

Supplementary Information for

The design of alternative anodic reactions paired with electrochemical CO₂ reduction

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Supplementary Table 1 Alternative anode reactions paired with CO₂RR.

$E_{\text{electrode}}$ (V)	J (mA cm ⁻²)	Cathode catalyst	Cathode product(s), FE (%)	Anode reaction	Anode catalyst	Anode product(s), FE/DE (%)	Cell type	Ref
E_{cat} -0.59, E_{an} 0.73V vs. RHE, E_{cell} 1.4V	67.79 (total)	GDL- deposited	CO (96.25)	Glycerol	Pt	HCOO ⁻ , C ₃ H ₆ O ₃	Flow cell	¹
E_{cat} -0.3, E_{an} 1.5V vs. RHE, E_{cell} 2.0V	~7 (total)	Fe- SAs/N-C	CO (99.6)	hypochlo rite	RuO ₂ /Ti	82	H-cell	²
E_{cat} -1.7V vs. SHE, E_{cell} 2.5V	100 (total)	Ag	CO (90)	urea oxidation	Ni foam	-	H-cell	³
E_{degra} -1.7V vs. Ag/AgCl	43 (cathode)	CNT40/E SGDE cathode	Formate (72.38)	MO	Ti/SnO ₂ -Sb anode	100	H-cell	⁴
E_{degra} -1.7V vs. Ag/AgCl	38 (cathode)	EBGDE- 60	Formate (91.46)	MO	Ti/SnO ₂ -Sb	100	H-cell	⁵

				crystal			two-	
E_{cell} 2.8V	9 (total)	Sn	HCOOH (14.1)	violet (CV)	Co_3O_4	52.6	electrode glass cell	6
E_{degra} 1.8V vs. Ag/AgCl	18 (anode)	Cu/Bi	Formate (84.63)	p-nitrophenol	Ti/SnO ₂ -Sb	97.31	H-cell	7
E_{degra} -0.8V vs. Ag/AgCl	-0.9 (cathode)	flower-like CuO	CH ₃ OH, C ₂ H ₅ OH (electron efficiency 73.1)	4-nitrophenol	Co_3O_4 arrays	99.2	H-cell	8
E_{degra} -1.3V vs. Ag/AgCl	-3 (cathode)	SnO ₂ /CC	HCOOH (24.1)	4-nitrophenol	3D gear shaped Co_3O_4	99.1	H-cell	9
-	24 (total)	Sn	formic acid (45mM)	Acid Orange 7 Alcohol to acetaldehyde and acetic acid 1,2-propanediol	boron-doped diamond	TOC (>80)	H-cell	10
E_{cat} -0.7V vs. RHE	-3.7 (cathode)	copper-indium cathode	CO >70	acetaldehyde and acetic acid 1,2-propanediol	platinum anode	>75	H-cell	11
E_{cell} 2.53-2.63V	-15 (cathode)	gold plate	CO (76)	iol to lactic acid	carbon felt	80	Flow cell	12
E_{cat} -1.1V vs. Ag/AgCl E_{cell} 2 V	0.09 (total, E_{cell} 2 V)	[(tpy)(Me bipy)Ru ^{II} (OH ₂)] ²⁺	CO&H ₂ (30-40)	Ph-CH ₂ OH oxidation	[Ru(bis-Mebimpy)(4,4'-((OH) ₂ OPC H ₂) ₂ -	Benzaldehyde (70)	H-cell	13

					bpy)(OH ₂)] ²⁺			
					ceric			
					ammonium			
E _{cat} -1.8, E _{an} 2.43		Re(bipy-		Syringald	nitrate			
V vs. Ag/AgCl,	2.4 (total)	tBu)(CO) ₃	CO (100)	ehyde to	(CAN)+syrin	65	H-cell	14
E _{cell} 4 V		Cl		benzimid	galdehyde+o			
				azole	-			
					phenylenedia			
					mine			
E _{cell} 2.5 V	2 (total)	BiO _x	Formate (81)	HMFOR	NiO NPs	36 for biomass	H-cell	15
						conversion		
						84.3 for HMFOR		
E _{cell} 2.7 V	103.5 (total)	PdO _x /ZIF-	CO (97)	HMFOR	PdO	(20.0 maleic acid,	H-cell	16
		8				64.3% of formic		
						acid)		
E _{cell} 3.8 V	100	TPPNi-	CO (~98.5)	CER	DSA	Cl ₂ (~80)	Flow cell	17
		CB/GDE						
E _{cat} -2.241, E _{an}	15.7	graphite						
1.36 V vs. SHE	(cathode),	rod	CO (92.23)	CER	Au foil	Cl ₂ (82.5)	H-cell	18
	2.53 (anode)							
				Br ⁻ to Br ₂				
				combined				
E _{cat} -1.01 V vs				*CHCH ₂			membranele	
RHE	-19 (cathode)	Cu foil	C ₂ H ₅ OH (12)	to form	Pt	2-bromoethanol (40)	ss cell	19
				BrCH ₂ C				
				H ₂ OH				
				Br ⁻ to				
E _{cell} -3.75 V	12 (cathode)	Au	CO (48), H ₂ (33),	Br ₂ , to	glassy	dimethyl carbonate	membranele	
			MeOH to MeO ⁻	form	carbon	(60)	ss cell	20

				dimethyl carbonate				
					N- bromoamino acids synthesis carboxylation	N-bromoamino acid (68) N-methyl-N- (phenylacetoxy)met hylformamide (69)	undivided cell one- compartmen t cell	21
-	10 (total)	Ni	-COOH	Au	n of benzyl halides tetraalkylam monium salt anion oxidation			
-	20 (total)	Pt plate	-COOH&-CHO	Pt wire				22
E _{cell} 3.22 V	15 (total)	Pt plate	-COOH	Pt net		Cyanoacetic Acid (24.7)	H-cell	23

Reference

1. S. Verma, S. Lu and P. J. A. Kenis, *Nat. Energy*, 2019, **4**, 466-474.
2. F. J. Quan, G. M. Zhan, H. Shang, Y. H. Huang, F. L. Jia, L. Z. Zhang and Z. H. Ai, *Green Chem.*, 2019, **21**, 3256-3262.
3. X. V. Medvedeva, J. J. Medvedev, S. W. Tatarchuk, R. M. Choueiri and A. Klinkova, *Green Chem.*, 2020, **22**, 4456-4462.
4. Q. N. Wang, X. Q. Wang, C. Wu, Y. Y. Cheng, Q. Y. Sun and H. B. Yu, *J. CO₂ Util.*, 2018, **26**, 425-433.
5. Q. N. Wang, C. Q. Zhu, C. Wu and H. B. Yu, *Electrochim. Acta.*, 2019, **319**, 138-147.
6. L. Chiayu, A. Balamurugan, L. Yihsuan and H. Kuochuan, *Talanta*, 2010, **82**, 1905-1911.
7. Q. N. Wang, W. L. Wang, C. Q. Zhu, C. Wu and H. B. Yu, *J. CO₂ Util.*, 2021,

- 47, 101497.
8. J. P. Zou, Y. Chen, S. S. Liu, Q. J. Xing, W. H. Dong, X. B. Luo, W. L. Dai, X. Xiao, J. M. Luo and J. Crittenden, *Water Res.*, 2019, **150**, 330-339.
 9. M. Zhu, L. S. Zhang, S. S. Liu, D. K. Wang, Y. C. Qin, Y. Chen, W. L. Dai, Y. H. Wang, Q. J. Xing and J. P. Zou, *Chinese Chem. Lett.*, 2020, **31**, 1961-1965.
 10. S. Sabatino, A. Galia, G. Saracco and O. Scialdone, *ChemElectroChem*, 2017, **4**, 150-159.
 11. T. F. Li, Y. Cao, J. F. He and C. Berlinguette, *ACS Cent.Sci.*, 2017, **3**, 778-783.
 12. E. Pérez-Gallent, S. Turk, R. Latsuzbaia, R. Bhardwaj, A. Anastasopol, F. Sastre-Calabuig, A. C. Garcia, E. Giling and E. Goetheer, *Ind. Eng. Chem. Res.*, 2019, **58**, 6195-6202.
 13. Y. Wang, S. Gonell, U. R. Mathiyazhagan, Y. M. Liu, D. G. Wang, J. M. Alexander and T. J. Thomas, *ACS Appl. Energy Mater.*, 2018, **2**, 97-101.
 14. M. Llorente, B. Nguyen, C. Kubiak and K. Moeller, *J. Am. Chem. Soc.*, 2016, **138**, 15110-15113.
 15. S. Choi, M. Balamurugan, K. Lee, K. Cho, S. Park, H. Seo and K. Nam, *J. Phys. Chem. Lett.*, 2020, **11**, 2941-2948.
 16. J. H. Bi, Q. G. Zhu, W. W. Guo, P. S. Li, S. Q. Jia, J. Y. Liu, J. Ma, J. L. Zhang, Z. M. Liu and B. X. Han, *ACS Sustain. Chem. Eng.*, 2022, **10**, 8043-8050.
 17. J. H. Guo and W. Y. Sun, *Appl. Catal. B-environ*, 2020, **275**, 119154.
 18. C. J. Li, J. Shi, J. X. Liu, Y. J. Duan, Y. X. Hua, S. Wu, J. Z. Zhang, X. G. Zhang, B. Yang and Y. N. Dai, *Electrochim. Acta.*, 2021, **389**, 138728.
 19. S. D. Zhong, Z. Cao, X. L. Yang, S. M. Kozlov, K. W. Huang, V. Tung, L. G. Cavallo, L. J. Li and Y. Han, *ACS Energy Lett.*, 2019, **4**, 600-605.
 20. K. M. Lee, J. H. Jang, M. Balamurugan, J. E. Kim, Y. I. Jo and K. T. Nam, *Nat. Energy*, 2021, **6**, 733-741.
 21. C. H. Li, X. Z. Song, L. M. Tao, Q. G. Li, J. Q. Xie, M. N. Peng, L. Pan, C.

- Jiang, Z. Y. Peng and M. F. Xu, *Tetrahedron*, 2014, **70**, 1855-1860.
22. H. Senboku, K. Nagakura, T. Fukuhara and S. Hara, *Tetrahedron*, 2015, **71**, 3850-3856.
23. B. Batanero, F. Barba, C. M. Sa'nchez-Sa'nchez and A. Aldaz, *J. Org. Chem.*, 2004, **69**, 2423-2426.