Proposal Title: Development of Advanced Mixed Electronic and Carbonate Ion Conducting Membranes and Reactors for Combined CO₂ Capture and Conversion

Abstract

Global warming and climate change resulted from CO₂ emissions have been increasingly observed to impact our daily life and damage our economy in recent human history. To deal with this grand challenge, carbon capture and storage (CCS) has been established as a key technology to curb CO₂ emission from fossil-fueled power plants. The core of the CCS technology is to capture CO₂ at emission sources and geologically bury it for permanent storage or enhanced oil recovery (OER). As the first step of CCS, carbon capture technologies are currently being developed for three power-generation related combustion processes that are responsible for ~78% of the global stationary carbon emissions: pre-combustion, post-combustion and oxy-combustion. A major challenge to the full implementation of the current carbon capture technologies such as imine-based “chemical washing” process is, however, the high-energy penalty, which significantly reduces plant efficiency and increases the cost of electricity. Developing cost-effective, energy-efficient and CO₂-selective carbon-capture processes/methods is, therefore, highly desirable.

The state-of-art CO₂ capture technologies are either based on a reversible chemical/physical sorption processes by liquid solvents and solid sorbents as CO₂ scrubber or on a membrane based molecular filter. However, both technologies have intrinsic drawbacks. Solvent and sorbent based CO₂ scrubber is usually costive, application of which into existing power plants adds a 30% parasitic energy. The membrane based technology is susceptible to poor selectivity at high permeability since it is size excluded. In particular, those polymeric membranes are incompatible with high temperature streams from which CO₂ is captured. So far, only a few of these technologies are commercially available for large-scale application.

The previous works carried out by our group have demonstrated a high-performance, dual-phase membrane for CO₂ capture from post-combustion flue gas. The dual phase consists of an electron conducting silver matrix witholding a carbonate-ion conducting molten carbonate phase, making the membrane a mixed electronic and carbonate ion conductor (MECC). The driving force for this new type of inorganic membrane is the gradient of electrochemical potentials of CO₂ and O₂ existing on the opposite surfaces of the membrane. Thus, no external electronic devices are needed to drive CO₂ and O₂ through the membrane, which makes it low cost and energy efficient. Furthermore, since only electrochemically active species such as CO₃²⁻ can pass through the membrane, the membrane selectivity is not bound by permeability like conventional polymeric counterparts, thus can be very high. Another advantage of this new membrane is that it operates at high temperatures in a continuous manner, making it well suited to directly capture CO₂ from high-temperature flue gas streams. Despite all these advantages and promises, the long-term stability of MECC membranes is a major challenge to be met for ultimate commercial applications.

Therefore, the first objective of this dissertation work is to develop methods to fabricate stable MECC membranes while maintaining high CO₂ capture rate at the operating temperature. Chemical dealloying and electrochemical dealloying methods have been selected for the first time to fabricate porous Ag matrix for MECC membranes. The result show that the porous Ag matrices derived from these two methods contain much smaller pores than traditional ones made by pore former method. Chemically dealloyed porous Ag matrix contains three types of pore structures...
with a larger pore around 10 µm and smaller pore less than 2 µm. Electrochemically dealloyed Ag matrix contains a very homogenous pore structure with an average pore size of less than 1 µm. Flux measurements indicate that the chemically dealloyed MECC membranes exhibit a superior CO₂/O₂ flux density and stability over 900 h testing period. It is concluded that the high CO₂/O₂ flux arises from H₂ in Ar as the presence of H₂ on the sweep side significantly increases the electrochemical gradient of O₂. The electrochemically dealloyed MECC shows a stability and high flux over 500 h with a very low N₂ leakage, which is attributed to its fine and homogenous microstructure. A bi-path gas transport mechanism is also proposed to explain the sudden change of CO₂ and O₂ ratio at 130-h marker in the test.

After CO₂ capture at the point sources, the next step is CO₂ storage. However, large-scale geological storage of CO₂ is still in the early development and has not been fully deployed in the US. An attractive alternative to geologic storage is to convert the captured CO₂ back into fuels. Several methods that have been developed so far for CO₂ conversion including thermolysis, thermochemical cycles and electrolysis. Among all those technologies, high-temperature co-electrolysis is of particular interest since it can utilize high-temperature steam/CO₂ directly from a point source, and convert it instantly into syngas without change process condition for the downstream F-T liquid fuel synthesis, which makes it an efficient fuel synthesis technology.

Thus, the second objective of this thesis is to theoretically analyze the energy efficiency and economics of a combined “MECC-SOEC” reactor that integrates the newly developed high-temperature MECC membranes with conventional high-temperature solid oxide electrolysis cell (SOEC). Life cycle analysis (LCA) has been carried out on a plant consisting of CO₂ capture reactor, SOEC reactor, heat recovery system and fuel delivery system. The analysis shows that the parasitic energy of MECC plant for CO₂ capture can be as low as 321 kJ/kg CO₂, about half of traditional monoethanolamine (MEA) plant. The whole system efficiency can be as high as 82%. It also shows that the active area of SOEC can significantly affect MECC parasitic energy, but has little effect on system efficiency. The price of syngas and resultant FT-fuels have also been estimated and the latter is further compared with that of biomass to liquid (BTL). In order to compete with the price of BTL-fuels, the analysis indicates that the price of nuclear/renewable (carbon neutral) electricity utilized in the steam/CO₂ electrolysis has to be lower than $0.06/kwh for Ag-MECC conversion/capture system and lower than $0.098/kwh for NiO-MECC conversion/capture system. This modeling work provides useful guidance for future development of combined CO₂ conversion/ capture reactor system.