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Silver-molten carbonate composite as a new high-flux membrane for electrochemical separation of CO_2 from flue gas

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ABSTRACT

One of the major concerns of consuming fossil fuels to produce useful form of energy is the emission of CO_2, a greenhouse gas that can cause climate change and ultimately threaten the survival of humanity. Controlling CO_2-emission is an urgent but only practical solution to stabilize CO_2 concentration in the atmosphere. In this paper, we report our effort to capture CO_2 from a simulated flue gas by utilizing a dual-phase mixed carbonate-ion and electron conducting membrane, namely molten carbonate and silver. The obtained CO_2 and O_2 flux densities are the highest among the published metal-molten carbonate systems and relatively stable over 80-h period. The measured CO_2 and O_2 flux densities not only exhibit similar activation energy but also have the ratio of 2:1, favorably confirming the surface electrochemical reaction of $CO_2 + 1/2O_2 + 2e' = CO_3{}^{2-}$. These results demonstrate the Ag–MC dual-phase composite as a promising high-flux membrane for high-temperature electrochemical CO_2 separation from flue gas with high selectivity.

1. Introduction

Fossil fuels are still the dominant energy source powering our modern society, largely due to their competitive cost and wide accessibility. However, one of the main byproducts from consuming fossil fuels is carbon dioxide (CO_2), a greenhouse gas that can cause climate change and ultimately threaten the survival of humanity. An alarming statistic published in 2008 shows that a nearly 40% of 5.8 billion metric tons of the total US anthropogenic CO_2 emissions was resulted from burning fossil fuels for power generation [1,2]. Therefore, to effectively mitigate CO_2 emissions from the use of fossil fuels has drawn a great deal of attentions globally in recent years. It has risen to be not only a scientific topic but also a political agenda.

There are four general strategies currently being considered for the abatement of CO_2 emissions: demand-side conservation, supply-side efficiency improvement, potential increase in nuclear and renewable energy supplies and implementation of carbon capture and storage (CCS) technology on fossil-fueled power plants [3,4]. Of all the options, CCS is regarded as the sole practical solution to achieve considerable CO_2 emission reduction from fossil-fueled power plants in the near term [4].

To realize the ultimate CO_2 storage/sequestration, separation and capture of CO_2 from a CO_2-containing industrial process stream is the first step. The CO_2 capture technologies currently being developed and demonstrated are targeting at three different stages/processes depending on the type of a power plant: post-combustion, oxyfuel combustion and pre-combustion [4–6]. The pre-combustion CO_2 capture is more suitable for integrated gasification combined cycle (IGCC) power plants whereas the post-combustion and oxygen-combustion captures are more applicable to conventional pulverized coal-fired (PC) and natural gas-fired power plants [3]. However, the existing state-of-the-art CO_2 capture technologies are primarily based on chemical/physical absorptions by a liquid solvent or a solid sorbent and are yet ready for commercialization at the larger scale necessary for power plant application. The parasitic loads (steam and power) required to support CO_2 capture would decrease power generation capacity by nearly one-third and increase levelized cost-of-electricity (COE) by as much as 80%. Even if successfully scaled up, it would not be cost effective at their current level of process development [3,7].

In comparison to solvent- and sorbent-based CO_2 capture processes, conventional membrane-based technology presents cost advantages when applied to pre- and post-combustion CO_2 capture: no steam or chemical load, delivering high-pressure CO_2 and driving CO shifting reaction to completion [8–10]. However, the major challenges are the limited selectivity, thus product purity, and poor compatibility with high-temperature process stream.

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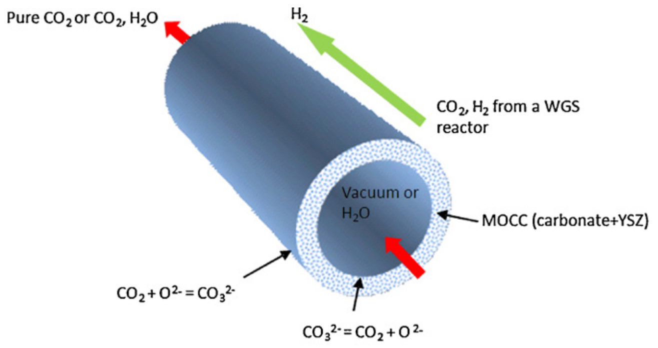
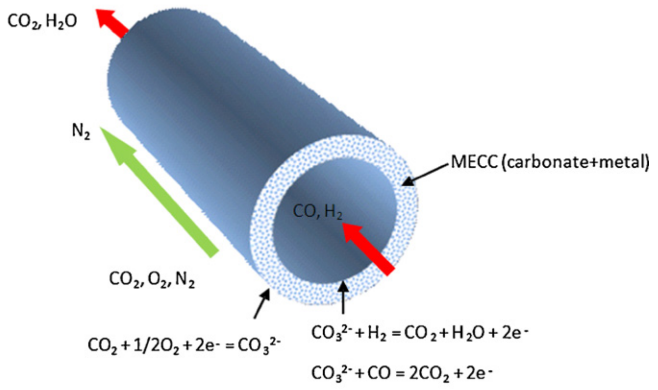


(a) MOCC



(b) MECC

Fig. 1. Schematic of the working principles of MECC and MOCC based CO_2 separation membranes: (a) MOCC; (b) MECC.

Therefore, developing an alternative high-temperature membrane technology to separate/capture CO_2 more selectively and efficiently for existing power plants is in great need.

One category of gas separation membranes that has the potential to meet these requirements is the mixed ionic and electronic conductors [11–14]. Different from those absorption and size-exclusion counterparts, an electrochemical transport membrane only allows the electrochemically active species to transport through the membrane. Therefore, its selectivity is exclusive. Since this membrane normally operates at elevated temperatures, it also has an excellent compatibility with any high-temperature process stream. The best example of this category of materials is the oxygen transport membranes, or OTMs, which have been demonstrated in producing pure oxygen and synthetic gas at large scale. The key feature of these materials is the concomitant fast oxide-ion and electronic transport enabling high oxygen flux. Applying this principle to the CO_2 separation membrane, two types of mixed conductors can be envisioned: (1) mixed carbonate-ion and oxide-ion conductor (MOCC); (2) mixed carbonate-ion and electron conductor (MECC). Fig. 1 shows the working principles of these two membranes along with CO_2-separation enabling surface reactions. Based on these fundamental reactions, it is evident that MOCC is more suitable for CO_2 separation from a reducing stream such as water-gas shift gas ($CO_2 + H_2$) where the chemical gradients of CO_2 and O_2 exist in opposite direction across the membrane. On the other hand, MECC is more adequate for CO_2 separation from an oxidizing stream such as flue gas (CO_2, O_2, N_2) where the chemical gradients of CO_2 and O_2 exist in the same direction across the membrane. In this case, both CO_2 and O_2 will permeate through the membrane, the mixture of which can be further separated by a downstream OTM or recycled back to the combustion chamber for oxy-combustion [6].

Since single-phase MOCC is presently nonexistent from a material perspective [12], the MOCC membrane in Fig. 1 is illustrated as a composite of two phases: one being carbonate-ion conducting and another being oxide-ion conducting. Compared to the carbonate-ion conductor, the oxide-ion conductor has much lower ionic conductivity in the temperature of 500–650 °C, making it the limiting factor to the total CO_2 flux. In fact, the highest permeability of CO_2 of a LSCF + MC dual-phase membrane measured so far is only in the order of magnitude of 10^{-9} mol m^{-2} s^{-1} Pa^{-1} at 650 °C in one study [13] and 10^{-12} mol m^{-1} s^{-1} Pa^{-1} for other ceramic-carbonates dual-phase materials (note: different unit is used for this study) at the same temperature in other studies by both experiment [14] and modeling [15].

Similarly, a MECC illustrated in Fig. 1 can also be comprised of two phases: one being a carbonate-ion conductor and another being an electronic conductor. Compared to the MOCC, the CO_2 flux of a MECC can be higher, simply because of higher carbonate-ion and electron conductivities (for example, $\sigma_{CO_3^{2-}} = 0.3$ S/cm and $\sigma_e = 6.3 \times 10^5$ S/cm at 650 °C). The first reported MECC was made of a stainless steel and molten carbonate (MC) dual-phase composite (SS–MC) [11]. The reported permeability is almost one order of magnitude higher than that of MOCC (e.g., 2.5×10^{-8} mol m^{-2} s^{-1} Pa^{-1} at 650 °C). However, the chemical interaction between SS and MC is a potential problem affecting long-term stability.

In this work, we report for the first time a new dual-phase MECC membrane comprising of Ag and MC. The selection of Ag against SS is primarily based on the fact that Ag has an excellent chemical compatibility with MC. The high and stable electronic conductivity of Ag along with its operatability in the temperature range of 500–650 °C can also favor a high and stable CO_2 flux. Since the research in this field is scarce at present time, these promising results are anticipated to inspire more studies to this important subject in the very near future.

2. Experimental procedures

2.1. Preparation of Ag–MC MECC

The molten carbonate (MC) phase used in this work is a binary eutectic mixture of Li_2CO_3 and K_2CO_3 (99%, Alfa Aesar) in a molar ratio of 62:38, prepared by solid state reaction at 600 °C for 2 h. The obtained melt was then broken up and ball-milled into sub-micrometer powders. The powders were then intimately mixed with silver powders (1–3 μm, 99.5%, Alfa Aesar) in a predetermined volumetric ratio of 50:50, followed by second-round ball milling. After drying, the obtained powders were pressed uniaxially into pellets of 19 mm in diameter with a static pressure of 150 MPa. The Ag–MC pellets were finally fired in air at 650 °C for 2 h.

2.2. Permeation characterization

The CO_2 permeation characteristics of the Ag–MC were studied with a homemade permeation cell, the configuration of which is schematically shown in Fig. 2. The Ag–MC pellet was first sealed to a supporting alumina tube using a modified sealant containing a mixture of a ceramic cement (Ceramabond 552-VFG, Aremco Products) and a commercial glass powder (Schott glass GM31107). A second short alumina tube was then bonded to the top of the sample for the purpose of guiding the feed gas. The assembly is then subject to the curing condition required by the Ceramabond 552-VFG cement: room temperature 1–4 h and 93 °C for a minimum of 4 h. The feed gas is a pre-mixed CO_2–O_2 gas in a molar ratio of 1:1 flowing at