 6065858.4\ \ A * \frac{1}{4e^- * 96485\frac{C}{mol}} * \frac{0.018\ kg}{mol} * \frac{0.2642\ gal}{kg} * \frac{86400\ s}{day}$$

$$= 6457.9\ \frac{gal}{day}$$

Then, the total gas flow rate is the sum of the CO_2 exit flow rate, the gas product flow rate ($0\ \frac{m^3}{hr}$) and the H_2 flow rate:

$$Total\ gas\ flow = 8047.2 + 0 + 542.6 = 8589.8\ \frac{m^3}{hr}$$

Capital Costs

From the DOE H_2A analysis for central grid electrolysis, the electrolyzer cost for the stack component is \$250.25/kW. The reference electrolyzer is operates at 0.175 A cm^{-2} and 1.75 V. The instillation factor is 1.2. Thus, the cost per area for the reference electrolyzer is:

$$Ref.electrolyzer\ cost = \frac{\$250.25}{kW} * \frac{0.175\ A}{cm^2} *\ 1.75\ V * \frac{10^4\ cm^2}{m^2} * \frac{kW}{1000\ W} * 1.2 = \frac{\$919.7}{m^2}$$

Then, the CO_2 electrolyzer capital cost is given by multiplying the total area:

$$Electrolyzer\ cost = 3032.9\ m^2 * \frac{\$919.7}{m^2} = \$\ 2789290$$

From the H_2A, the balance of plant capital cost is 35% of the total cost, while the stack is 65%:

$$Bop\ capital\ cost = \$\ 2789290 * \frac{0.35}{0.65} = \$\ 1501926$$

The distillation capital cost is calculated by the reference cost calculated in ref. 19 to the volumetric flow rate of the electrolyte:

$$Distillation\ capital\ cost = \$6896190 * \left(\frac{812.5\ \frac{L}{min}}{1000\ \frac{L}{min}}\right)^{0.7} = \$\ 5963289$$

If there is hydrogen byproduct, then the PSA capital cost is calculated by scaling the reference cost to the total flow rate:

$$PSA\ capital\ cost = \$1989043 * \left(\frac{8589.8\frac{m^3}{hr}}{1000\ \frac{m^3}{hr}}\right)^{0.7} = \$\ 7980731$$

So, the sum of capital costs is $ 19217069.

Operating Costs

The electricity cost is calculated from the power requirement and the price of electricity:

$$Electricity\ cost = 16.7MW * \frac{10^3\ kW}{MW} * 24\ hr * \frac{\$\ 0.03}{kWh} = \frac{\$\ 12010}{day}$$

The maintenance cost is assumed 2.5% of capital cost per year (from H_2A):

$$Maintenance\ cost = \frac{\$2789290 * \frac{0.025}{year}}{350\frac{days}{year}} = \frac{\$\ 199}{day}$$

The distillation and PSA costs are calculated by scaling the reference costs to the flow rates. Since we produce pure formic acid, we suppose the distillation capital cost of our product is 50% compared to mixed product:

$$Distillation\ operating\ cost = \frac{\$\ 32037.71}{day} * \left(\frac{812.5\ \frac{L}{min}}{1000\ \frac{L}{min}}\right)^{0.7} * 0.5 = \frac{\$\ 13015}{day}$$

$$PSA\ operating\ cost = \frac{0.25\ kWh}{m^3} * 8589.8\ \frac{m^3}{hr} * \frac{24\ hr}{day} * \frac{\$\ 0.03}{kWh} = \frac{\$\ 1546}{day}$$

The cost of CO_2 is:

$$CO_2\ cost = 95600.2\ \frac{kg}{day} * \frac{ton}{1000\ kg} * \frac{\$40}{ton} = \frac{\$\ 3824}{day}$$

The cost of water is:

$$water\ cost = \frac{6457.9\ gal}{day} * \frac{\$\ 0.0054}{gal} = \frac{\$\ 35}{day}$$

The yearly profit is given by the product income minus the sum of operating costs ($\frac{\$\ 30630}{day}$), the market price of pure formic acid is reported as $\frac{\$\ 0.735}{kg}$:

$$yearly\ profit = \left(\frac{10000\ kg}{day} * \frac{\$\ 0.735}{kg} - \frac{\$\ 30630}{day}\right) * \frac{350\ day}{year} = \frac{\$\ 15004495}{year}$$

Finally, the payback time should be:

$$payback\ time = \$\ 19217069\ (capital\ cost) \div \frac{\$\ 15004495}{year} = 1.28\ year$$

Thus, we can conclude here that our strategy is highly competitive with current commercial technologies for HCOOH production.

Supplementary References

1 Hagos, T. T. *et al.* Locally Concentrated $LiPF_6$ in Carbonate-based Electrolyte with Fluoroethylene Carbonate as a Diluent for Anode-Free Lithium Metal Battery. *ACS Appl. Mater. Interfaces* **11**, 9955-9963 (2019).

2 Jouny, M., Luc, W. & Jiao, F. General techno-economic analysis of CO_2 electrolysis systems. *Ind. Eng. Chem. Res.* **57**, 2165-2177 (2018).