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GHGT-11

## An electrochemically-mediated gas separation process for carbon abatement

Michael C. Stern<sup>a</sup>, Fritz Simeon<sup>a</sup>, Howard Herzog<sup>b</sup>, T. Alan Hatton<sup>a\*</sup>,

<sup>a</sup>Department of Chemical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Ave., Cambridge, MA 02139, USA

<sup>b</sup>MIT Energy Initiative, Massachusetts Institute of Technology, 77 Massachusetts Ave., Cambridge, MA 02139, USA

### Abstract

This work describes a promising alternative to conventional thermal processes for absorber/desorber processing of for removal of CO<sub>2</sub> from flue gas streams at fossil fuel fired power plants. Our electrochemically-mediated amine regeneration (EMAR) process offers the advantages of an electrical system coupled with the desirable high output purities typical of amine sorbents that are difficult to achieve with most electric systems such as pressure-swing sorption, membrane separation, and oxy-fuel combustion. Preliminary experimental results are presented that demonstrate the feasibility of using ethylenediamine as the CO<sub>2</sub> sorbent and copper electro-cycling to isothermally modulate the amine affinity for CO<sub>2</sub>. Cupric ions entirely deactivate ethylenediamine at a ratio of 2:1 diamine to copper. Open-circuit potential measurements at 50°C indicate the required energy to desorb CO<sub>2</sub> and regenerate the ethylenediamine is 18 kJ/mole CO<sub>2</sub> under open-circuit conditions. Kinetic over-potentials are sufficiently low to ensure acceptable energy losses. Lower energies can be achieved by increasing the temperature or by changing the amine.

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Keywords: Carbon capture; amine scrubbing; electrochemistry; ethylenediamine

### 1. Introduction

The compelling evidence for the role of anthropogenic carbon dioxide (CO<sub>2</sub>) in the Earth's atmosphere as a primary cause of global climate change that is a major threat to global public health and welfare highlights the need for the development and deployment of carbon abatement technologies and the legislation to enforce their implementation [1]. Carbon capture and sequestration (CCS) from large point-source emitters, such as fossil fuel burning power plants, is a potentially effective strategy for

\* Corresponding author. Tel.: +1-617-253-4588; fax: +1-617-253-8723.

E-mail address: [tahatton@mit.edu](mailto:tahatton@mit.edu).

carbon mitigation [2], although the high cost of implementation, which has been estimated to nearly double the cost of electricity, has deterred both political and industrial entities from supporting CCS [3].

Thermal amine scrubbing is the current benchmark technology for separating CO<sub>2</sub> from combustion flue gases in CCS systems [4]. CO<sub>2</sub> is absorbed by amine solutions, usually monoethanolamine in water, at flue gas temperatures between 40°C and 60°C and then desorbed in the stripper by low-pressure steam at between 100°C and 120°C [5]. The need for low-pressure steam generally requires a significant fraction of the steam be routed from the steam turbines to the amine stripper. For an existing power plant, retrofitting requires such a high capital cost to reconfigure the internals of the plant that a rebuild is often more economically feasible [3].

Alternative strategies that do not rely on low-pressure steam have been shown to be economically superior when considering a retrofit to an existing plant [6]. These processes, which include oxy-fuel combustion and membrane separation, use electric compressors to perform the work of separation, thereby avoiding the inherently difficult demands of thermal scrubbing, but at the expense of lower output purities of CO<sub>2</sub> [6,7]. This could be a significant drawback based on the downstream storage processes, since even small quantities of impurities in the CO<sub>2</sub> outlet can significantly alter the supercritical properties of the stream [8].

We have proposed a new strategy that combines the advantages of both electrical and traditional scrubbing systems using the process shown schematically in Figure 1. The Electrochemically-Mediated Amine Regeneration (EMAR) process operates in a manner akin to traditional amine scrubbing operations, but eliminates the cross-flow heat exchanger and stripper required in the usual configurations by replacing them with an electrochemical cell, where desorption and regeneration is achieved through the electrochemical cycling of a Lewis acid. The transition between copper and cupric ions is currently the most promising acid cycle for an EMAR process. This process has both logistical and operating advantages relative to thermal processes for desorption of the CO<sub>2</sub> and regeneration of the amine sorbents. Much lower lean loadings of CO<sub>2</sub> can be achieved due to the dramatically faster kinetics of the competitive desorption approach compared to those possible with thermal desorption operations; thus the hydraulic load on the scrubber can be reduced, leading to smaller scrubbers. Moreover, since the desorption does not require a sweep gas, the entire electrochemical cell can be pressurized allowing for elevated desorption pressures that lead to significantly lower compression requirements downstream. It should be possible to eliminate at least one compressor in the intercooled compressor train required to produce CO<sub>2</sub> at the 100 to 150 bars necessary for storage.

In this paper, we evaluate the potential utility of the proposed approach by reporting experimental results obtained using ethylenediamine (EDA) to demonstrate the ability to desorb CO<sub>2</sub> and then regenerate the amine isothermally by electro-cycling between copper metal and cupric ions. Because EDA is a strong chelating agent towards cupric ions [9], CO<sub>2</sub> can be released through the addition of cupric ions into a CO<sub>2</sub> saturated EDA solution. EDA is a viable CO<sub>2</sub> sorbent and has been investigated previously for thermal scrubbing processes [10].

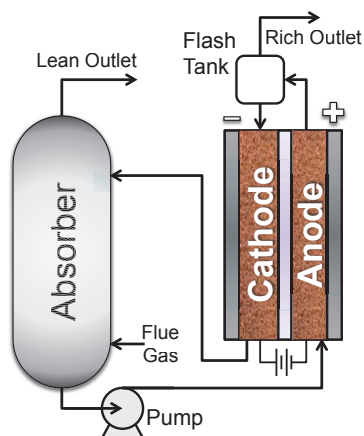


Fig. 1. Process diagram for an EMAR system for CO<sub>2</sub> scrubbing

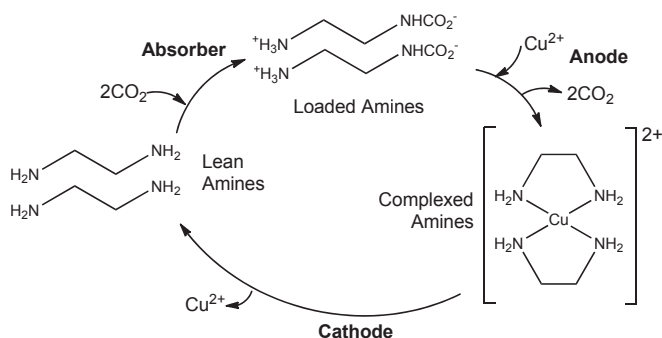


Fig. 2. Chemical transitions in an EMAR system based on EDA and copper

## 2. Experimental methods

### 2.1. Absorption experiments

Several 40 mL solutions containing 1M EDA, 1M potassium nitrate, and varying amounts of copper nitrate from 0 to 0.5 molar were prepared in 50 mL round bottom flasks. During the experiments, the solutions were heated to 50°C and vigorously stirred. Simulated flue gas (15% CO<sub>2</sub>, 85% N<sub>2</sub>) was bubbled through the flask at 66 mL/min for several hours. The outlet was sampled every 2 minutes using a gas chromatograph to determine the CO<sub>2</sub> concentration. The total quantity absorbed was calculated by subtracting the amount of CO<sub>2</sub> that exited the solution from the amount of CO<sub>2</sub> that was bubbled into the solution. All reported measurements were adjusted by subtracting out the quantity of CO<sub>2</sub> absorbed by a 1M potassium nitrate solution without any amine.

### 2.2. Open-circuit potential measurements

Experiments were performed by measuring the open-circuit potential between a copper wire electrode and a sealed Ag/AgCl reference electrode. All solutions contained 1M EDA and 1M NaNO<sub>3</sub> and varying amounts of copper nitrate from 0 to 0.5M. The difference in the open-circuit potential at a given copper

loading was calculated by subtracting the open-circuit potential of a solution that was under inert atmosphere from the potential of a solution with the same copper loading but saturated with CO<sub>2</sub>. CO<sub>2</sub> saturation was achieved by bubbling pure CO<sub>2</sub> through the solution until the open-circuit potential reached a steady value. All experiments were done at 50°C.

### 2.3. Kinetic over-potential measurements

Experiments using Normal Pulse Voltammetry (NPV) were performed on a model solution (1M EDA, 0.25M Cu(NO<sub>3</sub>), 0.5M KNO<sub>3</sub>, 0.5M NaCl). Non-Faradaic current was eliminated through measurement of the resistance and capacitance of the system using millisecond-long chronopotentiometric measurements followed by estimation of the charging current as an RC circuit. Copper electrodes were created through electroplating of cupric ions onto a smooth vitreous carbon electrode (diameter = 3mm) from a 1M H<sub>2</sub>SO<sub>4</sub> and 0.5M CuSO<sub>4</sub> solution at negative of overpotential of 100mV and gentle stirring for 15 minutes. The electrode was activated by application of a negative 200mV overpotential for 1 minute before an experiment.

## 3. Results and Discussion

In the process schematic for the EMAR system shown in Figure 1, carbon dioxide is absorbed in a traditional absorption column where it reacts with EDA to form the corresponding carbamate; in principle, one mole of EDA will be required per mole of CO<sub>2</sub>, in contrast to absorption with MEA, where two moles of the amine are required per mole of CO<sub>2</sub>. The CO<sub>2</sub>-loaded amine solution leaving the absorber is fed to the anode side of the electrochemical cell, where cupric ions released on oxidation of copper electrodes compete favorably with the CO<sub>2</sub> for the EDA. The displaced CO<sub>2</sub> is released as a gas, and compressed for subsequent sequestration or utilization. The Cu<sup>2+</sup>-complexed amine solution is then passed through the cathode side of the electrochemical cell, where the copper is reduced and plates out on the electrodes, and the amine is regenerated before being returned to the absorber.

The optimal anode desorption pressure depends on the need to reduce the lean loadings of the absorbent to acceptable levels, and on the avoided work of compression. Elsewhere in these conference proceedings, we have shown that to include the pressure in the analysis, the efficiency of the process with respect to a reversible system must be used instead of the work of separation. Eq. (1) shows the efficiency of an EMAR process as a function of the CO<sub>2</sub> binding constant  $K_{CO_2}$  and the partial pressures  $P_{CO_2}$  in the flue gas and the anode.

$$\eta_{EMAR} = \frac{-\ln P_{CO_2}^{Flue} - \frac{(1 - P_{CO_2}^{Flue})}{P_{CO_2}^{Flue}} \ln(1 - P_{CO_2}^{Flue}) + \ln P_{CO_2}^a}{\ln\left(1 + K_{CO_2} P_{CO_2}^a\right) \frac{1 + K_{CO_2} P_{CO_2}^{Flue}}{K_{CO_2} P_{CO_2}^{Flue}}} \quad (1)$$

The efficiency calculated in Eq. (1) is an increasing function of anode partial pressure, indicating that an efficient EMAR process should be operated at as high a pressure as possible. The maximum achievable efficiency of an EMAR process is shown as a function of desorption pressure in Fig. 3 for a CO<sub>2</sub> flue gas partial pressure of 0.1 bar. This result shows that, potentially, thermodynamic efficiencies of over 75% can be achieved. Kinetic and Ohmic overpotentials and other minor losses will, however,

reduce the actual operating efficiency of a real process. For competitive operation, then, desorption pressures should be above 10 bars and the  $\text{CO}_2$  binding equilibrium coefficient should not exceed 500.

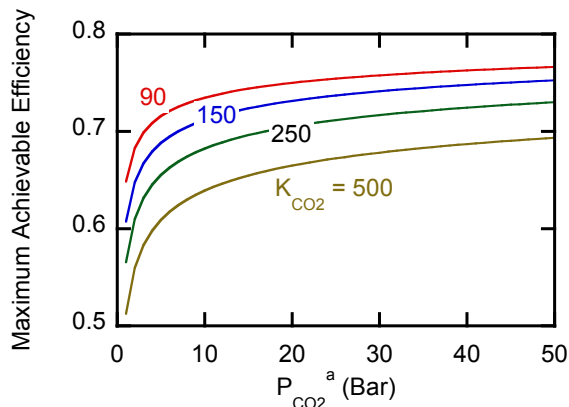


Fig. 3. Thermodynamically achievable efficiency of an EMAR process based on anode desorption pressure and  $\text{CO}_2$  binding constant,  $K_{\text{CO}_2}$ .

We evaluated the EMAR process through (i) absorption experiments to show the effect on the  $\text{CO}_2$  loading of the addition of cupric ions to the solution, (ii) measurements of the open-circuit potentials to enable determination of the electrical work required to separate the  $\text{CO}_2$  and to determine the binding constants, and (iii) a study of the kinetic over-potentials under various operating conditions to enable assessment of potentials needed to sustain a desirable current density.

Figure 4 shows the  $\text{CO}_2$  capacity per amine functional group as a function of the cupric ion loading per amine functional group, from which it is evident that as cupric ions are added, the  $\text{CO}_2$  capacity of an EDA solution drops by 2 moles  $\text{CO}_2$  per mole of  $\text{Cu}^{2+}$ . In the absence of cupric ions, the EDA binds slightly over 0.5 moles  $\text{CO}_2$  per mole of amine functional group, which indicates that carbamate formation dominates over bicarbonate formation. When the cupric ion concentration reaches half the ethylenediamine concentration, the  $\text{CO}_2$  capacity of the solution becomes negligible. Thus, we conclude that the change in  $\text{CO}_2$  capacity upon oxidation of a copper electrode is 1 mole  $\text{CO}_2$  per mole of electrons.

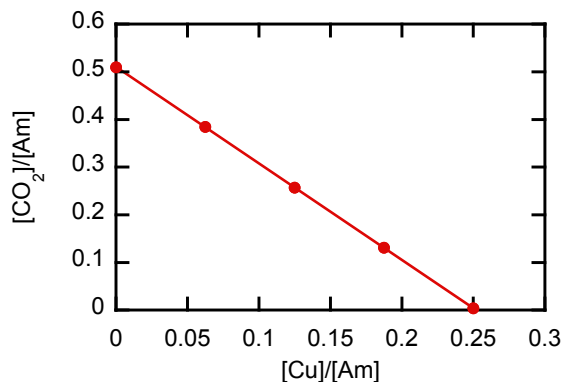


Fig. 4. Thermodynamically achievable efficiency of an EMAR process based on anode desorption pressure and  $\text{CO}_2$  binding constant,  $K_{\text{CO}_2}$ .

The open-circuit potential difference between anodic (CO<sub>2</sub> saturated) and cathodic (inert atmosphere) conditions based on an anode pressure of 1 atmosphere is given in Figure 5. The potential is nearly constant over the entire range of copper loadings and averages 0.19 volts at 50°C. A constant potential is expected since the EDA/copper complex does not change under the different copper loadings tested or due to the presence of CO<sub>2</sub>. UV-visible spectra (data not shown) confirm that the complex is consistent under all tested conditions. The slight drop in potential is likely due to concentrated solution effects.

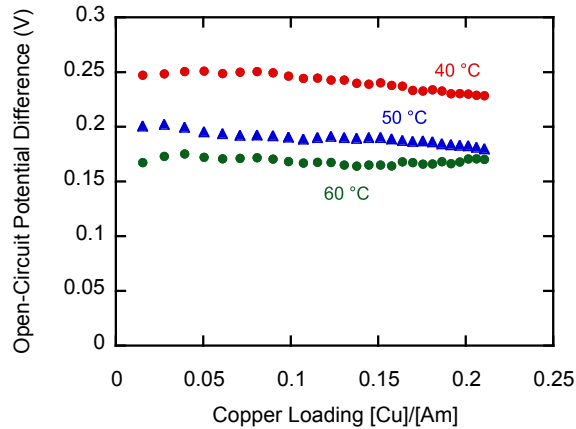


Fig. 5. Open-circuit potential difference of EDA/Cu<sup>2+</sup> solution between anodic and cathodic conditions at 40, 50 and 60 °C.

The work required is the product of the charge and voltage and equals 18.3 kJ/mole CO<sub>2</sub> separated at 50°C. This number is slightly more than double the reversible value required for complete separation of a 10% CO<sub>2</sub> in nitrogen stream at 50°C. By operating at higher temperatures, the open-circuit potential is reduced and leads to lower energies of separation. If the temperature is increased beyond 75°C, however, the loading of the CO<sub>2</sub>-saturated EDA solution will drop below 0.5 mole CO<sub>2</sub> per mole of amine functional group and begin to increase the charge required for separation. The work of separating one mole of CO<sub>2</sub> from flue gas conditions to a pure CO<sub>2</sub> stream at other anode pressures can be obtained from the equation

$$W_{CO_2} = RT \ln \left( 1 + K_{CO_2} P_{CO_2}^a \right) \frac{1 + K_{CO_2} P_{CO_2}^{Flue}}{K_{CO_2} P_{CO_2}^{Flue}} \quad (2)$$

Values of the CO<sub>2</sub> binding constant were determined as a function of temperature using measured open-circuit potentials in the presence of 1 bar CO<sub>2</sub> and in air using the equation

$$K_{CO_2} = \exp \left[ \frac{F}{RT} (V_{CO_2} - V_{air}) \right] \quad (3)$$

where  $V_{CO_2}$  and  $V_{air}$  refer to the open-circuit potentials under CO<sub>2</sub> and air atmospheres, respectively. Figure 6, which shows the variation of  $K_{CO_2}$  with temperature, indicates the optimal temperature range over which the value of  $K_{CO_2}$  is between 250 and 500 runs from about 63 to 70 degrees Celsius.

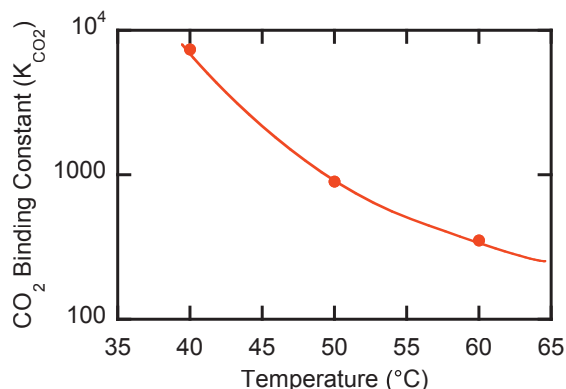


Figure 6: Calculated CO<sub>2</sub> binding constants based on open-circuit potential measurements at different temperatures.

For the EDA solution to demonstrate sufficiently facile kinetics, the total over-potential should be less than 50 mV for the anode and cathode combined in the thermodynamically desirable temperature range. Measurement of the cathode over-potentials was done in an air atmosphere (since the CO<sub>2</sub> should already have been removed before the solution enters the cathode) while anode measurements were done in CO<sub>2</sub> saturated solutions. If the process of copper oxidation is concerted (the CO<sub>2</sub> leaves the amine and the amine attacks the copper surface simultaneously), then we would not expect significant differences in the kinetic over-potentials when operating at CO<sub>2</sub> pressures above 1 atmosphere.

Figure 7 shows the anodic and cathodic overpotentials required at a given temperature to achieve a current density of 50 A/m<sup>2</sup>. In the thermodynamically desirable window of 63°C to 70°C, the kinetic over-potentials are below the 50mV goal, which is a strongly encouraging result. Note that these results are for a solution that is more dilute (four fold so) than the hypothetical working solution, and thus overestimates the needed overpotential. Conversely, the transport limitation encountered during these short pulses (0.1 to 0.2 seconds) is less than what might be encountered in a flow cell.

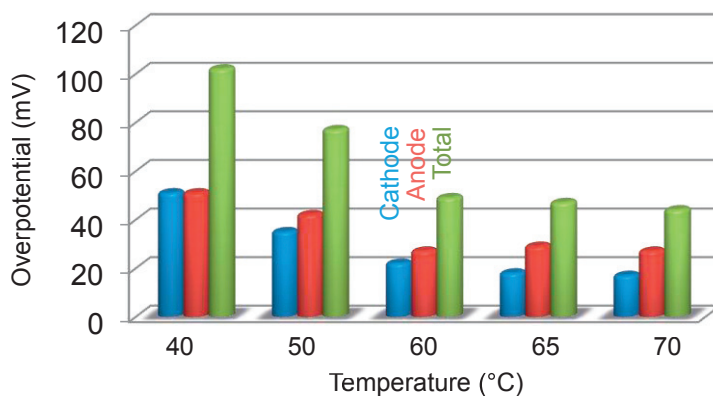


Figure 7: Kinetic overpotentials of the anode, cathode, and combined as a function of temperature.



#### 4. Conclusion

Electrochemically-mediated amine regeneration is a new strategy with the potential to drastically reduce the implementation costs of post-combustion CO<sub>2</sub> absorption separations, without the need for intrusive retrofitting of an existing power plant to extract low-pressure steam for the stripper. The process has the added advantage that the stripper will provide a considerably leaner solvent feed to an absorber, reducing the required absorber size. It has been shown that amines such as ethylenediamine (EDA) release captured CO<sub>2</sub> when they form soluble complexes with cupric ions in solution, and can be regenerated on reduction of the copper ions. Preliminary experimental results show the ability to desorb CO<sub>2</sub> and regenerate an ethylenediamine solution at only double the theoretically-reversible work. Optimization of the chemistry and operating conditions should lead to significantly higher attainable efficiencies, and are the subject of ongoing studies.

#### Acknowledgements

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