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Stabilizing electrochemical carbon capture membrane with Al_2O_3 thin-film overcoating synthesized by chemical vapor deposition†

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Development of high-efficiency and cost-effective carbon capture technology is a central element of our effort to battle the global warming and climate change. Here we report that the unique high-flux and high-selectivity of electrochemical silver-carbonate dual-phase membranes can be retained for an extended period of operation by overcoating the surfaces of porous silver matrix with a uniform layer of Al_2O_3 thin-film derived from chemical vapor deposition.

A wide range of creditable scientific evidence has suggested that manmade CO_2 emission through the combustion of fossil fuels is a major cause of global warming and climate change.[1,2] Although many alternatives to combustion are being considered, combustion will remain a principal component of the global energy system for decades to come. Instead, stabilizing the atmospheric CO_2 concentration is considered the best near-term solution to mitigate the "greenhouse" effect on the climate. The current mainstream approach to achieving this goal is to curb the emission of CO_2 by capturing at point-sources and geologically storing it. So far, three industrial combustion processes have been identified as the point-sources for carbon capture:[3–10] pre-combustion, post-combustion and oxy-combustion. Although significant progress has been made over the past decades, today's carbon capture technologies (capture, compression and storage or collectively CCS) are still too expensive, cumbersome and energy intensive. Implementation of CCS technologies into the existing as well as new fossil fuel power plants would significantly lower the overall plant efficiency and ultimately increase the cost of electricity.

Recently, our group as well as other groups has demonstrated two new classes of carbon capture membranes operated on electrochemical principles.[11–19] The first class is a mixed oxide-ion and carbonate-ion conductor (MOCC) comprised of an oxide and carbonate phase. The second class is a mixed electron and carbonate-ion conductor (MECC) consisted of a metal and carbonate phase. These two types of electrochemical membranes have fundamental advantages over conventional size-exclusion membranes in flux density, selectivity and high-temperature compatibility, and therefore have garnered growing attention in recent years.

Within the two new electrochemical membranes, the MECC membrane technology is of particular interest because of its ability to capture CO_2 from a flue gas stream emitted from coal-fired power plants;[17–19] the latter is one of the major industrial emitters of CO_2. However, our previous work showed that the flux of MECC membranes was unstable for a longer period of time to have any practical implications.[17–19] One of the root causes is the loss of MC during operation arising from the poor wettability between silver and molten carbonate (MC). Subsequently, we demonstrated that coating a thin film of Al_2O_3, a zero-contact-angle wetting agent to MC, on the surface of porous silver matrix through colloidal deposition can notably improve the stability of MECC membranes.[19] Due to a poor controllability of the colloidal deposition method, however, the coverage and thickness of the coating, thus the degree of stability improvement, were often inconsistent from batch to batch. Here we report that a uniform overlayer of Al_2O_3 can be consistently deposited over the surface of a porous silver matrix by chemical vapor deposition (CVD)[20,21] and the stability of a MECC membrane with the coated silver can be significantly improved.

The microstructures of a porous silver matrix before and after CVD Al_2O_3-coating are compared in Fig. 1(a) and (b). Details about fabrication of the porous silver matrix and deposition of Al_2O_3 thin-films can be found in the ESI.† The presence of a coating over the surfaces of silver grains is clearly discerned from Fig. 1(b) by the disappearance of grain-boundaries from the original uncoated silver matrix shown in Fig. 1(a). The coverage of Al_2O_3 is further verified by EDS

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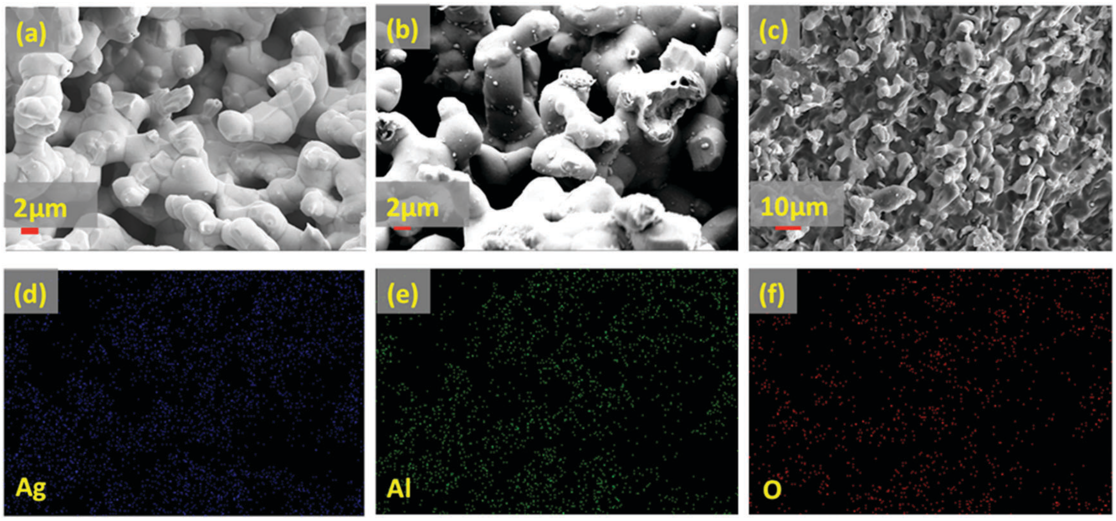

Fig. 1 SEM images of (a) porous silver matrix; (b) porous silver matrix coated by Al_2O_3; (c) silver matrix filled with molten carbonate; EDS mapping of Al_2O_3-coated silver matrix; (d) Ag; (e) Al; (f) O.

mapping of Ag, Al and O shown in Fig. 1(d)–(f), respectively. The high penetration ability of electrons of SEM also reveals silver footprint underneath the Al_2O_3 coating. The thickness of the Al_2O_3 overcoating is estimated to be $\sim$1 μm. Detail about the CVD process can be found in the ESI.† Finally, a dense microstructure of the silver-carbonate membrane after high-temperature impregnation of molten carbonate is shown in Fig. 1(c); pores in the Al_2O_3-coated matrix are clearly filled by MC with no apparent interfacial separation, indicating an excellent wettability between the two phases.

The flux density of permeated species is shown in Fig. 2 as a function of reciprocal temperature (Arrhenius plot). Note that the feeding gas was a simulated flue gas containing 15% CO_2, 75% N_2 and 10% O_2. As predicted from the enabling surface reaction $CO_3^{2-} = CO_2 + 1/2O_2 + 2e^-$ presented in the ESI,† both CO_2 and O_2 were observed in the sweeping helium at the permeate side. The ratio between the flux of CO_2 (J_{CO_2}) and O_2 (J_{O_2}) is very close to 2 : 1, reflecting the stoichiometry required by the surface reaction.

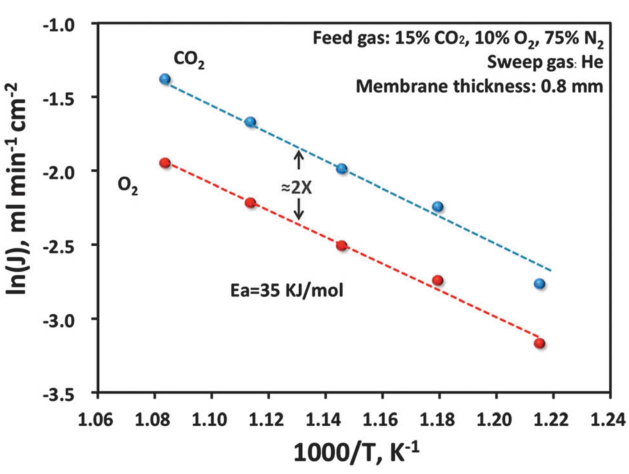

Fig. 2 Arrhenius plots of CO_2 and O_2 flux densities measured under a simulated flue gas.

In addition, J_{CO_2} and J_{O_2} shares a similar activation energy (E_a), implying that the permeation of CO_2 and O_2 is a closely coupled process by the surface reaction. It is also interesting to see that obtained E_a = 35 kJ mol^{-1} is in excellent agreement with E_a = 32 kJ mol^{-1} of the CO_3^{2-} conduction for molten carbonates.[22] This observation suggests that the CO_3^{2-} migration could be a rate-limiting step of the overall CO_2 transport through MECC membranes. In other words, the high-conductivity electron transport in the silver matrix is not limiting the flux of the CO_2 permeation. Overall, the membrane can achieve a flux density as high as 0.25 ml min^{-1} cm^{-2} at 650 °C. This value is compared to a unstable J_{CO_2} < 0.10 ml min^{-1} cm^{-2} for the uncoated sample under the same condition, demonstrating the criticality of an Al_2O_3 coating over the silver surface in enhancing J_{CO_2} of MECC membranes.

The long-term stability of CVD-Al_2O_3 coated MECC membrane is shown in Fig. 3(a) along with the uncoated baseline sample. It is starkly clear that the coated sample shows no sign of degradation over the 100 hour test, whereas the uncoated baseline sample losses nearly 50% of its original flux in just the first 20 hours. Furthermore, the selectivity of (CO_2 + O_2)/flue-gas is determined from the concentration of N_2 in the sweeping gas leaked through the membrane. When the N_2 concentration is 0.015% (equivalent to a flux density of 0.0225 ml min^{-1} cm^{-2}), the highest leakage encountered in this study, the selectivity of (CO_2 + O_2) is calculated to be 100. For a regular level of N_2-leakage at 0.001% (equivalent to a flux density of 0.0008 ml min^{-1} cm^{-2}), the selectivity is over 2000. The independent flux and selectivity is a unique feature of the electrochemical membranes contrasting to conventional membranes subject to the "Robeson Upper Bound".[23] It is also important to point out the ramification of using (CO_2 + O_2)/flue-gas as a measure of the selectivity. By the use of either H_2 or syngas (H_2 + CO) as the capture gas, the co-permeated CO_2 and O_2 can be fully converted into CO_2 and H_2O for easy downstream separation. We have demonstrated the concept in one of our early publications.[24] Therefore, O_2 is not considered non-selective to the CO_2 capture in this case.

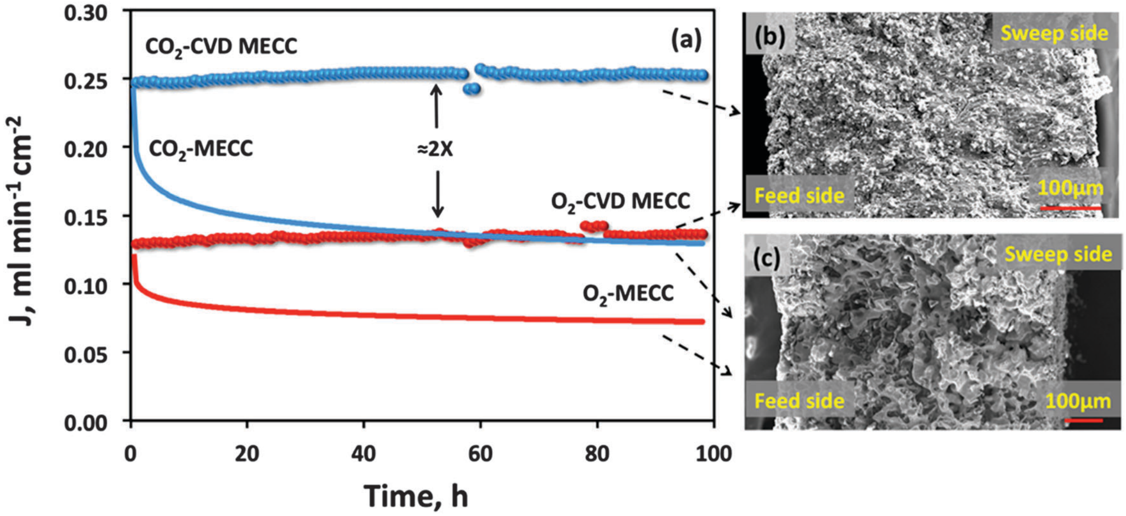

Fig. 3 (a) CO_2 flux as a function of time measured under a simulated flue gas composition at 650 °C; cross sections of a MECC membrane after 100 h test; (b) coated; (c) uncoated.

The relevant microstructural differences corresponding to the drastically different flux stability observed in Fig. 3(a) are shown in Fig. 3(b) and (c). It is very evident that, after running for 100 hours, the coated MECC membrane shows in Fig. 3(b) an intact and dense microstructure of silver and MC, whereas the uncoated membrane displays in Fig. 3(c) a large amount of porosity accompanied by apparent sintering of silver grains, implying that a loss of MC have occurred during the operation.

In summary, a stable silver-carbonate electrochemical membrane suitable for high-flux and high-selectivity post-combustion carbon capture has been successfully demonstrated by overcoating a uniform layer of Al_2O_3 on the surface of a porous silver matrix through CVD. The temperature dependence of J_{CO_2} and J_{O_2} suggests that the CO_2 and O_2 permeation is a closely coupled diffusion process with a very similar E_a. The similarity in E_a between the measured and that of CO_3^{2-} conduction implies that the CO_3^{2-} migration through the carbonate phase is a rate-limiting step of the overall CO_2 transport. The time dependence of J_{CO_2} and J_{O_2} shows no sign of degradation for the coated sample and nearly 50% of degradation in the first 20 hours for the uncoated sample. Overall, this study has demonstrated that long-term stability of high-flux and high-selectivity electrochemical MECC membranes can be effectively enhanced by an Al_2O_3 thin-film overcoating synthesized by CVD.

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