Development of Dual-Phase Oxygen Transport Membranes for Carbon Capture Processes

Fossil fuel based power plants and industrial production of cement and steel are major sources of anthropogenic CO2 emissions. One of the most promising approaches to capture and store CO2 from such large point sources is the oxy-fuel combustion route, where pure oxygen instead of air is used in the combustion, which greatly facilitates the down-stream CO2 capture. The main energy penalty for the oxy-fuel process is related to the production of the oxygen, which today commonly is done in cryogenic air separation units (ASUs). An alternative approach, which requires significant less energy is the use of oxygen transport membranes (OTMs), which has the potential to reduce the cost and energy penalty associated with the CO2 capture and storage.

This thesis focusses on the development and characterization of highly efficient and chemically stable planar asymmetric OTMs for direct integration in oxy-fuel combustion power plants. For the case of direct integration considered here the permeate side of the OTMs will be swept with recirculated flue gas whereby a driving force for oxygen transport through the membrane, which is fed with air on the other side, is directly established. It further facilitates thermal integration and thermal management in the combustion and avoids the need to handle pure oxygen. However, a direct integration scheme impose quite severe conditions on the membrane materials, such as stability towards both CO2 and SO2 and at low pO2 (1-10 mbar).

The development of planar asymmetric membranes in this work, required the parallel development of (i) stable porous supports, (ii) thin dense membrane layers, (iii) porous catalytic backbones and (iv) meso-porous nano-particulate catalytic coatings. For the dense membrane layers, dual-phase composites consisting of a stable ionic and a stable electronic conductor were used to overcome the stability limitations commonly observed with single-phase membrane materials (e.g. La1-xSrxCoy1-δ (LSCF), Ba1-xSrxCoy1-δ (BSCF)) in CO2 and SO2. Three composite materials, (ZrO2)0.99(Y2O3)0.01-δ (Sc2O3)0.10 - MnCo2O4 (10Sc1YSZ-MCO), (ZrO2)0.99(Y2O3)0.01-δ (Sc2O3)0.10 - AIO0.02Zn0.98O1.01 (10Sc1YSZ-AZO) and (ZrO2)0.99(Y2O3)0.01-δ (Sc2O3)0.10 - LaCr0.85Cu0.10Ni0.05O3-δ (10Sc1YSZ-LCCN) were prepared and applied in planar dual-phase asymmetric OTMs and finally characterized and tested in clean as well as flue-gas like atmospheres.

The work dedicated to 10Sc1YSZ-MCO (70-30 vol.%) dual-phase membranes entailed development and characterisation of of 7 μm thin asymmetric membranes supported on zirconia supports as well as 0.5 mm thick self-standing membranes. The thin asymmetric membranes were prepared by tape-casting, lamination, and fired in a two-step sintering process in order to obtain fully dense thin membrane layers in a sintering regime that avoids excessive Co and Mn diffusion and/or decomposition of the MCO phase. Long-term stability tests above 1700 °C in pure CO2 and 1700 °C in oxy-fuel conditions (250 ppm of SO2, 3 vol.% of H2O, 5 vol.% of O2 balanced with CO2) demonstrated the stability of the composite membranes under relevant application conditions. Oxygen permeation fluxes of 1.41 mL N cm-2 min-1 and 2.23 mL cm-2 min-1 at 940 °C in air/N2 and O2/N2 atmospheres, respectively, were obtained. To further improve the membrane performance, catalytic surface layers were developed and tested by electrochemical impedance spectroscopy (EIS). Oxygen permeation tests were realized on 10Sc1YSZ-MCO (70-30 vol.%) membranes coated with these porous catalytic layers. The tests demonstrated that layers based on mixed ionic and electronic conducting backbones worked best (e.g. Ce0.8Bo.2O2-δ (CTO)-NiFe2O4 (NFO) (40-60 vol.%)); increases in the oxygen permeation of about 50 % were observed for membranes coated with a such compared to those based on purely ionically conducting backbones.

10Sc1YSZ-AZO (50-50 vol.%) dual-phase composite membranes were also developed and characterized as thick (1 mm) self-standing membranes and thin (0.8 μm) supported membranes. The stability of these membranes in gas streams containing CO2, SO2 and H2O was found to be excellent. However, the high volatility of the Zn in the AZO phase under mildly reducing atmospheres makes the fabrication of thin asymmetric membranes challenging. Very limited oxygen permeation fluxes were measured through the 8 μm thick supported membrane (0.16 mL N cm-2 min-1 at 925 °C in air/N2), while 1 mm thick membranes, in which the Zn depleted part was removed by polishing, displayed higher oxygen permeation fluxes (0.33 mL N cm-2 min-1 at 925 °C in air/N2).

Finally, self-supported dual-phase membranes made of 70 vol.% of 10Sc1YSZ and 30 vol.% of LCCN were prepared and characterized (oxygen permeation measurements and stability tests under oxy-fuel conditions). Analyses using several characterization techniques (X-ray diffraction (XRD), X-ray fluorescence (XRF), attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), Raman spectroscopy and scanning electronic microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) underlined the excellent stability of the materials under application relevant atmospheres. Oxygen permeation fluxes of 0.27 mL N cm-2 min-1 and 1.02 mL cm-2 min-1 were obtained at 950 °C in air/N2 gradient for a 1000 μm thick and a 110 μm thick membrane, respectively. To further improve the oxygen permeation through 10Sc1YSZ-LCCN membranes, thin asymmetric and symmetric supported membranes were developed on 10Sc1YSZ-LCCN (40-60 vol.%) porous structures. Fully dense thin membrane layers (10-60 μm) were obtained, but the porous structures (support and activation layers) became to dense in the co-firing process. Consequently, further research and development is required to realize the full potential of this promising material combination.