Electrochemistry IV

Electrochemistry

Corrosion: A Case of Environmental Electrochemistry

Electrolytic Cells: Nonspontaneous Reactions

The Corrosion of Iron

About 25% of the steel produced in the United States is made just to replace steel already in use that has corroded. Rust arises through a complex electrochemical process.

1) Iron does not rust in dry air: moisture must be present.
2) Iron does not rust in air-free water: oxygen must be present.
3) The loss of iron and the deposition of rust often occur at *different* places on the *same* object.
4) Iron rusts more quickly at low pH (high [H^+]).
5) Iron rusts more quickly in contact with ionic solutions.
6) Iron rusts more quickly in contact with a less active metal (such as Cu) and more slowly in contact with a more active metal (such as Zn).

The Corrosion of Iron

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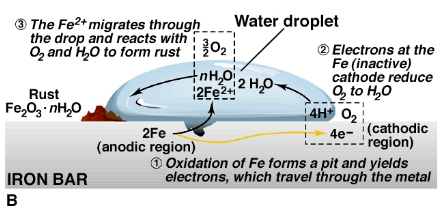
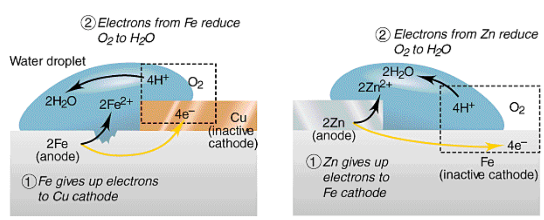


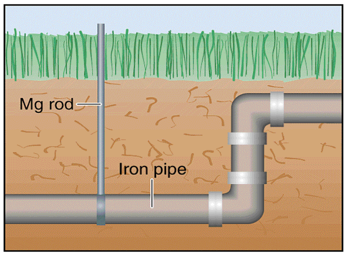
$$Fe_{(s)} \longrightarrow Fe^{2+}_{(aq)} + 2\ e^- \quad \text{[anodic region; oxidation]}$$
$$O_{2\,(g)} + 4\ H^+_{(aq)} + 4\ e^- \longrightarrow 2\ H_2O_{(l)} \quad \text{[cathodic region; reduction]}$$
$$2\ Fe_{(s)} + O_{2\,(g)} + 4\ H^+_{(aq)} \longrightarrow 2\ Fe^{2+}_{(aq)} + 2\ H_2O_{(l)}$$

The Effect of Metal-Metal Contact on the Corrosion of Iron



A Enhanced corrosion **B** Cathodic protection

The Use of Sacrificial Anodes to Prevent Iron Corrosion

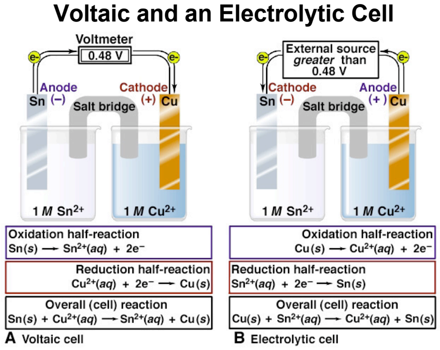


QUESTION

For cathodic protection used to prevent corrosion of iron to be effective which of the following must be true?

1. The anode used must be a better oxidizing agent than iron.
2. The sacrificial anode used must react with oxygen to protect the iron from reacting with oxygen.
3. Iron must have a reduction potential than the metal used as the anode.
4. In cathodic protection systems a metal is attached or connected to iron in such a way that electrons flow away from the iron.

The Tin-Copper Reaction as the Basis of a Voltaic and an Electrolytic Cell



Construction and Operation of an Electrolytic Cell

Let's use the tin-copper voltaic cell:

$Sn_{(s)} \longrightarrow Sn^{2+}_{(aq)} + 2\ e^-$ [anode; oxidation]

$Cu^{2+}_{(aq)} + 2\ e^- \longrightarrow Cu_{(s)}$ [cathode; reduction]

$Sn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Sn^{2+}_{(aq)} + Cu_{(s)}$ $E^o_{cell} = 0.48$ V and $\Delta G^o = -93$ kJ

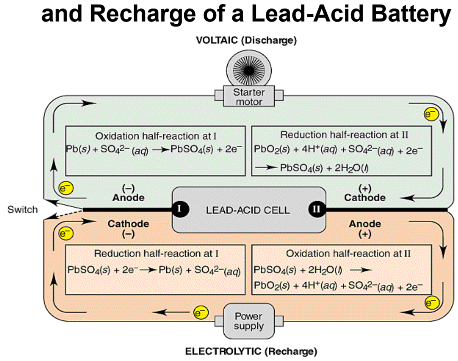
The spontaneous reaction of Sn metal through oxidation to form Sn^{2+}ions and the reduction of Cu^{2+} ions to form copper metal will produce a cell voltage of 0.48 volt. Therefore, the reverse reaction is *non*spontaneous and never happens on its own. We can make the reverse reaction occur by supplying power from an external source with an electric potential greater than E^o_{cell}. We convert the voltaic cell into an electrolytic cell and reverse the electrodes.

$Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^-$ [anode; oxidation]

$Sn^{2+}_{(aq)} + 2\ e^- \longrightarrow Sn_{(s)}$ [cathode; reduction]

$Sn^{2+}_{(aq)} + Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + Sn_{(s)}$ $E^o_{cell} = -0.48$ V and $\Delta G^o = 93$ kJ

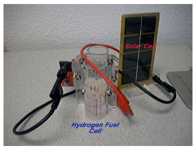
The Processes Occurring During the Discharge and Recharge of a Lead-Acid Battery

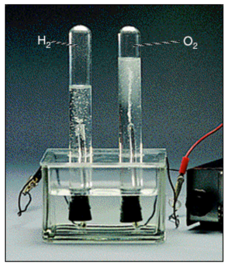


Comparison of Voltaic and Electrolytic Cells

			Electrode		
Cell Type	**ΔG**	**E_{cell}**	**Name**	**Process**	**Sign**
Voltaic	< 0	> 0	Anode	Oxidation	-
Voltaic	< 0	> 0	Cathode	Reduction	+
Electrolytic	> 0	< 0	Anode	Oxidation	+
Electrolytic	> 0	< 0	Cathode	Reduction	-

The Electrolysis of Water





Using Nernst's Eq.:

(+) Anode: -0.82 V

(-) Cathode: -0.42 V

E cell = -1.24 V

Oxidation half-reaction
$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$

Reduction half-reaction
$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$

Overall (cell) reaction
$2H_2O(l) \longrightarrow 2H_2(g) + O_2(g)$

Electrolysis of Aqueous Ionic solutions and the Phenomenon of Overvoltage

When two half-reactions are possible at an electrode, the one with the more positive (or less negative) electrode potential occurs.

For example, the electrolysis of KI: Cathode reaction:

$K^+_{(aq)} + e^- \longrightarrow K_{(s)}$ $E^o = -2.93$ V

$2\ H_2O_{(l)} + 2\ e^- \longrightarrow H_{2\,(g)} + 2\ OH^-_{(aq)}$ $E^o = -0.42$ V [reduction]

The less negative potential for water means that H_2 forms at the cathode.

Anode reaction:

$2\ I^-_{(aq)} \longrightarrow I_{2\,(s)} + 2\ e^-$ $-E^o = -0.53$ V [oxidation]

$2\ H_2O_{(l)} \longrightarrow O_{2\,(g)} + 4\ H^+_{(aq)} + 4\ e^-$ $-E^o = -0.82$ V

The less negative potential for I^- means I_2 forms at the anode.

For gases such as $H_{2\,(g)}$ and $O_{2\,(g)}$ to be formed at the metal electrodes an additional voltage is required; this is called the **overvoltage!**

Electrolysis of Aqueous Ionic Solutions and the Phenomenon of Overvoltage

An example of overvoltage is the electrolysis of aqueous NaCl.
Water is easier to reduce, so H_2 forms at the electrode even with an overvoltage of 0.6 V.

$Na^+_{(aq)} + e^- \longrightarrow Na_{(s)}$ $E^o = -2.71$ V

$2\ H_2O_{(l)} + 2e^- \longrightarrow H_{2\,(g)} + 2\ OH^-_{(aq)}$ $E = -\ 0.42$ V (~ 1 V with overvoltage) [reduction]

But Cl_2 forms at the anode, even though the electrode potentials suggest O_2 should form:

$2\ H_2O_{(l)} \longrightarrow O_{2\,(g)} + 4\ H^+_{(aq)} + 4\ e^-$ $-E = -0.82$ V (~ -1.4 V with overvoltage)

$2\ Cl^-_{(aq)} \longrightarrow Cl_{2\,(g)} + 2\ e^-$ $-E^o = -1.36$ V [oxidation]

Keeping the chloride ion concentration high favors the production of Cl_2, even though O_2 formation is still slightly favored with the overvoltage.

Predicting the Electrolysis Products of Aqueous Ionic Solutions

Problem: What products form during electrolysis of aqueous solutions of the following salts? (a) KBr (b) $AgNO_3$ (c) $MgSO_4$

Plan: We identify the reacting ions and compare their electrode potentials with those of water, taking the 0.4 to 0.6 overvoltage into consideration. Whichever half-reaction has the higher (less negative) electrode potential occurs at that electrode.

Solution:

(a) $K^+_{(aq)} + e^- \longrightarrow K_{(s)}$ $E^o = -2.93$ V

$2\ H_2O_{(l)} + 2\ e^- \longrightarrow H_{2(g)} + 2\ OH^-_{(aq)}$ $E^o = -0.42$ V

Despite the overvoltage, which makes *E* for reduction of water between -0.8 and -1.0 V, H_2O is still easier to reduce than K^+, so **$H_{2\,(g)}$ forms at the cathode**.

$2\ Br^-_{(aq)} \longrightarrow Br_{2\,(l)} + 2\ e^-$ $-E^o = -1.07$ V

$2\ H_2O_{(l)} \longrightarrow O_{2\,(g)} + 4\ H^+_{(aq)} + 4\ e^-$ $-E^o = -0.82$ V

Because of the overvoltage, it is easier to oxidize Br^- than water, so **Br_2 forms at the anode**.

Predicting the Electrolysis Products of Aqueous Ionic Solutions

Solution: Cont.

(b) $Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}$ $E^o = 0.80$ V

$2\ H_2O_{(l)} + 2\ e^- \longrightarrow H_{2\,(g)} + 2\ OH^-_{(aq)}$ $E^o = -0.42$ V

As the cation of an inactive metal, Ag^+ is a better oxidizing agent than H_2O, so **Ag forms at the cathode.** NO_3^- cannot be oxidized, because N is already in its highest (+5) oxidation state. Thus, **O_2 forms at the anode:**

$2\ H_2O_{(l)} \longrightarrow O_{2\,(g)} + 4\ H^+_{(aq)} + 4\ e^-$

(c) $Mg^{2+}_{(aq)} + 2\ e^- \longrightarrow Mg_{(s)}$ $E^o = -2.37$ V

Like K^+ in part (a), Mg^{2+} cannot be reduced in the presence of water, so H_2 forms at the cathode. The SO_4^{2-} ion cannot be oxidized because S is in its highest (+6) oxidation state. Thus, H_2O is oxidized, and **O_2 forms at the anode:**

$2\ H_2O_{(l)} \longrightarrow O_{2\,(g)} + 4\ H^+_{(aq)} + 4\ e^-$

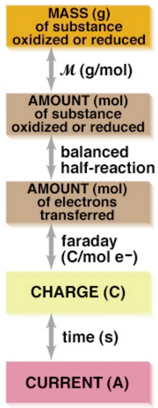
Electrolysis Products of Aqueous Ionic Solutions

1) Less active metals can be produced at the Cathode (reduction of their respective cations to the metal):
Au, Ag, Cu, Cr, Pt, Cd

2) More active metals are NOT produced: **Groups 1A and 2A plus Al**; **H_2O is reduced instead.**

3) Some anions react at the Anode (are oxidized): **Group 7A: Halides except for F^-**
Anions that are NOT oxidized besides F^- include common oxoanions: nitrate, carbonate, sulfate, phosphate.
H_2O is oxidized instead.

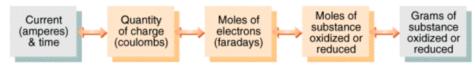
A Summary Diagram for the Stoichiometry of Electrolysis



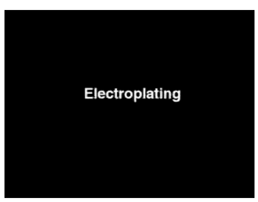
Electrolysis

Quantitative Aspects of Electrolysis

- We want to know how much material we obtain with electrolysis.
- Consider the reduction of Cr^{3+} to Cr.
  - $Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$.
  - 3 mol of electrons will plate 1 mol of Cr.
  - The charge of 1 mol of electrons is 96,500 C (1 *F*).
  - Since Q = I x t, the amount of Cu can be calculated from the current (I) and time (t) taken to plate.



Electrolysis: Electroplating



Electrolysis: Chrome Plating

Applying the Relationship Among Current, Time, and Amount of Substance

Problem: A technician needs to plate a bathroom fixture with 0.86 g of chromium from an electrolytic bath containing aqueous $Cr_2(SO_4)_3$. If 12.5 min is allowed for the plating, what current is needed?
Plan: We write the balanced half-reaction for Cr^{3+} reduction. We then know the number of moles of electrons per mole of Cr, and can calculate the current needed to do the electroplating.
Solution: Writing the balanced half-reaction:

$$Cr^{3+}_{(aq)} + 3\ e^- \longrightarrow Cr_{(s)}$$

$$e^-\ \text{transferred: } 0.86\ \text{g Cr} \times \frac{1\ \text{mol Cr}}{52.00\ \text{g Cr}} \times \frac{3\ \text{mol } e^-}{1\ \text{mol Cr}} = 0.050\ \text{mol } e^-$$

Calculating charge transfer:

$$\text{Charge (C)} = 0.050\ \text{mol } e^- \times \frac{9.65 \times 10^4\ \text{C}}{1\ \text{mol } e^-} = 4.8 \times 10^3\ \text{C}$$

Calculating the current:

$$\text{Current (A)} = \frac{\text{charge (C)}}{\text{time (s)}} = \frac{4.8 \times 10^3\ \text{C}}{12.5\ \text{min}} \times \frac{1\ \text{min}}{60\ \text{s}} = 6.4\ \text{C/s} = \textbf{6.4 A}$$

QUESTION

An antique automobile bumper is to be chrome plated. The bumper, which is dipped into an acidic $Cr_2O_7^{2-}$ solution, serves as a cathode of an electrolytic cell. The atomic mass of Cr is 51.996; 1 faraday = 96,485 coulombs. If oxidation of H_2O occurs at the anode, how many moles of oxygen gas will evolve for every 1.00×10^2 grams of Cr(s) deposited?

1) 2.88
2) 0.48
3) 11.5
4) 7.7
5) 1.44

Electrolysis

Electrical Work

- In an electrolytic cell an external source of energy is required for the reaction to proceed.
- In order to drive the nonspontaneous reaction the external emf must be greater than E_{cell}.
- From physics: work has units watts:

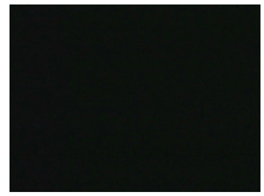
$$1\text{ W} = 1\text{ J/s}.$$

- Electric utilities use units of kilowatt-hours:

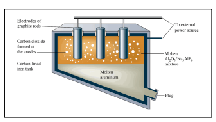
$$1\,\mathbf{kWh} = (1000\,\mathbf{W})(1\,\mathbf{h})\left(\frac{3600\,\mathbf{s}}{1\,\mathbf{h}}\right)\left(\frac{1\,\mathbf{J/s}}{1\,\mathbf{W}}\right)$$

$$= 3.6\times10^{6}\,\mathbf{J.}$$

Aluminum Production

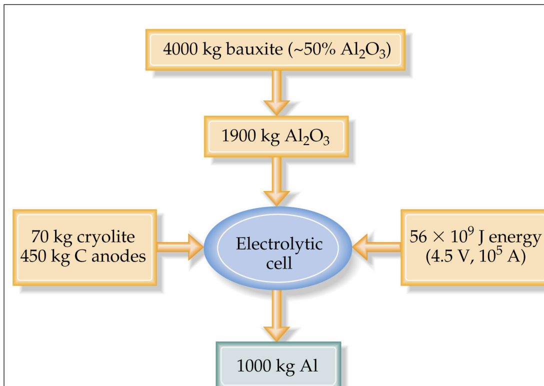


QUESTION



The extraction of aluminum from a mixture of molten Al_2O_3/Na_3AlF_6 (cryolite) is superior to the extraction from a solution of aluminum ions in water or from molten aluminum oxide because…

1. carbon dioxide bubbles can continuously provide agitation that effectively stirs the molten solution.
2. attempts at reducing Al^{3+} from water are hampered because Al^{3+} is a better oxidizing agent than water.
3. the process involves lower temperatures (therefore less energy) due to the ease of oxidation of aluminum in the presence of cryolite.
4. water is easier to oxidize than aluminum, so it would react first at a lower voltage.



QUESTION

What quantity of charge is required to reduce 40.0 g of $CrCl_3$ to chromium metal?
(1 faraday = 96,485 coulombs)

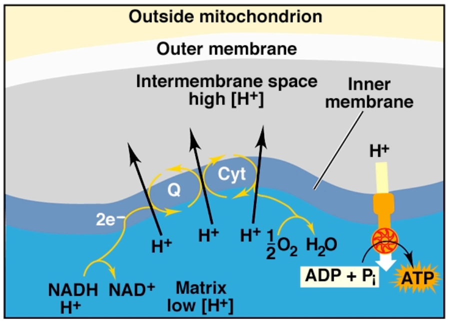
1) 2.45×10^4 C
2) 7.31×10^4 C
3) 2.20×10^5 C
4) 9.65×10^4 C
5) none of these

QUESTION

Gold (atomic mass = 197) is plated from a solution of chlorauric acid, $HAuCl_4$; it deposits on the cathode. Calculate the time it takes to deposit 0.50 gram of gold, passing a current of 0.10 amperes. (1 faraday = 96,485 coulombs)

1) 41 minutes
2) 2.0 hours
3) 1.0 hour
4) 6.0 hours
5) none of these

Coupling Electron Transport to Proton Transport to ATP Synthesis



The Main Energy-Yielding Steps in the Electron-Transport Chain (ETC)