Supporting Information

Harvesting Electrical Power during Carbon Capture using Various Amine Solvents

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S1 Power density from different membranes

In previous work, we created a CCRED system using ion exchange membranes supported by polyether ketone (PK): (Fumasep FKB-PK-130 (100-130 µm thick, PK reinforced, cation exchange) and FAB-PK-130 (100-130 µm thick, PK reinforced, anion exchange)).\(^1\) When using thin compartments (thickness: 2.5 mm) for the lean and rich compartments, we calculated that the membranes contributed the majority of the internal resistance. In our initial trials of the device presented in this article, we first used the PK reinforced membranes. As seen in Figure S1, the power density did not improve despite the fact that we had reduced the thickness of the lean and rich compartments to one fifth the thickness of the previous work (thickness: 0.5 mm). We decided to instead use membranes with no polymer reinforcement (FKS-50 (45-55 µm thick, cation exchange) and FAS-50 (45-55 µm thick, anion exchange)) and measured a 4-fold increase in maximum power density.
The maximum power density from the previous work is shown in blue with diagonal stripes. The thickness of the rich and lean compartments in the device presented in previous work was 2.5 mm, and the thickness of the PK-supported membranes was approximately 130 μm. When using the CCRED device presented here with the same PK-supported membranes (130 μm thick), we found no increase in maximum power density despite the fact that we used compartments that were 5x thinner (0.5 mm). When we used unsupported membranes (50 μm) instead, the maximum power density increased 4-fold. Only one trial was taken with the CCRED device presented here using PEEK-supported membranes. All trials were done with 3.28 M MEA rich and lean solutions. Trials that used PK-supported membranes are indicated with diagonal stripes. Trials using the CCRED setup presented in this work are indicated in red.

**Figure S1. Influence of different membranes on power density.** The maximum power density from the previous work is shown in blue with diagonal stripes. The thickness of the rich and lean compartments in the device presented in previous work was 2.5 mm, and the thickness of the PK-supported membranes was approximately 130 μm. When using the CCRED device presented here with the same PK-supported membranes (130 μm thick), we found no increase in maximum power density despite the fact that we used compartments that were 5x thinner (0.5 mm). When we used unsupported membranes (50 μm) instead, the maximum power density increased 4-fold. Only one trial was taken with the CCRED device presented here using PEEK-supported membranes. All trials were done with 3.28 M MEA rich and lean solutions. Trials that used PK-supported membranes are indicated with diagonal stripes. Trials using the CCRED setup presented in this work are indicated in red.

**S2 Open Circuit Voltage at increasing Flow Rates**

Previous work by Kim *et al.* demonstrated that the flow rate of solutions through a CCRED device influences the resulting open circuit voltage. We measured the open circuit voltage produced at different flow rates using two different CC solvents, MEA and MDEA (Figure S2). We found that increased flow rates resulted in increased open circuit voltage for both solvents. Increased flow rates reduces the amount of mixing that occurs across membranes, resulting in maintaining greater ion gradients across each membrane.
turn leads to a higher open circuit voltage (Equation S1-S4). Informed by this trial, the fastest flow rate, approximately 7.6 mL min\(^{-1}\) cell\(^{-1}\), was used for all experiments.

**Figure S2. The influence of flow rate on open circuit voltage.** Open circuit voltage increases when using either MEA or MDEA as flow rate increases.

*S3 Conductivity of MDEA and AMP at various concentrations*

We measured the conductivities of various concentrations of MDEA and AMP to find the most conductive rich and lean solutions. Because these values did not surpass the conductivity measured with ammonia solutions, and because ammonia had already demonstrated a much higher power density at similar concentrations, we concluded that running the CCRED device with optimized concentrations of MDEA or AMP would not result in a higher power density than that achieved when using ammonia.
**Figure S3. Conductivity of lean and rich solutions of MDEA and AMP at different concentrations.**

a) The conductivity of the lean solutions of MDEA and AMP at different concentrations. b) The conductivity of the rich solutions of MDEA and AMP at different concentrations.

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**S4 The pKₐ value and stability of the carbamates of different carbon capture solvents**

As discussed, only MEA and DEA form stable carbamates. The stability constant ($K^*$) for these CC solvents is shown in Table S1. The pKₐ of each carbon capture solvent also provides insight on the protonation equilibria of each CC solvent. The lower pKₐ of MDEA likely contributed to the different contributions to internal resistance compared to the other CC solvents, as discussed in the main text.

**Table S1. The pKₐ and the carbamate stability of different CC solvents.**

| CC solvent | MEA | DEA | MDEA | AMP | Ammonia |
|------------|-----|-----|------|-----|---------|
| **pKₐ (25 °C)** | 9.5 | 8.9 | 8.4  | 9.7 | 9.3     |
| **$K_c^*$ (40 °C)** | 12.5 | 2.0 | 0    | <0.1| --      |

All values except ammonia reported from Sartori and Savage, 1983. *$K_c$ represents the carbamate stability constant*
We calculated the expected open circuit voltage ($V_{oc}$) across each membrane (anion exchange membrane: AEM, cation exchange membrane: CEM) in conditions with perfect permselectivity. We used a version of the Goldman-Hodgkin-Katz Equation adapted for the concentrations of relevant ions when using an initial solution containing 3 M ammonia:\(^1,^7\)

$$V_{oc \text{CEM}} = \frac{RT}{F} \ln \left[ \frac{P_{\text{CEM NH}_4^+} [\text{NH}_4^+]_{\text{rich}} + P_{\text{CEM OH}^-} [\text{OH}^-]_{\text{lean}} + P_{\text{CEM HCO}_3^-} [\text{HCO}_3^-]_{\text{lean}}}{P_{\text{CEM NH}_4^+} [\text{NH}_4^+]_{\text{lean}} + P_{\text{CEM OH}^-} [\text{OH}^-]_{\text{rich}} + P_{\text{CEM HCO}_3^-} [\text{HCO}_3^-]_{\text{rich}}} \right] \quad (S1)$$

$$V_{oc \text{AEM}} = \frac{RT}{F} \ln \left[ \frac{P_{\text{AEM NH}_4^+} [\text{NH}_4^+]_{\text{lean}} + P_{\text{AEM OH}^-} [\text{OH}^-]_{\text{rich}} + P_{\text{AEM HCO}_3^-} [\text{HCO}_3^-]_{\text{rich}}}{P_{\text{AEM NH}_4^+} [\text{NH}_4^+]_{\text{rich}} + P_{\text{AEM OH}^-} [\text{OH}^-]_{\text{lean}} + P_{\text{AEM HCO}_3^-} [\text{HCO}_3^-]_{\text{lean}}} \right] \quad (S2)$$

Where $R$ is the universal gas constant (8.314 J·mol$^{-1}$·K$^{-1}$), $T$ is the absolute temperature (K), and $F$ is the Faraday constant (96,485 C·mol$^{-1}$). To estimate the theoretical $V_{oc}$ with perfect permselectivity, we set the permeabilities as follows: $P_{\text{CEM NH}_4^+} = 1$, $P_{\text{AEM OH}^-} = 1$, $P_{\text{AEM HCO}_3^-} = 1$, $P_{\text{AEM NH}_4^+} = 0$, $P_{\text{CEM OH}^-} = 0$, and $P_{\text{CEM HCO}_3^-} = 0$. In the rich solution, we assumed that all ammonia molecules had been protonated to become ammonium cations, and an equal number of bicarbonate anions had formed, resulting in a concentration of 3 M for each ion. At a pH of 7.9, the concentration of hydroxide ions are negligible. In the lean solution, at a pH of 12.1, we assume the concentration of bicarbonate is negligible and hydroxide is the predominant anion. We assume that the concentration of ammonium cations in the lean solution is equal to the number of hydroxide anions to preserve electroneutrality. With these values in mind, the equations can be rewritten as follows:

$$V_{oc \text{CEM}} = \frac{RT}{F} \ln \left[ \frac{[\text{NH}_4^+]_{\text{rich}}}{[\text{NH}_4^+]_{\text{lean}}} \right] \quad (S3)$$
$$V_{oc\text{ AEM}} = \frac{RT}{F} \ln \left( \frac{[HCO_3^-]_{\text{rich}}}{[OH^-]_{\text{lean}}} \right)$$ \hspace{1cm} (S4)

These values result in $V_{oc\text{ CEM}} = V_{oc\text{ AEM}} = 0.138$ V. With two membranes per cell, the maximum theoretical $V_{oc}$ of a RED cell would be 276 mV. We achieved 250 ± 5 mV per cell (Table 2).

**S6 Calculating Internal Resistance and Maximum Power Density**

The following equations represent the relationship between the power, voltage, current, and resistance of a RED system:

$$P = I \times V$$ \hspace{1cm} (S5)

$$I = \frac{V}{R}$$ \hspace{1cm} (S6)

$$P = \frac{V^2}{R}$$ \hspace{1cm} (S7)

where $P$ is power (W), $V$ is voltage (V), $I$ is current (A), and $R$ is resistance ($\Omega$). The maximum power transfer theorem states that a DC power source provides maximum power when the resistance of the load ($R_L$) is equal to the internal resistance ($R_{int}$) of the power source.\[1,2\] For a power source with a linear I-V relationship, this condition is met if the voltage across a load ($V_L$) equals half the $V_{oc}$.\[1,2\] To calculate $R_{int}$, we connect a $R_L$ of known value to the power source in series to create a voltage divider. Using the measured $V_L$, we calculated the internal resistance using the following equation:\[8\]

$$V_L = V_{OCR_L + R_{int}}$$ \hspace{1cm} (S8)
Alternatively, because of the linear nature of the I-V curve, we could solve for the internal resistance ($R_{int}$) of the device using the short circuit current ($I_{sc}$):  

$$R_{int} = \frac{V_{oc}}{I_{sc}}$$  \hspace{1cm} (S9)

Knowing that maximum power ($P_{max}$) results when $R_L = R_{int}$ and $V_L = V_{oc}/2$, we can solve for $P_{max}$ using known values:

$$P_{max} = \frac{V_{oc}^2}{4R_{int}}$$  \hspace{1cm} (S10)

We solved for maximum power density ($\rho_{P_{max}}$) by dividing this result by cross-sectional area ($A$, m$^2$) and number of cells ($N$):

$$\rho_{P_{max}} = \frac{V_{oc}^2}{4ANR_{int}}$$  \hspace{1cm} (S11)

**S7 Energy Analysis**

To calculate the theoretical exergy flow rate $X$ (W) from mixing the streams of rich and lean solutions, we used Equation 7 and 8 from the main text. When starting with a lean solution consisting of 3 M ammonia, we made the assumption that all the ammonia is converted into ammonium bicarbonate in the rich solution. To convert $X$ to the theoretical amount of free energy due to mixing $\Delta G_{mix}$ (J) available per volume of rich solution $v_{rich}$ (L), we divided by the flow rate of the rich solution $Q_{HSS}$ (L s$^{-1}$):  

$$\frac{\Delta G_{mix}}{v_{rich}} = \frac{X}{Q_{HSS}}$$  \hspace{1cm} (S12)

We estimated the theoretical free energy from complete mixing would be approximately 9.8 kJ per liter of rich solution. If we assume that each liter of rich solution captured 3 M of CO$_2$, we can use the molecular weight of CO$_2$ (44 g/mol) to convert this value
to approximately 74 kJ per kg of CO$_2$. To compare this with the energy we harvested from the CCRED device, energy $E$ (J) can be expressed as the product of power $P$ (W) for a period of time $\Delta t$ (s):

$$E = P \Delta t \tag{S13}$$

We used the maximum power density $\rho_{P_{\text{max}}}$ (W m$^{-2}$) multiplied by the effective membrane area $A$ (m$^2$) to solve for $P$. Because $\rho_{P_{\text{max}}}$ was calculated per cell, we can use the flow rate of rich solution through a single compartment $Q_{c_{-\text{HSS}}}$ (L s$^{-1}$) to solve for the amount of energy per volume of rich solution $v_{\text{rich}}$ (L):

$$
\frac{E}{v_{\text{rich}}} = \frac{A \rho_{P_{\text{max}}}}{Q_{c_{-\text{HSS}}}} \tag{S14}
$$

Note that, because there are two RED cells but three rich compartments, $Q_{c_{-\text{HSS}}}$ (5.1 mL min$^{-1}$) differs from $Q_{\text{HSS}}$ (7.6 mL min$^{-1}$). As the number of cells in a CCRED device increases, the difference between these two flow rates will decrease. We can then calculate $e_{\text{pct}}$, the percentage of energy we harvested compared to the theoretical free energy that could be made available from the complete mixing the rich and lean solutions:

$$
e_{\text{pct}} = \frac{E}{\Delta G_{\text{mix}}} \times (100\%) \tag{S15}$$

**S8 Sketches and models used for fabrication**

**Figure S4** shows the sketch that we provided for the machine shop at University of Fribourg to fabricate the end pieces. The 3D models and the Cricut designs used to build the CCRED device can be found at: [https://github.com/tkalkus/CCRED](https://github.com/tkalkus/CCRED)
Figure S4. A sketch of the 3D model for machining the end pieces of the CCRED device.
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