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Button Cell SOEC Co-Electrolysis of CO_2 and H_2O

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Summary

A review has been carried out to provide background knowledge of Solid Oxide Electrolysis Cells (SOECs) it was determined that SOECs produce ultra high purity (UHP) hydrogen, suitable for use in situations where the electricity grid cannot supply energy effectively such as automobiles and other forms of transport or remote energy users (Stoots, O'Brien et al. 2010). Such SOECs can also be used as an intermediate energy storage device which would complement intermittent energy sources such as wind and tidal power (Elangovan, Hartvigsen et al. 2007). These SOFCs can also be used to process CO2 in a carbon neutral manner. In this way syngas can be generated from water (steam) and carbon dioxide.

The purpose of this two month placement was to design, build and run an electrolysis button cell test rig which could be used in the future by other PhD students. This has been partially completed due to reasons discussed in the report. The rig has been designed and experimental procedures have been set in place, along with health and safety procedures.

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Background

SOECs make run at a high operating temperature of around 700-1000 °C (Jensen, Larsen et al. 2007). High cell temperature (thermal energy input) increases the efficiency of the cell by minimizing the Gibbs free energy of the cell reaction. A simple electrolysis cell produces Hydrogen and Oxygen from steam, this reaction can be described as follows in equations 1 to 3 (Elangovan, Hartvigsen et al. 2007):

$$H_2O + 2e^- \rightarrow H_2 + {O_2}^- \quad \text{Steam Electrode Reaction} \qquad [1]$$

$$O^{2-} \rightarrow \frac{1}{2}{O_2}^- + 2e^- \quad \text{Air Electrode Reaction} \qquad [2]$$

$$H_2O \xrightarrow{energy} H_2 + \frac{1}{2}O_2 \qquad [3]$$

Electrolysis of steam can also be modified to coelectrolysis of water and carbon dioxide as shown in equation 4 (Stoots, O'Brien et al. 2010). This is one carbon neutral method of making some use of CO_2.

$$H_2O + CO_2 \xrightarrow{electricity,heat} H_2 + CO + O_2 \qquad [4]$$

This mini-project will focus on the design, building and testing of a small experimental rig for the testing solid oxide fuel cells (SOFCs) to be used in reverse for the coelectrolysis of steam and carbon dioxide at elevated temperature. Cells purchased for this work were button cell size, less than 30mm in diameter.

Experimental data from the literature

In order to generate results comparable with the literature it was decided that the experimental equipment would use similar gas flow rates and concentrations to those published for use with button cells. Performance characteristics could then be compared between steam electrolysis and coelectrolysis of steam and carbon dioxide.

Paper	Cell active area	Furnace Temp. (°C)	N2 – flow (sccm)	H2 - flow (sccm) / component %	CO2 - flow (sccm) / Component %.	H20 - flow (sccm)/ component %	CO out- flow (sccm)/ component%
(Stoots , O'Brien et al. 2010)	2.5 cm^2	800	35	4/5-12%	8/12-17	10.7/	/2-5%

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(Stoots, O'Brien et al. 2009)	2.5cm^2	800	35	4/5-12%	8/12-17	10.7/	/2-5%
(O'Brien, Soots et al. 2007)	2.5cm^2	800	35 50 40	4/5-12% 3/2-9% 8/8-13%	8/17-12% 6/10-6% 8/4-7%	10.7 7.27 2.93	/5-2% /4-1% /21-7%

Table 1: Gas flow rates for SOEC design

Table 1 shows the available information regarding gas flow rates for co-electrolysis of CO2 and steam using SOECs. One of the flow rates has been quoted in three different papers since this is optimised for the size of button cell that has been used (2.5 cm^2 active area). As such this ratio of flow rates was chosen as the starting point of further experiments.

Experimental Design

It was decided that similar apparatus to that used in previous experiments ((O'Brien, Soots et al. 2007; Stoots, O'Brien et al. 2009) should be built and tested so that the experiments could be modified and optimized in future for further experimental work. Furthermore, experiments have already been carried out in the University of Sheffield's Chemical and Process Engineering Hydrogen Lab using Yttrium Stabilized Zirconia button cell membranes with other gasses. As a result some of the experimental equipment could be modified for the purpose of this experiment.

Other equipment had to be sourced specifically for the experiment including rotameters for the measurement of gasses provided to the electrolysis cell. These rotameters were sourced from Omega's flow measurement department (industrial measurement equipment suppliers) according to the flow rates required. Two FL3607ST rotameters were purchased for the measurement of steam and carbon dioxide gas. Two FL3845G type rotameters were also purchased for the measurement of nitrogen and hydrogen

Figure 1 illustrates the experimental apparatus planned to be used for syngas production. The reaction of interest occurs within a temperature controlled furnace inside of which a Solid Oxide Electrolysis Cell (SOEC) is held with two quartz membrane holders. Each of the membrane holders also delivers the gas supply to the experiment. Sufficiently long tubes are incorporated into the quartz glassware to allow the transfer of heat to the gasses form the furnace before reaching the membrane reaction surface. A graphical description of this work can be seen in Appendix figure 2.

The membrane holders are sealed to the SOEC membrane with gold foil gaskets to eliminate gas leakage from the system and must be leak checked and fully sealed before the experiment

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commences. The pressure test is carried out by passing inert gas through the permeate and the feed side of the membrane holder then measuring the difference between the gas delivery and exhaust flow rates. If there is a difference the equipment must be extracted from the furnace after cooling and the seal must be adjusted until air tight. Once leak checks have been completed and the apparatus has been correctly inserted into the furnace its entrance must be lagged to reduce heat loss.

Detailed calculations were completed to determine the Reynolds number of the fluid flow across the membrane holder in order to check that the flow was turbulent (Re>2000) and that mixing had been optimised. To complete this calculation the viscosity of the fluid has to be calculated as a compound viscosity with multiple components at elevated temperature. The compound density had to be determined in a similar way too. This information was then compiled into a spreadsheet, yielding that the flow was in fact turbulent, so mixing could not easily be enhanced by increasing the volumetric flow rate.

Cell Preparation

The button electrolysis cells have to be prepared before use in order to reduce the Nickel Oxide to Nickel. In order to reduce these cells safely and effectively they can be placed in a furnace, which is constantly purged with Nitrogen gas until the furnace reaches 900 ^{o}C. Once the furnace is heated Hydrogen gas is fed into the furnace with a concentration less than 4% in air (5% is the lower explosive limit in air) so that when the excess hydrogen exits the furnace it does not explode upon contact with air due to its high temperature. After two hours the furnace temperature is ramped down slowly to prevent cell fracture.

Methodology

This methodology has been designed around the specific experiment to be run using SOEC button cells, however inspiration was taken from previous work (Atkin 2009)

1. Connect the apparatus as described in the attached experimental apparatus diagram (pdf. file: SOEC apperatus_09072010.pdf). Before the first experiment ensure that all of the gas lines have been pressure checked with leak spray.
2. Attach the electrolysis cell the multi-meter with the positive terminal attached to the permeate side and the negative terminal to the feed side.
3. Turn on the lab computer, opening the oxygen analyser and power supply control software. Set the maximum voltage and time sweep as required in the power supply software. Remember the power supply software times out at 5400 seconds before which the data must be saved to file. The power supply software internal window (not the main program!) must then be closed and re-opened to record new data, appending to the old file. The O_2 sensor software runs out of power at about 3600 seconds, and so the same procedure must be carried out for this too.

4. Switch on the Furnace, set the temperature and turn on power to the heating element and the furnace to 750 ^{o}C for pretesting to ensure that the full system is functioning. Carry out the final test at 800 ^{o}C.
5. Apply a 17 ml/min flow rate of Nitrogen gas to the feed side and permeate side of the membrane for ten minutes prior to running the full test.
6. Feed **10.7 ml/min of steam, 35 ml/min N_2, 4 ml/min H_2 and 8 ml/min CO_2** to the membrane. Ensure that the pressure of the gasses on either side of the membrane is equal so to reduce the chance of deforming the membrane.
7. Set the power supply voltage to the voltage required. If this is the first time of operation start from zero volts and ramp up taking care to avoid the cell break down voltage. If continuing from previous work on the experimental rig, proceed from the last test point.
8. Allow the voltage cycle to repeat until the full set of conditions has been applied. Ensure that the software is renewed as described whilst running this process. Ensure that the gas pressures in the cylinders does not decrease sufficiently to cause a change in permeate or feed gas flow rates. Record the start and end time of the experiment along with the correlating data point number in each respective experimental software.
9. Once the experiment has been completed isolate all of the gas supplies apart from nitrogen. Purge the cell with nitrogen for ten minutes then switch off the furnace and nitrogen supply.
10. Save O_2 and power supply data to file systematically.

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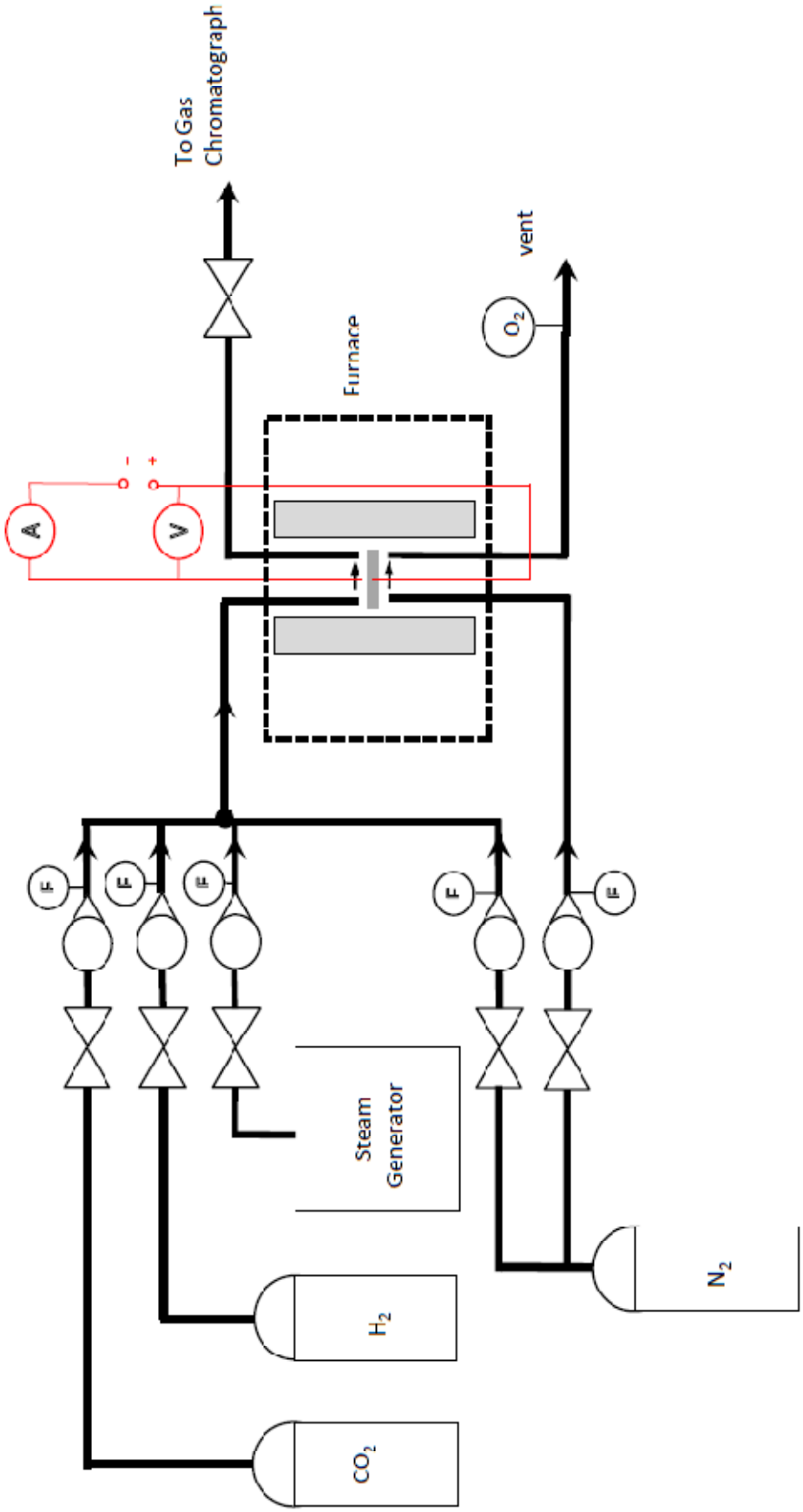

Figure 1: Design of the SOEC Syngas production apparatus

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Results

Due to illness in the early stages of the project and the fact that some of the component delivery times were over two weeks it has been difficult to assemble apparatus in the allotted two month time period, which was extended in order to complete the project to a satisfactory level.

As such the experiment and apparatus has been designed, and some of the preliminary characteristics of the apparatus have been determined through calculation. The rotameters for the delivery of gas to the feed side have been assembled with their stands and connected using Tygon tubing.

It was not possible to run produce good quality steam from the steam generator as the steam iron steam generator used delivered steam through an $1/8^{th}$ inch diameter copper pipe with a low mass flow, as such giving high heat losses. University technicians deemed the steam generator unsafe because of the lack of control of its high temperature heating filaments (up to 500 ^{o}C) hence no further work in calibrating the steam equipment was possible.

In discussions with the technicians it became evident that the best way to measure the quality of the steam was to measure its temperature and pressure (in order to use standard steam look up tables). Through conversations with instrument suppliers it became evident that rotameters were not suitable for steam measurement as their glass slips shatter. No other measurement alternative was suggested by the instrument suppliers engineering department for small steam quantities.

It was decided that experiments using steam equipment would be postponed until the delivery of a new steam generator (after the termination of this project)

Conclusion

This report documents the current state of work undertaken to develop an electrolysis cell test rig, however due to time constrictions and illness during the project the original aim of running the rig before the project completion date has been unachievable. The test rig is at a state ready to be assembled with a steam generator. Information has been gathered to determine how to run the experiment, the experimental equipment has been sized and schematics produced. Flow meters have been assembled and connected to one another. This experiment should run with relatively little work in the future, after the cells have been reduced, the steam generator delivered and the whole experiment assembled as a system.

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References

Atkin, I. (2009). Improvement of sulphur dioxide yield from the sulphuric acid thermal decomposition process by membrane separation. Department of Chemical and Process Engineering. Sheffield, The University of Sheffield. **Submitted for the degree of Doctor of Philosophy:** 236.

Elangovan, S., J. J. Hartvigsen, et al. (2007). "Intermediate Temperature Reversible Fuel Cells." International Journal of Applied Ceramic Technology **4**(2): 109-118.

Jensen, S. H., P. H. Larsen, et al. (2007). "Hydrogen and synthetic fuel production from renewable energy sources." International Journal of Hydrogen Energy **32**(15): 3253-3257.

O'Brien, J. E., C. M. Soots , et al. (2007). "High-Temperature Co-Electrolysis of Carbon Dioxide and Steam for the Production of Syngas; Equilibrium Model and Single-Cell Tests." International Topical Meetin on the Safety and Technology of Nuclear Hydrogen **INL/CON-07-12102**.

Stoots, C. M., J. E. O'Brien, et al. (2010). "High-temperature electrolysis for large-scale hydrogen production from nuclear energy - Experimental investigations." International Journal of Hydrogen Energy **35**(10): 4861-4870.

Stoots, C. M., J. E. O'Brien, et al. (2009). Idaho national laboratory experimental research in high temperature electrolysis for hydrogen and syngas production.

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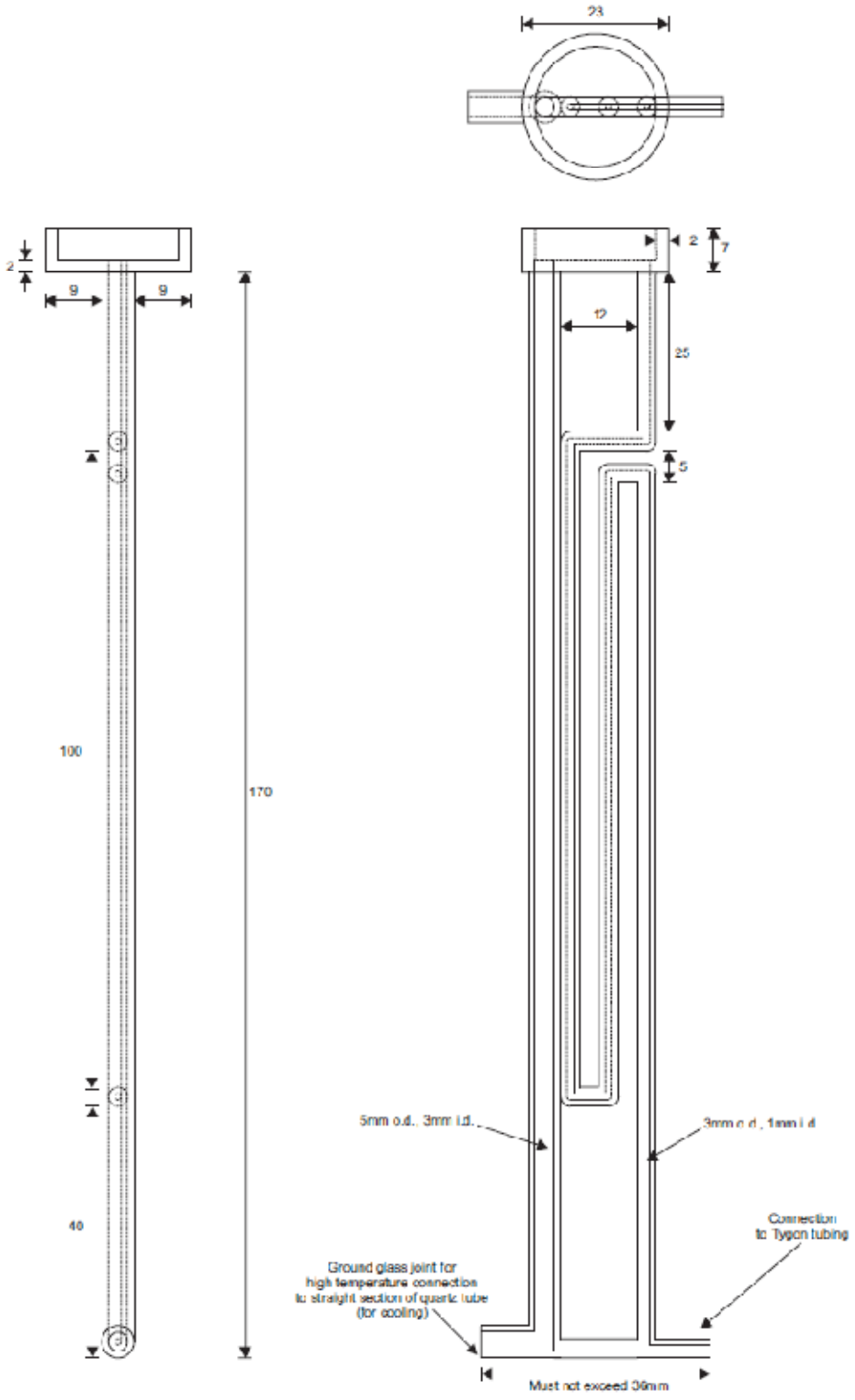

Appendix Figure 2: Quartz membrane holder equipment, two of these are held end to end in order to supply gas to the membrane. The junction between this glass ware and the membrane is sealed using gold foil. (Atkin 2009)

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GENERAL RISK ASSESMENT

Name: Jonathan Knapton

TASK OR ACTIVITY: High temperature Co-electrolysis of steam and CO_2 using Solid Oxide Electrolysis Button Cells

LOCATION: B9 **Expected duration of work** 2-3 weeks

PERSONS AT RISK Staff (**1**) Postgraduates (**1**) Undergraduates (0) Other(0)

List Persons: Jonathan Knapton, other persons working in lab B9 at the time

Maximum number Staff / Students / Others at risk

HAZARD IDENTIFIED	Risk of Injury & Details	Control Measure & Procedures To Reduce Risk of Injury	Final Risk Rating
Biological	n/a	n/a	n/a
Chemical	**H_2:** explosive/flammable between 4-75% in air, compressed gas, asphyxiant at high concentrations. **CO:** asphyxiation, flammable in air over a very wide range (reacts violently with oxygen diflouride and barium peroxide) **$H_20_{(g)}$:** burns **CO_2:** causes asphyxiation in high concentrations, compressed gas. **N_2:** asphyxiation at high	Carry out experiment in fume hood, wear heat proof gloves when handling the furnace. Wear a full length lab jacket. Do not breathe in any vapours. Pressure-test all equipment before experiments commences to reduce chemical Leaks. Leak test after assembly in the fume cupboard and after each adaption to the apparatus.	

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	concentrations, compressed gas.		
Dust	n/a	n/a	n/a
Electrical	Electrocution, fire	PAT tested equipment in good working order	Low
Explosion	Pressure up to 2 bar (multiple non flammable gasses and Hydrogen)	Vent non flammable gasses in fume hood if required. Visually check H_2 flow rate are correct during experiment in order to mitigate explosive risk. Visually check non-flammable gas pressures before use, vent safely if required	Low
Fire	Furnace (up to 800^{o}C), Hydrogen	Heat proof gloves to be used when handling the furnace under cooling conditions. In the event of a fire inform the fire brigade immediately of the hydrogen supply.	Low
Compressed Gas	Compressed CO_2 gas cylinder, whose failure are of a chemical and mechanical nature.	Ensure safely secured in appropriate stand, fitted with working regulator and appropriate delivery pipes for pressure. Do not tamper with bottle, shut off valve or regulator. If the regulator or shut off valves are stiff/showing signs of misuse/worn/difficult to use return equipment to supplier.	Low
Laser, UV, or Radiation	n/a	n/a	n/a
Mechanical	n/a	n/a	n/a
Noise	n/a	n/a	n/a
Physical	Risk of burns from heated equipment	Ensure that heated equipment is lagged to reduce surface temperature and that hazard identification signs are present.	n/a

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Pressure	Pressure up to 2 Bar	Visually check pressure, vent system safely if required. Leak test pressurised lines, ensure that all gas supply lines and connections are correctly specified to deal with relevant pressures.	
Slip, Trip & Falls	n/a	n/a	n/a
Other please specify!			

Activity Description: Co-Electrolysis of CO_2 and H_2O (gas) at elevated temperatures up to and including 900 ^oC. Solid Oxide Electrolysis Cells (of button type) will be held inside of the cylindrical furnace and housed inside a fume hood. Gasses are fed across the fuel cell surface using quartz tubes, sealed to the SOEC using gold sheet/graphite gaskets. Pressure is maintained over the gasket by means of applied weight which compensates for thermal expansion of the test apparatus inside the furnace.

The experimental control variables are furnace temperature, cell voltage and individual gas flow rates.

Required Personal protection equipment identified:

Heat proof gloves will be used when working handling the furnace. Goggles and a lab jacket must be worn whilst running the experiment. The fume hood must be closed whilst operating the experiment.

Could the procedure be made any safer? No

Any Special Accident requirements? No

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Level of Supervision required: **Category C**

Named supervisory staff if required

Dr Rachael Elder

Will the task or activity also be undertaken outside normal working hours? No

OPERATING PROCEDURES

RESEARCH TITLE: High temperature Co-electrolysis of steam and CO_2 using Solid Oxide Electrolysis Button Cells

SUPERVISOR: Dr Rachael Elder

OPERATORS: Jonathan Knapton

COULD THE APPARATUS BE LEFT RUNNING UNATTENDED ? YES / NO

HOW MANY PERSONNEL ARE REQUIRED FOR NORMAL START UP ? …….. /SHUTDOWN …….

EMERGENCY PHONE NUMBERS……

EMERGENCY SHUT DOWN PROCEDURE

1. **Isolate Hydrogen Supply**
2. **Isolate Power to the furnace**
3. **Isolate electrical power to the steam generator**
4. **Isolate power supply to steam heater**
5. **If safe to do so, increase nitrogen flow rate.**

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START UP PROCEDURE

Pleliminary Checks

Leak checks are to be carried out all gas lines and the membrane gasket seal, Electrical conductivity checked, furnace must be lagged after insertion of apparatus. Carry out all other preliminary checks before running the experiment, allowing half a day to perform full leak checks on the system. Ensure that Dr Elder is present during preliminary shake down testing.

Experimental procedure.

11. Connect the apparatus as described in the attached experimental apparatus diagram (pdf. file: SOEC apperatus_09072010.pdf). Before the first experiment ensure that all of the gas lines have been pressure checked with leak spray.
12. Attach the electrolysis cell the multi-meter with the positive terminal attached to the permeate side and the negative terminal to the feed side.
13. Turn on the lab computer, opening the oxygen analyser and power supply control software. Set the maximum voltage and time sweep as required in the power supply software. Remember the power supply software times out at 5400 seconds before which the data must be saved to file. The power supply software internal window (not the main program!) must then be closed and re-opened to record new data, appending to the old file. The O_2 sensor software runs out of power at around 3600 seconds, and so the same procedure must be carried out for this too.
14. Switch on the Furnace, set the temperature and turn on power to the heating element and the furnace to 750 ^{o}C for pretesting to ensure that the full system is functioning. Carry out the final test at 800 ^{o}C.
15. Apply a 17 ml/min flow rate of Nitrogen gas to the feed side and permeate side of the membrane for ten minutes prior to running the full test.
16. Feed **10.7 ml/min of steam, 35 ml/min N_2, 4 ml/min H_2 and 8 ml/min CO_2** to the membrane. **Nitrogen quantities to the feed and permeate side???.**
17. Set the power supply voltage to the voltage required. If this is the first time of operation start from zero volts and ramp up taking care to avoid the cell break down voltage. If continuing from previous work on the experimental rig, proceed from the last test point.
18. Allow the voltage cycle to repeat until the full set of conditions has been applied. Ensure that the software is renewed as described whilst running this process. Ensure that the gas pressures in the cylinders does not decrease sufficiently to cause a change in permeate or feed gas flow rates. Record the start and end time of the experiment along with the correlating data point number in each respective experimental software.

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19. Once the experiment has been completed isolate all of the gas supplies apart from nitrogen. Purge the cell with nitrogen for ten minutes then switch off the furnace and nitrogen supply.
20. Save O_2 and power supply data to file systematically.

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NORMAL OPERATIONAL

SHUT DOWN PROCEDURE

1. Flush the feed side of the apparatus with pure nitrogen for 10 minutes with no applied voltage

2. Stop gas flows

3. Switch furnace off

COSHH FORM B

February 2002

MAJOR ASSESSMENT OF HEALTH RISK ASSOCIATED WITH PROPOSED EXPERIMENTS

COSHH Ref. No.	*Laboratory No.* ***B9*** *Location:* ***Hadfield Building***	Risk Rating (H= High, M= Medium, L= Low) **M**
Title of Experiment/Procedure: **High Temperature Co-electrolysis of steam and CO_2 using Solid Oxide Electrolysis Button Cells** *Aim:* **Preliminary Experiment to determine running characteristics**		*Personnel involved:* *(incl. status)* **Dr R. Elder (Supervisor)** **J. Knapton (PhD student)**
Substances (including quantities): Hydrogen, H_2 **(4 ml/min input,**		*Hazards Identified:* H_2: explosive/flammable between 4-75% in

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16.5ml/min predicted output if fully reacted srt&p) Carbon Monoxide, CO **(6.8 ml/min predicted output if fully reacted)** Steam, $H_2O_{(g)}$, (11 ml/min input) Carbon Dioxide, CO_2, (8 ml/min input) Nitrogen, N_2 (35 ml/min) Oxygen, O_2 **(9.0 ml/min)** **These quantities need to be checked**	air, compressed gas, asphyxiant at high concentrations. CO: asphyxiation, flammable in air over a very wide range (reacts violently with oxygen diflouride and barium peroxide) $H_20_{(g)}$: burns CO_2: causes asphyxiation in high concentrations, compressed gas. N_2: asphyxiation at high concentrations, compressed gas.

Information sources:

http://cartwright.chem.ox.ac.uk/hsci/chemicals/hydrogen.html

http://www.energas.co.uk/downloads/015.pdf

http://www.vngas.com/pdf/g112.pdf]

Is there a less hazardous substance? No

If so, why not use it?

Control Measures to be adopted:

Appropriate PPE, i.e. gloves, eye protection, lab coat. Experiments to be carried out in fume hood. Carbon Monoxide alarm fitted outside of fume hood. Ensure Hydrogen/air, Hydrogen O_2 ratio in every instance is outside of flammability limits.

Required checks and their frequency, on the adequacy and maintenance of control measures during the course of the experiment:

Gas temperature will be monitored and recorded using computerised data-loggers, gas flow rates will be measured using rotameters. Output gas composition will be monitored using oxygen analysers and gas chromatography equipment.

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Is this procedure authorised to be done outside normal working hours: No

Is this procedure authorised to be left unattended: No Out-of-hours: No

Disposal procedures during and at end of experiment:	*Estimated cost of disposal £0*
Vent surplus gasses into fume hood, ensuring hydrogen: oxygen ratio is beyond limits of flammability or explosion.	

Name of Assessor:	*Name of Counter signatory:*	*Departmental Safety Officer*
Jonathan Knapton		
Status of Assessor:		
PhD Student		
Date:	*Date:*	*Date:*
13th July 2010		
Signed:	*Signed:*	*Signed:*

Emergency Procedures

If any of the substances or procedure identified overleaf is likely to pose a special hazard in an emergency, then identify below the action to be taken:

Spillage/uncontrolled release:

CO uncontrolled release. Evacuate Lab if carbon monoxide alarm activated.

H_2, N_2, CO_2 uncontrolled release: lab evacuation may be required depending on volume of release.

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Fire: Evacuate Lab if necessary, if safe to do so close all gas valves and isolate furnace power supply. Inform fire brigade of gasses present in the lab.
If personnel are affected (fume, contamination etc.) treatment to be adopted: H_2,N_2,CO_2, CO asphyxiation: remove patient to fresh air if safe to do so, if breathing has stopped, immediately give artificial respiration and immediately seek medical help. If it is not safe to enter laboratory immediately seek emergency services.