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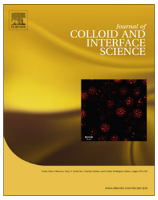

# Energy from $CO_2$ using capacitive electrodes – A model for energy extraction cycles

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ABSTRACT

A model is presented for the process of harvesting electrical energy from $CO_2$ emissions using capacitive cells. The principle consists of controlling the mixing process of a concentrated $CO_2$ gas stream with a dilute $CO_2$ gas stream (as, for example, exhaust gas and air), thereby converting part of the released mixing energy into electrical energy. The model describes the transient reactive transport of $CO_2$ gas absorbed in water or in monoethanolamine (MEA) solutions, under the assumption of local chemical equilibrium. The model combines the selective transport of ions through ion-exchange membranes, the accumulation of charge in the porous carbon electrodes and the coupling between the ionic current and the produced electrical current and power. We demonstrate that the model can be used to calculate the energy that can be extracted by mixing concentrated and dilute $CO_2$ containing gas streams. Our calculation results for the process using MEA solutions have various counterintuitive features, including: 1. When dynamic equilibrium is reached in the cyclical process, the electrical charge in the anode is negative both during charging and discharging; 2. Placing an anion-exchange membrane (AEM) in the system is not required, the energy per cycle is just as large with or without an AEM.

## 1. Introduction

This paper focuses on a new technology, “Energy from $CO_2$ emissions using capacitive electrodes”, that generates electricity from the mixing energy released when a gas with high $CO_2$ concentration, such as exhaust gas from power plants, dilutes into a gas with low $CO_2$ concentration, such as the atmosphere. This technology, that is compatible with post-combustion $CO_2$ capture treatments [1] and may increase the energy efficiency of power stations that release $CO_2$ emissions, was first demonstrated by Hamelers et al. [2] and was inspired by the use of capacitive electrochemical cells for energy extraction from mixing seawater with river water, a process called “capmix” [3–5]. These capacitive cells are built with a combination of porous electrodes, an anion-exchange membrane (AEM) and a cation-exchange membrane (CEM), see Fig. 1. Two ionic electrolytes at different concentrations flow alternately (cyclically) through the cell.

During the period that the concentrated electrolyte is flowing into the cell, defined as the “charging step”, ions are stored within the micropores of the porous carbon particles, where electrical double layers are formed [6]. Due to the presence of the membranes, mainly cations are transported to the cathode, which is the carbon electrode covered with the cation-exchange membrane, while anions are mainly transported to the anode, which is covered with the anion-exchange membrane, see Fig. 1. The resulting ionic current directed from anode to cathode is compensated by the transport of electrons through the external electrical circuit, also from the anode to the cathode, i.e., an electrical current is set up. During the discharging step, when the dilute electrolyte is flowing into the cell, the ions are released from the electrodes and are transported through the membranes back to the flow channel. Consequently, the electrons stored in the cathode are released, resulting again in an electrical current, now in the opposite direction.

The capmix technology was developed for the extraction of mixing energy from the salinity difference between seawater and river water at river mouths [7,8]. Hamelers et al. [2] demonstrated that it is also possible to apply the same technology for harvesting energy from the mixing of carbonated electrolytes, i.e., electrolytes equilibrated with $CO_2$ containing gases that have a different $CO_2$ concentration.

In Ref. [9], a theoretical discussion of the fundamental differences between the application of this technique using either saline

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or carbonated solutions was presented. Salinity difference systems are based on inert ions meaning that chemical reactions between them do not play an important role. $CO_2$ concentration difference systems, however, involve additional physical and chemical reactions that have to be taken into account for the understanding and the optimization of the technology. Among the differences discussed in Ref. [9] are the $CO_2$ gas/liquid equilibrium, the acid/base reactions that the ions can undergo (e.g., the ionic species $HCO_3^-$ can react to $CO_3^{2-}$ or $H_2CO_3$ depending on the pH), and the presence of neutral species, such as $H_2CO_3$.

The extraction of energy from carbonated solutions, using deionized water in equilibrium with air or pure $CO_2$, showed relatively low power densities compared to the results obtained from river water/seawater mixtures, due to the low conductivity of the electrolytes [2]. An aqueous electrolyte in equilibrium with pure $CO_2$ gas acts approximately as a binary 1:1 electrolyte of protons and bicarbonate ions with $\text{pH} \sim 4$, which means that the ionic strength is in the order of 1 mM [9]. These values are a few orders of magnitude lower than the concentration of NaCl in seawater ($\sim$0.5 M). To increase the absorption of $CO_2$ in the aqueous phase (in the form of bicarbonate and carbonate ions) and to increase the conductivity of the system, alkaline solutions can be used instead of pH neutral deionized water [2,9]. Aqueous solutions of ethanolamines, for example, are commonly used for the absorption of post-combustion $CO_2(g)$ and other acid gases from power stations and chemical plants [10–12]. The higher solubility of $CO_2(g)$ in amine solutions is due to the alkalization of the medium and due to the formation of carbamate ions.

For the development and optimization of the capacitive mixing techniques, theoretical studies and numerical models have to be proposed and compared with results obtained in laboratory experiments and pilot plants. This paper is a continuation of the experimental work presented in Ref. [2] and the theoretical discussion presented in Refs. [9,13]. In the present work, we present a mathematical model for the process of harvesting energy from $CO_2$ containing electrolytes (either pure water of monoethanolamine (MEA) solutions) using capacitive cells based on porous electrodes covered by ion-exchange membranes. We propose a model that couples the electro-diffusion transport of ions through the ion-exchange membranes into/from the porous carbon electrodes, with the electrical current running in the external circuit. At each position, in electrode, membrane and flow channel, we assume local chemical equilibrium, incorporating infinitely fast equilibration between the chemical species. With the model, we calculate the energy that can be extracted in a cycle that consists of sequentially flowing into the cell electrolytes that were contacted either with concentrated or dilute $CO_2$ containing gas streams. Note that whereas in Ref. [9] only the zero-current case was considered (open circuit), in the present paper real operation is modeled including non-zero currents.

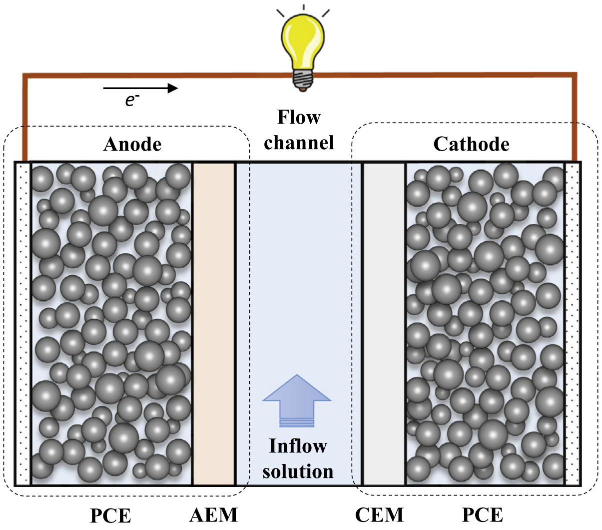

**Fig. 1.** Schematic picture of the capacitive cell (operating in the charging step). PCE is porous carbon electrode, AEM is anion-exchange membrane, CEM is cation-exchange membrane.

## 2. The model

### 2.1. The capacitive cell

The capacitive cell modeled in this paper, schematically depicted in Fig. 1, is based on that used in the experiments reported in Ref. [2]. The cell consists of a pair of porous carbon electrodes (270 cm length $\times$2 cm width $\times$200 μm thickness) placed between the flow channel and the porous carbon electrodes. Mixing energy is converted into electrical energy by sequentially flowing an air-flushed solution, with a low $CO_2$ concentration, and a $CO_2$-flushed solution, with a high $CO_2$ concentration, through the cell.

The different parts of the capacitive cell (the membranes, the flow channel and the electrodes) are modeled following specific approaches. We use continuity equations to describe the ionic transport through the membranes. In the model presented here, we assume that the transport resistance of the system is located in the membranes, and not in the flow channel or the porous carbon electrodes. Accordingly, the flow channel and the porous electrodes are modeled as continuous stirred-tank reactors (CSTRs). The numerical solution of the coupled mathematical model is achieved by means of a semi-implicit Runge–Kutta numerical method.

### 2.2. The chemical system

Carbonate solutions are obtained by the continuous bubbling of gas containing $CO_2$ through the electrolyte, the gas either being air ($p_{CO_2}$ = 390 ppm or $3.9 \times 10^{-4}$ atm) or pure $CO_2(g)$ ($p_{CO_2}$ = 1 atm). The electrolyte into which the $CO_2$ is absorbed is either pure water, or an aqueous solution of MEA. Henry's law is used to describe the $CO_2$ gas/liquid equilibrium, that is

$$[CO_2] = \frac{p_{CO_2}}{K_H} \qquad (1)$$

where $p_{CO_2}$ (atm) stands for the partial pressure of $CO_2$ and $K_H$ is the Henry constant, which is approximately 29.41 L atm mol$^{-1}$ at 298 K.

The mathematical model presented here is described for the general case of having a MEA solution as a solvent. In solution, MEA can be present in two forms: (1) the neutral monoethanolamine molecule (MEA) and (2) the protonated monoethanolamine ion ($MEAH^+$). In the case of having pure water, the concentrations of MEA and $MEAH^+$ are set to zero. Table 1 lists the chemical species included in the system, as well as the diffusion coefficients [14].

In aqueous solution, carbonic acid, $H_2CO_3$, is in equilibrium with non-hydrated carbon dioxide, $CO_2$ (aq), and the concentration of the former is much lower than the concentration of the latter. Based on this, in the chemical system considered here we include only the species $CO_2$ (aq), neglecting the hydrated form of carbonic acid. As mentioned in the introduction, the absorption of $CO_2$ in a MEA solution can also result in the formation of carbamate ions. This species is for the moment excluded from the model.