The University Of Sheffield.

EPSRC

Engineering and Physical Sciences Research Council

Electrocatalytic Reduction of CO_2 and H_2O to Form Syngas

Laura Platt

University of Sheffield

E-Futures DTC

Email: dtp09lcp@sheffield.ac.uk

Overview

- **Carbon Dioxide**
  - Storage
  - Activation
- **Solid Oxide Electrolysis**
  - Theory
  - Materials
- **Co-electrolysis of CO_2 and H_2O**
  - Syngas Production
- **Water Gas Shift Reaction**
- **Experimental Design**

Figure 1. Syngas Plant in Germany. Source http://www.linde-engineering.com/process_plants/hydrogen_syngas_plants/gas_products/syngas.php

Carbon Capture and Storage

- CO_2 from point sources:
  - Collection
  - Compression
  - Transportation
- Storage in geological formations:
  - Oil and gas reservoirs
  - Unminable coal seams
  - Deep sea reservoirs
- Additional fuel input for CCS enabled plant – 25% - 80%.

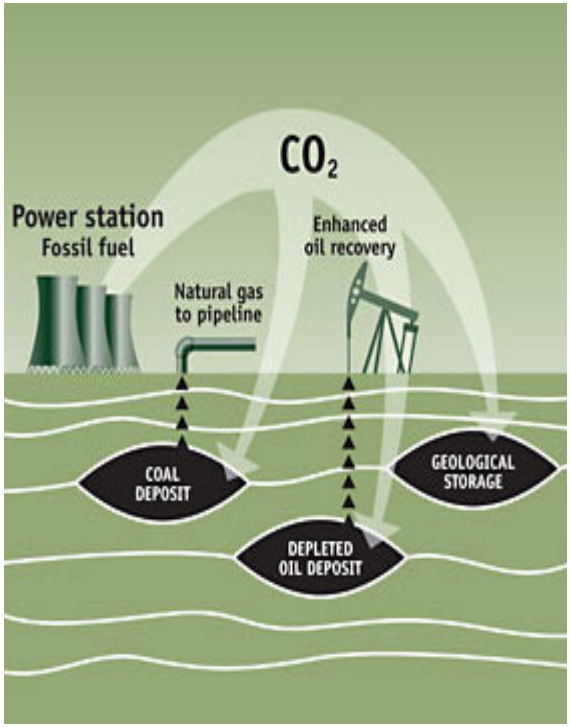


Figure 2. Carbon Capture and Storage. Source: http://www.nottingham.ac.uk/carbonmanagement

Solid Oxide Electrolysis

- Hydrogen/Oxygen production via the electrolysis of H_2O.
- Operating temperature 700°C – 1000°C.
- Three layers – anode, cathode and electrolyte material, for example, Yttria-stabilised Zirconia (good ionic conductivity).

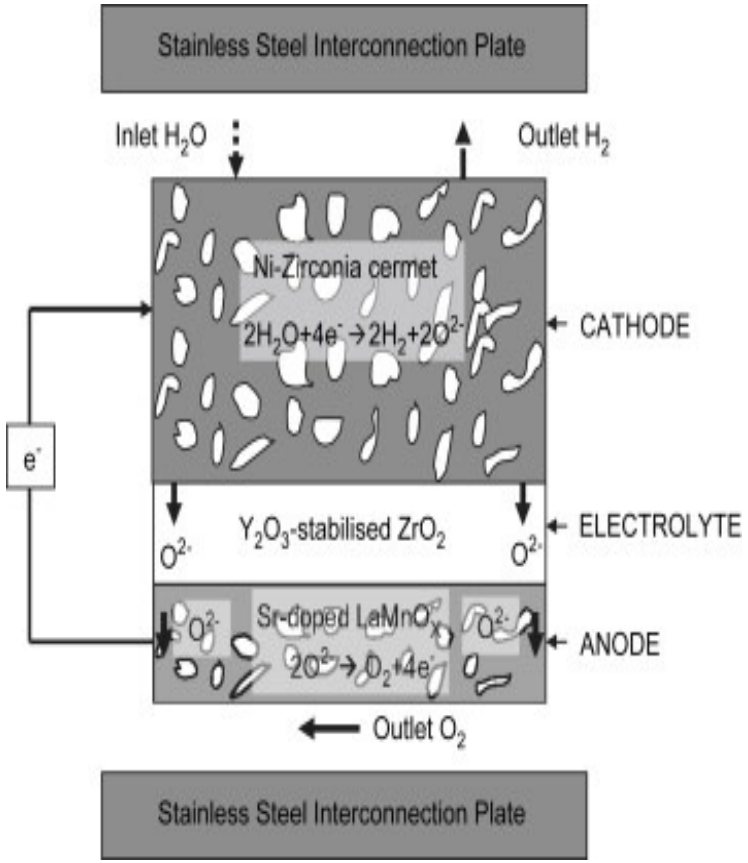


Figure 3. Schematic of a Solid Oxide Electrolysis Cell (Brisse, Schefold and Zahid, 2008).

Co-electrolysis of CO_2 and H_2O

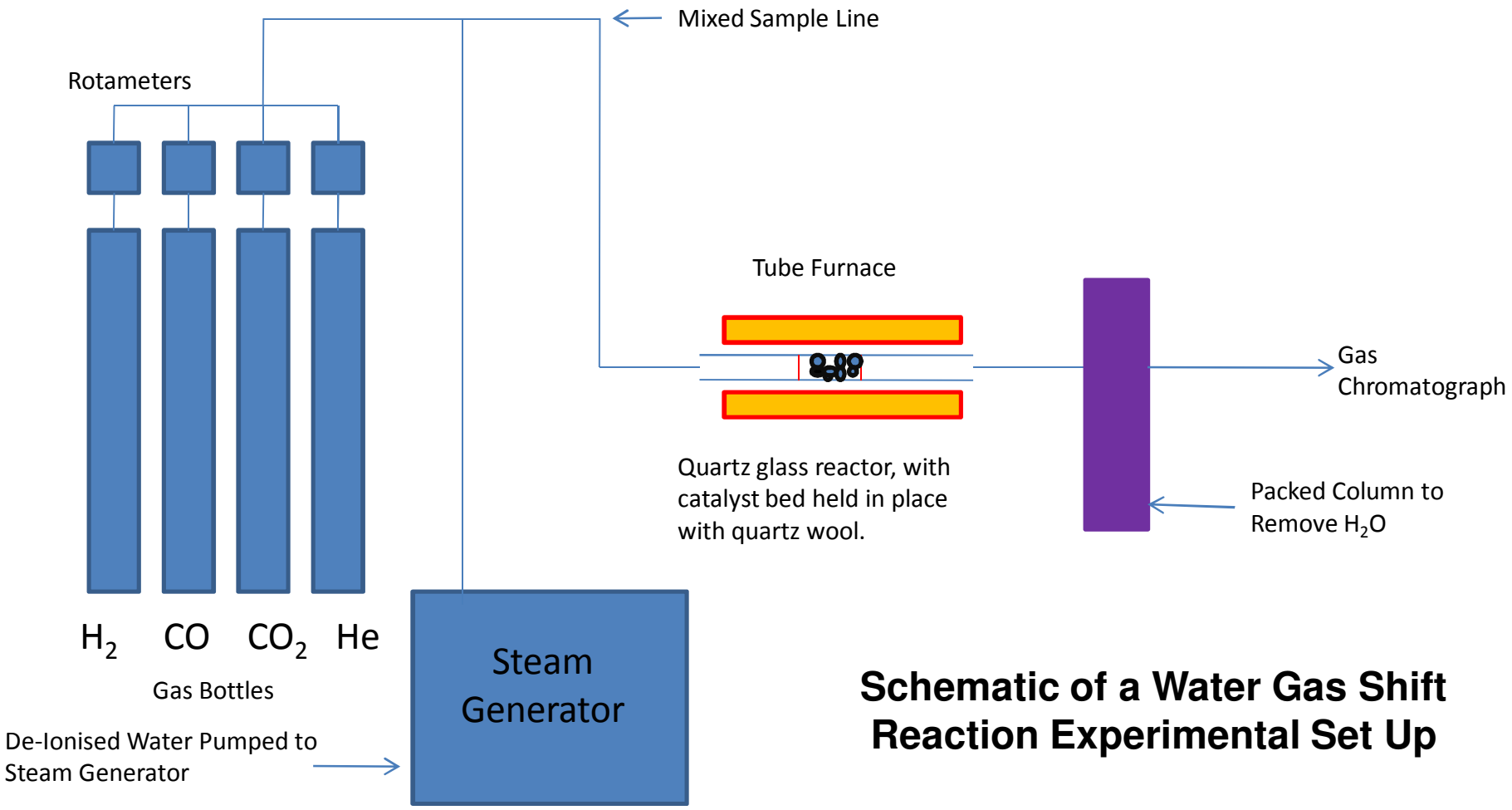
- Research groups looking at high temperature co-electrolysis of CO_2 and H_2O:
  - Risø National Laboratory, Denmark.
  - Northwestern University, USA.
  - Idaho National Laboratory, USA.
- Syngas can be converted to liquid hydrocarbon fuels via Fischer-Tropsch synthesis.
- **$CO_2 + H_2O \rightarrow H_2 + CO + O_2$**
- The mechanism for this process is not clear cut. Stoots, O'Brien and Hartvigsen (2009) propose that only H_2O is electrolysed and the CO_2 in the system reacts with the electrolysis products via a reverse water gas shift reaction.

Water Gas Shift Reaction

- **$CO + H_2O \leftrightarrow CO_2 + H_2$ $\Delta H = -41.4$ kJ mol^{-1}**
- Reversible reaction. Exothermic.
- High temperature reaction - 310°C - 450°C , Iron Oxide catalyst.
- Low temperature reaction - 210°C and 240°C, Copper/Zinc/Alumina catalyst.
- Two stage high and low temperature reactors used in the ammonia synthesis process.
- Studies investigate alternative catalysts, kinetics, mechanism and optimisation.

Experiment Design

- Baseline measurements of the water gas shift reaction as a precursor to co-electrolysis studies.
- Many experimental studies, for example, Hla *et al* (2009), Chen *et al* (2007), Choi and Stenger (2003).
- Quartz glass tube reactor with a fixed bed of catalyst.
- Gas Chromatograph to analyse the yield of reaction products.
- Testing at different temperatures and pressures.
- Safety considerations when working with Hydrogen, explosive mix with air.
- Sourcing of equipment and commissioning of the rig.



Schematic of a Water Gas Shift Reaction Experimental Set Up

Conclusions and Further Work

- Co-electrolysis is an emerging technology for the activation of CO_2.
- The process is not fully understood and further research and subsequent optimisation is required.
- The water gas shift reaction is well studied, however, experiments which consider it's possible role in co-electrolysis are required.
- Further Work:
    - Sourcing and commissioning of the test rig. Gas chromatograph testing and programming.
    - Design of experiments, this can change depending on preliminary results.
    - Economic analysis of the process and comparison with other technologies.

References

- Armstrong, E.F., Hilditch, T.P. (1920) **A Study of Catalytic Actions at Solid Surfaces. The Interaction of Carbon Monoxide and Steam as Conditioned by Iron Oxide and by Copper.** Proceedings of the Royal Society. A97, pp 265.
- Benson, E.E., Kubiak, C.P., Sathrum, A.J., Smieja, J.M. (2008) **Electrocatalytic and Homogenous Approaches to Conversion of CO_2 to Liquid Fuels.** Chemical Society Reviews. 38, pp 89-99.
- Brisse, A., Schefold, J., Zahid, M. (2008) **High Temperature Water Electrolysis in Solid Oxide Cells.** International Journal of Hydrogen Energy. 33, pp 5375-5382.
- Bustamante, F., Enick, R., Rothenberger, K., Howard, B., Cugini, A., Ciocco, M., Morreale, B. (2002) **Kinetic Study of the Reverse Water Gas Shift Reaction in High Temperature, High Pressure Homogenous System.** Fuel Chemistry Division Preprints. 47(2), pp 663.
- Choi, Y., Stenger, H.G. (2003) **Water Gas Shift Reaction Kinetics and Reactor Modelling for Fuel Cell Grade Hydrogen.** Journal of Power Sources. 124, pp 432-439.
- Ebbesen, S.D., Mogensen, M. (2009) **Electrolysis of Carbon Dioxide in Solid Electrolysis Cells.** Journal of Power Sources. 193, pp 349-358.
- Hla, S.S., Park, D., Duffy, G.J., Edwards, J.H., Roberts, D.G., Ilyushechkin, A., Morpeth, L.D., Nguyen, T. (2009) **Kinetics of High-Temperature Water-Gas Shift Reaction Over Two Iron-based Commercial Catalysts Using Simulated Coal-Derived Syngases.** Chemical Engineering Journal. 146, pp 148-154.
- Ni, M., Leung, M.K.H., Leung, D.Y.C. (2008) **Technological Development of Hydrogen Production by Solid Oxide Electrolyser Cell (SOEC)**. International Journal of Hydrogen Energy. 33, pp2337-2354.
- Rhodes, C., Hutchings, G.J., Ward, A.M. (1995) **Water-Gas Shift Reaction: Finding the Mechanistic Boundary.** Catalysis Today. 23, pp 43-58.
- Roy, S.C., Varghese, O.K., Paulose, M., Grimes, C.A. (2010) **Towards Solar Fuels: Photocatalytic Conversion of Carbon Dioxide to Hydrocarbons.** American Chemical Society Nano. 4(3), pp 1259-1278.
- Stoots, C., O'Brien, J., Hartvigsen, J. (2009) **Results of recent High Temperature Coelectrolysis Studies at the Idaho National Laboratory.** International Journal of Hydrogen Energy. 34, pp 4208-4215.
- Twigg, M.V. (1996) **Catalyst Handbook Second Edition.** Manson Publishing Ltd.
- Zhan, Z., Kobsiriphat, W., Wilson, J.R., Pillai, M., Kim, I.., Barnett, S.A. (2009) **Syngas Production By Coelectrolysis of CO_2/H_2O: The Basis for a Renewable Energy Cycle.** Energy and Fuels. 23, pp 3089-3096.