# Construction of a Silver/Silver Chloride Reference Electron
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## Introduction

An electrochemical cell involves two half cells, one which undergoes oxidation and one which undergoes reduction. The electrodes in each half cells are connected which results in a flow of electrons from the anode to the cathode. In order for these electrons to flow an energy potential is required; a potential for the anode to be oxidised and the cathode to be reduced. This potential is called the cell potential and is the difference of the potential of the anode and cathode to be reduced[1].

A potential-controlled electrochemical method involves measuring the current passing through the cell as a function of the potential applied to the working electrode. However, there is no way to measure the applied potential directly. Therefore, in order to determine the applied potential, the potential differences between two connected half cells can be measured, with one of the half cells having a stable and reproducible activity value.

To produce a half cell that is stable and reproducible, a reference electrode is placed in the cell. The potential is then measure using the energy difference between the two electrodes. Therefore, the potential of the working cell is based on the potential of the reference half-cell[2].

A Silver| Silver chloride electrode is a simple, low cost electrode commonly used as a reference electrode. The reference electrode consists of a silver wire coated in silver chloride and immersed in a sodium chloride solution saturated in silver chloride[23]. The reaction that takes place is $Ag_{(s)} + Cl^-_{(aq)} <> AgCl_{(s)} + e^-$ that has a potential of 0.196V. This experiment looks at the effects of solution concentration on the cell potential and the reliability of laboratory standard reference electrode provided cell potentials.

## Materials and Method[3]:

- Sodium Chloride (purity >99%)
- Nitric Acid (70% purity)
- Distilled water
- Voltmeter
- Potentiostat
- Laboratory standard Ag|AgCl 3M NaCl reference electrode
- AfterMath software

Prepared Solutions (Group B):

Solution 1: 25mL of 0.1M $HNO_3$: 150uL of $HNO_3$ in diluted to 25mL
Solution 2: 25mL of 1M NaCl: required 1.461g of NaCl. 1.461g used.
Solution 3: 50mL of saturated NaCl: required 17.95g. 17.99g used.

- Reference electrode glass holder was half filled with solution 3 and placed in a beaker containing solution 3.
- Silver wire was placed in solution 1 for a few seconds and rinsed with distilled water to remove oxide layer.
- Silver wire and Pt wire were placed into electrochemical cell and was filled with solution 2.
- The electrochemical cell was connected to potentiostat and 0.5V was run for 15minutes to coat the silver wire in silver chloride.

- The silver wire was washed with distilled water and placed into the reference electrode glass holder.
- The reference electrode was then tested with a voltmeter with the laboratory standard reference electrode.
- The reference electrode and laboratory standard reference electrode were connecter to potentiostat and the open circuit potential versus time was measured for 15 seconds.
- Reference electrodes were stored in solution 3.

**Results:**

**Group B solution preparation:**

25mL of 0.1M $HNO_3$: 150uL of $HNO_3$ in diluted with distilled water to 25mL
Vol(mL) = ([conc] x Vol of solution x Mr)/density x (100/purity)

= (0.1 x 0.025 x 63.01/1.5) x (100/70)
= 0.1499mL (149.9uL)

25mL of 1M NaCl: required 1.461g of NaCl. 1.461g used

n=CxV
n=1.0.025
=0.025mol
m=nxMr
m=0.025x58.44
=1.461g

50mL of saturated NaCl: required 17.95g. 17.99g used.

NaCl solubility = 359g/L
mass = 359x0.05
= 17.95g

**Cell potential calculations using Nernst Equation:**

E = 0.23V + 0.0592/1 log 1/[6.16]

6.16M NaCl (Saturated) = 0.183V

3M NaCl = 0.201V

2M NaCl = 0.212V

0.196 = 0.23V + 0.0592/1 log 1/[conc.]
[Conc] = 3.75M

Using the Nernst equation, the effect of concentration on the cell potential can be demonstrated. The increase in concentration results in a decrease in cell potential.

Therefore, the hypothesis stating that the Silver|Silver chloride reference electrode has a cell potential of 0.196V versus the SHE is true when referring to the cell potential at a concentration slightly above 3M (3.75M to be exact). However as seen in the calculations above, a change in the NaCl concentration will alter the cell potential, due to the Nernst Equation.

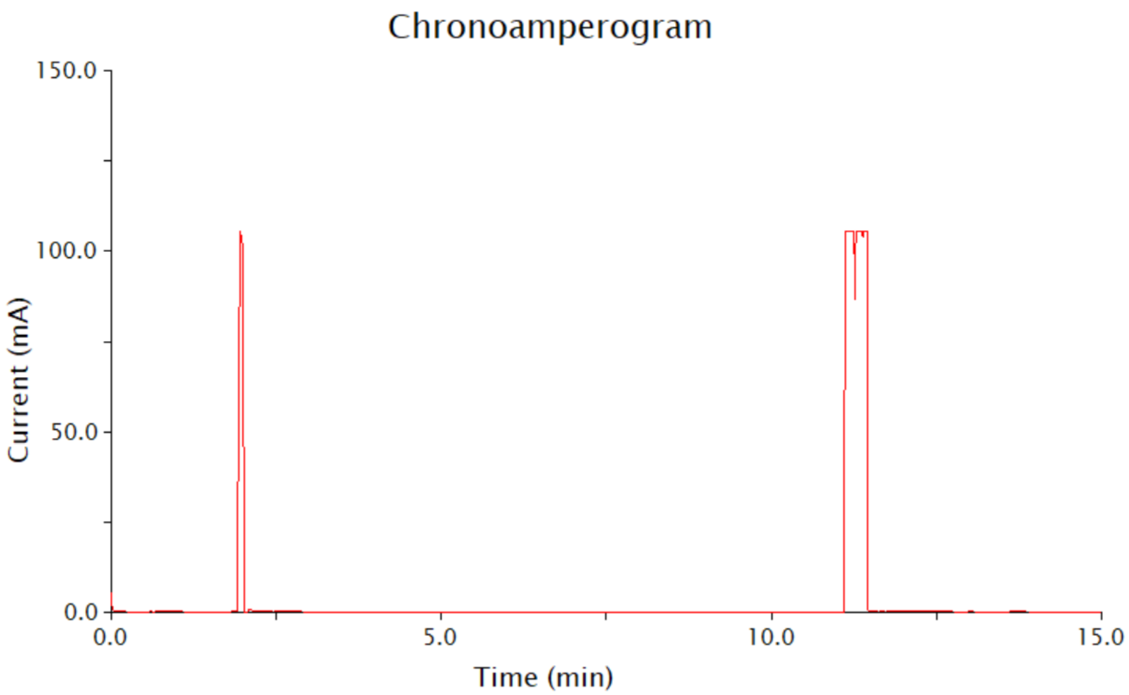

***Figure 1:*** *Aftermath software's chronoamperogram showing the AgCl depositing on the Silver wire. As the AgCl coating develops the electrons have to move through the coating first, resulting in the reaction slowing down, this results in a drop in current. The peaks in the results are due to accidental movement of the electrodes closer together.*

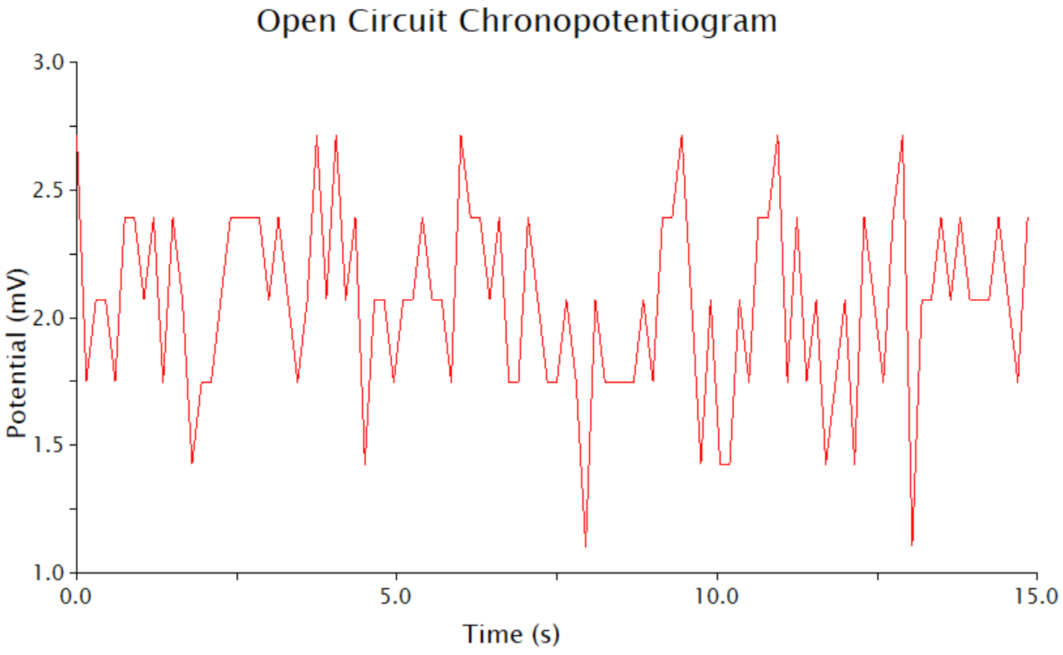

***Figure 2:** Aftermath software's Open Circuit Chronopotentiogram of the constructed reference electrode and the laboratory standard reference electrode. Shows an average cell potential of 2.057mV indicating the successful construction of the reference electrode.*

The potential of the constructed reference electrode can be determined by the equation:
$E_{RE2}=E_{meter} + E_{RE1}$
$E_{RE2} = 0.002V + 0.196V$
$= 0.198V$

The average reading of the open circuit potentiostat was 2.057mV or 0.002V. This reading indicates that there was only a 2mV difference (within the ± 20mv range) suggesting that the construction of the electrode had been successful.

**Discussion:**

In this experiment a Silver|Silver Chloride reference electrode was constructed. In order to construct this electrode, the oxide layer on the silver wire had to first be removed, this is done by placing the wire in a $HNO_3$ solution. This allows for the electrons to be able to flow directly between the solution and the metal in the half cell in order for the AgCl deposit to be strongly attached to the Ag wire.

The silver wire then needs to be coated in the AgCl. This is done by placing the Pt wire and Ag wire into the electrochemical cell containing a solution of NaCl. Platinum is used due to it being an inert metal and therefore does not participate in the redox reaction. The reaction occurring is $AgCl_{(s)} + e^- <> Ag^+ + Cl^-$ the cell potential of this reaction is 0.23V[1]. In order for the reduction reaction to take place a potential above 0.23V needs to be applied. However, if the voltage is too high other reaction will begin to take place such as reaction with oxygen and hydrogen. The electrochemical cell was then connected to the potentiostat and chronoamperogram was run with a potential of 0.5V applied for 15 minutes in order to sufficiently coat the silver wire. Figure 1 shows current versus time graph. The chronoamperogram was run for a second time for an extra 5 minutes due to the first run not sufficiently coating the wire, as seen by the lack of colouration on the wire.

Once the wire had been coated in silver chloride the wire can then be placed in the reference electrode glass holder containing the NaCl solution. The newly created reference electrode can then be evaluated. This is done by comparing the potential to a laboratory standard reference electrode. This is done using the potentiostat and measuring the open circuit potential versus time for 15 seconds. Figure 2 shows the difference between the two half cells, with an average of 2.057mV, this result is within ±20mV allowed variation. The potential of the laboratory standard reference electrode which is already known, can be added to the total potential value read by the potentiostat which gives the potential of the constructed reference electrode of 0.198V. However, this varies from the theoretical value of the Silver|silver Chloride electrode in a saturated solution, which would be 0.183V according to the Nernst equation. However, this is still within the allowed ±20mV variation. The higher potential of the constructed electrode may be a result of the concentration within the electrode being lower than intended. The solution of NaCl was expected to be saturated, at a concentration of 6.16M, however if there wasn't enough NaCl added to the water, or the solution wasn't mixed through the concentration of the solution would have been decreased. This pattern is seen in the results section where increase in concentration results in a decrease in potential.

**Conclusion:**

The construction of the Silver|Silver chloride reference electrode was successful as seen by the concordant results when the open circuit potential was compared to the laboratory standard reference electrode. However, the provided cell potential of the Silver|Silver chloride, 3M NaCl laboratory standard reference electrode proved to be incorrected when using the Nernst Equation. At 3M the potential should be around 0.2V, the potential at 0.196V would indicate the solution to be 3.75M. A correlation between solution concentration and cell potential was also shown, indicating that the increase in concentration results in a decrease in cell potential. The constructed reference electrode provided a cell potential of 0.198V which is 0.015V more than the theoretical value, this may be due to the concentration being less than what was intended.

**References**

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2. Baucke, F. G. K., *Handbook of reference electrodes*. Springer-Verlag: Berlin, 2013.

3. Torriero, A. A. J., Practical Class 1: Construction and Characterisation of a Silver|Silver Chloride Reference Electrode. In *SLE338 Electrochemistry for a Sustainable Future – laboratory instructions, CloudDeakin, Deakin University*, 2017.