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The Selective Electrochemical Conversion of Preactivated CO₂ to Methane

Oana R. Luca,^{a§} Charles C. L. McCrory,^a Nathan, F. Dalleska,^b Carl A. Koval^{a §}

^a Joint Center for Artificial Photosynthesis, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States.

^b Environmental Analysis Center, California Institute of Technology, Pasadena California 91125, United States.

[§]corresponding author

S1. Electrochemical Methods

S2. Product Separation and Quantification

S3. X-ray Photoelectron Spectroscopy of Electrode Materials

S4. Labeling Experiments

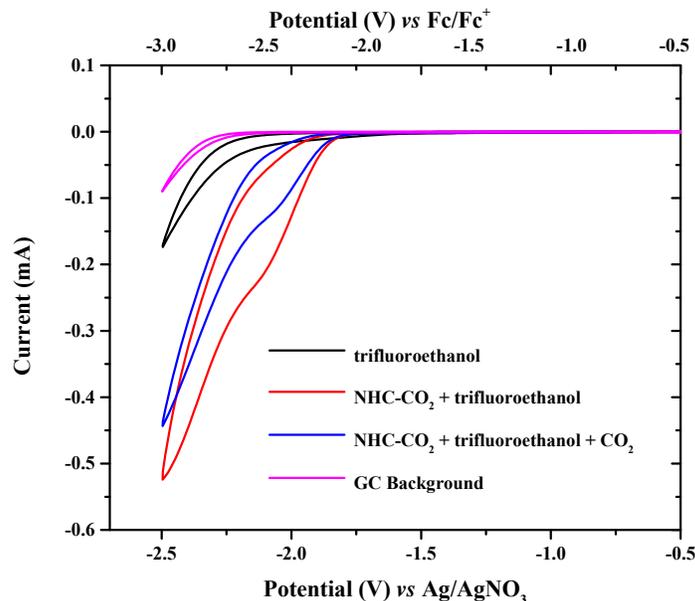
39 S1. Electrochemical Methods

40 All electrochemical experiments were performed using either a Bio-Logic VSP-300 multichannel
41 potentiostat/galvonostat or a BioLogic VSP-400 potentiostat/galvonostat. All electrochemical
42 data was recorded using the Bio-Logic EC Lab Express (5.53) software package.

43 The reference electrodes for all measurements was a Ag/AgNO₃ (0.5 mM)/CH₂Cl₂ nonaqueous
44 reference electrode (also contained 0.1 M *n*Bu₄NBF₄) separated from the solution by a Vycor frit
45 (Bioanalytical Systems, Inc.) and externally referenced to ferrocene (at 410 mV *vs* the reference).
46 We report the potentials *vs* Ag/AgNO₃, but we also provide an alternate Fc/Fc⁺ scale for
47 reference in each of the cyclic voltammogram figures.

48 Cyclic voltammograms in methylene chloride (0.1 M *n*Bu₄NBF₄) were collected at a glassy
49 carbon working electrode (3 mm diameter, BASi) with a C rod counter electrode (99.999%,
50 Strem) in 5 mL of solution. All CVs were recorded after rigorous exclusion of air via nitrogen
51 purge. Data workup was performed on OriginPro v8.0988.

52 Diagnostic cyclic voltammograms and backgrounds (Figures 2 and M1) show that a high-current
53 reduction response is observed at -1.5 V *vs* Ag/AgNO₃ in the presence of catalyst and
54 carboxylate (Figure 2), whereas low currents are observed in the absence of carboxylate (M1).



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56 **Figure M1.** Background cyclic voltammetry experiments for the diagnostic of CO₂ reduction in
57 0.1 M *n*Bu₄NBF₄ in CH₂Cl₂. The scan rate is 100 mV/s.

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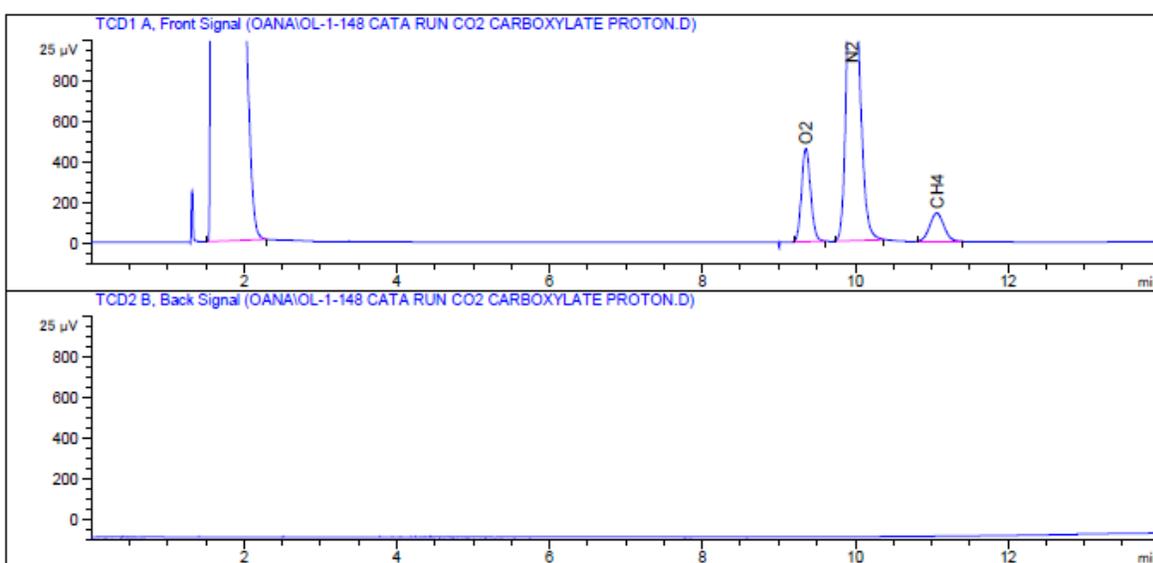
59 Controlled-potential electrolysis experiments were performed at ambient pressure in a sealed,
60 two-chamber H-cell where the solutions in the two chambers were separated by a fine ceramic
61 frit, but the two chambers shared a common headspace. The first chamber contained the
62 reference electrode and working electrode, a 6 cm x 1 cm x 0.3 cm glassy carbon plate (HTW
63 Hochttemperatur-Werkstoff GmbH), in 40 mL solution. During the experiment, the working

64 electrode was submerged such that about 75% the electrode was submerged in solution. The
65 second chamber contained the high-surface area reticulated vitreous carbon electrode counter
66 electrode, in 20 mL solution. The electrolyte solution was 0.2 M $n\text{Bu}_4\text{NBF}_4$ in a 4:2 (v:v)
67 methylene chloride/trifluoroethanol mixture. The total volume of the electrolysis cell was 142
68 mL (for electrolyses preceding GC-MS experiments) or 188 mL (for electrolyses preceding GC-
69 TCD measurements), leading to total headspace volumes of 82 mL and 128 mL, respectively.
70 For the GC-TCD measurements, 10 mL of headspace were sampled and analyzed.

71 **S2. Product Separation, Identification and Quantification Methods**

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73 GC-TCD measurements were performed using an Agilent Technologies 7890A GC system with
74 two TCD detectors. The oven was held at 50° C for 9 minutes, then the temperature was
75 increased 8°C/min to 80°C with the following column configuration: G3591-81143 0.5m x 1/8",
76 Ultimetel, Hayesep T 80/100 mesh , G3591-81144 0.5m x 1/8", Ultimetel, Hayesep Q 80/100
77 mesh, G3591-81145 1.5m x 1/8", Ultimetel, Molsieve 13X 80/100 mesh , G3591-81146 1m x
78 1/8", Ultimetel, Hayesep Q 80/100 mesh , G3591-81149 1m x 1/8", Ultimetel and a Molsieve 5A
79 60/80 mesh.

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82 **Figure M2.** GC-TCD trace output for headspace sampling of catalytic electrolysis run. No H_2
83 product observed (expected at 2min on the Back Signal channel, low pane), exclusive methane
84 formation observed.

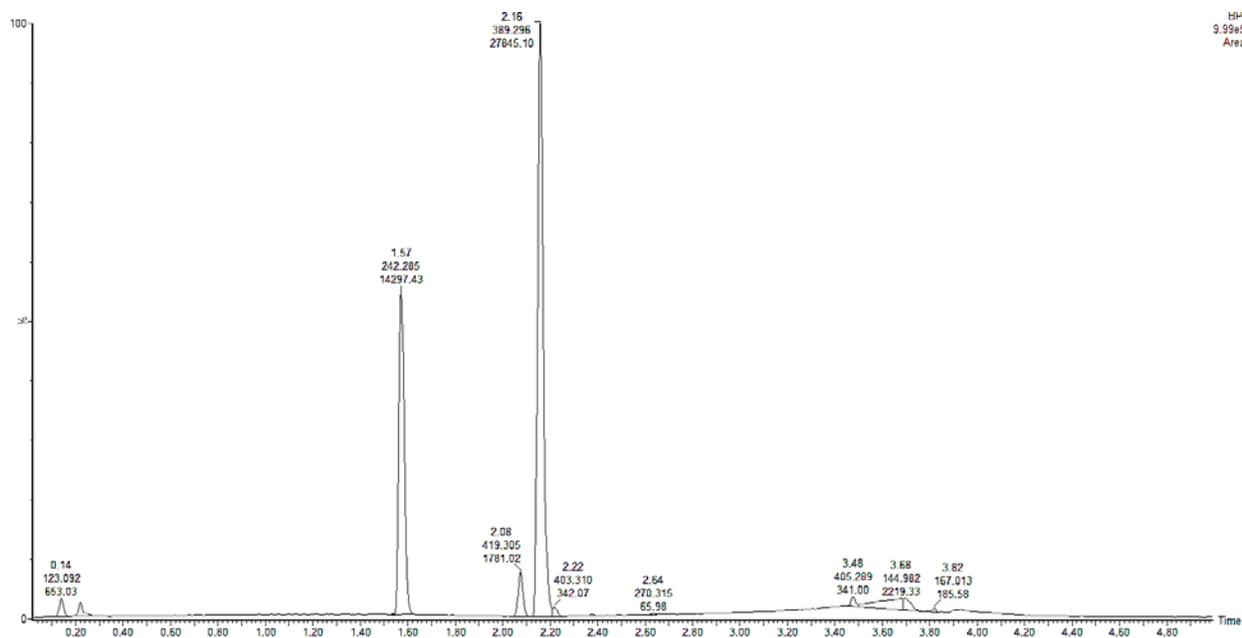
85
86 GC-MS-TOF measurements and exact mass analyses were performed on an Agilent 6890 gas
87 chromatograph interfaced to a Waters GCT Premier time-of-flight mass spectrometer with an
88 electron impact ionization source. Separation of methane from other headspace gases was
89 achieved on a 30m x 0.320 mm PLOT-Q capillary column (Agilent Technologies) operated with
90 helium carrier gas flowing at a linear velocity of 35 cm/s. The oven temperature was held at 40°
91 C for 1 minute and then raised to 45 °C at 5°/min. After 1 minute at 45 the temperature was
92 increased to 200°C at a ramp of 20° C/min and held constant for 4 minutes. 50 µL gas samples

93 were injected into a split-splitless inlet operating at 150 C and a split ratio of 1:5 and with a 1
94 mm ID liner installed. The GCT Premier was operated in electron impact ionization mode, with
95 low mass cutoff parameters adjusted to allow transmission as low as 14 m/z. Mass resolution
96 was 7000 at 131 m/z, and approximately 900 at 17 m/z.

97
98 GC-MS nominal mass data were acquired on an HP 5890 GC 5972 MSD quadrupole mass
99 spectrometer. Gas samples were manually injected with a 50 uL gastight syringe into a split-
100 splitless inlet operated in split mode and held at 125 C. Gases were separated on a 0.25 micron x
101 30m PLOT-Q GS column (Restek Corporation) using helium carrier gas flowing at 0.6 mL/min.
102 An oven temperature ramp was employed to ensure complete elution of all sample components
103 after each injection. The GC column transfer line was held at 300 C in order to keep the electron
104 impact source hot (approximately 180 °C). The electron impact ionization source was operated
105 with 70 eV electron energy. The ion focusing lenses were retuned on residual nitrogen (28 m/z)
106 and argon (40 m/z) in the helium carrier gas and the 131 m/z fragment of perfluorotributyl amine
107 so as to maximize sensitivity for low mass ions such as methane.

108 For the UPLC-MS analyses, the catholyte contents were added to a 250 mL round bottom flask
109 and the volatiles were removed via rotary evaporation. The solid residue was then extracted three
110 times with 75 mL diethylether. The combined organic fractions were dried over Na₂SO₄. After
111 the removal of the ether phase, we recovered 640 mg white crystalline solid. The workup did not
112 entirely remove the supporting electrolyte, but that remaining did not interfere with obtaining
113 UPLC-MS data. The solid sample was dissolved in a minimum amount of methylene chloride
114 and then diluted with a mixture of methanol, ethanol, isopropanol and acetonitrile. The analysis
115 of 4µL of the sample allowed us to identify 1,3-bis(2,6-diisopropylphenyl)imidazolium at 389
116 m/z as the major organic species in solution aside from supporting electrolyte (242 m/z). (Figure
117 M3). Instrument details above.

118 UPLC-MS analysis of this catholyte sample was performed using an Acquity I-Class UPLC
119 coupled to a Xevo G2-S time-of-flight mass spectrometer (Waters Corporation). Samples were
120 diluted sufficiently in 5% acetonitrile in water such that saturation of the fast electron multiplier
121 detector did not occur. Separation was performed on a BEH C18 column (2.1 x 50 mm, 1.7
122 micron particle size, Waters Corporation) using a 5 minute gradient from 5% to 90% acetonitrile
123 in water with 0.1% formic acid. Masses from 100 to 1000 m/z in positive ion mode were
124 recorded. The mass axis was calibrated with sodium formate cluster peaks and spectra were
125 referenced to the mass of singly charged leucine enkephalin. Measured m/z are considered
126 accurate to 2 millidaltons. Electrospray source conditions were capillary voltage, 2.5 kV;
127 sampling cone, 50V; cone gas, 40 L/hr; and desolvation gas 800 L/hr at 500° C.



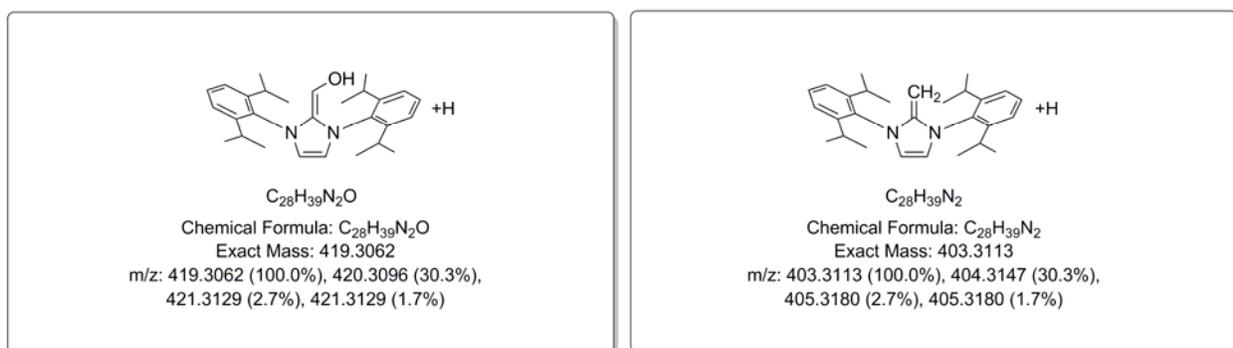
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129 **Figure M3.** UPLC-MS base peak ion chromatogram of extracted catholyte.

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131 **Major peaks in the UPLC chromatogram:** The species observed at 2.16 minutes and 389.296
 132 m/z corresponds to the protonated imidazolium core of NHC-CO₂. The peak at 1.57 minutes and
 133 242.285 m/z corresponds to the tetrabutylammonium cation of the supporting electrolyte. We
 134 also observe peaks at 2.08 minutes, 419.305 m/z and 2.22 minutes, 403.310 m/z. These masses
 135 are consistent with the structures we propose in M4.

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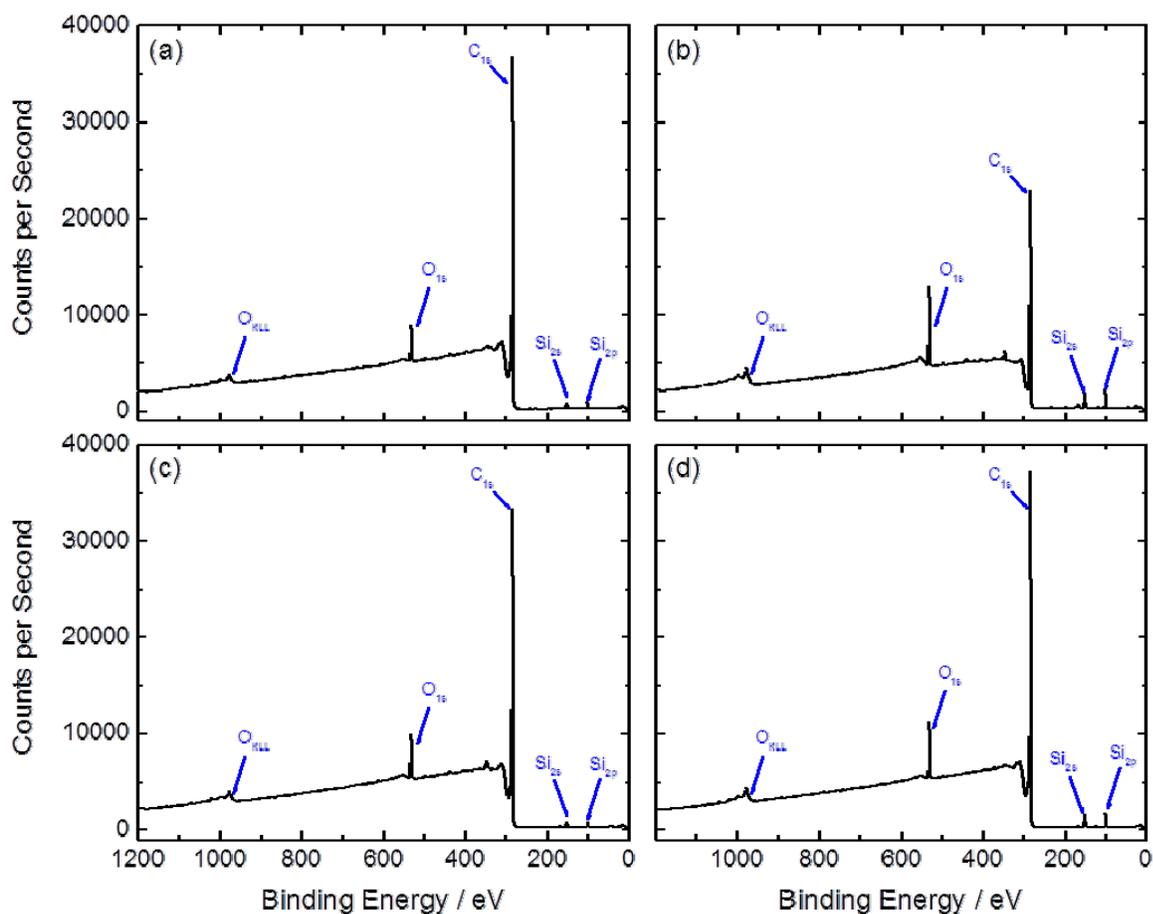
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138 **Figure M4.** Tentative structural assignments for organic fragments observed at 2.08 min and
 139 2.22 min.

140 **S3. X-ray Photoelectron Spectroscopy of electrode materials**

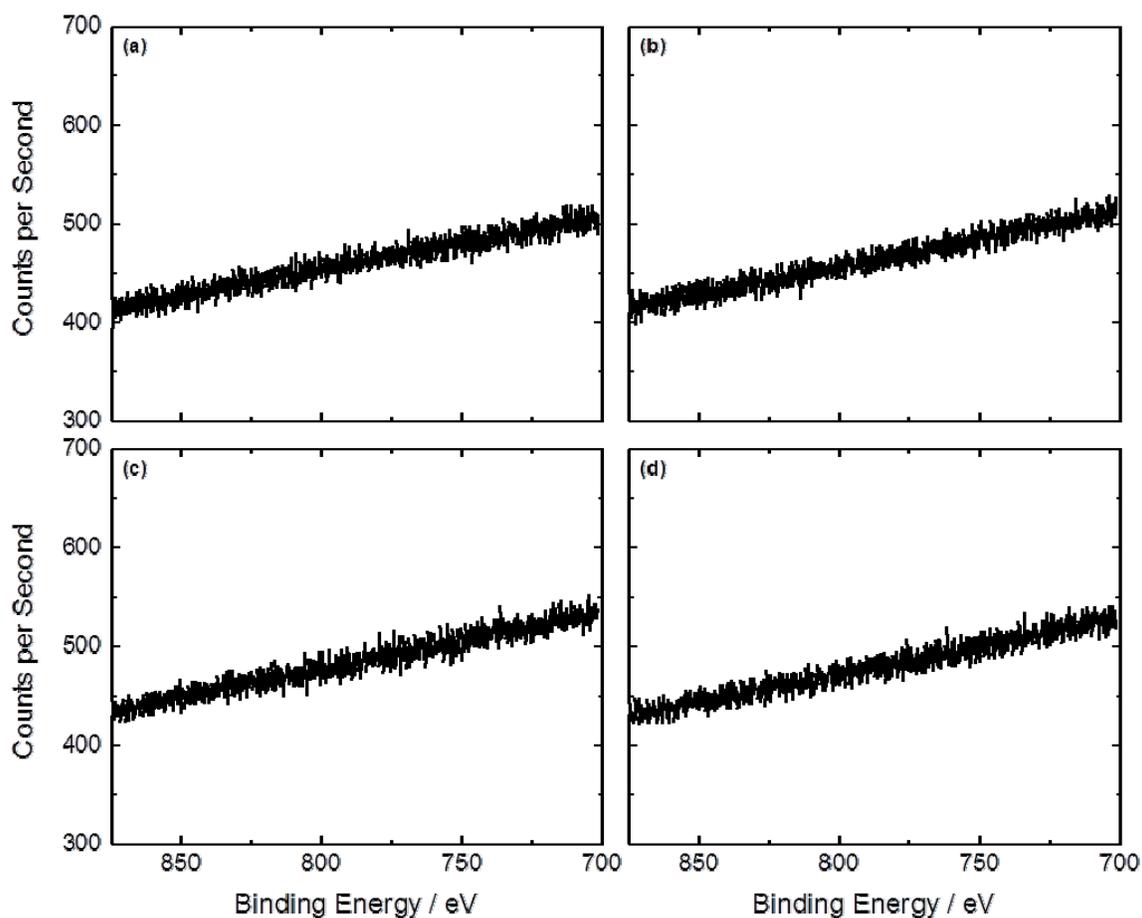
141 The surface speciation of the carbon electrode before and after electrolysis was determined via
142 XPS on a Kratos Axis Nova spectrometer with DLD (Kratos Analytical; Manchester, UK). The
143 excitation source for all analysis was monochromatic Al K α _{1,2} ($h\nu = 1486.6$ eV) operating at 30
144 mA and 15 kV. The angle of incident x-rays with respect to the surface normal is 54.5 degrees.
145 A base pressure of 1×10^{-9} Torr is maintained in the analytical chamber, which rises to 1×10^{-8}
146 Torr during spectral acquisition. All spectra were acquired using the hybrid lens magnification
147 mode and slot aperture, resulting in an analyzed area of $700 \mu\text{m} \times 400 \mu\text{m}$. Survey scans were
148 conducted using 160 eV pass energy, and narrow region high resolution scans used 20 eV. The
149 following sequence of scans was performed: Survey (0-1200 eV), Cu 2p (925-970 eV), N 1s
150 (410-389 eV), Sn 3d (479-500 eV), F 1s (695-674 eV), P 2p (126-140 eV), Ni 2p/Fe 2p/Co 2p
151 (701-885 eV), O 1s (525-543 eV), C 1s/Ru 3d (276-292 eV), and Ir 4f (56-71 eV).
152 Compositional analysis was performed using CasaXPS version 2.3.16 (Casa Software Ltd;
153 Teignmouth, UK). Energy scale corrections for the survey and narrow energy high resolution
154 regions was done by setting the large component in the C 1s spectrum to 284.3 eV, the expected
155 C 1s peak for graphitic carbon in glassy carbon.

156 Survey scans and narrow-region high-resolution scans of the Ni 2p/Fe 2p/Co 2p regions are
157 shown in Figures M4 and M5, respectively, for a pristine glassy carbon plate and working
158 electrodes from three independent catalytic electrolyses. After electrolysis, the working
159 electrodes were removed from the electrolyte solution and gently rinsed in CH₂Cl₂ prior to
160 analysis. In general, the survey scans and high-resolution scans both confirmed that there was no
161 Ni, Fe, Co, or other transition metal deposits on the surface within the detection limits of XPS (~
162 0.1 atom%).



163

164 **Figure M5.** XPS survey scans of (a) a pristine glassy carbon plate as received and (b)-(d)
 165 working electrodes from three independent controlled-potential electrolyses after rinsing with
 166 acetone. XPS and Auger peaks are assigned as labeled. The presence of Si is likely due to trace
 167 amounts of silicone grease. Small peaks barely above background in (b) and (c) at 346 and 437
 168 eV are not labeled, but are assigned as Ca 2p and Ca 2s peaks, respectively.



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171 **Figure M6.** XPS high-resolution scans of (a) a pristine glassy carbon plate after polishing and
 172 (b)-(d) working electrodes from three independent controlled-potential electrolyses in the Ni
 173 2p/Co 2p/Fe 2p region. There are no peaks evident in this region.

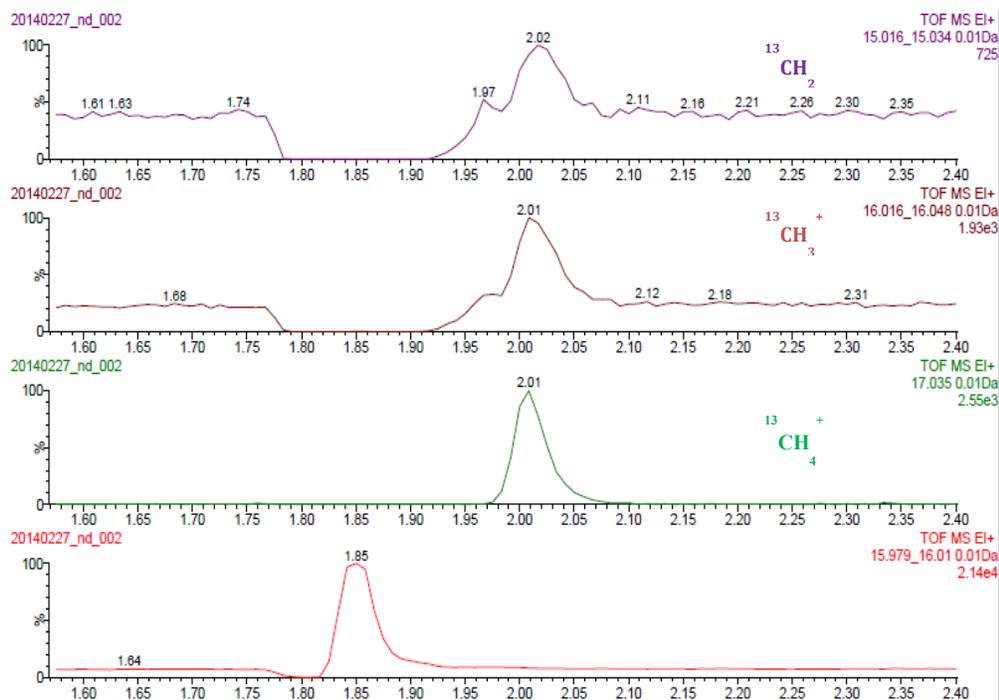
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175 **S4. Labeling experiments**

176 Isotopically labeled experiments were performed with an added 466 mg of the 1,3-bis(2,6-
 177 diisopropylphenyl)imidazolium-¹³C-carboxylate, NHC-¹³CO₂, (MW: 433.5 g/mol) and 3.4 mg
 178 [NiCyclam]Cl₂ (320 g/mol). Experiments done with CF₃CH₂OD as the proton source and
 179 CH₂Cl₂ as the solvent were analyzed by GC-MS with unit mass resolution using the HP 5890 GC
 180 5972 MS as described above. 50 μL of the gas sample was manually injected in the GC inlet.
 181 Experiments done with CF₃CH₂OH as the proton sources and CD₂Cl₂ as the solvent were
 182 analyzed with the GC-MS-TOF system as described above. For all analyses 5 mL of headspace
 183 gas was sampled from the reactor after 2h of electrolysis at -1.5 V (vs Ag/AgNO₃).

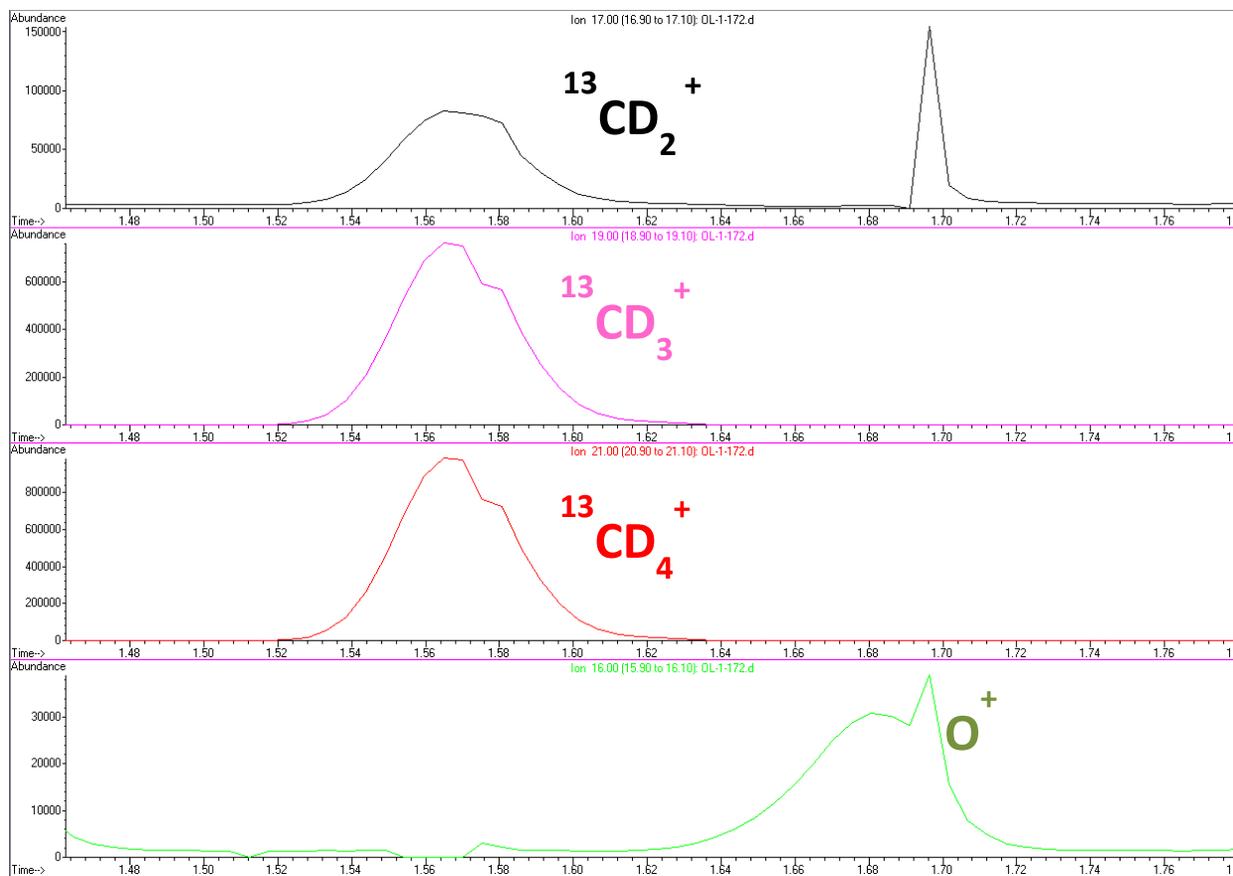
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187 **Figure M7.** GC-MS-TOF (accurate mass) extracted ion chromatograms for a 500 μ L headspace
 188 sampling of an electrolysis run with ^{13}C -labeled imidazolium carboxylate with 0.5 mol% [Ni
 189 (cyclam)] $^{2+}$ in deuterated methylene chloride under standard conditions. The first three traces
 190 qualitatively show the expected decrease in intensity from CH_4^+ to CH_3^+ to CH_2^+ . The bottom
 191 trace is the mass of OH^+ , demonstrated chromatographic resolution of water from labeled
 192 methane.



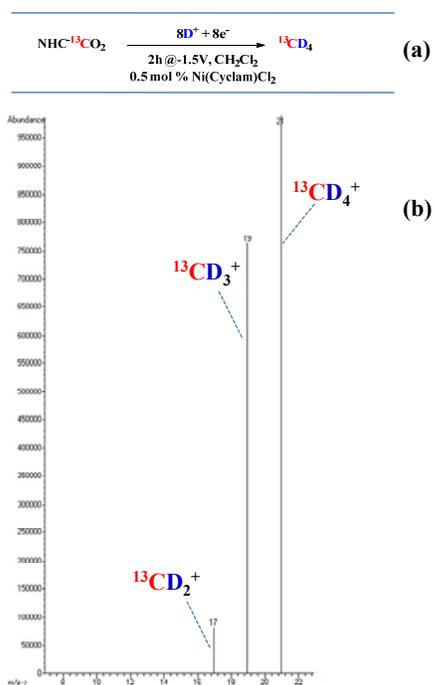
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194 **Figure M8.** GC-MS nominal mass extracted ion chromatograms of 17, 19, 21, and 16 m/z
 195 corresponding to $^{13}\text{CD}_2$, $^{13}\text{CD}_3$, $^{13}\text{CD}_4$ and H_2O . Areas under the peaks in the EICs decrease in
 196 the order 21, 19, 17, consistent with the spectrum expected for labeled methane. The spike
 197 observable in the top and bottom traces is an artifact associated with the polymeric stationary
 198 phase. Particles detached from the stationary phase produce spikes at nearly all masses when
 199 they arrive in the ion source. The spike is not visible in the middle traces as a consequence of
 200 normalization to the larger analyte peaks. Note that we observe water eluting after methane with
 201 the column used in the present data, but before methane in the data of M7. We attribute this to
 202 sourcing the columns from different manufactures and the columns having been subjected to a
 203 differing array of analyses.

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212 **Figure M9.** a. Reaction scheme for the 8e^- reduction of $\text{NHC}^{13}\text{CO}_2$ in the presence of
213 deuterated proton source. b. Mass spectrum at 1.57 min of the M8 GC trace.

214