Supporting Information

Gaseous CO_2 Electrolysis: Latest Advances in Electrode and Electrolyzer Technologies toward Abating CO_2 Emissions

*Kazuhide Kamiya,[*a,b] Sora Nakasone,[a] Ryo Kurihara,[a] Asato Inoue,[a] Hazuki Irie,[a] Shoko Nakahata,[a] Nishina Yuta,[c] Satoshi Taniguchi,[d] Thuy T.H. Nguyen,[d,e] and Sho Kataoka[*d,e]*

[a]Research Center for Solar Energy Chemistry, Graduate School of Engineering Science, The University of Osaka, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan.
[b]Innovative Catalysis Science Division, Institute for Open and Transdisciplinary Research [b]Initiatives (ICS-OTRI), The University of Osaka, 1-1 Yamadaoka, Suita, Osaka 565-0871, Japan
[c]Research Institute for Interdisciplinary Science, Okayama University, 3-1-1 Tsushimanaka, Kita-ku, Okayama, Japan
[d]Research Institute for Chemical Process Technology, National Institute of Advanced Industrial Science and Technology (AIST), Central 5, 1-1-1 Higashi, Tsukuba 305-8565, Ibaraki, Japan
[e]Integrated Research Center for CCUS Implementation, National Institute of Advanced Industrial Science and Technology (AIST), Central 5, 1-1-1 Higashi, Tsukuba 305-8565, Ibaraki, Japan

*Corresponding author: E-mail: kamiya.kazuhide.es@osaka-u.ac.jp
E-mail: s-kataoka@aist.go.jp

Table S1. Compilation of previous studies on CO_2 electroreduction in MEA-based electrolyzers.

Year	FE [%] of CO_2RR products							E	j_{total}	Single-pass conversion for C_2H_4 [%]	Stability			Cathode		Membrane	Anode	Anolyte	Electrode size	CO_2 flow rate	Ref.
	C_2H_4	EtOH	PrOH	AcOH	CO	HCOOH	H_2	[V]	[mA cm^{-2}]		Time [h]	j_{total} [mA cm^{-2}]	E [V]	Catalyst	Ionomer				[cm^2]	[sccm]	
2019	48	15	3	7	20	1	5	4.2	200	1.5	100	120	3.8	Cu[a]	Nafion	Sustainion or Aemion	IrO_2/Ti	0.1 M $KHCO_3$	5	80	1
2020	64	No Data	No Data	No Data	5	No Data	8	3.9	170	1.7	190	120	3.6	Cu	aryldihydropyridine oligomer	Sustainion	IrO_2/Ti	0.1 M $KHCO_3$	5	80	2
2020	66	8	2	0	10	5	10	3.9	300	3.1	100	220	3.9	Cu[b]	Aquivion	Sustainion	IrO_2/Ti	0.1 M $KHCO_3$	5	80	3
2021	57	16	2	5	11	2	6	3.8	175	1.6	236	175	3.8 ⇔2	Cu	Nafion	Sustainion	IrO_2/Ti	0.1 M $KHCO_3$	5	80	4
2021	65	10	2	2	7	1	13	4.1	330	3.4	55	300	4.1	Cu-SiO_x	Aquivion	Sustainion	IrO_2/Ti	0.1 M $KHCO_3$	5	80	5
2021	55	9	0	15	10	1	15	3.3	281	3.9	6	200	7.0[c]	Cu-KOH	Nafion	Sustainion	IrO_2/Ti	1 M KOH	10	100	6
2021	63	5	2	1	10	2	12	3.8	150	—[d]	180	90	3.6	Cu[e]	Nafion	Sustainion	IrO_2/Ti	0.1 M $KHCO_3$	No Data	50	7
2021	56	16	5	0	7	2	15	4.5	325	18.5	100	400	4.5	Ag-Cu[f]	Not in use	Fumasep	IrO_2/Ti	0.1 M $KHCO_3$	4	10	8
2022	49	6	0	14	14	0	9	3.3	700	2.3	5	200	2.9	porous Cu	QAPEEK[g]	QAPEEK[g]	IrO_2/Ti	pure water	1.6	60	9
2022	48	No Data	No Data	No Data	12	No Data	16	5.4	300	3.7	52	200	4.0	Cu	Nafion	SC-BPMA[h]	IrO_2/Ti	0.1 M $KHCO_3$	4	40	10
2023	40	3	2	4	10	0	17	3.7	500	—[d]	2	300	3.9	Cu	*p*TPN-Beim[i]	No Data	IrO_2/Ti	pure water	No Data	100	11
2023	44	44	0	3	2	1	10	2.7	300	4.5	400	200	3.2	Cu dendrites[j]	Nafion	Sustainion	IrO_2/Ti	1 M KOH[k]	4	30	12
2024	52	19	3	4	9	1	14	3.5	252	2.6	194	70	4.1	Cu	Nafion	PiperION	IrO_2/Ti	0.1 M $KHCO_3$[l]	6.25	80	13
2024	86	6	0	0	3	1	2	3.0	368	26.8	200	370	3.0	MP-Cuf20[m]	Not in use	Sustainion	Ni form	0.1 M $KHCO_3$	5	15	14
2024	43	6	2	1	10	1	30	4.3	300	1.1	1000	333	25[c]	surface-step-rich Cu	Sustainion	Sustainion +Nafion	Pt/Ti	pure water	1	30	15
2024	63	8	1	2	3	5	20	4.1	150	20.0	65	150	4.1	porous Cu	Nafion	PiperION +Nafion	IrO_2	0.1 M $KHCO_3$	1	1.2	16
2025	66	1	0	0	10	1	17	3.0	500	6.7	56	300	3.5	amorphous-rich Cu	Nafion	Sustainion	IrO_2/Ti	1 M KOH[n]	4	50	17

[a]with carbon nanoparticle and graphite powder
[b]with tetrahydro-phenanthrolinium
[c]Cell voltage measured in the stacked-cell configuration.
[d]Not calculated owing to the lack of electrode dimension data.
[e]quasi-graphitic C shell-protected Cu doping with N
[f]N_2SN functionalized Ag-Cu
[g]quaternary ammonia poly(ether ether ketone)
[h]PVDF+TiO_2-coated Nafion+PiperION
[i]terphenyl-trifluoroheptan-2-one-1-methyl-benzimidazolium
[j]Cu dendrites with ultrastable $Cu^{\delta+}$ sites and hydrophobicity
[k]0.02 M $KHCO_3$ was used for the stability test.
[l]Switching between 0.1 M $KHCO_3$ and dilute K^+ solution
[m]electrochemically depositing mesoporous Cu films on Cu foam
[n]1 M $KHCO_3$ was used for the stability test.

Note S1. Details of the experimental conditions for the data used in Table 1.[13]

Materials and Chemicals

CuONPs (copper(II) oxide, nanopowder, <50 nm particle size (TEM)) were purchased from Sigma-Aldrich. 5 wt% Nafion dispersion, 2-propanol, dimethyl sulfoxide (DMSO), potassium hydrogen carbonate ($KHCO_3$) and D_2O were purchased from Wako Pure Chemical. Carbon-based GDE (GDS2130, AvCarb) was purchased from the Fuel Cell Store. IrO_2/Ti mesh (porosity: 56%, wire diameter: 20 mm, thickness: 3 mm) was purchased from Tanaka Kikinzoku Kogyo. Anion-exchange menbrane (Sustainion X37-50 Grade RT) was purchased from Dioxide Materials.

Fabrication of cathode electrode

Cathode electrodes were fabricated by spray-coating a Cu catalyst ink onto a GDE. The catalyst ink was prepared by dispersing 100 mg of CuNPs in a mixture of 200 μL 5 wt% Nafion ionomer solution and 6800 μL 2-propanol. The catalyst ink mixtures were sonicated for 30 min and then sprayed onto a carbon-based GDE (electrode area: 6.25 cm^2) at room temperature. The mass loading of Cu catalyst on the GDE was controlled at ~0.2 mg cm^{-2}.

Electrochemical measurements

All electrochemical experiments were performed using an MEA-based electrolyzer (Figure S1). IrO_2/Ti mesh (electrode surface area: 6.25 cm^2) was used as an anode. Sustainion AEM was used as a solid electrolyte for the electrolysis. In all of the experiments, humidified CO_2 was set at a flow rate of 80 mL min^{-1} and was supplied to the cathode flow channel at room temperature using a mass flow controller (8500 MC, Kofloc, Japan). At the anode side, 90 mL of 0.1 M $KHCO_3$ was placed in a reservoir as an anode solution and was circulated in the anode flow channel at 10 mL min^{-1} using a diaphragm pump. An electrochemical workstation (HZ-Pro, Hokuto Denko, Japan) was used to conduct all of the electrochemical experiments.

Analysis of CO_2RR products

Liquid products such as ethanol, propanol, acetic acid, and formic acid were collected in a liquid trap and an anode solution reservoir at the cathode and anode side, respectively. Vaporized liquid products in the cathode outlet gas were collected by bubbling into a liquid trap filled with deionized water. The liquid products transported from the cathode surface to the anode through solid electrolyte membrane were collected in an anode solution reservoir. The liquid products captured in the liquid trap and in the anode solution reservoir were analyzed using ^{1}H nuclear magnetic resonance (^{1}H NMR) spectroscopy (JNM ECS-400, 400 MHz, JEOL, Japan). ^{1}H NMR spectra of freshly acquired samples were collected using the water suppression mode reported elsewhere.[18] A 500 mL sample of the electrolyte after electrolysis was mixed with 100 μL of D_2O containing DMSO as an internal standard. The gas products downstream of the liquid trap were analyzed using a gas chromatograph (GC 2030, Shimadzu, Japan), which was equipped with both a thermal conductivity detector (TCD) and a flame ionization detector (FID). The gas chromatograph, in which He was used as the carrier gas, was equipped with a MICROPACKED ST column.

(a)

(b)

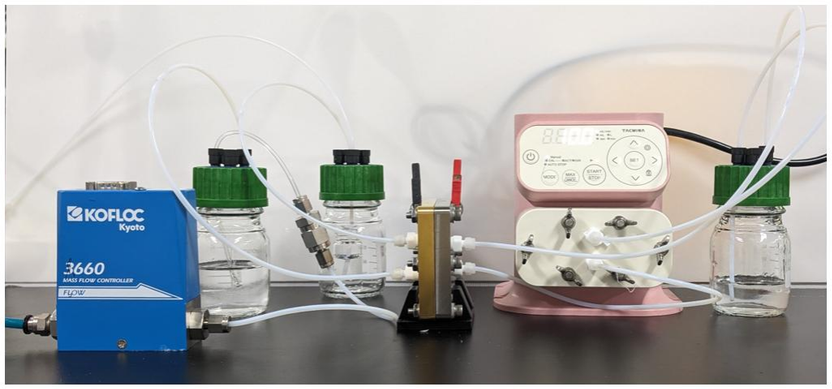

Fig. S1. Photographs of (a) MEA-based cell and (b) MEA system for CO_2RR used used for the data presented in Table 1.[13]

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