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Electrocatalytic Reduction of CO_2 and H_2O to Form Syngas

E-Futures Mini Project Specification

The activation of CO_2 is a critical area of energy research, the goal being to convert CO_2 into a useful fuel and so positively impact the global carbon balance. The electrocatalytic reduction of CO_2 and H_2O produces oxygen and a mixture of carbon monoxide and hydrogen termed syngas. Syngas can then be converted to liquid hydrocarbons via the Fischer–Tropsch process. This project investigates potential ways of carrying out the electrocatalytic step.

Contents

Aims and Objectives June/July 2010

The previous report for this study comprised a literature review covering Carbon Dioxide (CO_2), solid oxide electrolysis, co-electrolysis of CO_2 and H_2O and water gas shift reactions. Preliminary ideas for experiment design were also discussed.

Carbon sequestration technologies have attracted much attention in recent years as a way of mitigating anthropogenic carbon emissions from energy production, soil cultivation and process industry (Lal, 2008). Co-electrolysis would activate excess CO_2, using it to produce fuel.

The water gas shift reaction is a reversible reaction used in industry, including ammonia synthesis and hydrogen production. It has been cited by a number of governments and in academic papers as a route

for producing hydrogen (H_2) for use in a hydrogen economy scenario, for example, the US Department of Energy and Vlachos and Caratzoulas (2010).

For this experimental study the reverse water gas shift reaction is of interest:

$$CO_2 + H_2 \leftrightarrow CO + H_2O \tag{1}$$

It has been proposed that during the co-electrolysis of H_2O and CO_2 that only the H_2O is electrolysed producing H_2 and O_2, and subsequently the CO_2 and H_2 react to form CO and H_2O via a reverse water gas shift reaction (Stoots, O'Brien and Hartvigsen, 2009). The following equations indicate the mechanism of high temperature steam electrolysis within a solid oxide electrolyser cell:

$$H_2O + 2e^- \rightarrow H_2 + O^{2-} \tag{2}$$

$$O^{2-} \rightarrow \frac{1}{2} O_2 + 2e^- \tag{3}$$

$$H_2O \rightarrow H_2 + \frac{1}{2} O_2 \tag{4}$$

This would indicate that the reverse water gas shift reaction may be important in producing the syngas mixture required for conversion into liquid fuels, when the route of co-electrolysis is utilised.

The aim of this project is to look at the water gas shift reaction and gain baseline knowledge and measurements for future use in any co-electrolysis study. The aims for this section of the mini project are as follows:
- Designing a series of experiments and testing schedule, including operating parameters, number of tests, yield and analysis of products and safety considerations.
- Designing and obtaining a test rig for the reaction study.
- Commissioning the rig, including health and safety considerations.
- Undertaking experiments and analysing the data.

Apparatus and Experimental Set up

The initial apparatus set up would allow for the testing of both the forward and reverse water gas shift reactions:
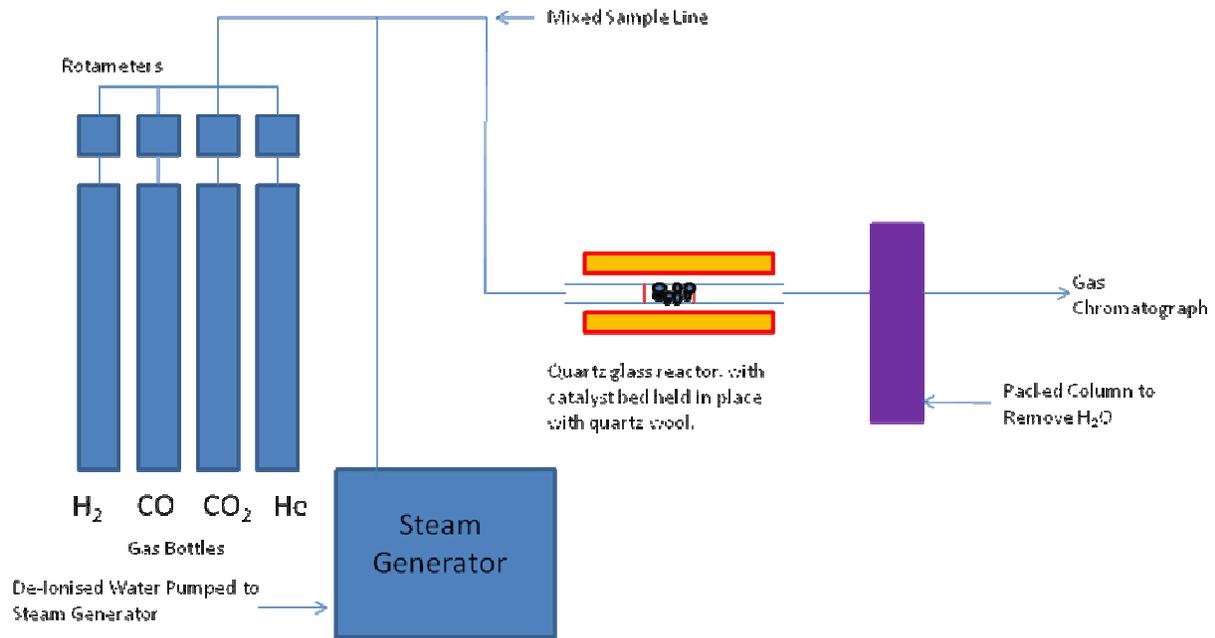
Fig 1. Schematic of Water Gas Shift Reaction Test Rig.

However, it was decided that as a starting point only the reverse water gas shift reaction would be investigated. Therefore, the steam generator and bottled CO gas were not required as part of the set up, so a revised testing rig would be made. Due to time constraints and product lead times, no experiments were able to be conducted. However, a detailed explanation of the experiments to be conducted and the apparatus used has been carried out.
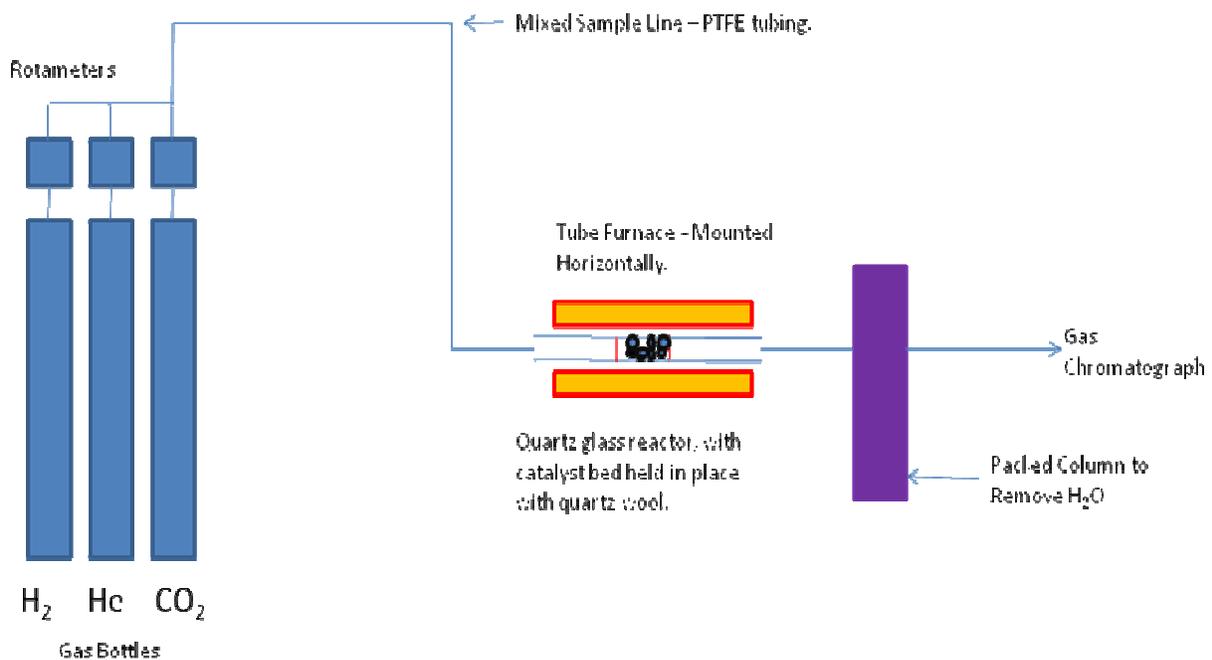
Fig 2. Revised Schematic of Water Gas Shift Reaction Test Rig.

Equipment was ordered to construct the test rig, these include:

- CO_2 cylinder – small portable cylinder and regulator.

- H_2 cylinder – small portable cylinder, regulator and flame arrestor. The flame arrestor will prevent any fire from surging back into the cylinder causing an explosion.

- Carbolite tube furnace (38mm diameter, 300mm length (250mm hot zone)) which can be mounted vertically or horizontally.

- Quartz tube reactor (see fig 3), this was commissioned from the glass blowing workshop in Chemistry.

- PTFE tubing.

- Iron-Chrome based catalyst from Alfa Aesar (COSHH form attached to the report).

- Quartz wool to hold catalyst in place within the tube reactor. The Quartz wool can also be used to pack the quartz tube into the tube furnace.

- A K type thermocouple and digital reader.

- Rotameters for each gas bottle allowing the correct flow of gas to the mixed gas steam.

Other pieces of equipment which would be useful when constructing the test rig include:

- Connectors for longer pieces of PTFE tubing, push fit fittings would be easy to use and three and four ways connectors can be bought to join the gas streams easily using PTFE tubing.   Cole Palmer http://www.coleparmer.co.uk/catalog/product_index.asp?cls=51236

- Heat resistant larger diameter (>10mm diameter) tubing to join the PTFE tubing to the quartz tube reactor, only small lengths required, a band clamp to stabilise the join on each side of the quartz tubing would also be useful.

- PTFE tape (http://www.diy.com/diy/jsp/bq/nav.jsp?action=detail&fh_secondid=9265394&ecamp=trf-005&CAWELAID=266880929) which may be useful for joints if the system appears to be leaking.

There are a number of other pieces of apparatus which are readily available in the laboratory, these include, clamp stands and general glassware.

The quartz tube was designed to fit inside the tube furnace and was specified to the following dimensions:
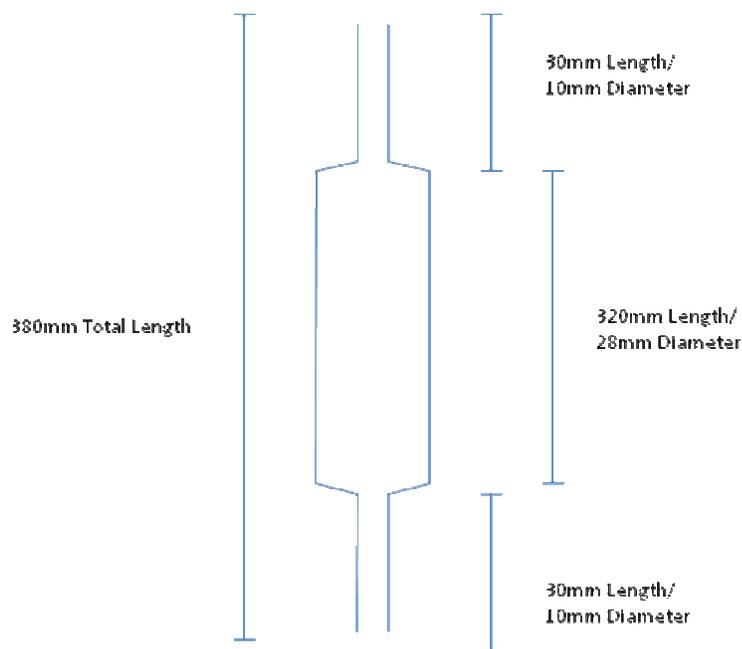
Fig 3. Quartz Reactor Tube Design.

The ends were left open with a diameter of 10mm so quartz wool and catalyst can be inserted into the tube. The quartz glass is 1.6mm with diameter measurements on Fig 3. referring to the external diameter.

The test rig should be set up as per the diagram and then tested for leaks using an inert gas, for example compressed air. The quartz reactor tube should be held with clamp stands to hold the tubing at either end and quartz wool used as insulator to stop movement in the actual tube furnace. The H_2 gas bottle should be in a fume cupboard. An extra product line which goes to a vent (fume cupboard) can be incorporated in to the system, allowing excess product gas to be vented without danger to people (CO is a toxic gas). The sample line carrying products from the reactor tube may need to be cooled before samples are injected into the GC. The thermocouple probe should be inserted into the tube furnace to check the temperature in the hot zone of the furnace.

Experimental Conditions

There are a number of different investigations which can be conducted using the same experimental set up. The variables to be changed are the temperature, presence of catalyst and reactant gas ratios. Regarding temperature, the iron chrome catalyst is a high temperature shift catalyst, indicating that it will perform effective catalysis between 310°C and 450°C (Rhodes *et al*, 1995). However, the operating temperatures of solid oxide fuel cells are approximately 700°C - 1000°C (Brisse, Schefold and Zahid, 2008). There are safety issues associated with hot gas mixtures which could potentially become explosive, so the experiment should be treated with caution. It may be more suitable to use stainless steel piping if high temperatures are to be used consistently, as although the heat throughout the system will dissipate, PTFE has a melting point of 327°C.

The residence time in the tube and flow rate of gases can be estimated using the Ideal Gas Law; it is thought that the residence of gas in the reactor should be 1 s or 2 s:

Volume of the Reactor $\pi r^2 h$ [5]

Ideal Gas Law $PV = nRT$ [6]

P – Pressure (Pa)
V - Volume (m^3)
n - Number of Moles
R - Constant (8.314472)
T – Temperature (K)
1 Mol of Gas (STP) = 22.4 litres

Total Gas Mixture					
Temperature			mol of Gas	1 s Residence Time Flow Rate	2 s Residence Time Flow Rate
(°C)	(K)	mol of Gas in the Reactor	(ml)	(ml/min)	(ml/min)
200	473.15	0.00474	106.16	6369.42	3184.71
250	523.15	0.00429	96.01	5760.67	2880.33
300	573.15	0.00391	87.64	5258.12	2629.06
350	623.15	0.00360	80.60	4836.22	2418.11
400	673.15	0.00333	74.62	4477.00	2238.50
450	723.15	0.00310	69.46	4167.45	2083.73
500	773.15	0.00290	64.97	3897.94	1948.97
550	823.15	0.00272	61.02	3661.17	1830.59
600	873.15	0.00257	57.53	3451.52	1725.76

Table 1. Example Flow Rate Table for Variable Temperatures.

The water gas shift reaction is a 1:1 ratio; therefore gas mixtures at this level or in excess will be suitable. Rotameters have a conversion factor depending upon the gas used, for example, CO_2 -1.23, He – 0.37 and H_2 – 0.26; conversion factors are calculated at standard temperature and pressure. The helium carrier gas with make up the bulk of the gas mixture. An example gas mixture would be 70% He and a 50:50 split of H_2 and CO_2 for the remaining 30%. Examples are included on the attached spreadsheet.

As a control, the experiment can be run omitting the catalyst just using a heated gas mixture, as a specific shift catalyst will not be present in a solid oxide electrolysis cell. When using the catalyst a set weight of catalyst powder, for example, 1g per experimental run will need to be used. The catalyst may be ground using a pestle and mortar to increase the surface area for reaction, this may not be necessary.

The product gas stream needs to be dried and cooled before being injected into the GC, a desiccant column would remove unwanted water but would not measure the amount produced. An estimate can be made if the amount of CO in the product stream is measured. A condenser or other method of

cooling and collecting the water could be used. However, the solubility of the gases in water may be a problem.

Gas Chromatograph Set up

The GC is an 8000 series, fitted with a Porapak Q column and flame ionization detector. A sample can be injected at a suitable interval, for example, every 3 minutes, throughout the test time, with excess sample products safely vented. CO would be the most suitable gas to test for initially. There are a number of papers which deal with the detection of CO using a GC. Kaminski *et al* (2003) modify the GC adding a short molecular sieve 5A column and a catalytic hydrogenation reactor (methanizer). The CO is separated from O_2 before entering the methanizer and the amounts calculated accordingly depending on the chromatograms and calibration data.

It would be useful to also test for the reactant gases, allowing yields to be calculated definitively. At present Helium is used as the carrier gas.

Safety Concerns

There are a number of safety issues associated with this investigation. H_2 is an extremely flammable gas and CO is toxic. The Iron Oxide based catalyst is also toxic and needs to be handled with caution. The elevated temperature may need to be considered, PTFE tubing may not be the best option for sample lines, with stainless steel more suitable. Good laboratory practice should be followed, will all trip hazards, for example, trailing pipes, labelled or moved.

COSHH forms and MSDS sheets are attached as appendices.

Discussion and Conclusions

Due to time constraints and equipment issues, no laboratory work was able to be carried out. The equipment is in place for a student to undertake the work. Further to the short tests outlined above there are a number of other tests which would be useful in understanding the role of the water gas shift reaction in co-electrolysis. A comparison of the results from these tests and tests on the product yields from solid oxide co-electrolysis may provide an insight into how much the water gas shift reaction contributes to the process of syngas production. Running tests under similar conditions would allow for scientific comparison. Changing the pressure of the experiment may also be undertaken.

An economic comparison of this activation technology and storage technologies would be an interesting piece of work. This comparison will change depending on the efficiency of the electrolysis and specific technology used for sequestration.

References

Brisse, A., Schefold, J., Zahid, M. (2008) **High Temperature Water Electrolysis in Solid Oxide Cells.** International Journal of Hydrogen Energy. 33, pp 5375-5382.

Kaminski, M., Kartanowicz, R., Jastrzebski, D., Kaminski, M.M., (2003) **Determination of Carbon Monoxide, Methane and Carbon Dioxide in Refinery Hydrogen Gases and Air by Gas Chromatography.** Journal of Chromatography A. 989, pg 277-283.

Lal, R. (2008) **Carbon Sequestration**. Philosophical Transactions of the Royal Society B-Biological Sciences. 363(1492), pg 815-830.

Rhodes, C., Hutchings, G.J., Ward, A.M. (1995) **Water-Gas Shift Reaction: Finding the Mechanistic Boundary.** Catalysis Today. 23, pp 43-58.

Stoots, C., O'Brien, J., Hartvigsen, J. (2009) **Results of recent High Temperature Co-electrolysis Studies at the Idaho National Laboratory.** International Journal of Hydrogen Energy. 34, pp 4208-4215.

US Department Of Energy (2008) **Hydrogen Production Natural Gas Reforming** [online] Available From: http://www1.eere.energy.gov/hydrogenandfuelcells/production/natural_gas.html

Vlachos, D.G., Caratzoulas, S. (2010) **The Roles of Catalysis and Reaction Engineering in Overcoming the Energy and Environmental Crisis**. Chemical Engineering Science. 68(1), pg 18-29.