

Coupling homogeneous and heterogeneous catalysis for enhancement of HCOOH electrooxidation via the dehydrogenation pathway

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IR-compensation of cyclic voltammetry performance.

Through electrochemical impedance spectrum measurement as shown in Fig. S1A, we find that the electrolyte resistance (R_u) slightly increases with increasing the $VOSO_4$ content in the electrolyte, as tabulated in Tab. S1. Regarding the measured electrolyte resistance, the compensation voltage (V_{comp}) is determined by following formula:

$$V_{comp} = V_{measured} - I_{cell} \times R_u$$

IR-compensation of the cyclic voltammetry performance is conducted on the basis of above formula and CV data (Fig. S1B). Here, $V_{measured}$ and I_{cell} refer the measured values of voltage and current during CV measurement, respectively.

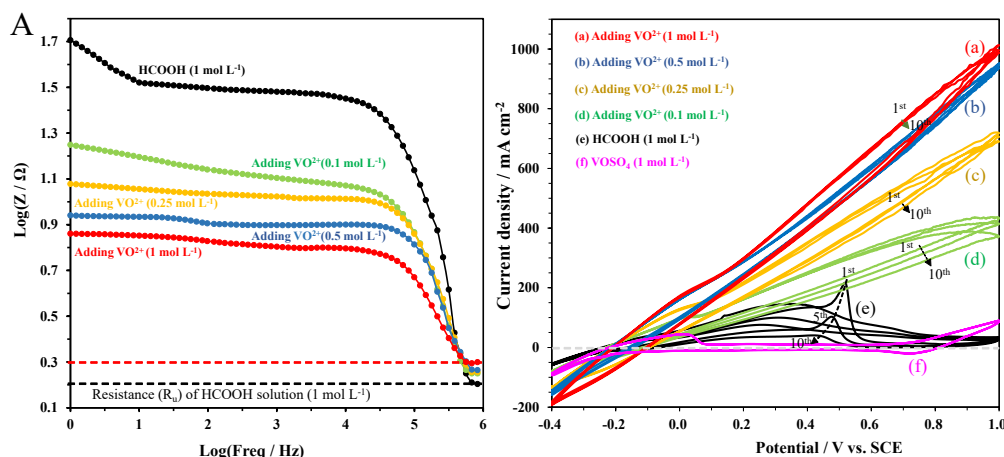


Fig. S1 (A) Bode plots of Pd/C electrode in $HClO_4$ -based electrolytes (1.0 mol L^{-1} of $HClO_4$) containing HCOOH (1.0 mol L^{-1}) or/and $VOSO_4$ with different concentrations. (B) Cyclic voltammetry performance of Pd/C electrode without IR-compensation at a stirring rate of 400 rpm, scan rate of 50 mV s^{-1} , and temperature of $30 \text{ }^\circ\text{C}$.

Tab. S1 Electrolyte resistance of $HClO_4$ -based electrolytes (1 mol L^{-1} of $HClO_4$) containing HCOOH (1 mol L^{-1} of HCOOH) and $VOSO_4$ with different concentrations

Electrolyte	HCOOH (1 mol L^{-1})	VO^{2+} -added electrolyte (mol L^{-1} of $VOSO_4$)			
		0.1	0.25	0.5	1.0
Solution resistance (R_u) / Ω	1.60	1.78	1.81	1.84	1.97

Composition of produced gas through identification of gas chromatography.

A gas chromatograph (Agilent Technologies 7820A) equipped with a thermal conductivity detector (TCD) and a TDX-01 column is operated as follows: injector $250 \text{ }^\circ\text{C}$, detector $300 \text{ }^\circ\text{C}$, oven initial temperature $60 \text{ }^\circ\text{C}$ for 2 min, then increasing at $25 \text{ }^\circ\text{C min}^{-1}$ to $260 \text{ }^\circ\text{C}$. Ar is the carrier gas flowing at 20 mL min^{-1} . The CO_2 reference gas is prepared by reaction of $CaCO_3$ with H_2SO_4 solution, showing a single component at retention time of 6.78 min. The created gas from HCOOH decomposition in HCOOH analyte for 1.8 h under catalysis of Pd/C via non-Faradaic dehydrogenation, shows two components at retention times of 0.40 and 6.78 min (Fig. S2), assigned to H_2 and CO_2 peaks with a molar ratio of H_2 to $CO_2 \approx 1:1$ (Tab. S2). The CO_2 content is significantly increased in the produced gas after HCOOH electrooxidation at a current density of 60 mA cm^{-2} for 1.9 h under the VO^{2+}/Pd combination, reaching the mole ratio of H_2 to $CO_2 = 1:18.72$.

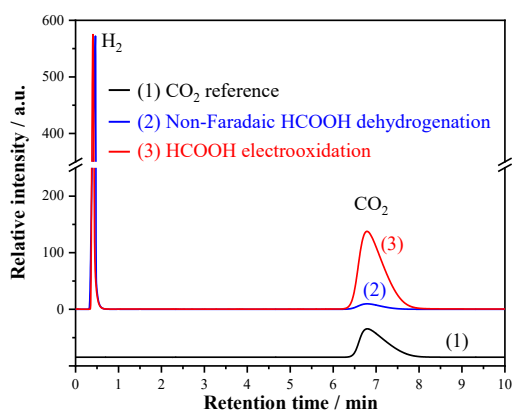


Fig. S2 Chromatogram (TCD) of gases from: (1) reaction of CaCO_3 with H_2SO_4 , (2) Non-Faradaic HCOOH dehydrogenation in HClO_4 -based HCOOH analytes containing 1.0 mol L^{-1} of HClO_4 and HCOOH, (3) HCOOH electrooxidation at Pd/C anode in VOSO_4 -added analytes on the basis of HCOOH anolyte (containing 1.0 mol L^{-1} of HClO_4 and HCOOH, and 0.5 mol L^{-1} of VOSO_4).

Tab. S2 Composition of the produced gas after HCOOH electrooxidation and non-Faradaic dehydrogenation identified by gas chromatography

Sample	CO_2 content / ppm	H_2 content / ppm	CO_2 proportion / %	H_2 proportion / %
Non-Faradaic HCOOH dehydrogenation	3.38×10^5	2.97×10^5	53.25	46.75
HCOOH electrooxidation	5.79×10^5	3.09×10^4	94.93	5.07
CO_2 reference	4.12×10^5	-	100	-

Colour variation of analytes during operation.

The colour variation of analytes during cell operation is illustrated in Fig. S3, using VOSO_4 and VOSO_4^- -added HCOOH analytes. The blue VO^{2+} anolyte (100 mL, 1 mol L^{-1} of HClO_4 , 0.5 mol L^{-1} of VOSO_4) turns to yellow, forming VO_2^+ -contained anolyte when discharge to cut-off voltage of 1.0 V. The colour of the as-prepared VOSO_4 -added anolyte (100 mL, 1 mol L^{-1} of HClO_4 and HCOOH, 0.5 mol L^{-1} of VOSO_4) turns from blue at operation stage (i) to green at operation stage (ii), indicating the formation of hydrated- V^{3+} . Then, the anolyte colour changes to blue again at operation stage (v), and finally to yellow at operation stage (vii).

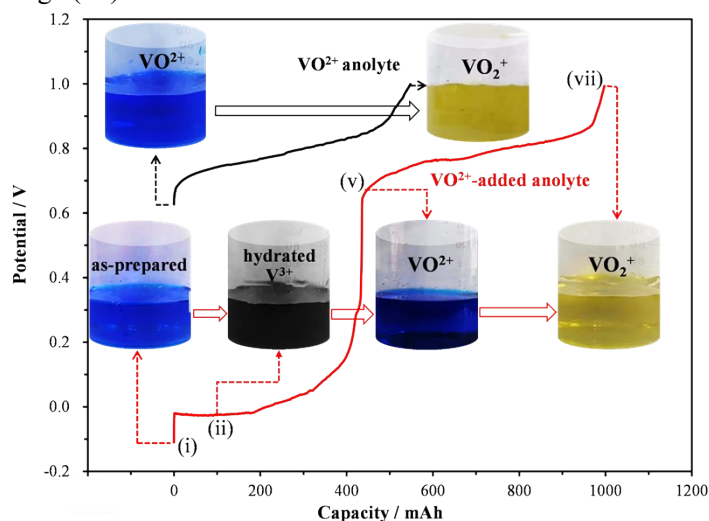


Fig. S3 Colour variation of the VOSO_4 -added anolyte during electrooxidation.

Tab. S3 Comparison of HCOOH oxidation under catalysis of Pd with and without VO²⁺

FAOR under catalysis of Pd		FAOR under coupling catalysis of VO ²⁺ /Pd
Pd + HCOOH → Pd-HCOOH		
Dehydrogenation pathway ^{S1-S4}	Dehydration pathway ^{S2,S5,S6}	Stepwise reaction pathway
Pd-HCOOH → Pd-HCOO + H ⁺ + e ⁻ Pd-HCOO → Pd-CO ₂ + H ⁺ + e ⁻ Pd-CO ₂ → Pd + CO ₂	Pd-HCOOH → Pd-COOH + H ⁺ + e ⁻ Pd-COOH + H ⁺ + e ⁻ → Pd-CO + H ₂ O Pd + H ₂ O → Pd-OH + H ⁺ + e ⁻ Pd-CO + Pd-OH → 2Pd + CO ₂ + H ⁺ + e ⁻	VO ²⁺ + Pd-HCOOH → VOH ²⁺ + Pd-HCOO VO ²⁺ + Pd-HCOO → VOH ²⁺ + CO ₂ + Pd 2VOH ²⁺ + 2H ⁺ → 2V[H ₂ O] ³⁺ 2V[H ₂ O] ³⁺ → 2VO ²⁺ + 4H ⁺ + 2e ⁻
totally, HCOOH → CO ₂ + 2H ⁺ + 2e ⁻	totally, HCOOH → CO ₂ + 2H ⁺ + 2e ⁻	totally, HCOOH → CO ₂ + 2H ⁺ + 2e ⁻

V[H₂O]³⁺: hydrated V³⁺

Estimation of HCOOH consumption.

Tab. S4 illustrates the HCOOH consumption result according to ion chromatography. 100 mL of HCOOH anolyte (1 mol L⁻¹) contains 100 mmol of HCOOH, theoretically producing an operation capacity of 5360 mAh. Ion chromatography result shows that 12.5 mmol of HCOOH is consumed but 87.5 mmol of HCOOH remains after operation of 1.9 h at a current of 240 mA. Regarding the operation capacity of 456 mAh, only 8.5 mmol of HCOOH participates the electrooxidation reaction with a coulombic efficiency of 68%, producing 8.5 mmol of CO₂. The molar ratio of CO₂ to H₂ reaches 3.125:1. However, according to the gas chromatography analysis (Tab. S2), the molar ratio of CO₂ to H₂ is measured to be 18.72:1. Based on this ratio, the coulombic efficiency is estimated to be 94.66% which is much larger than that estimated from ion chromatography result. Therefore, more detailed investigations are needed to estimate the coulombic efficiency accurately.

Tab. S4 Composition of the anolyte before and after operation of 1.9 h at a current of 240 mA.

Sample	Retention time / min	Peak height / μS	Peak area / μS min	Content / ppm	HCOOH consumption
Anolyte before operation	6.78	3.909	0.754	460.1073	-
Anolyte after operation	6.78	3.434	0.660	402.7256	12.5%

References

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