CO₂ Capture Performance of Silver-Carbonate Membrane with Electrochemically Dealloyed Porous Silver Matrix

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Abstract

Developing advanced cost-effective, energy-efficient and CO₂-selective carbon capture technologies to curb carbon emissions and mitigate global warming effect is of paramount importance to a sustainable future. In the present study, we report on the permeation performance of a silver-carbonate dual-phase CO₂ separation membrane with the porous silver matrix prepared by electrochemical dealloying method. The membrane exhibits excellent CO₂/O₂ flux densities of 0.6/0.37, 0.74/0.47, 0.89/0.59 and 1.02/0.75 ml/min·cm² at 600, 625, 650 and 675 °C respectively, and stability over 500 h with a very low leakage rate. A new transport mechanism involving the change of dominant reactive sites from triple phase boundaries to two-phase boundaries is also proposed to understand behaviors of the membrane exhibited during the CO₂/O₂ permeation process.

Keywords: carbon capture, membrane, metal, carbonate, electrochemical

I. Introduction

Stabilization of the atmospheric CO₂ concentration at its current level is a key to battle global warming and climate change that has been observed to disrupt our daily life and economy more frequently than ever before. The central task to stabilize the atmospheric CO₂ concentration is to capture CO₂ at the point sources and store it underground permanently for oil recovery (OER) [1, 2] or convert it into value-added chemicals [3-6]. Of all the CO₂ emission point sources, coal-fired power plants represent a major and stationary emission site of CO₂ easy to capture in comparison to the mobile vehicular counterpart. Therefore, flue gas emitted from coal-fired power plants has become a major target for today's carbon capture.

There are three industrial-scale combustion processes conceived for carbon capture: post-combustion, pre-combustion and oxy-combustion [7-9]. Carbon capture from post-combustion process makes the most sense because it is a primary industrial CO₂ emitter [10-12]. The flue gas emitted from a post-combustion process at a coal-fired power plant contains low-concentration of CO₂ (~13% CO₂), making the capture expensive and cumbersome. For example, the state-of-art imine-based “chemical washing” process for carbon capture from coal-fired power plants imposes a severe energy and cost penalty, making its full implementation into the existing coal-fired power plants less attractive [13-17]. Therefore, developing advanced cost-effective, energy-efficient and highly-selective CO₂ capture technologies is highly desirable.

Recently, electrochemistry-based methods have garnered much attention for carbon capture and conversion due to their intrinsically high efficiency and selectivity [18-39]. One

interesting class of electrochemical cells demonstrated for efficient and selective CO₂ capture is electrochemical-potential driven permeation cells composing of dual-phase mixed conducting membranes: mixed oxide-ion and carbonate-ion conductor (MOCC) and mixed electron and carbonate-ion conductor (MECC). Compared to the conventional CO₂ concentrator based on molten carbonate fuel cells (MCFCs), the driving force for the CO₂ transport is the electrochemical potential gradient of active species existing across the membrane, not the electrical potential as in MCFC CO₂ concentrators, thus eliminating the external circuit and saving cost.

The working principles of MOCC and MECC membranes differ slightly. The former operates on CO₃²⁻ in the carbonate phase as the sole CO₂ transporting charge carrier compensated by O²⁻ in the oxide-ion conducting phase. The enabling surface reaction is CO₂+O²⁻=CO₃²⁻. The latter also operates on CO₃²⁻ in the carbonate phase as the sole CO₂ transporting charge carrier, but charge compensated by electrons in the metal phase. The enabling surface reaction is CO₂+1/2O₂+2e⁻=CO₃²⁻. Previous studies have demonstrated the ability of these two types of membranes to separate CO₂ from flue gas, natural gas and fuel gas with high selectivity and flux densities [18-39].

For CO₂ capture from the flue gas of a post-combustion process, such as coal-fired power plants, MECC membranes are more advantageous than MOCC counterparts because of their higher flux density and favorable oxidizing flue gas composition [23-26, 34, 37-39]. One of the major challenges hindering MECC membranes from large-scale demonstration is, however, the poor long-term stability resulting from the loss of molten carbonate (MC)

during operation. The root cause for the loss of molten carbonate is the gradual sintering of porous Ag matrix at the operating temperature. Two ways have been so far demonstrated to mitigate the sintering of porous Ag matrix: coating the surfaces of porous Ag matrix with refractory Al_2O_3 or ZrO_2 [25, 26, 38, 39], and lowering the operating temperature of Ag-MC MECC membranes. The latter requires a high-flux Ag-MC membrane, which was previously demonstrated by the use of a nanoporous Ag matrix derived from chemically dealloying of Ag-Al as a result of the enhanced triple-phase boundary (3PB) density at the gas/membrane surfaces [37].

In the present study, we report on the performance of a similar silver-carbonate MECC membrane with a fine-structured, high 3PB-density, porous silver matrix prepared by electrochemical dealloying (or electro-dealloying) method, a known method to fabricate nanoporous metals [40-47]. The rationales behind this approach are: 1) the precursor alloy Ag-Zn forms a fine grain and single ζ -AgZn phase, the removal of the Zn phase can, therefore, lead to the formation of a composition-uniform microstructure. In the previous chemical dealloying of Ag-Al [37], the parent alloy consists of two phases and larger grains, the presence of which resulted in an heterogeneous porous Ag unfavorable to the stability and flux of the membrane; 2) the rate of electro-dealloying process can be better controlled by the current applied to an electrolysis cell at ambient temperature, thus increasing the reproducibility of making the porous silver matrix; 3) environment-friendly neutral solutions can be used as the electrolyte in electrochemical dealloying process. Hot-acid leaching method used for the chemical dealloying of Ag-Al alloy lacks a good control of Al-removal rate and promotes surface migration of silver atoms, causing a much faster coarsening of

porous silver matrix. In addition, long-term exposure to hot acid usually leads to a weakened mechanical strength of porous Ag matrix and thus could result in pellet breakup in the following carbonate infiltration process.

II. Experimental Procedures

2.1 Preparation of Ag-carbonate dual phase membranes

Silver is the metal phase of choice for MECC membranes since it is chemically unreactive to MC [23]. The first step of making a MECC membrane is to fabricate the porous Ag matrix. In this study, we show the use of electro-dealloying technique to make a uniform and nanoporous silver matrix. The silver alloy employed in the experiment was made of a 50 at% Ag and 50 at% Zn (from ACI alloys, donated as Ag50Zn50 hereinafter) with Zn as the fugitive element. The dealloying procedure is described as follows. A corrosion cell was employed consisting of a 1 L flask containing a 1 M NaCl electrolyte solution, two identical graphite counter electrodes and an Ag50Zn50 pellet with a diameter of 17 mm as the working electrode. A schematic illustration of the setup is shown in Fig. 1(a). One side of the working electrode pellet was covered with epoxy so that the dealloying process can only proceed in one direction to avoid delamination at the center of the sample.

The dealloying of zinc was carried out under the galvanodynamic mode using a Solartron 1287 potentiostat. The dealloying process was completed in two steps as schematically shown in Fig. 1(b). In the first step, a constant current of 10 mA was applied to the cell for a period of 50 h. In the subsequent second step, a linear current ramping down profile at a rate of 0.414 mA/h starting from 10 mA and ending at 0 mA was applied. The average current in

the second step was, therefore, 5 mA. The current scan rate (Δi) employed in the second step is calculated by

$$\Delta i = 10 \text{ mA} - 0 \text{ mA} / t_2 \quad (1)$$

The time, t_2 , needed for the second stage dealloying is determined by

$$t_2 = n \times F \times w_{2,Zn} / i_{2,average} \times M_{Zn} \quad (2)$$

The remaining Zn, $w_{2,Zn}$, in the alloy after the first stage dealloying process is determined by

$$w_{2,Zn} = w_{Ag50Zn50} \times M_{Zn} / M_{Ag} + M_{Zn} - i_1 \times t_1 \times M_{Zn} / nF \quad (3)$$

where M_{Zn} =65.38 g/mol; M_{Ag} =107.86 g/mol; n =2 is the charges transferred during the electro-dealloying process; F is the Faraday constant; $w_{Ag50Zn50}$ =2.0065g is the sample weight; i_1 =10mA is the current applied in the first stage; t_1 =50h is the deplating time used for the first stage; $i_{2,average}$ =5 mA is the average current applied in the second stage of dealloying. After dealloying, the sample was thoroughly washed in acetone for 5 minutes to remove the epoxy, followed by a 10 minutes washing in a DI water. The sample was finally dried in oven and annealed at 400 °C for 2 h before use. By annealing the as-dealloyed sample at 400 °C, the mechanical strength of the porous Ag can be enhanced. The MECC membrane developed by this procedure is donated as EC-10mA-400 hereinafter.

It is worth mentioning that thus created pores in Ag phase are expected to be fully connected because of the Zn-content in the original Ag-Zn alloy is above the percolation threshold. As the Zn-grains are gradually dissolved during the dealloying process, the resultant pores are expected to replicate the Zn-grains and be fully connected. The pore volume should be very close to the volumetric fraction of the Zn phase in the parent alloy after all the Zn is removed, which is $\sim 47\%$ after Zn phase has been completely removed.

Figure 1. (a) Schematic illustration of corrosion cell; (b) a typical electrochemical dealloying current profile employed.

The second step of making the final MECC membrane is to fill the porous Ag matrix with molten carbonate by infiltration at high temperature. The infiltration procedure is described as follows. The porous Ag pellets were first attached to a silver wire and then embedded in the solid carbonates contained in a crucible. The solid carbonates contain a eutectic composition of an alkaline carbonate mixture: 52 mol% Li_2CO_3 and 48 mol% Na_2CO_3 . The sample assembly was then placed in a furnace at 650°C . Driven by the capillary forces, the

molten carbonate (MC) would eventually fill into the porous Ag pellet. After a 2h soak, the pellet filled with MC was then pulled out of the MC and hung over the crucible, followed by a 3 °C/min cooling to room temperature. Thus made MECC membrane was finally polished with sandpaper in the presence of ethanol to remove the residual carbonates from surfaces.

2.2 Permeation measurement

A homemade permeation cell was employed to measure CO₂ and O₂ flux densities. Detailed information about this setup can be found in our early publications [19, 23, 25]. Below is a brief description. The MECC membrane was first sealed to a supporting alumina tube by silver paste (Synthetic Resins, Shanghai Research Institute), after which a second short alumina tube was placed on top of the membrane to confine the feed gas to MECC surface. After each round of silver paste sealant application, the membrane/alumina tube assembly was dried in furnace at 130 °C for half an hour. It usually took 4-5× silver paste applications to achieve a complete seal.

For all the measurements in this study, a simulated flue gas containing 15% CO₂, 10% O₂ and 75% N₂ was used as the feed gas, and Ar-9.44% H₂ was used as the sweep gas to enhance the flux density by promoting concentration gradient across the membrane via H₂-O₂ and CO₂-H₂ reactions. A commercial gas flow controller (Smart-Trak,50 series) was employed to control the mass flow rate of both feed and sweep gases, while an on-line 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). Pre-calibrations with five standard gases of interest (CO₂, O₂, N₂, H₂, CO) were conducted before measurement. The N₂

concentration in sweep gas was used as a tracer to correct for the leakage from sealing or membrane itself. The total flow rate of feed gas was set to 100 ml/min, while it was set to 50 ml/min for the sweep gas. The final CO₂ and O₂ flux densities were calculated from a leakage-corrected gas composition averaged from ten successive readings by Micro-GC multiplied by the sweep-gas flow rate. A 30-min stabilization time was given before each reading taken at each temperature.

2.3 Other characterization

The phase compositions of the precursor alloy as well as the dealloyed sample were examined by an X-ray diffractometer (Rigaku, Japan) with a graphite-monochromatized CuK α radiation ($\lambda=1.5418$ Å). The 2θ scans were performed at a rate of $10^\circ \text{ min}^{-1}$ in a range of $20\text{-}80^\circ$. The microstructures of porous Ag matrix as well as dense Ag-MC membrane before and after long-term test were also captured by a field scanning electron microscopy (FESEM, Zeiss Unltra) equipped with energy dispersive X-ray spectroscopy(EDS) analyzer.

III. Results and Discussion

3.1 Phases before and after dealloying

Figure 2 shows the phase compositions of the starting Ag₅₀Zn₅₀ alloy and the resultant EC-10mA-400 sample. Two phases were found in the original Ag₅₀Zn₅₀ alloy: hexagonal ζ -AgZn (PCPDF#29-1156) and β -AgZn (PCPDF#29-1155). According to the Zn-Ag phase diagram [48], however, only ζ -AgZn is expected to exist for this composition. The actual

fabrication method of Ag₅₀Zn₅₀ such as fast quenching may have resulted in formation of the metastable β -AgZn phase. Nevertheless, the XRD pattern of the dealloyed sample shows only fcc-Ag phase, indicating that Zn in either ζ -AgZn or β -AgZn has been removed, resulting in a pure fcc-Ag phase. The attainment of a pure fcc-Ag phase demonstrates the suitability of using Zn as the sacrificial element in making porous Ag.

Figure 2. XRD patterns of the starting Ag₅₀Zn₅₀ alloy and resultant EC-10mA-400.

3.2 Microstructures of porous Ag matrix

The microstructures of the original Ag₅₀Al₅₀ used in chemical dealloying and Ag₅₀Zn₅₀ used in electrochemical dealloying are shown in Fig. 3 (a) and (e), respectively. Unlike Ag₅₀Al₅₀ [37], neither grain boundaries nor phase boundaries in Ag₅₀Zn₅₀ can be observed under this magnification (both pictures were taken at the same magnification), suggesting a

much smaller but more uniform grain size in the parent alloy. Fig. 3(b) and (f) compare the microstructures (under same magnification) of porous Ag matrix made by chemical-dealloying and electrochemical-dealloying, respectively. Evidently, porous Ag derived from electrochemical methods shows a more porous microstructure with smaller pore-size than the chemical dealloying derived counterpart. In addition, unlike chemical-dealloying derived porous Ag that has two types of pore structures as shown in Fig. 3(c) and (d), electrochemical-dealloying derived porous Ag of Fig. 3(g) shows a single homogenous porous structure with the pore size ranging from 0.2 μm to 1 μm in the as-dealloyed state. The post-annealing at 400 $^{\circ}\text{C}$ increased pore size to 1~5 μm as shown in Fig. 3(h). It is worth mentioning that both chemical and electrochemical dealloying derived samples show much finer microstructures compared to the traditional pore-former derived porous Ag matrix with a pore size larger than 10 μm [24].

Figure 3. SEM images of (a) the original Ag50Al50 (b) porous Ag derived from Ag50Al50 with chemical dealloying (sample 48h-Ag50Al50); (c) porous Ag created from α -Al phase; (d) porous Ag created from Ag_2Al phase [37]; (e) the original Ag50Zn50; (f) porous Ag derived from Ag50Zn50 with electrochemical dealloying (sample EC-10mA-400); (g) image

(f) at higher magnification and (h) image (g) after 400 °C annealing.

There are two reasons conceived for the microstructural improvement. First, different microstructure of the original parent alloy leads to a different porous structure after dealloying. The Ag50Al50 used in chemical dealloying is composed of very large grains and long grain boundaries. Dealloying starts from the silver-depleted grain boundary areas [37, 49], resulting in the formation of large and long 3D channels. In contrast, the Ag50Zn50 used in the electro-dealloying shows no sign of large grain boundaries under SEM. In addition, the two phases contained in the original Ag50Al50 exhibits very different dealloying activity: α -Al phase dissolves faster than Ag₂Al phase, leading to the coarsening of α -Al derived pores/ligaments during the chemo-dealloying. Although Ag50Zn50 also contains two phases, they have a similar electrochemical activity and thus is dealloyed at a similar rate [50]. The second reason is associated with electrochemical method in which the zinc dealloying rate and Ag coarsening rate can be well controlled by the current applied in the electrochemical dealloying process, which ultimately results in a more uniform microstructure with a tight pore size distribution.

3.3 Flux density vs temperature

The permeation flux densities of CO₂ and O₂ measured from EC-10mA-400 sample are shown in Fig. 4 as a function of reciprocal temperature. A simulated flue gas containing 15% CO₂, 10% O₂, 75% N₂ was used as the feed gas, while 9.44%H₂-Ar was used as the sweep gas. Both CO₂ and O₂ follows closely the Arrhenius relationship, indicating the transport of

CO₂ and O₂ are thermally activated. The close activation energies for CO₂ ($E_a=48.57$ kJ/mol) and O₂ ($E_a=53.35$ kJ/mol) indicates a likely coupled transport process for those two gas species through MECC membrane. It is interesting to note that, unlike membrane made from pore-former method that has a tight 2:1 CO₂/O₂ flux ratio [23-26], the CO₂/O₂ flux ratio of this sample varied between 1.65 and 1.38 as temperature was increased from 550 to 675 °C. This new flux ratio lies between CO₂/O₂=2:1 and 1:1.5, where the 2:1 ratio infers CO₃²⁻ as the active surface species and 1:1.5 infers CO₄²⁻ as the active surface species [51]. Thus, two surface reactions including the primary reaction of CO₂+1/2O₂+2e⁻=CO₃²⁻ and a parallel secondary reaction of 1/2O₂+CO₃²⁻=CO₄²⁻ are proposed to occur simultaneously during the CO₂ separation process. Compared with the activation energy of CO₃²⁻ conduction in pure molten carbonates, *i.e.* 32 kJ/mol [52], the observed higher activation energy in this study may also support the secondary pathway mechanism involving bulkier CO₄²⁻ species.

Figure 4. Comparison of Arrhenius plots of CO₂/O₂ flux density of sample EC-10mA-400

and chemical dealloyed sample 48h-Ag50Al50 [37]. A simulated flue gas with composition of 10% O₂, 15% CO₂ and 75% N₂ was used as the feed gas, while 9.44% H₂-Ar was used as sweep gas.

The CO₂/O₂ flux densities for the chemical-dealloyed sample are also plotted in Fig. 4 for comparison. For the electrochemical-dealloyed sample, the CO₂/O₂ flux densities reached 0.6/0.37, 0.74/0.47, 0.89/0.59 and 1.02/0.75 ml/min·cm² at 600, 625, 650 and 675 °C respectively. Compared with the previous pore-former derived MECC membrane measured with pure He as the sweep gas [24-26], these flux densities represent 2~3× improvement, which could be attributed to a combined microstructural and H₂-containing sweeping gas effect aforementioned [37].

Compared to the chemo-dealloyed sample in Fig. 4 obtained at the very beginning of testing when the T-dependence study was conducted, the electro-dealloyed sample shows a slightly lower CO₂ flux density. At this point, the tortuosity (τ) of electro-dealloyed sample was higher because of the smaller pore size, leading to a lowered flux density according to the relationship that J is proportional to ϵ/τ (ϵ is the porosity). As the time-on-test increases, the silver matrix begins to coarsen, resulting in a simultaneous reduction in tortuosity and porosity. The degree of reduction in tortuosity by the coarsening mechanism is expected to be greater than porosity for a fine-grain and fine-pore microstructure as suggested in ref.[53], leading to a net increase of ϵ/τ , thus flux density. The latter is indeed observed in the time-dependence plot of Fig.5 for the first 100 hours.

3.4 Long-term stability test

The time-dependent flux density was investigated at 600 °C; the results are shown in Fig.5. The feed gas and sweep gas remained the same as in Fig. 4. The overall behavior of the time-dependent CO₂ and O₂ flux density can be generally characterized by a gradual initial increase for the first 100 h, a fast decrease between 118~147 h, and a slight increase for the next 400 h. Furthermore, the CO₂/O₂ flux ratio also varied drastically from the initial 1.6 to the eventual 1.15, inferring a change in CO₂/O₂ transport mechanisms.

Figure 5. CO₂, O₂ and N₂ flux densities as a function of time at 600 °C under a simulated flue gas containing 15% CO₂, 10% O₂, 75% N₂ as feed gas and 9.44% H₂-Ar as sweep gas.

On the other hand, the leakage N₂ flux is very low during the 500 h-testing in comparison to CO₂ and O₂ fluxes. For example, N₂ leakage rate of the electrochemical-dealloyed sample

was very low ($J_{N_2} < 0.02 \text{ ml/min.cm}^2$) for 300 h. Even at the end of test, the detected N_2 leakage rate was still $< 0.05 \text{ ml/min.cm}^2$. The CO_2/N_2 ratio is ~ 107 for the first 136h and then drops to ~ 58 between 138h and 300h and further to 27 at the 300h marker. For the O_2/N_2 ratio, it is ~ 65 for the first 136h, then decreases to 50 between 138h and 300h and finally to 23 after 138h. This is in striking contrast to the chemo-dealloyed counterpart, which showed a more rapid N_2 leakage after the first 100-h with CO_2/N_2 drop to 20 and O_2/N_2 to < 10 , respectively, after the first 100h [37]. Such a low leakage rate indicates a much better retention of molten carbonate by the electrochemical-dealloyed MECC membrane, which can be attributed to its much finer microstructure.

3.5 Understanding the time-dependent flux behavior

The dynamic change of CO_2/O_2 flux ratio shown in Fig.5 is scientifically intriguing. If the initial increase in flux and higher CO_2/O_2 flux ratio (~ 1.6) are attributed to the microstructural change (e.g. increased ϵ/τ) aforementioned and parallel CO_2/O_2 transport mechanisms, respectively, the sudden change in flux at 118-147-h marker implies a change in mechanism of CO_2/O_2 transport.

We herein propose a mechanism involving the state of the sweep-side surface to explain the behavior. The schematic illustration of the mechanism is shown in Fig.6. At the beginning of the test when Ag coarsening is still low, Fig. 6(a), the sweeping-side surface is full of 3PBs (MC/Ag/gas) to allow the reaction $CO_3^{2-} = CO_2 + 1/2O_2 + 2e^-$ to dominate, while the secondary reaction $CO_4^{2-} = CO_3^{2-} + 1/2O_2$ takes place at less populated MC/gas two-phase boundaries (2PBs). As the time-on-test increases and coarsening worsens, more and more MC is

“squeezed out” from the bulk of the porous Ag and accumulated on the bottom (sweep-side) surface. As the accumulation of MC on the sweep-side surface reaches a critical value, the primary 3PB-pathway is partially shut-down, while the secondary 2PB-pathway becomes a dominant reaction route as 2PB-sites are increased. Such a change in the dominance of the two parallel pathways has, therefore, led to a fast decrease in CO_2 flux and relatively flat O_2 (both pathways contribute to O_2 flux) flux observed in Fig. 5. We have shown strong evidence for the likelihood of a concurrent parallel CO_4^{2-} transport mechanism in our previous study [39]. The mechanism for the flux changes during the transition period is schematically illustrated in Fig. 6 (b).

Figure 6. Schematic illustration of the proposed bi-pathway transport mechanism (a) in the initial stage; (b) in the transitional stage.

3.6 Post-test microstructure analysis

The microstructures of the EC-10mA-400 sample before and after test are compared in Fig. 7. It is evident that the porous Ag has severely coarsened after 500-h operation. Although most of molten carbonate was still kept inside the porous Ag matrix, the loss of molten carbonate was obvious in some locations as indicated in Fig. 7 (b), explaining the gradual increase of N₂ leakage after the first 300-h.

Figure 7. Microstructures of EC-10mA-400; (a) before and (b) after 500-h permeation test.

To support the mechanism illustrated in Fig. 6, the sweep-side surface of the sample after test was examined by SEM; the image is shown in Fig. 8. It is evident that the sweep-side surface has been largely flooded/covered by MC as indicated by the yellow dash-lines. The 3PBs are also visible in Fig.8. The observed MC partially flooded/covered sweep-side surfaces provides experimental evidence to support the proposed mechanism in Fig. 6.

Figure 8. SEM image of the state of sweep-side surface after test.

The SEM images of post-test samples derived from chemical-dealloying [37] and electrochemical-dealloying both show a significant grain growth of silver after long-term exposure to high temperatures. The continual growth of silver grains and therefore the reduction of porosity can cause the porous Ag to lose its ability to retain molten carbonate as it not only repels MC from its volume, but also loses the capillary force to withhold MC as the pore size becomes larger, ultimately leading to gas breakthrough. Therefore, it is necessary to find a way to prevent silver sintering over time in our future study. One approach is to deposit a conformal layer of ZrO_2 over porous Ag before MC-infiltration by atomic layer deposition method to mitigate the silver sintering [38].

IV. Conclusion

In summary, a high-flux and stable silver-carbonate based electrochemical carbon capture

membrane has been successfully demonstrated at 600 °C for 500 hours with the porous silver matrix fabricated by electrochemical dealloying method. SEM observations reveal that the resultant porous Ag matrix contains sub-micron pores in the range of 0.2 to 1 µm. The temperature-dependent flux density plot indicates a similar activation energy for CO₂ and O₂ flux densities, suggesting a coupled transport mechanism. The observed higher O₂/CO₂ flux ratio is interpreted by a secondary pathway involving CO₄²⁻ as an active species for O₂/CO₂ transport. The long-term test shows that a high and stable CO₂/O₂ flux density could be retained for 500 hours with a very low N₂ leakage rate, implying that electrochemical-dealloying derived porous silver has a better retention ability to withhold MC for CO₂/O₂ transport than the conventional pore-former as well as chemical-dealloyed counterpart. A mechanism involving transition of primary reactive sites from 3PBs to 2PBs is also proposed to explain the observed sudden change of CO₂ flux and CO₂/O₂ ratio.

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