Electrolysis – predicting the products at each electrode.

Consider the following conditions when predicting products at each electrode during electrolysis.

- At the positive terminal (anode) oxidation will occur and it is the strongest reductant present, making contact with the anode or forming the anode, that will react.
- At the negative terminal (cathode) reduction will occur and it is the strongest oxidant present making contact with the anode, or forming the anode, that will react.

eg 1.

Consider the electrolytic cell shown in diagram 1

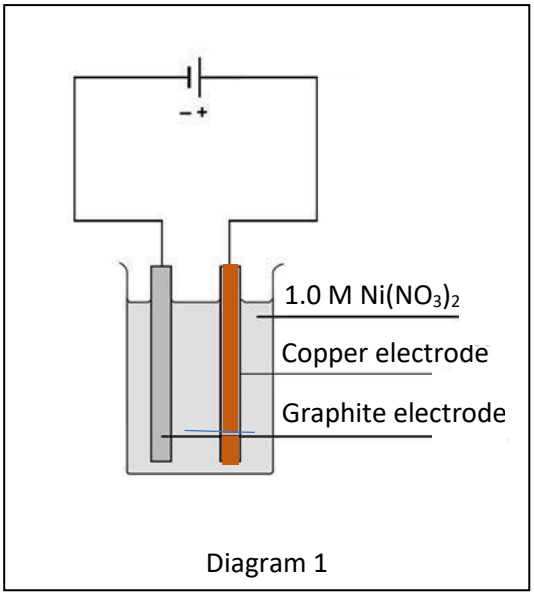


Diagram 1

Write the half reactions occurring at the anode and cathode.

Step 1 Find all the reductants present in the solution and in contact with the anode(+).

Cu(s)

$H_2O(l)$

Step 2 Find the strongest reductant in contact with the anode(+).

Cu(s) (in fact Cu is the anode)

Step 3 Find all the oxidants present.

$Ni^{2+}(aq)$

$H_2O(l)$

Step 3 Find the strongest oxidant in contact with the cathode(-).

$Ni^{2+}(aq)$

Step 4 Write the half equations

Reaction taking place at the anode

$Cu(s) \rightarrow Cu^{2+} + 2e^-$ (oxidation)

Reaction taking place at the cathode

$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$

1. Consider the electrolytic cell shown in diagram 2.

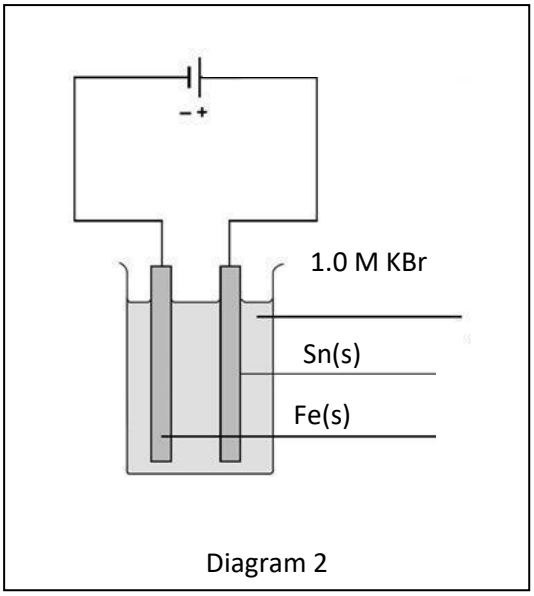


Diagram 2

   a. Write the balanced equations to the reactions occurring at the:

      i. Anode

Anode is the site of oxidation so Identify the reductants present.

$H_2O(l)$, $Br^-(aq)$, Fe(s), Sn(s).

Select the strongest reductant that makes contact or actually forms the cathode. In this case it is

$Sn(s) \rightarrow Sn^{2+}(aq) + 2e^-$

Cathode

Cathode is the site of reduction so identify the oxidants present.

$H_2O(l)$, $K^+(aq)$Select the strongest oxidant that make contact with the cathode or forms the cathode. In this case $H_2O(l)$ is the strongest oxidant.

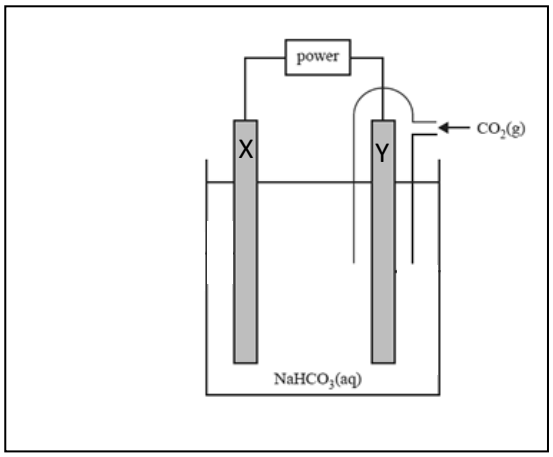
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

b. What will happen to the pH of the electrolyte solution? Explain.
The pH will increase since at the cathode OH^- is formed.

c. Explain how will each electrode change.
Cathode will decrease in mass ($Sn(s) \rightarrow Sn^{2+} + 2e^-$) the mass of the anode remains unchanged.

2. Consider the electrolytic cell shown on the right. It is used to produce ethanol from water and carbon dioxide gas. Given the following two half-cell reactions answer the following questions.

i. $O_2(g)+2H_2O(l)+4e^- \rightarrow 4OH^-(aq)$ $E^o = +0.40V$
ii. $2CO_2(g)+9H_2O(l)+12e^- \rightarrow C_2H_5OH(l)+12OH^-(aq)$ $E^o = -0.33V$



a. Identify the :
i. Anode __*X*_ , Polarity __*+*__
ii. Cathode __*Y*_ , Polarity __*-*__

b. Give the overall cell equation, states included.

$(O_2(g)+2H_2O(l)+4e^- \rightarrow 4OH^-(aq)$) X 3
+
$2CO_2(g)+9H_2O(l)+12e^- \rightarrow C_2H_5OH(l)+12OH^-(aq)$
$\Rightarrow 2CO_2(g) + 3H_2O(l) \rightarrow C_2H_5OH(l) + 3O_2(g)$

c. What material can be used for electrodes X and Y? Justify your answer.
Since no metal is part of the overall reaction, any inert conductive material such as Pt or graphite can be used.

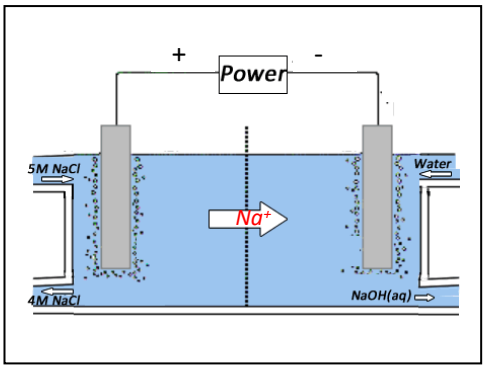
d. Identify the reducing agent in the cell and justify your answer with the use of oxidation numbers.
$OH^-(aq)$ is the reducing agent . Oxygen changes oxidation state from -2 in OH^- to 0 in O_2. Oxidation number is increased.

e. What cell voltage should be applied to run the electrolytic cell?

> 0.73V

f. How does the pH of the electrolyte change during the operation of this cell? Justify your answer. *No change*
In the overall equation the $OH^-(aq)$ does not appear as the amount of $OH^-(aq)$ used at the anode equals the amount of $OH^-(aq)$ produced at the cathode.

3. NaOH and Cl_2 gas are important chemicals in industry. They are both produced via the electrolysis of brine solution, which is concentrated NaCl. Consider the membrane electrolytic cell shown on the right. During the operation of this cell gas is produced at both electrodes. During the cell's operation a smell of chlorine is noticed coming from one of the electrodes.



   a. Give the balanced equation for the reaction occurring at the anode.

      Anode = +
      Identify the reductants in the brine and select the strongest reductant in contact with the anode.
      H_2O, Cl^- => Due to its high concentration $Cl^-(aq)$ is the strongest reductant present. This is supported by the smell of chlorine gas stated in the questions.
      $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

   b. Give the balanced equation for the reaction occurring at the anode.

   c. *Cathode = -*
      Identify the oxidants in the brine and select the strongest oxidant in contact with the cathode.
      H_2O, Na^+ => $H_2O(l)$ is the strongest oxidant present.
      $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

   d. Indicate in the diagram the ions that flow in the direction pointed to by the arrow.
      Positive ions flow to the cathode.

   e. Explain how the synthesis of NaOH and Cl_2 may be impacted if the fresh water supply to the cell was contaminated with nitric acid from a near by fertiliser synthesis facility. Make reference to the E^0 series in your explanation.
      Since $H^+(aq)$ is the strongest oxidant present, formation of $H_2(g)$ will still take place at the cathode according to the equation $2H^+(aq) + 2e^- \rightarrow H_2(g)$, $OH^-(aq)$, however, will not form as water is no longer the strongest oxidant according to the E^o series.

   f. A chemical engineer suggested making a change to this electrolytic cell in order to keep costs down. She suggested that an iron anode be used. Explain, with the use of a chemical equation and reference to the E^o series, how the products may change with the use of an iron anode.

      The following reaction will take place at the anode
      $Fe(s) \rightarrow Fe^{2+}(aq)\ ) + 2e^-$.
      The formation of $Cl_2(g)$ will not take place as Fe(s) is a stronger reductant than Cl^- (aq) according to the E^o series.

   g. The reaction between H_2 and Cl_2 is explosive. What is the purpose of the semi-permeable membrane in this cell and how does it function?
      The membrane prevents contact between H_2 and Cl_2 gases. It allows for the passage of Na^+ ions to flow from anode to cathode and hence from NaOH(aq).