Electronic Supplementary Material (ESI) for EES Catalysis.

Supporting Information for

High-Pressure Electrochemistry: A New Frontier in Decarbonization

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S1. Literature Summary

Application	Pressure	Cell potential	Efficiency	Current Density	Reference
CO_2 reduction to Formic Acid/Formate	50 bar	3.5 V	FE∼80%	∼30 mA/cm^2	[22]
CO_2 reduction to CO in ionic liquids	51 bar	-2 V	FE∼60%	0.22 mA/cm^2	[23]
CH_4 to CH_3OH	10 bar	1.5 V	≈2200 µmol/g$_{cat}$	-	[24]
CH_4 to CH_3OH	46 bar	-	FE∼91%	∼0.09 mA/cm^2	[25]
Measurement of molar volume changes of redox reactions	Upto 1500 bar	-	-	-	[26]
Measurement of molar volume changes of redox reactions	Upto 10000 bar	-0.2 and -0.1 V	-	-	[4]

S2. Advantages of PEM electrolyzers at high pressures

High pressures significantly enhance the kinetics of HER and OER. Faster kinetics lead to higher current densities, higher production rates, reduced overpotential, which results in improved electrolyzer efficiency. High pressures could lead to more compact designs enabling efficienct integration into various industrial processes. High pressure PEM electrolyzers can directly produce high pressure H_2 which would align with the storage and transportation requirements. This would eliminate the needs for additional compression steps reducing energy consumption and associated costs. High pressure operation could lead to intensified electrochemical processes enabling higher throughput and productivity without significant improvement in the system size.

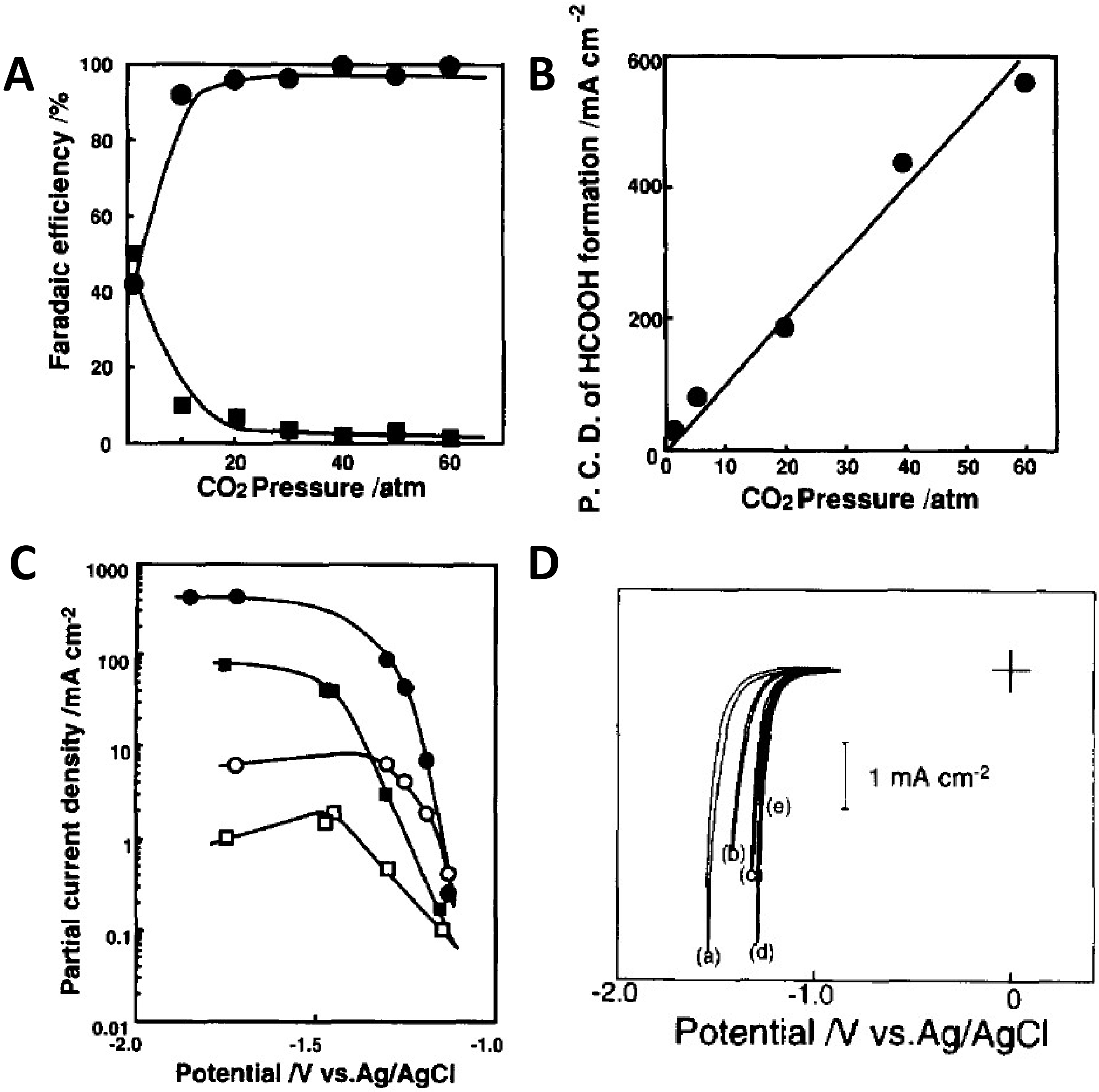

Figure S1: A) Effect of CO_2 pressures on the Faradaic efficiencies of HCOOH (circles) and H_2 (squares) when Pb electrode is used at a current density of -200 mA/cm^2. B) Effect of CO_2 on the partial current density of HCOOH when In electrode is used. C) Tafel plots of HCOOH (dark) and CO (light) at 5 atm (square) and 40 atm (circle) when In electrode is used. D) Cyclic Voltammetry profiles using In electrode for various pressures a) 1 atm Ar, b) 1 atm CO_2, c) 20 atm CO_2, d) 40 atm CO_2 and e) 60 atm CO_2. The figures are reproduced with permission from M. Todoroki et al., Journal of Electroananalytical Chemistry, 1995.[1]

S3. Energy Requirement to Pressurize Reactors

The work done for an isentropic expansion of an ideal gas is given by,

$$W = \frac{P_1 V_1}{k-1}\left[1-\left(\frac{P_1}{P_2}\right)^{\frac{1-k}{k}}\right] \quad \text{(S1)}$$

where W is the work done (kJ), P_1 and P_2 are the pressures at states 1 and 2 (kPa), V_1 is the volume of the reactor (m^3), and k is the ratio of specific heat capacities of an ideal gas, i.e., C_p (specific heat capacity at constant pressure), and C_v (specific heat capacity at constant volume).

The work done to pressurize an ideal gas can be calculated from the above equation of isentropic expansion, which is normalized with respect to the number of moles of the ideal gas. Here, N_2 is taken as the model system. **Error! Reference source not found.**A shows the energy required to pressurize a reactor normalized with respect to the number of moles of gas as a function of the pressure. The energy required to pressurize a reactor to 10 bar is 60% of the energy required to pressurize a 300 bar reactor.

Electrochemical Energy Savings with Increasing Pressure

For a general redox reaction, a species O undergoing reduction at a cathode to species R is given by,

$$\mathrm{O} + \mathrm{ne}^- \rightleftharpoons \mathrm{R} \quad \text{(i)}$$

with the corresponding Nernst equation written as,

$$E = E^o + \frac{RT}{nF}\ln\left(\frac{C_o}{C_R}\right) \quad \text{(S2)}$$

where E is the equilibrium potential (V), E^o is the standard equilibrium potential (V), R is the gas constant (J/mol.K), T is the temperature (K), n is the number of electrons transferred, F is the Faraday's constant (96485.33 C/mol), C_o is the concentration of O (mol/m^3), and C_R is the concentration of R (mol/m^3). For a system involving gas phase reactants, the concentration can be expressed in terms of mole fraction and the total pressure of the system. The difference in equilibrium potentials at two different pressures P_1 and P_2 can be shown to be,

$$\Delta E = \frac{RT}{nF}\ln\left(\frac{P_2}{P_1}\right) \quad \text{(S3)}$$

The difference in Gibb's free energy of the systems at pressures P_1 and P_2 can be obtained from equilibrium potential difference in eq. S3,

$$\Delta G = -RT\ln\left(\frac{P_2}{P_1}\right) \quad \text{(S4)}$$

Error! Reference source not found.B shows the electrochemical energy requirement decreases with increasing pressure. While the reduction in equilibrium potential depends on the number of electrons transferred per mole of the product (see eq. S3), the free energy reduction does not depend on the type of redox reaction (see eq. S4).

S4. Pourbaix Diagram Calculations

The calculations for the Pourbaix diagrams at elevated pressures for the considered reactions are given below:

1. $N_2\,(g) + 6\,H^+ + 6e^- \rightarrow 2NH_3\,(g)$ (E° = 0.05 V)

$$E=E^{o}-\frac{2.303RT}{zF}\log\frac{[\text{Product}]}{[\text{Reactant}]}$$

$$E=E^{o}-\frac{0.0591}{z}\log\frac{[\text{Product}]}{[\text{Reactant}]}$$

$$E=E^{o}-\frac{0.0591}{z}\log\frac{(P^{NH_3})^2}{(P^{N_2})[H^+]^6}$$

At, high pressure $P^{NH3} = P^{N2}$

$$E=E^{o}-\frac{0.0591}{6}\log\frac{(P)^2}{(P)[H^+]^6}$$

$$E=E^{o}-\frac{0.0591}{6}\log\frac{(P)}{[H^+]^6}$$

$$E=0.05-0.00985\times\log(P)-0.0591\times pH$$

2. $CH_4\,(g) + H_2O\,(aq.)\rightarrow CH_3OH\,(l) + 2H^+ + 2e^-$ (E° = 0.58 V)

Similarly,

$$E=0.58+0.02955\times\log(P)+0.0591\times pH$$

For $[CH_3OH]$ and $[H_2O]$ = 1 mol/mL

3. $2CO_2\,(g) + 12\,H^+ + 12e^- \rightarrow C_2H_4\,(g) + 4H_2O\,(aq.)$ (E° = 0.08 V)

Similarly,

$$E=0.08+0.004925\times\log(P)-0.0591\times pH$$

For $[CH_3OH]$ and $[H_2O]$ = 1 mol/mL

4. $2CO\,(g) + 8H^+ + 8e^- \rightarrow C_2H_4\,(g) + 2H_2O\,(aq.)$ (E° = 0.17 V)

Similarly,

$$E=0.17+0.007388\times\log(P)-0.0591\times pH$$

For $[H_2O]$ = 1 mol/mL

5. $CO_2\,(g) + 6H^+ + 6e^- \rightarrow CH_3OH\,(l) + H_2O\,(aq.)$ (E° = 0.03 V)

Similarly,

$$E=0.03+0.00985\times\log(P)-0.0591\times pH$$

For $[CH_3OH]$ and $[H_2O]$ = 1 mol/mL

6. $CO\ (g) + 4H^+ + 4e^- \rightarrow CH_3OH\ (l)$ ($E^o = 0.08$ V)

Similarly,

$$E=0.08+0.014775\times\log(P)-0.0591\times pH$$

For $[CH_3OH] = 1$ mol/mL

7. $2H_2O\ (aq.) \rightarrow O_2\ (g) + 4H^+ + 4e^-$ ($E^o = 1.23$ V)

Similarly,

$$E=1.23-0.014775\times\log(P)+0.0591\times pH$$

For $[H_2O] = 1$ mol/mL

8. $2H^+ + 2e^- \rightarrow H_2\ (g)$ ($E^o = 0.0$ V)

Similarly,

$$E=-0.02955\times\log(P)-0.0591\times pH$$

S5. Increasing Solubility and Deviation from Henry's Law

The solubility of non-polar gases such as H_2, N_2, CH_4, and O_2 follows Henry's law over a wide range of pressures.[21] The mole fraction of dissolved gases increases almost linearly with increasing pressures up to 100 bar. Such linear trends may bend if the pressurized gasses deviate from ideal gas behavior. For example, CO_2 solubility starts deviating from linear behavior from pressures exceeding 60 bar.[22] Another example is the gases that exist as vapor (e.g., H_2O). These vapor gases follow Henry's law only up to one-half to two-thirds of their saturation point. Such deviations from Henry's law directly affect the rate of redox reaction.

The solubility of gases in ion exchange membranes for PEM, alkaline electrolyzers, and other GDE-based electrolyzers is thoroughly discussed in the literature.[23] A single Fickian diffusion coefficient describes the diffusion of gases in rubbery homopolymers[24], whereas the "dual-mode" sorption model is used to study the diffusion of gases in glassy polymers.[25] The dual modes correspond to the sorption of gas into the porous polymer matrix and the free volume of the polymer, which is dependent on the pressure of the diffusing gas. Hence, for glassy polymer solid electrolytes, the pressure plays a vital role in determining the diffusion of the gases.

Some other effects that are important for gas solubilities at higher pressures are – i) competitive absorption of gas mixtures may lead to preferential absorption of one species over the other with increasing pressure, and ii) the solubility of gases decreases with increasing ionic strength of the electrolyte.

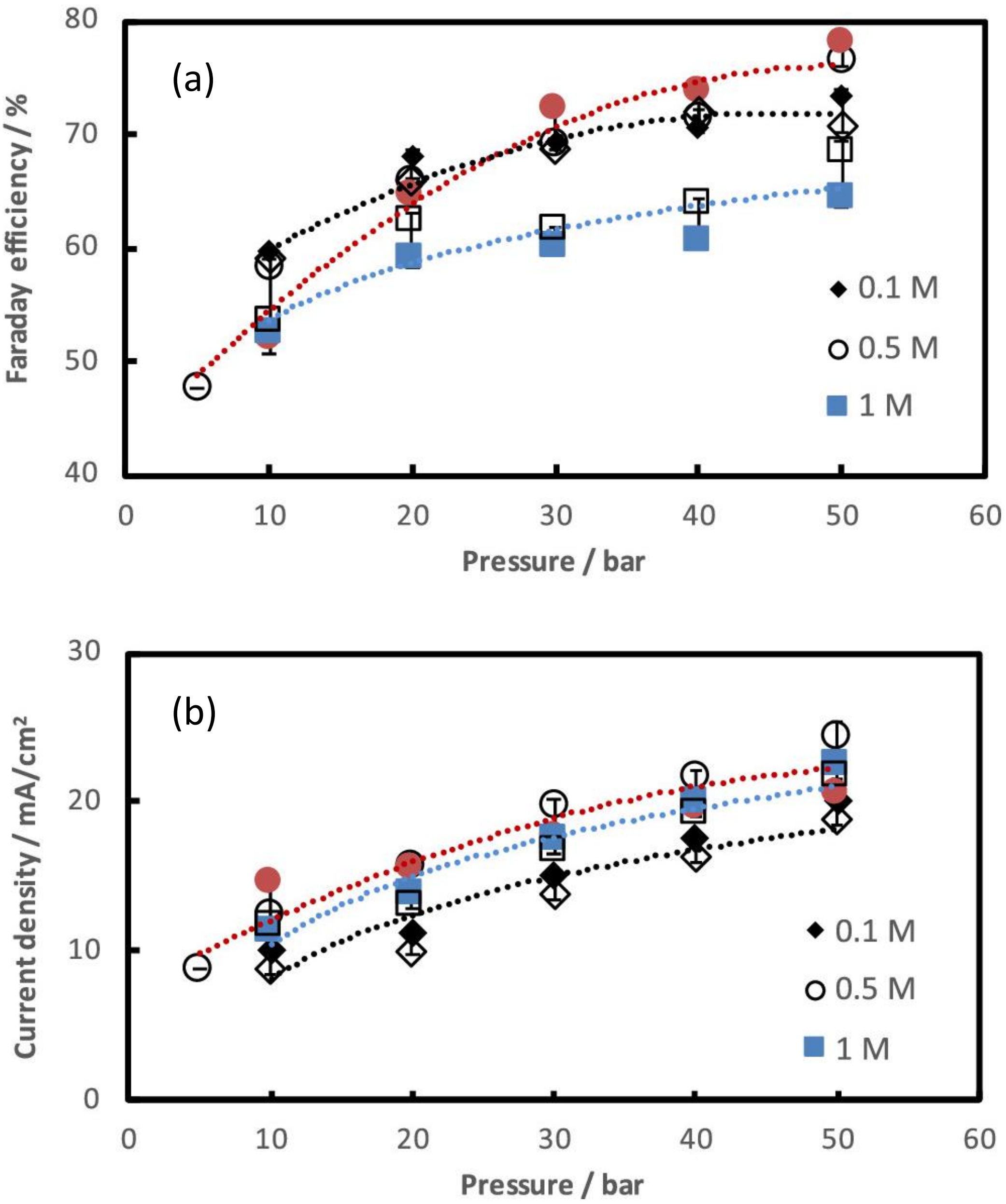

Figure S2. (a) Faraday efficiency, and (b) current density as a function of pressure for CO_2 electrolysis. Adapted from.[16] Copyright 2019 American Chemical Society.

Figure S3. Instrumentation for high pressure fundamental electrochemical studies A) Commercial high pressure high temperature cell from AZO Materials for FTIR analysis of solid samples. The image is taken from AZO Materials website (https://www.azom.com/). B) Diamond Anvil Cells (DAC) for characterization of materials at high pressures sold by Almax easyLab Inc. The image is taken from Almax easyLab Inc. website (https://diamondanvils.com/). C) Paris-Edinburgh cell developed by Oakridge National Laboratory for neutron diffraction studies. The image is taken from the Oakridge National Laboratory website (https://cci.chem.psu.edu/apparatus).

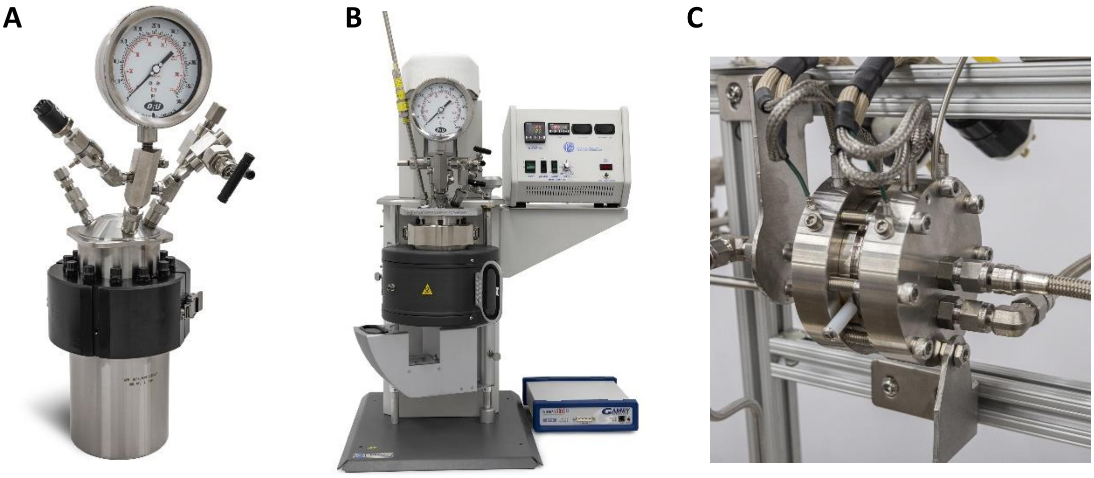

Figure S4. Commercial autoclave setups available in Parr Instrument Company for high pressure electrochemical studies A) Modified autoclave for batch high pressure electrochemical synthesis B) High pressure rotating disc electrode (RDE) setups C) Continuous high pressure electrochemical synthesis setups. The images are taken from Parr Instrument Company website (https://www.parrinst.com/)