Electronic Supplementary Material (ESI) for ChemComm.

# Electronic Supplementary Information

## 1. Preparation of Ag-MC membranes

### *1.1 Preparation of the porous Ag matrix*

The porous Ag matrix was prepared in the same way as our previous study.[1,2] Silver powder (1-3 micron, 99.9% metal basis, Alfa Aesar) was intimately mixed with carbon black in a volume ratio of 1:1 in the presence of ethanol. The dried powder mixture was then pressed into pellets under 70 MPa, followed by sintering at 650 $^{o}$C for 2 h in air.

### *1.2 ALD deposition of $ZrO_2$*

The porous silver matrices were coated with a nanoscaled $ZrO_2$ layer using ALD (Atomic Layer Deposition) system (Savannah S200, Cambridge NanoTech, USA). Tetrakis(dimethylamido)zirconium(IV), $[(CH_3)_2N]_4Zr$ (669016, Sigma-Aldrich®, USA) was used as the zirconia precursor, DI water as the oxidant and $N_2$ as the carrier/purge gas. Different from the conventional flow mode recipe, an exposure mode recipe was developed for our micro porous substrate. One deposition cycle consisted of eight steps: Vacuuming - Pulsing DI - Dosing DI - Purging DI - Vacuuming - Pulsing Zr - Dosing Zr - Purging Zr, while the reaction chamber temperature was controlled at 250 °C. The $ZrO_2$ precursor pulsing/dosing/purging times were 0.4/20/60 sec, respectively. The deposition rate of the film was determined to be 0.13 nm/cycle. A total of 200 cycles was performed, expecting ~26 nm $ZrO_2$ layer on the silver wall. The image and compositional of Ag and Zr were also examined by SEM and EDS at different lateral and depth locations of the sample, to confirm the uniformity of $ZrO_2$ coating by ALD.

### *1.3 Forming dense Ag-MC membranes*

Both the uncoated and $ZrO_2$-coated porous silver pellets were then impregnated with a 52 mol% $Li_2CO_3$-48 mol% $Na_2CO_3$ molten carbonate (MC) at 650 $^{o}$C for 2 h to form a dense MECC membrane. The weight increased after MC impregnation was ~20%. After MC infiltration, the surface of the Ag-MC was thoroughly cleaned by DI water.

## 2 Characterization of Ag-MC membranes

### *2.1 Scanning electron microscopy*

The cross-sectional views of the $ZrO_2$-coated porous Ag matrix and final Ag-MC membrane before and after testing were examined by a scanning electron microscope (SEM) (FESEM, Zeiss Ultra) equipped with Energy Dispersive Spectrometry (EDS).

### *2.2 Permeation measurements*

The flux densities of $CO_2$ and $O_2$ of the Ag-MC membranes fabricated in this study were measured using a homemade permeation cell. Details on the testing procedure can be found in our previous works.[2,3] In particular, the measurement of permeation flux as a function of temperature (550-850 $^{o}$C) was carried out in a mixture of 75% $N_2$, 10% $O_2$ and 15% $CO_2$ at a total flow rate of 100 ml min$^{-1}$ as the feed gas and high-purity Ar at a total flow rate of 50 ml min$^{-1}$ as the sweep gas. During all the tests, the $N_2$ was used as the tracer gas to detect and correct for any leakages resulting from the sealing and/or membrane. Commercial mass flow controllers (Smart-Trak, 50 Series) specifically calibrated for the gas under use were employed to control the mass flow rates of both feed and sweep gases. The compositions of the sweep gas were analyzed by an on-line micro-GC (Varian 490 GC, Varian) under ambient temperature and pressure conditions (t=25 $^{o}$C, P=1 atm). To ensure the accuracy, the GC was pre-calibrated with four standard gas compositions for each gas of interest ($CO_2$, $O_2$ and $N_2$) prior to the measurement. Approximately one hour was given at each temperature to ensure full stability before data were taken. The final $CO_2$ and $O_2$ flux densities were calculated using the following equations:

$$J_{CO_2} = \frac{C_{CO_2}}{(1 - C_{CO_2} - C_{O_2} - C_{N_2})} \times \frac{Q}{A}$$

$$J_{O_2} = \frac{C_{O_2}}{(1 - C_{CO_2} - C_{O_2} - C_{N_2})} \times \frac{Q}{A}$$

where $C_{CO_2}$, $C_{O_2}$ and $C_{N_2}$ are the measured concentrations of $CO_2$, $O_2$ and $N_2$, respectively; Q is the flow rate of the Ar sweep gas; and A is the effective area of the sample.

## References

1. J. Tong, F. Si, L. Zhang, J. Fang, M. Han, K. Huang, *Chem. Commun.,* 2015, 51, 2936-2938.
2. J. Tong, X. Lei, J. Fang, M. Han, K. Huang, *J. Mater. Chem. A,* 2016, **4**, 1828-1837.
3. L. Zhang, N. Xu, X. Li, S. Wang, K. Huang, W. H. Harris,W. K. S. Chiu, *Energy Environ. Sci.,* 2012, **5**, 8310-8317.