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_2, Ta_2O_5 and Nb_2O_5 as electrocatalysts for the electro-oxidation of SO_2” 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 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 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_2-C had a higher EAS area than Pt/Ta_2O_5-C, Pt/Nb_2O_5-C and Pt/C. The high EAS of Pt/ZrO_2-C can be explained by the low crystal size however after a series of linear polarisation scans Pt/ZrO_2-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 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_2O_5-C catalysts exhibited superior catalytic activity and stability compared Pt/Nb_2O_5-C, Pt/ZrO_2-C and Pt/C. The Pt/ZrO_2-C exhibited the most inferior catalytic activity and stability.

Keywords: Hydrogen, Hybrid sulphur, 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_2O	Water
H_2SO_4	Sulphuric acid
HyS	Hybrid sulphur cycle
LP	Linear polarisation
OCP	Open Circuit Potential
O_2	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_2 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^{-2}	Milliampere per centimetre squared
Energy/ Work	Petajoules	10^{15} joules
Potential	V	Volts
Concentration	Wt%	Weight percentage