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Stabilizing Electrochemical Carbon Capture Membrane with $\text{Al}_2\text{O}_3$ 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 $\text{Al}_2\text{O}_3$ thin-film derived from chemical vapor deposition.

A wide range of credible scientific evidence has suggested that manmade $\text{CO}_2$ emission through the combustion of fossil fuels is a major cause of the 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 $\text{CO}_2$ 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 $\text{CO}_2$ 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: 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-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 $\text{CO}_2$ from a flue gas stream emitted from coal-fired power plants$^{17,19}$; the latter is one of the major industrial emitters of $\text{CO}_2$. 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 $\text{Al}_2\text{O}_3$ 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 $\text{Al}_2\text{O}_3$ 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.

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The microstructures of a porous silver matrix before and after CVD Al$_2$O$_3$-coating are compared in Fig.1 (a) and (b). Details about fabrication of the porous silver matrix and deposition of Al$_2$O$_3$ 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$_2$O$_3$ is further verified by EDS mapping of Ag, Al and O shown in Fig.1 (d), (e) and (f), respectively. The high penetration ability of electrons of SEM also reveals silver footprint underneath the Al$_2$O$_3$ coating. The thickness of the Al$_2$O$_3$ overcoating is estimated to be ~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$_2$O$_3$-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$_2$ + O$_2$ + 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$_2$ ($J_{\text{CO}_2}$) and O$_2$ ($J_{\text{O}_2}$) is very close to 2:1, reflecting the stoichiometry required by the surface reaction. In addition, $J_{\text{CO}_2}$ and $J_{\text{O}_2}$ 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 is in excellent agreement with $E_a$~32 kJ/mol of the CO$_2$ conduction for molten carbonates $^{22}$. This observation suggests that the CO$_2$ 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 an unstable $J_{\text{CO}_2}$<0.10 ml·min$^{-1}$·cm$^{-2}$ for the uncoated sample under the same condition, demonstrating the criticality of an Al$_2$O$_3$ coating over the silver surface in enhancing $J_{\text{CO}_2}$ of MECC membranes.

The long-term stability of CVD-Al$_2$O$_3$ 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 2,000. 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$_2$O 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.
The relevant microstructural differences corresponding to the drastically different flux stability observed in Fig. 3 (a) are shown in Figs. 3 (b) - (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.

Conclusions

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 Al₂O₃ on the surface of a porous silver matrix through CVD. The temperature dependence of J_{CO₂} and J_{O₂} suggests that the CO₂ and O₂ permeation is a closely coupled diffusion process with a very similar E_a. The similarity in E_a between the measured and that of CO₃²⁻ conduction implies that the CO₃²⁻ migration through the carbonate phase is a rate-limiting step of the overall CO₂ transport. The time dependence of J_{CO₂} and J_{O₂} 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 Al₂O₃ thin-film overcoating synthesized by CVD.

Notes and references

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