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Surface modified silver-carbonate mixed conducting membranes for high flux CO₂ separation with enhanced stability

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ABSTRACT

In this paper, we demonstrate that a silver-carbonate CO₂ permeation membrane with the surface of silver matrix modified by a thin coating of Al₂O₃ can effectively improve the flux stability over an extended period. The CO₂ and O₂ flux densities reached 0.39 ml cm⁻² min⁻¹ and 0.20 ml cm⁻² min⁻¹ at 650 °C, respectively, and maintained > 90% of its original values for 130 h. This is in contrast with the untreated membrane in which only one-third of the original values can be retained even after 60 h. Overall, surface modification of silver matrix by a thin layer of Al₂O₃ coating is demonstrated as a viable method to fabricate stable silver-carbonate membranes for electrochemical CO₂ capture from flue gas.

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1. Introduction

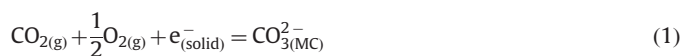
Manmade CO₂ through the use of fossil fuels is a major source of “greenhouse gas” for the global warming and climate change. The stabilization of atmospheric CO₂ concentration is conceived to be the best near-term solution to mitigate the negative environmental impacts of the “greenhouse” effect. The current mainstream technical approach to achieve this goal is to curb the emission of CO₂ by capturing CO₂ at point-sources and geologically storing it. The point-sources for carbon removal currently being developed and demonstrated are targeting three combustion processes: pre-combustion, post-combustion and oxy-combustion [1–10]. The state-of-the-art technologies for CO₂-capture are principally based on reversible chemical/physical sorption processes using liquid solvents and solid sorbents as a CO₂ scrubber [11–13] and on size-exclusion permeation using membranes as a CO₂ filter [14–19]. However, as aforementioned, the solvents and sorbents based technologies are costly, cumbersome and energy intensive [20–24]. The membrane technology is susceptible to poor selectivity and incompatibility to high temperatures [25–28]. As of today, only a few of CO₂ capture technologies such as amine-based solvent absorption are considered commercially viable for large-scale applications.

As an effort to advance the carbon capture technology, we as well as other research groups have recently studied a new type of electrochemical CO₂ separation membranes that are in theory exclusively permeable to CO₂ and compatible with elevated temperatures

[5,29–38]. The new electrochemical membranes are categorized by two types of mixed conductors: (1) mixed oxide-ion and carbonate-ion conductor (MOCC), which is more suited for pre-combustion application where the feedstock gas is a mixture of CO₂ and H₂; (2) mixed electron and carbonate-ion conductor (MECC), which is more adequate for CO₂ separation from an oxidizing stream such as a flue gas (CO₂, O₂, N₂) produced from conventional power plants.

In practice, the MECC membranes are more demanding for stabilizing the atmospheric CO₂ concentration as the majority of CO₂ in the atmosphere is emitted from the existing fossil-fueled power plants. In this type of membrane, the chemical gradients of CO₂ and O₂ exist in the same direction across the membrane, i.e., CO₃²⁻ is charge-balanced by e⁻ inside the membrane. Therefore, both CO₂ and O₂ will permeate through the membrane, the mixture of which has been suggested to either recycle back to the combustion chamber for oxy-combustion [7] or convert into a pure stream of CO₂ and H₂O by combusting the permeated O₂ in syngas [39]. For the latter case, the electrochemical reactions at the two surfaces of the membrane can be expressed by:

At the feed side:



At the permeate side:



The first MECC membrane reported was made of a stainless steel and molten carbonate (MC) dual-phase composite [32]. However, the chemical interaction between stainless steel and molten carbonate is

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a potential problem affecting long-term stability. Silver have been subsequently investigated by our group to replace stainless steel [33]. Silver is known to be chemically compatible with MC and possess a very high and stable electronic conductivity in the temperature range of 500–650 °C [33]. Initial flux measurements on the silver-carbonate membranes showed approximately six times higher CO₂ permeation flux than that of the stainless-steel-carbonate system published [33]. However, maintaining a stable permeation flux over an extended period has been identified as a primary issue [33]. The understanding on the unstable flux is that (1) MC phase does not wet silver phase very well, which leads to a poor retention of MC during high-temperature operation; (2) silver is prone to sinter at elevated temperatures and (3) carbonate salts have a tendency to volatilize [40], all of which can cause a gradual loss of MC during operation, thus a decay of flux. As a means of enhancing the flux stability of silver-MC membranes, improving the wettability between silver and MC seems to be a rational approach. It has been previously demonstrated in molten carbonate fuel cell research that MC can fully wet a solid LiAlO₂ matrix with a zero contact angle [41]. This observation implies that if a thin layer of LiAlO₂ can be engineered on the surface of a porous silver network, the MC with which silver makes contact can then be retained to the maximal degree. Similar methodology to improve the wettability of MC has also been recently reported [42]. In addition, refractory Al₂O₃ may mitigate the thermal coarsening of silver at the same time.

In this study, we report CO₂ permeation flux as a function of time of a surface-modified silver-MC membrane. A thin layer of γ -Al₂O₃ is coated on the surface of a silver porous matrix prior to MC impregnation. The subsequently impregnated MC is expected to react with Al₂O₃ to form a LiAlO₂ layer *in situ*, [43] which ensures a good wettability between the bulk MC phase and the solid silver porous network.

2. Experimental section

2.1. Synthesis of dual-phase silver-carbonate MECC membranes

A two-step approach was employed to synthesize the dual-phase silver-carbonate MECC membranes. The porous silver matrix was

first fabricated by intimately mixing silver powders (99.9%, Alfa Aesar) with microcrystalline methylcellulose (Alfa Aesar) as a pore former in a ratio of 30:70 (vol%). The powder was then ball-milled (Mix/Mill 8000 M, Spex Sample Prep) and uniaxially pressed at 200 MPa into pellets using a static mold press (18 mm in diameter), followed by firing at 650 °C for 2 h. After that, the sample was placed in a vacuum impregnation chamber (CitoVac, Struers). Al₂O₃ colloidal solutions (0.05 μ m, Alfa Aesar) with 5 and 10 wt% concentrations were then infiltrated into the porous silver scaffold for one time under vacuum. After drying at 110 °C for 4 h and firing at 650 °C for 2 h, the coated silver-MC membrane was immersed into a carbonate melt containing a eutectic mixture of Li₂CO₃ (\geq 99%, Alfa Aesar) and K₂CO₃ (\geq 99%, Alfa Aesar) in 62:38 (mol%). The detail about this procedure can be found in our previous work [5,44,45]. The fabricated membrane was finally polished using ethanol alcohol as a media to remove the residual molten carbonate on the surfaces, followed by gas tightness check using a homemade leakage check device before it is assembled into a permeation cell. The effective area of the membrane was 0.92 cm².

2.2. CO₂ flux measurement

The CO₂ permeation characteristics of the synthesized silver-MC MECC membrane were studied using a homemade permeation cell, the configuration of which is schematically shown in Fig. 1. The button membrane cell was first sealed to a supporting alumina tube with a commercial silver paste (Shanghai Research Institute of Synthetic Resins) as a sealant. A second short alumina tube was then bonded to the top of the sample for the purpose of shielding the feed gas. The feed gas was a mixture of 50 ml min⁻¹ O₂, 50 ml min⁻¹ CO₂ and 20 ml min⁻¹ N₂; N₂ was used as a tracer gas for leak correction if any. A high-purity helium (99.999%) at a flow rate of 50 ml min⁻¹ was used as the sweeping gas, the composition of which was analyzed by an on-line micro-GC (Varian 490-GC, Varian). To ensure the accuracy, the GC was calibrated with four standard gas compositions for each gas of interest (CO₂, O₂, and N₂). The final CO₂ flux density was calculated out from an average gas composition of a total of ten successive readings from the GC. For all gas flows, commercial mass flow controllers (SmartTrak, 50 Series) specifically calibrated for the gas under use

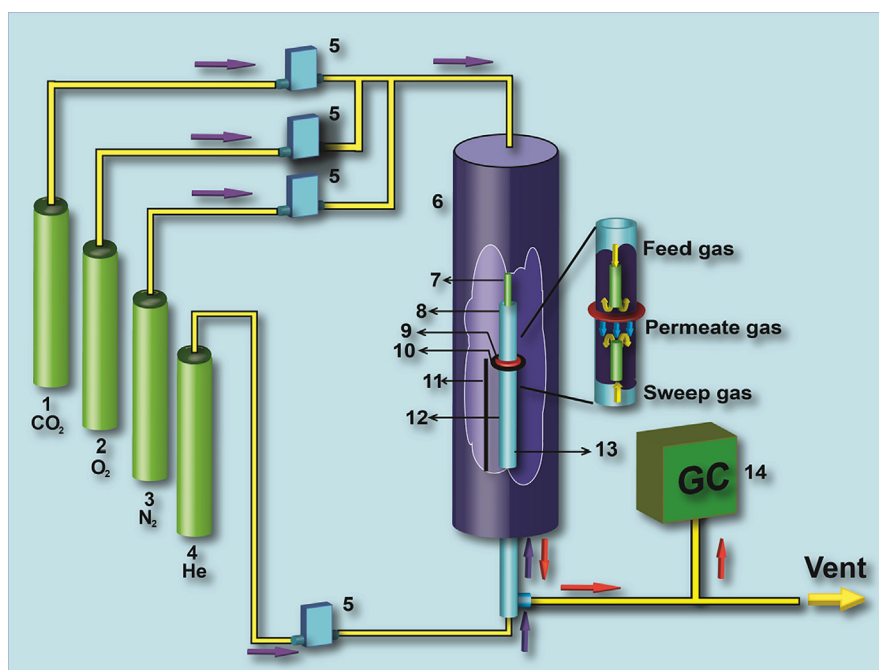


Fig. 1. Schematic of the CO₂ permeation cell configurations. (1) CO₂ cylinder; (2) oxygen cylinder; (3) nitrogen cylinder; (4) helium cylinder; (5) mass flow controllers; (6) furnace; (7) inner feed tube; (8) second short alumina tube; (9) MECC membrane; (10) solvent; (11) thermocouple; (12) supporting alumina tube; (13) inner sweep tube; and (14) gas chromatography (GC).

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