

## Supporting Information

### Electrosynthesis of *N,N*-Dimethylformamide from Market-Surplus Trimethylamine Coupled with Hydrogen Production

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## Experimental Section

### Chemicals and Materials

The main text of the article should appear here with headings as appropriate. Except noted, all chemicals were purchased and used without further purification. Deionized water was used throughout the experiments. Nickel nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), ferric nitrate nonahydrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), urea ( $\text{CO}(\text{NH}_2)_2$ ), potassium carbonate ( $\text{K}_2\text{CO}_3$ ), potassium hydrogen carbonate ( $\text{KHCO}_3$ ), potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ), potassium chloride (KCl), Glycerol ( $\text{C}_3\text{H}_8\text{O}_3$ ) and dimethylamine solution (DMA, 40 wt. % in  $\text{H}_2\text{O}$ ) were purchased from Aladdin Reagent Co. Ltd (Shanghai, China). Potassium hydroxide (KOH), trimethylamine solution (TMA, 30 wt. % in  $\text{H}_2\text{O}$ ), N,N-dimethylformamide (DMF), formaldehyde ( $\text{CH}_2\text{O}$ ) and ammonium fluoride ( $\text{NH}_4\text{F}$ ) were obtained from Macklin Reagent Co. Ltd (Shanghai, China). Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) was provided by Chuandong Chemical Reagent Company (Chengdu, China). Eschenmoser's salt was purchased from Meryer Biochemical Technology Co. Ltd (Shanghai, China). Nafion (5 wt%) solution was obtained from Sigma-Aldrich Chemical Reagent Co. Ltd. Nickel foams (1.6 mm thick) were obtained from China (PRC) MTI-Group. Graphite flakes, carbon paper, carbon felt were purchased from Beijing Jing Long Carbon Graphite Company.

### Synthesis of Ni-Fe LDH

The NiFe-LDH was prepared using a modified method. In a typical experiment, 0.75 mmol  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 0.25 mmol  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , 5 mmol  $\text{CO}(\text{NH}_2)_2$  and 2 mmol  $\text{NH}_4\text{F}$

were dissolved in 30 mL distilled water under vigorous stirring for 30 min, after adjusting the solution to pH = 10 with 1 M KOH. Then the mixture was transferred into a 50 mL Teflon-lined autoclave and maintained at 120 °C for 6 h. The system was allowed to cool down to room temperature, and the final product was collected by centrifugation, and washed with water for several times and then the final product was freeze dried overnight.

### **Synthesis of Ni(OH)<sub>2</sub>**

The procedure was similar with NiFe-LDH except that without Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, and the 0.75 mmol Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O changed to 1 mmol Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O.

### **Electrochemical measurements**

The electrochemical measurements of the samples in a H-type cell were performed with a CHI 760E electrochemical workstation (CH Instruments, Inc., Shanghai). The three-electrode system consists of Hg/HgO as the reference electrode, Pt foil as the counter electrode, and graphite flake as the working electrode. All potentials were 90% IR compensated using electrochemical impedance spectroscopy (EIS) techniques. The LSV curves with a scan rate of 5 mV s<sup>-1</sup> ranging from 0.2 to 1.4 V vs. Hg/HgO in 0.7 M K<sub>2</sub>CO<sub>3</sub> with or without 20 mM TMA. The reaction changes were then monitored by applying constant potential ranging from 0.9 V to 1.3 V vs. Hg/HgO. The electrochemical performances of the samples in a flow-type cell were tested using a CS1350 electrochemical analyzer (CS Instruments, Inc., Wuhan). The two-electrode

system consists of Ni foam as the counter electrode and graphite flake as the working electrode. The electrolyte is 0.7 M  $K_2CO_3$  with or without 20 mM or 200 mM TMA. The reaction was then manipulated by applying constant current ranging from 2.2 A to 4.0 A. The corresponding full-cell voltage was recorded while the experiments. Unless otherwise stated, all experiments were carried out at room temperature. Ice-bath condition provides the temperature at a range of 0–10 °C. Electrolyte passed through the cell in a single pathway with a constant flow rate of 1.35 mL min<sup>-1</sup> using a peristaltic pump. Electrolyte of constant volume of 120 mL was circulated through the cell with a constant flow rate of 5.4 mL min<sup>-1</sup>. LSV curves in the flow cell with a scan rate of 10 mV s<sup>-1</sup> ranging from 1.0 to 3.5 V in 0.7 M  $K_2CO_3$  with or without 200 mM TMA.

### **Products analysis**

The main text of the article should appear here with headings as appropriate. To analyze the products of DMF, 100  $\mu$ L aliquots of electrolyte solution were collected during chronoamperometry test, and were diluted by 900  $\mu$ L of water. The samples were then analyzed by a HPLC (Agilent 1200 Infinity Series) equipped with a refractive index detector (RID) and a variable wavelength detector (VWD). Oxidation products DMF and NMF were detected using an organic acid column (Coregel 87H3) and aqueous  $H_2SO_4$  (5 mM) mobile phase (0.6 mL min<sup>-1</sup>), and the VWD detector was set at 210 nm. NMR analysis was conducted as follows: 630  $\mu$ L aliquot of electrolyte was collected and mixed with 70  $\mu$ L of deuterated water. Glycerol was added as an internal

standard. The NMR spectra were measured on a Varian 400 instrument with water suppression. The Faradaic efficiency (FE) and product selectivity of the products were calculated with the following equations:

$$FE (\%) = \frac{\text{Mole of produced product} \times n \times F}{\text{total charge passed}} \times 100\%$$
$$\text{Selectivity} (\%) = \frac{\text{Mole of certain product}}{\text{Mole of all products detected}} \times 100\%$$

where  $n$  is the number of electron transfer for each product formation,  $n = 4$  for TMA oxidation to DMF. External standard curves of DMF and NMF were obtained to quantify the products.

### **Techno-economic Analysis**

To ascertain the economic potential of the generation of DMF from TMA powered by renewable electricity, we carried out a techno-economic analysis using a modified model which is already published.<sup>[1]</sup> There are two components, namely the capital costs and the operating costs, in the total costs. Capital costs consist of the electrolyser and gas/liquid separation equipment cost, since this might dominate any other components. Operating costs can be separated into four parts: electricity costs, product separation costs, plant operation costs and material costs (price of TMA).

An example TEA calculation for the case where the operating current density is assumed to be  $100 \text{ mA cm}^{-2}$  is performed as follows.

1. We assume a cost of \$10,000 per  $\text{m}^2$  of electrolyser and the plant will own a lifetime of 10 years to calculate electrolyser capital costs. Separation capital costs will be assumed to be 10% of the capital costs.

2. Electricity costs are variable, we will assume a price of 10 cents/kWh for the purposes of this calculation.
3. Separation costs are assumed to be 30% of electricity costs, containing two components that are distillation costs for separation of DMF and an TMA separation and recycle system.
4. Operation costs are assumed to be 10% of the capital costs.
5. Capacity factor, the fraction of time the plant, is anticipated to be operational on any day and this is assumed to be 0.8 resulting in where the plant will be operational 19.2 hours a day.
6. The faradaic efficiency to DMF is 54%, the total cell operating voltage is 2.5 V and the total operating current density is 100mA cm<sup>-2</sup>.
7. The plant will convert a ton of TMA to 1.24 ton of DMF.
8. The price of TMA and DMF is assumed to be \$1400 per ton and \$3000 per ton respectively.
9. The price of hydrogen is \$1900 per ton. The faradaic efficiency is assumed to be 100%.

### **Material costs**

$$\begin{aligned}
 \text{Material costs} &= \frac{\text{Cost of TMA} \times \text{Mass of TMA}}{\text{Mass of DMF produced}} = \frac{\$1400 \times 1}{1.24} = \$1129 \text{ per ton}
 \end{aligned}$$

### **Electricity costs**

We first calculate the total charge required to oxidize 1 ton of TMA per day.

$$Q = \frac{\text{Mass of TMA converted} \times F \times N}{\text{Molar mass of TMA} \times \text{Faradaic efficiency}} = \frac{1 \times 10^6 \times 96485 \times 4}{59.11 \times 0.8} = 1.21 \times 10^{10} \text{ C}$$

Where Q is the total charge. F is the Faraday's constant and N is 4 since TMA oxidation to DMF is a four-electron transfer process.

We then calculate the current required to sustain this process, with a capacity factor of 0.8.

$$I = \frac{Q}{\text{Time in a day} \times \text{Capacity factor}} = \frac{1.21 \times 10^{10}}{24 \times 60 \times 60 \times 0.8} = 1.75 \times 10^5 \text{ A}$$

Where I is the current.

The power required to sustain this process can be calculated, assuming an operating cell potential of 2.5 V.

$$P = 1.75 \times 10^5 \times 2.5 = 4.37 \times 10^2 \text{ kW}$$

The energy use per day can be calculated as follows:

$$\begin{aligned} \text{Energy use per day} &= P \times \text{Time in a day} \times \text{Capacity factor} = 4.37 \times 10^2 \times 24 \\ &\times 0.8 = 8.4 \times 10^3 \text{ kWh} \end{aligned}$$

Finally, the electricity cost per day, normalized by the mass of DMF produced can be calculated:

$$\begin{aligned} \text{Electricity cost per day} &= \frac{\text{Energy use per day} \times \text{Cost per kWh}}{\text{Mass of DMF produced}} = \frac{8.4 \times 10^3 \times 0.10}{1.24} \\ &= \$677 \text{ per ton of DMF} \end{aligned}$$

## Separation costs

The separation costs are 30 % of electricity costs.

$$\text{Separation costs} = 677 \times 0.3 = \$164$$

### Capital costs

We first calculate the electrolyser cost. Based on the current required and the assumed operating current density of 100 mA cm<sup>-2</sup> we can calculate the area of electrolyser needed.

$$\text{Area of electrolyser} = \frac{1.75 \times 10^5}{0.1} = 175 \text{ m}^2$$

The electrolyser cost can now be calculated based on the estimate of \$10,000 per m<sup>2</sup>.

$$\text{Cost of electrolyser} = 175 \times 10000 = \$1.75 \times 10^6$$

The capital costs are associated with the gas/liquid separations equipment are assumed to be 10 % of electrolyser cost and is calculated as:

$$\text{Cost of separation equipment} = 1.75 \times 10^6 \times 0.1 = \$1.75 \times 10^5$$

Therefore, the capital costs component can be calculated:

$$\begin{aligned} \text{Capital costs} &= \frac{\text{Cost of electrolyser} + \text{Cost of separations equipment}}{\text{Lifetime of plant} \times \text{Mass of DMF produced}} \\ &= \$425 \text{ per ton of DMF} \end{aligned}$$

### Operation costs

This is assumed to be 10% of the capital costs.

$$\text{Operation costs per day} = \$425 \times 0.10 = \$42.5 \text{ per ton of DMF}$$



### Total plant gate levelized cost

Finally, the total cost can now be calculated by adding up all 5 components:

$$\begin{aligned} \text{Total costs} &= \$1129 + \$677 + \$164 + \$425 + \$42.5 = \$2437.5 \text{ per ton} \end{aligned}$$

### Potential profit

The profit per day from this process can be calculated based on the market price of DMF, which we assume to be \$3000 per ton.

$$\text{Profit per tonne of DMF} = \$3000 - \$2437.5 = \$562.5 \text{ per ton of DMF}$$

$$\text{Profit per day} = \$562.5 \times 1.24 = \$697.5 \text{ per ton of DMF}$$

Then, we include the simultaneous production of hydrogen at the cathode, which has a 100% faradaic efficiency.

$$\begin{aligned} \text{Mass of hydrogen produced per day} &= \frac{Q \times \text{Molar mass of hydrogen}}{N \times F} = \frac{1.21 \times 10^{10} \times 2}{2 \times 96485} \\ &= 0.125 \text{ ton} \end{aligned}$$

Profit from hydrogen can now be calculated as:

$$\text{Profit per day} = \$1900 \times 0.125 = \$237.5$$

Normalising this based on the 1.24 ton of DMF produced per day:

$$\text{Profit from hydrogen per tonne of DMF} = \frac{237.5}{1.24} = \$191.5 \text{ per ton of DMF}$$

Finally, total profits per ton of DMF:

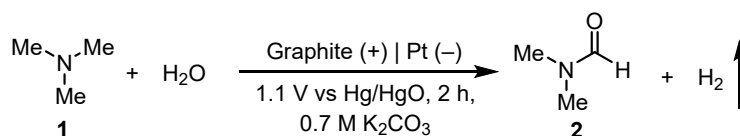
$$\text{Total profit per tonne of DMF produced} = \$562.5 + \$191.5 = \$754$$

### Breakeven point

To breakeven, the costs of producing one ton of DMF must be less than the relative market price of DMF and hydrogen.

$$\textit{Breakeven point} = \$3000 + \$191.5 = \$3191.5 = \$3200 \textit{ (rounded up)}$$

## **Supplementary Table and Figures**

**Table S1** Optimization of electrochemical oxidation of TMA. <sup>a</sup>

Entry	Anode	Yield (%)	FE (%)
1	Pt	3	5
2	NiFe-LDH	31	6
3	Ni(OH) <sub>2</sub>	58	13
4	Ni foam	64	25
5	Pd/C	68	54
6	Carbon paper	54	53
7	Carbon felt	72	65

[a] Reaction conditions: anode catalyst (1 cm×1 cm), Pt cathode (1 cm×1 cm), TMA (20 mM), K<sub>2</sub>CO<sub>3</sub> (0.7 M), at 1.1 V vs. Hg/HgO for 2 h at room temperature in an H-type cell. Ni(OH)<sub>2</sub> were synthesized following the procedures described in Methods of Supplementary Information.

The working electrode was fabricated as follows: 2.5 mg of catalyst powder was dispersed in a mixed solvent (water: ethanol: 5% Nafion = 245 μL:245 μL:10 μL) to form a concentration of 5 mg mL<sup>-1</sup> homogeneous black suspension under sonication. Then 200 μL of the suspension was carefully dropped onto the surface of C paper electrode with 1 cm×1 cm and was dried under ambient condition.

**Table S2** Calculations of the standard electrode potential ( $\phi^\theta$ ) of anodic TMA

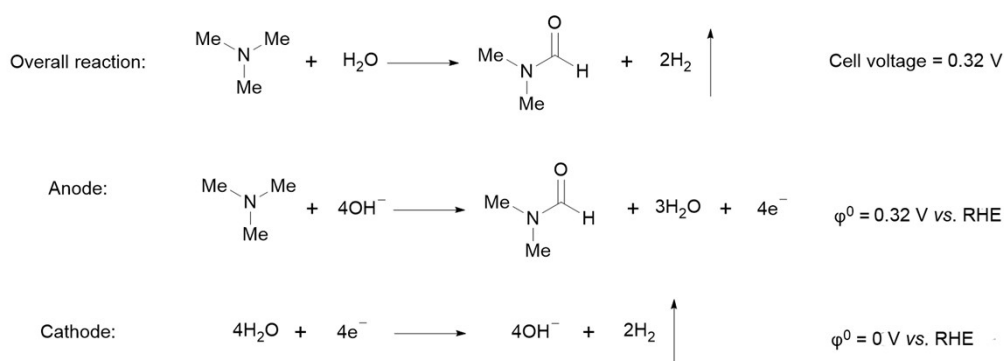
oxidation.

Compounds	$\Delta G_f^\theta$ (kJ mol <sup>-1</sup> )
Water	-237.1
Hydroxide	-157.2
TMA	98.98
DMF	-14.36

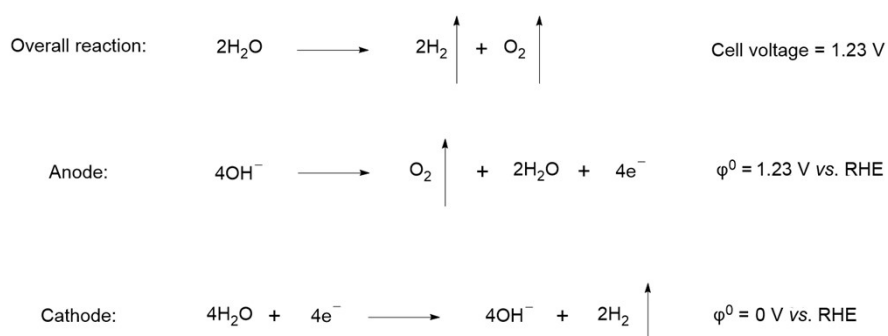
$$\Delta G^\theta(\text{reaction}) = \sum b_i \Delta G^\theta(\text{product}) - \sum a_i \Delta G^\theta(\text{substrate})$$

$$\varphi = -0.059pH + \varphi^\theta$$

#### TMA electrooxidation



#### Water electrooxidation



The data of standard reaction Gibbs energy of formation showing above are from Chemo. The overall reactions (TMA oxidation coupled with HER, and overall water splitting) are shown above, associated with the calculated standard reaction Gibbs energy ( $\Delta G^\theta$ ).  $\Delta G^\theta$  was calculated by the use of thermochemical data. Based on the

equation of  $\Delta G^\theta = -nFE^\theta$  (where  $n$  is the number of electrons transferred ( $n = 4$ ),  $E^\theta$  represents the standard electromotive force), in the respect of reaction thermodynamics, the standard electrode potential ( $\phi^\theta$ ) of TMA oxidation reaction is 0.32 V vs. RHE, while that of the oxygen evolution reaction (OER) is 1.23 V vs. RHE, indicating that TMA oxidation is more thermodynamically favorable than the OER.

**Table S3** DMF yield at different potentials. <sup>a</sup>

Potential (V)	Yield (%)
0.9	32
1.0	49
1.1	80
1.2	42
1.3	19

[a] Reaction conditions: Graphite flake anode (1 cm×1 cm), Pt cathode (1 cm×1 cm), TMA (20 mM), K<sub>2</sub>CO<sub>3</sub> (0.7 M), at different potentials vs. Hg/HgO for 2 h at room temperature in an H-type cell.

**Table S4** Faradaic efficiency at 1.3 V vs. Hg/HgO of all the detected products.

<b>Compounds</b>	<b>FE (%)</b>
DMF	5.6
NMF	1.9
Formaldehyde	1.4
Formic acid	1.9
Oxygen	85.4
Total	96.2

Graphite flake as the anode, Pt as the cathode, and Hg/HgO as the reference electrode, the reaction was carried out in 0.7 M K<sub>2</sub>CO<sub>3</sub> with 20 mM TMA at 1.3 V vs. Hg/HgO for 2 h in the H-type cell, and the O<sub>2</sub> was collected by drainage gas collection method. 25 mL O<sub>2</sub> was collected after 2 h (460.6 C), and the Faradaic efficiency of O<sub>2</sub> is 85.4%, indicating that the decrease of DMF yield at 1.3 V vs. Hg/HgO is mainly caused by the competition of OER.

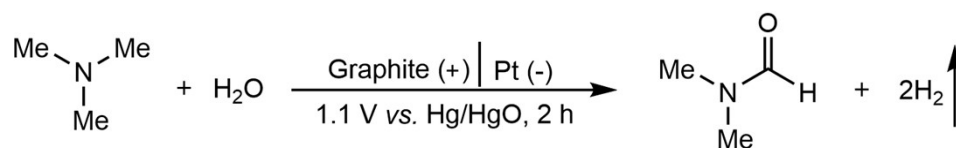
The volume (L) of a mole of gas was calculated with the following equation:

$$V = \frac{nRT}{P}$$

where n (mol) is the amount of substance, R (8.314) is thermodynamic constant, T (K) is thermodynamic temperature, and P (MPa) is atmospheric pressure.

## Green chemistry metrics [2, 3]

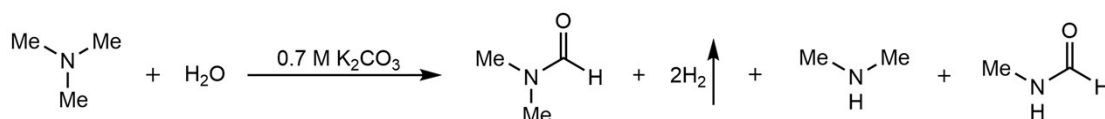
### (1) Atom Economy (AE)



For a given reaction, AE is defined as the molecular weight ratio of the desired product to all the reagents according to the stoichiometric equation. For electrochemical synthesis of DMF, AE was calculated to be 94.8%, as shown below.

$$AE = \frac{MW \text{ of desired product}}{MW \text{ of reagents}} = \frac{73.10}{59.11 + 18.02} = 94.8\%$$

### (2) Environmental factor (E-factor)



**Table S5** Calculation of environmental factor in electrochemical synthesis of DMF. <sup>a, b</sup>

Raw materials and byproducts	Quantity (kg per kg of DMF)
TMA	1.08 (residue of 0.01)
K <sub>2</sub> CO <sub>3</sub> (95% recycle)	4.41
DMA	0.05
NMF	0.15
Water	912.41
<b>E-Factor</b>	<b>4.62</b>

[a] H<sub>2</sub> is also the desirable product, and it is not included in the wastes for E-factor calculation. We excluded water used in the process from the calculation of the E factor.

[b] The data was based on the results shown in Figure 2a.

E-factor is defined as the mass ratio of waste to the desired product (the equation is shown below).



$$E - factor = \frac{Mass\ of\ wastes}{Mass\ of\ desired\ product}$$

E-factor is used to assess the environmental impact of a product in the production process, and a lower E-factor is desirable. The ideal E-factor is zero. Regarding electrochemical synthesis of DMF, we first summarized the quantities of the raw materials and byproducts normalized by per kg of DMF (Table S5; the data was based on the catalytic results shown in Figure 2a), and then calculated the corresponding E-factor. Note that H<sub>2</sub> is also the desirable product, hence it is not included in the wastes for E-factor calculation. As a result, E-factor for electrochemical synthesis of DMF was estimated to be 4.62, suggesting the synthetic method is environmentally benign.

### (3) Carbon efficiency (CE)

**Table S6** Calculation of carbon efficiency in electrochemical synthesis of DMF. <sup>a</sup>

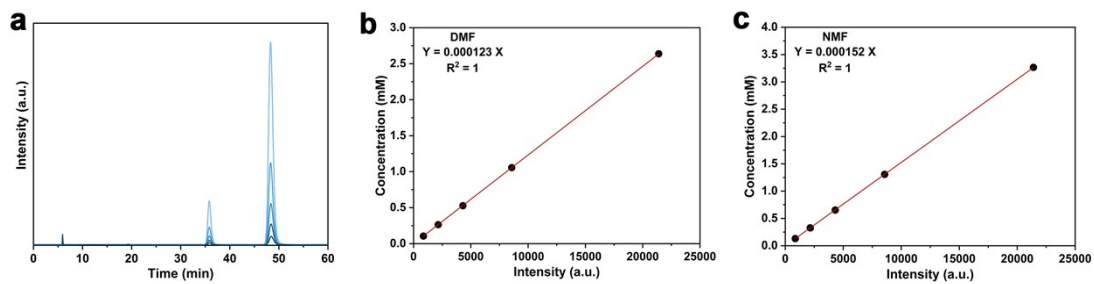
Carbonaceous chemicals	Mass of carbon (kg)
TMA	0.658
DMA	0.027
NMF	0.061
DMF	0.493

[a] The data was based on the catalytic results shown in Figure 2a.

CE is defined as the mass ratio of carbon in the product to the total mass of carbon in the reactants, as the equation shown below.

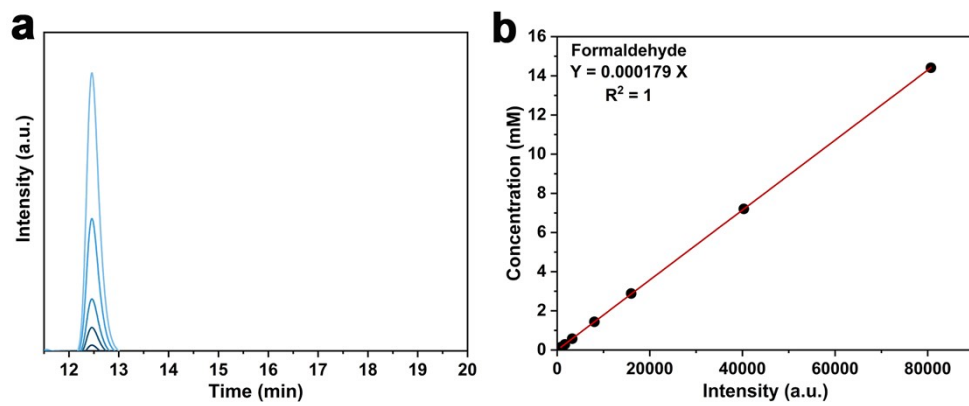
$$CE = \frac{Mass\ of\ carbon\ in\ the\ product}{Total\ mass\ of\ carbon\ in\ the\ reactants}$$

Table S6 shows the carbonaceous chemicals in electrochemical synthesis of DMF and the associated carbon mass. The data was based on the catalytic results shown in Figure 2a. The CE of electrochemical synthesis of DMF was calculated to be 88%.

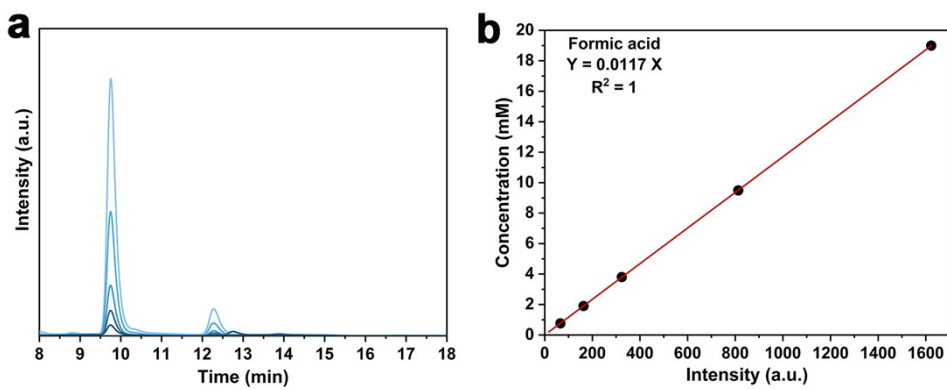


**Figure S1.** (a) HPLC spectra of DMF and NMF solutions with different concentrations.

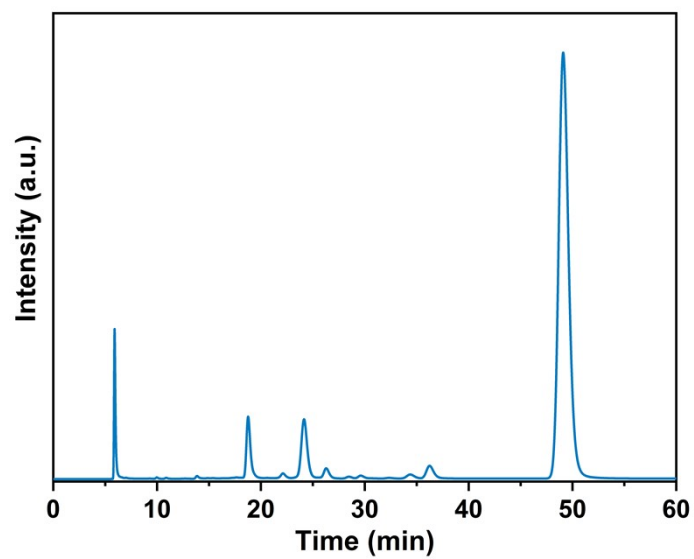
HPLC calibration curves of (b) DMF and (c) NMF.



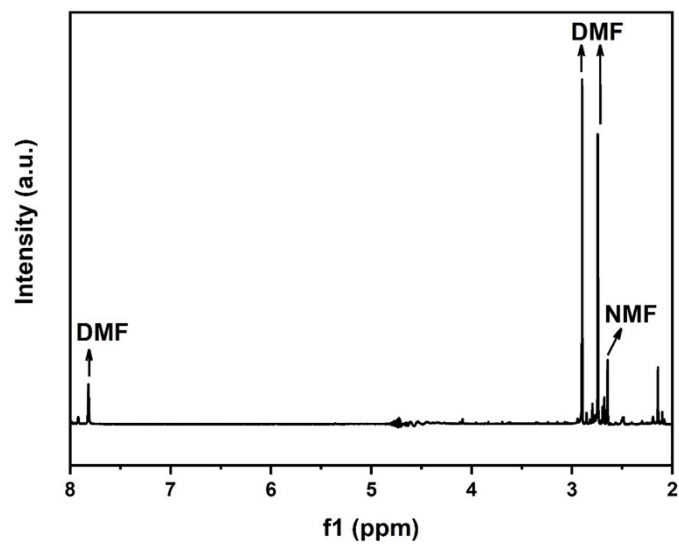
**Figure S2.** (a) HPLC spectra of formaldehyde solutions with different concentrations.  
(b) HPLC calibration curves of formaldehyde.



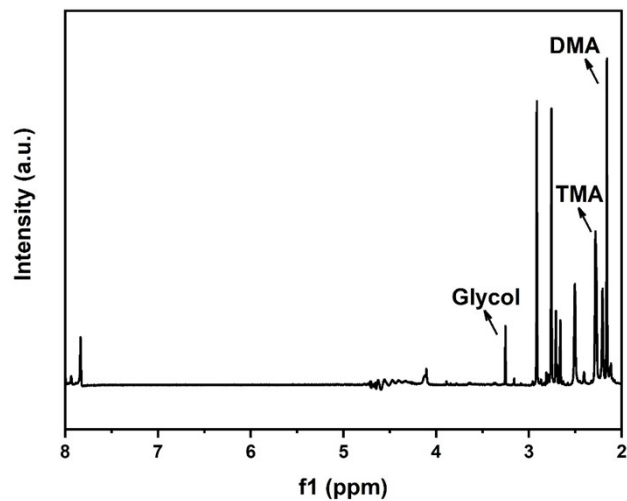
**Figure S3.** (a) HPLC spectra of formic acid solutions with different concentrations. (b) HPLC calibration curves of formic acid.



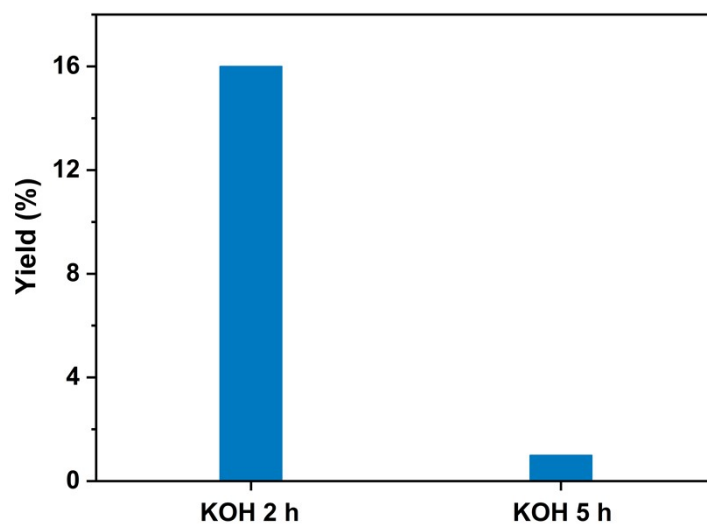
**Figure S4.** HPLC spectrum of the liquid products of 20 mM TMA oxidation at 1.1 V vs. Hg/HgO for 2 h.



**Figure S5.**  $^1\text{H}$  NMR spectrum of the liquid products of 20 mM TMA oxidation at 1.1 V vs. Hg/HgO for 2 h.

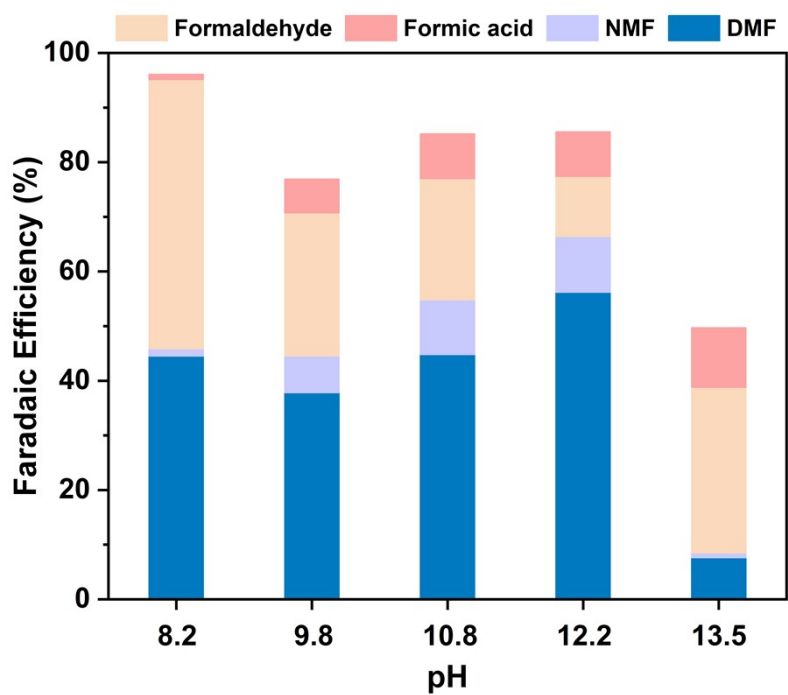


**Figure S6.** <sup>1</sup>H NMR spectrum of the liquid products of 20 mM TMA oxidation at 1.1 V vs. Hg/HgO for 1 h. Glycol was added as an internal standard.

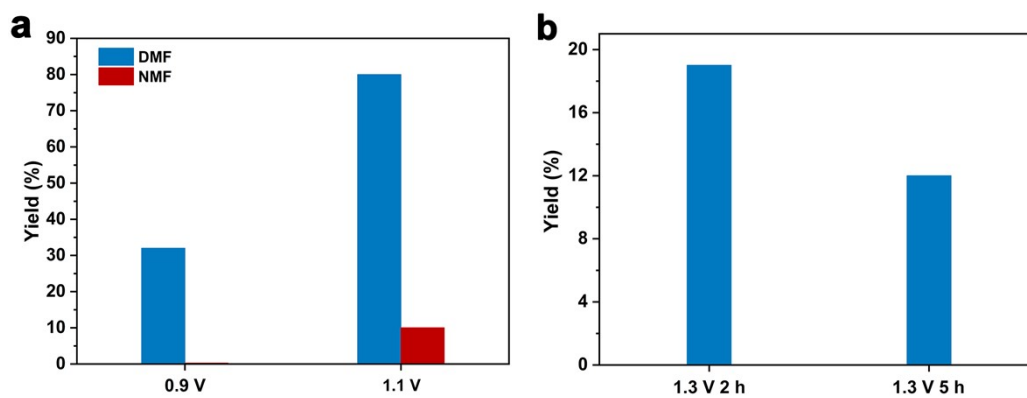


**Figure S7.** DMF yield in 0.7 M KOH with 20 mM TMA at 1.1 V vs. Hg/HgO for different time under the other standard conditions.

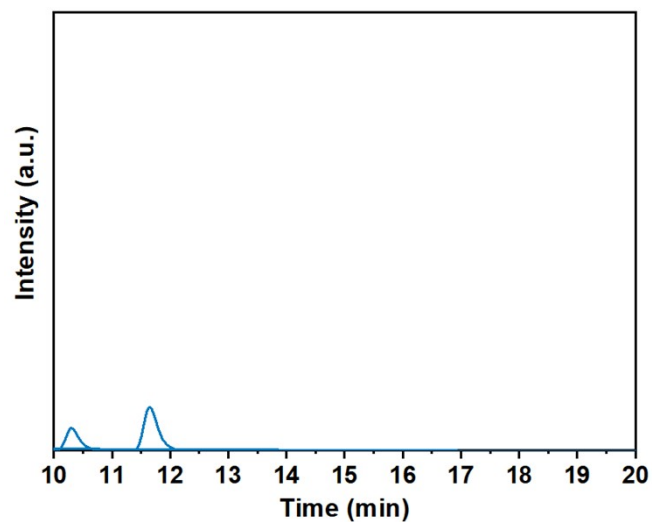




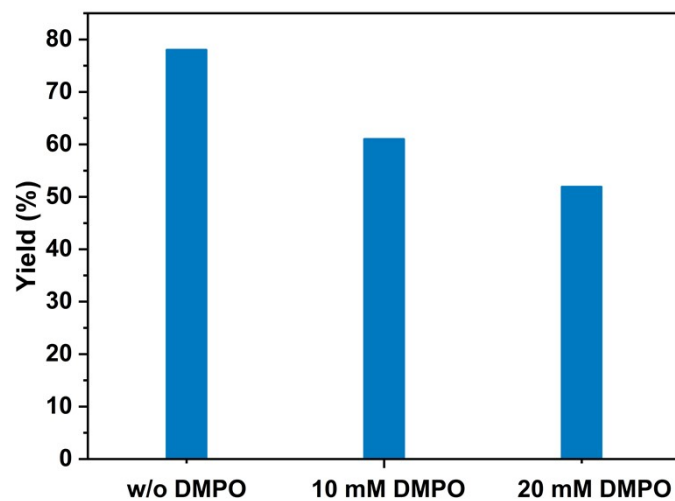
**Figure S8.** Faradaic efficiency as a function of pH for TMA oxidation under the other standard reaction conditions.



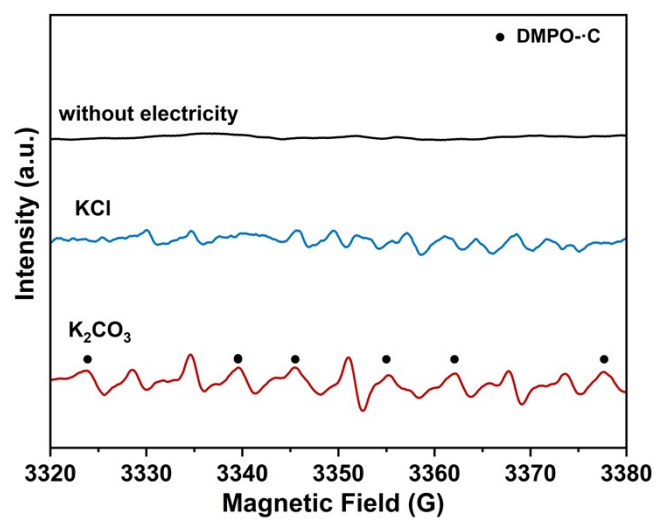
**Figure S9.** (a) DMF and NMF yields at different potentials under the other standard conditions (0.7 M  $K_2CO_3$  with 20 mM TMA, 2 h). (b) DMF yields at 1.3 V vs. Hg/HgO during different time under the other standard reaction conditions (0.7 M  $K_2CO_3$  with 20 mM TMA).



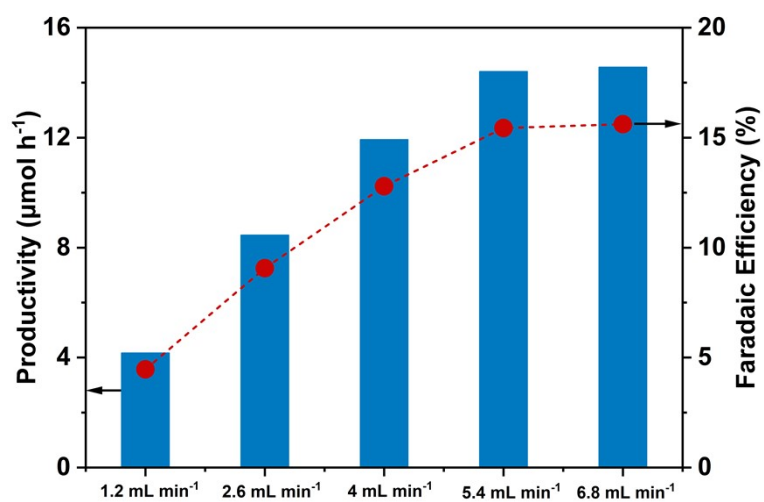
**Figure S10.** HPLC spectrum of the liquid products in cathode compartment (0.7 M  $\text{K}_2\text{CO}_3$  with 20 mM TMA oxidation at 1.1 V vs. Hg/HgO for 2 h in an H-cell). No HCHO was detected.



**Figure S11.** DMF yields under standard reaction conditions with different amounts of DMPO or without DMPO.

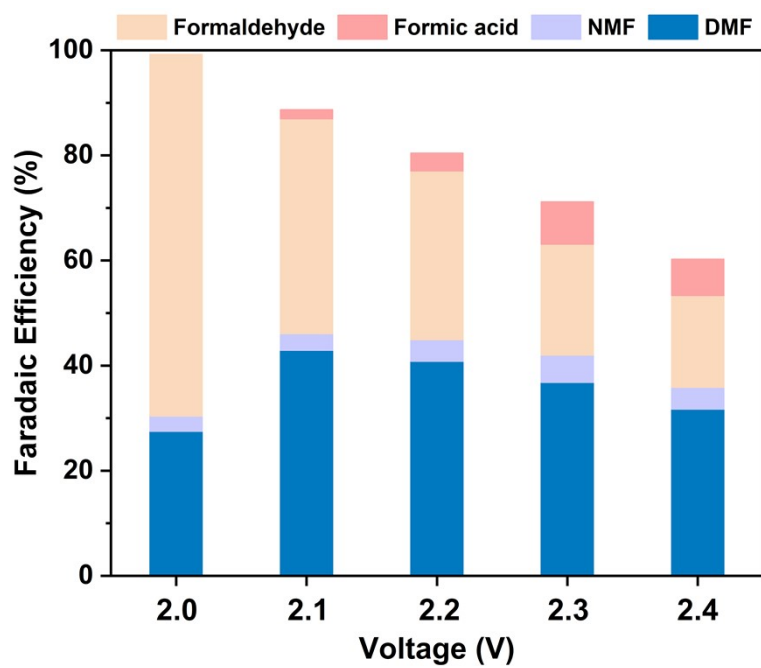


**Figure S12.** Comparison of EPR spectra between the reaction under standard conditions and that in 0.7 M KCl under the other standard reaction conditions.

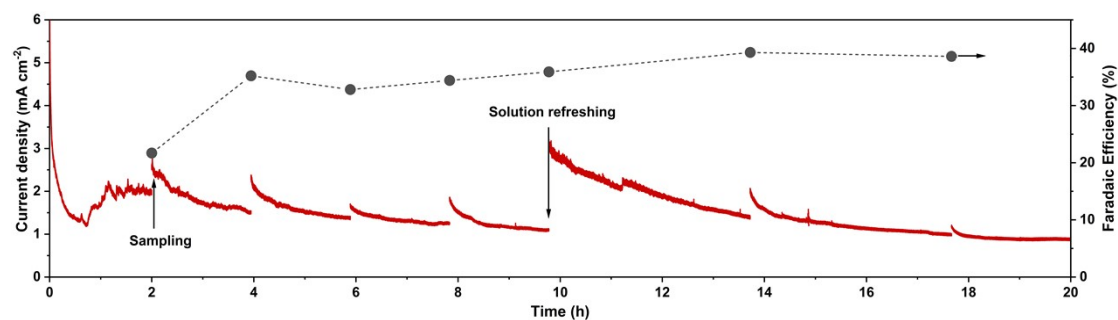


**Figure S13.** Productivity and Faradaic efficiency as a function of flow rate for TMA oxidation in flow reactor.

Reaction conditions: a graphite flake (2 cm×2 cm) as the anode and a Pt plate (2 cm×2 cm) as the cathode, 0.7 M K<sub>2</sub>CO<sub>3</sub> with 20 mM TMA at 2.1 V at room temperature for 2 h.



**Figure S14.** Faradaic efficiency as a function of applied potential for TMA oxidation in MEA flow reactor.

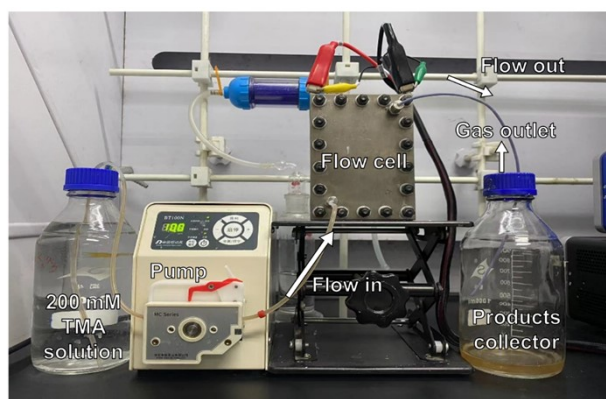


**Figure S15.** I-t curve at cell voltage of 2.1 V for 20-hours.

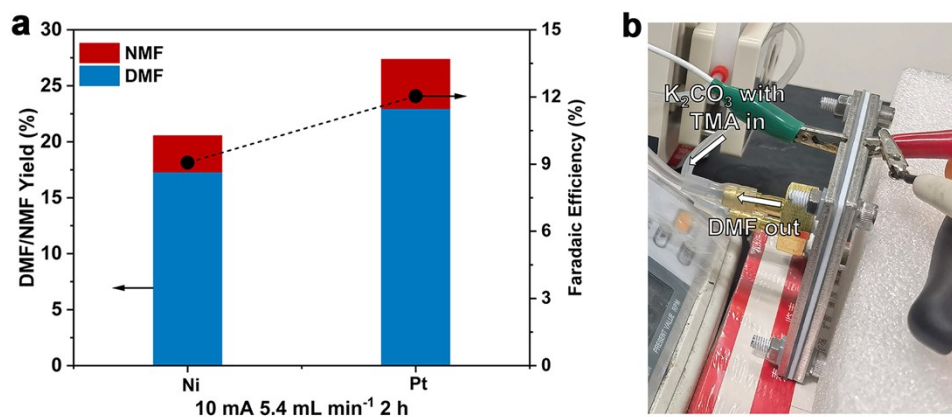
Reaction conditions: 0.7 M  $K_2CO_3$  with 20 mM TMA at a flow rate of  $5.4 \text{ mL min}^{-1}$ .

The discontinuous current density is due to sampling. Samples are taken every 2 h and 4 h for the first 10 h and after replaced fresh electrolyte, respectively. A 20-hour i-t test confirmed that the current density substantially restored by replacing the fresh electrolyte.

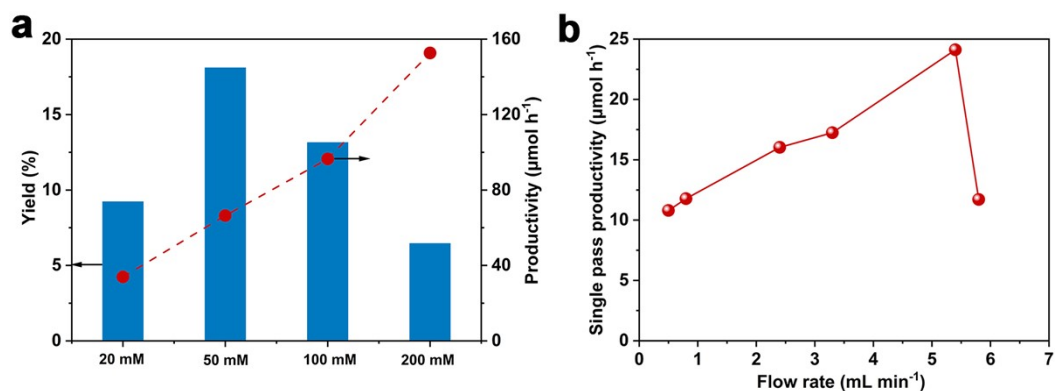




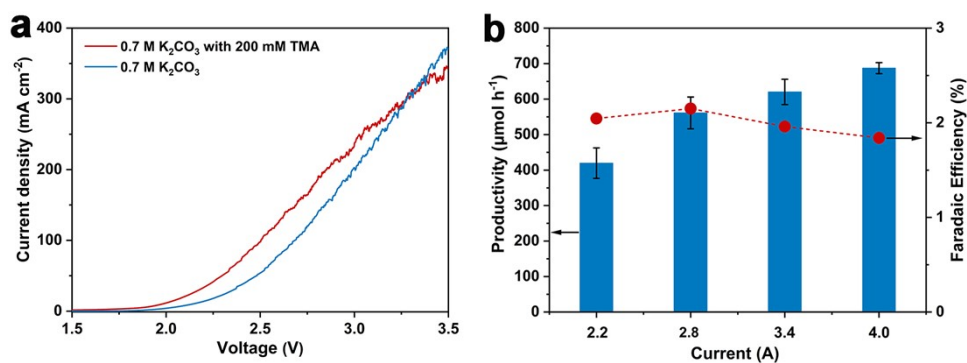
**Figure S16.** Set up of the membrane-free flow reactor.



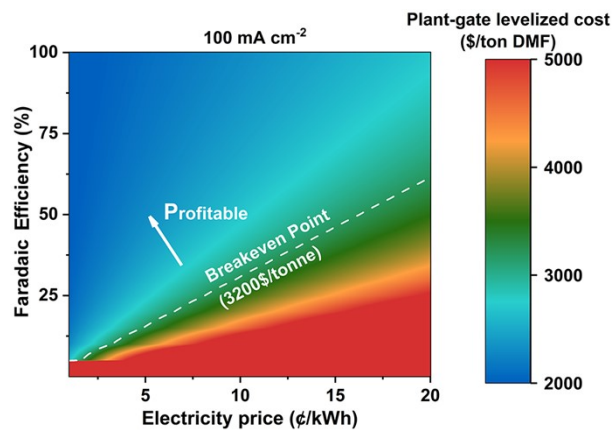
**Figure S17.** (a) Comparison of cathode electrodes in the membrane-free flow reactor in 0.7 M K<sub>2</sub>CO<sub>3</sub> with 20 mM TMA at 10 mA for 2 h at a flow rate of 5.4 mL min<sup>-1</sup> with a graphite flake (2 cm×2 cm) as the anode and Ni foam (2 cm×2 cm) or Pt (2 cm×2 cm) as the cathode. (b) Photograph of the membrane-free flow reactor.



**Figure S18.** (a) Yield and productivity with different TMA concentrations in the membrane-free flow reactor in 0.7 M  $\text{K}_2\text{CO}_3$  at 2.3 V for 2 h at a flow rate of 5.4  $\text{mL min}^{-1}$  with a graphite flake (2 cm $\times$ 2 cm) as the anode and Pt (2 cm $\times$ 2 cm) as the cathode. (b) Single pass productivity as a function of flow rate for TMA oxidation in the membrane-free flow reactor. Reaction conditions: a graphite flake (8 cm $\times$ 9 cm) as the anode and Ni foam (8 cm $\times$ 9 cm) as the cathode, in 0.7 M  $\text{K}_2\text{CO}_3$  with 50 mM TMA at 2.1 V at room temperature.



**Figure S19.** (a) LSV curves in membrane-free flow reactor flow reactor with a scan rate of 10 mV s<sup>-1</sup> ranging from 1.5 to 3.5 V in 0.7 M K<sub>2</sub>CO<sub>3</sub> with and without 200 mM TMA. (b) Productivity and Faradaic efficiency as a function of current in the membrane-free flow reactor in 0.7 M K<sub>2</sub>CO<sub>3</sub> with 200 mM TMA for 1 h at a flow rate of 5.4 mL min<sup>-1</sup> with a graphite flake electrode (8 cm×9 cm).



**Figure S20.** Plant-gate levelized cost per ton of DMF from a techno-economic analysis at  $100 \text{ mA cm}^{-2}$ . The region above the dashed white line indicates profitable production costs for DMF.

## Supplementary References

- [1] P.D. Luna, C. Hahn, D. Higgins, S.-A. Jaffer, T.-F. Jaramillo, E.-H. Sargent *Science*, 2019, **364**, 6438.
- [2] Roger A. Sheldon, *Chem. Soc. Rev.*, 2014, **41**, 1437-1451.
- [3] Roger A. Sheldon, *Chem. Commun.*, 2008, **29**, 3352-3365.