

## Experiment # 12 ELECTROLYSIS

### Objective

In this experiment you will construct a small electrolytic cell. Then using indicators you will determine the products formed at the anode and the cathode during several different electrolysis experiments.

### Introduction

Electrolysis is the process in which an electric current produces a chemical reaction. An electrolytic cell consists of two electrodes connected to an electrical power source. The positive pole of the power source, the anode, is connected to the electrode where oxidation is occurring and the negative pole, the cathode, is the site of reduction. The cell is constructed to keep the products of electrolysis separate so they don't react with each other.

Electrolysis is a very useful process, widely used in electroplating (i.e. chrome-, or silver-plating). The plating metal is the anode in the cell and the object to be plated is the cathode. Electrolysis is also used in purification of metal in the mineral processing industry. The best local example would be the electrolytic process of copper purification carried out every day at Kennecott. The electrolytic process is also used on a large scale to manufacture magnesium metal and chlorine gas at the nation's most infamous polluter, Utah's Magnesium Corporation (MagCorp).

As with any electrochemical reaction, an electrolysis experiment can be broken down into half-reactions. The emf of the cell ( $E_{\text{cell}}$ ) can then be calculated in the same way it is for any other electrochemical reaction (see Equation 1). The difference is that the  $E_{\text{cell}}$  will be negative, that is it is a non-spontaneous reaction. That is why we are putting energy into the system to drive the reaction.

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} \quad \text{Equation 1}$$

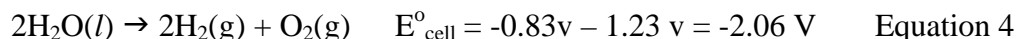
In electrolysis of a molten salt the possible half-reactions are limited to those involving the ions of the salt. In aqueous solution, however, you must be aware that water can also be involved in the electrolytic reaction. For example, if one were to place the leads of a 9 volt battery into pure water, the half-reaction at the cathode would be



The half-reaction at the anode would be

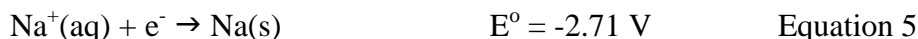


The overall reaction is



Note that the  $E^\circ$  for the cell is negative and will happen only if a minimum of -2.06 volts of electricity are available (there is plenty of voltage in our 9 volt battery). Note also that the pH at the cathode will become basic because of the production of hydroxide and the pH at the anode will become acidic because of production of hydrogen ions.

In an aqueous solution, you must consider half-reactions of all ions present in addition to water. For example, in an aqueous solution of sodium chloride, you must consider reduction of sodium ions to sodium metal (Equation 5) as a possible half-reaction at the cathode as well as the reduction of the hydrogen ions in water to form hydrogen gas and hydroxide (Equation 2)



Since the emf for reduction of water is much less than that of reduction of sodium ions, you would expect, under standard conditions, that water would be reduced in preference to  $\text{Na}^+$ .

At the anode of the sodium chloride solution you must consider the oxidation of water to form  $\text{O}_2$  and  $\text{H}^+$  (Equation 3) as well as the oxidation of chloride to chlorine (Equation 6).



$E^\circ$  for oxidation of the oxide in water is slightly lower than the  $E^\circ$  for oxidation of chloride (1.23V vs 1.36V). Therefore, under standard conditions the water should be oxidized in preference to chloride. However, in practice, since the potentials are close to each other, any over-voltages applied at the anode can result in production of  $\text{Cl}_2$ . In addition, according to the Nernst Equation (Equation 7) if a high concentration of NaCl or a low partial pressure of  $\text{Cl}_2$  is present (non-standard conditions),  $\text{Cl}^-$  may be electrolyzed in preference to water. Remember that for this reaction, Q equals the partial pressure of  $\text{Cl}_2$  divided by the molar concentration of chloride. So if  $\text{Cl}_2$  is very low or  $\text{Cl}^-$  is high, log Q will be negative and  $E_{\text{cell}}$  will be less than  $E^\circ_{\text{cell}}$ .

$$E_{\text{cell}} = E^\circ_{\text{cell}} - [(0.0592/n)\log Q] \qquad \text{where } n = \#\text{e}^- \text{ transferred} \qquad \text{Equation 7}$$

### About the experiment

In the first part of this experiment you will construct a small scale chlorine production plant. It is a miniature of the real, large scale process used for production of chlorine by the electrolysis of sodium chloride or brine (procedure written by Dr. Stephen Thompson, CSU, CO). You will then investigate the electrolysis of several other aqueous solutions. You will perform the electrolysis in a solution containing an indicator to help you identify the reaction products. Because chlorine gas is toxic, do not extend the time of the electrolysis unnecessarily, keep the electrodes in the solution only as long as you need to see the results and then remove them. Make sure not to short the electrodes to avoid complete drainage of the battery. ***Work on the set of questions provided in the discussion section as you perform the electrolysis.***

## Procedure

### Part I

#### *Pre-electrolysis investigation*

1. Place a drop of dilute mineral acid on the lid of a 24-well tray. Add a drop of bromocresol green (BCG).
2. Place a drop of dilute strong base on the lid of a 24-well tray. Add a drop of bromocresol green.

#### *Production of chlorine*

1. Obtain pins and pencil lead (graphite), 1/4" hole punch, one straw, and a small cap from the instructor's cart.
2. Cut the straw into three pieces: one about 8 cm long, and two pieces about 6 cm long.
3. Use the hole punch to punch two holes, about 0.5 cm apart in the longer straw.
4. Push the short straws through the holes in the long straw to make the set up (see Figure 1).
5. Using a pin, make a hole in the lower part of one of the short straws, so that you can insert the pencil lead into the center of the straw as shown in Figure 1.
6. Push the pin through the vertical straw and into the center of the other shorter straw as shown in Figure 1.

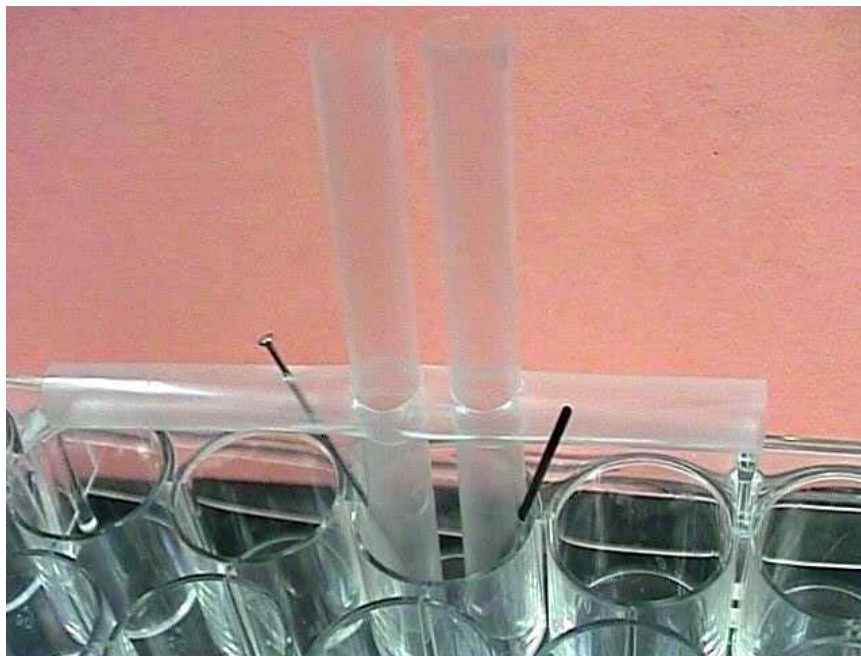


Figure 1. Set up for the production of chlorine.

7. Fill one well of a 24-well tray about 3/4 full with brine (saturated NaCl solution). Add three (3) drops of bromocresol green to the brine solution in the well. Record the color of the solution in the well.
8. Place the electrolytic set-up (straws and electrodes) in the well. Make sure that the electrodes are inserted deep into the solution.
9. Attach the alligator clips to the electrodes but do not attach the battery yet.
10. Place a small drop of starch/KI solution on the upper part of the inside wall of each straw.
11. Place a cap on the straw containing the pencil lead (the anode).
12. Attach the battery to the set up. Keep the battery on for about 3-5 seconds, long enough to observe the changes. Record your observations. If bubbles appear or solution colors change make sure that you record that. It is important to record the initial and final colors of the solution. Also note any change in the starch/KI solution in the straw at the anode.
13. Detach the alligator clips and clean the set up with distilled water. Shake off any excess water.

## **Part II.**

### **Investigating the electrolysis process of water and aqueous salt solutions**

For Part II of the experiment, use the lid of the 24-well tray to hold your solutions. Make sure that it is clean and dry. Use the same pin as in part I for one electrode and a second pin for the other electrode (no graphite used). To perform the electrolysis, attach the alligator clips to the pins and then connect the leads to the battery. Hold the alligator clips by their plastic insulation and insert them into the solution in such a way that they are as far apart as possible, yet immersed fully in the solution. Make careful observations and record what happens in the solution around each electrode for every investigation carried out.

#### **A) H<sub>2</sub>O**

1. Place 4 drops of **distilled** water in one of the circles on the lid. Perform electrolysis for about 3 seconds.
2. Repeat step 1, but use **tap** water.

#### **B) Na<sub>2</sub>SO<sub>4</sub> or K<sub>2</sub>SO<sub>4</sub>**

1. Perform electrolysis on 4 drops of 0.1 M Na<sub>2</sub>SO<sub>4</sub> (or K<sub>2</sub>SO<sub>4</sub>) solution for about 3 seconds.
2. Place 4 drops of 0.1 M Na<sub>2</sub>SO<sub>4</sub> (or K<sub>2</sub>SO<sub>4</sub>) solution in another circle, add one (1) drop of bromothymol blue, and electrolyze for about 3 seconds.

#### **c) KI or NaI**

1. Perform electrolysis on four drops of 0.1 M KI (or NaI) solution for about 3 seconds.
2. Place 4 drops of 0.1 M KI (or NaI) solution in another circle, add one (1) drop of starch solution, and perform the electrolysis for about 3 seconds.

### **Report**

The report for this experiment should contain a detailed Data Sheet documenting all observations for each experiment and a discussion of results including answers to the questions below followed by a short conclusion.

### **Questions for Discussion and Postlab**

#### **Part I.**

##### *Pre-electrolysis investigation*

What happens to BCG upon addition of acid?

What happens to BCG upon addition of base?

##### *Chlorine production.*

1. The redox reaction at the cathode is :  $2 \text{H}_2\text{O}(l) + 2 e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(aq)$ . How do you know it is not:  $\text{Na}^+(aq) + e^- \rightarrow \text{Na}(s)$  [or  $\text{K}^+(aq) + e^- \rightarrow \text{K}(s)$  if  $\text{K}_2\text{SO}_4$  is used]?
2. Why did the pH indicator (bromocresol green) change color around the cathode? Explain how this fact can be used to identify the product at the cathode.
3. What are two pieces of evidence for chlorine gas formation at the anode?
4. Write the equation for the reaction that occurs on the anode.
5. Write the overall net ionic reaction for the production of chlorine in the electrolysis process performed in Part I of this experiment.
6. Write a balanced chemical equation for the reaction of chlorine gas and KI (redox reaction that happens in the starch/KI drop placed on the inside wall of the straw. Hint,

starch is not undergoing a redox reaction).

7. What product of the reaction in question 4 reacts with starch?

Hint: An easy test for the presence of starch in bread is to place a drop of iodine solution on a bread slice and observe the brown dot of iodine change to a dark purple dot.

8. In the production of chlorine gas it is important to have the electrodes separated from each other in order to prevent the products from mixing and reacting (you really need that chlorine to react with the starch/KI). How is this separation achieved in the experiment performed?

## Part II

### **H<sub>2</sub>O**

1. What is observed in electrolysis of distilled water?
2. What is observed when tap water is used?
3. What is the difference between tap and distilled water?
4. If nothing was observed in the electrolysis of distilled water, why?

### **Na<sub>2</sub>SO<sub>4</sub> or K<sub>2</sub>SO<sub>4</sub>**

1. You may want to experiment by adding a drop of pH indicator (BTB) to a drop of dilute mineral acid and then add another drop to a drop of dilute strong base (NaOH) to verify your possible answers to this question.  
What is indicated by the color changes of bromothymol blue in the solution surrounding the electrodes?

2. How can the changes in BTB color be helpful in identifying the products formed at the electrodes and help identify the species being reduced and oxidized?

3. A. Write the equation for the redox reaction taking place at the cathode:

B. Write the equation for the redox reaction taking place at the anode:

**KI or NaI**

1. Can you easily determine the identities of the products formed on the electrodes based on the first part of this experiment (without starch)? Explain.

2. A. In the second part, why does the starch added to the solution change color?

B. How does the starch help in identifying the product of the oxidation reaction and the chemical species being oxidized?

3. Write the equation for the redox reaction taking place at the anode.

4. Write the equation for the redox reaction taking place at the cathode.

1. What is the cell emf ( $E^\circ_{\text{cell}}$ ) for electrolysis of molten nickel (II) iodide? (Use  $E^\circ$  values from Appendix E of your lecture text).
2. What reactions would take place at the anode and cathode during electrolysis of an aqueous solution of nickel (II) iodide?
3. Use the Nernst Equation (Equation 7) to calculate  $E_{\text{cell}}$  at  $25^\circ\text{C}$  for electrolysis of aqueous sodium chloride if the concentration of chlorine in the brine solution is 4.5 M and the partial pressure of  $\text{Cl}_2$  is 0.001 atmospheres.
4. Chlorine will spontaneously react with iodide to produce chloride and iodine. What is  $E^\circ$  for this reaction.