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Electrochemically Mediated Separation for Carbon Capture

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Abstract

Carbon capture technology has been proposed as an effective approach for the mitigation of anthropogenic CO₂ emissions. Thermal-swing separation technologies based on wet chemical scrubbing show potential for facilitating CO₂ capture at industrial-scale carbon emitters; however, the total operational and capital costs resulting from the high energy consumption are prohibitive for their implementation. Electrochemically mediated processes are proposed to be the next generation of CO₂ separation technology that can enable carbon capture to be a more viable option for carbon mitigation in the near future. This technology utilizes electrochemically active sorbents that undergo significant changes in their molecular affinity for CO₂ molecules as they progress through an electrochemical cycle. This nearly isothermal separation process consumes electrical energy to facilitate effective CO₂ capture and regeneration processes under more benign conditions of sorption and desorption than in traditional continuous wet-scrubber operations. This electrically driven separation process has the potential to significantly reduce the difficulty of retrofitting CO₂ capture units to existing fossil fuel-fired power generators. The ease of installing an electrically driven separation system would also allow its application to other industrial carbon emitters. The design of such a system, however, requires careful consideration since it involves both heterogeneous electrochemical activation/deactivation of sorbents and homogeneous complexation of the activated sorbents with CO₂ molecules. Optimization of the energy efficiency requires minimizing the irreversibility associated with these processes. In this study, we use a general exergy analysis to evaluate the minimum thermodynamic work based on the system design and the electrochemical parameters of quinodal redox-active molecules. Using this thermodynamic framework, our results suggest that the proposed technology could capture CO₂ from a dilute post-combustion flue gas and regenerate CO₂ at 1 bar with high efficiency, if a two-stage design is effectively implemented.

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1. Introduction

Anthropogenic carbon dioxide (CO₂) in the Earth's atmosphere has been cited as a primary cause of global climate change [1]. Since the industrial revolution, fossil fuels have become the primary energy source and the driving force for sustainable global economic growth [2]. Human dependence on fossil fuels will likely continue for the rest of this century with the remaining abundance of fossil fuels [3]. To mitigate the CO₂ emissions, major transformation of the global energy supply toward clean energy is necessary. Global efforts to increase the share of renewable energy have been initiated; however, during the coming decades, carbon mitigation and “clean-fossil fuel” development are essential for an effective transition to an environmentally responsible economy [4].

Carbon capture and storage (CCS) technology has been proposed as a promising direction for “clean-fossil fuel” development [5]. The technology works through the direct removal of CO₂ from large-scale carbon emitters and storage in secure geologic reservoirs. Implementation of CCS technology is a challenging task due to the scale at which CO₂ is produced, the energy requirements and the capital expense. Aqueous amine-based wet-scrubber processes have been investigated widely over the past two decades for CO₂ capture [6]. The technology can be implemented at large-scale

carbon emitters; however, the energy requirements and the economical costs of the technology are currently unacceptable for their immediate implementation. In this thermal-swing process, dilute CO₂ is separated from a gas mixture through chemical sorption by an aqueous amine solution. Considerable quantities of steam and heat are required to release the CO₂ after capture at low temperatures. Substantial parasitic energy losses result from the need to use excess steam and heat in order to meet the kinetic requirements of the process [7].

Electrically mediated separations offer a nearly isothermal alternative to the thermal-swing separation strategies typically used for CO₂ capture. The driving force in these systems is supplied through gradients in electric potential, which can be controlled precisely to reduce energy losses. Electrically mediated separations based on membranes impregnated with electrochemically active sorbents were first demonstrated by Ward in 1970 [8]. Shortly thereafter, membrane systems utilizing molten salts were developed for the electrically induced separation of acid gases by Winnick and coworkers [9,10]. The development of these systems was motivated by NASA for the removal of CO₂ during spaceflight due to their ability to effectively, and continuously, remove CO₂ at atmospheric concentrations. Implementation of these systems at industrial carbon emitters is difficult, however, due to extreme operational conditions, high temperature (>400°C) [11].

As an alternative to membrane processes, more classical electrochemically-mediated separation strategies were developed that utilized absorber/desorber cycles. The basis for these processes is an electrochemically active sorbent molecule with a redox state sensitive complexation affinity with the target species [12,13]. Both liquid/liquid extraction and gas stripping applications were shown to be possible at the lab-scale; however, these systems have yet to achieve industrial utility. A few studies considering the mass and energy balances on these processes have been reported by Jemaa *et al.* showing the benefits of such electrochemically modulated complexation (EMC) based separations [14,15], but they were unable to achieve theoretical energy efficiencies in lab-scale experiments [16]. Considering the success of other electrochemical processes (i.e., fuel cells, batteries, the Hall-Heroult process), examination of electrochemical systems for separation purposes could offer significant efficiency improvements over conventional separation techniques.

We propose a modified EMC process to be the next generation of CO₂ capture from dilute gas mixtures. The sorbents for this system are molecularly designed to have CO₂ selective binding sites and be capable of undergoing electrochemical cycles in the presence and absence of CO₂. The change in sorbent oxidation state alters dramatically the CO₂ sorption capacity and thereby facilitates CO₂ capture and regeneration. These redox active sorbents are based on quinone molecules (figure 1), similar to those that facilitate numerous essential biological redox processes [17].

In 1989, Wrighton and Mizzen [18] discovered that the electroreduction of quinones in the presence of CO₂ results in bis(carbonate) formation, and that upon oxidation the quinones, the CO₂ molecules are regenerated. These diketones undergo a reversible, consecutive two-electron reduction to form six-membered aromatic ring structures. Scovazzo *et al.* used quinoidal molecules in a batch EMC separation experiment to capture and regenerate CO₂ from a dilute gas stream [19,20]. Despite the encouraging proof-of-concept study, the system has low energy efficiency and further research was not pursued.

In this report we will use a generalized thermodynamic framework to analyze four possible process configurations of electrochemically mediated separation technology. An overview of the methodology and of an exergy model is provided; the specific details of the model would, however, be beyond the scope of this analysis. The purpose of the model for this report is to analyze the proposed CO₂ separation strategies and evaluate the feasibility of implementing the different configurations.

2. Process Description

An electrochemically mediated separation cycle can be broken down into four steps:

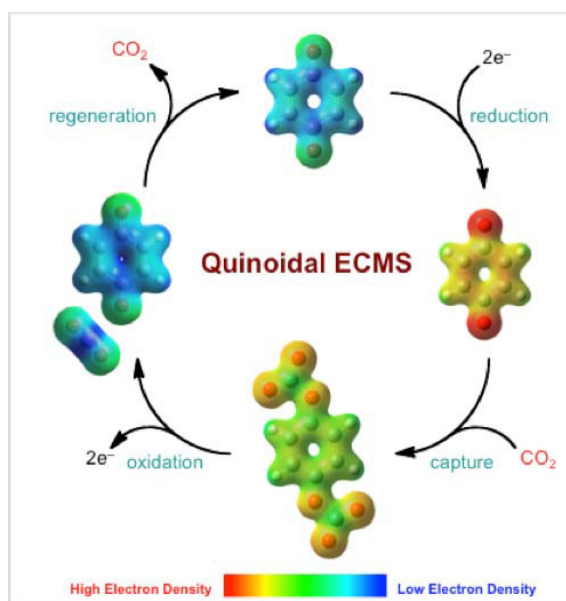


Figure 1. Schematic diagram of the electrochemical cycle of 1,4-benzoquinone during CO₂ capture and regeneration.

1. Activation of the sorbent through electrochemical oxidation or reduction
2. Capture of the target molecules with the activated sorbent
3. Deactivation of the sorbent through the reverse electrochemical process
4. Release of captured target molecules to a pure outlet stream

Previous studies of EMC processes have operated four-stage cycles where each step was performed independently from the other steps (configuration A in figure 2) [16]. Alternatively, these steps could be integrated in a two-stage configuration if steps 1 and 2 are combined or steps 3 and 4 are combined (configuration D in figure 2). Two different three-stage configurations are also possible if a single, two-step integration, is allowed (configuration B and C in figure 2).

Separation of individual stages does allow for less complicated equipment design, since each piece of equipment would be required to have either good gas/liquid transport or good electrochemical kinetics, but not both. Integration leads to the challenge of developing equipment where high gas/liquid contact and high electrode surface area are both accommodated. This is not unprecedented, though, as fuel cells are an apt example of an integrated electrochemical process.

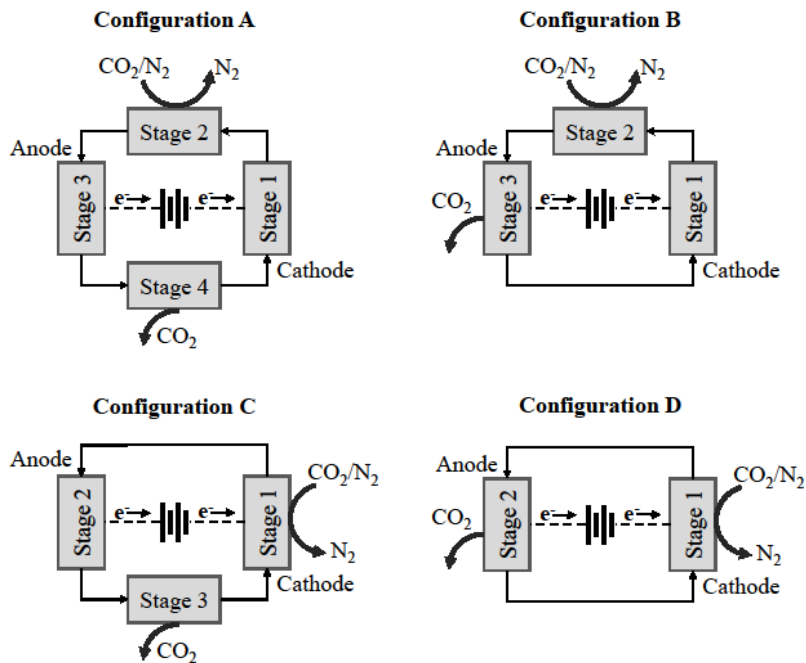


Figure 2. Diagram of the four configurations of an electrochemically-modulated complexation separation process.

In this analysis, we will assume that the gas sorption processes operate in a counter-current flow through configuration. We also will assume that the applied potential can be varied over the corresponding spatial coordinate for the integrated processes. Previous thermodynamic studies of these systems have only considered configuration A, and have not addressed configuration B, C and D. This analysis also considers the two-step reduction mechanism inherent to quinones, which adds significant non-linear elements to the system of equations and has not been previously considered in analyses of EMC systems.

3. Thermodynamic Model

To evaluate whether the efficiency benefits of an integrated system are worthwhile, a thermodynamic exergy analysis must be performed. In this analysis we will calculate how each configuration compares to the thermodynamic limit of a non-interacting (zero mixing enthalpy) gas mixture. The important metric to be evaluated is the electrical energy required to separate a given quantity of CO_2 . We can define this as the energy required to perform one cycle divided by the amount of CO_2 separated by that one cycle.

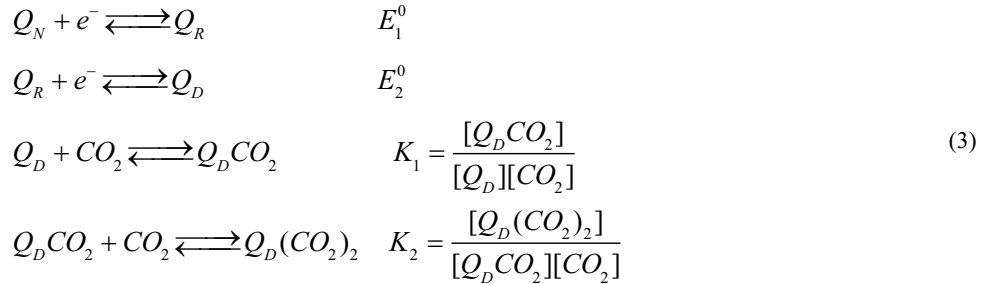
$$W_{sep} = \frac{W_{cycle}}{n_{CO_2}} \quad (1)$$

To calculate the work per cycle we can integrate the potential difference between the anode and cathode, ΔE , over the charge passed during the cycle.

$$W_{cycle} = \int_0^{q_{cycle}} \Delta E dq \quad (2)$$

where q_{cycle} is the amount of charge passed during one cycle. We can relate the difference in potential of the between the anode and cathode as a function of their state variables. If we assume electrodes have equal temperatures and, then we can define the voltages entirely by the concentrations of the different species in the solution. If we further assume that the non-reacting species (i.e., salts and solvents) are at similar activities, we find the concentration of the various quinone species and CO_2 are the only influential state variables if the activity coefficients can be assumed to be unity.

To relate these concentrations to the potential difference in an ideal system, we must first define the system of equilibria that exists in the solution:



where Q_N is neutral quinone, Q_R is radical anion quinone, and Q_D is dianion quinone. We can relate the potential using the Nernst equation for either of the two electrochemical reactions:

$$E = E_1^0 - \frac{RT}{F} \ln \left(\frac{[Q_R]}{[Q_N]} \right) \quad (4)$$

$$E = E_2^0 - \frac{RT}{F} \ln \left(\frac{[Q_D]}{[Q_R]} \right) \quad (5)$$

where E_1^0 and E_2^0 are the formal potentials. By subtraction of equation (5) from equation (4) we find:

$$E_1^0 - E_2^0 = \frac{RT}{F} \ln \left(\frac{[Q_R]^2}{[Q_N][Q_D]} \right) \quad (6)$$

We can define the equilibrium constant for the comproportionation reaction (where one neutral molecule and one dianion molecule form two radical anion molecules), K_{comp} as:

$$K_{comp} = \frac{[Q_R]^2}{[Q_N][Q_D]} = \exp \left(\frac{F}{RT} (E_1^0 - E_2^0) \right) \quad (7)$$

Because of the complexation reactions of the dianion quinone with CO_2 , the concentration of uncomplexed dianion quinone, Q_D , is a function of the equilibrium coefficients as well as the concentration of CO_2 in the solution. We can define the concentration of uncomplexed dianion quinone as a function of all dianion quinones, Q_{D0} :

$$Q_D = \frac{Q_{D0}}{\Psi} \quad (8)$$

where Ψ is equal to:

$$\Psi = 1 + K_1[\text{CO}_2] + K_1K_2[\text{CO}_2]^2 \quad (9)$$

Here, the terms K_1 and K_2 refer to the complexation equilibriums constants for the last two reactions in equations (3). Through incorporations of equations (5), (7), (8), and (9) as well as a total quinone balance and a charge balance, it is possible to derive an explicit expression for the potential as a function of CO_2 concentration (or Ψ), quinone reduction fraction, γ , and comproportionation constant:

$$E = f(\gamma, \Psi, K_{comp}) \quad (10)$$

where γ is defined by:

$$\gamma = \frac{q_{cycle}}{2Q_0F} \quad (11)$$

where Q_0 is the total quinone concentration. The reduction fraction defines the amount of reduction (electrons transferred) with respect to the maximum possible. A reduction fraction of zero would represent all of the quinones in the neutral form, while a value of one would signify all of the quinones in the dianion state.

Now that we can explicitly calculate the potential given the three dimensionless parameters of the system, we can revisit equation (2) and show:

$$W_{cycle} = 2Q_0F \int_0^{\gamma_{cycle}} \left(\left[f(\gamma, \Psi([\text{CO}_2]), K_{comp}) \right]_{anode} - \left[f(\gamma, \Psi([\text{CO}_2]), K_{comp}) \right]_{cathode} \right) d\gamma \quad (12)$$

where we have noted that the parameter Ψ is a function of the CO_2 concentration at the given electrode. To evaluate equation (12) we must know the concentration of CO_2 at both electrodes as the process progresses. This is where the configuration of systems makes a significant difference. Highly integrated processes (configuration D) have higher CO_2 concentrations at the cathode and lower concentrations of CO_2 at the anode compared to non-integrated systems (configuration A) leading to smaller potential differences and thus better efficiencies.

In some cases, determination of the CO_2 concentrations is trivial (such as there is no CO_2 present at the cathodes in configurations A and B). In other cases, however, the CO_2 concentration changes as the stage progresses through space (due to the counter-current flow-through setup). In these instances, the partial pressures of the CO_2 in the inlet and outlet streams become important. Table 1 shows a brief overview of the different equations for calculating the CO_2 concentration in the different configurations.

Table 1. Descriptions of the CO_2 partial pressures at the electrodes for the four different configurations.

	Configuration A	Configuration B	Configuration C	Configuration D
$[\text{CO}_2]_{\text{Cathode}}$	0	0	$g(P_{in}, x_{cap})$	$g(P_{in}, x_{cap})$
$[\text{CO}_2]_{\text{Anode}}$	$f(P_{in}, x_{cap})$	P_{out}	$f(P_{in}, x_{cap})$	P_{out}

Table 1 shows that when the first and second step are decoupled (configurations A and B), there is no CO_2 present in the cathode, and when they are coupled (configurations C and D), the CO_2 is a function of the incoming partial pressure,

P_{in} , and the capture fraction, x_{cap} . The function $g(P_{in}, x_{cap})$ can be considered an effective, or averaged, concentration similar to a log mean average used in counter-current heat exchanger problems.

The function $f(P_{in}, x_{cap})$ refers to concentrations at the anode. In the configurations A and C, the CO_2 is not released until after the quinones are oxidized back into their non-reactive form. In this case, a large quantity of CO_2 is trapped in the anode and cannot be released until the next stage. Thus, the concentration of CO_2 becomes very super saturated in the solution towards the exit of the anode. In contrast, since the last two steps are coupled in configurations B and D, we find that the CO_2 can be released at its desired pressure, P_{out} , which should lead to significantly reduced CO_2 concentrations in the solution.

The last unknown parameter value, seen in equation (1), is the number of moles separated per cycle. In the simple case where physical sorption into the solvent is negligible, we could assume that all the CO_2 that was bound entering the anode would be separated and removed. This assumes that both the physical sorption into the solvent and bonding by the deactivated quinones is negligible. In this analysis, we do consider the effects of sorption into the solvent by defining our complexation efficiency as:

$$\eta_{complex} = \frac{Q_{D0} \frac{K_1[CO_2] + 2K_1K_2[CO_2]^2}{\Psi}}{q_{cycle}/F} \Bigg|_{anode} - \frac{[CO_2]}{q_{cycle}/F} \Bigg|_{cathode} \quad (13)$$

where the first term considers the amount of captured CO_2 entering the anode and the second term considers the amount that must remain in the solvent when it re-enters the cathode.

4. Result and Discussion

Because the majority of calculations cannot be solved analytically, numerical methods were employed using codes developed in-house with MATLAB® software. For the analysis in this report we will assume that the total inlet and outlet pressures are at 1 bar. We define the approach to ideality as the efficiency of the given configuration with respect to the fully reversible one-stage thermodynamic limit. It is assumed that the configurations are operated at their own highest possible efficiency given the parameters of the system. A real system would not be expected to reach these idealized efficiency limits.

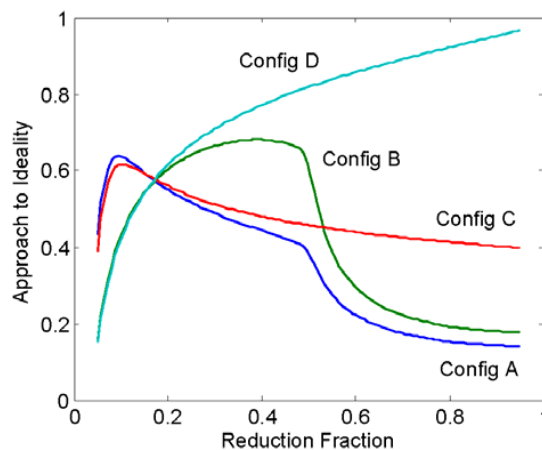


Figure 3. Comparison of the energy efficiencies for the four configurations as a function of reduction fraction. The parameters used were $K_{comp} = 7 \cdot 10^{11}$, $K_1 = 5 \cdot 10^{12} \text{ M}^{-1}$, $K_2 = 10^5 \text{ M}^{-1}$, $y_{CO_2}^{in} = 0.12$, $x_{cap} = 0.9$, $H = 100 \text{ bar/M}$ (where $[CO_2] = y_{CO_2} \cdot P/H$).

Figure 3 shows the efficiency (with respect to the ideal work of separation) of each of the four configurations as a function of the reduction fraction, γ . Figure 3 illustrates the dramatic effect that configuration and reduction fraction can have on the efficiency of the process. Several important trends can be deduced:

1. Systems without integration at the cathode (configurations A and B) suffer significant efficiency losses when the reduction fraction is greater than 0.5. This occurs because the systems must now use higher potentials to reduce the radical anions to the dianions without the stabilization afforded by CO_2 complexation.
2. Systems without integration at the anode (configurations A and C) suffer in efficiency as the reduction fraction increases because the concentration of CO_2 in the anode becomes very large as the CO_2 is desorbed without being removed.
3. Systems that are fully integrated (configuration D) perform the best, but still suffer some inefficiency at low reduction fractions. This is caused by the losses due to physical sorption of the CO_2 into the solvent as well as losses due to the abrupt increase in CO_2 partial pressure as the system changes from stage 1 to stage 2.

Using the model, we can also identify important metrics that must be considered when designing electrochemically-mediated separation processes with twice reduced sorbents. In the previous section we introduced the dimensionless parameters Ψ and K_{comp} , which both influence the energy efficiency and the sorbent capacity. The sorbent capacity is a strong function of the ratio of the two parameters at the inlet of the cathode. Figure 4 shows the complexation efficiency or capture fraction for different ratios of Ψ over K_{comp} .

Figure 4 shows that for ratios of $\Psi/K_{\text{comp}} < 0.1$, the capacity of the system is small when the reduction fraction is below 0.5. This is because it is more favorable for the quinone to exist in the radical form than the different CO_2 adducts. For systems where this low fraction exists, any configuration where the cathode is not integrated (A or B) would be impossible. As the ratio increases to unity and larger, the system approaches its capacity limit where the capture fraction equals the reduction fraction. This is representative of each electron being able to capture one molecule of CO_2 , which is the stoichiometric limit shown by the mechanism in equation (3). Ratios greater than ten do not appreciably increase the amount of CO_2 captured per quinones reduced, but may adversely affect the efficiencies in certain configurations.

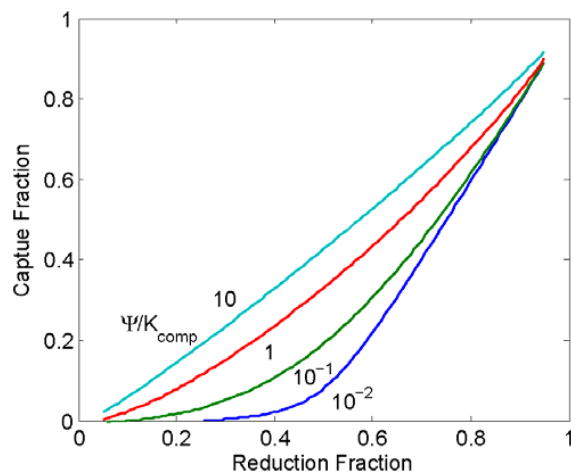


Figure 4. Influence of Ψ/K_{comp} (line labels) and reduction fraction on the sorbent CO_2 capacity (normalized by the maximum value of twice the quinone concentration).

5. Conclusion

A thermodynamic model has been introduced and utilized to determine the feasibility of an electrochemically-modulated complexation separation process for CO_2 separation using quinone sorbents. Both the system configuration and the properties of the electrochemically active sorbent strongly influence the thermodynamic efficiency and the capacity of the sorbent. It was demonstrated that integration of the four steps into a concerted two-stage system provides the highest efficiency process, while a four-stage process cannot be expected to perform with sufficient efficiency to justify its use for CO_2 capture. It is worth further investigation to determine the sensitivities of the two- and three-stage configurations to the operating and electrochemical parameters of the system as they afford much better performance than the four-stage system.

Before losses due to solution resistances and overpotentials, two and three stage processes offer approaches to ideality of >95% and >65%, respectively.

6. Acknowledgements

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