

Supporting Information

Enabling Technologies for the Continuous Electrically Driven Conversion of CO₂ and Water to Multi-Carbon Products at High Current Densities

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Working electrode fabrication for HER studies

20 μL of 5% Nafion solution was added to 50 mg of Ni_2P powder and mixed in mortar and pestle until dry. This composite was then pressed with a force of 5 tons in a 6 mm diameter die. The resulting pellet was then mounted on a Ti plate fixed to a Cu wire using Ag-paint, followed by threading the assembly through a glass tube. After drying, the Ag-paint, the sides of the catalyst pellet, and the Ti plate were isolated from solution by covering in Hysol 1C epoxy (Loctite) all the way up onto the glass tube. Fabricated electrodes were then allowed to completely dry overnight prior to any electrochemical analysis.

Roughness Factor Calculation

A roughness factor was obtained by dividing the ECSA with the geometric area of the sample. ECSA was obtained by dividing the capacitance of the Ni_2P electrocatalysts with the specific capacitance of metal phosphides ($40 \mu\text{F}/\text{cm}^2$). To measure the capacitance, potential was cycled between 0 and -0.1 V vs RHE at different scan rates in $0.5 \text{ M H}_2\text{SO}_4$ solution. Capacitive current was then measured at -20mV vs RHE and plotted versus scan rates. The slope of the linear fit is the capacitance of the sample.

Batch Cell Setup for CO_2RR

Each CO_2RR Faradaic efficiency value reflects the average of 3 replicates. The cell used was a custom-made glass-reinforced nylon-6,6 electrochemical cell, with silicon O-rings and PEEK fittings (IDEX HS). The working electrode was separated from the counter electrode by a Nafion 115 membrane (Fuel Cell Store). Platinum black deposited on Pt foil (Alfa Aesar, 99.9%) was utilized as the counter electrode. The $\text{Hg}/\text{Hg}_2\text{SO}_4$ reference electrode was calibrated daily against a pristine Accumet SCE electrode. This SCE was periodically calibrated against a freshly flame-annealed Pt electrode in $0.5 \text{ M H}_2\text{SO}_4$ under 1 atm H_2 to calibrate to the RHE scale. The working electrode was prepared by mixing 1.00 g of the catalyst with 3% (w/w) neutralized Nafion or PFAEM ionomer and mixing the slurry until it turned back to the dry powder. This powdered material was then pressed at 10 ton onto an aluminum die and dried overnight in vacuum oven at $60 \text{ }^\circ\text{C}$ to remove any excess volatile impurities. The die, containing the pressed catalyst pellet was employed directly as the working electrode and current collector, with only the Ni_2P exposed to the electrolyte. CO_2 (Air Gas, instrument grade, with a Supelco hydrocarbon trap) was supplied through the bottom of the cell to both the working and counter electrodes at a flow rate of 5 sccm (certified MKS P4B mass flow controllers). The headspace of the working electrode compartment was sampled every 30 minutes for gas chromatography.

Preparation of Cathode Catalyst Inks

The cathode catalyst inks were prepared by mixing Ni_2P catalyst, Vulcan carbon (XC-72R, FuelCellStore), isopropanol alcohol (HPLC Plus grade 99.9%, Sigma Aldrich), deionized water, and ionomer together. The ratio of ionomer, catalyst, and Vulcan carbon was kept at 3:5:5. The solvent ratio of deionized water to isopropyl alcohol 2:3 was used. The ink was first dispersed using a horn sonicator three times at 30 s intervals, and then the ink was placed in an ice bath sonicator for 1 h to ensure uniform mixing before being deposited onto the gas diffusion layer (GDL).

Cathode GDE Fabrication

A GDL (Sigracet 39BC, FuelCellStore) with a thickness of $325 \pm 25 \mu\text{m}$ was placed on a heated vacuum table at $95 \text{ }^\circ\text{C}$ with the micro porous layer (MPL) facing up. The catalyst ink was hand-painted onto the GDL. The catalyst loading was 0.5 mg cm^{-2} . Once fabricated, the cathode GDE was hot annealed at $120 \text{ }^\circ\text{C}$ for 2 hours.

Characterization

Methods for characterization of the catalyst by powder X-ray diffraction, atomic absorption of the electrolyte, online product analysis by GC and HPLC using refractive index and UV-vis detectors, and offline product analysis by $^1\text{H-NMR}$. Powder X-Ray diffraction (PXRD) was conducted at room temperature on a Philips X'pert system using Cu K-alpha 0.15418 nm x-rays, calibrated daily with a Si standard. The step size used for the diffraction patterns shown was 0.02° , and the scan speed $0.013^\circ/\text{s}$. Zeiss Sigma Field Emission SEM at 5 keV acceleration voltage was utilized to image samples. Samples were dispersed in ethanolic solution and drop casted on Al-stubs followed by drying in vacuum oven at $60 \text{ }^\circ\text{C}$ for 2 h. ICP-OES was conducted on a Perkin Elmer Optima 7300 DV to detect the amount of nickel that was dissolved from electrode during the catalysis. The samples were prepared by diluting $500 \mu\text{L}$ of the post-reaction electrolyte with $2500 \mu\text{L}$ of 2% (v/v) nitric acid in ultrapure water. Immediately prior to sample analysis, calibration was done with a serial dilution of a 1000-ppm nickel. Product detection and quantification of possible headspace products (hydrogen, carbon monoxide, carbon dioxide, methane, ethane, and ethylene) was performed by in-line auto-sampling on an HP 5890 Series II GC with serial connected thermal conductivity and flame ionization detectors. Liquid products were quantified on a Perkin-Elmer Flexar HPLC equipped with an auto-sampler, refractive index, and UV-vis detectors. Using an HPX 87H Aminex column, a flow rate of 0.3 mL min^{-1} at 65°C , standards were calibrated between 0.05 and 10 mM . Product assignment was confirmed by $^1\text{H-NMR}$ which also was used to verify the absence of other products

Calculation of the number of sites

First, the molar volume [$V_m(\text{cm}^3/\text{mol})$] of the Ni_2P was calculated from its formula weight [$F_w(\text{g/mol})$] and density [$\rho(\text{g/cm}^3)$]

$$V_m = \frac{F_w}{\rho}$$

The average surface occupancy (atoms/cm^2) was approximated using the equation below, where N_a is Avogadro's number:

$$\text{Average surface occupancy (atoms} \cdot \text{cm}^{-2}\text{)} = \left(\frac{\text{\#atoms per formula unit} \cdot N_a}{V_m} \right)^{0.67}$$

Finally, the number of surface sites was calculated using the product:

$$\text{\#Surface sites (mol)} = \frac{\text{surface occupancy} \cdot \text{Roughness factor} \cdot \text{Geometric area}}{N_a}$$

#Surface sites (μmol) for Ni_2P -CTAB= 7.58

#Surface sites (μmol) for Ni_2P -SSS= 3.28

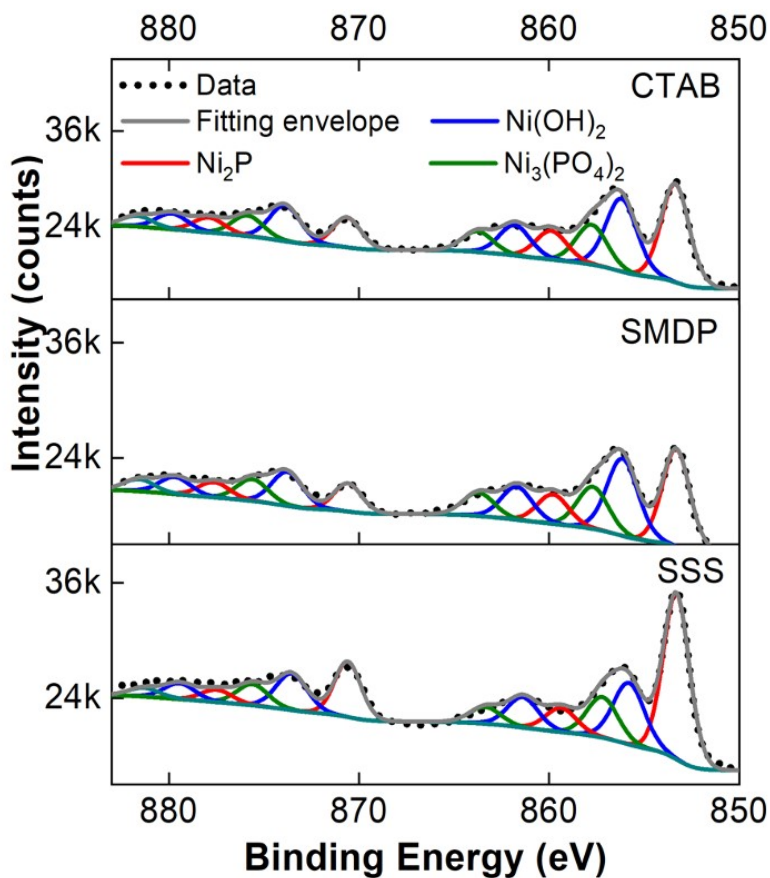


Fig. S1. Ni 2p XPS spectra of various Ni_2P catalyst with fitted spectra.

Table S1. Percent of dissolved Ni in 0.5 M H_2SO_4 solution as determined by ICP-OES analysis.

Catalyst	Average Ni% leached in the solution
SSS	0.027 ± 0.002
SMDP	0.227 ± 0.017

CTAB	0.243 ± 0.021
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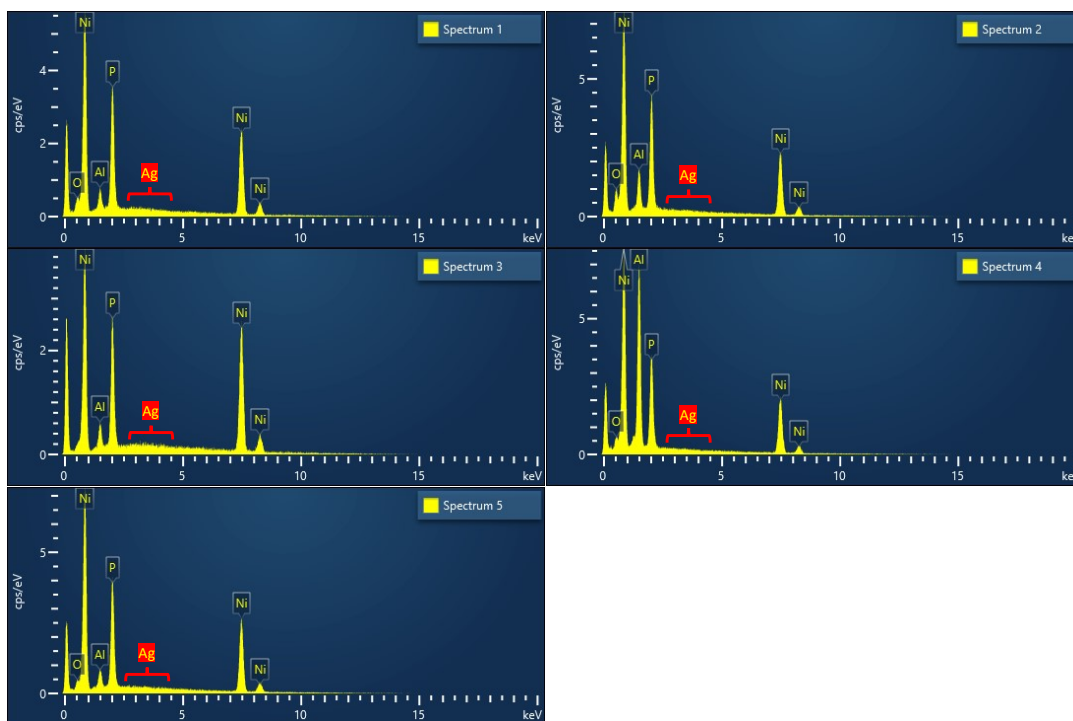


Fig. S2: SEM-EDS analysis performed on used Ni₂P-CTAB electrode to confirm the absence of any leached silver contaminant on the electrode surface.

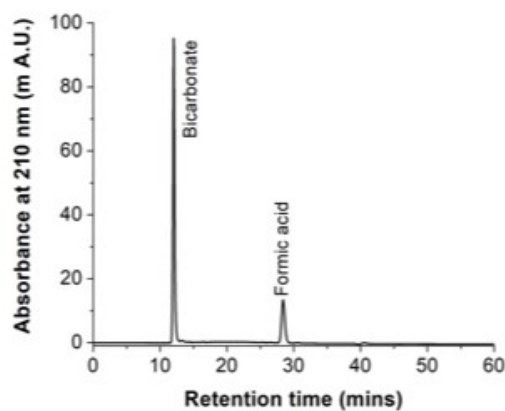
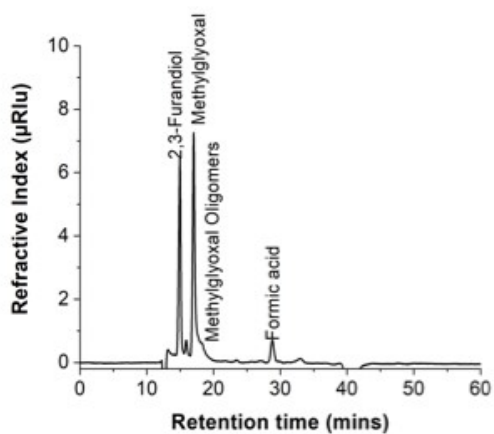


Fig. S3. Example of chromatographs for a CO₂RR sample on Ni₂P-CTAB at -0.1 V vs RHE obtained with the refractive index detector (left) and the UV absorbance detector (right), arranged in series

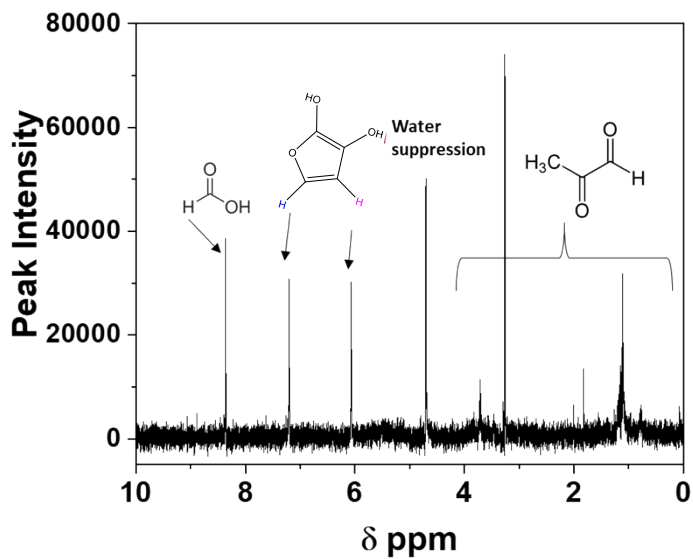


Fig. S4. ¹H NMR chemical shifts of an electrolyte sample from the electroreduction of CO₂ on Ni₂P-CTAB.

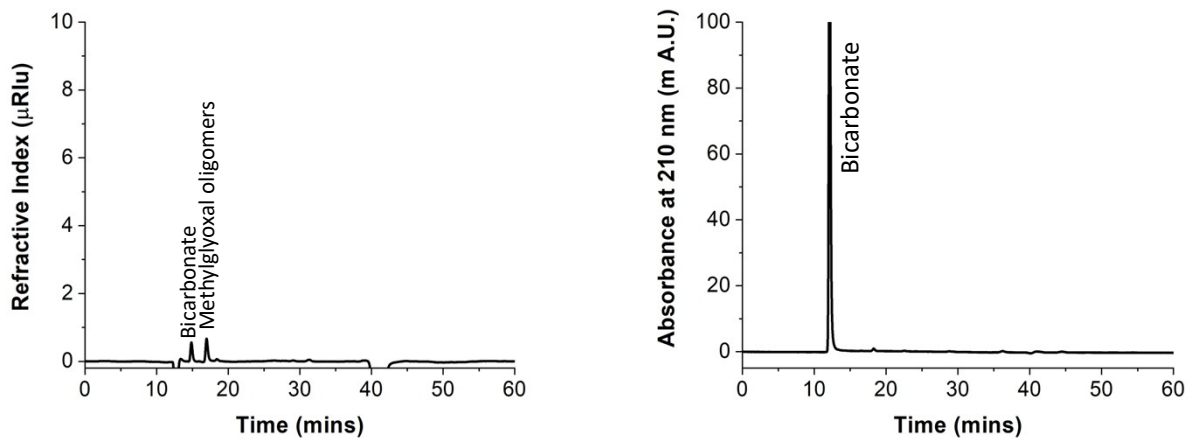


Fig. S5. Chromatographs for a CO₂RR performed at 100 mA cm⁻² on Ni₂P-CTAB as obtained with the refractive index detector (left) and the UV absorbance detector (right), arranged in series.

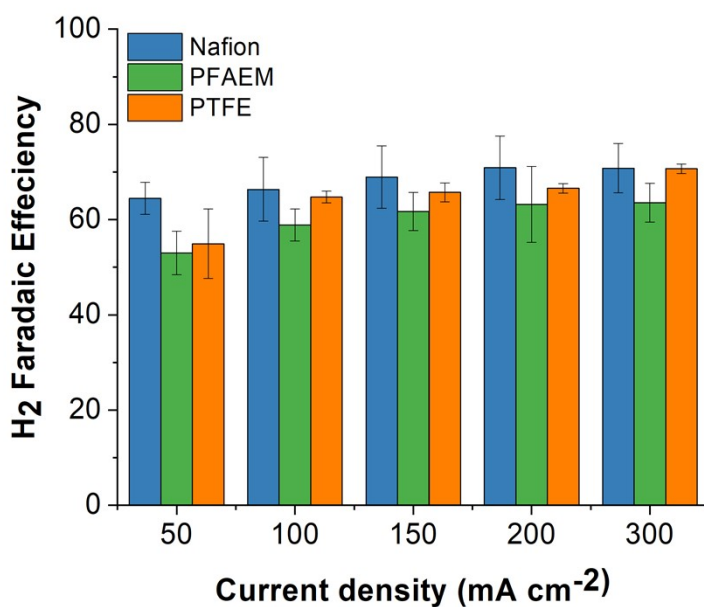


Fig. S6. H₂ Faradaic Efficiencies on Ni₂P-CTAB with different ionomers used. The remaining Faradaic efficiency is for CO₂ reduced products.

Table S2. Faradaic efficiency and partial current density of methylglyoxal (major products) for Ni₂P-CTAB catalysts at various current densities tested.

	Current density (mA cm ⁻²)	H ₂ FE (%)	Non-H ₂ FE (%)	Formate FE (%)	Methylglyoxal FE (%)	i _{mg} (mA cm ⁻²)
Ni ₂ P-CTAB + Nafion	50	64.46	35.54	4.36	19.78	9.89
	100	66.36	33.64	3.21	9.98	9.98
	150	68.93	31.07	3.16	10.35	15.52
	200	70.92	29.08	2.72	8.44	16.88
	300	70.82	29.18	2.95	5.49	6.47
Ni ₂ P-CTAB +	50	53.01	46.99	4.99	38.36	19.18

PFAEM	100	58.87	41.13	4.76	14.99	14.99
	150	61.75	38.25	3.84	10.78	16.17
	200	63.20	36.8	3.98	9.54	19.07
	300	63.56	36.44	3.76	6.03	18.09
Ni ₂ P-CTAB + PTFE	50	54.93	45.07	3.11	47.37	23.68
	100	64.74	35.26	2.70	20.23	20.23
	150	65.74	34.26	1.11	13.92	20.87
	200	66.57	33.43	0.79	9.89	19.77
	300	70.70	29.3	0.64	6.07	18.20

Fig. S7. Total cell potential and cathode cell potential for CO₂RR in flow cell configuration (single replicate). Catalyst= Ni₂P-CTAB with Nafion as the binder.

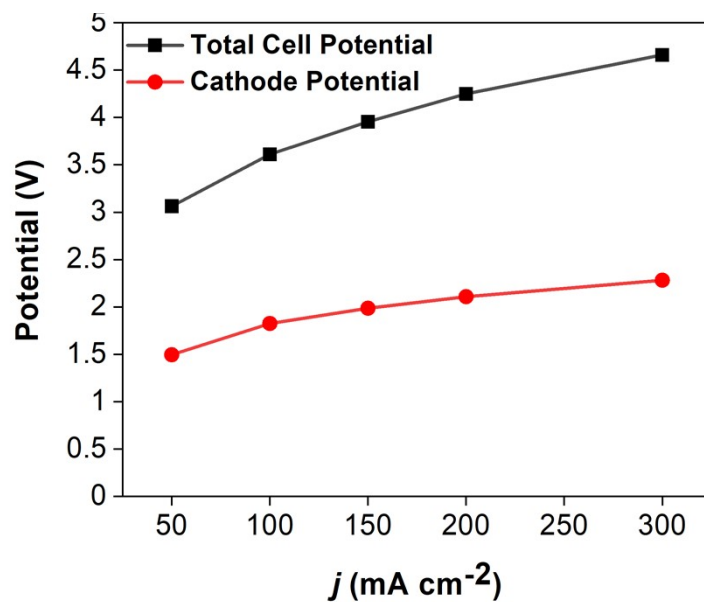


Table S3. ATR-FTIR spectrum data with peak positions and assignments.

Number	Wavenumber (cm ⁻¹)	Assignment
1	3400	OH
2	1530	C=C
3	1408	C-H
4	1100	C-O ether
5	1005	C-O ether
6	864	(CH ₂) _n with n>4 (alkane)