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Voltage pulsing for performance recovery of yttria-stabilised zirconia membranes in oxygen/sulfur dioxide separation

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ABSTRACT

The regeneration of yttria-stabilized zirconia (YSZ) membranes exposed to high concentration sulfur dioxide in oxygen at 850 °C using DC voltage pulses was investigated by in-situ impedance spectroscopy. The membranes consisted of a dense YSZ layer as the solid electrolyte coated with two platinum layers as electrodes. On operation in the presence of SO₂, the serial resistance and polarization resistance of the Pt/YSZ cell increased. This is most likely due to the formation of sulfide at the interface area of the electrode and electrolyte combined with sulfur adsorption on electrode surface. DC Voltage pulses were found to have an effect on the charge transfer and mass transfer properties of the Pt/YSZ cell, assisting the removal of sulfur on the cathode surface and leading to performance recovery of the cell. In these experiments, the greatest rate of membrane performance recovery is achieved with a cathodic DC bias of 10 V, applied for 0.08 s. Higher or longer voltage pulses may cause the rate controlling step for the oxygen reduction reaction to shift to oxygen supplied in feed from oxygen surface exchange and diffusion processes. A relatively steady membrane performance was achieved during 20 h SO₂ exposure tests. It is concluded that DC voltage pulses show promise as a method for reducing the performance degradation effects of poisoning due to sulfur containing gases in the fields of fuel cells and in the sulfur family of thermochemical cycles.

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Introduction

The demand for clean, secure, and sustainable energy sources has stimulated great interest in the sulfur iodine thermochemical cycle (SI cycle) and the hybrid sulfur (HyS) cycle, promising methods for the large scale production of hydrogen. The SI and HyS cycles share the decomposition of sulfuric acid as a common stage, typically at temperatures in

the range 800–900 °C. Higher temperatures tend to favour greater conversion. If the high temperature can be decreased to some extent, yet keeping conversion at the same level, then a great deal of energy can be saved. Process simulations showed that utilising a membrane to selectively remove oxygen from the decomposition reactor could increase the yield from 62.3% to over 90% at 1000 K [1]. An 80% conversion of SO₃ to SO₂ is obtained at 850 °C theoretically if no oxygen is removed from the products. However, the temperature of the

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same conversion reduces to about 750 °C if 90% of the oxygen is removed, and to around 590 °C when 99.9% of the oxygen is removed [2]. Yttria-stabilized zirconia (YSZ), a ceramic with high oxygen ion conductivity, was proposed to separate oxygen from the products of sulfuric acid decomposition reaction. In our previous research, the feasibility of applying high temperature oxygen separation using YSZ membrane to the sulfuric acid decomposition process was investigated [1], and the performance of Pt/8YSZ/Pt membrane exposed to gas mixtures of SO₂–O₂–He on the feed side was investigated at 850 °C [3].

Among the challenges of utilising YSZ membranes in the separation process after H₂SO₄ decomposition is severe degradation of membrane performance due to sulfur poisoning, also a common problem in solid oxide fuel cells (SOFCs). In the past few decades, extensive efforts have been devoted to characterizing sulfur poisoning behaviour of conventional electrodes (Pt is used as the electrode material here, however similar behaviour is seen with Ni electrodes used in many SOFC configurations), unravelling the mechanism of sulfur poisoning, and developing methods to reduce the degradation in performance. Sulfur poisoning of the cathode is characterized by a rapid initial drop in current upon exposure to sulfur dioxide (type I degradation), followed by a much slower but still significant rate for a long period of time (type II degradation) [3,4]. It is well accepted that type I degradation is caused by the dissociative adsorption of sulfur species around three-phase boundaries (the active sites for the electrochemical reactions) [4–8]. However, the mechanism of type II degradation during continuous exposure to sulfur containing gas over a long period of time is still not clear. It would be difficult to explain from the sulfur adsorption point of view. There are four different hypotheses for type II degradation:

1. H₂S may cause migration of metal in the electrode, thereby degrading the distribution of the pre-coating metallic phase in the electrode [4];
2. Surface reconstruction of the metal may lead to a new surface on the electrode [5];
3. A sulfide layer is formed on the electrode surface which increases the size of impedance arcs [9], impedes the transport of the reactant gas onto the electrode surface and

transport of products away from the active sites [10], causes microstructure change and reduces the TPB area for electrochemical reactions [11], contaminates the anode surface and increases the interface resistances between electrode from the YSZ membrane [12];

4. H₂S may lead to an irreversible increase of the serial resistance due to a loss of percolation of the metal particles in the layers closest to the electrolyte [13].

In previous work, platinum sulphite was observed on the cathode surface after SO₂ exposure by using surface analysis techniques (XRD, SEM-EDS and Raman Spectroscopy) [3].

Several studies have investigated ways to reduce sulfur poisoning, including:

- Remove sulfur containing impurities, which may achieve completely recovery [4,14,15] or partial recovery [11,16,17].
- Apply sulfur-tolerant electrodes. These can be categorized into three kinds of materials: thiospinels and metal sulfides, metal cermets, and mixed ionic and electronic conductors [18].
- High current density can increase performance regeneration [11,19], or application of short but strong DC polarization can alter chemical composition of the electrode surface and lead to an acceleration of the oxygen surface exchange reaction [20].

Application of a DC voltage pulse was investigated and a 2 min pulse was found to partially recover membrane performance [3]. Preliminary results using a much shorter pulse of 1 s also showed performance recovery. This paper investigates the effect of magnitude and duration of DC voltage pulses on performance recovery, with the aim of optimising performance based on oxygen separation and applied voltage. Firstly, membrane performance degradation by SO₂ poisoning and recovery by DC voltage pulse is experimentally investigated with *in-situ* electrochemical impedance spectroscopy (EIS). Secondly, the magnitude and duration of DC voltage pulses are optimised to obtain the greatest rate of performance recovery. Finally, longer-term experiments on membrane performance in He–O₂–SO₂ are demonstrated with periodic voltage pulses.

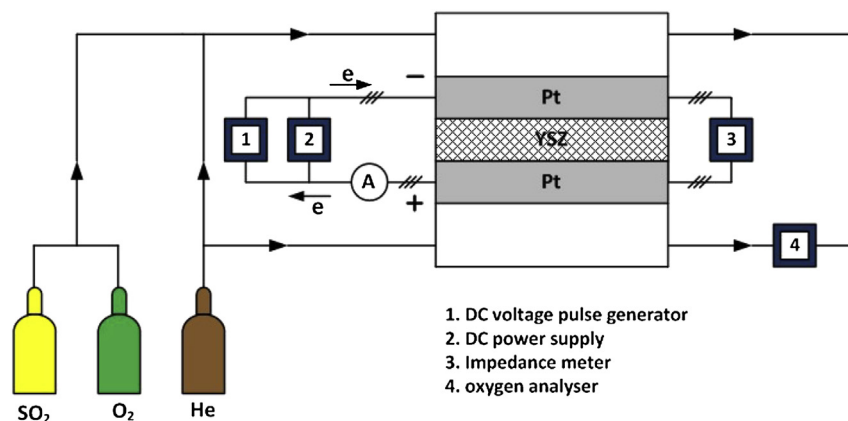


Fig. 1 – Experimental setup.

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