Plasma Enhanced Chemical Vapor Deposition Synthesis of Metal Carbide Membranes for High Temperature H₂ Separations

Donal Finegan, Mayur Ostwal, J. Douglas Way and Colin Wolden

Motivation

1. Approximately 80% of the global energy demand comes from fossil fuels and this reliance is expected to increase at least until the year 2020. Combustion of these fossil fuels to generate power produces CO₂.

2. Hydrogen gas is a highly sought after chemical within industry and its uses in society are continuously increasing. The annual production of H₂ currently stands at around 50 million tonnes. The primary method of production of H₂ is steam reforming which produces a gaseous mixture of H₂ and CO₂.

Consequently, methods are sought to separate CO₂ and purify H₂.

Results

1. With the RF power set to 100 Watts and varying the MoF₀ flow rate between 2.8 sccm and 3.7 sccm, the MoO₂ rates of deposition were measured.

2. After achieving operating conditions for Mo(CO)₆, the temperature and thus the flow rate was measured against the rate of deposition. MoO₂ powder began to form at around 50°C.

3. SiO₂ was deposited on a GTC tube for 15 minutes at 200W. The pore size distribution is shown before and after SiO₂ deposition. Further deposition is required to prevent viscous flow of H₂, N₂, and He and perform selective separation.

4. Permeation testing for a carburized Praxair tube before and after SiO₂ pore repair; The SiO₂ film appears to break apart at higher temperatures above 300°C. The H₂/He separation factor calculated from the testing was between 1.4 and 1.6. The fluxes exhibited viscous behaviour.

Challenges

• MoF₀ is a functional but undesirable component for the deposition of a MoO₂ film. MoF₀, F and HF are environmentally damaging, toxic, corrosive and reactive chemicals. MoF₀ is also an expensive raw material to be used, costing $780 per canister ($15.6 per gram).
• Mo(CO)₆ costs about $2.66 per gram and the syngas produced by reaction (CO and CO₂) with H₂ under low temperature PECVD conditions is significantly safer and more environmentally friendly.

Conclusion

Synthesis of β-Mo₅C thin film membranes was analyzed involving a two step process. First step involves the PECVD of dense molybdenum oxide using initially a mix of MoF₀/H₂/O₂ at optimum conditions. Mo(CO)₆ was experimented with but reproducible functional conditions are not yet found. Second step is the conversion and characterization of oxide films into β-Mo₅C using TPR in CH₂/H₂. In-situ SiO₂ deposition is done by counter flow PECVD to eliminate the big pores and defects formed during carburization. This helps in the formation of nanoporous surface diffusion Mo₅C carbide membrane. H₂ dissociation at high temperatures, >300°C is still under research.

Acknowledgements

• Chemical Engineering department, University College Dublin
• Martin McAdam, Pat Mc Adam Scholarship
• Department of Energy Award, # DE-FEE0001009
• Renewable Energy Materials Research Science and Engineering Centre