

CHAPTER III EXPERIMENTAL

3.1 Materials

The high temperature reference electrode was constructed for operating in high temperature water, to 300°C, and pressures up to 10.3421 MPa. The silver/silver-chloride (Ag/AgCl) reference electrode was chosen for its ease of manufacture. In addition, it can be used in any orientation and does not usually significantly contaminate the medium in which it is immersed if the chloride concentration is kept low.

The electrode body was constructed from a titanium tube which is 0.9525 cm in diameter and 27.9400 cm long. The titanium tube was oxidized in a furnace at a temperature of 850°C for 8 hours such that the oxide film would act as an electrical insulator. The internal pressure of the electrode is the same as operating conditions in the autoclave, thus, the electrode body wall thickness must be greater than the minimum required wall thickness, 0.1702 cm, calculated by the Barlow and Lamé equations for straight metal pipes under an internal pressure of 13.7895 MPa (Perry, 1984). A Conax fitting was used to seal the top end. A small leak from the oxidised titanium plug at the bottom end serves as the ionic conducting electrical pathway between the inside of the reference electrode and bulk of test solution (Macdonald; private communication, 2004).

The filling solution inside is potassium chloride, the most widely used electrolyte because it does not generally interfere with pH measurements. Also, the nearly equal mobilities of the potassium and chloride ions minimize liquid junction potentials. An excess of KCl crystals in saturated KCl solution extends the time before the reference cell starts to drift due to the depletion of chloride ions in the electrolyte. However this may lead to increased contamination of the test environment.

Since the Ag/AgCl redox couple can not be used at high temperature due to the instability of the silver chloride layer, the upper part of the

electrode body is cooled. Cooling water flows through the cross at a maximum flow rate of 0.13 litre/hour to maintain the electroactive element at low temperature. The electrode is connected to the high temperature environment via a non-isothermal electrolyte bridge.

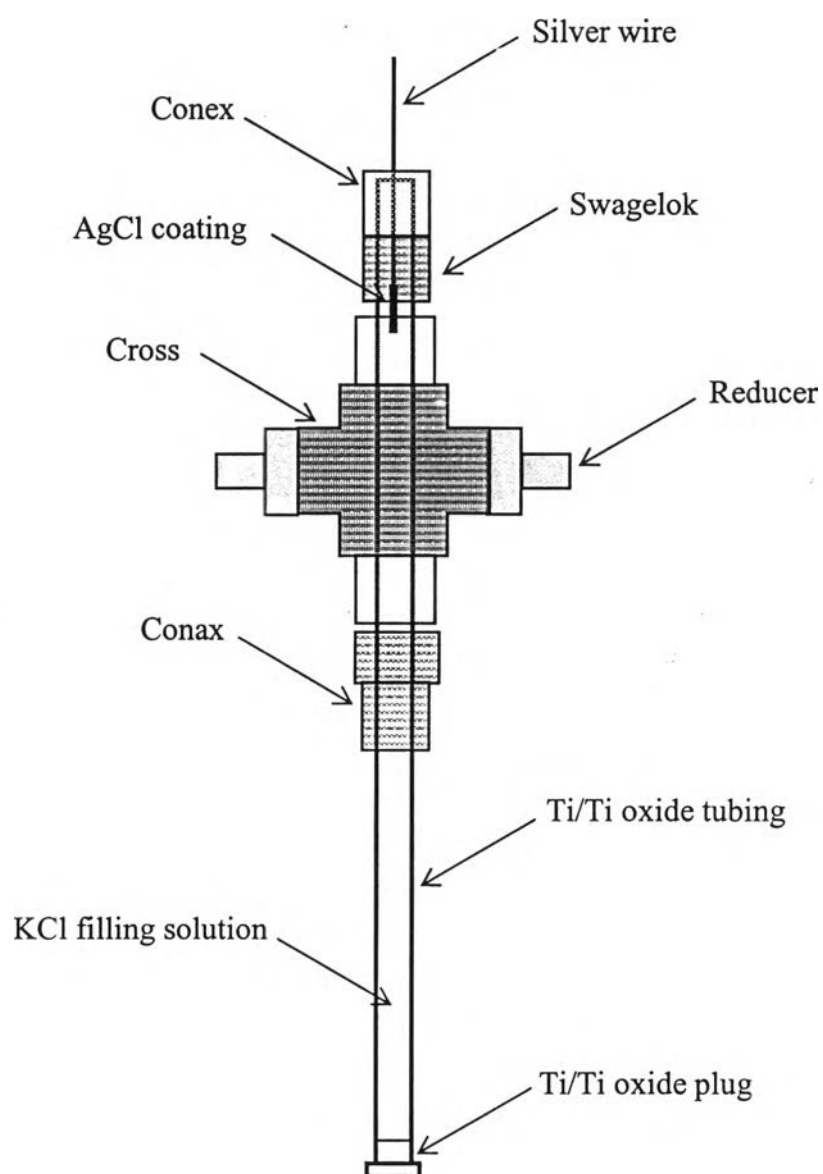


Figure 3.1 Reference electrode assembly.

3.2 Experimental Equipment

A potentiostat was used in this work for two functions. Firstly, the potentiostat was used in the potentiostatic mode to monitor potential differences between electrodes with time. Secondly, the potentiostat was used in the galvanic mode for applying current for the process of silver-chloride coating. A power supply was used to provide the higher current in the platinum black coating process.

For the titanium oxidation procedures, a furnace was used in which a titanium tube was placed and raised in temperature to 850°C. After the oxide film had been formed, a multi-meter was used to measure the resistance of both inside and outside surfaces to verify the electrical insulation property of the titanium tube as an electrode body. The titanium oxide composition and surface morphology on the inner surface was characterized by SEM, EDAX, and XRD techniques.

During the high temperature test of the Ag/AgCl electrode, the tube surface temperature above the cross was measured by a thermocouple for each test to give the AgCl's temperature. A stop watch was used to determine the flow rate of cooling water flowing in the cooling line with a fully open valve.

3.3 Methodology

3.3.1 Silver-chloride Coating

To produce the silver/silver-chloride element, a 1 mm diameter silver wire was first cleaned with 3 M nitric acid and washed thoroughly with water. The silver wire acts as an anode and a coiled platinum wire as the cathode. Both wires were immersed in a 0.1 M hydrochloric acid solution. The experiment arrangement is shown in Figure 3.2. The potentiostat provided the current at 0.1 mA/cm² for 24 hours. The following details show the conditions of the potentiostat for the AgCl coating process.

Galvanostat mode

Setting: Resistance: auto
Polarisation: +1 mA - Pol I
0 V - Pol V
DVM : Range : 20 V
Trigger : recycle
Driftcurrent : on
Avg : off
Null : off
Digits : 4x9-60Hz

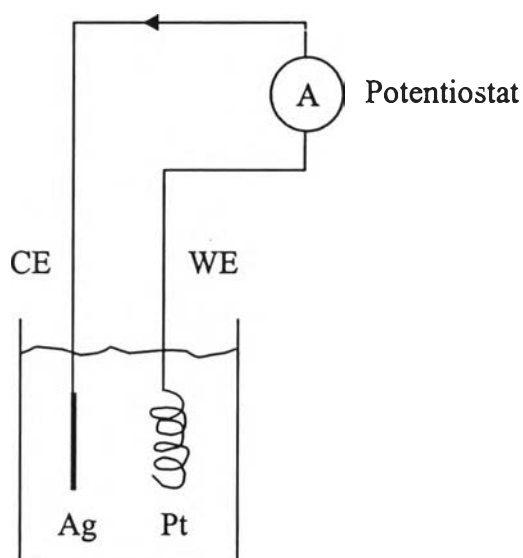


Figure 3.2 Experimental setup for AgCl coating.

The electrodes were then thoroughly washed again and were kept in saturated KCl solution. The color of the fresh electrodes was dark gray but after use, the color usually changed to light gray. The silver-chloride can be re-coated by soaking the wire in concentrated ammonium hydroxide in order to remove the old silver chloride coating. The procedures for re-coating were the same as mentioned above.

The potential of the Ag/AgCl electrode is sensitive to light. Even though light of ordinary intensity does not have a marked effect on the potential of the electrodes, exposure to direct sunlight should be avoided. Moreover, electrodes prepared by this method are suitable for potentiometric titrations or routine voltammetric use. Mechanical strains in the silver wire introduced in the drawing process and impurities in the silver or in chloride electrolyte generally cause the bias potentials of such electrodes to be rather high (~ 5 mV). Nevertheless, they are reasonably stable with time (Sawyer *et al.*, 1974).

3.3.2 Platinum Black Coating

Platinum black was coated on a platinum wire for the purpose of enhancing the stable potential measurement by increasing the contact surface area of the cathode. Two of the 0.5 mm diameter platinum wires were used, one was coiled at the end and serves as the anode and the straight wire acted as the cathode. In Figure 3.3, the setup is shown in which the 5 g/l chloroplastic acid was the test solution. The current was passed through the wires at 20 A/cm^2 . The platinum black was deposited on the anode for 5 minutes. After completion, the coated platinum black was washed with deionized water and acetone.

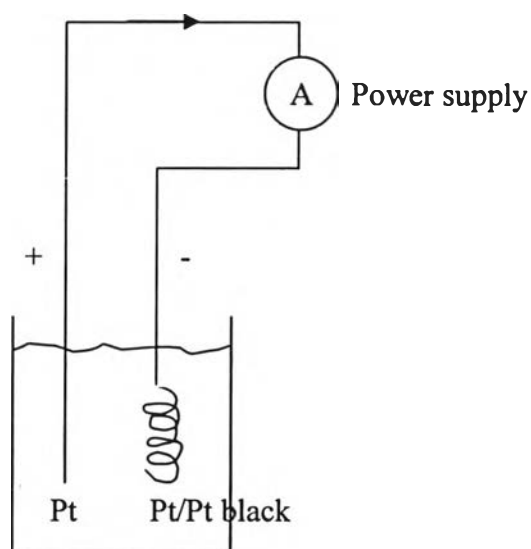


Figure 3.2 Experimental setup of platinum black coating.

3.3.3 Potential Measurement

In order to assess the viability and behaviour of the reference electrode, comparing theoretical and experimental values, potential measurements were performed. The potential of the Ag/AgCl reference electrode was measured against a standard calomel electrode (SCE) on the bench to check the reliability of the electrode at room temperature. Potassium chloride was chosen as the filling solution at the concentrations of 0.1 M, 1 M, 3.5 M, and 4.2 M (saturated). In high temperature conditions, experiments were carried out in a one litre titanium autoclave in which two electrodes were fitted. The Ag/AgCl electrode potential was first checked versus a calomel electrode on the bench before being installed in the autoclave in which DI water, presaturated with hydrogen is the test solution.

The high temperature Ag/AgCl electrode's performance was verified by means of potential measurements and compared to that of the platinum electrode which behaves as a reversible hydrogen electrode (RHE). A potentiostat was provided for continuous data acquisition and determination of potential at various temperatures. The potentiostat settings are as follows.

Potentiostat mode

Setting: Resistance: auto
Polarisation: 0 A - Pol I
 0 V - Pol V
DVM : Range : 20 V
 Trigger : recycle
 Driftcurrent : on
 Avg : off
 Null : off
 Digits : 4x9-60Hz

The experiment was operated continuously in the temperature range of 25-300 °C. The temperature was raised in steps to a maximum of 300 °C, resting at each temperature until the potential difference reached a

steady value. Following these increases, the temperature was then decreased in steps and the cell potential recorded in the descending direction. These temperature increasing and decreasing cycles were repeated to test the reproducibility and reversibility of the reference electrode. The experimental setup for the measurement is shown in Figure 3.4. After high temperature testing, the Ag/AgCl electrode potential was again checked versus SCE.

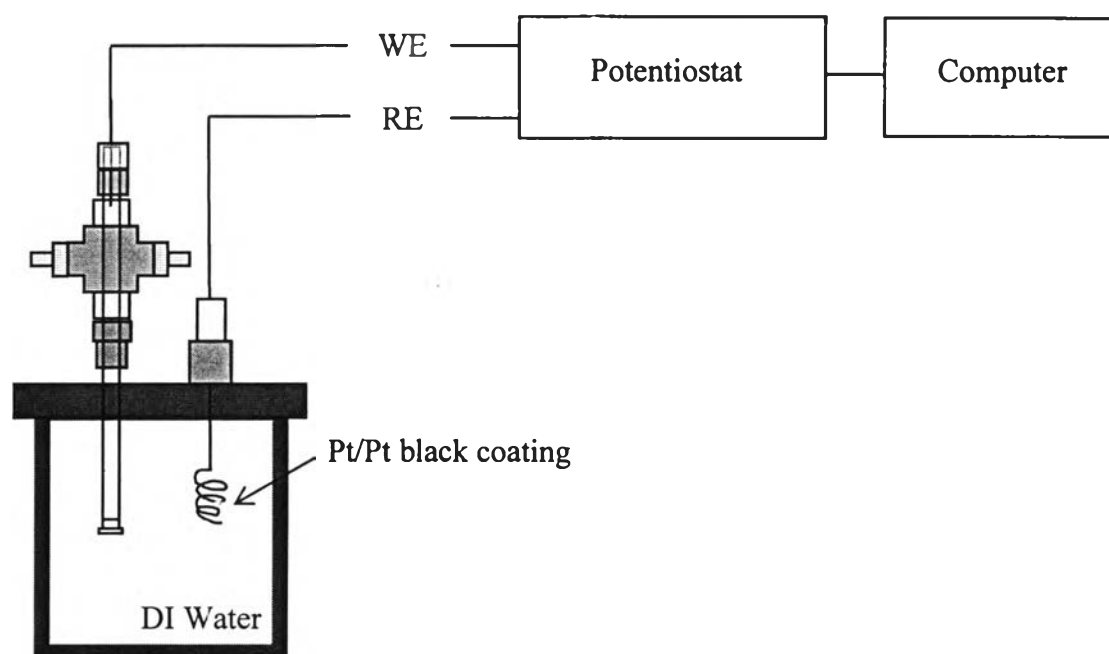


Figure 3.4 Experimental apparatus for potential measurement between Ag/AgCl electrode and Pt electrode.

3.3.4 Electrode Verification

After the electrode potential of the Ag/AgCl was established on the SHE scale, the Ag/AgCl electrode was used as a reference electrode for measuring the potential of a carbon steel coupon. The carbon steel coupon, 2 x 2 cm, was polished with 280, 400, and 600 grit sand paper and rinsed with deionized water until the oxide film was removed. The potential difference was measured between the carbon steel coupon and the Ag/AgCl electrode

using deionized water as a test solution. The data were collected every two hours after the autoclave temperature was raised according to the following steps 50, 100, 150, 200, 250, and 300 °C. Figure 3.5 schematically shows the experimental set up for potential measurements using Ag/AgCl as a reference electrode. After the experiment was completed, the carbon steel coupon was polished to remove the deposition on both surfaces and used for the next experiments.

The measured carbon steel potentials were corrected by empirical corrections to the SHE scale. The two sets of corrected carbon steel potentials, measured against Ag/AgCl electrode at 0.1 and 0.5 M KCl, were compared to validate the accuracy of the correction terms.

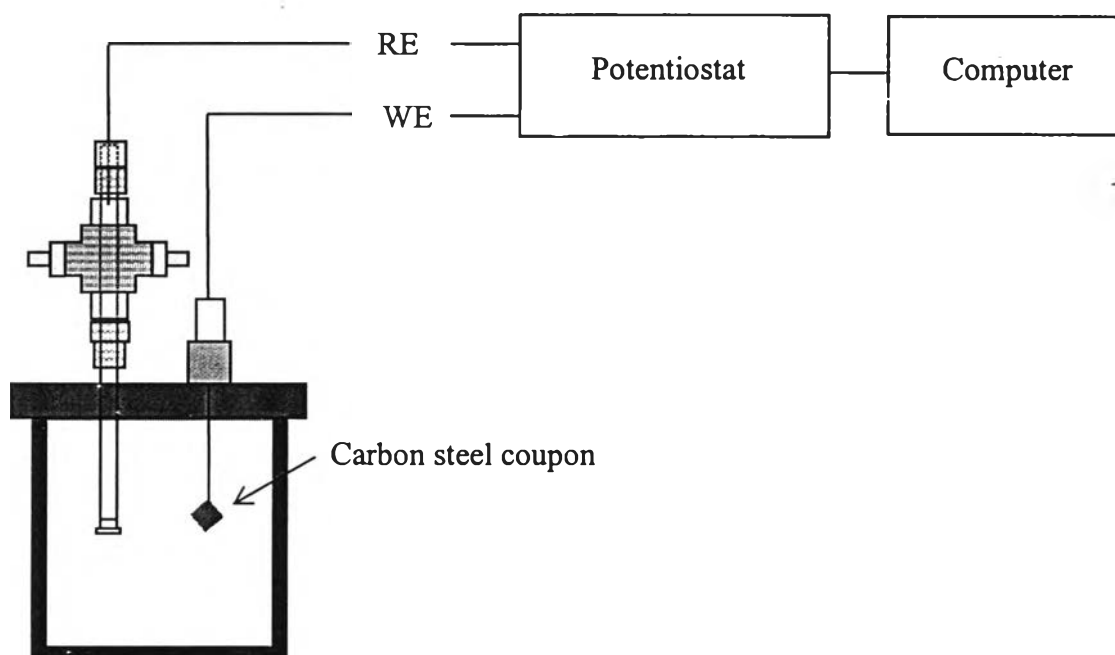


Figure 3.5 Experimental set up for testing Ag/AgCl as a reference electrode.

In order to eliminate concerns and ensure the viability of all reference electrodes in use, calibration tests were performed. The test consisted of a voltmeter, reference electrodes, and a beaker of DI water as a

test solution. The potential differences were measured for each couple of electrodes against a SCE.

Ideally, the potential difference between two electrodes of the same type should be zero. However, in actual practice there was some variation. For the same type of electrodes, the potential difference on the bench should have a reproducibility of $\pm 5\text{mV}$. In high temperature water, $\pm 20\text{mV}$, would be acceptable.