Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information for:

Optimising the Electrochemical Reduction of CO_2 to Oxalic Acid in Propylene Carbonate

*Halilu Sale[1,2], Gangi Reddy Ubbara[1], Mark D. Symes[1]**

1. WestCHEM, School of Chemistry, University of Glasgow, G12 8QQ Glasgow, UK.
2. Energy Commission of Nigeria, Plot 701c Garki-Abuja, Nigeria

**Corresponding Author: Mark.Symes@glasgow.ac.uk*

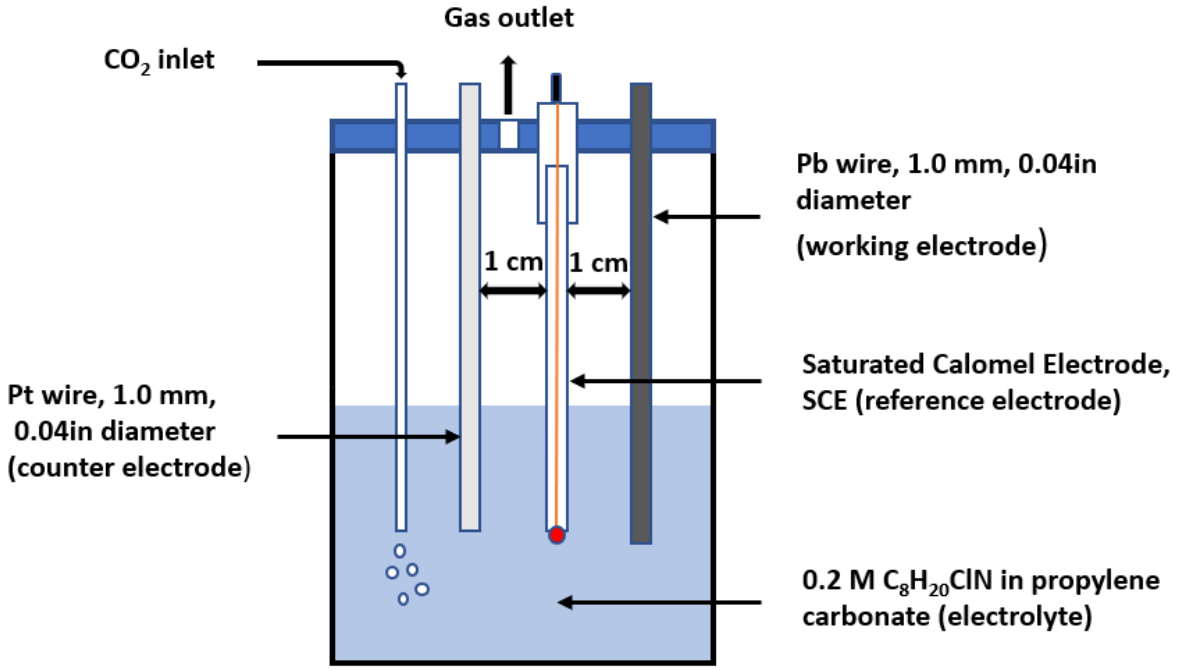

Figure S1: *Schematic diagram of the single-cell experimental set-up used for the cyclic voltammetry experiments, using lead as a working electrode, platinum as a counter electrode and a saturated calomel electrode as the reference electrode at a temperature of 25 °C.*

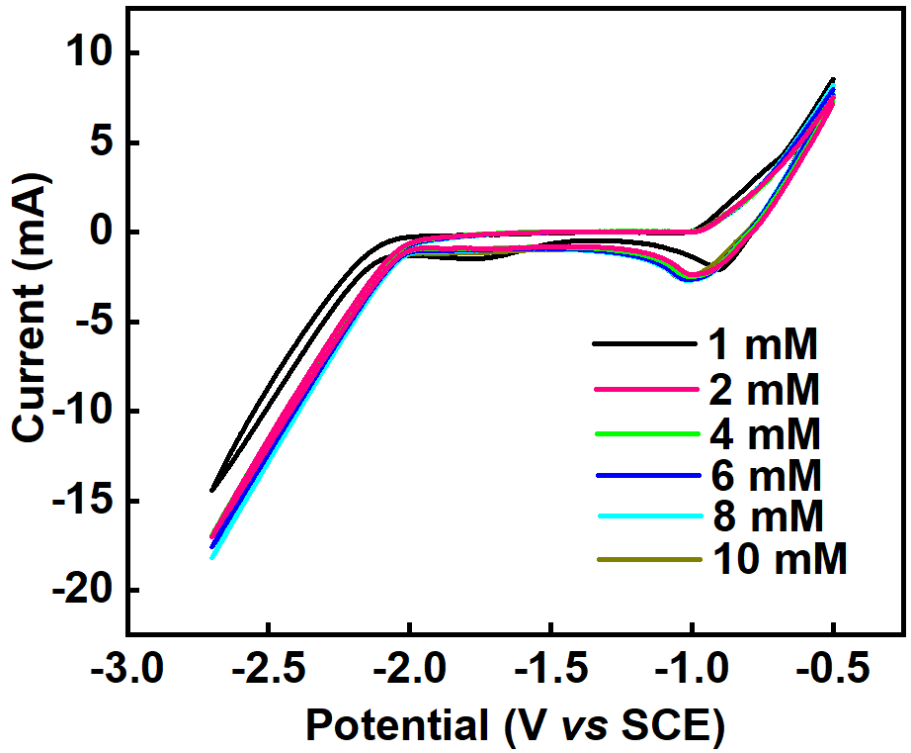

Figure S2: *Cyclic voltammetry investigating the optimum concentration of the benzonitrile electrocatalyst needed for the electrochemical reduction of CO_2 in propylene carbonate, using lead as a working electrode with a surface area of 1.40 cm^2, platinum as a counter electrode and a saturated calomel electrode as the reference electrode at a temperature of 25 °C and scan rate of 50 mV/s.*

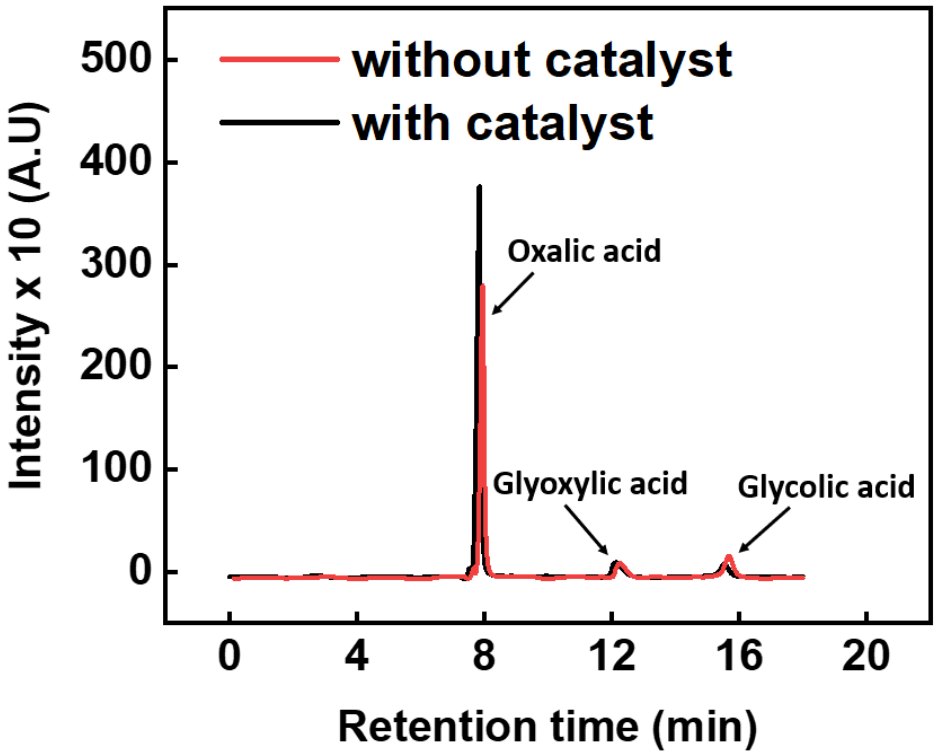

Figure S3: *Example HPLC signal showing the chromatograms retention time for the carboxylic acids detected at −2.2 (V vs SCE) in propylene carbonate (red) and propylene carbonate/benzonitrile (black).*

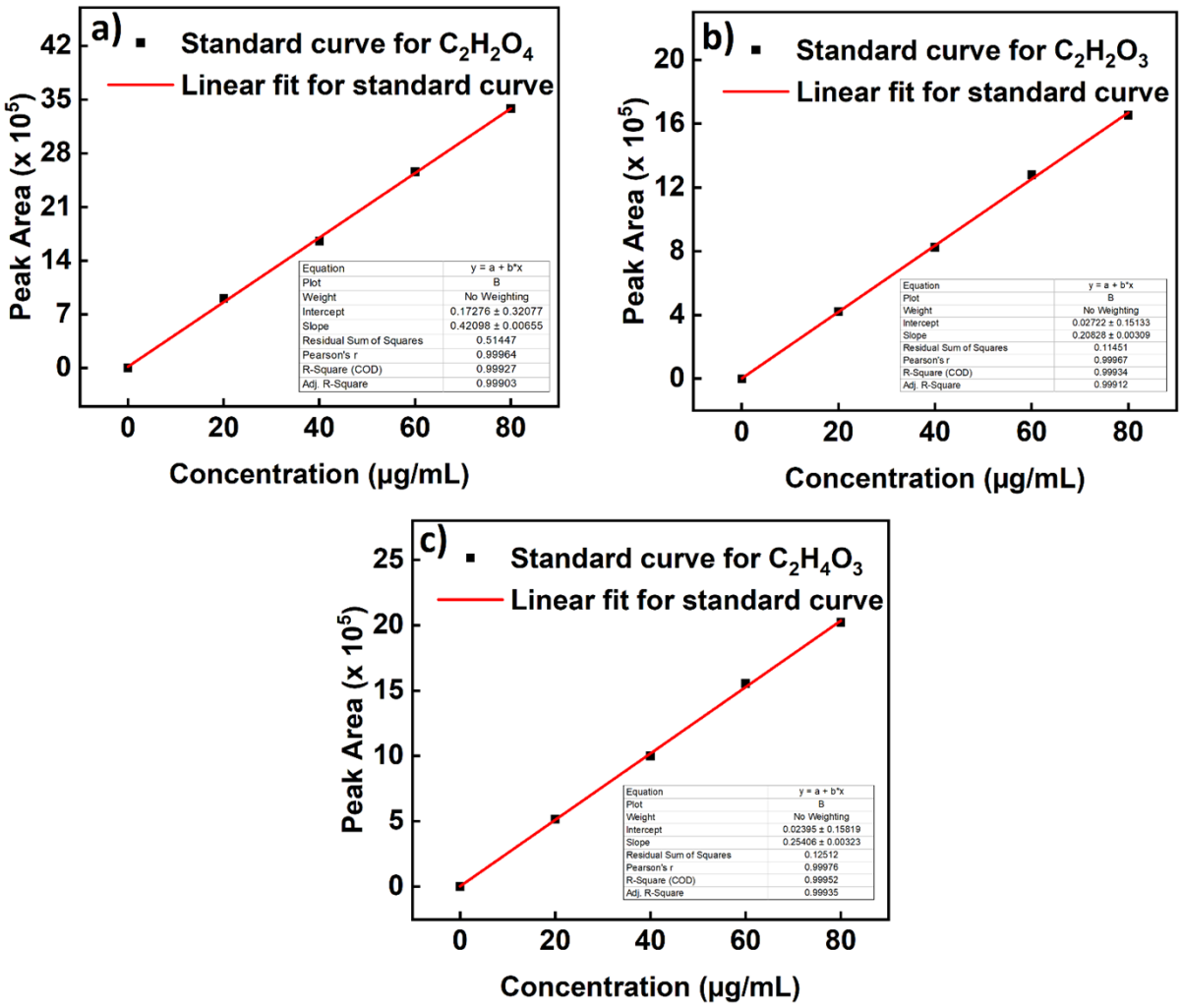

Figure S4: *Calibration curves for (a) Oxalic acid, (b) glyoxylic acid and (c) glycolic acid obtained from HPLC analysis of the standard solutions of the respective carboxylic acids.*

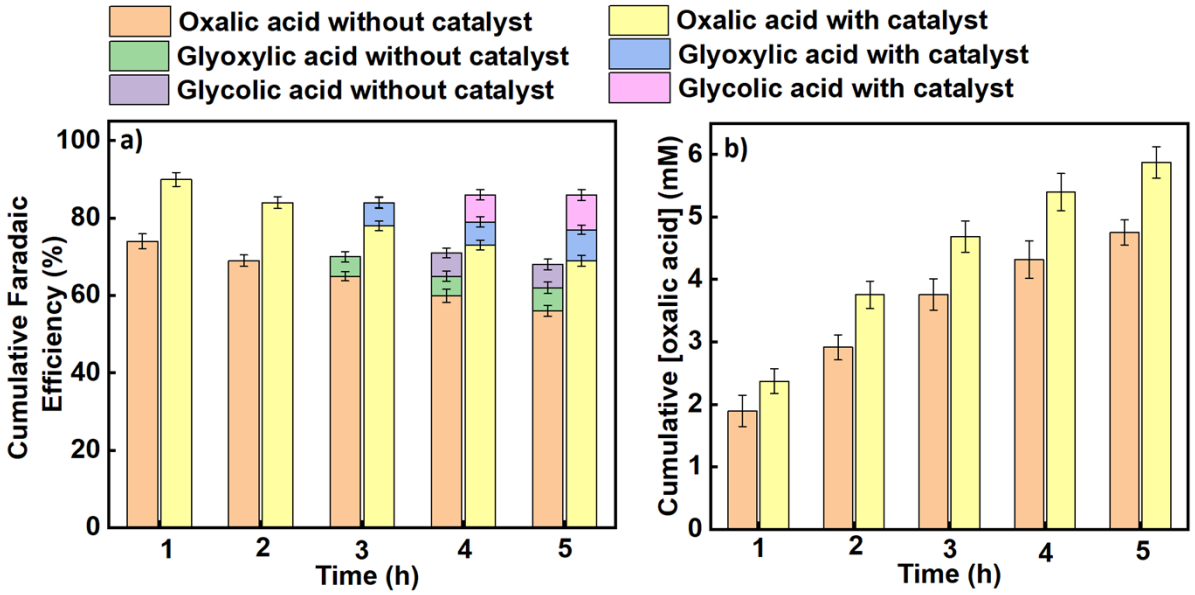

Figure S5: *The effect of benzonitrile on (a) the cumulative Faradaic efficiencies for the production of oxalic acid and its accompanying by-products in propylene carbonate, (b) the cumulative concentration of oxalic acid formed using Pb as a working electrode and Pt foil as a counter electrode at an applied potential of –2.3 V vs SCE in an H-cell at a temperature of 25 °C. Triplicate experiments were performed to obtain the error margin, and the results are calculated as the mean ± standard deviation (n = 3).*

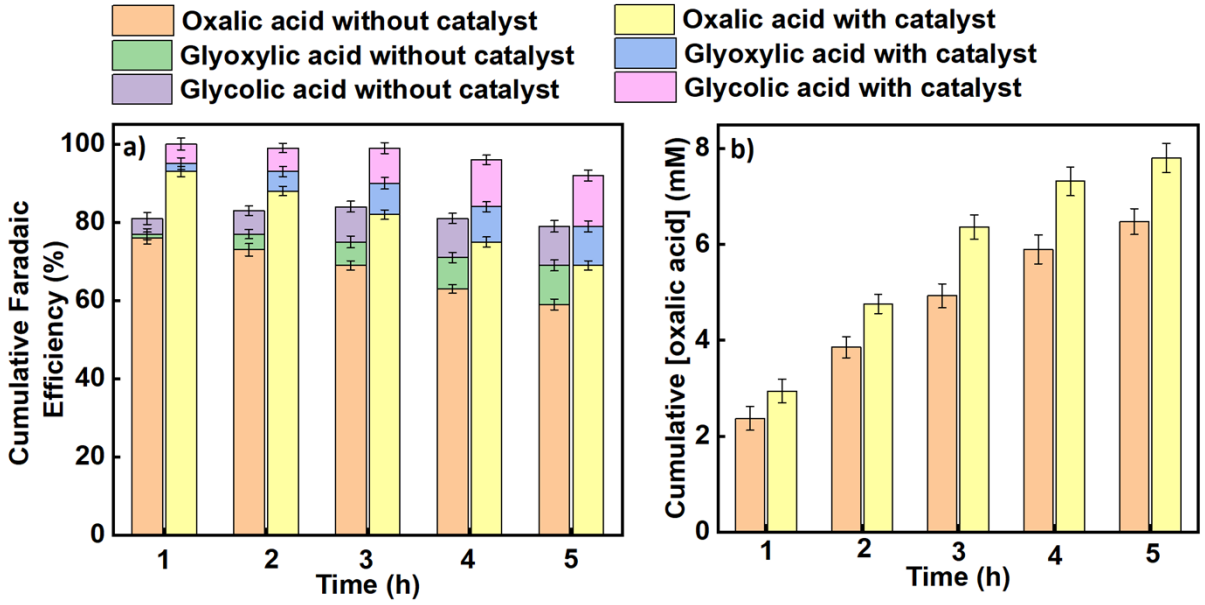

Figure S6: *The effect of benzonitrile on (a) the cumulative Faradaic efficiencies for the production of oxalic acid and its accompanying by-products in propylene carbonate, (b) the cumulative concentration of oxalic acid formed using Pb as a working electrode and Pt foil as a counter electrode at an applied potential of –2.4 V vs SCE in an H-cell at a temperature of 25 °C. Triplicate experiments were performed to obtain the error margin and the results are calculated as the mean ± standard deviation (n = 3).*

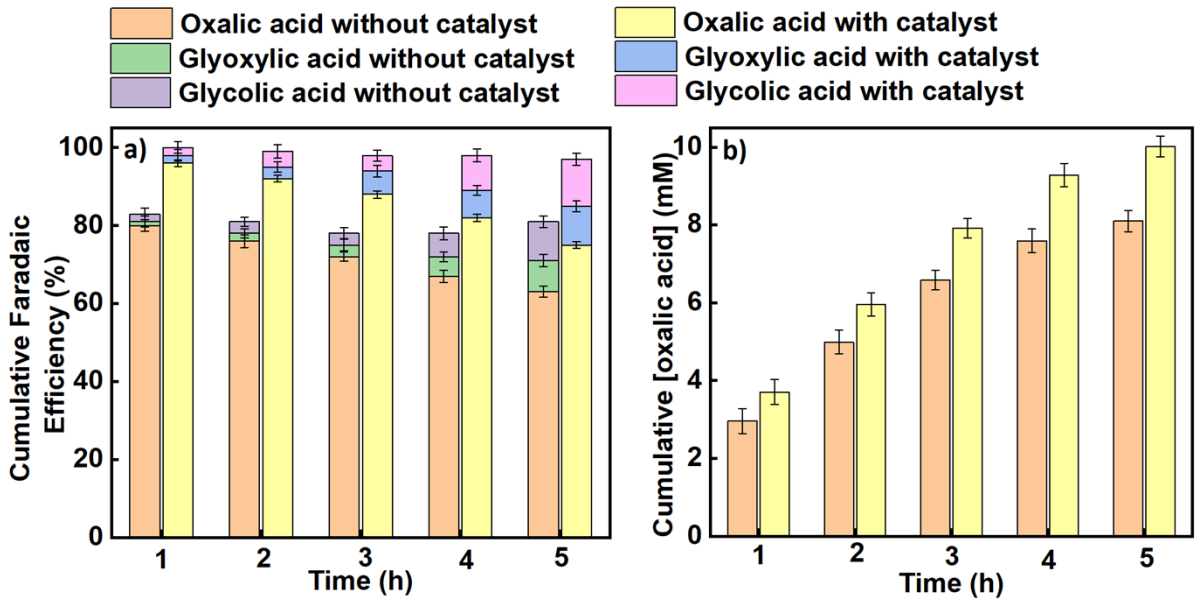

Figure S7: *The effect of benzonitrile on (a) the cumulative Faradaic efficiencies for the production of oxalic acid and its accompanying by-products in propylene carbonate, (b) the cumulative concentration of oxalic acid formed using Pb as a working electrode and Pt foil as a counter electrode at an applied potential of –2.5 V vs SCE in an H-cell at a temperature of 25 °C. Triplicate experiments were performed to obtain the error margin and the results are calculated as the mean ± standard deviation (n = 3).*

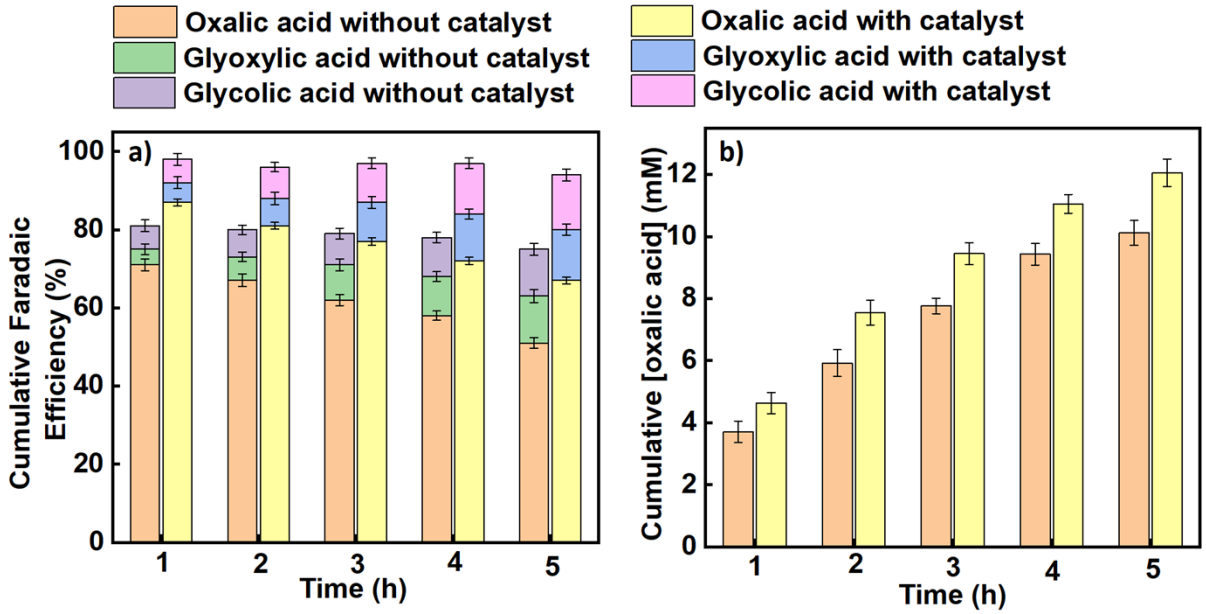

Figure S8: *The effect of benzonitrile on (a) the cumulative Faradaic efficiencies for the production of oxalic acid and its accompanying by-products in propylene carbonate, (b) the cumulative concentration of oxalic acid formed using Pb as a working electrode and Pt foil as a counter electrode at an applied potential of –2.6 V vs SCE in an H-cell at a temperature of 25 °C. Triplicate experiments were performed to obtain the error margin and the results are calculated as the mean ± standard deviation (n = 3).*

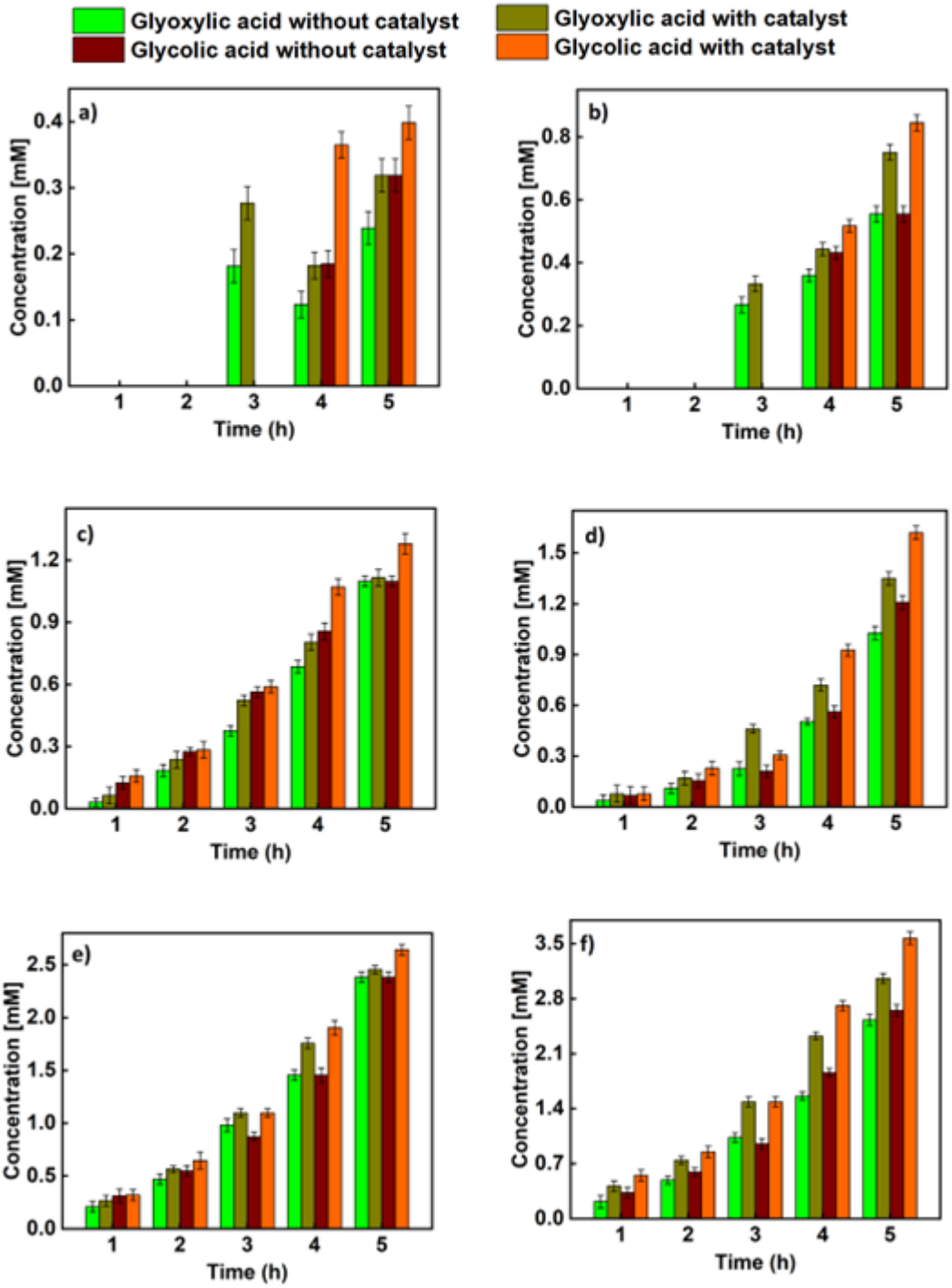

Figure S9: *The concentration of notable by-products accompanying the electrochemical reduction of CO_2 to oxalic acid in propylene carbonate and propylene carbonate/benzonitrile on a Pb cathode at an applied potential of a) −2.2 V, b) −2.3 V, c) −2.4 V, d) −2.5 V, e) −2.6 V, f) −2.7 V vs. SCE in an H-cell at 25 °C for 5 hours.*

***Table S1**: The effect of benzonitrile on current densities for electrochemical reduction of CO_2 to oxalic acid in propylene carbonate on a Pb cathode at an applied potential of −2.2 to −2.7 (V vs. SCE) in an H-cell at 25 °C, averaged over 5 hours.*

Entry	Applied Potential (V vs SCE)	Average Current Density (mA/cm^2)	
		Without catalyst	With catalyst
1	−2.2	−4.49	−5.11
2	−2.3	−5.61	−7.10
3	−2.4	−7.00	−8.71
4	−2.5	−8.77	−10.96
5	−2.6	−11.0	−13.68
6	−2.7	−13.7	−16.90

***Table S2:** The effect of benzonitrile on the average Faradaic efficiencies of the notable products of electrochemical reduction of CO_2 to oxalic acid in propylene carbonate on a Pb cathode at an applied potential of −2.2 to −2.7 (V vs. SCE) in an H-cell at 25 °C, averaged over 5 hours.*

Entry	Applied Potential (V vs SCE)	Average Faradaic Efficiency of the Products (%)					
		Oxalic Acid		Glyoxylic Acid		Glycolic Acid	
		Without catalyst	With catalyst	Without catalyst	With catalyst	Without catalyst	With catalyst
1	−2.2	61.17	75.40	1.80	2.60	1.40	2.25
2	−2.3	64.40	78.84	3.20	4.0	2.40	3.20
3	−2.4	68.22	82.25	5.80	6.83	7.80	9.01
4	−2.5	71.60	86.60	3.80	5.60	4.8	6.20
5	−2.6	63.80	77.80	8.2	9.40	8.60	10.20
6	−2.7	59.60	72.40	8.2	9.40	9.2	10.8

***Table S3:** The effect of benzonitrile on the yield of the notable products of electrochemical reduction CO_2 in propylene carbonate on a Pb cathode at an applied potential of −2.2 to −2.7 (V vs. SCE) in an H-cell at 25 °C, averaged over 5 hours.*

Entry	Applied Potential (V vs SCE)	Product Concentration (mM)					
		Oxalic Acid		Glyoxylic Acid		Glycolic Acid	
		Without catalyst	With catalyst	Without catalyst	With catalyst	Without catalyst	With catalyst
1	−2.2	4.05	4.68	0.23	0.31	0.35	0.39
2	−2.3	4.75	5.88	0.56	0.75	0.60	0.84
3	−2.4	6.47	7.81	1.09	1.11	1.09	1.45
4	−2.5	8.10	10.12	1.12	1.35	1.21	1.62
5	−2.6	10.14	12.05	2.38	2.45	2.38	2.64
6	−2.7	12.65	15.81	2.53	3.06	2.65	3.57