Journal of Membrane Science 455 (2014) 162–167

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Flux of silver-carbonate membranes for post-combustion CO_2 capture: The effects of membrane thickness, gas concentration and time

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ARTICLE INFO

Article history:
Received 13 November 2013
Received in revised form
15 December 2013
Accepted 29 December 2013
Available online 7 January 2014

Keywords:
CO_2 separation
Critical thickness
CO_2 concentration
Surface-modification
Stability

ABSTRACT

In this paper, we systematically studied the effects of membrane thickness, CO_2 concentration, and operating time on the CO_2 flux density of an Al_2O_3-surface-modified and carbon-black-pore-former derived silver-carbonate membrane. It was found that the CO_2 transport through a silver-carbonate membrane exhibited a critical thickness of 0.84 mm, below which no flux enhancement could be achieved. The CO_2 flux was also observed to be proportional to the difference of ($P_{CO_2}P_{O_2}^{1/2}$) at the two reacting surfaces, and not the commonly assumed logarithmic partial pressure difference. The CO_2 flux tested against time at 650 °C increased by 200% for the first 160 h, followed by a gradual decrease. At the 326-h marker, the flux was still the same as the original value when the test was started. Overall, the use of carbon black as a pore-former and Al_2O_3 as a surface modifier for silver-carbonate membranes has been proven effective and necessary to achieve a higher and more stable CO_2 flux density.

1. Introduction

Capture of post-combusted CO_2 from predominant fossil-fueled power plants is of technological importance to the stabilization of atmospheric CO_2 concentration and mitigation of global warming and climate change. The conventional solvent and sorbent based CO_2 capture technologies are costly, cumbersome and energy intensive [1–4]. With the existing material systems and engineering designs, it seems difficult to overcome the grand challenges in cost and energy penalty for years to come. Development of new, cost-effective and energy-efficient CO_2 capture technologies is, therefore, imperative.

Recently, we demonstrated high-flux silver-carbonate mixed electron and carbonate-ion conducting (MECC) membranes suitable for post-combustion CO_2 capture. This new class of electrochemical membranes in theory can exclusively and continuously separate CO_2 from a CO_2 source such as flue gas at high temperatures [5–7]. The working principle of the membrane is based on a concomitant migration of CO_3^{2-} and e^- under a chemical gradient of CO_2 and O_2 across the membrane, thus transporting CO_2 and O_2 from higher concentration to capture side. The captured CO_2–O_2 has been suggested to convert into a mixture of easily separable CO_2 and H_2O mixture by combusting in a syngas. The large amount of heat can be recovered to produce steam for electricity [8]. It has also been suggested to recycle back to the combustion chamber for oxy-combustion. Therefore, MECC membrane has great potential to play an important role in stabilizing the atmospheric CO_2 concentration by capturing CO_2 emitted from the existing fossil-fueled power plants. Since the capture process is continuous and operated at elevated temperatures, the new membranes have great potential to be a cost-effective and energy-efficient CO_2 capture technology. We also showed that the long-term stability of the membrane can be significantly improved by modifying the surface of porous silver networks with a thin layer of Al_2O_3 [9].

In previous study, the microcrystalline methylcellulose has been used as a pore-former to fabricate the porous silver matrix. Based on the knowledge we have learned from mixed oxide-ion and carbonate-ion conductor (MOCC), smaller pore size and uniform porous structure are among keys to achieving high CO_2 flux density [10–13]. In this study, we further expand the previous study by investigating the effects of membrane thickness, CO_2 concentration and time on the flux of CO_2 permeation. While the same Al_2O_3 surface modification on silver network was kept for the present work, a new pore-former carbon black, which is one of the widely used pore-former [14,15], was tested with a goal to create a better connected porous silver network.

2. Experimental procedure

2.1. Synthesis of silver-carbonate membranes

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

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http://dx.doi.org/10.1016/j.memsci.2013.12.077

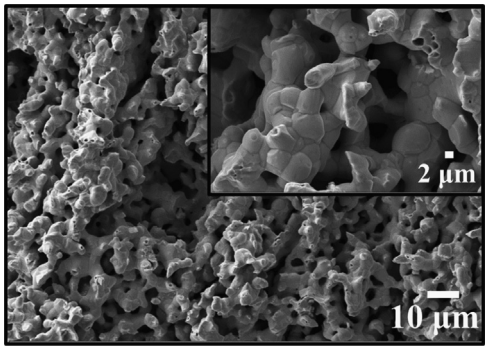

Fig. 1. The cross-sectional view of microstructure of a porous Ag matrix created by carbon black as a pore former.

matrix was first fabricated by intimately mixing silver powders (99.9%, Alfa Asear) with carbon black as a pore-former (Alfa Asear) in a ratio of 60:40 (vol%). The powder was ball-milled (Mix/Mill 8000M, Spex Sample Prep) and uniaxially pressed at 200 MPa into pellets using a static mold presser (18 mm in diameter), followed by firing at 650 °C for 2 h. After that, the sample was loaded into the vacuum impregnation unit (CitoVac, Struers). An Al_2O_3 colloidal solution (0.05 μm, Alfa Asear) with 5 wt% concentrations was then infiltrated into the porous silver scaffold for one time under a vacuum condition. After drying and firing at 400 °C for 2 h, the coated silver membrane was immerged into a carbonate melt containing a eutectic mixture of Li_2CO_3 (≥99%, Alfa Asear) and K_2CO_3 (≥99%, Alfa Asear) in 62:38 (mol%). The detail about this procedure can be found in our previous work [10,16–18].

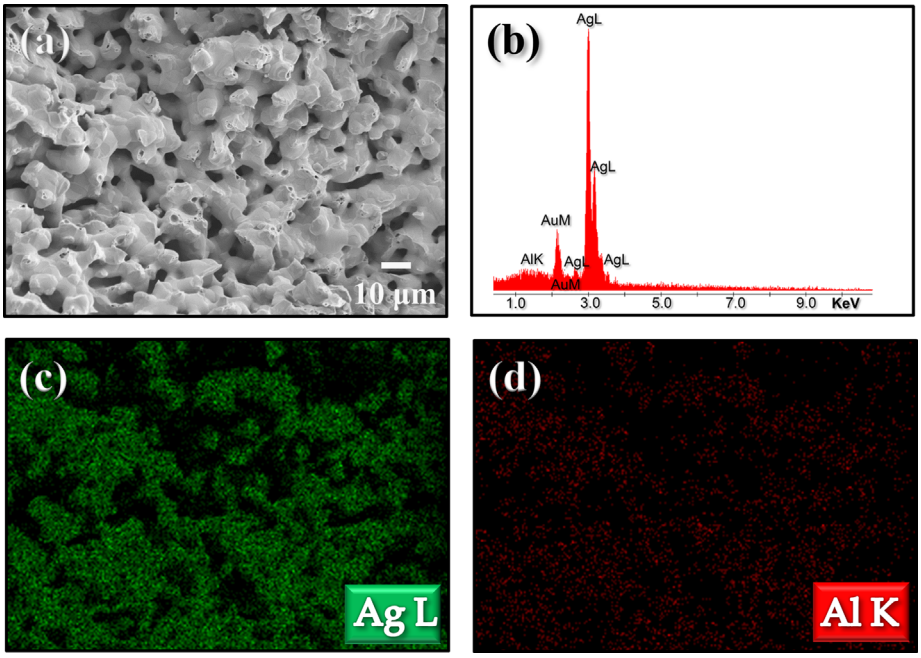

Fig. 2. (a) Microstructure and (b) EDS compositions of a porous Ag matrix coated with 5% Al_2O_3 colloidal; elemental distributions of Ag matrix with 5% Al_2O_3 colloidal (c) Ag mapping and (d) Al mapping.

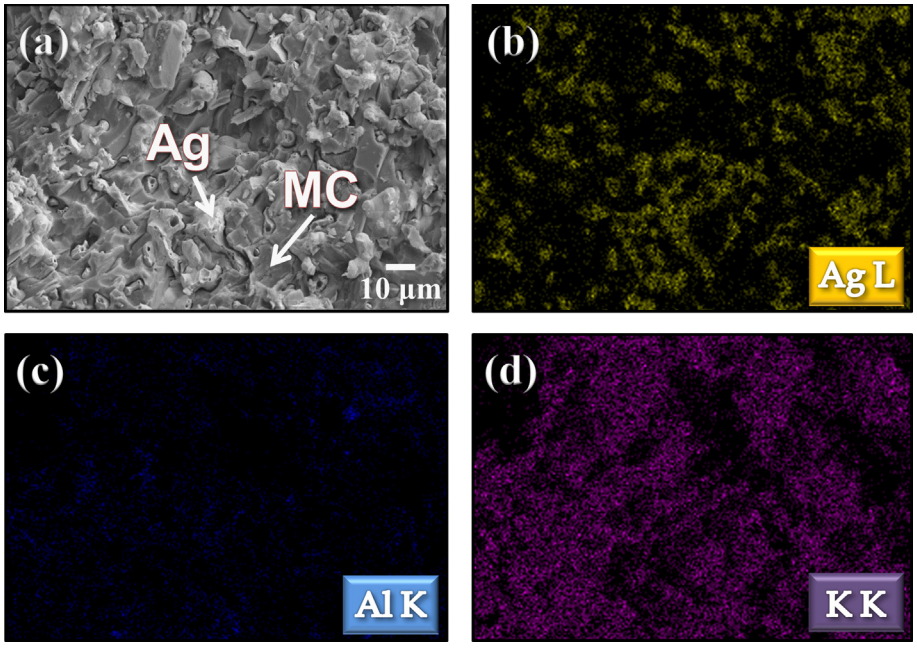

Fig. 3. Microstructure and elemental distributions of silver-carbonate MECC membrane decorated with Al_2O_3 coating (5% colloidal) before testing (a) SEM image; (b) Ag mapping; (c) Al mapping; and (d) K mapping. *Note*: Li is not detectable by EDS.