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

Investigators
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Objective
The purpose of this project is to develop hydrogen and CO₂ membranes to allow combination of natural gas reforming with H₂ or CO₂ 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 CO₂ 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 H₂ and CO₂ separation: functionally-graded H₂ membranes; hydrotalcite membranes; and ionic liquid membranes for CO₂ separation.

Background
Membrane materials for H₂ separation must be able to transport hydrogen as a molecule or as protons; they must operate at temperatures ≥400°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.

Among the requirements for CO₂ separation membranes, the three most critical are that materials must physically or chemically bind to CO₂ while hydrogen should not be adsorbed; that CO₂ release must be achieved with low-energy input; and finally that they must be able to operate at temperatures compatible with hydrogen production (≥400°C in the case of natural gas reforming). This project focuses on hydrotalcites (HTC) and ionic liquid membranes. HTC is an excellent CO₂-adsorbent composed of double-layered compounds, with divalent metal ions (e.g., Mg²⁺, Zn²⁺) and trivalent metal ions (Al³⁺) in the first layer and negatively charged ions (e.g., CO₃²⁻, oxalates) in the second layer (see Figure 1). The main challenges in developing HTC membranes are...
to enhance desorption of CO₂ and to stabilize their structure against changes occurring during uptake and release of CO₂ that might cause high mechanical stresses in the membrane layer. Ionic liquids based on imidazolium show very high CO₂ 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 CO₂ versus CO and H₂. 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 (≥150°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/CO₂-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 H₂ only. After fabrication, the feasibility of H₂ 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 CO₂-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.