GCEP

Global Climate & Energy Project

STANFORD UNIVERSITY

Advanced Membrane Reactors in Energy Systems
A Carbon-Free Conversion of Fossil Fuels

Investigators

Daniel Jansen, Wim Haije, Jan Wilco Dijkstra and Ruud van den Brink, Energy Research Centre of the Netherlands; Cor Peters and Joop Schoonman, Technical University of Delft

Objective

The purpose of this project is to develop hydrogen and CO_2 membranes to allow combination of natural gas reforming with H_2 or CO_2 separation in separation enhanced reactors, *i.e.*, membrane reactors, for carbon-free hydrogen production or electricity generation. These devices offer multiple advantages, such as eliminating the requirement of water gas shift reactors with associated costs reductions; offering higher conversion efficiencies at lower temperatures; and decreasing primary energy use for CO_2 separation/capture associated with electricity generation.

This project, a collaborative effort between Energy Research Centre of the Netherlands (ECN) and Technical University of Delft (TU-Delft), focuses on three potentially game-changing membrane materials for H_2 and CO_2 separation: functionally-graded H_2 membranes; hydrotalcite membranes; and ionic liquid membranes for CO_2 separation.

Background

Membrane materials for H_2 separation must be able to transport hydrogen as a molecule or as protons; they must operate at temperatures $\geq 400^{o}C$ for compatibility with natural gas reforming. Among the various materials that have been identified (*e.g.,* multi-component alloy metal membranes and metal-organic framework membranes), functionally-graded membranes have the highest potential with respect to efficiency and costs. Nano-porous ceramic structures will be built in tubular geometry, with the goal of producing stable, inorganic high-selectivity and high-permeability membranes that are capable of operating in high temperature and pressure environments.

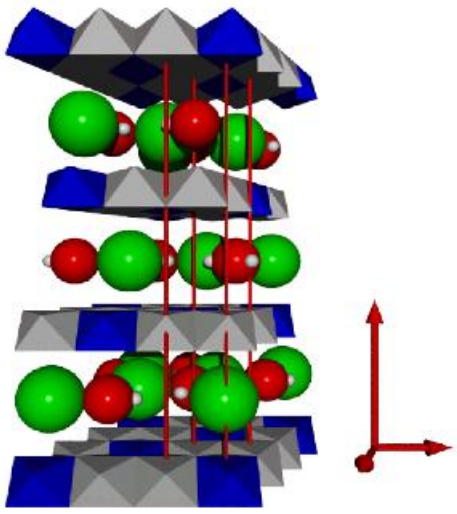

Figure 1. Hydrotalcite host lattice: grey: $Mg(OH)_6$-octahedron; blue: $Al(OH)_6$-octahedron; red: H_2O; green: CO_3^{2-} ions. A unit cell is shown in red.

Among the requirements for CO_2 separation membranes, the three most critical are that materials must physically or chemically bind to CO_2 while hydrogen should not be adsorbed; that CO_2 release must be achieved with low-energy input; and finally that they must be able to operate at temperatures compatible with hydrogen production ($\geq 400^{o}C$ in the case of natural gas reforming). This project focuses on hydrotalcites (HTC) and ionic liquid membranes.

HTC is an excellent CO_2-adsorbent composed of double-layered compounds, with divalent metal ions (*e.g.,* Mg^{2+}, Zn^{2+}) and trivalent metal ions (Al^{3+}) in the first layer and negatively charged ions (*e.g.,* CO_3^{2-}, oxalates) in the second layer (see Figure 1). The main challenges in developing HTC membranes are

to enhance desorption of CO_2 and to stabilize their structure against changes occurring during uptake and release of CO_2 that might cause high mechanical stresses in the membrane layer. Ionic liquids based on imidazolium show very high CO_2 solubility (*e.g.,* 0.4 mole fraction for 1-butyl-3-methylimidazolium hexafluorophosphate [bmin][PF6]) that can be further increased by proper choice of cation, anion, and alkyl chain length. Additionally, ionic liquids have good selectivity properties for CO_2 versus CO and H_2. In order to optimize their properties, fundamental understanding of their thermodynamic and phase behavior has still to be understood. Another challenge to render them operational at high temperatures ($\geq 150^{o}C$) is to include them in a porous membrane structure.

In membrane reactors, catalysts are required to reduce the operation temperature and to take full advantage of the membrane principle. In advanced membrane reactors the temperature is low (400 - 500°C) and could thus promote coke formation. Furthermore, at low temperatures kinetic barriers are high, so very active catalysts are required to limit the amount of catalyst necessary.

Approach

During the first year of the project, an integrated hydrogen/CO_2-capture production system is being designed and evaluated. The results of these system analysis studies and thermodynamic evaluations will guide investigation on materials, catalysts and membrane developments. Numerical models will be used to develop appropriate process schemes, perform second-law thermodynamic assessments, and identify the required membrane properties and performances.

Following the initial phase of the project, nano-porous ceramic membranes capable of separating hydrogen from gas mixtures containing methane, steam and carbon monoxide, will be fabricated. A two-step process will be followed where the pore size of a starting macro-porous membrane is decreased first by chemical vapor infiltration (CVI) and then by atomic layer deposition (ALD) to allow control of the pore size at the nano-scale. The ultimate pore size of the membrane allows diffusion of H_2 only. After fabrication, the feasibility of H_2 separation along with conversion enhanced reforming or water gas shift will be verified experimentally.

In parallel tasks, HTC and ionic liquid membranes will also be developed. In particular, gas-tight layers of HTC will be deposited on membrane supports, and their CO_2-adsorption and release mechanisms will be investigated and optimized. Finally, their performance will be tested in a separation-enhanced reactor for steam reforming and water gas shift. As for ionic liquids membranes, their thermodynamic, structural, and transport behavior will be simulated for a range of materials to provide fundamental insight. Accurate quantum chemical calculations are required to investigate the inter-ionic interactions in these materials. The inter-ionic potentials will subsequently be used in Monte Carlo simulations to study thermodynamics and phase behaviors. By varying the interactions, the effect of molecular parameters such as shape and polarity on the macroscopic behavior can be investigated in a systematic manner, guiding the design and optimization of their properties.

In combination with the development of the membrane materials, commercial catalysts will be selected and low-temperature reforming capabilities and mechanisms of coke formation will be investigated.