Analysis and Design of Electrochemically-Mediated Carbon Dioxide Separation

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Design of Electrochemically-Mediated Carbon Dioxide Separation

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ABSTRACT

Large-scale carbon dioxide (CO₂) separation is essential in the efforts to curb climate change, with applications in power stations, natural gas purification and enhanced oil recovery. Current CO₂ capture technology is energetically intensive, and challenging to deploy in existing power stations.

Electrochemical CO₂ separation is a novel technology that has the potential to reduce CO₂ capture costs. By cycling of metal ions to modulate the CO₂ affinity of amine sorbents, energy and capital requirements can be significantly cut. The feasibility of this approach was previously demonstrated with a proof-of-concept device, but was limited by low energy efficiency and instability. This thesis describes a systematic effort to optimize this technology by exploring its design space, and identifying conditions for robust, energy efficient operation.

The large effect of electrolytes on activation kinetics was explored via galvanostatic pulse voltammetry and bench-scale experiments. In the presence of halide electrolytes, energy efficiency was improved for short times, but bench-scale experiments showed an increase in resistance for longer operation, possibly due to electrolyte inclusion in the metal deposit. For the set of the electrolytes tested, nitrates were found to drive the most stable kinetics at moderate energy efficiencies.

To explore the electrochemical cell performance for a range of designs and operating conditions, a modeling framework combining thermodynamics, electrode reactions and mass transfer was developed. Model predictions suggest the cell will operate in a mixed kinetic-mass transfer regime at the desired current densities. Model results further predict that introducing flow field disturbances to induce mixing between the bulk and boundary layer will improve energy efficiency significantly.

A bench-scale system with modular internals was constructed and used to investigate performance effects of flow field designs. Model predictions were found to be in good qualitative agreement with experimental results. Under optimized conditions, an almost 70% lower voltage at 50 A/m² was demonstrated. Electrochemical impedance spectroscopy experiments provide further evidence to the mixed kinetics-mass transfer regime of operation. A detailed energy and cost analysis was performed, and results suggest that this technology can cut capture costs significantly if the performance improvement can be sustained for longer operation.

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Chapter 1

Introduction

Executive Summary

As the world population grows and standards of living improve, providing low cost energy to drive the global economy while addressing risks associated with climate change becomes more challenging. Current greenhouse gas emission rates from fossil fuel-based energy infrastructure run the risk of exceeding the world’s carbon budget, the limit for total emissions to keep atmospheric carbon dioxide (CO₂) concentrations below levels predicted to cause significant climate change. The transition of energy generation infrastructure to renewable sources will occur over decades, exacerbating the climate change challenge. This thesis focuses on developing a novel, electrochemical CO₂ separation technology that has the potential to allow for cost-effective energy from existing infrastructure at a fraction of emissions.

Cost-effective separation of CO₂, the most prevalent greenhouse gas, and its subsequent utilization or sequestration, can open a path to a low carbon economy with existing energy infrastructure. However, current technologies for CO₂ separation suffer from low energy efficiencies and massive capital requirements, which hinders their large-scale deployment beyond natural gas separations. Thermal amine scrubbing, the *de facto* state-of-the-art CO₂ separation technology, uses amine sorbents to reversibly bind CO₂ molecules from gas mixtures, followed by a temperature swing to regenerate the sorbent and produce a pure CO₂ stream. Thermal amine scrubbing shows excellent performance with high selectivity and durability, but requires massive amounts of steam for operation, limiting the technology’s utility in capturing emissions from power plants and industrial sources.

Electrochemically-mediated Amine Regeneration (EMAR) technology offers an alternative approach to sorbent regeneration that can potentially cut capture costs significantly. The reversible binding of metal
ions with amine sorbents under a voltage swing was shown to effectively control the capture and release of CO₂. The process costs are intrinsically competitive: commodity materials, amine sorbents and copper metal, are controlled by a targeted electrical current in a potentially high energy process that eliminates the need for expensive modifications to existing CO₂ sources for deployment.

A proof-of-concept device demonstrated the feasibility of the EMAR technology: copper ions generated at the anode of a simple electrochemical cell strongly bind a polyamine sorbent loaded with CO₂, forcing gas release and bubble formation, and at the cathode side of the cell, these copper ions were redeposited from their polyamine complex, and the rate of CO₂ generation was controlled by applied current.

This thesis provides a systematic exploration of the EMAR technology's design space, combining modeling and experiments to understand underlying processes and optimize process performance. The proof-of-concept device design suffered major limitations, resulting in energy consumption significantly higher than required for feasible operation. An analysis of the electrochemical cell performance suggests a significant opportunity for improvement by design optimization. The design space for the technology is vast, and requires a systematic effort to evaluate various energy contributions, a modeling framework to explore design parameters effects on performance, and high throughput experiments to test designs.

Chapter 2 is focused on the evaluation of possible electrolytes for the process, and their significant effects on stability and energy performance. Small-scale three-electrode experiments are used to explore the effect of electrolytes and their behavior as additives. Open circuit experiments supported by UV-VIS spectroscopy suggest electrolytes have no appreciable impact on copper/amine complex formation, and that their mechanism of action is kinetic in nature. Galvanostatic pulse experiments are used to probe the activation overpotentials at various current densities for a set of electrolytes. Results demonstrate a significant change in behavior under EMAR anodic and cathodic conditions. Bromide salts are found to reduce activation overpotentials, while nitrates and chloride salts show a slower but reasonable performance. Bench-scale testing of bromide salts finds their enhancement effect to subside quickly. XPS analysis of the formed copper deposit suggests that the electrolyte is co-deposited and is possibly causing an increase in contact
Nitrate salts are found to have more stable performance, and are utilized in further studies. A mechanistic discussion suggests that electrolytes act to modulate activation overpotentials by acting as ligand-bridges for an inner-sphere electron transfer mechanism. Further screening of a larger set of electrolytes guided by this hypothesis is recommended.

Chapter 3 develops an analysis of the effects of design and operating parameters on the electrochemical cell performance. A two dimensional modeling framework is built to explore those effects, tracking the copper ion concentration in each electrode compartment. Electrochemical thermodynamics are modelled through the Nernst equation, and activation kinetics are represented by the semi-empirical Butler-Volmer equation with experimentally derived parameters. Ohmic losses are modeled by a linear solution and contact resistance measured using Electrochemical Impedance Spectroscopy. Bubble overpotentials are included through an estimate of their electrode blocking effects. Half-cell coupling is achieved through a constraint on applied voltage distribution. The system equations are solved numerically, and a parametric study is performed. Model predictions suggest large mass transfer limitations, manifesting in a large difference in concentration at the electrode surface and in the bulk and a thick boundary layer. Higher superficial velocities, through smaller channel depth and higher flowrates, will improve mass transfer and lower thermodynamic penalties, but result in lower utilization. The design rules inferred from modeling predictions are used to guide prototype optimization.

Chapter 4 critically assesses the current EMAR cell design, and discusses design improvements aimed at facilitating high throughput design testing and stable operation. An upgraded modular design, EMAR 5.0, is designed and constructed with the purpose allowing rapid design changes and tests. A multi-electrode prototype, EMAR 6.0, is developed to allow spatial resolution of current distribution and allow further probing of internal cell processes. Finally, a high pressure operation prototype, EMAR 7.0, is designed as a step towards demonstrating the technology's ability to capture and release compressed CO₂ by pumping the electrochemical cell to higher pressures.
Chapter 5 explores the performance of bench-scale prototypes designs through their polarization curves and electrochemical impedance spectra. Parametric studies of channel depth and operating flowrate effects qualitatively confirm model predictions, and show high energy efficiency for maximized superficial velocity. Experimental trends suggest cell operation at desired current-densities is in a mixed mass-transfer/activation control regime. To limit the loss of utilization for higher superficial velocity, an optimization strategy utilizing serpentine flow fields is tested. Modeling predictions suggest that efficient remixing of bulk and surface streams inside the cell will improve performance significantly. Serpentine flow fields are tested, and shown to successfully improve energy efficiency, demonstrating a record 30 kJ/mole CO₂ captured at a current density of 50 A/m². Electrochemical Impedance Spectroscopy experiments at the bench-scale provide further evidence on the mixed regime operation of the process, and the effect of flowrate on performance. A short-study of membrane effects suggests an important effect of membrane pore size on performance, indicating a potential electrolyte migration effect can be important, particularly at higher current densities.

Chapter 6 serves to combine the modeling and experimental results into a holistic performance analysis of the EMAR technology. Energy performance and capture costs are analyzed for an upper bound scenario assuming no mass transfer limitations, and a scenario building on bench-scale results. The analysis finds that the EMAR process, if long stable operation is feasible, can potentially cut capture costs significantly. A sensitivity analysis shows that the cost structure is most sensitive to energy costs and project lifetime.

Chapter 7 provides an outlook of the EMAR technology, and the major priorities for further research and development. Optimization targets for the current prototype generation are outlined. A scaled-up version of the cell to demonstrate cell stacking is discussed. Exploration of other promising chemistries and extension to other Sulphur acid gases are also proposed. Chapter 8 reiterates the main conclusions of this work, and Chapter 9 complements it with a financial and business analysis of industrial deployment contexts and a potential go-to-market strategy.
The remainder of this chapter provides a more detailed motivation for cost-effective CO₂ separations technology, analyzing the climate change challenge and the role of existing energy infrastructure. A short discussion of existing CO₂ separation technologies contrasts the state-of-the-art with the potential advantages of the EMAR technology. An analysis of previous EMAR development efforts serves to bring context to the work performed in this thesis, and to outline its guiding methodology.

Motivation

**Climate Change and Carbon Dioxide**

Climate change is one of the most critical global challenges in the 21st century. Scientific consensus on the effect of anthropogenic carbon dioxide emissions on climate change is strong. Numerous studies and reports, including by the Intergovernmental Panel on Climate Change (IPCC) (1) and the National Academy of Sciences (2), critically compiled and assessed scientific evidence and concluded that greenhouse gas emissions from human industrial activity are the main driving force for climate change (3).

Since 1970, the rate of global temperature increase has nearly tripled from pre-industrial rates, to 0.16°C per decade (4). Figure 1-1 shows historical mean temperatures by the National Aeronautics and Space Agency (NASA), demonstrating a clear upwards trend.

![Global Land-Ocean Temperature Index](image)

Figure 1-1: Global land-ocean Temperature Index from 1880 till present. Data by NASA's Goddard Institute for Space Studies, reproduced from (5)
Greenhouse gases, like CO\textsubscript{2}, accumulate in the atmosphere and alter the earth’s ability to undergo radiative cooling, gradually causing changes in surface and ocean temperatures (6), thought to be irreversible (7). Major climate changes include change in extremes in temperature and precipitation, increase of sea levels (8) and water CO\textsubscript{2} concentrations, and many other secondary effects (9). Atmospheric CO\textsubscript{2} concentration has risen from 280 ppm before industrialization and reached 400 ppm in May 2013; Figure 1-2 shows the historical trends. Anthropogenic CO\textsubscript{2} emissions from energy infrastructure and industrial activity are the major driver for this increase in CO\textsubscript{2} concentration (10).

![Figure 1-2](image)

**Figure 1-2**: Average atmospheric CO\textsubscript{2} concentration, as measured by Mauna Loa Observatory, Hawaii. Figure reproduced from data the National Oceanic and Atmospheric Administration (NOAA).

Continued increase in global temperature and climate change at current rates is predicted to have a massive negative global impact (11). Agricultural yields are predicted to be dramatically affected. For example, corn and soybeans production in the United States which currently account for about 40% of the world’s production of these crops, can fall by up to 30%-50% under the slowest warming scenario (12). A potential increase in the frequency of occurrence of extreme weather events, like hurricanes, floods and droughts, will result in massive economic losses (13). Overall ocean acidification due to CO\textsubscript{2} absorption, around 0.1 pH unit since preindustrial periods, will significantly reduce aquatic diversity and disrupt marine ecosystems (14).
Energy Infrastructure and Emissions

Thus, significant reduction in carbon emissions, primarily from fossil fuels, is necessary to avoid the adverse effects of climate change (15) (16). However, current global energy infrastructure is dominated by fossil fuels, and various outlooks and analyses predict that a shift to renewable energy will require several decades to occur (17) (18). The US Energy Information Administration (EIA) outlook predicts that by 2040 fossil fuels will continue to supply more than 75% of the US primary energy needs (19).

![Figure 1-3: US primary energy consumption by fuel, 1980-2040. Reproduced from (19).](image)

For example, coal-fired power plants, responsible for 40% of US missions (20), will remain an important component of electricity production, and are projected to account for 38% of electricity generation in 2035 (21). At current emissions levels, the 2°C threshold for global temperature increase (the limit predicted to precede massive climate change effects) will be exceeded.

Carbon Capture and Sequestration

Emissions from existing infrastructure must therefore be addressed in the interim period as the global energy infrastructure transitions to low emission sources. To that end, carbon capture and sequestration
CCS is a critical component of environmental policy aimed at curbing greenhouse gas emissions in the next few decades (22). Analysis by the International Energy Agency predicts that over 100 GW of coal-fired power plant capacity must be retrofitted with CCS to achieve climate change mitigation objectives (23). The IPCC report on CCS provides a detailed analysis of the importance and feasibility of this approach in contributing to the transition to a low carbon economy (24).

CCS relies on cost-effective separation of CO₂ from flue or industrial gases, compression (to around 150 bars) and transport via pipeline to a sequestration site. Sequestration can also involve transformation, and a growing body of literature exists for development of technologies to convert CO₂ to higher value products, including reduction to carbon monoxide, methanol and formate among other target molecules (25) (26).

However, given the billions of tons of CO₂ that must be sequestered, larger-scale approaches are necessary, as the markets for high value-added chemical can quickly become saturated with the massive possible amounts of CO₂ based products. Sequestration of captured CO₂ into deep saline aquifers is feasible in terms of scale (25), but economically challenging without significant government subsidies.

A more economically feasible approach is the sequestration of CO₂ in mature oil fields. The pressurized gas can serve to extract large volumes of oil from existing oil fields at a competitive cost. Figure 1-4 shows a schematic of the process. Supercritical CO₂ injected into a mature oil reservoir becomes miscible with oil. A component of the injected CO₂ dissolves in the crude, reduces its viscosity and increases its flow, but the majority of the gas remains in the oil reservoir (26).

The subsequent combustion of oil implies the substitution of higher carbon-footprint from traditional reservoirs with oil from CO₂ EOR, cutting the carbon footprint of oil by more than two-thirds (27). CCS coupled with enhanced oil recovery (EOR) can sequester massive amounts of CO₂ by producing low carbon footprint oil using existing infrastructure (28).
**CO₂ Separation in Natural Gas Purification**

In addition to being a centerpiece technology for CCS applications, separation of CO₂ from gas mixtures is important in a number of other contexts that are worthwhile to outline briefly. The most prominent application is in natural gas purification, where the acid gas must be removed before natural gas is transported by pipeline or in liquefied form, to avoid corrosion and solid formation, respectively. This application has been historically the driving force for the inception and development of carbon dioxide separation technologies. Today, a large number of commercial scale plants exist to purify natural gas by removal of CO₂.
Carbon Dioxide Separation

The previous section outlined the necessity for addressing the climate change challenge, and the importance of minimizing greenhouse gas emissions from existing energy infrastructure, as we transition to a renewable energy world. In this section, we further motivate this thesis by briefly analyzing existing carbon dioxide separation technologies and their limitations.

The CO₂ separation challenge involves developing means to effectively remove CO₂ from associated gas mixtures with the highest selectivity, and deliver it in a pure form for further use, sequestration, or venting (in natural and fuel gas applications). The most relevant gas mixtures are coal-fired power plant flue gases where CO₂ concentration is between 0.12 and 0.15 on a molar basis. For gas-fired flue gas, CO₂ concentration is in the range of 0.05 molar. Other important gas mixtures include natural gas, where CO₂ concentrations range from less than 1% by volume, to more than 20% for reserves in Malaysia and Indonesia.

From a thermodynamic perspective, separating CO₂ from a gas mixture can be thought of as a de-mixing process, where the entropy of an ensemble of molecules system is reduced, and thus a net energy input is required to drive this separation.

The fundamental energy consumption limit for CO₂ separation is the Gibbs free energy arising from the entropic penalty of separating a gas into its components, which can be computed as:

\[ W_{lim} = RT \sum x_i \ln x_i \]

where R is the Universal Gas Constant, T is the operating temperature and \( x_i \) is the mole fraction of gas.

For coal-fired power plant flue gas, this penalty amounts to 7-9 kJ/mole CO₂ captured. This presents a lower bound for energy consumption for any CO₂ separation process.

A number of different approaches for carbon dioxide separation in power plants and industrial settings have been developed, and are summarized in Figure 1-5. Pre-combustion and oxyfuel are promising approaches,
but relevant only in the case of new power plants, as they require fundamental modifications to the combustion and power generation processes. Post-combustion capture is an approach where \( \text{CO}_2 \) is separated from flue gas after oxidation in a boiler and power generation, and is the most promising approach relevant to CCS applications.

Figure 1-5: Summary of approaches to capture \( \text{CO}_2 \) in power plants and industrial settings. Reproduced from (24)

Many post-combustion technologies are in development, and can be categorized according to the separation mechanism to thermal swings, pressure swings and membrane separation. Thermal swing technologies, the most prevalent category, involve capturing \( \text{CO}_2 \) chemically by a sorbent molecule that undergoes a large change in its \( \text{CO}_2 \) affinity between two temperatures. At the absorption temperature, the sorbent readily takes up \( \text{CO}_3 \) from a gas mixture, and subsequently releases \( \text{CO}_2 \) at a higher desorption temperature. From a molecular perspective, a thermal swing relies on an increase in entropic effects with higher temperatures to dominate enthalpic interactions. Pressure swing processes rely on a large change in partial pressure of \( \text{CO}_2 \) to force the gas into and out of a capture material, through a physical or chemical mechanism. Membrane processes utilize materials with high \( \text{CO}_2 \) selectivity and reduced permeability for other gases.
to capture a pure gas stream from a pressurized mixture. A large number of candidate sorbents and processes have been developed and proposed, and a full review is outside the scope of this work. The interested reader is directed to a number of comprehensive reviews (31) (32) (33) (34).

The state-of-the-art technology in CO$_2$ separation for CCS applications is by far thermal amine scrubbing, a technology that has been commercially deployed since before mid-20$^{th}$ century, as early as 1930 (35). Since then, the technology has witnessed wide-scale deployment in the natural gas industry and in refineries across the world, due to its ability to generate CO$_2$ streams of high purity and remove the gas from mixtures to the very low specifications required for natural gas transport. A molecular schematic of the process is shown in Figure 1-6. Due to their basicity, amines have a high affinity for the weakly acidic CO$_2$, and together they form a stable complex that is dissociated at high temperature to release pure CO$_2$ and regenerate the amine solvent.

![Figure 1-6: Schematic of thermal amine scrubbing process](image)

At the process scale, thermal amine scrubbing benefits from decades of equipment optimization, commercial operation and in-depth modeling, and is thought to be rapidly approaching its performance.
limits. Proprietary processes have been developed by many companies including Fluor, Alstom, Siemens, and Mitsubishi, differing primarily in capture agent solution. Figure 1-7 shows an example process flow diagram, featuring Fluor’s Econamine process. In a lower temperature absorber, lean amine is contacted with flue gas to enable CO₂ capture. The CO₂-bound amine then goes to a high temperature stripper, where an entropic driving force facilitates solvent regeneration and the release of a pure CO₂ stream.

Thermal amine scrubbing technology, however, suffers high costs of capture in CCS contexts, especially in retrofit applications (29). This high cost is the result of large energy consumption that significantly derates the power plant electrical output, and high capital cost associated in part with power plant modifications required to enable extraction of low pressure steam for the stripping operation (30) (31). In addition, deploying thermal amine scrubbing in high emission industrial settings where steam is not readily available, such as steel, aluminum and cement plants, presents a further challenge and requires dedicated steam generation equipment.

Thus, a novel post-combustion technology that combines the excellent removal and durability properties of thermal amine scrubbing with electrically-driven operation at high energy efficiency would present a powerful combination and promising approach.

Figure 1-7: Fluor’s Econamine Process Flow Diagram
Electrochemically Mediated Amine Recovery (EMAR)

We recently proposed a novel approach to CO₂ capture that has the potential to significantly improve the economics of CCS. This approach, Electrochemically-Mediated Amine Regeneration (EMAR), is an electrically-driven, highly targeted approach to CO₂ capture that does not require large-scale steam extraction or any expensive power plant modifications. Instead, the EMAR process utilizes redox responsive metal ions to modulate the affinity of amine solvents for CO₂ by competitive complexation. The steam-free nature of the EMAR process eliminates the need for expensive retrofits, and provides for a plug-and-play, drop-in solution. In addition, 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 options.

The EMAR technology replaces thermal stripping operation in an amine-based CO₂ flue gas scrubbing process, and relies on almost isothermal electrochemical cycles rather than the large temperature swings required in conventional absorption/stripping processes. In the stripper, the CO₂ is released upon the acidification of the absorbent stream through the oxidative addition of Lewis acid transition metal cations from a metal anode. Once the released CO₂ is removed, the amines themselves are regenerated for recycle to the absorber by reduction of the metals on electrode surfaces in a cathode chamber, recycling the metal. The flow directions and the polarity of the two electrodes are switched after a period of time to maintain the integrity of the electrodes.

A previously tested EMAR chemistry uses a polyamine solvent to capture CO₂ from flue gas in an absorber operating at a relatively low temperature. To regenerate the solvent and provide a pure stream of CO₂, the CO₂-loaded polyamine solution is pumped to the anode side of an electrochemical cell, where copper ions are generated by electrochemical dissolution. The copper ions formed chelate strongly with the polyamine molecules, releasing CO₂ in the form of gas bubbles by a competitive complexation mechanism. The CO₂ gas is flashed off at the exit to the anode chamber. After the gas bubbles are removed, the copper-loaded amine solution is recycled to the cathode side of the electrochemical cell. At the cathode, copper ions are

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removed from their amine complex by electrochemical deposition. The lean amine solvent is then pumped to the absorber where it performs further separations. The cycle is described schematically in Figure 1-8.

Figure 1-8 Schematic of the EMAR process, showing the competitive complexation of the amine solvent by metal ions formed by electrodissolution, followed by removal of metal ions by electrodeposition.

There are several advantages to the EMAR process:

1. Direct targeting of electroactive metal ions that modulate amine/CO₂ affinity results in higher energy efficiency, in contrast to thermal cycling where significant entropic losses occur as heat is added to the entire medium.

2. Due to the electrically-driven nature of the EMAR process, integration with existing CO₂ sources is straightforward, eliminating the need for expensive retrofits to deliver steam.

3. The electrochemical cell can potentially operate at high pressures, with the CO₂ released as a compressed gas. In the context of power station emissions, captured CO₂ needs to be compressed to around 150 bars to facilitate transportation to a final sequestration site. Since the pumping of a liquid to raise the pressure is significantly more energetically favorable than the compression of a
gas, high liquid pressure operation of the EMAR process can result in significant savings in downstream compression requirements (32).

With a focus on copper metal and polyamines, previous development work showed that the thermodynamics of electrochemically-controlled copper-amine complexation can be energetically efficient and highly favorable. The electrochemical kinetics of copper ion formation and subsequent deposition from its amine complex were studied experimentally for a range of polyamines, and shown to be most facile with ethylenediamine (EDA) (34). A proof-of-concept system was developed and demonstrated, with sustained control of CO₂ capture rate with cycling of electric current (33). There remains, however, a number of challenges that must be addressed to develop the EMAR technology further.

**EMAR Development Challenges**

Early proof-of-concept prototypes were successful in demonstrating the feasibility of the EMAR technology. Fundamental thermodynamic analysis and open circuit experiments for the EMAR system using copper/ethylenediamine chemistry predict high efficiencies that have the potential to significantly change the economic feasibility of large scale CCS in power stations. However, the proof-of-concept prototype operates at significantly lower energy efficiencies than economically feasible for large-scale applications. In addition, the prototype features dendrite formation and transport limitations at high flowrates. Figure 1-9 shows a post-operation cathode for the proof-of-concept system, where copper deposition is on top of a cloth covering the cathode and meant to support the separator. The resulting uneven deposition of copper powder on top of the fabric lead to dendrite formation and caused short-circuiting of the cell.
Figure 1-9: Cathode of proof-of-Concept device after a short duration of operation. The electrode surface is covered with a fabric covered in deposited copper to prevent collapse of separator onto electrode. Such a design imposes a significant limit on stability: Reproduced from (34)

Figure 1-10 shows the current proof-of-concept system energy consumption compared with the thermodynamic limit of the process, based on open circuit potential measurements. The thermodynamic energy penalty using copper/EDA chemistry is only around $15 \text{kJ/mole CO}_2$; however, the proof-of-concept device operates at around $100 \text{kJ/mole}$ at a moderate current density of $50 \text{A/m}^2$.

Figure 1-10: Electrochemical Capture Energy Consumption Profile. Proof-of-concept device consumes more than $100 \text{kJ/mole CO}_2$ at $50 \text{A/m}^2$, significantly higher than the minimum thermodynamic penalty for the EMAR process, $10-15 \text{kJ/mole}$. The estimated limit for economic feasibility is around $55-65 \text{kJ/mole}$.

Bridging the performance gap between the working prototype and theoretical predictions is critical to the continued development of the EMAR process and in bringing it closer to commercial application. It is instructive here to analyze the major processes occurring in the electrochemical cell to understand potential sources of energy inefficiencies and the methodology applied in this work.

Figure 1-11 shows a schematic of the electrochemical cell processes. At the anode side, copper ions are
formed by electrodissolution at the electrode, and must diffuse to the bulk to react with the aqueous CO$_2$-loaded EDA solution according to the reactions:

$$\text{Cu} \rightarrow \text{Cu}^{+2} + 2\text{e}^- \quad (1-1)$$

$$\text{Cu}^{+2} + 2\text{EDA.CO}_2 \rightarrow \text{Cu}^{+2}(\text{EDA})_2 + 2\text{CO}_2 \quad (1-2)$$

The first reaction is thought to occur through a two-step mechanism and to be charge-transfer controlled. The second reaction is much faster, due to the large driving force offered by the strong chelation between copper and EDA. As the dissolved CO$_2$ concentration increases above supersaturation levels, bubbles form spontaneously and are entrained with the flow. The anode outlet solution thus consists of a two-phase mixture with the aqueous phase containing both CO$_2$-loaded and copper-loaded EDA. Gas bubbles are disengaged in an external flash tank, and the aqueous solution reenters the cell at the cathode side. Copper/EDA complex ions must diffuse to the electrode surface where copper is deposited on the surface as per the reaction:

$$\text{Cu}^{+2}(\text{EDA})_2 + 2\text{e}^- \rightarrow \text{Cu} + 2\text{EDA} \quad (1-3)$$

Finally, the regenerated EDA solution is sent to the absorber to once again be available to bind CO$_2$. 

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For a perfectly reversible thermodynamic process, the major energy penalty in this process is the EDA/CO₂ decomplexation energy, since other reactions in the system are reversible and, theoretically, no net change in copper ion concentration should occur at steady state. However, additional thermodynamic losses due to Nernstian concentration terms (i.e. copper concentration differences between the two electrode compartments) occur, as discussed in detail in Chapter 3.

The electrochemical reactions at the anode and cathode will also require an energy input (an activation overpotential) to drive the large currents necessary for industrial operation. As the current density is ramped up, reactant and product concentration profiles will develop, changing the surface concentrations and, consequently, the thermodynamics and kinetics of the process.

The system and cell design parameters can have major nonlinear effects; the flow field (planar in the proof-of-concept device), electrolyte and membrane choices will affect mass transfer and thereby change the
thermodynamic and kinetic behavior of the cell. Operating conditions, like temperature and flowrate, will change the solution properties, including conductivity and viscosity.

**Methodology**

The energy performance of the EMAR system is the nonlinear product of thermodynamics, kinetics and mass transfer properties of the system. The large number of design decisions, including selection of electrolytes, cell flow field and operating conditions, requires a systematic framework to evaluate these choices. The focus of this work, therefore, is to develop a consistent methodology to evaluate energy sinks and their underlying mechanisms, and to link them with the design space. Through a systematic investigation of parameter effects, guided by a modeling framework, the optimization of process energy consumption and stability can be addressed.

The Cu/EDA chemistry demonstrated efficient thermodynamic energy needs, with a minimum energy of less than 15 kJ/mole and compares favorably to the fundamental entropic limit of 7-9 kJ/mole. In addition, Cu/EDA chemistry has a linear behavior at a range of loadings, with stable complexation properties that are conducive to effective operation. For those reasons, this chemistry is used throughout this work, with recommendations for future work to evaluate other potential sorbents. The electrochemical kinetics of copper, and indeed of many metal ion systems, is a strong function of the electrolyte utilized. A logical starting point for this work is to explore this effect, and identify optimum electrolytes that drive stable and energy efficient kinetics. This is explored in Chapter 2, using both small-scale experiments to isolate and quantify activation kinetics, followed by larger bench-scale experiments to evaluate performance at longer time scales.

Building on models of thermodynamics (guided by a Pourbaix diagram for the Cu/EDA system) and kinetics, a cell modeling framework is then developed to improve our understanding of how the electrochemical reaction rates are coupled with flow and mass transfer. Chapter 4 develops this framework, and numerical solution to the developed model with a parametric study of major cell design and operating
conditions.

Chapter 5 analyzes the proof-of-concept device, highlighting its limitations, and efforts to address them. Experiment-specific prototype generations are designed and constructed: EMAR 5.0 with modular internals for parametric study and cell internals optimization; and EMAR 6.0 for analytical resolution of axial distribution of current density to probe internal cell processes. Chapter 6 puts the modeling and experimental results in perspective, by evaluating process energy and costs in the context of power stations at current and upper bound performance. The results are used to identify the main development priorities for the technology, summarized in Chapter 7. Chapter 8 reiterates the main conclusions of this project, while Chapter 9, the capstone paper, complements this work with a financial and business analysis of the deployment of this technology in the market place.

**Specific Aims**

- Understand the thermodynamic landscape for copper/EDA complexes, oxides and other side products.

- Evaluate kinetics with different additives, and develop an understanding of their mechanism of action. The results will help determine additives with the highest voltage and current efficiency.

- Model and optimize flow geometry and membrane materials for high throughput operation. Model results will guide process design towards a more favorable transport profile.

- Redesign, build and operate an optimized EMAR system capable of running at high temperatures and pressures, and evaluate its performance.

- Develop a process-level performance and economic analysis of the system.

- Analyze the EMAR deployment markets and develop a go-to-market thesis.
Chapter 2

Electrochemical Kinetics under Additives

This chapter summarizes investigations of the kinetics of copper deposition and dissolution in an aqueous ethylenediamine solution, and in particular, the effect of electrolyte additives on activation overpotentials. Open circuit experiments and UV-VIS spectroscopy show that additives have no effect on copper complex thermodynamic stability. Fast galvanostatic pulse experiments in the presence and absence of CO₂ demonstrate an appreciable difference in activation kinetics, with bromide salts demonstrating the fastest kinetics. To test electrolytes behavior over longer time scales, an electrochemical cell is constructed and used to probe additive effects. Bromide additives cause a gradual increase in voltage for a given current density, while nitrate salts demonstrate stable, relatively efficient operation (activation overpotentials of 20 kJ/mole of CO₂ captured at 250 A/m²). Mechanistic analysis supported by XPS experiments suggests additives can facilitate charge transfer by acting as a ligand bridge, and that their inclusion in the formed deposit causes an increase in contact resistance. Our results also suggest that copper electrodissolution and deposition kinetics are moderately fast and stable under a nitrate electrolyte.

Additives and Metal Deposition and Dissolution Kinetics

The thermodynamics of electrochemically-controlled copper-amine complexation were previously shown to be energetically efficient and highly favorable for the CO₂ separation application (33). The electrochemical kinetics of copper ion formation and subsequent deposition from its amine complex was studied experimentally for a number of polyamines, and shown to be most facile with EDA (34). Those studies also found a large change in EDA kinetics under sodium chloride and sodium nitrate, particularly in the presence of CO₂, but did not explore this phenomenon in detail. In this work, we further investigate the kinetics of copper deposition and dissolution in EDA, focusing in particular, on the effect of electrolytes.
The enhancing effect of additives on metal deposition and dissolution kinetics is well studied. Bockris and Enyo (35) used galvanostatic transients to study the short time deposition and dissolution of copper under different electrolytes in H₂SO₄, including perchlorate, sulphate and acetate. Their results showed a significant effect of electrolytes on kinetics, where perchlorate ions drove the fastest rates.

Ramos et al. (36) studied the effect of chloride and nitrate anions on copper electrodeposition in ammonia media using cyclic voltammetry and chronoamperometry. They found a small but appreciable effect of the electrolyte choice on peak currents for deposition, with no additive influence on the complex formed. Low charge recovery was observed, and explained by disproportionation reactions, where Cu²⁺ ions react with copper atoms to form Cu⁺ ions.

Soares et al. (37) studied the mechanism of chlorides catalysis on copper ion reduction in acidic media using electrochemical quartz-microbalance experiments. They found a proportional relationship between chloride ion concentration and deposition kinetics. Scanning electron microscopy confirms the presence of CuCl crystals on the copper surface during deposition, suggesting a parallel pathway of copper ion reduction that is modulated by chloride ions.

Similar effects of halide ions on metal deposition were shown by Tsuru et al. (38) for high-speed Nickel electroplating. Campion et al. (39) studied the accelerating effects of chlorides on iron electrochemistry, and explained their findings by the formation of an intermediate anion-bridged complex that facilitates charge transfer. Even with trace amounts of chlorides of less than 1 millimole, Nagy et al. (40) demonstrated significant catalytic effects that are consistent with the anion-bridged complex mechanism, as their theoretical calculations suggest.

Brolo et al. (41) showed that copper dissolution in acidic bromide media proceeds through the formation of a porous copper-bromide film at high overpotentials. A passivating film is formed by the addition of hexamethylenetetramine (HMTA), but only at a higher pH when HMTA deprotonates. Additives have also
been well studied in the context of the damascene copper plating process, where a mixture of inhibitors and accelerators is used to control the properties of the copper deposit (42).

Here, we investigate the effect of additives on the electrochemical dissolution and deposition kinetics of copper in EDA, in the presence and absence of CO₂. These conditions correspond to those prevailing in the EMAR cell, where the cell anode operates under CO₂ rich conditions and the cathode in the absence of CO₂.

The additives tested in this work include two halide anions, bromides and chlorides, widely reported in literature to modulate copper activation kinetics, as well as nitrates. In addition, two cations, sodium and ammonium, are also tested to explore any potential cationic effects on reaction kinetics.

**Experimental Methods**

**Materials**

Solutions were prepared with distilled and deionized 18 MΩ water (Milli-Q). All chemicals used were purchased from Sigma-Aldrich. The background electrolytes used were sodium nitrate (NaNO₃, purity >99%), sodium chloride (NaCl, purity >99%), sodium bromide (NaBr, purity > 99%), ammonium chloride (NH₄Cl, purity >99%) and ammonium bromide (NH₄Br, purity >99%). Cupric ions were added to solutions through the addition of copper nitrate semi(pentahydrate) (Cu(NO₃)₂, purity >98%). Ethylene diamine (EDA) used was of 99% purity. Copper working electrodes and Ag/AgCl reference electrodes were purchased through BASi (West Lafayette, IN).

**Open circuit potential measurements**

Solutions of 1M EDA, 1M electrolyte, and varying quantities of copper nitrate were tested for their open-circuit potential with a copper working electrode versus a Ag/AgCl reference electrode. Measurements were done under argon and pure CO₂ atmospheres with constant bubbling. The potentials were measured using a VersaStat 3 potentiostat (Princeton Applied Research) under light stirring at temperatures ranging from
40°C to 80°C. Temperature was controlled by submerging the electrochemical cell in a temperature
controlled oil bath.

**UV-VIS spectroscopy**

The absorbance of diluted solutions of copper nitrate and EDA was measured for their electromagnetic
absorbance from 400 nm to 1000 nm, in the presence of electrolyte salts. CO₂ saturated systems were
prepared by using CO₂ saturated EDA. All experiments were done at room temperature. Measurements
were taken with an Evolution 220 spectrophotometer from Thermo-Scientific.

**Three-Electrode Experimental Setup**

Electrochemical experiments were performed using a three electrode setup controlled by a Princeton
Applied Science VersaStat 3 potentiostat. The working electrode was a 3.1 mm diameter copper. The length
of the working electrode was sheathed by heat-shrink FEP insulation, which was then wrapped with a
copper mesh that acted as the reference electrode. Another layer of insulation was placed around the
reference electrode, which was covered by another layer of copper mesh that acted as the counter electrode.
This configuration minimizes the distance between electrodes and consequently reduces uncompensated
resistances.

**Galvanostatic pulses**

The galvanostatic pulse experiments applied here follow those of Mattson and Bockris (51) and further
developed for the Cu/EDA system by Stern (34). The electrochemical kinetics of copper deposition and
dissolution, in the absence of mass transfer effects, were investigated with constant-current pulses from
1250 A/m² to 0.25 A/m². Highest current density pulses were performed first, starting always with cathodic
pulses. Pulse length was set according to pulse amplitude (i.e. current density): for current densities larger
than 125 A/m², pulse length was set to 0.01 seconds, while for smaller pulses (≤ 125 A/m²), total applied
charge density was kept constant at 1.25 C/m². Therefore, lower current densities had progressively longer
pulse lengths with a maximum length of 5 seconds for the 0.25 A/m² pulses.
Between each set of experiments (i.e. a set of cathodic and anodic pulses), the electrode was polished with a series of progressively finer polishing solutions. Before each set of pulses, a fresh layer of copper was formed on the electrode by electroplating in the solution at 15 A/m² for 10 minutes.

The kinetic experiments were performed under conditions similar to those in the anode and cathode of the electrochemically-mediated amine regeneration cell. Anodic conditions were simulated by performing experiments under CO₂, saturating the solution for 60 minutes prior to plating, and bubbling CO₂ for the duration of the plating and pulse experiments. Cathodic conditions were simulated by running the experiments under an inert atmosphere, by bubbling argon into the cell during both the pulsing and the electroplating steps. All experiments used 10 mL of solution, gently stirred. Temperature was controlled by submerging of the electrode-cell assembly in a temperature regulated oil bath. The experiments are performed for the entire set of additives at temperatures between 25°C and 75°C. For each pulse, 1000 data points were taken. The experiments were performed in duplicate for each electrolyte under each condition.

**Dynamic Pulse Analysis**

Here, we follow the analysis approach developed by Mattsson and Bockris (51) for copper in acidic media and extended by Stern (34) for copper in amine solutions. Figure 2-1 shows an example of short constant-current pulses in a 1M EDA solution with 0.25M copper nitrate and 1M NaCl electrolyte. The voltage required to drive these cathodic pulses quickly reached steady state, after a steep rise in voltage at the beginning of the pulse due to fast, transient double layer charging.
Activation kinetics parameters are estimated from the experimental data by fitting pulse dynamics to the equivalent circuit shown in Figure 2-2. The circuit includes an uncompensated resistance, $R_u$, a double layer capacitance, $C_{DL}$, in addition to the resistances $R_1$ and $R_2$ and the capacitance $C_2$. These resistances and capacitance are based on the assumption that deposition and dissolution reactions follow a two-step mechanism, as is widely reported for copper metal. Each resistance represents the reaction rate for a step in the two-step mechanism, and the capacitance $C_2$ is a measure of the net generation of the intermediate species (likely Cu⁺) which modulates the reaction rate. It is important to note here that equivalent circuits are not unique, i.e. the same data can be represented by a number of equivalent circuits. Nevertheless, this approach is helpful in quantitatively comparing the performance of different electrolytes in a consistent manner.

If we assume that the double layer capacitance is significantly small compared to $C_2$ so that $R_1C_{DL} \ll R_2C_2$, the circuit can be simplified to that shown in Figure 2-2. This is a reasonable assumption, given the small double layer capacitance of the copper surface in comparison with the faradaic reaction. The voltage response under a constant-current pulse for this circuit can be modeled by:
\[ \eta = i \left[ R_u + R_1 \left( 1 - \exp \left( -\frac{t}{R_1 C_{DL}} \right) \right) + R_2 \left( 1 - \exp \left( -\frac{t}{R_2 C_2} \right) \right) \right] \]  

(2-1)

Here, \( \eta \) is the voltage response, \( i \) is current density and \( t \) is time. For this experimental setup, the measured voltage response of the copper working electrode is against a copper reference electrode, and thus the open circuit potential is zero, and the measured voltage is equivalent to the overpotential.

![Equivalent Circuits](image)

Figure 2-2: Equivalent Circuits. (Top): The equivalent circuit proposed to fit the charge resistance of the system. (Bottom): Simplified equivalent circuit used to fit pulse dynamics data to estimate kinetic parameters. Reproduced from Stern (34).

The difference in time scales is then exploited to isolate the short-term response, which is associated with double layer charging and uncompensated resistances. Stern (34) found that the RC time constant for a Cu/EDA system is less than 0.1 milliseconds and that for shorter times (< 0.05 millisecond), uncompensated resistance and capacitive effects are dominant. The same strategy is followed here, and the first and middle terms in the voltage response equation (2-1) are linearized to yield a linear dependence of voltage on time for short times:

\[ \frac{\eta}{i} = R(t \leq 50 \mu s) = \left[ R_u + \frac{t}{C_{DL}} \right] \]  

(2-2)
The short-time response can thus be used to estimate the uncompensated resistance and double layer capacitance using equation (2-2). This approach to estimate the double layer capacitance follows that utilized by Bockris and Enyo (35). Figure 2-3 shows the resistance versus time for high current density pulses in 1M EDA with 0.25M copper nitrate at 55°C under sodium chloride at short times, comparing experimental data with the fit from equation 2-2. The intercept value is \( R_u \) and the slope is the double layer capacitance. The results show that the short-time response model reasonably represents the experimental behavior.

![Figure 2-3: Short time response model fitted to experimental data for 1M EDA, 0.25M copper nitrate and 1M sodium chloride at 55°C for three pulses (1250, 1000 and 500 A/m²). (Left): Anode. (Right): Cathode.](image)

The values for uncompensated resistance and double layer capacitance are then used in fitting the entire dynamic response to equation (2-1), and to compute \( R_1 \), \( R_2 \) and \( C_2 \). The model fit and experimental data are shown in Figure 2-4 to agree well, suggesting the equivalent circuit proposed reasonably models the pulse dynamics.
Figure 2-4: Dynamic pulse resistance values for 1M EDA, 0.25M copper nitrate and 1M sodium chloride at 55°C, fit to the equivalent circuit model proposed, showing good agreement. Reduced data for three pulses (1250, 1000 and 500 A/m²) are shown here. (Left): Anode. (Right): Cathode.

The pseudo-steady state overpotential value for each pulse is calculated by equation (2-4), an extrapolation of equation (1) to infinite time after subtraction of the uncompensated resistance.

$$\eta(t \to \infty) = i(R_1 + R_2)$$

(2-3)

where the resistances R₁ and R₂ are obtained through the fitting procedure outlined. This pseudo-state overpotential is used as the voltage for a specific current density reported in the results section.

To ensure the current densities tested are not transport limited, we can estimate the time-dependent limiting current for this system as:

$$i_{Limit} = 2F\left( \frac{D}{\pi t} \right)^{1/2} C_0$$

(2-4)

Integration of this equation can provide an estimate of the total charge transported during a pulse in a diffusion limited system for a pulse of length t. For the copper ion complex, the diffusivity is on the order of 10⁻⁹ m²/s. Given an initial copper concentration of 0.25M, the maximum ratio of charge transferred for the highest current density of 1250A/m² is less than 10% of the diffusion limited charge. Transport effects
were therefore assumed negligible and not included in the analysis of galvanostatic pulse experiments.

**Bench-scale Experiments**

The electrolytes were further tested at the bench-scale to evaluate their performance for longer time scales. The closed loop system used for the bench-scale tests consists of an absorber vessel, a flash tank and an electrochemical cell. A CO$_2$-saturated 1M EDA and 0.25M Cu(NO$_3$)$_2$ solution was continuously circulated through the system by a dual-channel MasterFlex pump. The absorber was a 200 mL three neck flask, whose temperature was controlled by submersion in an oil bath heated by a digital hot plate. The flash tank was a 25 mL three neck flask, with a liquid inlet and outlet, and a gas outlet. Before the experiments started, the amine solution was saturated overnight with CO$_2$ by flowing pure gas into the absorber. The saturation was continued until the pH of the EDA solution dropped to 7, indicating full CO$_2$ loading of EDA. The electrochemical cell consisted of two 9" by 3" flow channels, cut out from silicone gaskets, placed on top of the copper plates, with an external aluminum chassis. Copper 101 alloy (purity > 99.99%) was used for the copper plate electrodes and copper wire. A Celgard® 3501 surfactant-coated porous polypropylene membrane separating the two flow channels to prevent gas cross-over was used. A power supply delivered a constant current or voltage to the copper plates through side-protruding copper wires. Between experiments, the copper plates were sandblasted to restore their surfaces. The setup is described in more detail in Chapter [4].

**X-ray Photoelectron Spectroscopy**

To probe the metal deposits formed at the bench-scale, X-ray Photoelectron Spectroscopy (XPS) experiments were performed. After operation, deposits from the cathode of the cell were left to dry overnight and analyzed by XPS for binding energy. A Physical Electronics Versaprobe II X-ray Photoelectron spectrometer was used to perform x-ray photoelectron spectroscopy on the surface. The analysis was performed at ultra-high vacuum (1e-08 bar) with an argon-gun neutralizer. The survey scans
were performed with 10 cycles from 1400 eV to 50 eV at 200 kV with a pass energy of 80 eV and a step size of 0.5 eV.

**Effect of Electrolytes on Complexation Thermodynamics**

The impact of electrolytes on the deposition and dissolution of copper in an EDA solution can be due to either a thermodynamic or a kinetic effect. For example, electrolytes can potentially alter the stability of the copper/EDA complex (CuEDA$_2^{2+}$), experimentally found to be the most stable complex in this system (44), or drive the formation of a different complex. The copper/ethylenediamine complex is very stable with a binding constant on the order of $10^{18}$ (45), and thus, the presence of an electrolyte additive is not expected to disrupt its behavior. To confirm that electrolytes affect the system performance mainly through a kinetic mechanism, their effect on complexation thermodynamics was first evaluated.

First, open circuit potential experiments were performed in the presence and absence of carbon dioxide, simulating the environment of the anode and cathode, respectively, in the electrochemical cell. Figure 2-5 shows no appreciable effect of different electrolytes on cathodic and anodic voltages, except for NH$_4$Br, where the change in pH (as NH$_4$Br is a weak acid and not a neutral salt as with the others in this set) is reflected in a small change in open circuit potential (around 40 mV).
UV-VIS spectroscopy experiments were performed to further confirm that copper/EDA complex stability is independent of the presence of additives. Both the free copper and the copper/EDA complex have distinct signatures, shown in Figure 2-6.
The UV-VIS experiments were repeated with different electrolytes. The results, shown in Figure 2-7, indicate no shift in peak position in the presence of additives. This result provides further evidence that complex formation is independent of electrolyte.

![Figure 2-7: Effect of Additives on UV-VIS Spectra. (Left): Copper/EDA complex. (Right): Uncomplexed copper ions. All solutions were 1M EDA, 0.25M copper nitrate and 1M electrolyte before dilution.](image)

**Effect of Additives on Electrochemical Kinetics**

Next, we probe the effect of electrolytes on copper dissolution and deposition activation kinetics. Following the procedure outlined earlier, the voltage-current profile for an activation controlled system is estimated by fitting dynamic pulse data to a proposed equivalent circuit that includes the widely reported two-step deposition/dissolution mechanism for copper:

\[
\text{Cu} \rightarrow \text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}^{2+} + \text{e}^-
\] (2-5)

Figure 2-8 summarizes the post-processed experimental results for conditions simulating the anode and cathode sides of the electrochemical cell. Under CO₂, reflecting conditions similar to those in the cell anode, the dissolution of copper under CO₂ appears to be hindered with NaNO₃, whereas experiments with bromide salts (NaBr and NH₄Br) demonstrated much more facile dissolution kinetics. For deposition under CO₂, the
trends are similar, where bromide salts followed by sodium nitrate showed the most facile kinetics, while sodium and ammonium chloride kinetics were slowest.

Figure 2-8: Effect of additives on EDA-complexed copper deposition and dissolution activation overpotentials (Left): Under CO$_2$. (Right): Under Argon. All solutions used 1M EDA, 0.25M copper ions and 1M electrolyte at 55°C.

Under conditions simulating the cathode side of the electrochemical cell, in the absence of CO$_2$, copper dissolution kinetics were generally faster than in the presence of CO$_2$. Again, the fastest kinetics were in the presence of bromide salts. For deposition, relevant to the electrochemical cell cathode, chloride salts led to relatively slower kinetics, while bromide salts and nitrate drove almost equally fast kinetics.

An increase in temperature translates to a direct improvement in reaction kinetics. Figure 2-9 shows the activation overpotentials at current densities between 0.25-1250A/m$^2$ for copper under ethylenediamine in 1M KCl, under Argon and CO$_2$. Deposition kinetics with KCl, relatively slow at 25°C, are around 30% faster with a temperature increase to 65°C.
The same behavior is observed with other electrolytes, for example, with NaBr, as shown in Figure 2-10.

The effect of temperature becomes small for fast kinetics, but can be significant for slower kinetics.

For the EMAR process, the results above are important, demonstrating a strong effect of electrolytes on the energy efficiency of the capture process. The activation overpotentials required for copper dissolution in the presence of CO₂ and copper deposition in its absence represent the anode and cathode of the
electrochemical cell, respectively. The performance in different electrolytes suggests that bromide salts provide for the highest energy efficiency at high current densities, while other electrolytes are only moderately efficient. The results above are based however on short pulses, and therefore, further evaluation is necessary.

**Bench-scale Experiments**

The high energy efficiency in the presence of bromide electrolytes in galvanostatic pulse voltammetry is promising, but the stability of the deposition and dissolution process must also be tested over longer time scales. The galvanostatic pulse experiments performed can only capture short time scale phenomena, and thus, electrolytes must be tested in a more practical setup. A relatively large-scale cell with dimensions of 9” length and 3” wide was constructed and used to test the performance in the presence of different electrolytes. The details of the cell design are discussed in Chapter 5.

For a given current density, results with bromide salts initially featured low voltages, followed by a large increase in voltage after the first few minutes of operation. Figure 2-11 shows the changes in voltage required to drive a current density of 50A/m² in sodium bromide.

![Figure 2-11: Applied potential difference change with time in NaBr electrolyte system tested at the bench-scale. Solution consists of in 1M EDA, 0.25M Cu(NO₃)₂ and 1M NaBr.](image-url)
The same behavior was observed with NH₄Br, where the voltage starts at a low value then quickly increases. To probe this phenomenon further, the cell was disassembled to inspect the electrodes post-operation, and for both bromide salts, a purple colored deposit was observed.

The deposit was further analyzed using XPS. The results, shown in Figure 2-12, indicate the presence of copper metal as expected, in addition to bromide ions. This suggests that the mechanism of deposition involves bromides that are inserted into the deposit.

Figure 2-12: XPS results for bench-scale cell cathode with NaBr electrolyte. Solution: 1M EDA, 0.25M Cu(NO₃)₂ and 1M NaBr at 55°C
In contrast, nitrate salts provide a high level of stability, operating for hours without any appreciable change in voltage. Figure 2-13 shows the steady-state voltage-current density profile under sodium nitrate after 1 hour of continuous operation. It is important to note here that results from the electrochemical cell include strong mass transfer limitations, and thus do not reflect pure activation kinetics.

Despite the high performance in the presence of bromide salts at short-time scales, their longer term instability renders their application in the EMAR process infeasible, given the need for long, stable operation. Chloride salts did not show a significant performance improvement over sodium nitrate, and previous testing of their performance at the bench-scale by Stern found that copper powder deposits were formed in the bulk, potentially due to disproportionation reactions. It is therefore the conclusion of this study that within the set of electrolytes tested, sodium nitrate offers the best tradeoff, and will be used in further bench-scale experiments. It is important to note, however, that further testing of a larger set of electrolytes can yield important process improvements, and is therefore recommended.

Figure 2-13: Steady-state voltage-current density profile in NaNO₃. Solution contained 1M EDA, 0.25M Cu(NO₃)₂ and 1M NaNO₃ at 55°C.
Data Fitting

The activation kinetics behavior of the electrolytes can be readily fit to the Butler-Volmer (BV) equation, a phenomenological equation widely used to represent electrochemical kinetics:

\[
i = i_0 \left\{ \exp \left( \frac{\alpha_a n F}{RT} \right) \eta - \exp \left( \frac{(1 - \alpha_c) n F}{RT} \right) \eta \right\}
\]  

(2-6)

where \( i_0 \) is the exchange current density, \( n \) is the number of electrons exchanged, \( F \) is Faraday’s constant, \( R \) is the universal gas constant, \( T \) is the operating temperature, \( \alpha_a \) and \( \alpha_c \) are the anodic and cathodic symmetry factors respectively, and \( \eta \) is the overpotential.

The form of the BV used here employs two symmetry factors in each reaction direction, and reflects the asymmetry of the reaction due to EDA complexation. The BV equation with experimental parameters will be used later, in Chapter 4, to represent the electrode reactions in a model of the cell processes. Voltage-current density data for the sodium nitrate system under EMAR anodic and cathodic conditions at a temperature of 55°C are shown in Figure 2-14. The 95% confidence interval fits computed through a Levenberg-Marquardt optimization are summarized in Table 1.

<table>
<thead>
<tr>
<th>Condition</th>
<th>( i_0 )</th>
<th>( \alpha_a )</th>
<th>( \alpha_c )</th>
<th>R-square</th>
</tr>
</thead>
<tbody>
<tr>
<td>Under Argon</td>
<td>162.9</td>
<td>0.45</td>
<td>0.55</td>
<td>0.993</td>
</tr>
<tr>
<td>Under CO₂</td>
<td>42.6</td>
<td>0.18</td>
<td>0.30</td>
<td>0.991</td>
</tr>
</tbody>
</table>

Table 1: Butler-Volmer parameters for the EMAR system under CO₂ and argon with NaNO₃ electrolyte. Solution contained 1M EDA, 0.25M Cu(NO₃)₂ and 1M NaNO₃ at 55°C.
Mechanistic Analysis

There are two major modes of charge transfer in an electrochemical reaction: outer-sphere, and inner-sphere electron transfer. Outer-sphere electron transfer, first explained in seminal work by Marcus (46), involves electron hopping between a metal surface and a metal center for a heterogeneous reaction system. The rate of charge transfer is heavily influenced by the reorganization energy, an estimate of the energy required to reorganize the inner coordination shell and the surrounding solvent shell.

Inner-sphere electron transfer, explained in landmark work by Taube (47), involves the formation of a ligand bridge between two metal redox centers, through which the electron is transferred. The ligand bridge forms part of the coordination sphere for both metal ions involved in the reaction (48). A precursor complex is first formed, bridging the metal centers by the ligand, followed by activation of the complex and charge transfer, and finally, deactivation and formation of a successor complex. The bridging ligand must be a good conveyor of electrons, and thus must have one or more lone electron pairs, to act as an electron donor to the oxidant and reductant. Before electron transfer, ligand bridging first occurs. The bridged structure can be in the ground state (stable), a transition state, or a transition-formed intermediate. Figure 2-15 contrasts inner- and outer-sphere charge transfer.
Figure 2-15: Schematic contrasting two modes of charge transfer a) Outer-sphere b) Inner-sphere

For charge transfer reactions where the donor and acceptor atoms have dissimilar inner coordination shells, outer-sphere charge transfer is slow, as with the well-studied example of ammonia-complexed cobalt ions:

\[ \text{Co(NH}_3\text{)}^6^{+2} \rightarrow \text{Co(NH}_3\text{)}^6^{+3} + e^- \]  \hspace{1cm} (2-7)

where a large difference in Co-N bond length in the two valence states is thought to hinder the reaction (46), an effect that can be explained by the Franck-Condon principle (49).

In contrast, for those electron transfer reactions involving large structural changes, an inner-sphere charge transfer mechanism can accelerate the reaction rate by orders of magnitude. For example, the rate constant of reaction of \( \text{Cr}^{2+} \) with \( \text{Co(NH}_3\text{)}_5\text{Cl}^{2+} \) was found to be around \( 10^8 \) larger than that with \( \text{Co(NH}_3\text{)}_6^{3+} \) (47)

\[ \text{Co(NH}_3\text{)}_6^{3+} + \text{Cr}^{2+} \rightarrow \text{Co}^{2+} + \text{Cr}^{3+} + 6\text{NH}_3 \]  \hspace{1cm} (2-8)

\[ \text{Co(NH}_3\text{)}_5\text{Cl}^{2+} + \text{Cr}^{2+} \rightarrow \text{Co}^{2+} + \text{CrCl}^{2+} + 6\text{NH}_3 \]  \hspace{1cm} (2-9)

This distinction in charge-transfer mechanisms can potentially explain our experimental results. Haim (48) posits that complexes with basic ligands, like EDA, act as ligand-bridges, but can be strongly affected by the concentration of hydrogen ions. EDA undergoes two protonation reactions, at pH around 6.8 and 9.9, as explained in more detail in Chapter 4, in the context of a Cu/EDA Pourbaix diagram. Thus, in the case of copper/EDA, at low pH under \( \text{CO}_2 \) saturation conditions, the protonation of EDA can prevent it from acting as a ligand bridge, switching the charge transfer to a slow outer-sphere mechanism. This hypothesis
can explain the significantly slower deposition and dissolution kinetics in EDA under CO₂. The decrease in pH due to the presence of CO₂ can retard EDA’s ability to act as a ligand bridge, as hydrogen ions compete for EDA sites with the copper surface.

Halides, as discussed previously, are also recognized to act as ligand bridges in metal dissolution and deposition. Under CO₂, they can act as an alternative to the EDA ligand bridge, accelerating the reaction rate and reducing activation overpotentials. This is consistent with our experimental findings, where kinetics under CO₂ in the absence of halides is slower than in their presence. In the absence of CO₂ and the higher prevailing pH, EDA deprotonates and becomes available to act as ligand bridge.

However, the ability of halides to act as ligand bridges results in their inclusion in the formed copper deposit, increasing its contact resistance. Thus, despite their accelerating effect on kinetics for short time-scales, the energy efficiency of the process gradually drops due to their inclusion in the formed metal deposit.

Conclusions

We investigated the effect of a set of electrolytes on the electrochemical kinetics of dissolution and deposition of copper in EDA and found the following:

- We find no evidence for an effect of electrolytes on the stability of the copper/EDA complex.
- Kinetic experiments at short time scales show an appreciable effect of additives on the activation overpotentials, with bromide salts driving the fastest kinetics.
- Upon testing in a bench-scale electrochemical cell at longer time times, a large increase in voltage is caused by bromides, and the formed deposit was found to include bromide ions.
- Mechanistic arguments suggest additives act as ligand bridges, but that they are gradually included in the deposit and can cause an increase in contact resistance.
- Nitrate electrolytes were found to be relatively energy efficient and stable over longer operations.
Further experimental work and analysis is required to conclude definitively that the mechanism of action of electrolytes is through a ligand bridge inner-sphere charge transfer one, and that the inclusion of bromides in the deposit is responsible for the increased voltage. Molecular modeling of the bond distances between copper metal centers in the presence of halide anions can provide useful insights into these effects. Electrochemical Quartz Crystal Microbalance (EQCM) experiments can determine the Faradaic efficiency of deposition and dissolution, and whether the inclusion hypothesis is consistent with observed weight changes.

The work in this chapter serves to provide a methodology to screen electrolytes for performance, first evaluating their short-time dynamics using galvanostatic pulses, and then testing promising candidates for longer-term behavior. Sodium nitrate serves to drive stable and moderately efficient kinetics, though the activation potential required for a given current is large under CO$_2$ in the presence of this salt. Although this electrolyte is used in the remainder of this work, further screening of other molecules electrolytes is strongly recommended, given the large potential contribution of electrolytes to the overall process efficiency.
Chapter 3

Cell Prototype Modeling Framework

This chapter describes the formulation and solution of a two-dimensional electrochemical cell model with mass transfer, convection and electrode reactions. The purpose of the model is to analyze the effects of design and operating parameters on the electrochemical cell performance. The model tracks copper ion concentration in each electrode compartment, accounting for convection and diffusion, with electrode reactions imposed as boundary conditions. Electrochemical thermodynamics are modelled through the Nernst equation, and activation kinetics are represented by the semi-empirical Butler-Volmer equation with experimentally derived parameters. Ohmic losses are modeled as a product of linear contact and solution resistance, measured using Electrochemical Impedance Spectroscopy. Bubble overpotentials are included through an estimate of their electrode blocking effects. Half-cell coupling is achieved through a constraint on applied voltage distribution. The system equations are solved numerically, and a parametric study is performed. Model predictions suggest large mass transfer limitations at high target current densities, resulting in a large concentration difference between the electrode surface and bulk, and formation of a thick boundary layer. Higher superficial velocities, through smaller channel depth and higher flowrates, are predicted to improve mass transfer and lower thermodynamic penalties, but result in lower utilization for a constant cell length. The design rules inferred from modeling predictions provide valuable insights for bench-scale prototype optimization.

Electrochemical Flow Modeling

Modeling provides effective means to accelerate the development cycles of new technologies, while reducing associated costs of extensive experimentation. A validated model can be a powerful tool in optimization, linking system design parameters to its performance, and generating insights into the
fundamental processes underlying this performance. Given the large design space of the EMAR process and the variety of open design decisions, a modeling framework that describes the major electrochemical cell processes as a function of chemistry, operating conditions and cell design is a valuable tool.

In guiding the model formulation, literature on modeling other electrochemical flow systems is a useful starting point. Electrochemical flow systems are growing in importance, particularly in energy storage applications. There are important similarities between redox flow batteries (RFBs) and the EMAR system: a redox-responsive molecule is cycled between two states through a flow configuration along or through an electrode, and two external tanks hold catholyte and analoyte solutions. RFBs have been an important source of inspiration in EMAR development.

Extensive literature on optimization of chemistry, flow patterns and operating conditions for RFBs by building comprehensive models is available. An early example is work by Fedkiw and Watts, who modeled an iron-chromium RFB using a two-dimensional model, and used it to optimize electrode thickness and electrolyte flowrate (50). More recently, Walsh et. al. modeled a Vanadium RFB, building two-dimensional dynamic cell models to understand flowrate and concentration effects (51), which they later extended to include heat effects (52). Roberts et al. developed a one-dimensional RFB model and fitted it to pilot-scale data for a bromide-polysulphide flow batter, and used it to predict cell performance at optimized conditions to evaluate the technology’s performance at the utility scale (53) (54). Braff et al. developed a two-dimensional modeling framework to aid the design of their novel membraneless hydrogen bromide battery (55).

Higher dimensional modeling efforts have also been employed, though less frequently. Xing et. al. for example developed a three-dimensional model of the negative compartment of a Vanadium RFB, to examine how local velocity changes will affect overpotentials distribution and cell performance (56).
Model Overview

This section describes the modeling framework developed to capture the interplay of processes inside the EMAR electrochemical cell (a schematic is provided in Figure 1-8). A quick summary of these processes follows, and a more extensive discussion is provided in Chapter 1.

The CO₂ saturated aqueous EDA solution enters at the anode side of the cell, where copper ions are formed from the electrode surface according to the reaction:

\[ \text{Cu} \rightarrow \text{Cu}^{2+} + 2e^- \]  

(3-1)

The dissolved copper ions react rapidly with EDA to form a chelate complex and release CO₂:

\[ 2\text{EDACO}_2 + \text{Cu}^{2+} \rightarrow \text{CuEDA}_2^{2+} + 2\text{CO}_2 \]  

(3-2)

The decomplexed CO₂ surpasses its supersaturation limit in water and evolves in the form of gas bubbles. The two phase solution is pumped from anode exit to a flash chamber, where bubbles are allowed to disengage. The copper-loaded EDA solution is then recycled back to the electrochemical cell. At the cathode, the copper ions are deposited from their amine complex according to the reaction:

\[ \text{CuEDA}_2^{2+} + 2e^- \rightarrow \text{Cu} + 2\text{EDA} \]  

(3-3)

In both cell compartments, a distribution profile for copper ion concentration develops as a voltage is applied due to electrode reactions, and mass transfer between electrodes and bulk becomes important. Copper exists in both compartments primarily in its amine-complexed form, due to the strong binding and amine concentrations higher than stoichiometrically required for a 2:1 EDA:Cu binding ratio. The formation of gas bubbles in the anode compartment is also likely to play an important role in the electrode availability, solution conductivity and mass transfer.

Here, we develop a model with two objectives: to validate our physical understanding of the major effects governing the cell performance, and to relate the cell and process design space to its energy efficiency.
A two-dimensional convection-diffusion model captures the concentration distribution of copper ions, and the mass transfer effects on surface concentration of copper ions, where electrochemical reactions occur. A Nernst-based open circuit potential (OCP) model is used to describe complexation thermodynamic and concentration effects. A Butler-Volmer (BV) model with experimentally determined parameters, as described in Chapter 2, is used to model electrodissolution and electrodeposition kinetics. Finally, the coupling of the half-cell reactions is modeled through the distribution of applied potential over the equilibrium voltage, activation overpotentials and ohmic losses, with the constraint that cathodic and anodic current densities must be equal. In addition, we include the effects of bubble formation on electrode availability as a linear resistance. The model is described in more detail in the next sections.

**Species concentration distribution**

The current design of the electrochemical cell consists of two planar copper metal electrodes sandwiching two flow compartments divided by a separator. In each of the compartments, a convective flow parallel to the electrodes carries solution through the cell. Copper metal ions formed at the anode surface diffuse to the solution bulk, and on the cathode side, copper/amine complex ions must diffuse to the electrode surface where copper is deposited.

The bulk reaction between amine and copper is assumed to go rapidly to equilibrium, given the large magnitude of the binding constant \( \beta = \frac{[CuEDA^{2+}]}{[Cu^{2+}][EDA]^2} = 10^{18} \), and therefore, copper/amine complex ions are assumed to be the dominant species in the anode compartment. The concentration of EDA molecules bound to CO\(_2\) \([EDA.CO_2]\) is the balance of total amine concentration \([EDA]_0\) minus copper-bound EDA \([CuEDA^{2+}_2]\), i.e.

\[
[EDA.CO_2] = [EDA]_0 - 2[CuEDA^{2+}_2] \tag{3-4}
\]
Spatially, the model can be simplified significantly by recognizing that concentration changes occur laterally (i.e. perpendicular to electrodes) and axially (along the electrodes), and by ignoring edge effects, a two-dimensional model will suffice.

Figure 3-1 shows a schematic of the physical picture described by the model, where the x-axis is perpendicular to the electrodes and spans the flow channel depth, and the z-axis is parallel to the electrodes.

The concentration of the copper ions in each electrode compartment can be modeled by the partial differential equation (PDE):

\[ u_z(x) \frac{\partial c_i}{\partial z} - D \frac{\partial^2 c_i}{\partial x^2} = 0 \]  

(3-5)

where \( u_z(x) \) is the fully-developed laminar velocity, subscript “i” refers to anode and cathode concentrations, and \( D \) is the diffusivity of the ions, assumed equal for anode and cathode. This PDE models ion concentration as the balance between an axial convective flow and a lateral diffusive flux.

Axial diffusion can be shown to be small compared with the convective flux (axial Peclet number is large) and is therefore ignored. Lateral components of velocity are assumed to be small, and the flow profile \( u_z(x) \) is assumed to be fully developed throughout the channel and is treated as a model input.

Migration effects are assumed to be negligible, as the high electrolyte concentration will result in screening of electrode electric field effects over a small region close to the electrode, a double layer, and is thus not included in this analysis. The double layer can have complex non-linear effects on electrode reactions, and future iterations on this model should account for its presence.

A major limitation of this model formulation is the assumption of a single phase flow in the anode compartment. As the current density is increased and more bubbles are formed, a two phase flow will develop in this anode compartment, which would affect the superficial velocity of the liquid phase. A full multi-phase flow treatment would however significantly increase the complexity and computational cost of this model. Moreover, bubble modeling will require a number of currently unavailable parameters to
accurately model the nucleation, growth and coalescence of bubbles. Instead, the model only tracks the liquid phase in the anode, and accounts for bubble effects on electrode surface availability as an ohmic loss, as described in more detail in a following section.

\[ u_x(x) \frac{\partial c_i}{\partial z} - D \frac{\partial^2 c_i}{\partial x^2} = 0 \]

\[ u_z(x) \frac{\partial c_i}{\partial z} - D \frac{\partial^2 c_i}{\partial x^2} = 0 \]

**Figure 3-1**: Schematic of model physics describing the two dimensional treatment of the two electrode compartments to be dominated by a convective axial flow and a diffusive lateral flux.

**Initial and Boundary Conditions**

At the entrance to the anode, the inlet copper concentration \( c_0 \), is set to be

\[ c_i(x, 0) = c_0 \]

(3-6)
where $c_0$ is the laterally-averaged inlet concentration, set by the conditions in the absorber.

The same condition applies at the entrance to the cathode, with an added constraint: the laterally-averaged anode exit concentration must be equal to the laterally-averaged cathode inlet concentration. This condition reflects reentry of the anode outlet solution (after flashing to disengage gas) into the cell via the cathode inlet. Numerical implementation of this condition is described in the model solution section.

At the electrodes, the boundary condition imposed is that the diffusive flux to and from the electrode must equal the electrochemical reaction occurring at the surface:

$$ \frac{\partial c_i}{\partial x} (H, z) = \frac{i_{BV}}{nFD} $$  \hspace{1cm} (3-7)

where $H$ is the channel depth measured from the separator to each electrode, $i_{BV}$ is the BV current density, described in the kinetics formulation section.

At the separator, we impose a no-flux BC:

$$ \frac{\partial c_i}{\partial x} (0, z) = 0 $$  \hspace{1cm} (3-8)

This condition is not strictly true, as species cross-over through the permeable separator occurs, but serves as a reasonable initial assumption in the absence of experimental measurements of species permeability through various separators.

**EMAR Thermodynamic Analysis**

This section describes the thermodynamic treatment of the EMAR process in the cell modeling framework presented in this chapter. First, previous thermodynamic experiments and analyses are summarized. Next, the thermodynamic analysis is extended to account for pH changes between the anode and cathode, and their impact on complex formation. Finally, a Nernst-based thermodynamic model of the cell is derived to describe the process quantitatively.
**Thermodynamics and pH**

The thermodynamics of the EMAR process were studied experimentally in previous work by Stern (41), and the EDA/Cu system was found to have efficient thermodynamic requirements. In addition, EDA and copper were found to bind with a 2:1 ratio throughout the loading range between 0% and 100% copper, as confirmed by UV-VIS studies.

This previous treatment however did not account for the effect of pH changes on complex stability. The pH of pure 2M EDA, conditions close to those prevailing at the EMAR cathode outlet, is around 12, while the pH of CO₂ saturated EDA, as at the EMAR anode inlet, is close to 7. In order to develop a clearer understanding of the range of stability of Cu/EDA complex across a range of pH, copper and EDA reactions and their thermodynamics must be considered, as well as other potential species.

Aksu and Doyle (52) (65) developed an extensive analysis of the Cu/EDA reaction system considering 10 species, 31 reactions and their thermodynamics. Potential-pH equilibria and polarization curves were used to develop Pourbaix (65) diagrams for the system across pH and standard potentials. Some of their results are reproduced in Figure 3-2, for the case where EDA concentration is an order of magnitude higher than that of copper.

EDA undergoes two steps of protonation (dotted vertical lines in the Pourbaix diagram), with protonation occurring at pH 6.8 and 10 respectively, following the reactions:

\[
H_2En \rightleftharpoons Hen + H^+ \quad (3-9)
\]

\[
Hen \rightleftharpoons En + H^+ \quad (3-10)
\]

For an electrochemical cell with pH changes between 7 and 12, a thermodynamic model must account for the protonation of EDA in that range, which will impact the complexation thermodynamics and associated open circuit potential, as can be seen from the changing gradient of lines separating copper complex and copper atom regions. However, for the current bench-scale prototype (described in Chapter 4) modeled in
this chapter, copper loading changes are small and operation is mostly in the $7 < \text{pH} < 10$ range where the dominant EDA species is HEDA.

\[ \text{Figure 3-2: Pourbaix diagram for copper/EDA system with EDA concentrations one order of magnitude higher than copper ion at 25°C, reproduced from work by Aksu and Doyle (52). Red dotted lines correspond to water splitting reactions.} \]

Other interesting features are briefly discussed. The most stable Cu/EDA complex in the entire range of interest is CuEDA$_2^{2+}$ as consistent with previous experimental findings. The 1:1 ratio complex, CuEDA$_2^{2+}$, only forms in a narrow range of low pH, a favorable finding as the 1:1 ratio would increase the electrons per molecule of CO$_2$ required, i.e. decrease the Faradaic efficiency.

At high pH (around 12), the risk of forming cupric and cuprous oxides increases, particularly under cathodic currents. A 2M solution of EDA in the absence of CO$_2$ has a pH of around 12. Thus, in the absence of CO$_2$, the Pourbaix diagram suggests that conditions would be favorable for oxide formation. Operation of the electrochemical cells with large copper loading swings can therefore be challenging.

It is important to note that the pH-potential equilibria above are for low ion concentrations at room temperature, and thus have limited utility in describing the EMAR system under current operating
conditions, but serve as an indicator for the ranges of stability for some of the process parameters and the importance of pH, which can change significantly in the electrochemical cell. In future work, this analysis should be extended through an activity model.

**Thermodynamic Model Formulation**

For fully reversible, competitive complexation of EDA with copper metal ions without spatial distribution, the open circuit potential can be described with the Nernst equation in the form:

\[
\Delta E^{eq} = -\frac{RT}{nF} \ln(KP_{CO2} / P_0)
\]  

(3-11)

where \( R \) is the universal gas constant, \( T \) is the operating temperature, \( n \) is the number of electrons transferred, \( F \) is Faraday’s constant, \( K \) is the binding constant for EDA and CO2, \( P_{CO2} \) the partial pressure of CO2 in the anode and \( P_0 \) is the reference pressure. This model was proposed by Stern et al. (42), and assumes perfectly reversible thermodynamics with no concentration effects. However, due to the distributed nature of the electrochemical cell, concentration gradients develop and their effects on the thermodynamic voltage must be included.

Starting with the Nernst equation,

\[
\Delta \psi_{eq} = \Delta \psi^0 + \frac{RT}{nF} \ln \frac{[Red]}{[Ox]}
\]  

(3-12)

We can write the following equations for the interfacial potential drop at each electrode at equilibrium:

\[
\Delta \phi_{eq,a} = \Delta \phi^0 + \frac{RT}{nF} \ln \left[ Cu^{2+} \right]_{anode}
\]  

(3-13)

For simplicity, we assumed activity coefficients of unity. Copper species exist in either free form, or complexed with EDA. At the prevalent pH in the anode, the most stable EDA form is protonated, HEDA. The EDA/Cu complex under those conditions is defined by the binding constant:
\[ \beta_{\text{HEDA/Cu}} = \frac{[\text{CuEDA}^{2+}_2][\text{H}^+]^2}{[\text{HEDA}][\text{Cu}^{2+}]} \]  

(3-14)

HEDA also exists in CO\(_2\)-bound form, defined by the binding constant:

\[ K = \frac{[\text{EDA.CO}_2]}{[\text{HEDA}][P_{\text{CO}_2}/P_O]} \]  

(3-15)

The total species concentrations for copper and HEDA can be written in terms of the HEDA/CO\(_2\) and the HEDA/Copper binding constants, \( K \) and \( \beta_{\text{HEDA/Cu}} \):

\[ [\text{Cu}^{2+}_0] = [\text{Cu}^{2+}] \left( 1 + \frac{[\text{HEDA}]^2 \beta_{\text{HEDA/Cu}}}{[\text{H}^+]^2} \right) \]  

(3-16)

\[ [\text{HEDA}]_0 = [\text{HEDA}] + 2[Cu\text{EDA}^{2+}_2] + \frac{K_{\text{CO}_2} P_0}{P_0} [\text{HEDA}] \]  

(3-17)

By assuming that free copper ions have a significantly lower concentration than amine-bound copper ions, due to the large binding constant, we can simplify the equations considerably:

\[ [\text{HEDA}] = \frac{[\text{HEDA}]_0 - 2[Cu^{2+}_0]}{1 + \frac{K_{\text{CO}_2}}{P_0}} \]  

(3-18)

\[ [\text{Cu}^{2+}]_{\text{anode}} = \frac{[Cu^{2+}_0][\text{H}^+]^2 \left( 1 + \frac{K_{\text{CO}_2}}{P_0} \right)^2}{\beta_{\text{HEDA/Cu}} \left( [\text{HEDA}]_0 - 2[Cu^{2+}_0] \right)^2} \]  

(3-19)

Subscript 0 denotes total ion concentration for each component including all complexes. This is an important expression and it is helpful to highlight its physical implications. The concentration of free copper ions at the anode is inversely proportional to the square of the HEDA concentration (in the denominator) and the HEDA/copper binding constant, reflecting the complexation of copper by amines. The binding of
amine and CO₂, represented by the expression in the numerator, reflects the competitive complexation between copper and CO₂ in binding EDA. An increase in pH favors larger concentrations of copper ion formation, consistent with the pH-potential equilibria of the system (Pourbaix diagram Figure 3-2) where reduction of copper ions to copper becomes less favorable with an increase in pH.

We can repeat the same analysis for the cathode, to obtain the equation:

\[
\left[ Cu^{2+} \right]_{cathode} = \frac{\left[ Cu^{2+}_0 \right] \left[ H^+ \right]^2}{\beta_{HEDA/Cu} \left( [HEDA]_0 - 2[CU^{2+}_0] \right)^2}
\] (3-20)

Combining the two electrodes expressions together, we arrive at the following OCP model:

\[
\Delta E_{eq} = \frac{RT}{nF} \left\{ \ln \left( \frac{\left(Cu^{2+}_0\right)_c}{\left(Cu^{2+}_0\right)_a} \right) + 2\ln \left( \frac{\left(E DA\right)_0 - 2Cu^{2+}_0}{\left(E DA\right)_0 - 2Cu^{2+}_c} \right) - 2\ln \left( \frac{K_{CO_2} P_a}{P_0} \right)_a + 2\ln \left( \frac{[H^+]}{[H^+]_a} \right) \right\}
\] (3-21)

where the subscript “0” represents the total concentration of a species, including different complexed forms, and subscripts “a” and “c” are for concentrations at the anode and cathode, respectively. The first term reflects the effect of total copper ion concentration in each compartment, which can be understood as a mass action effect where a higher product concentration forces an energetic penalty on further product formation. The second term represents the effect of amine complexation of copper ions. The third term is the Gibbs Free Energy of binding EDA with CO₂, and is temperature dependent (equal to around 14 kJ/mole at 55°C). The last term represents pH effects on the thermodynamic voltage. The binding constant of HEDA/Cu does not appear in the equation, since the binding is reversed across the cell, and thus does not strongly impact open circuit potential (though the binding constant must be large enough to satisfy the assumption of most copper ions being amine-bound, for this model to be valid). The concentrations referred to in this equation correspond to surface concentration of species, an important distinction for copper ions.
Operating Conditions and Open Circuit Potential

It is instructive here to assess the energy contribution of various terms in the open circuit potential model across operating loadings. The first two terms, copper ion concentration and amine complexation effects, have opposing effects on OCP. For a counter-current flow, where the anode outlet solution enters the cathode at the opposite end, this term will be eliminated and have no impact, since at each point along the electrode length, the contributions in the two compartments will cancel each other out. For a co-current flow, used in the current bench-scale setup and modeled in this work, the contributions are symmetrical (i.e. OCP for half the cell is opposite in sign and equal in magnitude to the second half OCP). However, the effect on current density through the distribution of applied voltage is exponential, as will be shown later in this chapter.

The third term, the amine/CO₂ binding energy penalty, is a function of temperature and pressure in the anode compartment, and previous tests by Stern et al. suggest it varies between 10-20 kJ/mole within relevant operating conditions.

The hydrogen-ion concentration effects term can be rewritten in terms of pH as:

\[
\frac{2RT}{nF} \ln \frac{[H^+]_a}{[H^+]_c} = \frac{4.606RT}{nF} \left( pH_a - pH_c \right) \tag{3-22}
\]

The pH of EDA for different CO₂ loadings was measured by saturating an EDA solution with CO₂ overnight and mixing at different proportions with fresh EDA to prepare a range of loadings. The results are shown in Figure 3-3. For a high Faradaic efficiency in the electrochemical cell, the pH swing range of the process is defined by the maximum and minimum CO₂ loadings. At a pH of 10, EDA (unprotonated form) becomes the dominant form and pH no longer affects OCP. Thus, the maximum change in OCP occurs for a pH swing of 7-10, and we can estimate the OCP contribution to reach up to 190 mV (or 18.8 kJ/mole CO₂). This is an important result that suggests that the operation of the EMAR process between CO₂ loadings of
95% and 5% would double the thermodynamic energy penalty of the process, relative to that calculated based on the Gibbs Free Energy of EDA/CO₂ binding only.

Figure 3-3: Experimental measurement of EDA aqueous solution pH vs. CO₂ loading, for a 1M EDA solution.

For the simulations in this chapter, aimed at providing insight for the bench-scale system discussed in Chapters 4 and 5, the effect of pH is negligible, as the change in CO₂-loading of EDA is small. The maximum loading change for the bench-scale prototype (with a length less than 10") is around 5% (i.e. CO₂ loading at anode inlet is 100% and exit is 95%) and therefore the pH change is around 0.4-0.5 pH units, which corresponds to a maximum OCP change as small as 30 mV. Thus, for the current setup, pH effects are not included in this model, but future simulations of a full-scale system with larger pH swings should include those effects.

**Electrochemical Kinetics**

In Chapter 2, the electrochemical kinetics of copper/EDA using galvanostatic pulse experiments under different electrolytes were studied, and nitrate salts were found to drive the most stable reaction system with reasonable energetic efficiency. Here, we use the semi-empirical BV model with experimentally determined parameters to model the anode and cathode kinetics:
\[ i_a = nFk_{0_{CO2}}[Cu^{(2+) \text{CO2}}]^{(\alpha_{CO2,a})}\left(\exp\left(\frac{\alpha_{CO2,c}nF}{RT}\eta_a\right) - \exp\left(-\alpha_{CO2,c}\frac{nF}{RT}\eta_a\right)\right) \]

(3-23)

where \( k_{0_{CO2}}, \alpha_{CO2,c} \) and \( \alpha_{CO2,a} \) are the intrinsic rate constant, and cathodic and anodic transfer coefficients for copper electrodissolution under CO₂, respectively, and \( \eta_a \) and \( \eta_c \) are the activation overpotentials for the anode and cathode respectively. As with the OCP model, the concentrations referred to here are surface species concentrations. In the simulations in this chapter, aimed at reflecting actual conditions in the bench-scale system, the rate expression above represents electrode kinetics both at the anode and cathode. As the change in CO₂ loading along the relatively short bench-scale prototype length is small, the kinetics can be well represented by those measured in a CO₂-saturated system. For a larger-scale system, it would be necessary to include the kinetics measured in the absence of CO₂, as described in Chapter 2.

**Half-cell coupling**

A primary difference between heterogeneous chemical reactions and electrode electrochemical reactions is the coupling for two spatially separated half-cell reactions for electrochemical reactions. This half-cell coupling is implemented here by imposing the following constraint:

\[ V_{\text{app}} = \Delta E_{eq} + \eta_a - \eta_c + iR_{\text{ohm}} \]

(3-24)

where \( V_{\text{app}} \) is the applied potential difference between the two electrodes and \( R_{\text{ohm}} \) is the total ohmic resistance. This constraint serves to distribute the input energy, in the form of applied potential, between the potential drop due to open circuit, electrode activation and ohmic overpotentials.

The activation overpotentials are further coupled through the condition that the total current for each electrode must be equal in magnitude to conserve charge. This condition requires the solution of a Differential Algebraic Equation (DAE) system, which can be computationally expensive. To simplify the solution method, we assume here that this condition is equivalent to assuming an equal local current density at each axial position.
An important potential source of energy loss in the electrochemical cell arises from ohmic resistances, dominated by contact and solution resistances, and are readily determined from EIS experiments and modeled as a linear (i.e. current independent) resistance.

**Bubble resistance**

The formation of bubbles on the anode side of the cell can affect the cell performance by reducing the anode electrode area available for electrochemical reaction. Bubbles can also contribute to better mixing, but can decrease the conductivity of the solution. A full model of bubble effects will require a complicated two-phase treatment of the system.

Here, we develop an estimate of the bubble resistance as a linear resistance, and focus in particular on its electrode blocking effects. A linear resistance is a reasonable assumption, as an increase in current will drive the formation of more bubbles and more blocking of the electrode surface. For very high currents, the effect of bubbles on electrode availability and activation overpotentials will deviate significantly from linearity, as the polarization curve enters its exponential phase.

For systems with and without bubbles, the total applied current is constant:

\[
\bar{i}_B A_B = \bar{i}_{NB} A_{NB}
\]

(3-26)

where \( \bar{i} \) is the average applied current density and subscripts “B” and “NB” represent the bubbles and no bubbles cases, respectively.

Assuming uniform gas distribution in the lateral direction, we can estimate the electrode area available in presence of bubbles from the volume fraction of gas \( \alpha_G \):

\[
A_B = (1 - \alpha_G) A_{NB}
\]

(3-27)
We can then write $\alpha_G$ in terms of applied current density, using Faraday’s law of electrolysis and assuming ideal gas behavior in the anode chamber (a reasonable assumption given the relatively low pressure):

$$\alpha_G = \frac{V_{CO_2}}{F_{total}} = \left( \frac{i_{NB}A_{NB}}{F} \right) \left( \frac{RT}{P} \right) F_{total}$$  \hspace{1cm} (3-28)

where $F_{total}$ is the total volumetric liquid and gas flowrate through the flow compartment. We can rewrite this equation in terms of the current density and electrode area values in the absence of bubbles using eq. (3-18):

$$\alpha_G = \frac{V_{CO_2}^0}{F_{total}} = \left( \frac{i_{NB}A_{NB}}{F} \right) \left( \frac{RT}{P} \right) / F_{total}$$  \hspace{1cm} (3-29)

Rearranging the above equations, we can write the real current density in the presence of bubbles in terms of the current density, assuming bubbles do not block the electrode, as

$$\bar{i}_B = \frac{A_{NB}}{A_B} \bar{i}_{NB} = \left( \frac{1}{1 - \alpha_G} \right) \bar{i}_{NB}$$  \hspace{1cm} (3-30)

which can be expanded to:

$$\bar{i}_B = \left( \frac{F_{total}}{F_{total} - \left( \frac{i_{NB}A_{NB}}{F} \right) \left( \frac{RT}{P} \right) F_{total}} \right) \bar{i}_{NB}$$  \hspace{1cm} (3-31)

Thus, given the model estimate of current density in the absence of bubbles, we can estimate the real current density, and use it compute the difference in activation overpotentials due to bubbles through the BV equation, i.e.:

$$\eta_{bubbles} = \eta(i_B) - \eta(i_{NB})$$  \hspace{1cm} (3-32)
The gradient of bubble overpotential change as a function of applied current density can be used as an estimate of resistance caused by bubble blocking of electrodes. We focus on the significantly less facile anode kinetics. In this formulation, the dependence of bubble overpotential on total flowrate is explicit, where for the same current density, the volume fraction of bubbles and their potential blocking of the electrode surface will become less pronounced.

**Solution Approach**

The system of equations outlined above consists of two 2nd order linear PDEs, with Neumann boundary conditions and algebraic constraints. The solution approach here exploits the parabolic nature of the equations, which allows the solution for the lateral distribution of concentration at each axial point, and treatment of the axial direction as a time-like variable. We therefore utilize a marching algorithm.

First, the initial concentrations are used to compute lateral equilibrium potential, voltage distribution, activation overpotentials and local current density from equations (3-13) through (3-17), using a nonlinear equation solver. Then, we use the local current density to solve the parabolic PDE (3-1) with BCs (3-3 and 3-4) on a radial mesh, and march the solution with a small axial step to ensure the lateral concentration does not change significantly ($\Delta c_i < \text{tol,}$).

After the small axial step (typically less than 0.1 mm), the voltage distribution and current density are updated according to the new lateral concentration distribution. This process is repeated until the end of the cell is reached.

We apply the shooting algorithm to ensure the equality of the laterally-averaged anode inlet and the cathode exit concentration. The error is estimated as:

$$error = \left| \bar{c}_a (z = L) - \bar{c}_c (z = 0) \right|$$ (3-33)
and required to be less than a tolerance of 0.1 mole/m³. If the error exceeds this tolerance, the solution sequence is repeated using the anode exit concentration as a guess for the cathode inlet. The equations are solved with an in-house code implemented in the commercial solver MATLAB.

Table 2: Values of physical parameters used in the simulations, for a temperature of 55°C.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{CO_2}$</td>
<td>300</td>
<td>-</td>
</tr>
<tr>
<td>D</td>
<td>0.6e-09</td>
<td>m²/sec</td>
</tr>
<tr>
<td>$R_{ohm}$</td>
<td>0.05</td>
<td>ohm</td>
</tr>
</tbody>
</table>

**Model Assumptions**

The electrochemical cell model outlined above includes several important assumptions, which are summarized and rationalized here:

1) Electric field distribution and migration effects are ignored, since the use of a high concentration of supporting electrolyte (1M) screens the solution bulk from interface electric field effects, and causes nearly all the potential drop to occur within a few angstroms from the electrode/electrolyte interface.

2) Electrolyte concentration distribution was not modeled and assumed to be equal to its bulk value.

3) Current density was assumed to be locally equal for the two electrodes. The more strictly physical condition is the equality of total applied current. However, this assumption is acceptable for a system where electric field distribution effects are minimal. Future work explicitly modeling bubble effects should allow for local variations in current density between the two electrodes.
4) EDA species distribution was not explicitly modeled, and the EDA/Cu\(^{2+}\) reaction was assumed to instantaneously reach equilibrium (and due to the very high binding constant, approaches 100% complexation).

5) Double layer ion distribution effects are not included in this analysis, and electroneutrality is assumed to prevail across the entire flow channel.

6) Activity coefficients of ions assumed to be unity, and dilute solution behavior is assumed.

7) Bubble effects are assumed to be limited to blocking of electrode surface and can be estimated as a linear resistance stemming from a change in activation overpotentials due to higher effective current density at the same applied voltage.

8) Edge effects are ignored and a Poiseuille flow profile is assumed, as the ratio of the channel length to depth is very large.

9) No cross-over of gas or ionic species through the separator occurs.

10) The cell is assumed to operate at 55°C with isothermal and isobaric conditions. This assumption should be revised in future work, as EDA/CO\(_2\) decomplexation is strongly endothermic, and a pressure drop will be incurred along the flow length. However, given the limited extent of CO\(_2\) desorption in the bench-scale system and the relatively short residence time, those effects are not as important for the cases simulated here.

11) The Faradaic reactions had an ideal efficiency.

**Model Results**

The model provides detailed insights into the distribution of main primary variables inside the electrochemical cell, as a function of applied voltage, channel depth, inlet concentrations, cell length and total flowrate. Extensive details from an example run with operating conditions similar to those utilized in bench-scale experiments (Chapter 5) are presented for a 1/8" deep channel and 0.35V applied potential
difference, demonstrating clearly the effect of mass transfer limitations. Following that, superficial velocity effects are explored through polarization curves, for brevity.

Figure 3-4 shows the axial distribution of current density along the length of the cell. The current density is highest at the cell entrance, reaching more than 55A/m², then drops significantly to 35A/m² with an average current density of 42A/m².

Figure 3-4: Sample model run results. (Top): Current density and equilibrium potential. (Bottom): Anode activation overpotentials. Channel depth is 1/8" depth channel with cell length and operating conditions similar to bench-scale experiments.
The sharp variation of current density can be understood through the axial distribution of equilibrium potential and anode activation overpotentials, shown in Figure 3-4. The equilibrium potential increases by almost 20% from less than 0.16V at the entrance to 0.2V near the exit, which in turn reduces the anode overpotential from 0.12V to less than 0.105V following eq. [3-16], which governs applied voltage distribution.

Those changes in applied voltage distribution and current density are the direct results of the copper ion concentration changes along the axial and lateral directions of the cell. Figure 3-5 shows the laterally averaged copper ion concentrations in the anode and cathode compartments. The concentration changes are symmetric due to the imposed constraint on local current densities. The changes in equilibrium potential are driven by the increase in anode copper concentration, and a decrease in cathode copper concentration along the cell length. This can be understood as a thermodynamic effect of change in copper loading of amines.

Figure 3-5: Sample model run results, showing the axial variation of laterally-averaged concentration of copper ions. Channel depth is 1/8'' depth channel with cell length and operating conditions similar to bench-scale experiments.
Lateral concentration profiles, shown in Figure 3-6 for the cathode compartment, more clearly illustrate the changes in current density and open circuit potential, and the effects of mass transfer. As the solution flows across the cell, a copper ion concentration gradient builds between the solution bulk and the surface of the electrode, creating a depletion zone, and the concentration boundary layer becomes thicker. Thus, since the open circuit potential and the exchange current density both operate at the surface concentrations, different from those in the bulk, giving rise to an energy penalty. For example, on the cathode side, the copper ion concentration at the surface drops by more than 75% between the inlet and outlet.

![Figure 3-6: Sample model run results, showing the cathode concentration distribution along the lateral direction. Channel depth is 1/8" depth channel with cell length and operating conditions similar to bench-scale experiments.](image)

Thus, boundary layer development significantly affects the electrode reaction rates, as the higher anode and lower cathode surface concentrations act to reduce the exchange current density and reaction rate. In addition, the thermodynamic impact of the surface concentration manifests itself in a higher equilibrium potential.

This sample run serves to show the utility of this model and the detailed information it provides. In Chapter 5, a comparison with experimental results shows the model results are in reasonable agreement. Here, we note however the clear importance of mass transfer in governing the predicted performance of the cell.
Given the significant role played by surface concentration, design and operating condition changes are expected to have a noticeable impact on performance.

The effect of superficial velocity on cell performance is explored next. The superficial velocity can be increased by either reducing the flow channel depth, or increasing the total flowrate. Polarization curves, shown in Figure 3-7, summarize simulations for flowrates ranging from 75 – 300 mL/min with a channel depth of 1/8". The model predicts first an initial linear range, where activation kinetics dominate system performance, with few superficial velocity effects. At higher current densities, energy efficiency increases with superficial velocity, where both activation and mass transfer are important. Finally, at higher current densities, diffusion effects dominate the voltage requirements, as a limiting current density is approached. The limiting current density is a strong function of superficial velocity. This behavior is similar to that encountered for redox flow batteries and other electrochemical flow systems.

![Figure 3-7: Modeling predictions of effect of superficial velocity on polarization curves for flowrates between 75 – 300 mL/min. Channel depth is 1/8" depth channel with cell length and operating conditions similar to bench-scale experiments.](image)

On closer inspection of the axial distribution of current density in the activation-mass transfer control region, superficial velocity effects can be discerned. Figure 3-8 shows the axial distribution of current density, laterally-averaged anode concentration and activation overpotentials, under an applied voltage of
0.35V, in the activation-mass transfer region. Following a short development length, current densities quickly drop as the surface concentrations become less thermodynamically favorable. The drop from maximum to minimum current density becomes smaller as the flowrate is increased, reflecting the improvement in mass transfer.
Figure 3-8: Model predictions of superficial velocity effect on axial variation of cell variables, for flowrates between 75 – 300 mL/min and 0.35V (kinetics-mass transfer controlled zone). (Top): Current density. (Middle): Laterally-averaged copper ion concentration at anode. (Bottom): Anode overpotential variation. Channel depth is 1/8” depth channel with cell length and operating conditions similar to bench-scale experiments.
In contrast, the bulk concentration increases faster for slower velocities, which drives the OCP higher and reduces the activation overpotentials. This larger change in bulk concentration with a decrease in flowrate is due to an increase in utilization: when less solution passes through the system, the impact of copper formation on the solution concentration becomes larger.

Another important aspect of superficial velocity effects is best demonstrated through the lateral concentration distribution. Figure 3-9 shows the lateral distribution of cathode copper ion concentration at three locations along the axial direction for same conditions discussed above, at an applied voltage of 0.35V, where both activation kinetics and mass transfer are important.

A diffusion boundary develops along the axial direction, and the thickness of that boundary layer becomes smaller with increased superficial velocity. The surface concentration of copper increases with higher superficial velocities at all locations along the cell length, for example, at the outlet of the cell, the surface concentration of copper drops from 0.26M in the bulk to less than 0.075M for a flowrate of 75 mL/min, whereas for a flowrate of 300 mL/min, the surface concentration drops to only 0.15M.
Figure 3-9: Model predictions of superficial velocity effect on lateral distribution of copper concentration in the cathode compartment, for flowrates between 75 - 300 mL/min and 0.35V (kinetics-mass transfer controlled zone). (Top): Cell inlet. (Middle): Cell middle section. (Bottom): Cell outlet. Channel depth is 1/8" depth channel with cell length and operating conditions similar to bench-scale experiments.
Thus a higher superficial velocity has three effects. First, as more solution passes through the cell, the changes in average concentration are smaller, reducing the thermodynamic OCP. Second, the higher velocity improves mass transfer and compresses the boundary layer, allowing the surface reactions to proceed at higher concentrations. Finally, a higher flowrate reduces the ratio of gas evolved to total flowrate, reducing bubble overpotential and electrode blocking effects. The downside however of a fast superficial velocity is the reduced utilization of the solution. Thus, at a high flowrate with more efficient mass transfer conditions, a longer electrochemical cell is required to bring the amine-CO₂ loading low enough for efficient absorber operation.

Conclusions

In this chapter, we developed a modeling framework to evaluate the effect of designs and operating parameters on the performance of the EMAR electrochemical cell:

- A two-dimensional model balancing axial convection and lateral mass transfer was developed to describe each compartment.
- A Nernst-based thermodynamic model of the cell as a function of copper surface concentrations was derived. The model predicts a thermodynamic penalty up to 190 mV for large pH swings.
- Electrode reactions were incorporated as boundary conditions and described using the Butler-Volmer equation with experimentally-determined parameters.
- Model results predict cell operation in a mixed kinetic-mass transfer regime, where concentrations are significantly different between bulk and surface, leading to the development of a thick boundary layer.
- Boundary layer development raises the equilibrium potential and reduces exchange current densities, resulting in a sharp decrease in current density over the length of the cell.
- Increase in superficial velocity, through reducing channel depth or increasing flowrate, will serve to compress the boundary layer, reduce bubble overpotentials and improve energy efficiency.
• However, a higher superficial velocity leads to a reduction in utilization of amine to less than 2% over the short length of the bench-scale system.

The model predictions above serve to provide guidelines for optimization of cell performance. They show that the Cu/EDA system can have high energy efficiency for CO$_2$ separation if mass transfer limitations are reduced. One path to reducing these limitations is through increasing the operating superficial velocity which acts to make the boundary layer more compact. However, the associated reduction in utilization will affect the EMAR process by increasing the size of absorber required, or increasing the total length of the cell. In chapter 5, we explore an alternative strategy to reduce mass transfer, by introducing flow disturbances to induce mixing of bulk flow and boundary layer.
Chapter 4

Bench-Scale Prototypes

This chapter describes design modifications to the EMAR bench-scale system to facilitate high throughput experiments and cell optimization. The previous prototype generation, EMAR 4.0, suffered limitations in its stability and ease of modification. New prototype generations are developed to address specific needs: EMAR 5.0 offers stable operation with modular internals; EMAR 6.0, the ability to control local current density along axial direction; and finally, EMAR 7.0 is optimized to demonstrate high pressure operation.

Prototype Components and Functions

It is helpful to first provide an anatomy of the cell components and their respective functions. The EMAR technology rests upon the ability to generate metal ions reversibly, and facilitate their reaction with a CO$_2$-loaded sorbent. For copper-polyamine chemistry, shown thermodynamically and kinetically to have favorable properties, an effective system must provide the following functionality:

1. Formation of copper ions at an electrode/solution interface under an oxidative anodic current.
2. Rapid mixing of formed copper ions into bulk solution to facilitate copper-amine complexation and accompanying CO$_2$ release, and the formation of a gas/liquid mixture.
3. Flow of anode-side gas/liquid mixture that minimizes contact with cathode side solution where the amine solution is regenerated.
4. Return of anode-side solution into the cell, after most gas has been removed, at the cathode side inlet, and effective mixing to bring copper/amine complex molecules to the electrode/solution interface.
5. Reduction of copper/amine complex molecules at the cathode metal/solution interface, and removal of copper metal atoms formed from solution.

There are a number of design configurations that can provide those functions. Conceptually, any design with two electrically connected electrodes immersed into solutions containing amine solution with an effective electrolyte would be sufficient.

A continuous flow system would be necessary to prevent CO₂ gas build-up inside cell, as well as effective mixing without the need for mechanical stirring. We could potentially envision a system where gas bubbles are not formed in the electrochemical cell, as discussed at the end of this chapter. For copper/EDA chemistry, such an arrangement is not possible without reducing utilization significantly, and thus bubble formation in the current cell design is allowed.

Mixing of flows from the anode and cathode must be minimized, to prevent formed gas bubbles from recombining with regenerated amines formed at opposite electrode. This can be achieved either by control of flowrate, as proposed for a membraneless Vanadium RFB (58), or with the recently developed membrane-free hydrogen bromide flow battery, where flow characteristics are carefully tuned (59), or by using a separator that forms a physical barrier and limits gas permeation. The separator must however allow ions to pass through with low ionic resistance, to limit ohmic losses across the cell. [Separator paper reference]

An important structural consideration is effective sealing to prevent leaks. Effective sealing balances leak prevention with ease of operation of the cell: permanent seals for example are ineffective. A commonly utilized approach in electrochemical cells design is to use an external chassis that holds the cell assembly together, and apply pressure (using bolts or clamps for example) to reduce clearance between chassis to where an effective seal is formed. Introducing an external chassis adds a few complications: inlet and outlet flows must pass through the external chassis into the cell, and electrical connection between electrodes and external circuit must be maintained.
Thus, the prototype essentially consists of two (flat or porous) electrodes with flow across or through them, with a membrane or separator dividing the two flow compartments, with an external chassis forming a tight seal. In the following we discuss various prototype generations which implement this design through a number of configurations.

**EMAR 4.0 - Previous Prototype Design**

The previous generation of the proof-of-concept system and electrochemical cell, EMAR 4.0, is shown in Figure 4-1. The EMAR 4.0 cell consists of two aluminum sheets forming the external chassis, sandwiching two copper electrodes and two Teflon gaskets with a straight rectangle cut through it to allow fluid flow along the electrodes. The chassis is held together by uniformly distributed bolts with insulating PTFE thread wrapped around bolts to prevent short-circuit. The aluminum sheets act as current collectors, and are electrically connected to the copper electrodes through conductive solder. Electrical connection between the aluminum chassis and external circuit is maintained by plugging wires into the chassis. Inlets and outlets to and from the flow channels are created by drilling holes through the copper and aluminum, and threading plastic fittings through the aluminum. The Teflon gaskets are cut to provide a planar flow field. A separator is sandwiched between the Teflon flow fields to minimize gas cross-over. Frequent collapse of the separator onto the planar flow field prompted the use of a fabric on top of the electrode.

In addition to the cell, the bench-scale system also consists of two three-neck flasks functioning as absorber and flash tanks, a dual-head pump to drive flow across cell, and an external power supply.

**Challenges with EMAR 4.0**

Through operational experience, a number of shortcomings in the design of EMAR 4.0 were observed. Those challenges are listed below:

- The use of a fabric to prevent collapse of the separator adds contact resistance, drives non-uniform copper deposition and associated dendrite formation. Dendrites were found to grow vertically
through the separator and ultimately cause a short-circuit. Figure 1-8 shows the cell cathode after a short-operation.

- The dual function of aluminum sheets as external chassis and current collectors results in a series of complications. The electrical connection between the chassis and copper electrodes by solder was ineffective as the solder frequently detached. When the solder was replaced by a wire coil, contact resistance increased. In addition, the clearance between the chassis and electrodes allowed fluid to leak from flow channels to surface of voltage-connected aluminum. The corrosive nature of amines quickly resulted in discoloring of the internal-facing surface of the aluminum, and a faradaic reactions are suspected to occur. This behavior reduces the energy efficiency of the cell by drawing current, as well as reducing the structural integrity of the chassis by electrochemical degradation.

- Similarly, threading inlet and outlet fittings into the chassis allowed small leaks between electrodes and aluminum, and drawing a faradaic current from the chassis.

- Teflon gaskets forming the flowfield suffer from the incompressibility of Teflon: applying stronger force to seal the cell can result in deformation of the gaskets causing leaks. Thus a balanced torque must be carefully applied to find the balance between insufficient force to form a seal, and too much force that causes deformation. The assembly and disassembly of EMAR 4.0 is thus a lengthy process (around 30 minutes each).

- EMAR thermodynamics and kinetics perform best at higher temperatures. High pressure operation is an important feature of the technology as it generates compressed CO₂ by pumping of liquid pressure. However, EMAR 4.0 is designed only for ambient operation.
Figure 4-1: EMAR 4.0 – previous generation of bench-scale cell prototype and system. Reproduced from (34)
EMAR 5.0 – Modular Internals and Stable Configuration

The purpose of EMAR 4.0 was to demonstrate the feasibility of the EMAR process, and to that end, this proof-of-concept fulfilled its mission. As the focus shifts to understanding the effect of design parameters on cell performance, and optimizing the cell design, the cell must be redesigned to allow for two core features:

- **Modular internals:** High throughput experiments, in the relative sense, which allow the exploration of a design parameter’s impact on performance, allows for a shorter and more resource efficient development cycle. EMAR 4.0 suffers a number of limitations that limit the robustness of the cell as it is assembled and disassembled, in addition to slow nature of assembly. EMAR 5.0 was designed to allow for flow fields to be rapidly constructed and deployed, and the electrodes to be returned to a fresh reproducible state between experiments, or quickly replaced. The assembly and disassembly is significantly shorter (5 mins each). This design generation was effective in facilitating the testing of a number of designs as discussed in Chapter 5.

- **Stable configuration:** To effectively demonstrate improved performance, longer operation times are required. Thus, issues like dendrite formation and chassis degradation must be effectively addressed.

We first explored replacing the bolt and nut assembly to reduce time and effort required for cell assembly and disassembly. The external chassis was made to be 50% thinner than before at 1/16” thickness for each sheet, to allow for a lighter system that needs less force to seal. The clamped system, shown in Figure 4-2, was unsuccessful: the clamps did not provide enough force to effectively seal the cell. In addition, clamps provide a non-uniform pressure distribution, which is not conducive to effective sealing, where uniform distribution is more desirable.
The bolt assembly was then simplified by decoupling the external chassis from its function as current collector. Instead of requiring electrical connection between the aluminum sheets and copper electrodes, the two layers are electrically insulated using a silicone adhesive layer and holes are drilled through the side of the electrodes. A copper wire is then brazed into the holes, and connected to the external circuit. Another important modification is drilling a large sized hole through the chassis, to allow direct threading of the inlet and outlets fittings into the copper electrode. Thus, the aluminum chassis are completely isolated from the solution and from electric current, protecting it degradation and preventing side reactions.

The Teflon gaskets were replaced by the more compressible Silicone sheets. Silicone is easily cut into complex shapes, can withstand a large seal pressure, and doubles as a gasket that makes the entire assembly more leak-proof.

To address the membrane collapse challenge, small baffles were added to the Teflon gasket along the flow direction, to act as supports for the membrane and minimize the area over which it can buckle under slight pressure differentials between the two compartments. This strategy, in addition to make the membranes slightly taller than the channels and stretch them before operation to prevent wrinkles, was successfully in eliminating the need for a fabric between the electrode and flow channels and the accompanying complications.
The dimensions of various components are modified to allow the aluminum chassis to essentially act as a “cage” for the copper electrodes, and the bolts do not go through the electrodes. Quick fit bolts are used to assemble the chassis together. A motor drive can be used to rapidly assemble and disassemble the cell, as the internal components are robustly set in place.

Thus, with this design, flow fields can be rapidly designed and deployed, the electrode surface can be restored with sandblasting or replaced without need to make other changes, since no connections are permanent. Finally, a large number of bench-scale experiments can be quickly performed, given the much higher speed of assembly. Figure 4-3 shows a photo of the assembled cell.

![Photo of Assembled Cell](EMAR 5.0 - Photo of Assembled Cell)

**EMAR 6.0 – Multi-electrode Analytical Cell**

As shown in Chapter 4, the axial variation of variables along the electrode surface has important effects on cell performance, both with regards to energy efficiency and stability. By tuning the cell design, the operating conditions and flow field, efficient and stable operation can be reached. Thus, in addition to the modeling capabilities developed, an analytical approach that allows measurement of local conditions along the electrode would provide valuable information.

EMAR 6.0 is a multi-electrode analytical cell, where the voltage or current applied at different axial positions can be precisely controlled. The design employs electrode segments that are electrically insulated
from each other. An External Aluminum chassis to provide structure, and is held down by sleeved bolts. A polypropylene layer between the chassis and electrode segments provides insulation for the former and structure for the latter. The copper electrode segments are held together in a pocket formed by the polypropylene layer, with wires passing through their rear to create electrical connection. Silicone gaskets, as with EMAR 5.0, are used as flow channels and to forms the seal, and sit between the polypropylene/copper segments layer. In addition, the polypropylene layer also allows multiple connections to the cell that are not individually attached to the electrode segments. Polypropylene (or alternatively, the more expensive PEEK) is necessary in lieu of a compressible material like silicone, which would not allow threading of a liquid fitting.

Figure 4-4 shows sketches of the cell design. The gray plates on the outside are similar to the aluminum clamping plates in use on the current reactor. Some longer, sleeved 3/8" bolts hold the assembly together and locate the internals during assembly. The tan plates represent PEEK plastic frames. These allow for threading fittings, 1/4" NPT for fluid flow and 1/8" NPT for electrode connection seals. The red areas near the edges represent silicone gasket material that can be customized to provide flow field designs. The inlet and outlet fluid connections are symmetrical, but the cut gaskets could be trimmed to feed flow to and from a corner of the first and last electrode if desired.

The electrodes are formed from 2" X 3" X 1/8" thick pure copper plate. Each electrode plate is brazed to a copper rod at its rear. This rod passes through a compression seal fitting to allow external electrical connection. This rod seal also serves to hold the electrodes in place during system assembly while the upper plate is lowered in place. After assembly, the copper electrodes are also pinned down at their ends by the pressure of the silicone gasket. All the fittings shown are made from either polypropylene or 316 stainless steel.
Figure 4-4: EMAR 6.0: CAD sketches of design. (Top): Front view along an axial cross-section of unassembled cell. (Middle): Isometric view of cross-section along center axis of cell. (Bottom): Isometric view of an electrode segment.

The fully assembled EMAR 6.0 prototype is used in a bench-scale system with multiple power supplies. Each power supply delivers a current or controls the voltage along two specific electrode segments, with
the other variable measured. This design thus allows investigations into the axial variations inside the cell and their interactions with different design parameters. Figure 4-5 shows a photograph of the cell.

![Figure 4-5: EMAR 6.0 - Photograph of Cell. (Top): Assembled cell. (Bottom): Front view of multi-electrodes held inside pockets in polypropylene layer.](image)

**EMAR 7.0 – High Pressure System**

EMAR cells 5.0 and 6.0 are both specifically developed for a particular purpose, though they can be repurposed. Both prototypes can be operated at higher temperatures, however, high pressure operation requires a different design approach. In particular, safety considerations must be prioritized, given the corrosive nature of the amine solution, and the risks associated with its high pressure operation.
EMAR 7.0 is therefore developed to act as a proof-of-concept for high pressure operation, and demonstrate the ability to efficiently regenerate pressurized amines and to generate high pressure CO₂ by evolution from the high pressure liquid phase.

The design of EMAR 7.0 uses two large 3/16" diameter racetrack gaskets to contain the high pressure solution and ensure cell is sealed. An engraving into the chassis fits O-rings that form a seal. The electrodes are held in place with #4-40 flat head machine screws near the ends. The connection to the electrode is via the 1/8" diameter copper rod shown pressed into a recess on the rear of the electrode. The channel size can be adjusted by inserting silicone strips during assembly. The external chassis is made from chemically-resistant PEEK plastic held together with a series of 1/4"-20 stainless steel bolts washers and nuts. Compression fittings are used for all inlets and entrance.
Peripherals

A few changes to the peripheral components of the bench-scale system are also necessary. Most importantly, temperature control capability is added to the system by immersing the three-neck absorber flask in a water bath whose temperature is controlled by a hot plate. The temperature inside the absorber and flash tank is monitored using thermocouples. A pH meter is used to track the CO₂ saturation of amines in the absorber flask. A gas mass flow meter is used to measure the output flowrate of released CO₂. Gas cylinders with a flowmeter are used to provide pure CO₂ or CO₂/N₂ mixture into the system. A power supply (or several in case of EMAR 6.0) is used to deliver the current/voltage required.

A number of challenges must still be resolved for effective monitoring of the system, the most critical of which is the flash tank design. The current design used here utilizes a three-neck flask. At one neck, the anode outflow enters and gas is disengaged, where it leaves from the second neck. The liquid solution is pumped through a piece of tubing to exit from the third neck. This design however does not efficiently
disengage the gas. Future designs of the system should focus on optimizing this component, to allow for accurate measurements of collected gas and of the Faradaic efficiency.

**Automation**

The operational mode of the EMAR process involves periodic switching of electrodes to maintain their integrity and prevent structural degradation that can be destabilize the cell. The switching time is a function of the current density and its distribution, the depth of flow channel and the thickness of the copper metal sheets. For long-term testing of the process, manual switching of electrodes becomes impractical, and the need arises for an automated approach. A first attempt at automation was attempted and is outlined here.

The automation setup was targeted at controlling the routing of flows to and from the absorber and flash tank, and the switching of polarity. An Arduino microprocessor, mounted on a breadboard, was used to control communication between a Python computer code and the system components. The MasterFlex pump is programmable through a serial connection cable, which allows control of flowrate through a circuit mounted on the breadboard connecting to the serial cable output wires, and controlled by the microprocessor. The programmable power supply was connected through a serial control cable directly to a computer running the Python control code. However, as the power supply did not have intrinsic polarity reversal features, its output was rerouted through the breadboard, and an H-gate circuit was used to reverse polarity, and was mounted on the same breadboard. Finally, flow switching was attempted through 8 two-way solenoid valves, connected to the breadboard and controlled by the microprocessor. Figure 4-8 shows a photograph and schematic of the circuit logic and assembled components.

This control strategy was however unsuccessful: the large number of solenoid valves required long tubing and therefore, large pressure drops that caused the system to be unstable. An alternative strategy is replacing the 8 two-way valves by 4 three-way or 2 four-way valves, despite the significantly higher cost, to improve the robustness of the process. The control platform developed can be modified to this more robust configuration when resources are available, and tested for smooth operation.
Conclusions

In this chapter, previous generations of EMAR prototypes are explored in-depth, describing their limitations and proposing design modifications. Modified prototype designs that are tailored for specific experimental
or analytical functions are proposed and constructed. Changes in peripheral components and an automated setup are also described.

- The previous generation of prototypes, EMAR 4.0, suffered limitations to its stability, ease of design modification, and control of operating conditions.
- EMAR 5.0 is designed to allow for faster assembly/disassembly and modular internals that allow for design testing, and is thus more tailored for exploring the design parameter space.
- EMAR 6.0 features multiple electrode segments that allow control of voltage/current along the axial direction, and is designed for analytical experiments and model validation.
- EMAR 7.0 uses a racetrack O-ring design that offers a more reliable seal, and is designed to demonstrate high pressure operation.
Chapter 5

Bench-Scale Device Experiments

This chapter describes bench-scale EMAR experiments, performed with the purpose of design parameter exploration and optimization. First, EMAR 5.0 performance as a function of flowrate and channel depth was tested. Experimental results indicate that at the desired current densities, the cell is operating in a mixed mass-transfer and kinetics control regime, in qualitative agreement with model predictions. To minimize mass transfer limitations without sacrificing utilization, mixing between the bulk and boundary layer must be induced. A serpentine channel design was constructed and tested, and results suggest a significant improvement in energy efficiency, with around 0.3 V demonstrated for a current density of 50A/m². Electrochemical impedance spectroscopy experiments further confirm mass transfer control effects on the bench-scale cell performance. Multi-electrode prototype experiments demonstrated the axial variability of current density for large applied voltages, as predicted by the model.

EMAR 5.0: Straight Channel Tests

This section describes bench-scale experiments with the modular EMAR 5.0 design. The objective of those experiments is to probe how polarization behavior of the cell changes as the cell design is modified, and in particular, the effect of superficial velocity on cell performance. The relative importance of kinetics and mass transfer can be inferred from the system behavior.

Device Design

Chapter 4 describes the prototype design process and rationale in detail. The electrochemical cell consists of two 9” by 3” variable-thickness flow channels, cut out from silicone gaskets placed on top of copper plates, with an external aluminium chassis. The total electrode surface area was between 0.015 and 0.018
Copper 101 alloy (purity > 99.99%) was used for the copper plate electrodes. A Celgard® 3501 surfactant-coated porous polypropylene membrane separating the two flow channels to prevent gas crossover was used. A power supply was used to deliver a constant current or voltage to the copper plates through side-protruding copper wires. Between experiments, the copper plates were sandblasted to restore their surface. The design of the cell is highly modular, allowing rapid modification of channel designs and membrane used. Flow fields of different thicknesses and flow configurations were designed and built. Initial experiments utilized straight channels with slight baffles to support the separator and reduce buckling, and thus prevent separator collapse on one side of the flow channel. Figure 5-1 shows an example of the basic design. The depth of the cell is easily controlled by choice of initial silicone gasket thickness. Flow channels of depth 1/8", 1/16" and 1/32" were tested, at flowrates ranging from 75 mL/min to 300 mL/min (superficial velocities between 5.2e-03 – 8.3e-02 m/sec)

Figure 5-1: Straight Flow field used in initial EMAR 5.0 experiments. Channel depth is easily controlled by choice of initial silicone gasket thickness.

Bench-Scale Experiments Protocol

The closed loop system used for the bench-scale tests, described in more detail in Chapter 4, consists of an absorber vessel, a flash tank and an electrochemical cell. A CO₂ saturated 1M EDA, 1M NaNO₃ electrolyte and 0.25M Cu(NO₃)₂ solution was circulated continuously through the system using a dual-channel MasterFlex pump. The absorber was a 200 mL three neck flask, whose temperature was controlled by submersion in an oil bath heated by a digital hot plate. The flash tank was a 25 mL three neck flask, with a liquid inlet and outlet, and a gas outlet. Before the experiments started, the amine solution was saturated
overnight with CO₂ by flowing pure gas into the absorber. The saturation was continued until the pH of the EDA solution dropped to around 7, indicating full CO₂ loading of EDA. The experimental setup allows control of operational temperature, flowrates and applied voltage. For each experimental condition, after steady-state flow was reached, a set voltage or current was applied, and allowed to equilibrate for 10 minutes before measurements are taken. In all experiments using sodium nitrate electrolyte, the current/voltage reached a steady-state with no fluctuations in less than 1 minute. The voltage or current was then recorded, before operating conditions were changed. Some experiments requiring disassembly of the cell to change internal components. The same EDA solution was used in all experiments, and did not exhibit any signs of degradation.

**Effect of Channel Depth and Flowrate**

The polarization curves of the bench-scale prototype cell for channel depths of 1/8”, 1/16” and 1/32” are shown in Figure 5-2. It is important to note here that the operating flowrates were limited by pressure build up inside the cell as the superficial velocity increased, and thus the maximum operating flowrate was successively smaller for smaller channel depths.

For the 1/8” deep channel, we first observe a linear phase, where current density increased slowly at a linear rate as the voltage was ramped up. Under the moderately fast system electrokinetics under a nitrate electrolyte (as discussed in chapter 3), this linear phase can be attributed to activation kinetics control, where small overpotential Tafel behavior is observed. The effects of superficial velocity in this region are limited, but still apparent. At a low current density of around 15A/m², the voltage required drops from around 0.52 V at a flowrate of 75 mL/min to 0.41 V at a flowrate of 300 mL/min, or around 20% change with a 4-fold increase in flowrate.

This limited effect of flowrate on polarization behavior at low current densities is due to comparable values of reactant surface concentration of reactants (and therefore, the exchange current density) over this range of flowrates. However, a higher flowrate will result in a drop in utilization and consequently, lower loading
changes and a lower OCP. At a lower OCP, more of the applied voltage is utilized to drive surface reactions, and thus the voltage required to drive the same current density becomes smaller.

At an onset potential (which varies with flowrate) an exponential current density phase starts where a small change in voltage results in a large increase in current density at a gradually increasing rate. In this region, the effect of flowrate in the 1/8" deep channel is apparent at all flowrates. For example, at 75 mL/min, a voltage of 0.75 V is needed to drive a current density of around 60 A/m², while only 0.61 V are needed at 300 mL/min.

**Figure 5-2:** Polarization curves for straight-flow channels with decreasing depths. (Top): Depth of 1/8". (Bottom): Depth of 1/16". Lines are for purpose of showing trends only. Experiments are at 55°C, 1M EDA, 0.25M Cu(NO₃)₂ and 1M NaNO₃.
In the exponential region, the effect of flowrate on performance is due to both the thermodynamic change in voltage, as well as an increased surface concentration at the cathode and reduced surface concentration of copper ions at the anode, and the resulting improvement in exchange current density.

Further inspection of the flowrate effects for the 1/8" deep channel draws attention to how the performance enhancement is significantly higher between 150 and 300 mL/min as compared with 75 and 150 mL/min. This change suggests that at higher flowrates, another effect is at play, in addition to the thermodynamic voltage and exchange current density enhancement.

Model predictions suggest that bubble effects become particularly important at higher current densities (and faster formation of cupric ions and release of CO₂). As bubble formation increases, the ratio of gas to total fluid will increase and less of the electrode is available for reaction. An increase in flowrate reduces the residence time of bubbles and their ratio to total fluid, and thus, increases electrode surface availability. This bubble effect can explain the improvement enhancement effect of flowrate for higher current densities.

In the 75 mL/min flowrate in a 1/8" deep channel, there is a noticeable deceleration at current densities higher than around 60 A/m², where a significantly higher voltage is required to drive an 85 A/m² current density. This sharp increase in voltage is potentially due to the onset of a diffusion controlled zone, as the limiting current density is approached.

For smaller channel depth, the behavior is qualitatively similar, where at low current densities, a linear phase is observed in the case of the 1/16" depth channel, followed by an exponential current density phase.

A significant performance improvement is observed as channel depth is reduced and flowrate increased. For example, at a current density of 50 A/m², the voltage required drops from around 0.6 V in the slowest flowrate for the 1/8" deep channel to 0.43 V for the fastest flowrate and 1/16" deep channel. As detailed in the model discussion and in this section, this improvement is a combination of lower thermodynamic
voltage, higher mass transfer and exchange current density, as well suppression of bubble effects on electrode availability.

Figure 5-3: Effect of channel depth on polarization curves – comparing 1/16" and 1/8" channel depths under the same flowrate. Lines are for purpose of showing trends only. Experiments are at 55°C, 1M EDA, 0.25M Cu(NO₃)₂ and 1M NaNO₃.

A comparison of voltage-current density behavior for the two channel depths at the same flowrate of 75 mL/min is shown in Figure 5-3. At high current densities, the exponential phase behavior is very similar, though limiting current density is not approached in the 1/16" depth channel for the range of voltages tested.

The low current density behavior follows a different trend, where it appears that the onset of exponential phase requires a much higher current in the case of the 1/8" depth channel. This difference in behavior at low current densities persists for different flowrates. If the polarization curves are compared for the same superficial velocity (shown in Figure 5-4), the large difference at low current densities is very clear. As the current density increases, performance at the same superficial velocity for 1/8" and 1/16" depth channels reached close agreement. The low current density discrepancy is possibly due to migrational resistance to electrolyte diffusion through the membrane. Further experiments to probe this behavior further can be performed; however, from a practical perspective, the low performance of 1/8" depth channels does not encourage further inspection.
Figure 5-4: Effect of channel depth at equal superficial velocity on polarization curves - comparing 1/16" (blue) and 1/8" (maroon) channel depths at the same superficial velocity of 10.3 and 20.6 mm/sec. Lines are for purpose of showing trends only. Experiments are at 55°C, 1M EDA, 0.25M Cu(NO₃)₂ and 1M NaNO₃.

An important conclusion here is the relative importance of mass transfer at higher current densities, and the demarcation of activation-controlled from mixed activation-mass transfer zones. As shown in Figure 5-5, an increase in flowrate has a monotonically enhancing effect on energy efficiency. The magnitude of this effect increases steadily with current density. Linear dependence of voltage on flowrate is observed for current densities starting 50 A/m². This linear dependence demarcates activation control from mass-transfer control.

Thus, for industrially relevant current densities, we expect the EMAR cell to operate under conditions where both the intrinsic electrode kinetics and the prevailing flow characteristics control performance. This is an important finding: it suggests that even without an improvement in the electrochemical kinetics, a significant performance enhancement is possible if the flowfield is optimized.
It is important to note, that the bench-scale experiments above did not allow for estimation of true Faradaic efficiency (CO₂ captured per unit charge). The current design of the flash tank did not separate the formed gas from the liquid efficiently, and thus the captured gas could not be accurately quantified. Previous kinetic and bench-scale experiments have found that the EDA/Cu system under nitrates features faradaic efficiencies above 90%. Qualitative observation of bubble formation and their increase with current was possible visually, and documented by video recording. Future work should focus on redesigning the gas/liquid disengagement zone to allow efficient gas capture and quantification.
Design Optimization

The electrochemical kinetics of the system with nitrate electrolytes (discussed in depth in Chapter 2) allow for energy efficiencies up to 25 kJ/mole at current densities around 50A/m². The trends observed in the initial bench-scale experiments suggest that an optimized design must address mass transfer limitations in current cell designs. An increase in superficial velocity has been found to greatly improve performance at all current densities by maintaining high ion concentration at the cathode and low concentrations at the anode, in addition to the potential effect on bubble suppression. Increasing superficial velocity can be achieved by reducing channel depth and increasing flowrates. Figure 5-6 shows the significantly improved performance for a 1/32” channel operating at higher superficial velocities. The performance demonstrated by this cell design reduces energy consumption to around 30 kJ/mole at a current density of 50A/m², more than 70% less than the original proof-of-concept device. This represents a significant improvement that can help bring this technology closer to application.

![Figure 5-6: Polarization curve for a 1/32” depth channel. Lines are for purpose of showing trends only. Experiments are at 55°C, 1M EDA, 0.25M Cu(NO₃)₂ and 1M NaNO₃.](image)

There are limits, however, to the extent of how depth and flowrate can be modulated. Channel depth less than 1/32” require customized construction methods used for microfluidic devices, adding a significant manufacturing cost that is infeasible given the large-scale target applications of this technology. Flowrate
increase is limited by the resulting pressure drop across the system, and the mechanical instability observed when flowrates higher than 300 mL/min were utilized.

In addition, a higher superficial velocity will reduce utilization (at a rate proportional to the square root of velocity) and limit the operating amine loadings. The energy efficiency of drawing a large current (and releasing a large amount of CO₂) while operating within a small range of amine CO₂-loading is at the expense of a dramatically rising capital costs, as the CO₂ absorption driving force becomes smaller and a larger absorber is required.

An alternative strategy is to address the mass transfer limitations inside the cell by an increase in mixing, without the need for higher flowrates and a reduced utilization. The introduction of internal mixing in the flow field can force the remixing of the surface boundary layer with the bulk, and in essence, “restart” the boundary layer development. This would in effect ensure that the average boundary layer thickness is kept small and thus the average exchange current density remains high enough to result in high performance. Internal mixing can be achieved through a number of strategies, such as the use of static mixers, for example. Here, we opted for the use of baffles in the flow field, due to their simplicity and ease of deployment.

The design and optimization of the baffles requires a more involved model that combines high resolution of flow field with modeling of electrochemistry and species distribution. We employ here a modified version of the model introduced in Chapter 4 where perfect mixing of boundary layer and bulk flow is achieved computationally by averaging the lateral concentration and reintroducing it at the next axial position as an undeveloped, single-front profile. This implementation amounts to an assumption that each turn will result in perfect remixing of the bulk and boundary layer streams.

A sample of the results is shown in Figure 5-7. With baffles (or some form of mixing), the boundary layer quickly develops, and towards the exit of a 10” long cell (the dimensions employed in bench-scale experiments), the surface concentration is an order of magnitude smaller than the bulk concentration. The
exchange current density and therefore, the cell performance, drops quickly. However, if evenly separated
turns are introduced, the surface concentration is maintained relatively high.

It is important to notice as well that baffle-induced mixing results in a drop in the bulk concentration. The
baffles thus effectively deliver surface changes occurring at the electrodes to the bulk of the system,
allowing high concentrations and current densities at the electrode while maintaining a high utilization.

Although this modeling approach to serpentine design effects is not sufficient to develop quantitative
estimates, given the important velocity effects that will dominate the cell performance, it provides a
promising qualitative picture of baffle effects.

Figure 5-7: Model results contrasting straight and serpentine channel designs. (Left): Straight channel
design. (Right): Serpentine channel design.

To test these effects experimentally, a number of different channel designs (Figure 5-8) were constructed
and tested. The fully serpentine design caused vibrations in the system due to the large pressure drop, and
thus was not used further. The short perpendicular baffles design did not result in a significant performance
improvement: upon inspection, the flow was found to channel through in the middle section, and thus the baffles were ineffective.

Figure 5-8: Samples of flow fields tested. All channels were cut from 1/16” silicone gaskets, with a length of 10” and a width of 3.25”. a) Vertical serpentine arrangement. b) Short baffles perpendicular to flow. c) Protruding baffles perpendicular to flow.

When the protruding baffles were designed for a longer length, a significant performance improvement resulted. Inspection of the cell electrodes post-operation suggest this baffle design was effective in rerouting the entire flow. Figure 5-9 shows picture of the electrodes. The removed and deposited layer at anode and
cathode respectively closely track the flow field shown in Figure 5-8. At the anode, the inlet point for the channel was placed opposite to the first baffle, and static liquid filled the pocket formed by the first baffle was static. This area featured formation of a dark deposit due to high changes in pH that can potentially result in copper hydroxide formation. This observation shows that the fluid closely tracks the serpentine flowfield.

![Image](image_url)

**Figure 5-9: Cell anode post-operation hour using a long baffled channel, with removed layer of copper.**

The polarization curve using this flow field is shown in Figure 5-10. The performance enhancement, where again a current density of 50A/m² can be achieved with an energy consumption of around 30 kJ/mole CO₂ (down from 100 kJ/mole for the proof-of-concept device), demonstrates that flow field can be effectively used as an additional lever to minimize mass transfer limitations, and allows current densities above 130 A/m² to be reached at a reasonable energy consumption (~60 kJ/mole CO₂).
In comparing with the proof-of-concept device, it is important not to discount the effect of temperature on the system performance. The proof-of-concept runs were operated at ambient conditions (around 25°C), while the results above are at around 55°C. For a better comparison, the baffled channel design system was tested at a range of temperatures from 25°C to 55°C.

The results show the important effect of temperature on system performance, particularly at higher current densities. An increase in temperature reduces the thermodynamic voltage of the cell, improves kinetics as well as mass transfer (by reducing viscosity and increasing diffusivity).

Even at low temperatures, however, an improvement in performance is apparent. At 25°C, the long baffled channel design requires around 50kJ/mole at 50A/m², still 50% better than the proof-of-concept device operated at the same temperature.

However, higher current densities can only be accessed if the temperature is increased to 55°C (as they require a voltage less than that where water splitting becomes a concern), due to the relatively slow kinetics of the system.
The design optimization rules validated for the EMAR process in this work thus suggest that maximizing superficial velocity while introducing significant mixing inside the flow channel can allow for a system operating close to its kinetic limits, without any significant changes to the chemistry utilized. Experimental results are thus in good qualitative agreement with modeling predictions.

**Note on Faradaic Efficiency**

The results for the experiments described in this chapter report the measured current and voltages for the bench-scale prototype, and interpret those results to indicate the energy efficiency of the process. However, two important limitations of these results are important to highlight.

The first concerns the true Faradaic efficiency of the system, specifically, whether each electron passing through the external circuit corresponds to the formation of half a mole of copper ions and the release of one mole of CO\(_2\) in the anode. To accurately evaluate the true Faradaic efficiency, all the released gas must be disengaged from the liquid phase and quantified. The current bench-scale setup utilizes a simple three-neck flask for disengagement, and observations suggest it had limited ability to disengage all formed bubbles. Bubble formation, observed at the inlet to the flash tank, was qualitatively found to increase with
current, but a better designed gas/liquid disengagement system should be utilized in future experiments to allow for better faradaic efficiency measurements.

The second limitation concerns the copper species deposited on the cathode side of the cell, and the Faradaic efficiency of copper deposition from its EDA-complex. The potential-pH equilibria of the EDA/Cu system discussed in Chapter 3 suggests that at high pH, there is a possibility of copper hydroxide and oxide formation under reduction potentials. Further probing of the deposited layer of copper using XPS experiments (as in Chapter 2) should be performed, to ensure that atomic copper is deposited. The deposition of copper oxide or hydroxide would result in increased voltages during their dissolution, and thus should be avoided.

**Electrochemical Impedance Spectroscopy**

This section describes Electrochemical Impedance Spectroscopy (EIS) experiments performed to further probe the electrochemical cell behavior and confirm proposed hypotheses on relative importance of kinetics and mass transfer.

EIS is an effective tool in testing the behavior of electrochemical cells. Alternating Current (AC) inputs at variable frequencies allows the separation of electrochemical processes by time-scale, and can provide important information on their relative importance.

**Experimental Setup and Analysis Methodology**

Electrochemical Impedance Spectroscopy experiments were performed using a VersaStat 4 potentiostat. The frequency range tested was 1mHz to 1kHz. In all experiments, the temperature of the cell was controlled by setting the temperature of the fluid in the upstream absorber through submersion in an oil bath whose temperature is controlled by a hot plate. The solutions used had the same composition as in direct current bench-scale experiments. The amplitude of the applied sinusoidal voltage waves was 10 mV and the waves were either centered on the open-circuit potential (OCP), or around -0.1V vs. OCP. For the
copper/EDA system, the electrochemical cell OCP reflects the Gibbs Free Energy of binding for EDA and CO₂, around 0.14V at T=55°C.

Static experiments with no flow through the system, as well as flow experiments with flowrates between 75 mL/min to 300 mL/min, were performed. In a typical experiment, a steady flow rate is first established by cycling CO₂ saturated amine solution with a 50% copper loading and 1M supporting electrolyte. For static experiments, the flow is stopped before an AC current is applied. For flow experiments, the solution is circulated through the cell at a set flow rate while the EIS experiment is performed.

**EIS Results**

EIS experiments were initially performed on EMAR 5.0 under static conditions. Figure 5-12 shows the Nyquist plots for a channel depth of 1/32” under static conditions. The EIS behavior is typical of a Randles cell, where a semi-circle beginning at zero R_{corr} is observed at high frequencies, followed by a straight line at approximately 45° at lower frequencies. The x-axis intersection corresponds to pure resistance stemming from contact and solution resistance. The radius of the semi-circle is proportional to resistance to charge transfer, while the low-frequency straight line is associated with diffusion-control. The features of the static EIS Nyquist diagram suggest a strong mass transfer effect, as expected. Results also suggest a low contact and solution resistance (0.0289 Ω), consistent with the use of a high concentration of supporting electrolyte and good electrical connection with the electrodes.
Figure 5-12: EIS results for EMAR 5.0 under static conditions. Channel depth was 1/32", and solution used was 1M EDA, 1M NaNO$_3$ and 0.25M Cu(NO$_3$)$_2$ at 55°C. Line indicates trend only. Perturbation was centered around OCP.

Figure 5-13: EIS results for EMAR 5.0 with flow. Channel depth was 1/32", flowrate 75 mL/min, and solution used was 1M EDA, 1M NaNO$_3$ and 0.25M Cu(NO$_3$)$_2$ at 55°C. Line indicates trend only. Perturbation was centered around OCP.

In contrast, the Nyquist behavior changes significantly under flow conditions. Figure 5-13 shows the Nyquist diagram for the cell at a flowrate of 75 mL/min. The high frequency response is similar, but with a lower peak than observed in the static experiments, indicating smaller activation resistance.
The effect of flowrate becomes apparent when the Nyquist diagram for two different flowrates is compared. Figure 5-14 shows the effect of increasing flowrate on the EIS behavior of the cell. The results are qualitatively similar, however, the magnitude of resistance decreases significantly.

![Nyquist diagram showing effect of flowrate on EIS behavior](image)

**Figure 5-14: Effect of flowrate on EIS results. Flowrates of 75mL/min and 150 mL/min. Channel depth was 1/32", and solution used was 1M EDA, 1M NaNO₃ and 0.25M Cu(NO₃)₂ at 55°C. Line indicates trend only. Perturbation was centered around OCP.**

The x-axis extrapolation of the semi-circle is linked to the activation resistance of the cell, and is a function of the exchange current density. The decrease in its value suggests that a higher flowrate results in a larger exchange current density. This increase can be attributed to either a change in surface concentration, or in electrode availability.
Figure 5-15: Comparing static and flow EIS results for 1/16" depth long baffle channel. Flowrate is in mL/min. Solution used was 1M EDA, 1M NaNO3 and 0.25M Cu(NO3)2 at 55°C. Line indicates trend only. Perturbation was centered around OCP.

Similar results are obtained for the long baffle 1/16" depth channel, though with a more complex behavior and higher kinetic resistances. Under static conditions, the system displays signs of mass transfer limitations at low frequencies, though not through the classic Warbug diffusion resistance behavior (45° angle). Under flow conditions, the straight line behavior at low frequencies is replaced by a more complex elliptical behavior, which requires further analysis to determine the underlying physics.

This complex behavior however appears to be a strong function of mass transfer and superficial velocity, as it quickly reduces to a semi-circle on the x-axis as the flowrate is increased, indicating a switch to an activation controlled regime as the flowrate is increased.
Figure 5-16: Flowrate effects on EIS results for long baffle 1/16" depth channel. Flowrates are in mL/min. Solution used was 1M EDA, 1M NaNO₃ and 0.25M Cu(NO₃)₂ at 55°C. Line indicates trend only. Perturbation was centered around OCP.

The experiments above are all performed with a sinusoidal wave centered around OCP, where current density is zero. To further probe the long baffle system, experiments centered around a voltage of -0.1V vs. OCP are performed, in order to investigate the effect of flowrate at higher currents. Figure 5-17 shows the results, contrasting static and low flowrate conditions. The trends are similar to previous cases, where low frequency response for static case are diffusion-controlled, and the introduction of flowrate transforms performance to a semi-circle that suggests activation control is dominant.
Figure 5-17: EIS experiments centered around -0.1V vs. OCP for long baffle 1/16" depth channel. Flowrate is in mL/min. Solution used was 1M EDA, 1M NaNO₃ and 0.25M Cu(NO₃)₂ at 55°C. Line indicates trend only. Perturbation was centered around -0.1V.

In the case of higher voltage centered sinusoidal waves, however, the behavior at higher flowrates shows an important qualitative difference, as shown in Figure 5-18: the intersection of two semi-circles appears to be underlie the performance of the system. The presence of two semi-circles can be explained a two-step charge transfer mechanism, as is consistent with what is known for copper electrochemistry. This can potentially mean that for other impedance spectra, the second reaction step underlies part of the low frequency response of the system, but is only resolved at higher currents and in the absence of strong mass transfer control. An alternative explanation is the prevalence of some side reaction at these conditions. Further investigation, and in particular, fitting to equivalent circuits, can help better explain the system behavior.
Figure 5-18: EIS experiments centered around -0.1V vs. OCP for long baffle 1/16" depth channel and higher flowrates. Flowrates are in mL/min. Solution used was 1M EDA, 1M NaNO₃ and 0.25M Cu(NO₃)₂ at 55°C. Line indicates trend only. Perturbation was centered around -0.1V.

**Fitting EIS Data**

Fitting EIS data to an equivalent circuit model can provide valuable insight into the processes occurring in the system. It is important to note that equivalent circuit models are not unique, and that it is possible for a number of different models to accurately fit a given data set, and thus quantitative physical interpretations of results should be approached conservatively. A Randles equivalent circuit, shown in Figure 5-19 was used to fit the electrochemical cell experimental data. This frequently utilized equivalent circuit assumes the system behavior can be reduced to a solution resistance \( R_\Omega \), a double layer capacitance \( C_D \), and an impedance representing faradaic reaction, consisting of a charge transfer resistance \( R_{ct} \), and Warburg impedance \( Z_w \).
A Generalized Finite Length Warburg element was used to represent the Warburg impedance, in the form:

\[
Z = \frac{R_c \tanh \left( \left( \frac{i\omega L^2}{D} \right)^p \right)}{\left[ \frac{i\omega L^2}{D} \right]^p}
\]  

(5-1)

where \( L \) is the diffusion length-scale, \( i \) is square-root of -1, \( \omega \) is the frequency and \( p \) is an exponent related to the ideality of the Warburg element. This equivalent circuit assumes the behavior of the cell is a balance between reaction and diffusion, with solution resistance and double layer charging effects.

The results were fit using the commercial software, ZView (Scribner Associates Inc.). The results from the 1/32" deep channel were fitted for flowrates of 75 and 150 mL/min. The equivalent circuit proposed showed good agreement with experimental data for both cases (with an error sum of squares of 0.03 and 0.05 respectively). The values of the fitted parameters are summarized in Table 3.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>75 mL/min</th>
<th>150 mL/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_1 )</td>
<td>0.07</td>
<td>0.06</td>
</tr>
<tr>
<td>( R_1 )</td>
<td>0.05</td>
<td>0.04</td>
</tr>
<tr>
<td>( R_{ct} )</td>
<td>1.34</td>
<td>0.96</td>
</tr>
<tr>
<td>( L^2/D (W_T) )</td>
<td>9.665</td>
<td>4.206</td>
</tr>
<tr>
<td>( W_p )</td>
<td>0.324</td>
<td>0.327</td>
</tr>
</tbody>
</table>

Table 3: Equivalent circuit fitted parameters for the 1/32" depth channel with flowrates of 75 and 150 mL/min.

The values for the capacitance and solution resistance (\( R_1 \)) were consistent for both flowrates. \( W_p \), the exponent representing departure from ideal Warburg behavior, also had similar values between the two
Experimental conditions, which suggests that similar processes are at play for both cases. Other Warburg impedance parameters were significantly different: the large change in \( W_T \), which is equal to \( L^2/D \), suggests that the average diffusion-length scale, an indicator of the boundary layer thickness, is reduced by around 1.5 as the flowrate is doubled, in agreement with model predictions and the mixed kinetics-mass transfer hypothesis. The change in charge transfer resistance, \( R_{ct} \), can also be explained in the same context; as the improvement in mass transfer with superficial velocity increase will result in a higher surface concentration and consequently, a larger exchange current density and lower charge transfer resistance.

**Role of Membrane**

The primary role of the separator is to prevent the cross-diffusion of evolved \( \text{CO}_2 \) from the anode to cathode compartment where it will recombine with the regenerated amine solvent. A secondary feature, however, is to prevent unwanted cross-over of reactant species, while allowing for ionic migration. When a voltage is applied between the two electrodes, faradaic reactions proceed. The dissociated electrolyte ions will migrate to the corresponding electrode to counter the change of charge and maintain electroneutrality. This ionic current passes through the membrane, and thus, the ionic conductivity of the membrane is important for efficient operation.

This section describes experiments performed to probe membrane effects. First, a number of anion exchange membranes were tested to explore their effect on performance. Fumasep® anion exchange membranes were purchased and used in the EMAR 5.0 cell design. The rationale for anion exchange membranes is to prevent copper ions from migrating from the anode compartment to the cathode, where they can recombine with regenerated amine molecules and therefore reduce the efficiency of the system.

However, experiments found that the anion exchange membrane caused a large increase of voltage at low current densities (0.8V at 50 A/m\(^2\) in a 1/32” depth channel). In addition, the membrane suffered strong discolouring even after short operation, suggesting its inability to withstand the chemical environment in
the cell. Further testing of anion exchange membranes utilizing different polymer chemistries may still useful but was not pursued further in this work.

In contrast, Celgard® separators, made from microporous polypropylene with a surfactant coating showed excellent performance and resistance for long operations. The effect of the separator pore size is pronounced: Celgard® 3501 and 3401 separators (pore size of 0.064 and 0.043 μm respectively) were tested in EMAR 5.0. Figure 5-20 shows the polarization curves, where the voltage required to drive the same current density increases significantly for smaller pores, particularly at higher currents. This effect of pore size suggests a membrane resistance to ionic current that becomes important with smaller membrane pore size.

![Figure 5-20: Effect of membrane porosity on polarization curve in a 1/32” depth channel. Solution used was 1M EDA, 1M NaNO₃ and 0.25M Cu(NO₃)₂ at 55°C. Line indicates trend only.](image)

EIS experimental results, shown in Figure 5-21, show two important differences: with a larger pore membrane the height and radius of the first semi-circle is smaller, suggesting smaller charge transfer resistance. In addition, the small pore membrane system shows signs of mass transfer control at low
Those preliminary experiments clearly show that the separator selection is critical to efficient performance. Further tests of other chemistries and pore sizes can provide valuable information of the underlying cell processes, and can potentially result in better performance at high current densities.

**EMAR 6.0**

A sample run of EMAR 6.0 with a 1/8" depth channel was performed to demonstrate the utility of this prototype in probing the axial distribution of current. The multi-electrode cell consisted of four equally sized copper anodes and cathodes, where each set of electrodes was connected to a separate power supply, with a flow channel guiding the solution along the electrodes. The current density for each anode/cathode couple was measured after applying an equal voltage at all locations. Figure 5-22 shows the change in current along the axial direction. At lower voltages, a flat profile was observed, and as the voltage is increased, the current density near the inlet becomes significantly higher, reaching around 75% higher at the inlet for an applied voltage of 0.8 V. This finding agrees with previously discussed modeling predictions and experimental results, where mass transfer is thought to play a dominant role for higher current densities.
and the development of a boundary layer results in a drop of current density along the axial direction due to thermodynamic concentration effects as well as a reduction in exchange current density. EMAR 6.0 can thus be used effectively in further optimization of more complicated flow fields, and in obtaining a better understanding of spatially distributed phenomena occurring inside the cell.

![Figure 5-22: Multi-electrode prototype bench-scale experiments; showing the change in current vs. axial location. A flow channel with depth of 1/8" was used, with a 1M EDA, 0.25M Cu(NO₃)₂ and 1M NaNO₃ solution at 55°C.](image)

**Conclusions**

In this chapter, bench-scale experiments were performed with the purpose of exploring the cell design and operating conditions impact on performance.

- For straight flow fields, the polarization curves show evidence for activation control at current densities below 25 A/m², and a transition to a mixed kinetics-mass transfer control region for higher current densities, and in thus in qualitative agreement with modeling predictions.
- The performance of the straight flowfield cell was found to be a strong function of the superficial velocity and channel depth, as expected for a kinetics-mass transfer controlled system.
To optimize cell performance and minimize mass transfer limitations while maintaining a reasonable utilization, disturbances to the flow field to remix the solution and minimize boundary layer thickness were introduced using a serpentine flow channel design.

In agreement with modeling predictions, the serpentine flow channel design was effective in improving mass transfer and raising the cell performance.

Electrochemical impedance experiments confirmed the activation-mass transfer hypothesis, with results suggesting a change in activation resistance for increased flowrates.

Membrane pore size was found to have an important impact on performance, possibly due to an added resistance to electrolyte migration for smaller pore size.

The multi-electrode prototype, EMAR 6.0, confirmed model predictions on the axial distribution of current density due to thermodynamic and kinetic effects of surface concentration.

The work done in this chapter expands our understanding of the EMAR technology, and the coupling of electrode reactions to flow. It also provided important findings in which design parameters and operating conditions have the most impact on performance. However, the experiments described here focused on one electrochemical cell with a limited total length and electrode surface area. A similar experimental investigation of a cell stack consisting of a number of cells is a necessary step to further validate the findings described here, as well as a more detailed investigation of changes in Faradaic efficiency.
Chapter 6
Performance Analysis

This chapter analyzes the current performance of the EMAR process in terms of energy contributions and cost of CO₂ capture. Two scenarios are established; a best case scenario assuming operation at thermodynamic and kinetic penalty of EDA/Cu chemistry, and a current case scenario assuming observed bench-scale polarization curves can be scaled up. Energy consumption was estimated for each scenario, including compression and pumping. The cost of capture was estimated based on a framework utilized for thermal amine scrubbing, with modifications and assumptions to apply it to the EMAR technology. A sensitivity analysis was performed to assess the most critical cost parameters. Results are compared with thermal scrubbing and current technology objectives, to evaluate the technology’s feasibility.

Motivation and methodology

The EMAR process is developed to provide a plug-and-play and cost-effective alternative technology to address the challenge of CO₂ separation, particularly in the context of climate change applications. For some niche applications, e.g. fuel gas purification in oil fields to obviate need for diesel usage in engines, features like the ability to deploy at a small-scale or ease of operation can provide significant benefits, but fundamentally, CO₂ mitigation for reduction of climate change related emissions is highly cost-dependent. It is therefore important to develop reliable estimates of capture costs on a consistent basis. Those estimates must be revised at every scale of the technology’s development, but remain critical, even with significant uncertainty.

Ideally, pilot scale tests run for long periods, and augmented by detailed, dynamic process modeling should be employed for performance analysis and cost estimation. Pilots tests however are expensive, require
significant time, and ultimately, significant capital committed to the technology’s development. Dynamic process models require significant experimental inputs, otherwise the quality of their predictions suffer considerably. Instead, bench-scale prototype experiments, similar to the ones described in Chapter 5, can provide reasonable performance estimates, and modeling frameworks, like those developed in Chapter 4, can help extend the reliability of those estimates to a wider range of conditions.

Here, higher bound estimates of energy efficiency for the EMAR process were developed, based on thermodynamic and kinetic considerations. In addition, bench-scale experimental results were utilized to develop estimates of current process energy efficiency. An NETL cost estimation framework for thermal amine capture (developed and implemented based on pilot scale experiments) was modified with explicit assumptions to account for the EMAR process changes. Best-case and current case capture costs were computed, and a sensitivity analysis was performed to determine the most critical design parameters. The findings of this analysis were used to evaluate the feasibility of the EMAR process at its current performance for further development, and to outline optimization areas where most value can be unlocked.

**Energy Efficiency**

**Upper Bound**

Upper bound estimates of efficiency for new technologies, particularly in the energy field, are easily critiqued on the premise that they are almost always overly optimistic. However, those estimates are also critically important.

First, they allow policymakers and technology developers to decide whether a new technology has the potential, if sufficient resources are invested, to address the societal need that prompted its inception. If a technology, even at its upper bound efficiency, is incapable of satisfying the performance level dictated by the parameters of the problem being addressed, the utility of the technology and the case for its development become questionable.
Second, upper bound estimates provide key insights into development priorities, especially when they are contrasted with demonstrated performance. This gap in performance, especially if it is dissected to its components and related to underlying physics, directs development to high value optimization targets, and thus guides further research more effectively.

The upper energy efficiency for the Cu/EDA system with a nitrate electrolyte can be estimated as the sum of the thermodynamic and kinetic energy consumption, assuming the electrochemical cell design can be optimized to significantly minimize mass transfer and other resistances. Chapter 8, Future Work, will discuss a few promising approaches in that regard.

On a basis of coal-fired power plant flue gas exhaust, consisting of around 0.12 mole fraction CO$_2$, the thermodynamic energy consumption due to the Gibbs Free Energy of binding CO$_2$ to EDA was previously shown to be around 15 kJ/moles CO$_2$ captured (33). Under a nitrate electrolyte, the activation overpotential behavior discussed in chapter 3 can be fit to the semi-empirical Butler-Volmer equation. The total energy consumption is thus a function of the operating current density, and implies a performance trade-off between capital and operating cost. Figure 6-1 summarizes the upper bound energy efficiency of the process for different current densities. It is clear that the process electrokinetics are relatively slow, with a progressively larger energy penalty for higher current densities. Cost estimation analysis will more clearly elucidate the relative importance of energy efficiency and current density.
It is important to note that better electrochemical kinetics performance is possible, and that the results above suggest it should be a main priority for further development of the technology. Chapter 8 discusses approaches to address this need.

**EMAR 5.0 Energy Efficiency**

A preliminary estimate of the energy efficiency for the EMAR process can be derived from the best experimental performance observed at the bench-scale. It is important to note that the reliability of this estimate is restricted by the limited amine utilization at the prevailing bench-scale conditions. Here we define utilization as the ratio of CO$_2$ released at the anode to the total CO$_2$ loading of the amine solution. The CO$_2$ capacity of a fully saturated circulating EDA solution can be approximated by $F_{total}[EDA]_0$ where $F_{total}$ is the liquid flowrate and $[EDA]_0$ is EDA concentration. This expression ignores uncomplexed EDA, given the relatively high binding constant (on the order of 100 for relevant temperatures).

The CO$_2$ released at the anode is a product of the current density and total electrode area:

$$n_{CO_2}^0 = \frac{i}{F}.A_{elec} \quad (6-1)$$
And amine utilization $\gamma_{EDA}$ is estimated by:

$$\gamma_{EDA} = \frac{i}{F} \frac{A_{elec}}{F_{total} [EDA]_0}$$  \hspace{1cm} (6-2)

Thus, for the EMAR 5.0 experiments outlined in Chapter 5, utilization is less than 1% (i.e. less than 1% of CO$_2$ circulated is released), and thus the change in amine loading would be too small for an effective absorber design.

This is not a serious limitation of the technology: a larger scale system would stack a number of cells to provide for a larger surface area. However, it is uncertain whether a stack of cells, connected in series, would have the same performance as the best-case results established for the bench-scale system in this work. As the loading of the amine solution changes, we expect a larger thermodynamic penalty and lower exchange current densities, as modeling results suggest.

However, this energy efficiency estimate still provides an important indicator of the current technology development status, and its energy efficiency. Assuming an ideal faradaic efficiency, we utilize the performance demonstrated at 55°C for a long baffle 1/16" depth channel, shown in Figure 6-2, as a performance indicator and use it in further analysis.

![Figure 6-2: Demonstrated bench-scale EMAR energy efficiency](image-url)
**Benchmark Technology Energy Efficiency**

Estimates of energy consumption for the benchmark technology, thermal amine scrubbing, are important in developing a consistent basis for energy efficiency comparisons. For thermal scrubbing, heat of sorption of around 176 kJ/mole CO₂ is required (29). Heat is supplied by low pressure steam, drawn from a power plant’s boiler, and thus acts to derate the generation capacity of the plant. Assuming a power plant efficiency of 20-25% steam-to-electricity conversion, the energy requirement for thermal scrubbing on an electrical basis is between 30 – 45 kJ/mole.

**Pumping/Compression**

In order to transport captured CO₂ 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 CO₂ at ambient conditions to 150 bars is around 10 kJ per mole CO₂ compressed, as calculated by the Peng-Robinson equation of state. In practice, with a compressor efficiency of around 65%, compression energy reaches around 15 kJ of electrical energy equivalent per mole of CO₂ compressed.

For the thermal amine stripping process, CO₂ desorption from amines occurs at pressures close to atmospheric pressure. A further increase in pressure would increase the CO₂ partial pressure and consequently, render desorption harder. In addition, it would require higher quality steam (i.e. at higher pressure), further derating a power plant’s efficiency.

One of the main advantages of the electrochemical process is its ability to desorb CO₂ under high pressure, since the dissociation kinetics of CO₂ 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 CO₂ 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. (34)
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.

Figure 6-3 shows the total compression and pumping energy to 150 bars for the EMAR process changes with anode operational pressure. The total energy can be reduced to less than 7 kJ/mole if the anode is operated at a pressure around or above 10 bars, i.e. 30% lower than baseline case of desorption at atmospheric pressure.

![Figure 6-3: Ideal pumping and compression energy requirements for the electrochemical process operating at different anode pressures. (32)](image)

**Comparing Energy Efficiency**

We can combine the estimates above to compare the performance of the EMAR process to thermal capture, on the basis of energy consumption, as a function of current density. A summary of this analysis is shown in Figure 6-4. At low flux (25 A/m²), the prototype performance is almost identical to the estimated upper bound, and both are well below the thermal process energy consumption range (30-50% less). At a moderate
flux of 50 A/m², the prototype performance departs from its upper bound, by approximately 30%, but is still higher performing than optimistic estimates for the thermal process. The upper bound energy consumption increases modestly, as large energy activation energy penalties become significant at much higher current densities in the case of nitrate electrolyte.

At a higher flux, 100 A/m², the prototype performance is predicted to be significantly less efficient than the upper bound energy, and comparable to low performing thermal scrubbing processes. Thus, the current version of the prototype still suffers voltage losses at higher current densities, due to mass transfer limitations, thermodynamic loading penalty and ohmic resistances.

![Figure 6-4: Energy Efficiency Comparison. Experimental bench-scale prototype results (blue) vs. upper bound limits for Cu/EDA chemistry based on thermodynamic and kinetic experiments, and contrasted with thermal scrubbing reported range. All values are on an electrical basis.](image)

**Cost Estimation**

This energy analysis performed above demonstrates the potential of the technology, and justifies the case for its development. It is however important to extend this analysis to analyze capture cost using EMAR holistically. A large number of cost estimation studies for carbon capture technologies, and specifically, thermal amine scrubbing has been performed. We follow here the methodology outlined in a study by the...
National Energy Technology Laboratory (NETL), Alston Power Inc. and ABB Corporation on retrofitting an existing coal-fired power plant with a thermal amine scrubbing system to capture carbon dioxide (60).

The study provides a detailed analysis of the required process changes and the associated costs, and provides a consistent methodology to estimate the cost of capture. Equipment sizing and costs for thermal scrubbing are modified with assumptions for the EMAR process, and updated for price changes using the CPI index to 2015.

**Case Study Description**

A coal-fired power station at Conesville, Ohio generates a total of 2080 MW of electricity through 6 units, of which 4 are operational. The study conducted by NETL focuses on unit #5 of the plant, which generates a net power of 433 MW through a subcritical pressure steam cycle. In the power plant, superheated steam generated in the boiler enters the high pressure turbine and undergoes expansion, supplying the work required for the electrical generator to generate around 466 MW of electricity. The plant requires about 30 MW of auxiliary power, used primarily in operating process pumps and compressors, and the net electrical power generation is therefore around 433 MW.

The hot flue gases from the boiler first preheat the feed water in an economizer, then the boiler air stream in an air heater. The flue gases then pass through an Electrostatic Precipitator unit where fly ash is removed, then a flue gas Desulphurization unit where acidic gases are removed. The flue gas stream is then vented, adding 3.375 million tons of CO$_2$ to the atmosphere each year. The CO$_2$ capture target is 90% of the emitted gas, i.e. 8485 tons per day, or 3.097 million tons per year.

**Thermal Amine Scrubbing**

The thermal amine scrubbing process uses a thermal swing to change the affinity of an amine sorbent to capture carbon dioxide from a gas stream then release it. Monoethanol Amine (MEA) was used in this study.
Flue gas enters at the bottom of the absorber, where it is contacted with the lean MEA entering at the top in a counter-current arrangement. The treated flue gas with low carbon dioxide content leaves from the top of the absorber, and is directed towards the stack. The rich MEA leaving at the bottom is divided into 2 streams. The first stream is first preheated by semi-lean MEA coming from the stripper, and then enters the stripper at the top. The second stream is first preheated by the bottoms of the stripper, and then enters the stripper at the middle section. The stripper uses low pressure steam to heat the rich MEA and drive the CO₂ desorption, which leaves in gaseous state at the top.

In order to supply the thermal amine scrubbing process with the steam required for carbon dioxide desorption, the main power station boiler must be modified to extract low pressure steam for desorption. To provide the low pressure steam necessary for the operation of the stripper, the steam cycle system is heavily modified. Several modifications are possible, and in this study, steam from the intermediate pressure is extracted from the system and expanded in a new turbine, from 200 psi to 65 psi (4.5 bars). The addition of a let-down turbine improves the overall energy efficiency of the process, and its capital cost was found in the study to be offset by the power gains. Other modifications required were a compression system for carbon dioxide to raise pressure to 150 bars, and retrofit modifications to optimize heat integration of the process.

**EMAR Modifications and Assumptions**

In the EMAR process, flue gas enters the absorber where it meets the amine in a counter-current arrangement, and exits at the top of the absorber after CO₂ is captured. This component of the system is almost identical to the absorber section of the thermal amine scrubbing process. The rich amine leaves the bottom of the absorber to enter the electrochemical cell (operating at a high pressure to reduce CO₂ compression requirements), where cupric ions generated at the anode bind to the amine creating cupric-amine complexes and releasing carbon dioxide. The gaseous carbon dioxide is separated from the amine-copper solution in an intermediate flash tank. The liquid stream then passes through the cathode, where the
copper ions are reduced to copper and release the amine, which is recycled to the absorber. The external current is reversed after some operation to reverse the position of the anode and cathode.

Most of the base case process design is largely unchanged, which demonstrates an important advantage of the EMAR process over other novel CO₂ separation technologies: the EMAR process benefits significantly from state-of-the-art technology knowledge, and indeed the only novel component is the electrochemical regeneration cells.

The boiler section, the steam cycle and turbine generator are completely unmodified. The absorber design provided in the NETL study is also retained, the changes in sizing for EDA vs. MEA should be not considerable. Future work should include a detailed absorber design to accurately assess required changes.

The electrochemical cell, which replaces the stripper in the thermal amine scrubbing process, is assumed here to operate at a high pressure, of around 10 bar_{abs}. As the efficiency of E-MAR increases with an increase in partial pressure of CO₂ in the anode, a high pressure condition is desirable. Additionally, since most of the energy required to compress carbon dioxide is consumed between 1 – 15 bar, maintaining the pressure of the flue gas will significantly reduce the power and capital requirements of captured carbon dioxide compression, and that of the entire process.

The following are the main design assumptions used in evaluating the cost of deploying EMAR technology to in this case study:

- Two scenarios for energy efficiency are used: upper bound and bench-scale prototype Experimental results at bench-scale are assumed to be reproducible in a large-scale system and stable for long periods.
- The absorber design provided in the NETL study for the thermal amine scrubbing process can be used for the EMAR process.
- The dimensions of the electrochemical cell are assumed to be a modular scale-up of the system used at lab bench-scale. This assumption can be revisited in the next stage of experimental work, where a cell stack will be tested to understand scale-up issues.

In estimating the equipment cost for the EMAR process, several significant assumptions were made. A true estimate of equipment sizing and cost requires a detailed process model and vendor quotations. However, the estimates developed here provide a preliminary indicator. Investment cost assumptions are:

- Both the compression energy consumption drops and associated investment costs of compressors will be reduced by the same ratio, reflecting the reduction in compression equipment required.
- The investment cost associated with heat transfer equipment is assumed to be eliminated: the EMAR does not involve costly retrofits to optimize heat integration, since the steam cycle is left unchanged. Similarly, the cost of a letdown turbine is eliminated since no modifications to the power cycle are required.
- Absorber costs remains as in thermal scrubbing.
- The cost of EMAR cells is equivalent to the sum of the cost of thermal scrubbing desorber in addition to the cost of copper metal.

**EMAR Design Basis**

To capture 90% of the CO₂ emissions from the 433 MW unit, a system must be designed for a capture rate of 3.051 million tons per year, or around 2230 mole/s. The total current required for the EDA/Cu system (where one electron drives the separation of one CO₂ molecule) is thus:

\[
I_{total} = n^0_{CO₂} \cdot F
\]

The power consumption is the product of the total current and the voltage required to drive it:

\[
P = I_{total} \cdot V_{app}
\]
The total copper surface area is a function of the total current, and the operating current density:

\[ A_{elec} = \frac{n_{CO_2}^0 F}{i} \]

where the total copper surface area is that of the anode.

Calculating the total mass of copper utilized requires an estimate of the acceptable electrode thickness. For a 1/16" depth channel, assuming up to 10% change of channel depth is acceptable, i.e. less than 0.8 mm, the minimum copper thickness must be larger than this value.

However, for a large current density, such a small thickness implies rapid switching of electrodes and polarity, in a manner that will be disruptive to operation. The thickness changes (assuming uniform deposition) as a function of current density and switching time is estimated by:

\[ \Delta \delta_{elec} = \frac{i M_{wt,Cu}}{2. F \cdot \rho_{Cu} \cdot t_{switch}} \]

where a factor of two is used reflecting that two electrons are required for each molecule of copper. Thus for a current density of 1000 A/m², the switching time to maintain changes in channel depth below 10% is slightly more than an hour, whereas for a current density of 50A/m², the switching time would be more than 24 hours. Here, we constrain the switching time to be around 24 hours to provide for stable operations. In effect, this constraint eliminates the effect of current density on total copper utilized and its contribution to the operating cost. The footprint of the technology, however, is a sensitive function of the current density.

Thus, the total power consumed can be estimated as outlined above, and used with the above assumptions to calculate the capital and operating costs, as shown next.

**Results**

The total cost per ton of CO₂ due to power consumption is an important metric, and is shown in Figure 6-5. The results show clearly that the total cost of capture will be dominated by energy consumption, as the energy cost almost doubles as energy consumption changes from 30 to 60 kJ/mole. For applications
where technology footprint is not a major concern (i.e. where cost of land or space constraints are secondary), this result suggests using a lower current density and maximizing energy efficiency to the most extent possible. The calculations assume a power cost of $0.05/kWh. A sensitivity analysis to the cost of electricity for total cost per ton CO₂ is explored in the next section.

![Figure 6-5: Cost of energy as a function of energy consumption. Major assumptions include a $0.05/kWh cost of electricity.](image)

However, a low current density quickly results in untenable total membrane surface areas, especially for large-scale coal-fired power plant applications. In this case study, where the unit generates 460 MW, the surface area requirements grow exponentially larger with lower current densities. Figure 6-6 shows the variation of membrane area with current density. It is important to note here that the net footprint of the system would be significantly smaller than the membrane area, since the cells can be effectively stacked. However, this analysis suggests that current densities lower than 300 A/m² would result in dramatically larger area requirements. For example, the area required drops 3-fold between 100 and 300 A/m².
With the design basis above, and using the methodology outlined in the NETL study, total capital and operating costs for this case study can be calculated. The cost of capture with capital amortized over 10 years without including energy costs is around $15/ton of CO$_2$. The cost of copper represents about 25% of the capital costs. Operating costs are 3-times the capital costs, reflecting the importance of energy efficiency and demonstrating the improved capital costs of the EMAR process. The estimated cost of capture per ton of CO$_2$ as a function of energy consumption is shown in Figure 6-7. The total capture cost for this specific case study ranges from around $23 to $35 per ton CO$_2$ for energy consumption between 25 – 60 kJ/mole ranges.
Figure 6-7: Total cost of CO₂ capture as function of energy consumption; the maroon bar represents total capture costs excluding energy, while the blue bar is the cost of energy.

Those estimates have important implications: at the upper bound energy efficiency of the process, capture costs lower than $25/ton CO₂ would be possible, comparing extremely favorably for the US Department of Energy’s current estimate cost of thermal capture of around $60/ton, and its R&D program targeting $40/ton. For the current bench-scale performance, even when operating at a current density of 100A/m² and energy consumption of around 60 kJ/mole, the cost of capture is still favorable, of around $35/ton. However, the total membrane area is likely infeasible at this current density for large-scale applications.

It is important to note that the estimates developed here are scale-specific, and more involved equipment sizing and costing would be required to apply this analysis for smaller-scale applications. In addition, the results are based on flue gas mix from coal-fired power stations: for other emission sources, like steel and aluminum plants, the costs would likely be appreciably lower, whereas for natural gas fired power stations and purification, CO₂ is more dilute and capture costs would likely rise.

Sensitivity Analysis

The results developed above are very sensitive to make-up power costs and lifetime of project. The cost of electricity varies significantly with region, energy source and time of day. A detailed sensitivity analysis
would therefore require a more specific project context. We show here how the cost of capture varies significantly with electricity prices (Figure 6-8), to demonstrate the sensitivity of the results above to the project context: for example, capture costs can increase by 25% between $0.05/kWh and $0.07/kWh for an energy consumption of 60 kJ/mole.

![Figure 6-8: Sensitivity of CO₂ capture cost to electricity price.](image)

The lifetime of most of the plant components should be between 10-20 years, except for the EMAR process, where the durability and lifetime of the process are unproven. A shorter life time of the project increases the annual charge of the capital cost; however, as the cost of capture is a stronger function of operating costs, the effect of life time is less pronounced. Figure 6-9 demonstrates the project lifetime effect on the capture costs, assuming high energy efficiency and a low electricity price, conditions which increase the ratio of capital to operating costs. The capture costs are sensitive to the project lifetime, especially for shorter lifetimes: a drop of almost $10/ton CO₂ is expected if the project lifetime can be extended from 5 to 10 years, while a change of less than $5/ton CO₂ is expected for an extension from 10 to 20 years of operation.
This analysis clearly demonstrates the importance of long-term experiments and models of the robustness of the EMAR process. Capture costs estimated based on bench-scale performance demonstrated for short periods can deviate significantly from real estimates, by several fold.

**Conclusions**

In this chapter, an analysis of the energy consumption and cost of CO$_2$ for the EMAR technology is developed:

- Two scenarios are established: an upper bound scenario based on thermodynamics and kinetics of EDA/Cu, and a current estimate, based on bench-scale performance.
- Accounting for energy contributions including compression and pumping, the EMAR process is predicted to be significantly more energetically efficient than thermal scrubbing in the upper bound case, and more efficient for low current densities based on bench-scale performance.
- An NETL cost estimation framework for thermal amine scrubbing is modified with a number of assumptions to compute cost estimates for the EMAR technology.
• The cost of capture, including amortized capital and operating costs, is estimated between $22 and $35 per ton CO₂, for energy consumption between 25 – 60 kJ/mole CO₂, and thus for upper bound and bench-scale performance under low flux conditions, the EMAR technology is very competitive.

• The cost of capture is dominated by operating costs, which are around 3-times capital costs assuming a 10-year lifetime of the plant.

• Energy costs are the largest and most variable component of the capture costs. Consequently, capture costs are very sensitive to electricity price.

• Capture cost is also found to be very sensitive to lifetime of project.

The analyses provided in this chapter, despite its many limitations, provide a helpful evaluation of the EMAR technology at its current and upper bound performance. The importance of reducing energy consumption, potentially through eliminating mass transfer limitations and improving electrokinetics, is clearly an important next step to the development of this technology.
Chapter 7

Future Directions

Building on the experimental and modeling work described throughout this thesis, this chapter presents recommendations on the major potential questions and issues that are critical to further development of the EMAR technology. Four important directions are discussed: optimizing current performance, demonstrating a larger scale cell stack system, exploring other EMAR chemistries, and extending the process to other acid gases.

Overview

The EMAR technology offers a compelling approach to address the climate change challenge through reducing emissions from power stations and unlocking significant value in oil and gas production at a lower carbon footprint, and all by utilizing existing infrastructure. With significant advantages in ease of deployment, capital requirements, and potentially, energy efficiency, the technology can cut gas separation costs significantly. The development of the technology has been rapid and promising, and further development is recommended.

There are four important future directions recommended, based on this work, to bring the EMAR technology closer to commercialization: optimizing the technology performance further, demonstration of a scaled-up version, exploring other chemistries, and extension to other acid gases. Each of those directions is discussed below.
Optimization Targets

In Chapter 6, cost analysis shows the sensitivity of capture costs to energy efficiency and to the stability of the EMAR system, and the rapid increase in membrane area required for lower operating current densities.

Electrolyte Screening

The current density and energy efficiency relationship is a function of activation kinetics and mass transfer. Efforts to optimize the technology’s performance were explored in this work. The effect of additives on activation kinetics was tested and quantified in Chapter 3, with the moderately fast and highly stable sodium nitrate as an electrolyte. However, the set of electrolytes tested was limited, and a much larger potential set of possible electrolytes should be systematically investigated. Further confirmation of the inner-sphere electron transfer hypothesis can help guide that search, and if validated, aided by molecular scale simulations to estimate binding energies for target electrolyte categories. High throughput testing at the bench-scale will allow rapid evaluation of target electrolytes. XPS studies of the electrode surface post-deposition can confirm whether electrolyte inclusion occurs, and the conditions that minimize it.

Amine Screening and Degradation

In addition to the importance of the choice of amines on thermodynamics, activation kinetics, and rate of bubble formation, that choice is critical for process stability. The long-term stability of the EMAR process is critical for capture economics. The stability of amine solvents in commercially used thermal scrubbing is known to be limited; both thermal and oxidative degradation occur, and are addressed by proprietary additives to hinder degradation, as well as a sharp cost for make-up amine.

For the EMAR process, thermal degradation has a smaller probability due to the relatively low temperature of operation. However, oxidative degradation may be further exacerbated by the presence of metal ions, which are reported to accelerate amine degradation. For bench-scale experiments reported in this work, such effects have not been observed, and the amine activity did not deteriorate over the period of days. However, oxidative degradation can occur over much longer time-scales on the order of weeks and should
thus not be dismissed. The choice of amine can have a considerable effect of oxidative degradation rates, and for thermal scrubbing, degradation is the driving force for active research in developing more stable amines.

For the EMAR process, our investigations have been limited to polyamines, due to their ability to strongly chelate copper metal ions, specifically focusing on EDA due to its demonstrated high performance. However, a large number of other polyamines should be explored, particularly in regards to their stability in the presence of oxygen and metal ions.

**Porous Electrodes & Insertion/Deinsertion Cycles**

An important limitation observed experimentally in this work, is the high mass transfer requirements at high current densities required to limit the aerial footprint of the process, which scales exponentially to current density. This work demonstrated improvements by using high superficial velocities and serpentine flowfields, with reasonable energy efficiencies at current densities up to 100 A/m². The analysis outlined in Chapter 6 however shows that current densities lower than 300 A/m² will require membrane areas that can be infeasible for large-scale applications. It is therefore desirable to explore further increases in current density.

Porous electrode systems are widely used in electrochemical flow systems, due to their ability to minimize transport limitations by providing a higher surface area of reaction. However, significant challenges are associated with use of porous electrodes for the EMAR process.

Entrapment of bubbles inside porous electrodes and associated voltage overpotential has been experimentally observed, and strategies to address are discussed in the next section. Another challenge concerns the periodic dissolution and deposition of the electrodes, required to cycle copper ions between electrodes. A copper electrode with a porous microstructure will quickly fail upon repeated operation, as the surface reformation is not precise. Instead, using carbon based electrodes as insertion electrodes can allow for smoother deposition and dissolution with smaller risk of morphological instabilities limiting the
number of operational cycles possible. Early experiments using carbon aerogels showed promising results, and further investigations are recommended.

**Bubbles Effects**

As modeling work in Chapter 5 showed, bubble formation inside the anode compartment can contribute to rising energy requirements, and limit the range of operating current densities feasible. The effect of bubbles may be larger than predicted through modeling their effects on electrode availability. Further and in more in-depth modeling is recommended, to properly account for bubble effects. Modeling of bubbles should account for their distribution, their rate of growth and rate of coalescence. Such bubbles will likely require a three-dimensional treatment of the electrochemical cell to accurately capture distribution effects on electrode availability. Models should also include effects of bubbles on increasing solution resistance, and the associated ohmic losses. Accurate modeling can significantly contribute to the rapid evaluation of designs and modifications aimed at limiting bubble effects.

We potentially envision a system where gas bubbles are not formed in the electrochemical cell. One approach would be to use very fast flowrates across cells with a short length. The residence time of the solution inside the cell must be tuned to be significantly shorter than the time scale for ion diffusion from electrode to bulk and the consequent reaction with amines. A different approach involves exploring amine chemistries where copper/amine reaction is slightly slower, and thus reasonable residence times can be used and bubble formation occurs mostly in the gas/liquid disengagement chamber.

**Faradaic Efficiency**

As explained in Chapter 5, the current version of the bench-scale setup and the design of the flask tank did not allow for efficient disengagement of gas bubbles, and it was therefore difficult to quantify the true Faradaic efficiency of the system i.e. gas captured per unit charge. Previous study at lower current densities (where gas volumes were formed were smaller and easier to disengage) suggest that the Faradaic efficiency
is above 90%. However, in exploring electrolytes and amines, a better gas/liquid disengagement design is needed to allow for accurate Faradaic efficiency estimation to evaluate potential candidate molecules.

**Scale-up Demonstration**

The current version of the technology demonstrates promising results, with high energy efficiency at moderate current densities, and costs estimates suggesting the technology’s capture cost is competitive. However, the costs estimate feature large uncertainties, given the small-scale nature of current prototypes. One major potential advantage of the EMAR technology is its modularity: where an increase in scale requires the addition of more unit cells, rather than the redesign of major units (e.g. reactor scale-up for a new chemical technology).

Experimental results and modeling predictions in this thesis suggest at the current length of the electrochemical cell, only a small fraction of the cycled amine solution is utilized, and the required absorber sizes would thus be infeasible. A larger stack of cells is required to bring the utilization to a sufficiently high range (ideally, amine/CO₂ loadings should cycle between 5% and 95%; for thermal scrubbing those values are around 10%-90%) A module of the EMAR technology would thus consist of a stack of cells with sufficient surface area for high utilization at the high flowrates required to maintain efficient mass transfer.

If the EMAR technology is demonstrated at the module scale for realistic flue gas mixtures, it would be a major development and step to its commercialization, as it would show the success of the modular scale-up strategy, and provide more reliable estimates for capture costs. It is therefore recommended that such a stacked cell design is built and tested.

The peripherals necessary for reliable module operation are significantly different from those used in the current setup. An absorber column with sufficient length and optimized internal design for efficient mass transfer would be required. A gas/liquid disengagement strategy capable of addressing multiple inflows from the individual cells and separating gas bubbles rapidly would be critical for realistic performance evaluation. An automated operation and data acquisition system will enable long operations and testing. A
modular cell design, like that employed in this work, will allow surface finishing to be restored between experiments.

The main metrics of performance will be the Faradaic, or current, efficiency and the required voltage per cell. The Faradaic efficiency is the ratio of molecules of CO$_2$ separated over electrons sent through the cell. Side reactions, physical solubility, and unwanted diffusion through the membranes will cause losses in current efficiency. The voltage efficiency will be affected by the solution conductivity, mass transport, and electrode kinetics. Long duration, multi-day, experiments will also be performed to test the stability of the sorbent solution, the electrodes, and the materials of construction. Field testing of the cell module would enable potential industrial partners to directly test the performance and reliability of the technology under realistic conditions.

**Exploring Other Chemistries**

Given the initial demonstration of the feasibility of electrochemically-mediated capture with polyamines and copper, it is desirable to explore the thermodynamic and kinetic feasibility of utilizing other sorbents and metal ion systems, with potentially lower costs and energy requirements.

The minimum thermodynamic penalty associated with the electrochemical capture process is a function of the Gibbs Free Energy of binding between the sorbent and CO$_2$. In addition, the kinetic overpotentials required to drive the process at high current density can have a large contribution to the process energy consumption. And as chapter 6 shows, the cost of copper is a large component of estimated capital costs at scale. A zinc or iron variation of the system would be an order of magnitude lower cost than copper, and can thus significantly reduce the capture costs. It is therefore desirable to expand the range of CO$_2$ sorbents and metal ions suitable for the electrochemically-mediated capture process.

Metal ion systems that should be considered include zinc and iron. Both metals are relatively cheap and electrochemically responsive with promising deposition and dissolution kinetics, and capable of chelating amines. The challenge lies in identifying a sorbent/redox couple which will form a stable soluble complex...
under high pH conditions. The CO₂ sorbents to be tested include amino acids, ammonia, and amine-functionalized ionic liquids, similar to those proposed in this work. For ammonia and ionic liquids, the likelihood of successfully developing a high energy efficiency process is high, while other operational challenges (high volatility, high viscosity, etc.) might present barriers to further development. The solubility of amino acids and their metal complexes will likely be the key challenge for this category of capture sorbents.

The testing and characterization will involve experimental techniques similar to those outlined in this work and its predecessor. Metal ion/amine pairs that show reasonable solubility should be first tested for their open circuit potentials in presence and absence of CO₂, the kinetics of deposition and dissolution, and the stability and reversibility of the formed complexes.

The modeling framework developed in Chapter 4 can be customized for different pairs by modifying the thermodynamic, kinetic and flow parameters, and can allow rapid evaluation of potential pairs. The highly modular prototype proposed in Chapter 5 can be used for bench-scale testing of promising candidates, in quick and informative experiments. The cost estimation framework developed in Chapter 6 can allow develop ballpark estimates of cost improvements based on upper bound and demonstrated performances, and comparison with benchmark technologies and other novel approaches. This work flow can allow a large number of potential pairs suggested by a thermodynamic analysis to be tested and evaluated in a short time and with a minimal cost.

**Extension to Acid Gases**

As this thesis has highlighted, CO₂ separation is important in many different contexts, from power station flue gases to natural gas purification. In almost all contexts, however, the gas mixture containing carbon dioxide also involves other acid gases. In coal-fired power plant applications, SO₂ and other SOₓ gases from the combustion of elemental Sulphur impurities in coal are an important impurity. Natural gas is frequently associated with H₂S and mercaptans.
Thus, a CO₂ separation technology must be capable of robust operation in the presence of Sulphur acid gases. If the EMAR technology can be demonstrated to effectively address Sulphur acid gases, its utility will be significantly expanded. Specifically, separating H₂S would enable deployment of the EMAR technology in natural gas purification applications without the need for expensive pretreatment and dedicated H₂S separation equipment.

Amines are capable of binding Sulphur acid gases (SOₓ and H₂S) and forming stable compounds. However, the strength of the bond is significantly stronger than that in the case of CO₂, due to the higher acidity of Sulphur acid gases. In thermal amine scrubbing, a desorber operating at significantly higher temperatures (above 250°C) is used to regenerate amines bound to Sulphur acid gases. Some of the formed complexes are heat-stable, and require a more involved process for separation. At present, sulphur physical scrubbing processes (e.g. Selexol) are dominantly used for H₂S removal from flue gas and natural gas, with an energy consumption up to 4.7% of power plant output.

The EMAR process can be used for H₂S separation (and potentially the more acidic SOₓ though that is more challenging) by exploring the regeneration of the amine solvent electrochemically. In theory, the main difference between CO₂-bound and H₂S-bound amine is the binding strength, and thus the open circuit potential required for regeneration would be higher for H₂S. Potentially, a cell operating at higher voltages can possibly be used to regenerate H₂S-bound amine once the CO₂ has been removed. This multi-stage system with successively higher voltages can be used to regenerate amines and supply high purity CO₂ while also providing a stream with high H₂S concentrations.

A number of challenges are anticipated. Side reactions of H₂S and CO₂ (to from carbon sulphides and water), and metal-sulfide reactions can provide major obstacles to implementation. A chemical screening investigation guided by thermodynamic analysis of amine-H₂S and metal sulphide thermodynamics and solubility should be performed to identify candidate amines and metal ions capable of electrochemical regeneration.
Electrochemical-based separation of H₂S and SO₃ has been long proposed and demonstrated. Townley and Winnick (61) demonstrated and evaluated an electrochemical system for flue gas desulphurization, where sulphate ions are cycled between two electrodes. They estimated the costs based on open circuit potential estimates from the Nernst equation and overpotentials from similarly operated molten-carbonate fuels cells.
Chapter 8

Conclusions

This thesis focuses on the continued development of a novel electrochemically-mediated CO₂ separation technology that has the potential to significantly cut the cost of capture, and enable wide-scale deployment in energy and climate change applications.

Previous technology development efforts showed the promising thermodynamic performance of the EMAR technology, and developed a proof-of-concept device that shows its technical feasibility. However, performance of the proof-of-concept prototype was significantly lower than what is thermodynamically possible, and not yet at the levels necessary for economic feasibility. The work in this thesis focused on addressing this performance gap, by systematically studying the underlying energy contributions, exploring the design space and extending our knowledge of this novel system.

First, the large effect of electrolytes on activation overpotentials was experimentally studied at small-scale using galvanostatic pulse voltammetry, and in a larger-scale prototype cell. Experimental results show a large change in voltage-current behavior in the presence of electrolytes. Small-scale experiments found a large improvement under bromide salts, but larger-scale testing indicated that this improvement was only sustained for a short time. XPS analysis and mechanistic arguments suggest bromides and other halide salts can act as ligand bridges for inner-sphere electron transfer, and that bromides were included in the formed deposit, possibly causing an increase in contact resistance. Nitrate salts were found to drive more stable kinetics, with moderate energy efficiency.

Next, an electrochemical cell modeling framework was developed to capture the coupling of electrode reactions with flow. Diffusion and convection were explicitly modeled using a set of PDEs, and electrode reactions were modeled as boundary conditions. A Nernst-based thermodynamic model accounting for
concentration and pH effects was derived, and used to show the potentially large increase in OCP for large CO₂ loading changes. The thermodynamic model was incorporated in a constraint for the distribution of applied voltage between OCP, activation overpotentials and ohmic losses.

The resulting model was solved numerically, and the effect of operating conditions on the cell performance was analyzed. Model predictions suggest the cell will operate under mixed activation-mass transfer control for the desired current densities. The model also predicts that the superficial velocity will have a significant effect on the boundary layer thickness, and a large resulting change in exchange current density and OCP.

To allow for high throughput experiments exploring different designs, the limitations of the proof-of-concept device were analyzed, and an upgraded prototype with modular internals was designed and constructed. The prototype enables quick assembly/disassembly and easy modification of flow fields. A multi-electrode prototype to analytically explore axial variations of current density was also designed and constructed. Finally, a high pressure prototype design is proposed and constructed.

Building on modeling predictions and prototype upgrades, an experimental investigation of the effect of channel depth and flowrates is performed. Experimental trends suggest that the cell indeed operates in a mixed activation-mass transfer regime, in qualitative agreement with the model. A large effect of superficial velocity at moderate current densities is observed, with an improved energetic performance as the velocity is increased, at the expense of utilization.

Alternatively, induced mixing between the bulk and boundary layer is proposed as an alternative strategy, and a serpentine channel design was constructed and tested as one implementation approach. Current-voltage behavior is significantly improved using this design, suggesting the success of this strategy.

Electrochemical impedance experiments were performed, and provided more evidence on mass transfer effects and how superficial velocity affects them. A fitted equivalent circuit suggests increased flowrate acts to reduce activation resistance.
Multi-electrode experiments showed that the current density shows a nonuniform axial distribution, particularly at high current densities, and suggest that such an analytical cell can be effective in future studies of axial variation inside the cell, and their potential effects.

To evaluate the feasibility of the EMAR technology at its upper bound efficiency and current performance, energy and cost estimates were computed. Energy analysis including compression and pumping energy suggest that at its upper bound efficiency, the EMAR technology is much more energetically efficient than thermal amine scrubbing, and that at the demonstrated bench-scale polarization curves, the technology is competitive at low current densities. Cost estimates find that the EMAR capture costs can be very attractive, promising a significant reduction over thermal amine scrubbing, provided high energy efficiency closer to its upper bound, and stable long-term operation can be demonstrated.
Chapter 9
Capstone Paper

Executive Summary

Scalable, efficient and cost-effective carbon dioxide capture technology is critical for a number of applications, ranging in scale and nature. Through the technical work in this thesis, we have advanced the EMAR process from concept to working prototype, developing a framework for optimization and scale-up of the system, and characterization of its long-term behavior. Previous chapters provide an in-depth understanding and a technoeconomic analysis of the technology, and the results suggest significant potential to reduce separation costs across a number of different use cases. The advantages of the electrochemically-mediated separation over other CO₂ separation technologies were previously discussed and quantified, suggesting significant cost advantages in addition to easier deployment and potential weight/footprint advantages.

In this chapter, the commercial case for the EMAR technology is further explored, with a focus on specific use case performance objectives and competitive edges, as well as understanding potential paths towards deployment. Current state-of-the-art CO₂ capture technology is more than 60 years old, requires large amounts of steam to drive it, is difficult to integrate with existing infrastructure, and is ultimately prohibitively energy intensive and expensive. The EMAR process is potentially plug-and-play, energy-efficient, electrochemically-controlled process for CO₂ capture. The technology utilizes an inexpensive redox-responsive material (i.e. a material that switches states with the application of an electric voltage) to modulate CO₂ capture by a solvent. Electric current drives the removal of CO₂ from gases, in lieu of the state-of-the-art thermal-driven. However, from a commercial view point, the technology does not only compete with other CO₂ separation solutions, but must also compete in the wider markets for CO₂ as a
product and its separation as a service. This chapter explores these issues to develop a potential
commercialization strategy.

Demand for CO₂ as an end-product is around 80 Million tons per annum (Mtpa) across diverse uses, from
the food-industry to enhanced oil recovery via tertiary methods, with several new utilization routes
emerging, including potential production of chemicals and fuels. Demand for CO₂ separation as a service
is relatively more nascent, but with significant potential. Applications requiring separation as a service
include life-support systems, building energy efficiency, natural gas purification, and most critically for
climate change mitigation, separation of CO₂ from power station and industrial flue gases.

Despite the large demand for CO₂, current supply is significantly larger, with more than 500 Mtpa of
potential concentrated sources, such as industrial production of ethanol, and natural CO₂ wells, in addition
to more than 18,000 Mtpa of dilute sources possible. Clearly, there is a significant mismatch between supply
and demand suggesting that absent a policy to price CO₂ externalities, technology alone would be unable
to provide an economically feasible solution that addresses the climate change risks through capture and
utilization of CO₂.

There are, however, compelling market opportunities for the EMAR process for commercial deployment.
An analysis of the CO₂ value chain shows the strong sensitivity of prices to transportation costs, as
evidenced by the large discrepancy in CO₂ prices across bulk and merchant markets, at $3-$25/ton versus
$100-$300/ton, respectively. Geographical concentration of low cost, bulk sources of concentrated CO₂ is
heterogeneous, with areas like the North East of the US (as well as several global markets) having
significantly less supply and higher prices, compared with the Midwest (where ethanol fermentation is
widespread) and the South of the US (where natural reservoirs are strongly utilized for EOR).

Consequently, there are potential market gaps that can be filled by the EMAR process across a range of
points in its scalability and development. First, by capitalizing on the technology’s ease of deployment and
plug & play nature, a commercial service to generate CO₂ on-site can be competitive in specific markets
with merchant prices for CO₂. EMAR units would be operated at customer sites to separate CO₂ from existing flue gas sources, to replace the need for expensive and complex sourcing of gas needs. This phase would offer the technology valuable insights into operations and longer-term stability, in addition to creating sufficient revenue for further development of the technology, without the price and reliability constraints of other applications.

If the first phase is successful, the EMAR process after further optimization can potentially be deployed at a larger scale for applications that are most cost-sensitive. Potential applications include energy efficiency in buildings, where more conditioned air can be recycled after lowering CO₂ contents below thresholds for comfortable environments. Other promising applications at this stage include on-site natural gas utilization after removal of CO₂ and H₂S; life-support systems for planes and submarines if reliability metrics can be met, and larger-scale off-shore natural gas recovery, especially with reservoirs containing large amounts of CO₂ such as those prevalent in Malaysia. The choice between these applications depends on the degree of maturity of the technology at this phase of development, as well as its price point.

Ultimately, if the technology continues to see success along these two phases, it would be sufficiently validated and demonstrated across various contexts and scale to derisk its deployment at a larger, commercial scale. Given the capital needs of such a deployment, partnerships with leading companies in oil & gas, chemicals, or gas separation would be necessary to facilitate deployment. At this stage of maturity, EOR applications can be attractive especially when no natural sources of CO₂ are available, and when large stationary emitters are co-located. When/If eventually policy changes to place a price of CO₂ emissions, the EMAR process would be well-positioned for wider deployment, at a scale and magnitude that allows it to play its role in addressing the climate change challenge.

**Market Analysis – Demand for CO₂ Separation**

Carbon dioxide separation technology is used across a variety of contexts, broadly either to produce carbon dioxide as an end-product for direct utilization, or as a necessary step towards purifying a gas stream. In
this section, market demand for CO\(_2\) separation technology is explored to understand the range of applications possible for the EMAR technology.

**Market for CO\(_2\) as an end-product**

CO\(_2\) is an important input material as well as final end product across a variety of applications that range in their requirements for volumes, purity and price. There exists both mature, well-established markets, as well as niche and relatively new markets, both of which are briefly summarized.

**Overview of Mature Markets**

- **Food:** An old and relatively well-known usage of CO\(_2\) is in carbonating beverages. Another food-related application is for chilling and cooling using solid CO\(_2\) ("dry ice"), particularly during transportation. Food grade applications require the highest standard of purity, with more than 99.9% purity.

- **Industrial:** CO\(_2\) is used to provide an inert atmosphere during metal fabrication via welding, usually mixed with Argon. Purity requirements are high (>99.5%) with the added constraint that oxygen cannot be present in trace amounts.

- **Safety:** CO\(_2\) is used as a fire extinguishing material, particularly for electrical components that would be damaged by using water. Purity requirements are similar to those of the metal fabrication application, given the similar function of CO\(_2\) in providing an inert atmosphere.

- **Chemicals:** CO\(_2\) is used as a raw material for urea, methanol and other chemicals production processes, and as a non-toxic industrial solvent. Use in algae production is still in its infancy but presents a large potential application.

- **Agriculture:** in greenhouses, plant growth is enhanced by increasing CO\(_2\) content of the environment by adding pure CO\(_2\). Here, purity constraints are less stringent, and CO\(_2\) mixtures with gases like nitrogen and oxygen are sufficient, provided that the composition results in a sufficient enrichment of the growth environment with CO\(_2\).
EOR with anthropogenic CO₂: As oil wells age, their natural pressure drops and an external source of pressure is necessary to continue production from the reservoir. One common approach is to inject CO₂ into oil wells to stimulate oil production, in what is termed Enhanced Oil Recovery, one of several secondary and tertiary production approaches. This activity is one of the largest consumers of CO₂ today and will be discussed in more detail.

Overview of Potential Markets

The above applications are relatively well established. Due to the abundance of CO₂ and the growing need for its mitigation, many new applications are being explored. Although these applications are less attractive for the short-term development of the process, they are potentially important in the future of this space:

- **Building blocks production**: Various research is underway to explore the production of a range of building materials using CO₂, e.g. sustainable concrete.

- **Conversion to commodity chemicals**: For example, Skyionic Corporation (Austin, TX) converts CO₂ to solid carbonate materials, such as sodium bicarbonate (baking soda), hydrochloric acid, and household bleach. The company has developed a commercial scale facility, though it is still unclear whether the process is cost-effective given the commodity nature of the resulting chemicals.

- **Conversion to fuel and specialty chemicals**: Given the large demand for liquid fuel and the ubiquitous infrastructure available for its management, many research groups and companies have attempted to reduce CO₂ to produce fuels and specialty chemicals. Companies like Dioxide Materials and Joule Unlimited are exploring electrochemical and biological pathways, respectively, to allow for this conversion. In most cases, high margin small volume chemicals are first targeted to validate the technology and improve its performance, with the objective of reaching the cost point where high volume fuel production is competitive with fossil fuels. It is important to note here that CO₂ conversion to fuels is thermodynamically unfavorable (essentially amounts to
reversing combustion) and there are open questions on the value of this approach from a climate change mitigation perspective if the input energy is not derived from a renewable resource.

- **Power generation**: Supercritical CO\textsubscript{2} is proposed for use in the Brayton cycle as the working fluid in gas-fired power stations, as it is shown to increase energy efficiency and reduce capital costs.

- **Biomass production**: One potentially promising utilization path for CO\textsubscript{2} is in algae production. Similar to the case of fuel conversion, CO\textsubscript{2} is reduced against a thermodynamic barrier. However, here the process is driven by photons utilized in photosynthesis, in lieu of electrons that can be expensive or from a high carbon foot print source. Ideally, algae would be grown in unutilized land with low quality water. The biomass grown can potentially become a large sink of massive quantities of CO\textsubscript{2}. The lipid portion of the produced biomass is then separated and processed to produce biodiesel. Despite its promise, the CO\textsubscript{2}-to-algae technology has yet to materialize its full potential, with many companies in the space forced to shut down. Yet, today, companies like Algenol and Cellana among several others continue to develop this technology platform.

**Demand Breakdown**

In understanding the existing market for CO\textsubscript{2} as an end-product, it is important to highlight the large difference in potential demand for different applications. Today, the market for carbon dioxide utilization is estimated globally to be around 80 Million tons per year (Mtpa), with the potential to reach 140 Mtpa by 2020. The current utilization market is dominated by EOR (around 50 Mtpa in North America). A breakdown of consumption is provided in the following figure.
To put these numbers into perspective, the Global CCS Institute estimates current CO₂ production to reach around 500 Mtpa from concentrated sources, and 18,000 Mtpa of high-volume (>0.1 Mtpa) dilute CO₂ from power stations and industrial CO₂ producers. From a climate change perspective, it is clear that absent a major policy change, demand for CO₂ utilization is not on track to place a serious dent in the total accumulation due to supply. It is important to note that these consumption numbers only include non-captive applications (i.e. where CO₂ externally sourced to the process and not produced as an intermediate, as in the case in the urea process).

**Enhanced Oil Recovery with CO₂**

Given the relative importance of CO₂ EOR in defining demand for CO₂, it is instructive to further explore the EMAR process potential in this context. In general, only 1/3 – 2/3 of oil in an existing oil reservoir can be produced via natural pressure and water-based secondary recovery approaches, leaving behind a significant volume of oil, as well as expensive stranded capital. By pumping supercritical CO₂ downhole, millions of barrels of lower marginal cost oil (where capital has already been deployed) can be produced. Figure 9-2 shows a schematic of CO₂-EOR.
Today, 5% of US oil production utilizes CO₂-EOR in wells across the Permian Basin and Gulf of Mexico areas. However, operators supply the CO₂ required for EOR from an unusual source: operators (directly or through suppliers) drill for naturally-occurring CO₂ and transport it over hundreds of miles from source to production wells. This significantly limits EOR to areas where infrastructure has already been deployed. In addition, natural CO₂ sources are rapidly decreasing in reserves. For example, sources in Colorado supplying the Permian basin are getting depleted, presenting a major threat to deployed investments. Figure 9-3, by Denburry Resources, shows the EOR infrastructure in the Gulf of Mexico, Texas, and contrasts it with the potential for EOR. Note that other regions have tremendous EOR potential, and no existing natural CO₂ reservoirs and infrastructure.
If anthropogenic sources of CO₂ can be utilized, the reach of CO₂-EOR would be significantly extended (US Department of Energy estimates the potential to be more than 60B barrels, compared with 2016’s annual oil production of 10m bpd), secure supply indefinitely, and most importantly, generate low carbon-footprint oil at a competitive cost.

From a climate change mitigation perspective, EOR holds significant promise. The carbon footprint of CO₂-EOR oil is more than 60% lower than oil produced with other means, as most of the CO₂ stays underground. CO₂ injection has been practiced safely, without leakage or detrimental effects since 1970s.

The major challenge in this application is cost: naturally-occurring CO₂ costs around $40/ton, while thermal technology is estimated by the US DoE to cost more than $60-80/ton and is thus uneconomical. Due to the high energy efficiency and simple deployment of our electrochemical capture, costs can be cut to 1/3 of today’s benchmark. At the performance of the EMAR process demonstrated in lab bench-scale tests, our estimates suggest we can capture CO₂ and deliver it in compressed form at less than $30/ton. As discussed in the technoeconomic section of this thesis, the EMAR process can potentially reduce the cost further to
less than $20/ton through further optimization. This represents a major step change and an attractive opportunity to produce low cost oil at a fraction of the carbon footprint. To be competitive in this market, the EMAR process must demonstrate high, cost-competitive performance at scale.

*Market for CO₂ Separation as a Service*

In addition to the potential demand for CO₂ separation technology for the purpose of utilization, some applications require separation technology with the purpose of purifying a gas stream. In that case, CO₂ is primarily a waste stream that is vented to the atmosphere. The EMAR technology can be a good candidate for these applications which often value the ease of deployment over the separation cost. Three important applications in that regard are the removal of CO₂ from enclosed systems as part of a life-support system; the potential for improving energy efficiency in buildings via recycling of conditioned air after reducing CO₂ content; and the purification of natural gas. In addition, large-scale separation from flue gases generated by power plants is the major long-term application for EMAR with impact on climate change mitigation, and is discussed here.

*Removal of CO₂ for Life-Support Systems*

There is a potential need for CO₂ removal technology in enclosed spaces with limited oxygen supply, such as in aircraft, spacecraft and submarines, as a component of life support systems. In terms of worker safety, the Occupational Safety and Health Administration (OSHA) has set a permissible exposure limit for CO₂ of 5,000 parts per million (ppm) over an 8-hour work day, or 0.5% by volume of air. A value of 40,000 ppm is considered immediately dangerous to life and health based on the fact that a 30-minute exposure to 50,000 ppm produces intoxication, and concentrations greater than that (7-10%) produce unconsciousness. Currently, physical adsorption systems based on zeolite materials are used in life-support systems, e.g., on the International Space Station. These systems use a thermal swing process with large energy consumption. Other removal systems include chemical adsorption within Lithium Hydroxide canisters, a non-regenerable process that limits the duration of operation. In addition to potential energy savings, the EMAR process can
obviate the need for high temperatures, which can pose a safety hazard, and requires only electricity to drive its performance at relatively low temperatures. Boeing estimates a demand of around 35,000 new civilian aircraft of various sizes over the next two decades (http://www.boeing.com/boeing/commercial/cmo/).

Based on the assumption of a linear rate of growth, the number of new aircraft built annually could be in range of 1,000, each requiring a CO₂ removal system.

It is difficult to estimate the number of new underwater vehicles, submarines and spacecraft, but this market segment is expected to be small in size. The main barrier to entry for this segment is safety, reliability and footprint of the device (both volume and weight). The efficiency of the technology must therefore first be demonstrated, including its ability to uphold the high levels of safety expected by aircraft manufacturers and air carriers, and the high level of engineering precision necessary for spacecraft and submarines. To that extent, the EMAR offers the advantage of operating at low temperatures (25 to 55°C), and can be optimized to work with different solvents (with lower volatility).

**Reduction of building energy consumption in buildings by recycling conditioned air**

HVAC systems are large-scale energy consumers. Much of the consumption is due to exchange of indoor air with fresh air in order to maintain CO₂ at comfortable levels: significant energy is expended to condition the fresh air to the desired temperature and humidity. By using the EMAR process to capture CO₂ from indoor air, the air exchange requirements can potentially be cut to reduce HVAC energy consumption. The potential size of this market segment is immense, with over 5 million commercial buildings in the US alone. Initial target markets are buildings in hot, humid and extreme environments where HVAC loads are highest.

The EMAR technology is scalable for this application, is able to run using electricity, and requires no other retrofit, which makes it suitable as a drop-in solution for existing buildings. The ability to access this opportunity rests on the development of a working demonstration unit with data to make the case for the energy savings and the return on investment in energy efficiency. The key requirements are to build a
demonstration unit that can capture appreciable amounts of CO₂ and operate stably over long periods, and to establish the process models that can feed a more detailed financial feasibility study.

**Natural gas purification**

Natural gas consists primarily of methane, short-chain hydrocarbons and CO₂, as well as other impurities like H₂S. There are several niche applications for the EMAR process in natural gas purification.

In the case of oil production sites, small amounts of gas are frequently produced. With small volumes, large-scale purification systems employing thermal regeneration of amine solvents are not economically feasible. Consequently, the gas is usually flared. Given the remote nature of some of these sites, there is a potential opportunity in replacing expensive diesel that is delivered to the site to run power generation equipment necessary for drilling and other site activities. One potential niche market for the technology is small-scale purification units that can empower oil site operators to utilize produced gas in replacing expensive and complicated procurement of diesel and propane to run generators. In this context, our electrochemical capture technology offers a significant advantage over other acid gas removal technologies, due to its modular nature which enables deployment at any scale, whereas standard thermal capture is only economical at larger scales.

Another small-scale application is biogas upgrading. Biogas production results in gas with more than 25-50% carbon dioxide, lowering its calorific value and inhibits its transport and widespread use. CO₂ removal units must operate at small-scale; be simple to deploy and have high selectivity, features where our technology outcompetes other solutions.

Finally, for reservoirs with high CO₂ content must be purified to facilitate transportation. Such reserves, particularly prevalent in Asia, require a technology solution with a smaller weight and area footprint, due to high cost of space on an off-shore rig. Thermal CO₂ capture is not suitable due to its steam-drive and massive footprint, while pressure-driven membrane separation suffers low selectivity (up to 1/3 of the methane product is lost). Electrochemical capture offers significant weight, area and energy efficiency...
advantages presenting significant improvements over today’s technology. Natural gas utilization is growing fast due to competitive prices and lower carbon footprint, presenting a compelling opportunity for the EMAR process.

**Mitigating Emissions from Fossil Fuel-Based Power Plants**

Driven by regulatory pressure, utilities need to reduce CO₂ emissions from their coal- and gas-fired power stations. In 2013, the EPA has issued two directives on power plants. For new power plants, new EPA regulations impose limits on CO₂ emissions, effectively requiring carbon capture and sequestration for new plants. For existing power plants, the EPA established rules that also require reduction of emissions, which can be satisfied by either fuel switching, cap-and-trade, or the deployment of carbon capture technology. These rules will drive increasing demand in the medium-term for effective CO₂ capture technology.

The overarching rationale is that fossil fuels will continue to play an important role in the world’s energy generation for the next few decades, given the large existing infrastructure. However, significant evidence suggests that in absence of an intervention, CO₂ content in the atmosphere will reach levels that will result in an increase of temperature above the 2°C threshold established by climate scientists that will precede major detrimental climate change. CO₂ emissions reduction solutions that are cost-competitive, pragmatic and compatible with existing energy infrastructure are critical in addressing the energy and climate change challenge.

The technology cost presents the largest barrier to deployment. The current state-of-the-art technology, thermal amine scrubbing, (discussed in detail in previous chapters) is estimated to cost around $70/ton CO₂ captured. This would lead to a doubling of the cost of electricity, and effectively render capture prohibitively expensive. The Department of Energy targets $40/ton of CO₂ by 2020 as capture cost. Our initial calculations reveal that if our electrochemical technology can perform at large scale at its current laboratory level performance, it can surpass that cost goal. Moreover, we believe we can drive our current
performance levels even closer to the experimentally verified upper efficiency bound, and reduce cost further.

The market size is tremendous; in the United States alone, more than 300 GW of coal-firing capacity is already installed, generating more than 2 billion tons of CO₂ per year. This translates to a total annual expenditure on CO₂ reduction of $25 billion at the DOE objective abatement cost of $40/ton and the EPA's current directive to reduce power station emissions by 30%. At present, there are few large-scale CO₂ capture and sequestration plants in the US, with a total sequestration of around 15 Million tons/year.

Ultimately, as regulatory pressure on coal-fired power stations increases, the utility companies will be forced to either shut down entire plants or deploy carbon capture technology. If capture technology is to be deployed, we envision that the electrochemical system would be an attractive "drop-in" solution to the carbon abatement problem in existing power plants, as these retrofits would not require any internal re-configuration of the steam cycle and power train. Figure 9-4 shows schematically how such arrangement might be deployed downstream of a power station, requiring only a connection to the outlet flue gas and the electricity output from the plant.

Figure 9-4: A schematic depiction of the large-scale electrochemical CO₂ capture process deployed downstream of a power station
The business model for the large-scale system will focus on licensing the technology, and providing maintenance and operational consulting services. Based on conversations with large players in this space, derisking the technology from a technical standpoint by demonstrating it at a small-scale will have significant impact on the ability to attract these industrial partnerships.

The long-term goal for the EMAR process is to help address the global challenge of reducing CO₂ emissions from coal- and gas-fired power plants. Carbon capture and sequestration is a critical technology for efforts to curb climate change resulting from large-scale electricity generation. However, adoption at the utility scale has been slow as existing technology is too expensive relative to existing policy incentives. The technology’s potentially significant cost reductions can drive faster adoption, especially when proven in other smaller-scale applications. With the advent of a carbon price, and US and global policy shifts to reduce emissions, the landscape can shift quickly and proven capture technologies will witness significant growth. International markets, like China, represent a major opportunity due to their recent shift in policy focus and growing interest in reducing emissions.

**Market Demand Forecast**

The market for point source CO₂ management is expected to grow exponentially over the next few years, driven in part by the Asia-Pacific region’s growing need to offset emissions due to rapid industrial development. Frost & Sullivan forecast a growth rate of 25% between 2015 and 2019, with the market reaching a size of $6.8b by 2019. These forecasts suggest that there is a large market opportunity around CO₂ capture across different applications.
Market Analysis – Supply Side

Next, we explore the supply side of the CO₂ equation. The CO₂ market potential is clearly large from the demand side, however, the challenge is that supply unequivocally far overshadows demand in terms of available quantities. Here, we explore the supply side in more detail.

**Anthropogenic Sources of CO₂**

First, we focus on anthropogenic sources of CO₂. Fossil fuel combustion dominates generation of CO₂, where the vast majority of these anthropogenic emissions are not captured or utilized, as previously discussed in this thesis.

For stationary sources, power plants dominate production with the balance shared among other industrial applications, like cement, iron and petrochemicals, as shown in figure XX. Similarly, mobile CO₂ point-source production is largely due to fossil fuel combustion. From a commercial perspective, such sources are less competitive as CO₂ suppliers with stationary sources, given the lower concentration and diffuse production of mobile sources. Despite the promise of on-board capture in a few contexts, the economics of such systems would be significantly more challenging than those where large volumes of concentrated CO₂ streams are to be processed. We therefore focus on outlining some of the major stationary point sources
used commercially today in the following discussion of CO₂ sources. Emissions from coal-fired and gas-fired power stations, as discussed in the previous section, are not included in this discussion, given their limit commercial use as of today.

![Figure 9-6: Breakdown of stationary point-source production of CO₂. Source: “Point Source Carbon Dioxide Management Tech Vision,” Energy & Power Systems, 2016](image)

Potential industrial sources for commercial CO₂ utilized today include ammonia/hydrogen plants, fermentation, lime-kiln operation, sodium phosphate manufacturing and sodium/potassium carbonate production. Most of today’s production of CO₂ in the cement and iron industries remain unutilized. Liquid carbon dioxide is usually recovered as a gaseous by-product of industrial operations, such as hydrogen production by the steam reforming of natural gas or the production of ethanol by fermentation. Figure 9-6 shows a breakdown of current CO₂ sources globally utilized industrially.

**Ammonia and Hydrogen plants:** The reaction of hydrocarbons with steam, as part of the ammonia production process, results in large quantities of carbon dioxide. Global ammonia production is on the order of 10⁷ tons/year, with more than 1 ton of CO₂ produced per ton of ammonia. The produced CO₂ is separated from the resulting gas stream to allow further processing of the gas mixture in the ammonia production process. The large majority of commercial CO₂ supply, particularly for urea production, is satisfied through by-products of ammonia production.
**Fermentation and Ethanol:** As a byproduct of the fermentation process, large amounts of CO₂ are produced. Most of today’s supply of CO₂ for commercial uses outside petrochemicals and EOR is supplied by ethanol production plants.

![Pie chart showing breakdown of CO₂ sources for utilization globally](image)

**Figure 9-7: Breakdown of CO₂ sources for utilization globally (71)**

**Examples of Commercial Projects for Industrial CO₂ Utilization**

There are many examples of industrially sourced CO₂ utilized commercially. For example, ExxonMobil provides more than 4 million tons of CO₂ per year from its gas processing facility in Wyoming to oil producers in the area for EOR activities. At the border between the US and Canada, the Weyburn oil field utilizes industrially sourced CO₂ from the lignite-fired Dakota gasification Company synthetic fuels plant in North Dakota. More recently, CO₂ from a commercial carbon capture facility at the Boundary Dam Coal-fired Power station is utilized to drive EOR at the Weyburn field.

**Natural sources of CO₂**

In addition to anthropogenic sources, there is an abundance of naturally generated and stored CO₂ that is available for commercial use and contributes to potential oversupply. Naturally released CO₂ is mostly offset by natural utilization in a delicate balance. Natural release processes include ocean/atmosphere
exchange, plant and animal respiration, soil respiration and decomposition, and volcanic eruptions. Some of these processes have contributed to naturally occurring reserves of almost pure CO₂. Some of the most important reservoirs are located in Colorado (McElmo Dome), Mississippi (Jackson Dome) and New Mexico (Bravo Dome).

Today, CO₂ production for utilization purposes in the US is dominated by natural sources. Of the 80 Mtpa utilized, 40 Mtpa are from (non-renewable) natural reservoirs and are directly utilized by the oil industry in EOR activities. According to the National Energy Technology Laboratory (NETL, more than 1.6 billion cubic feet of CO₂ from natural reservoirs are injected into oil well in the Permian Basin to incrementally generate around 170,000 bpd of oil.

However, even with the abundance of natural reservoirs, transportation infrastructure from production sites to injection wells is expensive, with an estimated cost of $1b of CO₂ pipeline infrastructure spent by the industry. Even in the Permian basin where such infrastructure has already been developed, NETL suggests that there is pent-up demand for more than 25,000 tons of CO₂ per day from field operators seeking to expand their EOR activity.

**Major Players in CO₂ Supply**

In the US, Linde has a dominant position in the CO₂ supply market (outside the natural reservoirs and EOR space), followed by Air Liquide, Praxair and Airgas. EPCO and Reliant Holding have strong positions in a few regional markets, particularly the South West.

In the New England region, our current knowledge based on information provided by CryoGas International is that no local production facilities exist (where the closest source are Ethanol plants in New York state), potentially suggesting an opportunity for localized production using the EMAR process. In the larger Mid-Atlantic region, there are four production facilities with a total capacity of 1500 tpd (two of which are from ethanol facilities), as well railroad transportation infrastructure, which reduces transportation costs relative
to trucks. In contrast, the South East region of the US has a significantly larger production volume including those from natural reservoirs, in addition to extensive pipeline systems.

In the US Corn Belt region (primarily the Midwest), the large ethanol production facilities based on corn result in significant amounts of byproduct CO₂, resulting in low merchant prices for the gas due to the abundant supply. Even if demand increases in these regions, supply can be ramped up rapidly since many ethanol plants currently vent their byproduct CO₂.

**Carbon Dioxide Value Chain and Pricing**

Fundamentally, CO₂ production a by-product of industrial applications is more cost-effective in today’s market than most potential separation approaches, even from the most concentrated flue gases. However, there are two business drivers for separation to be more competitive than production in the market place:

The first is transportation: Given its gaseous state at ambient conditions, CO₂ transportation is relatively expensive. Small amounts of CO₂ are transported via truck after compression and liquefaction, whereas large amounts (as with enhanced oil recovery) require the use of pipelines that are expensive to build and operate. A sizeable opportunity for separation technologies exists where CO₂ production is spatially separated from natural or industrial production sources, and an impure source is collocated with the utilization site.

The second is purity: In most applications, high standards of CO₂ purity are necessary for effective utilization (e.g. supercritical properties of CO₂ are unfavorably altered by the presence of gas impurities). In addition, industrially produced CO₂ mixtures can include other valuable gases (like H₂). Separation technologies are thus necessary to enable the necessary purity standards for the desired application.

**Bulk Prices**

There is significant variance in pricing CO₂ across the value chain and according to geographic location. As expected, the bulk price of CO₂ can be significantly lower than retail prices for low quantities. Given the dependence of CO₂ costs on transportation, in a manner similar to natural gas, there is no market price
but prices are rather set via bilateral agreements. A few data points can be used to provide a range. For example, ammonia producers are reported to purchase CO₂ at a price between $3 - $15/ton, whereas pipelined CO₂ ranges between $9 - $26/ton (accounting for capital and operating expenses of the infrastructure). Transportation can therefore account for a large fraction of the final price paid by bulk buyers, suggesting a significant opportunity for localized separation from existing flue gases. (72)

Another data point on CO₂ price point is that due considering its external costs (i.e. the climate change related externality of CO₂ as a greenhouse gas). In the European Union Emissions Trading System (EU ETS), CO₂ currently (March 2017) trades at around $5.2/ton though prices are extremely volatile, reaching a peak of more than $30/ton in 2008. In conclusion, bulk CO₂ prices are expected to have an upper bound in the range of $20-$25/ton, with some dependence on oil prices given the role of EOR in CO₂ utilization.

![EUA closing prices](image)

**Figure 9-8:** European Union Emissions Trading System Prices over the period 2006 – 2016. (73)

**Merchant Level Prices**

Raw CO₂ gas prices range from $5 to $25/ton whereas consumer market prices usually average around $90 to $100/ton; and in some high priced markets with little regional competition or no local supply can be $200
to $300/ton (74). This clearly points to the potential of distributed CO\(_2\) production and separation for small-scale applications where consumers face such extreme prices.

**EMAR Commercialization Strategy**

A few highlights are clear from the previous analysis of the demand and supply side of CO\(_2\). First, there is clearly more supply of the gas than current demand, and accordingly, the deployment of the EMAR technology would either be through replacing existing sources, or by unlocking new applications.

Second, there is a large difference in prices between bulk and consumer market prices ($5-$25/ton vs. $90-$100/ton and up to $200-$300/ton in absence of local competition). Given the modular nature of the EMAR process, there is a significant case to be made for direct access to the consumer market, though consumer markets would incur a large cost of sales per unit given the need to access and secure a more diffuse and volatile consumer base.

Third, there is a large discrepancy in scale of deployment across applications. For example, producing CO\(_2\) for building energy efficiency applications requires far smaller throughputs in comparison to EOR. For a new and unproven technology, this presents an opportunity to deploy in small-scale applications to prove out the technology. Similarly, reliability needs vary significantly: life-support systems require rigorous testing and certification, whereas biogas purification will be more tolerant of performance variations.

Finally, competing with industrial and natural sources of CO\(_2\) is primarily a question of co-location. When large-scale industrial producers are close by and the infrastructure exists for transport, it would be exceedingly difficult for any separation process include the EMAR process to compete. However, if there is no infrastructure and a closer source where CO\(_2\) can be separated is close-by, the cost competition can favor separation.

In deciding on the optimal commercialization strategy for the EMAR process, it is helpful to understand the benefits of the technology over other existing separation alternatives. Table XX shows a comparison of the EMAR process with thermal and pressure-driven CO\(_2\) separation, assuming the bench-scale
performance of EMAR can be sustained at scale. The EMAR process has significant advantages over both technologies in cost, ease of deployment and simplicity of operation, in addition to being modular and amenable to deployment at various scales.

<table>
<thead>
<tr>
<th>Criterion</th>
<th>EMAR</th>
<th>Thermal</th>
<th>Pressure-Driven</th>
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<td>Energy (w/o compression)</td>
<td>20 – 45 kJ/mole</td>
<td>50-70 kJ/mole</td>
<td>50-80 kJ/mole</td>
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<tr>
<td>Low Temperature Operation</td>
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</tr>
<tr>
<td>High Pressure Desorption</td>
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<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Purity of outgoing stream</td>
<td>High</td>
<td>High</td>
<td>Low</td>
</tr>
</tbody>
</table>

Table 4: Comparison of EMAR with thermal and pressure-driven CO$_2$ separation technologies

Given the above analysis of market needs, the following commercialization strategy is proposed with the objective of combining technical derisking at a small-scale with a go-to-market strategy that offers revenue from the outset. The purpose here is to avoid the fate of many technology startups that require significant upfront funding and spend the entire R&D phase without generating significant revenue, and ultimately fail to deliver sufficient returns to investors and therefore, frequently run out of funding before reaching sufficient technology maturity to address a commercially viable segment.
In this proposed strategy, the EMAR process would first be deployed for small-scale applications to replace CO₂ in merchant markets where prices exceed $100/ton. By building a large, concentrated customer base in strategically chosen geographies with limited natural and industrial CO₂ production, revenue generation would be combined with small-scale deployment iterations. Once the technology reaches sufficient maturity, deployment in energy efficiency and natural gas purification would be targeted next, to demonstrate pilot-scale deployment of the technology in contexts that are less capital-intensive and less sensitive economics. Finally, if pilot-scale deployments reach reasonable maturity, the technology would be ready for large-scale commercial application in EOR markets. Given the large capital needs and immense scale and complexity of such projects, deployment would occur through licensing agreements with large players that have sufficient resource for such a scale. The strategy is discussed in more detail as follows.

- **Phase 1: Validate performance at small-scale**

In this stage, modular stacks of the EMAR process would be deployed at small-scale to compete with merchant CO₂ uses, which are by definition distributed and small-scale. Geographical areas like the North East are potentially attractive (pending more detailed market research) given the lack of unutilized natural and industrial CO₂ and the high merchant market prices.

Deployments at 1-10 kg/day of CO₂ for consumer applications including academic institutions, universities, hospitals and food facilities, the EMAR technology can provide customers with on-site ability to supply CO₂, from flue gas and other sources.

This market segment would help create reasonable revenue for the company that in addition to research grants and other funding sources would help finance the company. Moreover, deployments across this scale would allow for extensive testing of the technology under various operational constraints, with limited downside and liability in case of lower performance, given the large price cushion (where EMAR is projected to produce at less than $40/ton whereas merchant prices are higher than $100/ton).
There are significant risks in this phase of the strategy: the first is developing a customer-ready version of the technology, which requires significant automation and ensuring fail-safe, given the use of specialized chemicals (like the amine solvent). Other risks include the commercial costs of reaching such a wide and diffuse customer base, and the potential acceptance of this category of the technology in presence of existing supply chains and supplier relations. Finally, there are risks associated with the quality and final purity of the supplied gas, given the remote operation of the technology.

- **Phase 2: Medium-Scale Deployment**

Once the technology performance is proven out at a small-scale, with more than 1 year of operation of units and a better understanding of the longer-term performance of the technology, costs per ton of CO₂ are expected to drop while the reliability increases. If these conditions are satisfied, the EMAR process would be well-positioned for medium-scale deployment (on the order of 1-10 ton/day).

A potentially attractive opportunity would be building energy efficiency, where a small EMAR unit can help recycle more conditioned air in an HVAC system, operating as a drop-in solution that reduces energy efficiency. With current densities above 200 A/m², the technology footprint and costs would be sufficient to allow for an attractive offering in energy efficiency.

This is a difficult market to enter, first because of the deployment complexity (where an HVAC system needs to be retrofitted with an EMAR process), the heterogeneity of buildings, and the untested value of such a system. Significant business development efforts would be necessary to deploy the technology in the first few projects, but if the benefits are clear and material, wider adoption is possible.

Another potential risk in this case is that of competition: small-scale zeolite systems that utilize waste heat can potentially be more competitive than the EMAR process, depending on relative costs of electricity versus the zeolite systems running costs.
If successful, however, this market segment could prove out to be a game changer for the EMAR process commercialization. With a huge market size and room for international expansion, the EMAR process can generate significant revenue while validating its performance at a much more substantial scale.

Another interesting mid-scale application is in on-site energy generation using natural gas. If the EMAR process demonstrates its ability to remove other acid gases (like the widely abundant natural gas impurity, H₂S), it could see tremendous demand in purifying small volumes of gas in oil-sites for energy generation, in lieu of expensive and difficult diesel supplies. This is a much more niche application in comparison with building energy efficiency, but requires a much larger scale per deployment.

Life-support systems would also be attractive: airplane builders are expected to be less price sensitive than other customers, and their high standards for quality and safety would pose a serious test to the EMAR technology reliability. If successful in this application, the technology would have strong validation of its performance and safety, an important stepping stone towards wider adoption.

With sufficient validation across these opportunities, the EMAR technology can target off-shore natural gas purification, where footprint and weight are critical given the expensive real-estate on an off-shore facility. Scale here would be significantly larger (10 – 100 tons of CO₂/day), and would likely require partnerships with large players, like Petronas (given the large presence of CO₂ in Malaysian natural gas wells) and Middle Eastern gas companies, in Qatar and the UAE. If the EMAR technology is deployed in such a context, it would be a significant milestone towards commercialization, equivalent to a successful pilot plant study.

- **Phase 3: Commercial Deployment at Scale**

Given the ultimate purpose of the EMAR process in addressing the climate change challenge, previous stages would have little impact even if successful: virtually all separation efforts are carbon neutral, with the exception of the resulting emissions savings from increased building energy efficiency. These phases
are however critical in demonstrating the technology at various scales before seeking commercial scale deployment in applications with a relatively large climate change impact.

Commercial deployment at scale would primarily target CO₂ EOR, the only large-scale sequestration process with accompanying commercial value. For such deployments, commercial partnerships with large players like Denbury or Exxon, or with chemical system providers like BASF and Dow Chemicals, would be critical. The following table provides a list of oil & gas players with significant CO₂ EOR activity:

<table>
<thead>
<tr>
<th>Company</th>
<th>Miscible Projects</th>
<th>Locations</th>
<th>Incremental Production (MMB/MD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Occidental</td>
<td>29</td>
<td>TX, NM</td>
<td>90.2</td>
</tr>
<tr>
<td>Hess</td>
<td>6</td>
<td>TX</td>
<td>25.3</td>
</tr>
<tr>
<td>Kinder Morgan</td>
<td>1</td>
<td>TX</td>
<td>24.2</td>
</tr>
<tr>
<td>Chevron</td>
<td>4</td>
<td>CO, TX, NM</td>
<td>21.3</td>
</tr>
<tr>
<td>Denbury Resources</td>
<td>13</td>
<td>MS, LA</td>
<td>17.8</td>
</tr>
<tr>
<td>Merit Energy</td>
<td>7</td>
<td>WY, OK</td>
<td>13.6</td>
</tr>
<tr>
<td>ExxonMobil</td>
<td>2</td>
<td>TX, UT</td>
<td>11.7</td>
</tr>
<tr>
<td>Anadarko</td>
<td>4</td>
<td>WY</td>
<td>9.0</td>
</tr>
<tr>
<td>Whiting Petroleum</td>
<td>3</td>
<td>TX, OK</td>
<td>6.9</td>
</tr>
<tr>
<td>ConocoPhillips</td>
<td>2</td>
<td>TX, NM</td>
<td>5.5</td>
</tr>
<tr>
<td>12 other independents</td>
<td>28</td>
<td>TX, OK, UT, KS, MI</td>
<td>14.9</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>99</strong></td>
<td><strong>TX, OK, UT, KS, MI</strong></td>
<td><strong>240.4</strong></td>
</tr>
</tbody>
</table>

* thousand barrels of oil per day

**Table 5: Major US CO₂ Operators** (Source: OGJ Biennial EOR Survey)

Alternatively, gas providers like Linde, Praxair and AirProducts could also be attractive partners to enter this space. In terms of commercial risk, the key question involves which markets to focus on for a demonstration project. Given the current oil price environment, identifying opportunities where our technology is not competing only at cost, but on other features (ease of deployment, reduced weight and area footprint) will be key.
Conclusions

In this capstone paper, the markets for CO₂ as a product and for separation are explored to develop a commercialization thesis for the EMAR technology:

- Demand for CO₂ as an end-product is on the order of 80 Mtpa in food, EOR and new utilization routes. However, supply at 500 Mtpa of concentrated CO₂ sources and 18,000 Mtpa from dilute sources significantly outweighs demand. Absent a policy change, the climate change challenge will not be addressed organically under these market conditions.

- Demand for CO₂ separation as a service is growing, with niche applications in building energy efficiency and small-scale natural/biogas separation, as well significant potential for CCS.

- Despite the overall challenge in the CO₂ markets, an analysis of the value chain finds that merchant prices are between $100-$300/ton, due to transportation costs. This suggests an opportunity for the EMAR process around localizing generation of CO₂.

- A potential commercialization thesis for the EMAR process would consist of three phases. In the first phase, the plug&play nature of the technology can be leveraged to compete in the merchant market through an on-site CO₂ generation solution. In the second phase, we propose targeting the CO₂ separation as a service through air reconditioning services for energy efficiency and on-site natural gas purification. Finally, in the third phase, if the EMAR process can evolve to satisfy the cost and reliability needs of large-scale operation, the EOR market would offer a massive, large-scale opportunity for deployment.
References


69. NETL. Carbon Dioxide Capture from Existing Coal-Fired Power Plants. 2007. DOE/NETL-401/110907.


