CHAPTER 3

EXPERIMENTAL

3.1 Catalyst preparation

3.1.1 Reagents

Hydrogen hexachloroplatinate (IV) hydrate (ACS Reagent ≥ 37.5% Pt basis), zirconium dioxide nanopowder (< 100nm), tantalum pentoxide (< 5µ 99.9% metal basis), niobium pentoxide (99.9% metal basis), 99.9% tetrahydrofuran anhydrous (inhibitor free), sodium carbonate (ACS reagent), 14wt% sodium borohydride in 14M NaOH, and 5wt% Nafion perfluorinated ion-exchange resin in a mixture of lower aliphatic alcohols were obtained from Sigma-Aldrich. Absolute ethanol (99.9%) was obtained from Merck.

All solutions were prepared using demineralised water which was prepared using a Milli-Q Plus ultra-pure water system. Perchloric acid (60%) was obtained from Merck and sulphuric acid (98%) analytical reagent was obtained from Rochelle chemicals.

3.1.2 Synthesis of Pt/M_xO_y-C

Various mass ratios of the selected metal oxide (either zirconium dioxide, or tantalum pentoxide or niobium pentoxide) were mixed with hydrogen hexachloroplatinate (IV) hexahydrate (shown in Table 3.1). The mixture was then added to a suspension of 30mg Vulcan XC-72 carbon in 10ml of tetrahydrofuran (THF) and H_2O with the volume ratio of THF:H_2O solution= 1:1. The mixture was ultrasonicated for 19h and the reducing agent, 10ml $NaBH_4$ was added followed by drop-wise addition of 0.5M Na_2CO_3, used for pH control to 10. The catalyst mixture was agitated for 1h at 10℃ and was then washed and filtered with deionised water and ethanol. The sample was then vacuum-dried at 80℃ for 4h. The final dry product will be noted as Pt/M_xO_y-C. This preparation method is a modification from Chen et al. [129].

The mass ratio of the precursor salts were selected such that all the Pt/M_xO_y-C catalyst powders comprised of 30 percent catalyst material and 70 percent support material, as this was (in a number of instances) the ratio communicated in literature for the production of electrocatalysts.

Table 3.1 Mass ratio of precursor salts used to synthesise catalysts

Catalyst number	g				
	Platinum	Vulcan carbon XC-72	Nb_2O_5	Ta_2O_5	ZrO_2
1	3.0	7.0	-	-	-
2	3.0	3.5	3.5	-	-
3	3.0	3.5	-	3.5	-
4	3.0	3.5	-	-	3.5

3.1.3 Electrode preparation

Catalyst ink was prepared by mixing 18mg of the catalyst powder (Pt/MO_x-C) with 3.25ml of a solution made from water, absolute ethanol and a 5wt% Nafion perfluorinated ion-exchange resin in a mixture of lower aliphatic alcohols (as a binder) from Sigma-Aldrich. The mixture was ultrasonicated for 30min and 5µl of this suspension was deposited on the glassy carbon disk electrode (5mm diameter) using an electronic micropipette, then placed in the vacuum oven for 1h at 30˚C at 400millibar. Prior to deposition of the catalyst ink, the glassy carbon was polished with 0.05µm alumina from Pine Instruments. Electrode catalyst assembly pieces are shown in Figure 3.1.

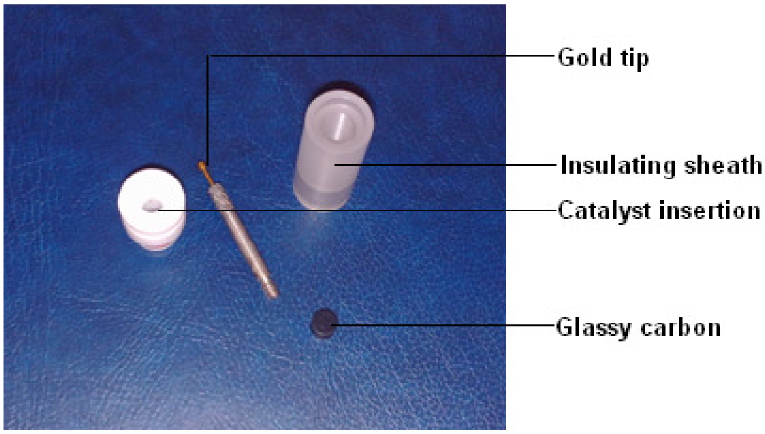

Figure 3.1 Electrode assembly kit from Pine Instruments

Subsequent to electrode preparation the RDE was connected to the shaft of a rotator (Pine Instruments). In the experimental set-up the working electrode was the RDE consisting of carbon-metal oxide supported platinum, as shown in Figure 3.2 and 3.3. Oxidation of SO_2 would take place at the RDE (the working electrode) and H_2 would be formed at the counter electrode.

3.2 Characterization

3.2.1 X-ray diffraction (XRD)

The X-ray diffractograms of the composite catalysts were recorded using a XPert Pro (PW 3040/60) with a Cu Kα radiation source, operated at 40mA and 45kV. The 2θ angular regions between 10° and 90° were explored at a scan rate of 6°min^{-1} with steps of 0.017°. Two samples of each catalyst powder as well as the original metal oxides were sent for XRD analysis. The XRD analysis was conducted in the XRD laboratory of the Geology Department at the North-West University (Potchefstroom Campus).

3.2.2 Transmission electron microscopy (TEM)

Prior to TEM analysis, the catalyst powder was dissolved in water, then ultrasonicated for 10min. Using a plastic Pasteur pipette, a drop of the sample was placed on 200 mesh Cu grids covered with a thin formvarfilm. The Cu grids act as sample holders for the transmission electron microscope. Excess liquid was removed with a filter paper, the Cu grids were air dried and viewed under the Phillips CM10 transmission electron microscope at an applied voltage of 100kV with a magnification range of 28500X and 73000X. TEM analysis was conducted at the Electron Microscopy Lab of the Chemical Resource Beneficiation research focus area at the North-West University (Potchefstroom Campus).

3.3 Electrochemical measurements

Electrocatalytic tests are conducted on the electrode materials by employing linear polarization and cyclic voltammetry. The parameters of the electrochemical measurements (for CV and LP scans) are given in Table 3.2.

Table 3.2 Experimental parameters for CV and LP

Parameters	Linear polarisation	Cyclic voltammetry
	Electrode kinetics	**EAS measurements and preconditioning**
Potential range	-0.3 to 1.8V	-0.3 to 1.2V
Scan rate	20mV/s	100mV/s
Electrolyte	0.5 to 1.5M H_2SO_4	0.1M $HClO_4$
Temperature	20 and 30℃	25℃
Rotation speed	0-2500rpm	static

3.3.1 Preconditioning

Preconditioning and electrochemical active surface area experiments were conducted in 0.1M $HClO_4$. In literature, however, 0.1M H_2SO_4 was used, but we chose 0.1M $HClO_4$ in order to minimise exposure to sulphur species in sulphuric acid as HSO_4^- and SO_4^{2-} adsorbs strongly on the <100> and <111> planes of Pt. The experiments were done using cyclic voltammetry.

3.3.2 Catalyst testing

A standard thermostated three electrode potentiostatic system (shown in Figure 3.3) was assembled, consisting of Pine research instrumentation electrodes, VMP3 Bio-logic two channel Potentiostat connected to a computer (shown in Figure 3.2). EC-Lab (V9.55) software was used to operate the potentiostat to obtain cyclic voltammograms and linear polarisation curves and to automatically compensate for iR drop by the PEIS method for which the frequency was set at 100000 kHz. A scan rate of 20mV/s, electrode rotation rates of 0, 100, 400, 900, 1600 and 2500rpm and a potential range between -0.3 and 1.8V was employed. The electrolyte temperature was manually controlled in the range 20-30˚C by water circulation through the double wall of the cell using a Julabo F12-ED thermostat.

Prior to electrochemical experiments, an aqueous H_2SO_4 solution was thoroughly deoxygenated for 10min by bubbling with purified nitrogen gas. SO_2 was then bubbled through the supporting electrolyte for 30 minutes. Working electrode material were Pt/M_xO_y-C, platinum wire was used as counter electrode and Ag/AgCl as the reference electrode. All potentials were corrected and communicated relative to the Standard Hydrogen Electrode (SHE). The use of an open three electrode electrochemical cell limited the experiment to atmospheric pressure conditions. Increasing pressure could therefore not be studied. All the experiments were conducted in the fume extraction cupboard.

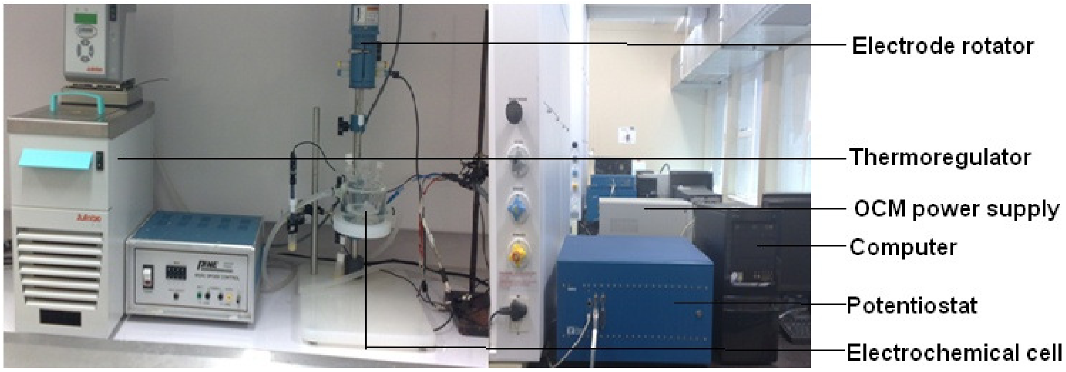

Figure 3.2 Photograph of the actual experimental setup

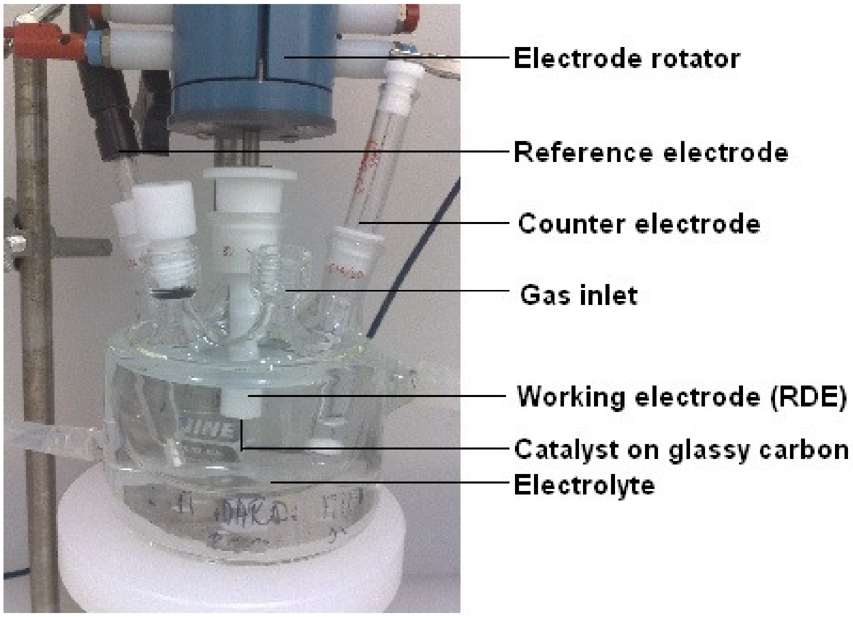

Figure 3.3 Photograph of the actual electrochemical cell

3.3.3 Inductively coupled plasma optical emission Spectroscopy

The sulphuric acid electrolyte was collected after each cyclic voltammogram to test stability. Two dilutions of each sample were taken for ICP-OES (iCAP 6000 series Thermo scientific Duo utilising iTEVA) analysis at the chemistry department at the Northwest University. The analysis was performed to determine the amount of platinum that had dissolved in the electrolyte during the experiment.

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