Journal of Electroanalytical Chemistry 799 (2017) 156–166

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Transient modeling of electrochemically assisted CO_2 capture and release

Shobhana Singh[a], Ellen B. Stechel[b,*], Daniel A. Buttry[b]

[a] *Department of Energy Technology, Aalborg University, Pontoppidanstræde 111, Aalborg 9220, Denmark*
[b] *School of Molecular Sciences, Arizona State University, Tempe, AZ 85287, United States*

ARTICLE INFO

Keywords:
CO_2 capture
Electrochemical cell
Ionic liquid
Transient modeling
Finite element method

ABSTRACT

The present work aims to develop a model of a new electrochemical CO_2 separation and release technology. We present a one-dimensional transient model of an electrochemical cell for point source CO_2 capture and release, which mainly focuses on the simultaneous mass transport and complex chemical reactions associated with the separation process. For concreteness, we use an ionic liquid (IL) with 2 M thiolate anion (RS^-) in 1 M disulfide (RSSR) as an electrolyte in the electrochemical cell to capture, transport and release CO_2 under standard operating conditions. We computationally solved the model to analyze the time-dependent behavior of CO_2 capture and electro-migration transport across the cell length. Given high nonlinearity of the system, we used a finite element method (FEM) to numerically solve the coupled mass transport equations. The model describes the concentration profiles by taking into account the individual transport of all participating species, charged as well as neutral. The model predicts performance characteristics of electrochemically assisted CO_2 capture and release in terms of faradaic efficiency and cell current density as the cell dynamics evolves and approaches the steady state. The model provides an opportunity to better understand electrochemically assisted CO_2 capture and release, and when coupled with experimental results will provide an early assessment of feasibility for large-scale application in realistic conditions.

1. Introduction

In view of adverse environmental impacts of global warming, capturing and utilizing CO_2 emissions from power generation or other large stationary sources can provide an opportunity to reduce CO_2 emissions and mitigate the risk of climate change. Currently, the most amenable sources for CO_2 generation are industrial processes, chemical production, and power plants. According to a recent report on greenhouse gas emissions (GHGs) from the existing power plants, emissions are expected to increase around 1942 million mt (from 2015 levels) in 2030 [1]. Fossil fueled power plants are the largest sole sources of greenhouse gas emissions in the United States. The flue gas from coal-fired power plants has 12–15 mol% of CO_2 concentration at atmospheric pressure [2–4]. There exist numerous novel approaches to capture CO_2 from power plant flue gas streams such as chemical [5–7], absorption [8–10], adsorption [11,12], cryogenic [13], membrane separation [14,15], and electrochemical separation [16–19]. The most conventional and commercially available post-combustion CO_2 removal is adsorption with amine solvents like monoethanolamine (MEA) [20,21]. MEA reacts quickly with CO_2 but requires substantial energy to regenerate CO_2 [22–24].

Ionic liquids (ILs) have the potential to capture post-combustion CO_2 and reduce the energy parasitics associated with conventional amine-based solvents [25,26]. ILs are organic salts with melting points lower than 100 °C, which can have remarkable selectivity for CO_2 in comparison to CH_4, CO, N_2, O_2 present in the flue gas mixture from power plants [27,28]. Researchers have explored the solubility of CO_2 gas in ILs for more than a decade [26,28–30]. ILs exhibiting unique properties such as low vapor pressure, high thermal stability, non-flammability, tunable polarity, and good solubility, have a wide parameter space for optimizing carbon capture and sequestration (CCS) or utilization (CCU) technologies [30–32]. Solvent regeneration without evaporation can reduce the replacement requirement pointing towards an advantage of ILs [33,34]. Although ILs have many advantageous properties, the release of CO_2 from the IL and the regeneration of the solvent still entail a substantial energy penalty. Higher viscosity than conventional MEA solution leads to an additional energy penalty of pumping. In addition, low CO_2 concentrations in the flue gas make the task of energy efficient capture even more difficult [35]. Furthermore, commercially viable implementation on a meaningful industrial scale will require high solubility with a fast absorption rate of CO_2 by the solvent and low-cost regeneration of the solvent. However, there are approaches to overcome these challenges in the existing literature. For example, in a recent study [26], a wide variety of Aprotic Heterocyclic

---

[*] Corresponding author.
E-mail address: Ellen.Stechel@asu.edu (E.B. Stechel).

http://dx.doi.org/10.1016/j.jelechem.2017.05.045
Received 15 February 2016; Received in revised form 23 May 2017; Accepted 24 May 2017

Anion (AHA) ILs having different enthalpies of reaction with CO_2 is studied in order to reduce the energy demand for CO_2 capture at low pressures between 0 and 1 bar at room temperature.

Development of numerical models and simulation tools can elucidate the dynamics of complex CO_2 capture from stationary sources, and thus contribute in predicting the dynamic behavior of the integrated chemical processes coupled with physical phenomena. Intensive steady-state modeling efforts have already been carried out for several CO_2 capture technologies based on new solvents or for novel integrated processes [36–38]. Freguia and Rochelle [39] developed a steady-state performance model of a stripping system for CO_2 removal from a flue gas by means of aqueous MEA solution. Dugas and Rochelle [40] developed a steady-state model of CO_2 absorption/desorption by aqueous MEA and piperazine in a wetted wall column and demonstrated the variation of CO_2 mass transfer coefficient with CO_2 loading, temperature, and amine concentration. In addition, Ramasubramanian et al. [14] have performed a detailed modeling study of a membrane based process of carbon capture and determined the effect of operating parameters and economic factors on the overall cost of the capture. Some researchers have also developed dynamic models for transient operation of CO_2 absorbers and desorbers using different computational frameworks (CO2SIM and gPROMS) [41–43]. However, none of the literature can be directly applied to model an electrochemically assisted CO_2 capture and release, which has the promise of a very low energy penalty because very little of the energy goes into spectator degrees of freedom.

The overall process involved in the electrochemically assisted capture and release is governed by heterogeneous surface reactions, mass transport, and homogeneous chemical reactions. The set of coupled differential equations describing the molecular transformations and transport of multiple interacting species (charged as well as neutral) often introduce numerical challenges. Nevertheless, a numerical method such as finite element method (FEM) has proved to be effective in calculating solutions of the coupled equations and have frequently been used for modeling many complex electrochemical systems. Recently, Razavi et al. [44] developed a two-dimensional mathematical steady-state model to describe the CO_2 capture through hollow-fiber membrane contactors based on a solution of 2-amino-2-methyl-1-propanol and piperazine as the chemical solvent and used FEM to computationally solve the mass transfer equations. Many innovative CO_2 capture technologies based on ILs are under development and mostly limited to laboratory scale. They have not yet been optimized for the scale required in, for example, coal-fired power plants. Increased modeling and simulation effort would help facilitate and guide experimental research for the ultimate goal of commercialization.

In this paper, we report on the development of a one-dimensional (1D), time-dependent, simplified numerical model of an electrochemical cell using FEM. The model is based on an electrochemical capture method in which electrochemical reduction of a disulfide (RSSR) generates a thiolate (RS^-) that binds CO_2 to produce a thiocarbonate ($RSCO_2{}^-$), which with subsequent oxidation regenerates the disulfide and free CO_2. It provides insights into the electrochemical approach with an IL electrolyte for CO_2 capture and release bridging from the laboratory to ultimately a large scale practicable technology, which can work under realistic operating and economic conditions. The applicability of the proposed numerical model can be extended by coupling model predictions with the experimental observations for validation and to provide guidance. The model incorporates multiple physical processes simultaneously including,

- Butler-Volmer reaction kinetics of the electrode processes;
- non- faradaic chemical reaction in the cell;
- transport by convection, diffusion, and electromigration;
- CO_2 transport across the cell;
- concentration profiles of participating species;
- cell performance characteristics such as faradaic efficiency, and cell current density.

The organization of this article is as follows - Section 2 describes the overall model development including a schematic diagram, operation, geometric domains, and the governing equations. Section 3 illustrates the computational algorithm, which outlines the boundary conditions and the procedure to reach a numerical solution. Section 4 presents and discusses the results obtained. Section 5 concludes with a summary and brief evaluation of the model in the context of real-world requirements.

2. Model development

2.1. Electrochemical cell

Here we use an electrochemical cell that consists of an IL electrolyte, which for our purposes in this paper is modeled as a mixture of 2 M RS^- salt and 1 M RSSR. The cell design consists of an IL layer, which is sandwiched between the cathode and anode. The technology uses RS^-, which exists in the IL, but can also be electrochemically generated from RSSR by applying an external potential. RS^- acts as the capturing agent for CO_2, producing $RSCO_2{}^-$ [45]. The reaction set involved can be written as:

$$\mathrm{RSSR} + 2e^- \rightleftharpoons 2\mathrm{RS}^- \tag{1}$$

$$\mathrm{CO}_{2,l} + \mathrm{RS}^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{RSCO}_2^- \tag{2}$$

$$2\mathrm{RSCO}_2^- \rightleftharpoons \mathrm{RSSR} + 2\mathrm{CO}_2 + 2e^- \tag{3}$$

We note that the faradaically active reactions in Eqs. (1) and (3) involve multiple reaction steps as reported previously [46], for example, stepwise reduction such as $RSSR + 1e^- \rightarrow RSSR^-$, $RSSR^-$ dissociation to $RS\cdot + RS^-$, and finally $RS\cdot + 1e^- \rightarrow RS^-$. For simplicity, we model the redox couples as concerted two-electron processes. This simplification reduces complexity in the model and focuses attention on the balance of transport between the neutral and charged species, which is a unique aspect of the present study. This comes at a cost of oversimplifying the electrode kinetics, which is a common strategy in simulating multielectron redox processes.

The forward reaction in Eq. (1) shows the cathodic two-electron reduction of one RSSR to generate two nucleophilic RS^- [47]. The anode reaction regenerates RSSR and releases CO_2 (Eq. (3)). The mechanism for trap and release of CO_2 using electrochemical activation was recently demonstrated [48,49], where the trap and release reactions of CO_2 using 4,4′-bipyridine are reversible, proceed rapidly with low energy barriers. Fig. 1 shows the simplified schematic diagram of

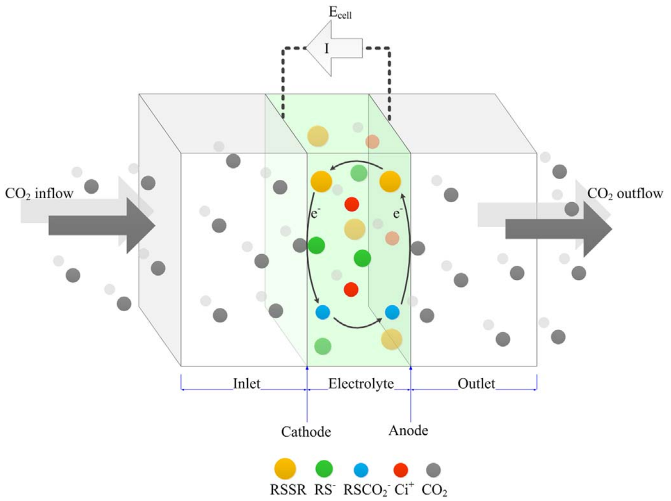

Fig. 1. Schematic diagram of the electrochemical cell for CO_2 capture and release.