Supplementary Information

Transforming the Carbon Economy: Challenges and Opportunities in the Convergence of Low-Cost Electricity and Reductive CO_2 Utilization

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Energy Intensity of CO_2R Products:

Table S1: Energy Intensity in GJ/tonne of Top 6 CO2R Products as Ranked by Ease of Formation

Product	Net Reaction (Anode = H_2O Oxidation)	ΔG_{prod} (kJ/mol)	ΔG_{react} (kJ/mol)	ΔG_{rxn} (kJ/mol)	MW (g/mol)	Energy Intensity (100% EE, GJ/tonne)	Energy Intensity (50% EE, GJ/tonne)
CO	$CO_2 \rightarrow CO + 0.5O_2$	-137.16	-394.41	257.25	28.01	9.18	18.37
C_2H_4	$CO_2 + 2H_2O \rightarrow C_2H_4 + 3O_2$	53.95	-1264.15	1318.10	28.05	46.99	93.98
HCOOH	$CO_2 + H_2O \rightarrow HCOOH + 0.5O_2$	-358.71	-632.07	273.37	46.03	5.94	11.88
CH_4	$CO_2 + 2H_2O \rightarrow CH_4 + 2O_2$	-50.60	-869.73	819.14	16.04	51.07	102.14
CH_3COOH	$2CO_2 + 2H_2O \rightarrow CH_3COOH + 2O_2$	-385.10	-1264.15	879.05	60.05	14.64	29.28
CH_3OH	$CO_2 + 2H_2O \rightarrow CH_3OH + 1.5O_2$	-166.94	-869.73	702.79	32.04	21.94	43.87

Example Energy Intensity Calculation (CO) Assuming **100% Energy Efficiency** Conversion Process:

$$257.25\,\frac{kJ\ Required}{mol\ CO\ formed} * \frac{1\ mol\ CO}{28.01\ g} * \frac{10^6 g}{tonne} * \frac{GJ}{10^6 kJ} = 9.18\,\frac{GJ}{tonne\ CO}$$

Example Energy Intensity Calculation (CO) Assuming **50% Energy Efficiency** Conversion Process:

$$257.25\,\frac{kJ\ Required}{mol\ CO\ formed} * \frac{1\ mol\ CO}{28.01\ g} * \frac{10^6 g}{tonne} * \frac{GJ}{10^6 kJ} = 9.18\,\frac{GJ}{tonne\ CO} * \frac{1}{0.5\ Efficiency} = 18.37\,\frac{GJ}{tonne\ CO}$$

Renewable Capacity to CO_2R products:

From the International Renewable Energy Agency, an estimated 2,351 GW of renewable energy capacity available at the end of 2018.[1]

$$2351\ GW = 2351\frac{GJ}{second}$$

Using the energy intensity of the products in Table S1, an estimate for the potential for CO_2 utilization can be calculated. For this exercise, we selected formic acid (11.88 GJ/tonne) and methane (102.14

GJ/tonne) as lower and upper bounds for electrochemical CO_2 utilization, assuming a net process energy efficiency of 50%. Note the CO_2 utilization range would be affected when other conversion technologies are incorporated.

$$Formic\ Acid: 2351\ GW = 2351\frac{GJ}{second} \cdot \frac{tonne\ FA}{11.88\ GJ} \cdot \frac{31{,}536{,}000\ seconds}{year} \cdot \frac{44.01\ tonne\ CO_2}{46.03\ tonne\ FA} = 5.97\frac{GT\ CO_2}{year}$$

$$Methane: 2351\ GW = 2351\frac{GJ}{second} \cdot \frac{tonne\ CH_4}{102.14\ GJ} \cdot \frac{31{,}536{,}000\ seconds}{year} \cdot \frac{44.01\ tonne\ CO_2}{16.04\ tonne\ CH_4} = 1.99\frac{GT\ CO_2}{year}$$

Standard Reduction Potential:

The thermodynamic reduction potential can be calculated using equation S-1. Further, the reduction potential can be converted in terms of different reference electrodes, such as the standard hydrogen electrode (SHE) and the reference hydrogen electrode (RHE) using equation S-2.

$$E^* = -\frac{\Delta G}{nF} \qquad \text{Equation S-1}$$

ΔG_{rxn} = Gibbs free energy of reaction. $\Delta G_{rxn} = \Delta G_{products} - \Delta G_{reactants}$

n = number of electrons transferred during the reaction

F = Faraday's constant (96,485 C mol^{-1})

$$E_{std}(SHE) = E_{std}(pH\ 0, RHE) - 0.059 * pH \qquad \text{Equation S-2}$$

Table S2: Calculating standard reduction potential in RHE and SHE (pH 7)

Product	**Cathodic Half Reaction**	**n**	**ΔG_{prod}**	**ΔG_{react}**	**ΔG_{rxn}**	**E_{std} RHE (V)**	**E_{std} SHE @ pH 7 (V)**
CO	$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	2	-374.8	-393.6	18.7	-0.10	-0.51
Ethylene	$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O$	12	-896.6	-787.1	-109.5	0.09	-0.32
CNT	$CO_2 + 4H^+ + 4e^- \rightarrow C + 2H_2O$	4	-475.3	-393.6	-81.8	0.21	-0.20
Formic Acid	$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$	2	-358.7	-393.6	34.9	-0.18	-0.59
Ethanol	$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_5OH + 3H_2O$	12	-887.0	-787.1	-99.9	0.09	-0.33
Oxalic Acid	$2CO_2 + 2H^+ + 2e^- \rightarrow C_2H_2O_4$	2	-685.1	-787.1	102.0	-0.53	-0.94
Propanol	$3CO_2 + 18H^+ + 18e^- \rightarrow C_3H_8O + 5H_2O$	18	-1356.6	-1183.2	-173.3	0.10	-0.31
Acetic Acid	$2CO_2 + 8H^+ + 8e^- \rightarrow C_2H_4O_2 + 2H_2O$	8	-860.3	-787.1	-73.2	0.09	-0.32
Methane	$CO_2 + +8H^+ +8e^- \rightarrow CH_4 + 2H_2O$	8	-525.8	-393.6	-132.3	0.17	-0.24

MeOH	$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	6	-404.5	-393.6	-11.0	0.02	-0.39
Allyl Alcohol	$3CO_2 + 16H^+ + 16e^- \rightarrow C_3H_6O + 5H_2O$	16	-1260.3	-1180.7	-79.6	0.05	-0.36
Glycolaldehyde	$2CO_2 + 8H^+ + 8e^- \rightarrow C_2H_4O_2 + 2H_2O$	8	-739.3	-787.1	47.8	-0.06	-0.47
Acetaldehyde	$2CO_2 + 10H^+ + 10e^- \rightarrow C_2H_4O + 3H_2O$	10	-850.9	-787.1	-63.8	0.07	-0.35
Propionaldehyde	$3CO_2 + 16H^+ + 16e^- \rightarrow C_3H_6O + 5H_2O$	16	-1314.3	-1180.7	-133.6	0.09	-0.33
Ethylene Glycol	$2CO_2 + 10H^+ + 10e^- \rightarrow C_2H_6O_2 + 2H_2O$	10	-798.0	-787.1	-10.9	0.01	-0.40
Acetone	$3CO_2 + 16H^+ + 16e^- \rightarrow C_3H_6O + 5H_2O$	16	-1342.7	-1180.7	-162.0	0.10	-0.31
Hydroxyacetone	$3CO_2 + 14H^+ + 14e^- \rightarrow C_3H_6O_2 + 4H_2O$	14	-1251.3	-1183.2	-68.1	0.05	-0.36
Glyoxal	$2CO_2 + 6H^+ + 6e^- \rightarrow C_2H_2O_2 + 2H_2O$	6	-667.8	-787.1	119.3	-0.21	-0.62
H_2	$2H^+ + 2e^- \rightarrow H_2$	2	0	0	0	0.00	-0.41
H_2O	$2H_2O \rightarrow 2H_2 + 2O_2$	4	0	-475.3	-475.3	1.23	0.82

Table S3: Reference Thermodynamic Parameters at 298K

Reference (298 K)	**ΔG**	**ΔH**	**ΔS**
CO2 (g)	-394.415	-393.55	0.002901
O2 (g)	-0.03491	-0.0094	8.56E-05
H2O (l)	-237.66	-287.74	-0.16797
CO (g)	-137.145	-110.5	0.089369
C2H4 (g)	54.05665	52.4639	-0.00534
FA (l)	-358.691	-417.506	-0.19727
EtOH (l)	-174.043	-278.127	-0.3491
OA (g)	-685.092	-777.929	-0.31138
PrOH	-168.271	-300.115	-0.44221
Acetic Acid (l)	-385.029	-478.636	-0.31396
CH4 (g)	-50.5281	-74.5381	-0.08053
MeOH (l)	-166.89	-241.294	-0.24955
Allyl Alcohol (l)	-71.9611	-169.158	-0.326
Glycolaldehyde (l)	-263.955	-369.86	-0.35521
Acetaldehyde (l)	-137.894	-171.165	-0.11159
Propionaldehyde (l)	-125.999	-215.272	-0.29942
Ethylene Glycol (l)	-322.681	-454.121	-0.44085
Acetone (l)	-154.383	-247.508	-0.31234
Hydroxyacetone (l)	-300.67	-425.472	-0.41859
Glyoxal (l)	-192.52	-246.672	-0.18163
Isopropanol (l)	-180.817	-312.177	-0.44059
Propionic Acid (l)	-380.21	-505.241	-0.41936
C(s)	122.102	75.489	-0.15634

Table S4: Calculated Energy Efficiencies for LTE Products Based on Equation 1.

Product	Whole Cell Rxn	η (V)	FE (%)	T (K)	ΔG rxn (kJ/mol)	ΔS (kJ/mol)	ΔH (kJ/mol)	EE (%)
CO	CO2 --> CO + 0.5 O2	0.67	99.9	1073	189.3	0.087	282.4	88.6
CO	CO2 --> CO + 0.5 O2	1.67	98	298	257.7	0.087	283.0	47.9
C2H4	2H2O + 2CO2 --> C2H4 + 3O2	1.05	63	298	1318.1	0.325	1415.0	35.2
CNT	CO2 -> C + O2	2.18	81.7	298	516.5	-0.159	469.0	28.2
Formic Acid	CO2 + H2O -> HCOOH + 0.5O2	1.44	88.3	298	273.4	-0.032	263.8	42.3
Ethanol	2CO2 + 3H2O -> C2H5OH + 3O2	1.068	26	298	1327.7	0.149	1372.2	13.9
Oxalic Acid	2CO2 + H2O -> C2H2O4 + 0.5O2	4.98	50	298	341.4	-0.149	296.9	11.4
Propanol	3CO2 + 4H2O -> C3H7OH +3O2	1.66	5.1	298	1965.5	0.221	2031.5	2.1
Acetic Acid	2CO2 + 2H2O -> CH3COOH +2O2	1.19	3	298	1354.4	0.352	1459.4	1.9
CH4	CO2 + 2H2O -> CH4 + 2O2	1.82	76	298	819.1	0.253	894.5	30.6
MeOH	CO2 + 2H2O -> CH3OH + 1.5O2	0.45	98	298	702.8	0.084	727.7	74.0
Allyl Al	3CO2 + 3H2O -> C3H6O + 4O2	1.42	1.6	298	1824.1	0.170	1874.7	0.7
Glycolaldehyde	2CO2 + 2H2O -> C2H4O2 + 2O2	1.41	0.62	298	1000.1	-0.025	992.7	0.3
Acetaldehyde	2CO2 + 2H2O -> C2H4O + 2.5O2	1.4	0.34	298	1126.2	0.219	1191.4	0.2
Propionaldehyde	3CO2 + 3H2O -> C3H6O + 4O2	1.45	0.48	298	1770.1	0.196	1828.6	0.2
Ethylene Glycol	2CO2 + 3H2O -> C2H6O2 + 2.5O2	1.59	0.15	298	1179.0	0.057	1196.2	0.1
Acetone	3CO2 + 3H2O -> C3H6O + 4O2	1.25	0.08	298	1741.7	0.183	1796.3	0.0
Hydroxyacetone	3CO2 + 3H2O -> C3H6O2 + 3.5O2	1.77	0.04	298	1595.4	0.077	1618.4	0.0

Table S5: Calculated Energy Efficiencies for MES Products Based on Equation 1.

Product	Whole Cell Rxn	η (V)	FE (%)	T (K)	ΔG rxn (kJ/mol)	ΔS (kJ/mol)	ΔH (kJ/mol)	EE (%)
Formic Acid	CO2 + H2O -> HCOOH + 0.5O2	0.321	4.1	298	273.4	-0.032	263.8	3.2
Ethanol	2CO2 + 3H2O -> C2H5OH + 3O2	0.785	11.6	298	1327.7	0.149	1372.2	7.1
Acetic Acid	2CO2 + 2H2O -> CH3COOH +2O2	1.12	99	298	1354.4	0.352	1459.4	65.1
CH4	CO2 + 2H2O -> CH4 + 2O2	1.36	70	298	819.1	0.253	894.5	33.5

Isopropanol	$3CO_2 + 4H_2O \rightarrow C_3H_7OH + 3O_2$	0.947	21.8	298	1953.0	0.223	2019.4	12.2
Propionate		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Table S6: Technology Readiness Levels as Suggested by the U.S. Department of Energy.[2]

TRL 1: Basic principles observed and reported	This is the lowest level of technology readiness. Scientific research begins to be translated into applied R&D. Examples might include paper studies of a technology’s basic properties or experimental work that consists mainly of observations of the physical world. Supporting Information includes published research or other references that identify the principles that underlie the technology.
TRL 2: Technology concept and/or application formulated	Once basic principles are observed, practical applications can be invented. Applications are speculative, and there may be no proof or detailed analysis to support the assumptions. Examples are still limited to analytic studies. Supporting information includes publications or other references that outline the application being considered and that provide analysis to support the concept. The step up from TRL 1 to TRL 2 moves the ideas from pure to applied research. Most of the work is analytical or paper studies with the emphasis on understanding the science better. Experimental work is designed to corroborate the basic scientific observations made during TRL 1 work.
TRL 3: Analytical and experimental critical function and/or characteristic proof-of-concept	Active research and development (R&D) is initiated. This includes analytical studies and laboratory-scale studies to physically validate the analytical predictions of separate elements of the technology. Examples include components that are not yet integrated or representative tested with simulants. Supporting information includes results of laboratory tests performed to measure parameters of interest and comparison to analytical predictions for critical subsystems. At TRL 3 the work has moved beyond the paper phase to experimental work that verifies that the concept works as expected on simulants. Components of the technology are validated, but there is no attempt to integrate the components into a complete system. Modeling and simulation may be used to complement physical experiments.
TRL 4: Component and/or system validation in laboratory environment	The basic technological components are integrated to establish that the pieces will work together. This is relatively "low fidelity" compared with the eventual system. Examples include integration of ad hoc hardware in a laboratory and testing with a range of simulants and small scale tests on actual waste. Supporting information includes the results of the integrated

	experiments and estimates of how the experimental components and experimental test results differ from the expected system performance goals. TRL 4-6 represent the bridge from scientific research to engineering. TRL 4 is the first step in determining whether the individual components will work together as a system. The laboratory system will probably be a mix of on hand equipment and a few special purpose components that may require special handling, calibration, or alignment to get them to function.
TRL 5: Laboratory scale, similar system validation in relevant environment	The basic technological components are integrated so that the system configuration is similar to (matches) the final application in almost all respects. Examples include testing a high-fidelity, laboratory scale system in a simulated environment with a range of simulants and actual waste. Supporting information includes results from the laboratory scale testing, analysis of the differences between the laboratory and eventual operating system/environment, and analysis of what the experimental results mean for the eventual operating system/environment. The major difference between TRL 4 and 5 is the increase in the fidelity of the system and environment to the actual application. The system tested is almost prototypical.
TRL 6: Engineering/pilot-scale, similar (prototypical) system validation in relevant environment	Engineering-scale models or prototypes are tested in a relevant environment. This represents a major step up in a technology's demonstrated readiness. Examples include testing an engineering scale prototypical system with a range of simulants. Supporting information includes results from the engineering scale testing and analysis of the differences between the engineering scale, prototypical system/environment, and analysis of what the experimental results mean for the eventual operating system/environment. TRL 6 begins true engineering development of the technology as an operational system. The major difference between TRL 5 and 6 is the step up from laboratory scale to engineering scale and the determination of scaling factors that will enable design of the operating system. The prototype should be capable of performing all the functions that will be required of the operational system. The operating environment for the testing should closely represent the actual operating environment.
TRL 7: Full-scale, similar (prototypical) system demonstrated in relevant environment	This represents a major step up from TRL 6, requiring demonstration of an actual system prototype in a relevant environment. Examples include testing full-scale prototype in the field with a range of simulants in cold commissioning. Supporting information includes results from the full-scale testing and analysis of the differences between the test environment, and analysis of what the experimental results mean for the eventual operating system/environment. Final design is virtually complete.
TRL 8: Actual system completed and qualified through test and demonstration.	The technology has been proven to work in its final form and under expected conditions. In almost all cases, this TRL represents the end of true system development. Examples include developmental testing and evaluation of the system with actual waste in hot commissioning. Supporting information includes operational procedures that are virtually complete. An ORR has been successfully completed prior to the start of hot testing.
TRL 9: Actual system operated over the full range of expected conditions.	The technology is in its final form and operated under the full range of operating conditions. Examples include using the actual system with the full range of wastes in hot operations.

Supporting Information References:

1. Renewables 2018: Market Analysis and Forecast from 2018-2023, https://www.iea.org/renewables2018/, (accessed 5/16/2019, 2019).
2. R. Sanchez, *Technology Readiness Assessment Guide*, United States Department of Energy, 2011.