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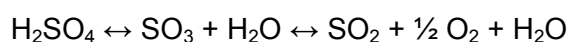
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# Improving Sulphur Dioxide Yield in the Sulphuric Acid Thermal Decomposition Process through the Application of High Temperature Ceramic Membrane Separations

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## 1 Introduction

Sulphuric acid thermal decomposition is part of a number of promising thermochemical water splitting cycles, including the hybrid sulphur (HyS) [1, 2] and sulphur iodine (SI) [3] cycles. The decomposition reaction is endothermic and occurs in two stages, as seen in the reaction equation below [4]. Sulphur trioxide decomposition to sulphur dioxide exhibits a poor yield in the temperature range accessible by conventional heat sources. As such the reaction must be carried out at very high temperature ( $\geq 700^{\circ}\text{C}$ ) in order to achieve an appreciable yield of sulphur dioxide [5].



It is proposed that by preferentially removing oxygen from the equilibrium reaction products, the equilibrium will be in effect shifted, allowing super-equilibrium  $\text{SO}_2$  yields at a given temperature. This would allow conventional heat sources such as current nuclear reactors to be used, as well as increasing the yield where a higher temperature heat source, e.g. solar energy, is used. This work investigates the feasibility of preferentially removing oxygen through the use of oxygen separation membranes.

## 2 Membrane Simulations

A membrane separation stage for the preferential removal of oxygen could take two forms:

- Standard catalytic reactor, with a membrane separator downstream and retentate recycling
- Use of a catalytic membrane reactor (CMR) in lieu of the standard catalytic reactor

A series of simulations were carried out in ProSimPlus to investigate both membrane reactor types, operating with both dense membranes and porous Knudsen regime membranes. These simulations showed that use of a selective separation process can increase yield at a given temperature. Figure 1 shows the ProSimPlus flowsheet for a downstream membrane separation as well as results for the same system. The 'F' values represent the selectivity of the dense membranes. Porous membranes which exhibit Knudsen separation produce a small yield improvement, however dense oxygen separation membranes produce significantly greater yield increases. The simulations also showed that CMRs produce greater  $\text{SO}_2$  yield improvements than the downstream separation process. Given this evidence, use of a CMR may seem preferable to using downstream separation. However, a

CMR may be significantly more difficult to engineer in practice and hence the smaller  $\text{SO}_2$  yield improvement offered by the downstream separation process may be more economic.

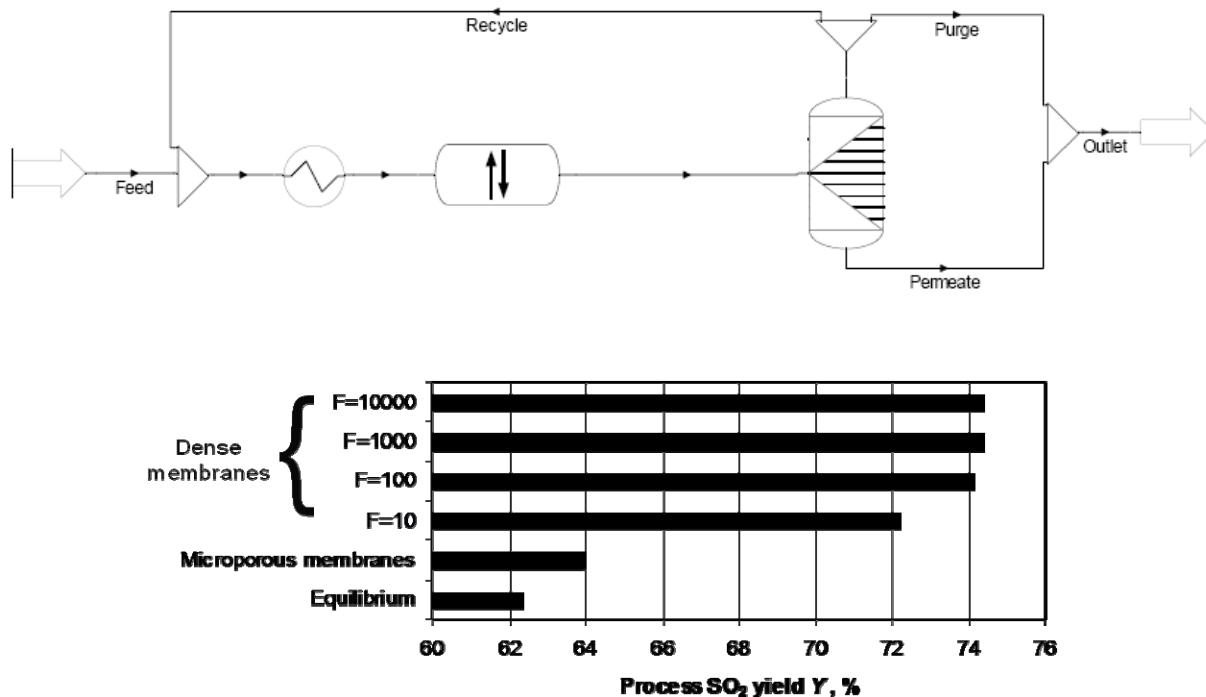


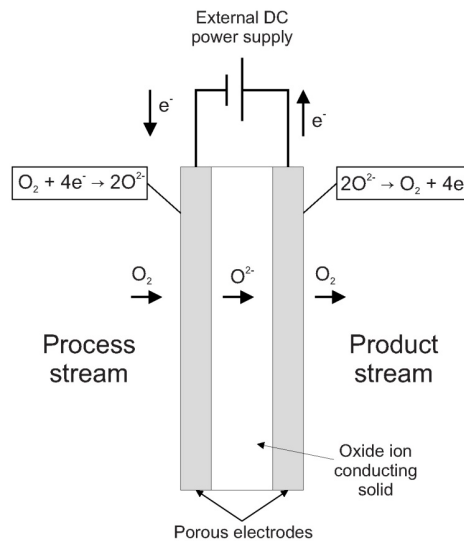
Figure 1: The ProSimPlus flowsheet and some results for the downstream membrane separation. F values indicate the selectivity of the membrane.

### 3 Membrane Material Selection

A review of electrically driven and mixed ion/electron conducting dense membranes was carried out and a number of candidate materials were identified. Calculations were performed in *HSC Chemistry* to evaluate the process stability of the candidate materials under the harsh process environment. Yttria and zirconia were both calculated to be stable in the temperature range of interest, except for zirconia at  $<750^\circ\text{C}$  and 20 bara. Because of this, YSZ (yttria-stabilised zirconia) is considered to be a good candidate material and was selected for experimental testing. Based on the results of the equilibrium calculation, the majority of other metal oxides encountered/employed in ion conducting or MIEC membranes are not suitable for use with a sulphuric acid thermal decomposition process. The equilibrium data for silica strongly suggests it will be stable in the reaction environment, confirming the widespread use of quartz for high temperature apparatus.

YSZ belongs to a group of solid electrolytes that conduct oxygen ions at high temperatures, but which conduct electrons poorly. In order for the membrane to function, an external electron conduction path must be provided. Molecular oxygen from the process stream dissociates on contact with the porous cathodic membrane surface. The adsorbed atomic oxygen then moves across the electrode surface to the boundary with the electrolyte, at which point it is incorporated into the electrolytic membrane. Following transport through the

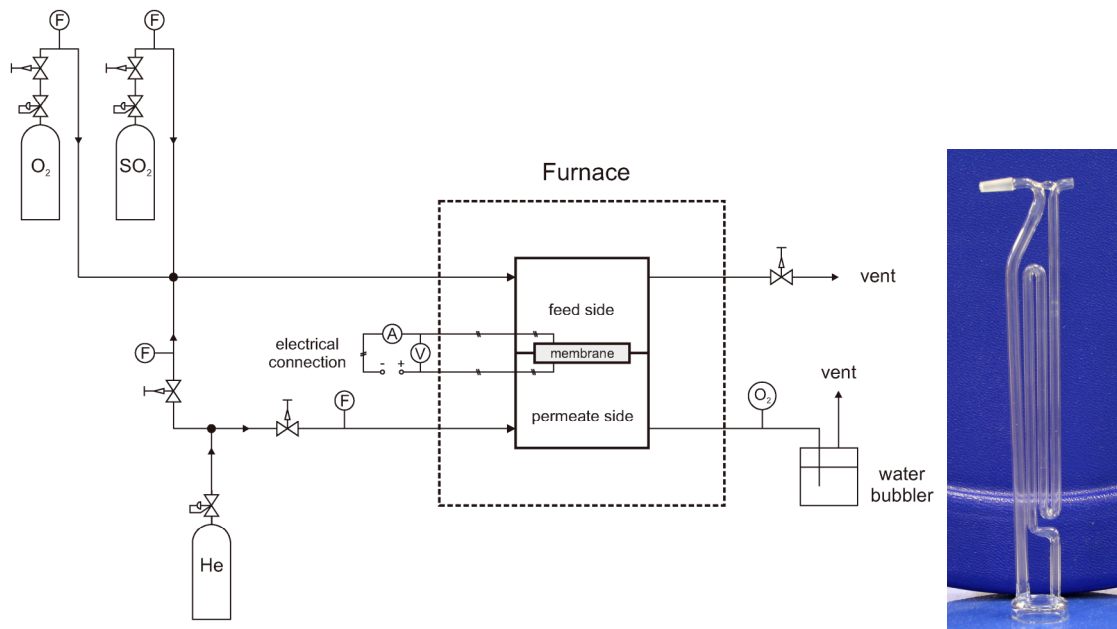
membrane, the ions recombine at the opposite porous anodic surface and pass into the product stream. A schematic of such a membrane is shown in Figure 2.



**Figure 2: Schematic of an electrically driven dense oxygen separation membrane.**

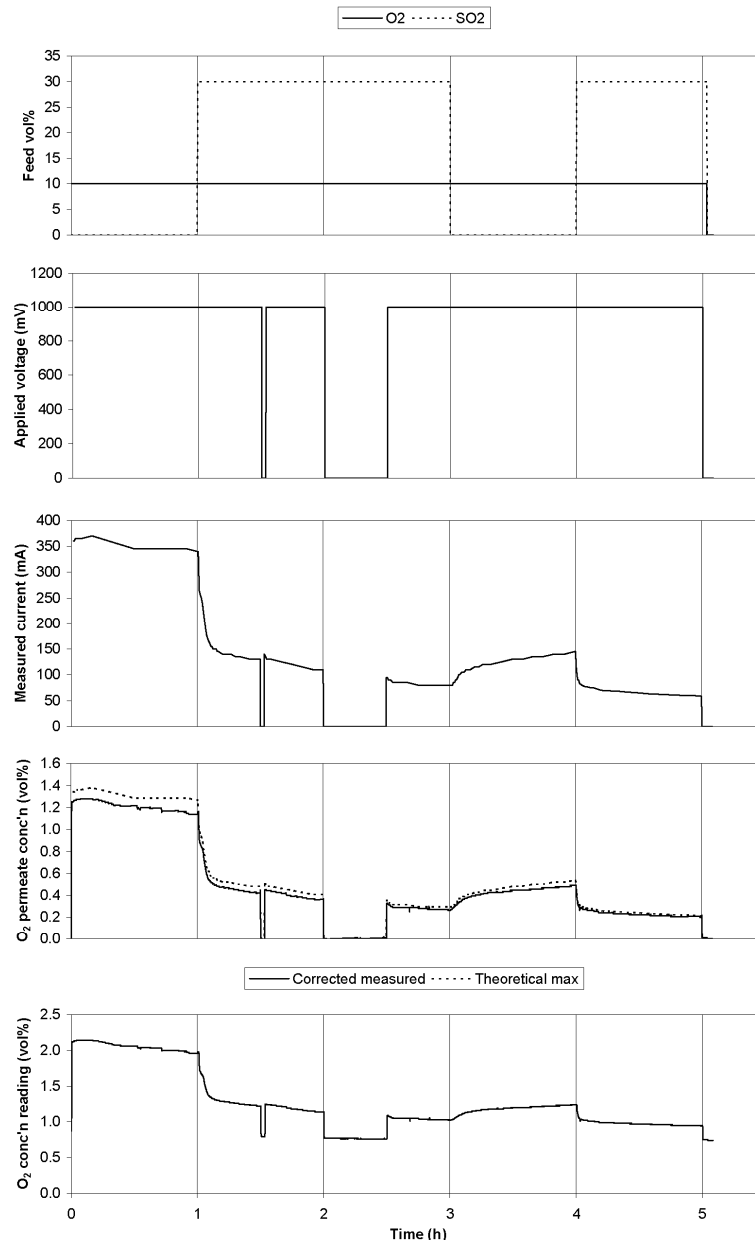
#### 4 Experimental Work

The experimental rig process schematic is presented in Figure 3. The rig was designed to allow a measured mix of GC grade helium, high purity oxygen, and/or sulphur dioxide to be fed from high pressure cylinders to the feed side of the membrane.



**Figure 3: High temperature membrane separation rig schematic and Quartz membrane holder.**

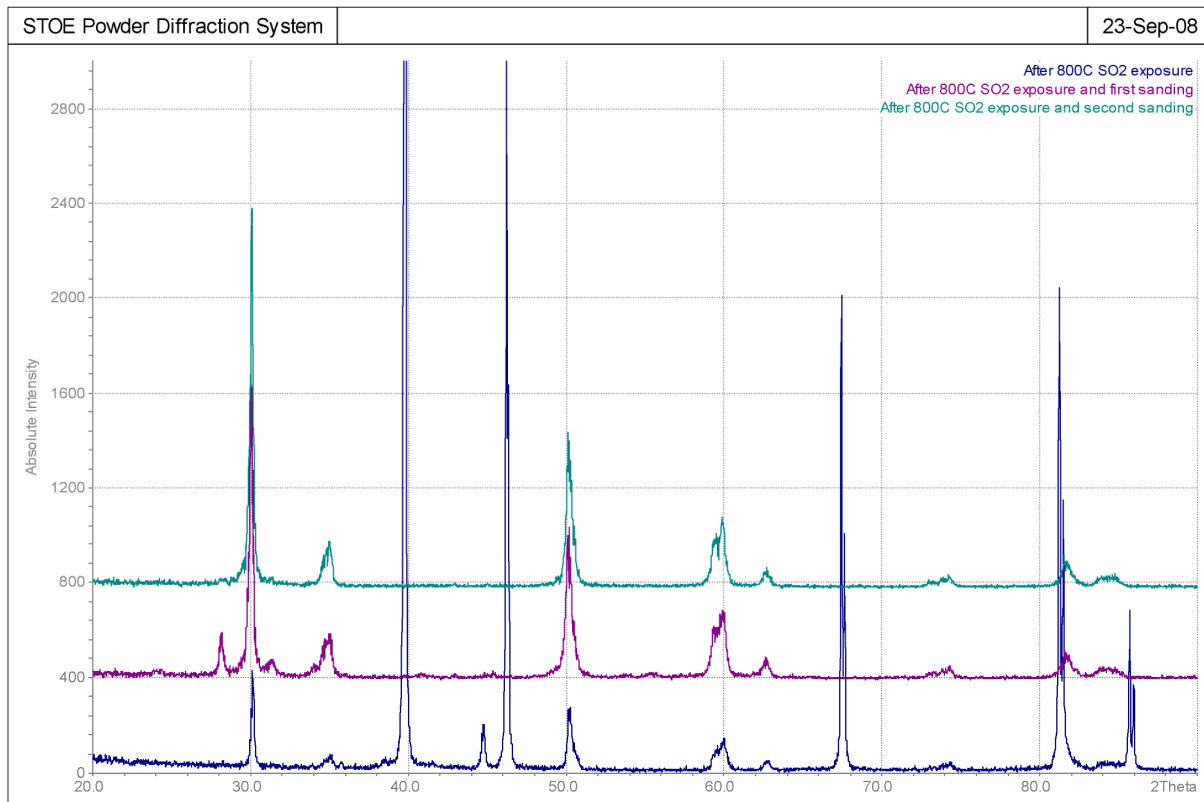
A measured supply of helium is fed to the permeate side to act as the sweep gas, maintaining zero oxygen partial pressure on the permeate side. A bespoke quartz membrane holder was designed, as seen in Figure 3, which is held inside a furnace whose temperature can be varied as required. A paramagnetic gas analyser in the permeate stream allows measurement of the oxygen concentration. Commissioning work verified the satisfactory operation of the rig and also showed gold foil to be a suitable sealing material.



**Figure 4: Experimental data for exposure of 8% YSZ/Pt pellet to SO<sub>2</sub> and O<sub>2</sub> at 800°C.**

Experiments have been carried out at 800°C, 850°C and 900°C with an applied voltage of 1 V and a feedgas of 10% O<sub>2</sub> in helium for one hour, followed by 30% SO<sub>2</sub> and 10% O<sub>2</sub> in helium. Initial results at 800°C, seen in Figure 4, show that O<sub>2</sub> is conducted through the YSZ

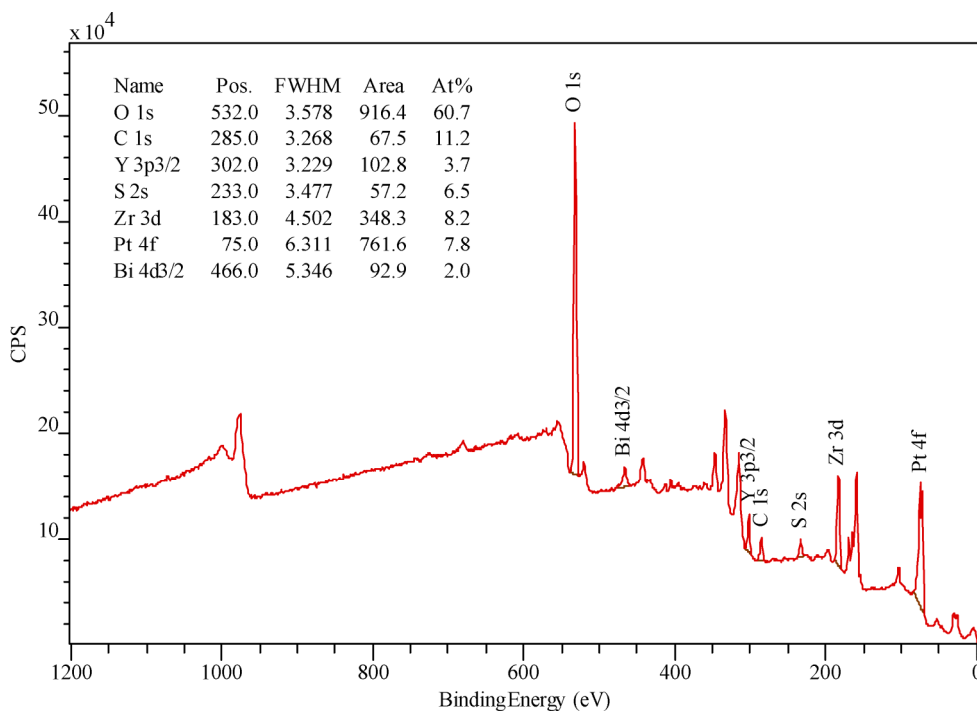
membrane, however when  $\text{SO}_2$  is introduced to the feed the permeate concentration decreases dramatically with an accompanying decrease in current. The IS (impedance spectroscopy) data showed no changes in the bulk or grain boundary electrical conductivity, but did indicate the presence of a surface layer on the YSZ/Pt pellet following  $\text{SO}_2$  exposure.



**Figure 5: XRD data for YSZ/Pt membrane after initial 800°C  $\text{SO}_2$  exposure and during post-exposure sanding.**

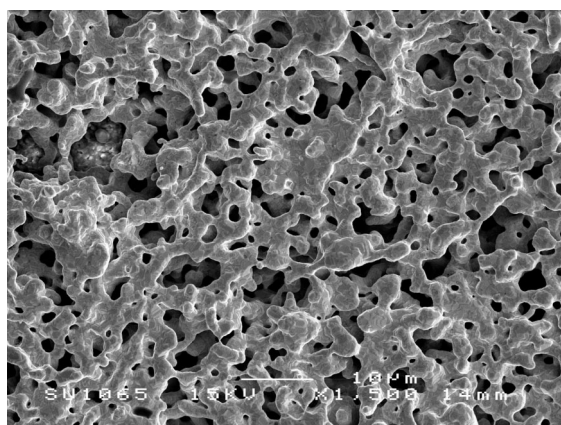
Removal of the electrode and surface of the YSZ by sanding, followed by application of a new electrode and retesting, showed oxygen permeability comparable to that at the start of the test. The XRD (x-ray diffraction) data shows an extra peak after the first sanding, indicating a surface layer on the YSZ (Figure 5). Further experiments were carried out at 850°C with a greater emphasis on surface analysis to investigate the cause of this surface layer. XPS (x-ray photoelectron spectroscopy) of an unused membrane disk showed the presence of bismuth as well as yttria, zirconia and platinum. This was determined to be from a bismuth based frit in the platinum ink used for the electrodes. Figure 6 shows the XPS data for a used membrane disk. The following observations can be made from these spectra:

- There is now sulphur present on the pellet surface;
- The proportion of oxygen on the surface has increased significantly;
- The ratio of yttria to zirconia has increased following the  $\text{SO}_2$  exposure;
- None of the metal peaks have shifted significantly following exposure.



**Figure 6: XPS wide scan of used 8YSZ/Pt pellet - thin electrode point.**

The experiment at 850°C was repeated using a fuel cell grade platinum ink which does not contain a bismuth frit. This yielded similar IS and XRD results to those above, showing that the bismuth is not the cause of the surface layer. Figure 7 shows an SEM image of the electroded YSZ using the fuel cell grade platinum ink. No significant changes were seen in the SEM images after exposure to SO<sub>2</sub>.



**Figure 7: SEM image of electroded YSZ pellet (GEM ink), 1500x magnification, JEOL6400 SEM.**

The results suggest that the drop in membrane performance is due to adsorbed sulphur species on the surface of the membrane. Work is ongoing to investigate ways to recover the membrane performance and thereby make it a viable option for increasing SO<sub>2</sub> yield in the sulphuric acid decomposition process.

## 5 Conclusions

Process Simulations showed that a selective membrane system could increase SO<sub>2</sub> yield in the sulphuric acid decomposition process at a given temperature. Experiments have shown that YSZ membranes are capable of separating oxygen from SO<sub>2</sub>, although a rapid decrease in performance is seen compared to initial flux values. This decrease was found to be due to absorbed sulphur species on the surface of the membrane. Further testing is on going to investigate ways of recovering the initial performance.

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