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## Energetics of electrochemically-mediated amine regeneration

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### Abstract

Cost-effective, large-scale carbon dioxide capture is a critical technology for mitigating greenhouse gas emissions, and current capture technologies are energy intensive and difficult to deploy in existing power plants. We have previously introduced a novel electrochemically-mediated process for amine regeneration, and demonstrated its feasibility with a proof-of-concept system that can efficiently modulate amine affinity to carbon dioxide under the effect of redox-responsive molecules. The electrochemical process is simple to install, obviating the need for expensive retrofits. In addition, due to its targeted nature, the process has the potential for lower energy consumption as compared with the thermal amine capture process. In this work, we analyze the energy consumption of the electrochemical process, building from thermodynamic lower bounds, and addressing electrochemical kinetics, transport requirements as well compression and pumping energy. The analysis suggests that the electrochemical process can generate carbon dioxide at the conditions required for transportation with an electrical energy consumption of less than 50 kJ per mole of carbon dioxide captured and compressed. The electrochemical process efficiency can be further improved by optimizing flow design and utilizing additives to reduce activation overpotentials.

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### 1. Introduction

Overwhelming evidence for the detrimental impacts of CO<sub>2</sub> emissions on the environment is well documented by a number of groups, including the Intergovernmental Panel on Climate Change and the National Research Council, which recommend significant reductions in carbon emissions. [1,2] Carbon capture and sequestration (CCS) has

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been identified as a necessary component of any environmental policy that aims to achieve significant reduction in emissions over the next few decades.[3,4] To this end, the International Energy Agency predicts that over 100 GW of coal-fired power plant capacity will need to be retrofitted with carbon capture capabilities. [5] Currently, retrofit costs for existing thermal amine scrubbing technology, the benchmark for CO<sub>2</sub> capture in CCS applications, are prohibitive. [6] There are two main elements to the retrofit cost: the high energy consumption of the thermal process that significantly derates the power plant electrical output, and the high capital cost associated in part with the required internal reconfiguration of the steam turbine train; this reconfiguration is required to enable extraction of low pressure steam for the stripping operation.[7,8]

Recently, our group introduced a novel approach to CO<sub>2</sub> capture that requires only the application of an electrical driving force for the stripping operation, freeing it from the need for large-scale steam extraction and disruption of the power plant internal steam cycle. The electrochemically-mediated amine regeneration process utilizes redox responsive materials to modulate the affinity of amine solvents for CO<sub>2</sub>, under the action of electric voltage. [9,10]

This electrochemical approach offers several advantages over the thermal stripping process, the first of which is that it is driven by electricity rather than steam, obviating the need for expensive retrofits to the steam configuration in the power plant. Second, due to its more targeted nature and ability to operate under high liquid pressures, the electrochemical approach can potentially be more energy efficient than thermal stripping. In previous work, we demonstrated a proof-of-concept system that utilizes copper metal and sustained control of CO<sub>2</sub> capture rates with the cycling of electric current. [9]

In this work, we provide an analysis of the energy consumption of the electrochemical process, based on our most recent kinetic experiments results. This analysis serves to explain the energy landscape of the process, to highlight its advantages and to create a roadmap for future development and research needs.

### Nomenclature

$C_j^{bulk}$	Bulk concentration of species $i$
$F$	Faraday's constant
$\Delta G$	Gibbs free energy of reaction
$\Delta H$	Enthalpy of reaction
$i$	Current density (A/m <sup>2</sup> )
$K$	Equilibrium constant for CO <sub>2</sub> /amine complexation
$R$	Universal Gas Constant
$\Delta S$	Entropy of reaction
$T$	Temperature (K)
$P_a$	Partial pressure of CO <sub>2</sub> on the anode side of the electrochemical cell
$P_F$	Partial pressure of CO <sub>2</sub> in the flue gas
$u_x$	Flow velocity of fluid in the direction perpendicular to the electrodes
$\nu_j$	Stoichiometric coefficient of species $i$
$W_{CO_2}$	Work of capture per mole of CO <sub>2</sub>

## 2. Theoretical Basis and Experiments

In this section, energy consumption and losses of the electrochemical capture process are outlined, with a brief discussion of relevant models and experiments required to estimate and measure these losses.

## 2.1. Thermodynamics

The thermodynamics of capturing CO<sub>2</sub> with amine sorbents are favorable due to the attractive forces between the basic amine molecules and the acidic dissolved CO<sub>2</sub>. However, the stability of the amine-CO<sub>2</sub> complex poses a significant challenge for large-scale CCS during solvent regeneration. The thermal absorption and stripping cycle shown in Figure 1(a) relies on an increase in entropy, driven by the addition of heat, to raise the temperature of an aqueous amine-CO<sub>2</sub> complex solution. As the entropic component of the Gibbs free energy increases, it dominates the enthalpic interactions between the amine and CO<sub>2</sub> molecules, reducing the complexed fraction as measured by the equilibrium constant of the amine/CO<sub>2</sub> complex. This effect can be summarized by the relationship:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} = -RT \ln K \quad (1)$$

The released CO<sub>2</sub> is of high purity, and the regenerated amine from the stripper must be cooled down before it returns to the absorber, usually in a heat exchanger with the cooler stream from the absorber, which is itself heated by this exchange before entering the stripper. However, even with significant heat recovery, the thermal amine stripping process consumes large amounts of energy, more than 50 kJ of electrical energy equivalent per mole of CO<sub>2</sub> captured and compressed. [6] The fundamental nature of the stripping process and its reliance on an increase in entropy results in that high consumption.

In contrast, the electrochemically-mediated amine regeneration process relies on competitive complexation of amines by Lewis acids that can cycle between active and inactive states under the action of electric voltage. In one embodiment of this process, metal ions capable of strongly chelating amine molecules are formed from a metal surface under anodic current. The affinity of amines for the formed metal ions allows for rapid release of CO<sub>2</sub> and formation of amine/metal ion complexes. For example, the stability constant of the copper complex with ethylenediamine (EDA) is on the order of 10<sup>18</sup>. [11]

Under a cathodic current, the metal ions are reduced to metal atoms, deposited onto a cathode surface, and regenerating the amine solvent for recycling into the absorber. Thus, instead of relying on an increase in entropy to separate amines from CO<sub>2</sub>, the electrochemical process introduces a more favorable enthalpic interaction. Figs. 1. and 2. contrast the thermal and electrochemical processes at the molecular scale.

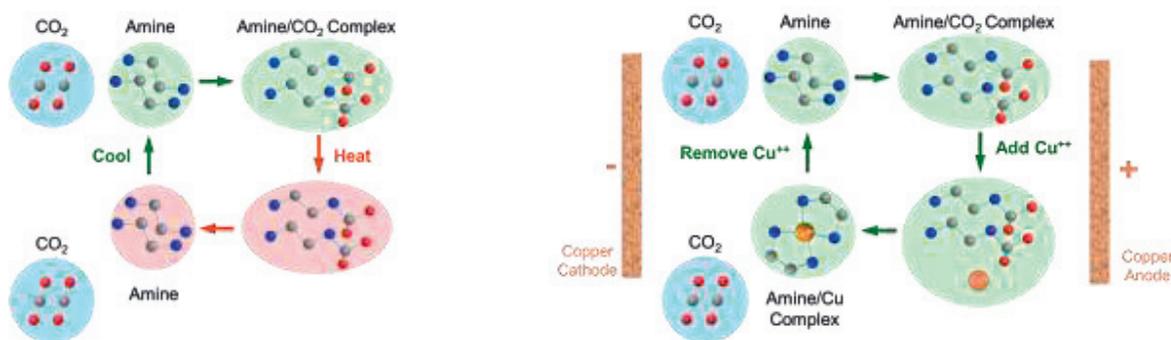


Fig. 1. (a) A simple molecular schematic of the thermal amine stripping process. An amine solvent at low temperature captures CO<sub>2</sub> from a gaseous mixture to form a complex, which is then dissociated at high temperature to regenerate the solvent. (b) A simple molecular schematic of an example of the electrochemical amine regeneration process. An amine solvent at low temperature captures CO<sub>2</sub> from a gaseous mixture to form a complex. The complex is then dissociated by competitive complexation by a metal ion formed by oxidation of a metal electrode. After the released gaseous CO<sub>2</sub> is separated from the aqueous solution, the metal ions are removed from the amine complex by electrochemical deposition on the surface of the metal electrode.

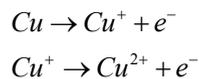
As shown in previous work [9] the thermodynamic work of capture in the electrochemical process for an example system utilizing copper metal and ethylenediamine (EDA) can be computed from:

$$W_{CO_2} = RT \ln \left( 1 + \frac{K_{CO_2} P_a}{P_o} \right) \left( 1 + \frac{K_{CO_2} P_f}{P_o + K_{CO_2} P_f} \right) \quad (2)$$

Experimentally, the same quantity can be determined by measuring the open circuit potential for copper under both argon and CO<sub>2</sub>-saturated environments and subtracting the two values. [10] This open circuit voltage difference arises from the differences in copper ion concentration between the two identical electrodes under anodic (CO<sub>2</sub> rich) and cathodic (CO<sub>2</sub> free) conditions. The open circuit potential is thus a measure of the energetic penalty of dissociating the copper-amine complex in the presence and absence of CO<sub>2</sub>.

## 2.2. Electrochemical Kinetics

Fig.2. shows a molecular schematic of the dissolution and deposition processes in the electrochemical cell. On the anode side, the metal (in this case copper) is oxidized to form copper ions according to the half reactions:



For uncomplexed copper, experiments suggest that the first reaction is fast and the second step is rate determining. [12] Once the copper ions are formed, the reaction with amines is rapid, driven by the large thermodynamic driving force, as evidenced by the high stability complex of the formed complex. CO<sub>2</sub> is then released by the amine molecules in gas form.

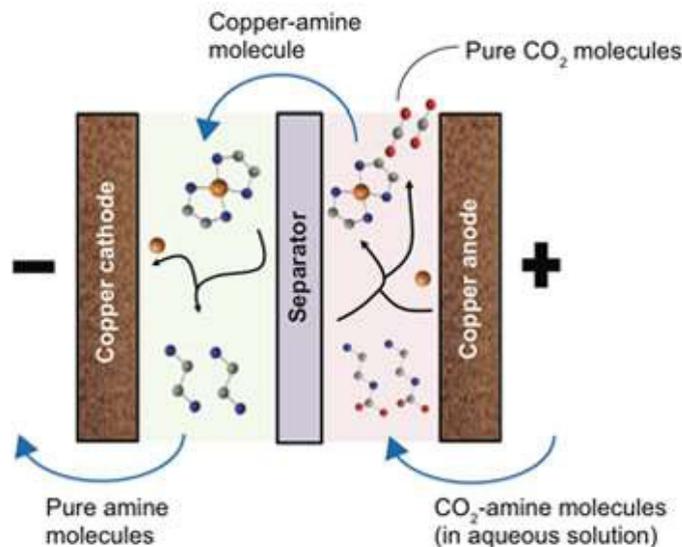
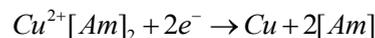


Fig. 2. A schematic of the electrochemical cell component of the electrochemical amine recovery process. The right hand side of the cell depicts the anode section, where metal ions formed at the surface of the electrode chelate amine molecules and break their complex with CO<sub>2</sub>. On the left hand side of the cell, metal ions are deposited on the metal surface in the cathode side of the cell.

The aqueous solution of the copper amine complex enters the cathode side of the electrochemical cell once the the gaseous CO<sub>2</sub> is separated in a simple flash tank. A cathodic current reduces the copper from its amine complex to deposit copper atoms according to the reactions:



CO<sub>2</sub> capture in the context of power stations is, by definition, large-scale; consequently, the feasibility of a CO<sub>2</sub> capture process is partly a function of its ability to operate at scale. For an electrochemical process, a major metric

of scalability is the current density at which the process can operate efficiently. The activation overpotentials represent the energetic penalty of operating a process at a rapid rate of reaction, as measured by the current density. A scalable electrochemical process must be able to operate at high current densities (above 500 A/m<sup>2</sup>) without requiring high overpotentials (i.e., no more than about 100 mV per electrode).

For the electrochemically-mediated amine regeneration process, both the dissolution and deposition of the metal ions must be facile if the process is to be feasible. The effect of additives on the overpotentials required to drive the process at relevant current densities are well known for metal ion systems, especially copper. [13,14,15] To explore the prospects for effective modulation of copper deposition and dissolution in the presence of amines, galvanostatic pulse experiments were performed following the procedures outlined by Mattsson and Bockris. [16] The details of these experiments and their results for the copper amine system under different additives are described elsewhere. [17]

### 2.3. Transport

Transport overpotentials represent the energy losses due to the concentration difference between the bulk solution and the electrode surface in an electrochemical system. That concentration difference is usually a result of diffusion limitations of ions to the electrodes. Our analysis of the performance of a flat plate electrode system for the electrochemical process was based on an integral solution to the partial differential diffusion equation, based on the assumptions of fully developed parabolic flow between two parallel, infinitely wide plates. [18] The surface flux due to the formation of copper ions or the consumption of copper-amine complexes was captured by the Butler-Volmer equation. The equations describing the transport for each species *i* can be written as:

$$u_x \frac{\partial C_j}{\partial x} = D_j \frac{\partial^2 C_j}{\partial y^2} \quad (3)$$

with the boundary conditions

$$\begin{aligned} C_j(x=0, y) &= C_j^{bulk} \\ \frac{\partial C_j}{\partial y} \Big|_{y=0} &= -v_j \frac{i}{nFD_j} \\ \frac{\partial C_j}{\partial y} \Big|_{y=H} &= 0 \end{aligned} \quad (4)$$

where  $u_x$  is the flow velocity in the direction parallel to the electrode,  $D_i$  is the diffusion coefficient of species *i*,  $C_j^{bulk}$  is the inlet concentration of the electrochemically active species,  $v_i$  is the stoichiometric coefficient of the corresponding species,  $x = 0$  represents the inlet zone,  $y = 0$  represents the electrode surface,  $y = H$  represents the center line between the plates, which is where the separator is located. The first boundary condition represents the inlet conditions; the second describes the flux at the surface, while the third describes the zero flux across the separator condition.

For the porous electrode systems, we utilized a volume-averaged approach with the assumption of perfect mixing in the direction normal to the flow. [18]

### 2.4. Compression and Pumping

In order to transport captured CO<sub>2</sub> to its final location for sequestration in saline formations, for enhanced oil recovery, or for utilization in other ways, it must first be compressed to around 150 bars. The theoretical energy (assuming an ideal compressor) required to compress CO<sub>2</sub> at ambient conditions to 150 bars is around 10 kJ per

mole CO<sub>2</sub> compressed. In practice, with a compressor efficiency of around 65%, compression energy reaches around 15 kJ of electrical energy equivalent per mole of CO<sub>2</sub> compressed.

For the thermal amine stripping process, CO<sub>2</sub> desorption from amines occurs at pressures close to atmospheric pressure. A further increase in pressure would increase the CO<sub>2</sub> partial pressure and consequently, render desorption harder. One of the main advantages of the electrochemical process is its ability to desorb CO<sub>2</sub> under high pressure, since the dissociation kinetics of CO<sub>2</sub> from amines under the action of metal ions are fast and driven by a large thermodynamic force (due to the strong amine affinity for the metal ions). Consequently, and based on previous analysis of irreversible losses due to the re-absorption of CO<sub>2</sub> in the solution under the higher desorption pressure, the energy consumption of the electrochemical process under pressures up to 10 bars did not significantly change with the increase in pressure. [18]

Here, we estimate the energy savings due to operating desorption at higher pressures by calculating the work of compression from the desorber pressure to 150 bars using the Peng-Robinson equation of state as a first approximation, and including the pumping energy consumption of the aqueous solution up to the desorber pressure.

### 3. Results and Discussion

For the electrochemical process, experimental results and thermodynamic models described previously suggest that the minimum energy consumption for cycling copper in the presence and absence of CO<sub>2</sub> can be as low as 15 kJ per mole of CO<sub>2</sub> captured. [9] Under different electrolytes, experimental measurements of open circuit potential under 50% copper loading and a temperature of 25°C (Fig.3.) yielded values of around 250 mV, while lower open circuit potentials were possible by going to slightly higher temperatures (around 55°C). [10,17]

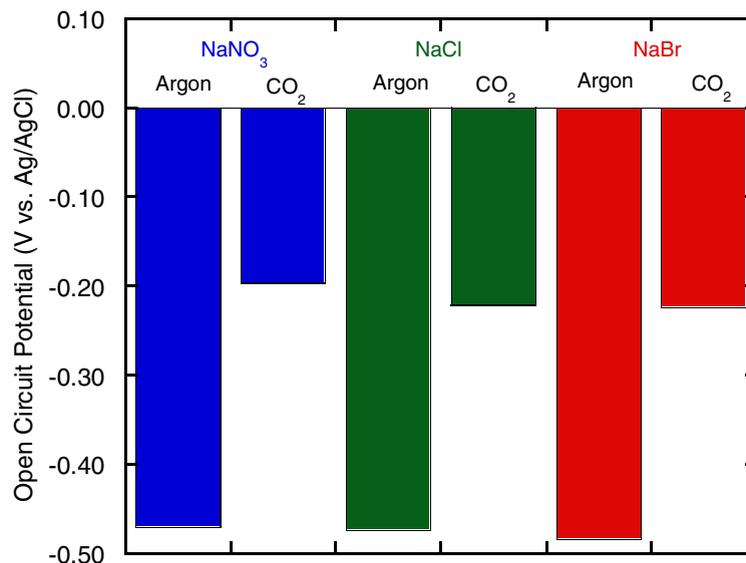


Fig. 3. Open circuit potential measurements under different electrolytes for the copper-EDA system at 25°C and 50% copper loading demonstrate energy consumption for separation of 250 mV.

Activation overpotentials for the copper-EDA system under nitrate electrolytes were found to be around 200 mV for anodic dissolution and 100 mV for cathodic deposition for a high current density of 1000 A/m<sup>2</sup> at 55°C. Under these conditions, the energy required to run the electrochemical process at industrially feasible rates would be around 50

kJ of electrical energy equivalents per mole of CO<sub>2</sub> captured, not including transport overpotentials or compression energy.

In our recent work, the effect of electrolyte additives was found to reduce activation overpotentials significantly. [17] Fig. 4. shows the voltage-current profile in the presence and absence of CO<sub>2</sub> under sodium bromide. The overpotentials required are as low as 90 mV for anodic dissolution (under CO<sub>2</sub>) and 80 mV for cathode deposition (under argon, representing the case where CO<sub>2</sub> is absent). Further investigations are underway to understand the underlying mechanism of additive modulation, which has been observed repeatedly for metal deposition and dissolution. One possible explanation is that additives cause a switch of mechanism for electron transfer, the rate limiting step for a two-step electron transfer system, from outer-sphere to inner-sphere. [19]

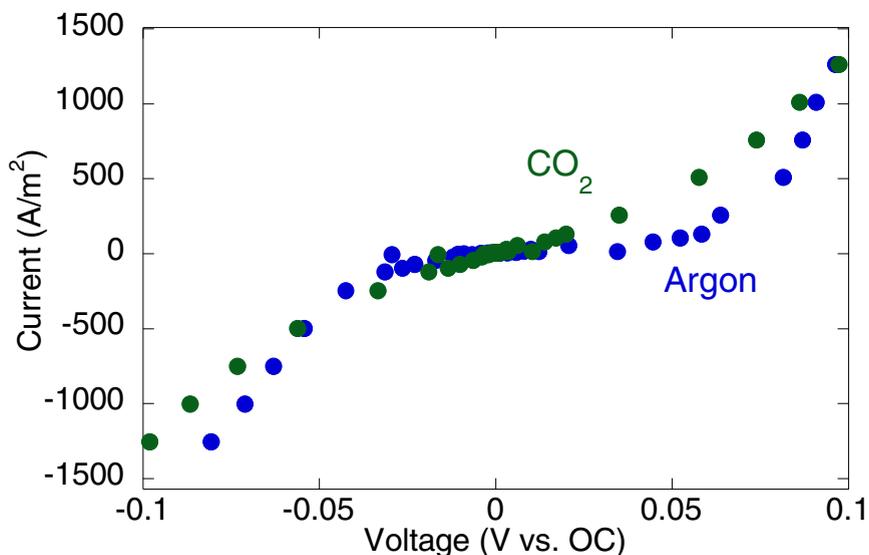


Fig. 4. Current-voltage profile for 1M copper-2M EDA system at 55°C measured using galvanostatic pulses in the presence and absence of CO<sub>2</sub>. The overpotentials required for a high current density of around 1000 A/m<sup>2</sup> are significantly lower than in the baseline case of a nitrate electrolyte.

Preliminary estimation of the transport overpotentials calculated by the methods outlined above suggests that the flat plate electrode system can operate at less than 100 mV per electrode. To reduce transport overpotentials further, it would be necessary to utilize porous electrodes, which are predicted to require less than 50 mV per electrode for high current densities. Further detailed analysis and experiments are currently underway to optimize the electrode design as well as the ensuing flow conditions.

Estimation of compression and pumping energy required for to produce carbon dioxide at a pressure of 150 bars as required for transportation to sequestration sites demonstrate the advantages of operating the electrochemical desorption cell at higher pressures. Fig. 5. summarizes the combined energy requirements for pumping and compression assuming ideal processes. On the assumption of 65% efficiency for both processes, with the anode operated at pressures above 9 bars, the total compression and pumping energy can be reduced from 15 kJ per mole to around 10 kJ per mole of CO<sub>2</sub> compressed to 150 bars.

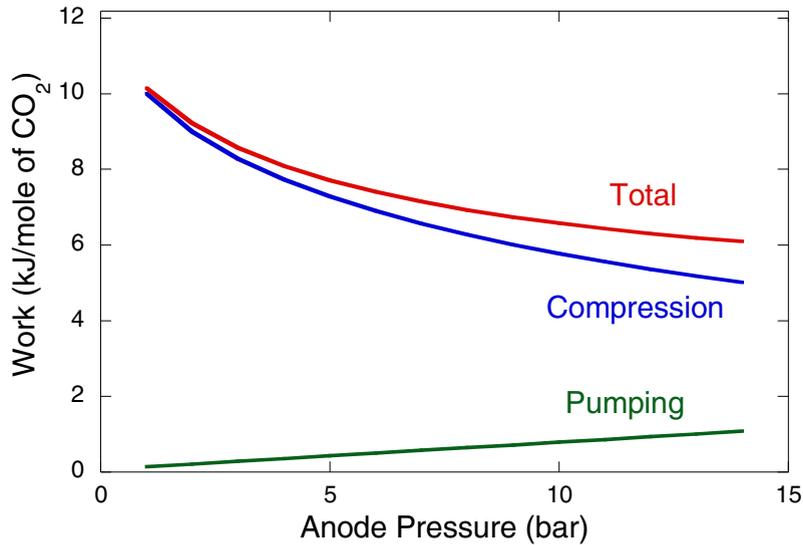


Fig. 5. Ideal pumping and compression energy requirements for the electrochemical process operating at different anode pressures. Analysis results suggest that an increase in the electrochemical cell desorption pressure can result in significant energy savings due to the lower energy required for pumping the aqueous solutions to the anode pressure.

Thus, we can estimate the expected overall energy consumption of the electrochemical process by summation of the thermodynamic limit, the activation and transport overpotentials, and the compression and pumping energy. Based on the estimates discussed above for the copper-EDA example system, the overall energy consumption is dominated by the activation overpotentials (around 20 kJ/mole) with important energy savings possible by choice of additives. Compression and pumping energy requirements for the process are significantly minimized, as desorption can be done at high pressures.

Fig. 6. compares the overall energy consumption of the electrochemical process with ideal consumptions figures, representing the minimum entropic penalty for separating a 15% CO<sub>2</sub> mixture, and ideal compression to 150 bars. The electrochemical process, at current performance, is expected to achieve around 35% efficiency.

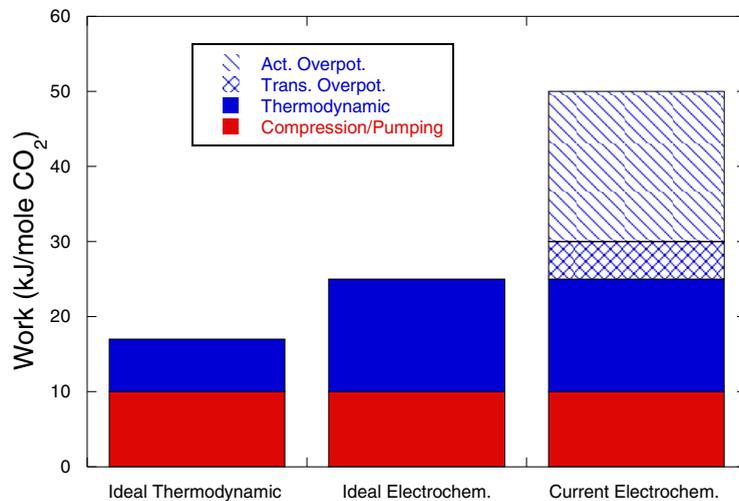


Fig. 6. Overall energy consumption of the electrochemical process, compared with the ideal thermodynamic and ideal electrochemical limits. Most of the energy consumption of the electrochemical process is the result of high overpotentials required to drive the process at current densities necessary for large-scale operation. Compression and pumping energy are significantly minimized because of the ability of the electrochemical cell to operate at high pressures.

#### 4. Conclusions

The analysis described in this work suggests that the electrochemical process at its current performance will operate at efficiencies comparable to, or higher than, those achieved with the thermal amine stripping process. The major losses in the process are a result of the high activation overpotentials required to drive high current densities. Operation of the electrochemical cell at high pressures should result in significant energy savings, by reducing the compression energy requirements. The energetic advantages of the electrochemical process, along with its plug and play nature, promise lower carbon capture costs and simpler implementation.

To optimize the electrochemical process further, it is necessary to explore more fully the role of additives in reducing activation overpotentials, as well as to optimize the flow profiles in the electrochemical cell to minimize transport overpotentials. Moreover, further exploration of potential metal/solvent chemistries can result in a system with lower thermodynamic minimum energy consumption. Further work is currently underway to explore those possibilities, as well as demonstrate stable operation at relevant operating conditions.

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