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A superior mixed electron and carbonate-ion conducting metal-carbonate composite membrane for advanced flue-gas carbon capture



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ABSTRACT

Developing cost-effective, energy-efficient and CO₂-selective advanced carbon capture technologies for carbon intensive flue gas is of vital importance to the reduction of carbon pollution and mitigation of global climate change. In the present work, we report that an electrochemistry-based mixed electron and carbonate-ion conducting metal-carbonate composite membrane with porous metal matrix fabricated by a chemical dealloying method exhibits superior CO₂/O₂ flux density and stability over a 900-h testing period. The results also demonstrate that the presence of H₂ in the sweeping gas can significantly enhance the CO₂ flux density as a result of increased gradient of chemical potential of oxygen and produce a pure stream of CO₂ and H₂O for easy downstream conversion. The fundamental mechanisms leading to the superior performance are also discussed.

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1. Introduction

Carbon capture and storage (CCS) has been established as a key technology to curb CO₂ emission from fossil-fueled power plants, thus to mitigate global climate change that has been increasingly observed to impact our daily life and damage our economy in recent human history. The core of the CCS technology is to capture CO₂ at emission sources and geologically bury it for permanent storage or enhanced oil recovery (OER) [1,2]. As the first step of CCS, carbon capture has been developed for three power-generation related combustion processes that are responsible for ~78% of the global stationary carbon emissions: pre-combustion, post-combustion and oxy-combustion [3–10]. A major challenge to the full implementation of the current carbon capture technologies such as imine-based “chemical washing” process is, however, the high energy penalty, which significantly reduces plant efficiency and increases the cost of electricity. Developing cost-effective, energy-efficient and CO₂-selective carbon-capture processes/methods is, therefore, highly desirable.

Electrochemical methods have been increasingly investigated as a new approach to capture CO₂ from combustion products such as flue gas in recent years. One approach is to use molten carbonate fuel cells (MCFCs) operated under a reverse mode that relies upon electricity as the driving force to concentrate CO₂ from a carbon source [11,12]. While such a high-temperature electrolysis

process (or “electrical pump”) can achieve high efficiency and selectivity, the requirement for electricity and external electronics complicates the system design and thus raises the overall system cost.

With a similar electrochemical principle, our group as well as others recently proposed two new types of carbon capture membranes made of ceramic-carbonate and metal-carbonate dual-phase composites [13–31]. The driving force for these new membranes is the gradient of electrochemical potential(s) of CO₂ (and O₂) existing on the opposite surfaces of the membranes. No electricity, thus no external electronics, is needed to drive CO₂ through the membrane, making it a promising low-cost carbon capture option. Ceramic-carbonate membranes consist of an oxide-ion conductor (ceramic) and carbonate-ion (molten carbonate denoted as MC hereinafter) conductor and follow upon the reversible electrochemical reaction $\text{CO}_2 + \text{O}^{2-} = \text{CO}_3^{2-}$ at the opposite surfaces to separate CO₂ from a carbon source. Similarly, metal-carbonate membranes comprise of an electron (metal) and carbonate-ion (MC) conductor and follow upon the reversible electrochemical reaction $\text{CO}_2 + 1/2\text{O}_2 + 2\text{e}^- = \text{CO}_3^{2-}$ to separate CO₂. Previous studies have demonstrated that these two types of membranes are effective separators of CO₂ for flue gas, natural gas and fuel gas with high flux and excellent selectivity [13–31].

Of these two electrochemical membranes, metal-carbonate based mixed electron and carbonate-ion conductor (MECC) membranes are of particular interest due to their ability to capture CO₂ from flue gas (a mixture of CO₂, O₂, H₂O, N₂) emitted from coal-fired power plants, a major stationary CO₂ emission source

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[18–21,29]. The reversible electrochemical reaction $\text{CO}_2 + 1/2\text{O}_2 + 2\text{e}^- = \text{CO}_3^{2-}$ takes place at the two opposite surfaces of the membrane with the forward reaction (left→right) occurring at the feed gas surface and backward reaction (right→left) occurring at the permeate surface. However, one of the major obstacles hindering MECC membranes from being demonstrated at a larger scale is their long-term instability. Our previous studies have shown that the root-cause for the instability of a silver-carbonate membrane is closely related to the large pore size within the silver matrix synthesized by a traditional pore-former method [18–21]; the large pores cannot generate a sufficient capillary force to immobilize molten carbonate during high-temperature operation, resulting in a gradual loss of carbonate and thus degradation of flux. In addition, large pores of low-surface-area yield a low density of triple phase boundaries (TPBs), a critical factor determining the rate of permeation, thus leading to a lower CO_2/O_2 flux density.

In the present study, we report that flux density and stability of a silver-carbonate MECC membrane can be substantially enhanced by fabricating the microstructure of porous silver matrix with a chemical dealloying approach, a well-known method to produce nanoporous metal structures for various applications [32]. This is the first study that utilizes chemical dealloying derived porous metal substrates for carbon capture. The resultant submicron pores in the silver matrix are expected to offer high density of TPBs and increase the capillary force to reinforce the immobilization of molten carbonate that resides inside pores, thus improving both the magnitude and stability of the permeation flux. In addition, we also report for the first time the effect of H_2 in the sweeping gas on the CO_2/O_2 flux density, laying ground for future use of reducing gas to capture CO_2 and O_2 , producing a stream of CO_2 and H_2O for easy downstream conversion.

2. Experimental procedures

2.1. Preparation of Ag-carbonate membranes

The metal of choice for MECC membrane is Ag, which is chemically inert to MC [18]. The first step to prepare an Ag-carbonate composite membrane is to fabricate a porous Ag matrix into which the MC phase can be impregnated. Chemical dealloying technique was employed with a goal of making nanoporous silver matrix to enhance the retention of MC. The alloy of choice for chemical dealloying is 50at% Ag and 50at% Al (from ACI Alloys, denoted as Ag50Al50 hereinafter) with Al as the fugitive element. The dealloying procedure is described as follows. Ag–Al alloy pellets in a diameter of $\phi 17$ mm are first soaked in a hot 3 M HCl aqueous solution at 90 °C for a predefined period of time (48 h and 72 h). The samples synthesized are denoted as 48 h-Ag50Al50 and 72 h-Ag50Al50, respectively. Then the de-aluminized samples are thoroughly washed in an ultrasonic cleaner with DI water. The samples are finally dried in oven and annealed at 650 °C for 2 h. The total weight losses for the 48 h- and 73-h dealloyed samples are ~12% and 15%, equivalent to a pore volume of 29.6% and 37%, respectively.

The second step to prepare an Ag-carbonate composite membrane is to infiltrate molten carbonate into the porous Ag matrix. The impregnation procedure is described as follows. The porous Ag pellets are first suspended by a silver wire over a carbonate bath containing a eutectic composition of alkaline carbonate mixture: 52 mol% Li_2CO_3 and 48 mol% Na_2CO_3 . After reaching 650 °C and melting of the carbonate, the porous matrix is slowly immersed into the carbonate melt and soaked for 2 h. The MC-saturated Ag pellet is finally pulled out of the melt at 600 °C during the cooling process. The final product of membrane is surface polished with sandpaper using ethanol as a medium to

remove any residual molten carbonate.

2.2. Permeation measurement

The flux densities of CO_2 and O_2 were measured with a homemade permeation cell. Details of the experimental setup can be found in our early studies [18,20]. A brief description is as follows. The MECC membrane was first sealed to a supporting alumina tube by silver paste sealant (synthetic resins, Shanghai Research Institute), followed by bonding a second short alumina tube on the top; this short alumina tube was used to confine the feed gas to the surface of Ag-MC membrane. Ag paste is applied in a layer-by-layer manner. After each application, the assembly is dried at 130 °C for an hour. A complete seal usually requires 4–5 applications. For all the measurements, a simulated flue gas containing 15% CO_2 , 10% O_2 and 75% N_2 was used as the feed gas, while Ar with different H_2 concentrations (0, 4.35% and 9.41%) was used as the sweep gas. The temperature range studied was 550–700 °C. The long-term stability testing was conducted at 600 °C with 9.41% H_2 -Ar as the sweep gas and the aforementioned simulated flue gas as the feed gas.

A commercial mass flow controller (Smart-Trak, 50 series) was employed to control the gas flow. A Micro-GC (model 490, Agilent Technologies) was used to analyze the compositions of the sweep gas at room temperature and ambient pressure ($T=25$ °C, $P=1$ atm). Prior to use, it was pre-calibrated with five standard gases of interest (CO_2 , O_2 , N_2 , H_2 and CO). The N_2 concentration in the sweep gas was used to correct for the leakage from sealing or membrane itself. The flow rate of the sweep gas, regardless of the H_2 concentration, was set to 50 ml/min, and that of the feed gas was set to 100 ml/min. The final CO_2 and O_2 flux densities were calculated from a leakage-corrected gas composition collected and averaged from ten successive readings by Micro-GC and the known sweep-gas flow rate. A 20-min stabilization period was given before a measurement was taken at each temperature.

2.3. Other characterization

The phase compositions of the original and de-aluminized samples were examined by an X-ray diffractometer (Rigaku, Japan) equipped with a graphite-monochromatized $\text{CuK}\alpha$ radiation ($\lambda=1.5418$ Å). The 2θ scans were performed at a rate of 10°min^{-1} in a range of 20–80°.

The microstructural features of the porous Ag matrix as well as Ag-MC membrane before and after long-term test were captured by a field emission scanning electron microscopy (FESEM, Zeiss Ultra) equipped with energy dispersive X-ray spectroscopy (EDS) analyzer. The BET surface areas of the dealloyed porous Ag matrix were measured by Krypton adsorption using Autosorb-iQ from Quantachrome Instruments.

3. Results and discussion

3.1. Phases in the original alloy and de-aluminized silver matrix

According to the Ag–Al phase diagram [33,34], the starting 50 at%Ag–50 at%Al alloy (denoted as Ag50Al50 hereinafter) contains a minor α -Al and primary γ - Ag_2Al phase. Fig. 1 shows x-ray diffraction (XRD) patterns of the original alloy confirming the presence of primary γ - Ag_2Al and minor α -Al phase. After de-aluminizing, the primary phase in the sample is silver with a very small amount of γ - Ag_2Al phase. The small residual γ - Ag_2Al phase is not a concern because Al element when oxidized into Al_2O_3 is an excellent wetting agent for molten carbonates [23,31].

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