

# Investigation of Pt supported on carbon, $ZrO_2$ , $Ta_2O_5$ and $Nb_2O_5$ as electrocatalysts for the electro-oxidation of $SO_2$

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## DECLARATION

I declare that this dissertation entitled "Investigation of Pt supported on carbon, ZrO<sub>2</sub>, Ta<sub>2</sub>O<sub>5</sub> and Nb<sub>2</sub>O<sub>5</sub> as electrocatalysts for the electro-oxidation of SO<sub>2</sub>" is my own work and that it has not been submitted for any degree or examination in any other university, and that all sources I have used or quoted have been indicated and acknowledge by complete references.

Boitshoko Goitseone Modingwane

Signature .....

Date.....

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## ABSTRACT

The gradual depletion of and dependence on fossil fuels, air pollution and global warming have all accelerated the development of alternative energy systems which use hydrogen as an energy carrier. The hybrid sulphur cycle (HyS) is the foremost electro-thermochemical process that can produce hydrogen as the energy carrier.

The HyS cycle consists of two units, namely the sulphuric acid decomposition reactor and the sulphur dioxide electrolyser (SDE). The SDE is responsible for the  $\text{SO}_2$  electro-oxidation to sulphuric acid and protons at the anode and the electro-reduction of protons to hydrogen at the cathode. This research study focuses on the kinetic data collected from the prepared catalysts for  $\text{SO}_2$  electro-oxidation at the anode.

Platinum dispersed on carbon, niobium pentoxide, tantalum pentoxide and zirconium dioxide as electrocatalysts were prepared using sodium borohydride as a reducing agent. These electrocatalysts were characterized using transmission electron microscopy and x-ray diffraction. Cyclic voltammetry was used to study the electrochemical active surface area (EAS) and the results showed that Pt/ZrO<sub>2</sub>-C had a higher EAS area than Pt/Ta<sub>2</sub>O<sub>5</sub>-C, Pt/Nb<sub>2</sub>O<sub>5</sub>-C and Pt/C. The high EAS of Pt/ZrO<sub>2</sub>-C can be explained by the low crystal size however after a series of linear polarisation scans Pt/ZrO<sub>2</sub>-C experiences a much greater area loss than all the other catalysts.

Linear polarisation scans for each of the catalysts revealed that the influence of increased temperature and sulphuric acid concentration were showed improved results. Levich and Koutecky-Levich plots revealed that the  $\text{SO}_2$  oxidation is a multistep reaction on all the prepared catalysts and that there are regions which are kinetic and diffusion controlled and diffusion-only controlled. Pt/Ta<sub>2</sub>O<sub>5</sub>-C catalysts exhibited superior catalytic activity and stability compared Pt/Nb<sub>2</sub>O<sub>5</sub>-C, Pt/ZrO<sub>2</sub>-C and Pt/C. The Pt/ZrO<sub>2</sub>-C exhibited the most inferior catalytic activity and stability.

**Keywords:** Hydrogen, Hybrid sulphur,  $\text{SO}_2$  electro-oxidation, platinum, tantalum pentoxide, niobium pentoxide and zirconium dioxide

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## LIST OF ACRONYMS

| Abbreviation                   | Description                              |
|--------------------------------|--|
| CV                             | Cyclic voltammetry                       |
| H <sub>2</sub> O               | Water                                    |
| H <sub>2</sub> SO <sub>4</sub> | Sulphuric acid                           |
| HyS                            | Hybrid sulphur cycle                     |
| LP                             | Linear polarisation                      |
| OCP                            | Open Circuit Potential                   |
| O <sub>2</sub>                 | Oxygen                                   |
| OLI-MSE                        | OLI Mixed Solvent Electrolyte            |
| Ot-HyS                         | Once-through Hybrid sulphur cycle        |
| MEA                            | Membrane electrode assembly              |
| PEMFC                          | Proton exchange membrane fuel cell       |
| RDE                            | Rotating disc electrode                  |
| SDE                            | SO <sub>2</sub> Depolarised Electrolyser |
| SEM                            | Scanning electron microscope             |
| SRNL                           | Savannah River National Laboratories     |
| TEM                            | Transmission electron microscope         |
| THF                            | Tetrahydrofuran                          |
| XRD                            | X-ray diffraction                        |

| Property        | SI units           | Description of the SI units        |
|-----------------|--------------------|------------------------------------|
| Temperature     | °C                 | Degree Celsius                     |
| Pressure        | bar                | Bar units                          |
| Current density | mA/cm <sup>2</sup> | Milliampere per centimetre squared |
| Energy/ Work    | Petajoules         | 10 <sup>15</sup> joules            |
| Potential       | V                  | Volts                              |
| Concentration   | Wt%                | Weight percentage                  |