3.014 MATERIALS LABORATORY
MODULE – BETA 1
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GEETHA P. BERERA

LEAD-ACID STORAGE CELL

OBJECTIVES:

- Understand the relationship between **Gibbs Free Energy** and **Electrochemical Cell Potential**.
- Derive Nernst Equation (**Cell Potential** versus **Activity** of reacting species) for a lead-acid cell.
- Verify the effect of **Temperature** on the **Cell Potential**.
- Verify the effect of **Activity** (effective concentration) of reacting species on the **Cell Potential**.
- Examine the effect of Electrode Composition on the Cell Potential.

BACKGROUND:

A lead-acid cell is a basic component of a lead-acid storage battery (e.g., a car battery). A 12.0 Volt car battery consists of six sets of cells, each producing 2.0 Volts. A lead-acid cell is an electrochemical cell, typically, comprising of a lead grid as an anode and a second lead grid coated with lead oxide, as a cathode, immersed in sulfuric acid. The concentration of sulfuric acid in a fully charged auto battery measures a specific gravity of 1.265 – 1.285.[1] This is equivalent to a molar concentration of 4.5 – 6.0 M.[2,3]

The cell potential (open circuit potential or battery voltage, OCV) is a result of the electrochemical reactions occurring at the cell electrode interfaces. The electrochemical reactions that convert chemical energy into electrical energy in a lead-acid cell, are shown in equations 1 and 2. [3,4]

$$Pb + SO_4^{-2} \text{ --------------> } PbSO_4 + 2\,e^{-1} \qquad (1)$$

Oxidation (anode)

$PbO_2 + 4H^{+1} + 2e^{-1} + SO_4^{-2}$ -----------------> $PbSO_4 + 2H_2O$ (2)

Reduction (Cathode)

Reactions 1 and 2, are half-cell reactions occurring simultaneously, at the anode and cathode.
The cell voltage is dependent on several factors, such as electrode chemistry, temperature and electrolyte concentration. The Nernst equation establishes the relationship between the cell voltage and these various parameters. [3,4]

NERNST EQUATION FOR THE ELECTROCHEMICAL REACTIONS IN A LEAD-ACID STORAGE CELL [5,6]

The Nernst equation is a fundamental equation in electrochemical reactions which expresses the electrochemical cell potential in terms of reactants and products of the reaction. It can be derived based on Gibbs Free Energy Criterion for chemical reactions.

The maximum amount of electrical energy (or work done) that can be delivered, by an electrochemical cell (or battery) in a given state, nFE, depends on the change in Gibbs Free Energy, ΔG as shown in equation 3.

$$\Delta G = - nFE \qquad (3)$$

where n is the number of moles of electrons exchanged in an electrochemical reaction, F is the Faraday's constant (96,485 C / mole), and E is the cell potential. For cell conditions, in a standard state,

$$\Delta G^0 = - nFE^0 \qquad (4)$$

where, E^0 represents standard electrochemical cell potential, and ΔG^0 represents the Gibbs Free Energy changes in the standard state.

For a general chemical reaction, the changes in Gibbs Free Energy is related to the reactants and products of reaction, as shown in equations 5 and 6.

$$\Delta G - \Delta G^0 = RT \ln [a_{products} / a_{reactants}] \qquad (5)$$

or

$$\Delta G - \Delta G^0 = 2.303 \times RT \log[a_{products} / a_{reactants}] \qquad (6)$$

where, ΔG and ΔG^0, represent changes in the free energy of products and reactants in non-standard and standard states, respectively, R is the gas constant (8.314

J/deg.mole), T is the absolute temperature, $a_{products}$ and $a_{reactants}$ are the activities (effective concentrations) of products and reactants, respectively.

Equations, 3, 4 and 6, establish the **NERNST** equation, which relates the cell potential in any state, to the standard cell potential, and the products and reactants of the electrochemical reaction.

$$E - E^0 = - [2.303 \times RT / nF] \times \{\log[a_{products} / a_{reactants}]\} \qquad (7)$$

Or $$E = E^0 - [2.303 \times RT/nF] \times \{ \log[a_{products} / a_{reactants}]\} \qquad (8)$$

The Nernst equation for the lead-acid cell can be written by adding the two half-cell reactions given in equations 1 and 2.

Overall reaction:

$$PbO_2 + Pb + 2SO_4^{-2} + 4H^{+1} \text{ ---------------------> } 2\,PbSO_4 + 2\,H_20 \qquad (9)$$

OR

$$PbO_2 + Pb + 2H_2SO_4 \text{ ------------------> } 2PbSO_4 + 2H_2O \qquad (10)$$

Note: The affect of sulfuric acid concentration on the electrode potential, is clearly seen in equation 10, which is a simpler form of equation 9. Using equation 8, the Nernst equation for the lead acid cell is,

$$E = E^0 - [2.303\, RT / nF] \times \{ \log [a^2_{PbSO4} * a^2_{H2O}] / [a_{PbO2} * a_{Pb} * a^2_{H2SO4}]\}$$

where a s' are the activities of the reactants and the products of the cell, defined as an effective concentration. It is related to the actual concentration of the species, via, $a = \gamma C$ [C: molal concentration, γ is an activity coefficient]. $a < C$, except in very dilute solutions where γ 1 and a C.

R = 8.314 J / K-mole, is the gas constant
T, is the absolute temperature (K)

Since $a_{PbSO4} = 1$, $a_{H2O} = 1$, $a_{PbO2} = 1$, $a_{Pb} = 1$
[The activity of a pure solid = 1, activity of water = 1]

$$E = E^0 - [2.303\, RT / nF] \times \{ \log [1 / a^2_{H2SO4}]\}$$

$$E = E^0 - [2.303\ RT / nF] \times \{ - 2 \log a_{H2SO4}\}$$

$$E = E^0 + [2 * 2.303\ RT / n F] \times \{\log a_{H2SO4}\} \qquad (11)$$

Note: n= 2
n = # of moles of electrons involved in the oxidation-reduction reactions in equations, 1 and 2, above.

Equation 11, clearly shows the effect of temperature and the activity (effective concentration) of H_2SO_4, on the cell potential.

Note:

1. The activity of sulfuric acid is related to the actual electrolyte concentration as shown below: [6]

   $$a_{H2SO4} = 4 * \gamma_m^{3} * C^{3}$$

   where C is the MOLAL concentration (MOLALITY) and γ_m is defined as a mean activity coeffcient.
   Typically, a < C, except in very dilute solutions (< 0.001 M) when $\gamma_m \approx 1$ and a C. The activity approaches unity for acid concentration in the range, 3.5 – 4.0 M.

2. The activity coefficient is generally temperature and concentration dependent, and is experimentally determined. The values of γ_m for H_2SO_4 as a function of molal concentration is provided in the handout.[6]

MATERIALS:

ELECTRODES: Lead (Pb) and lead oxide electrodes from Leoch Battery Technology Company, LTD.
Tin (Sn) and Pb-Sn (50% by mass) wires from Amerway Inc.
Pb (99.998%) foil, 1.0 mm thick from Alfa Aesar

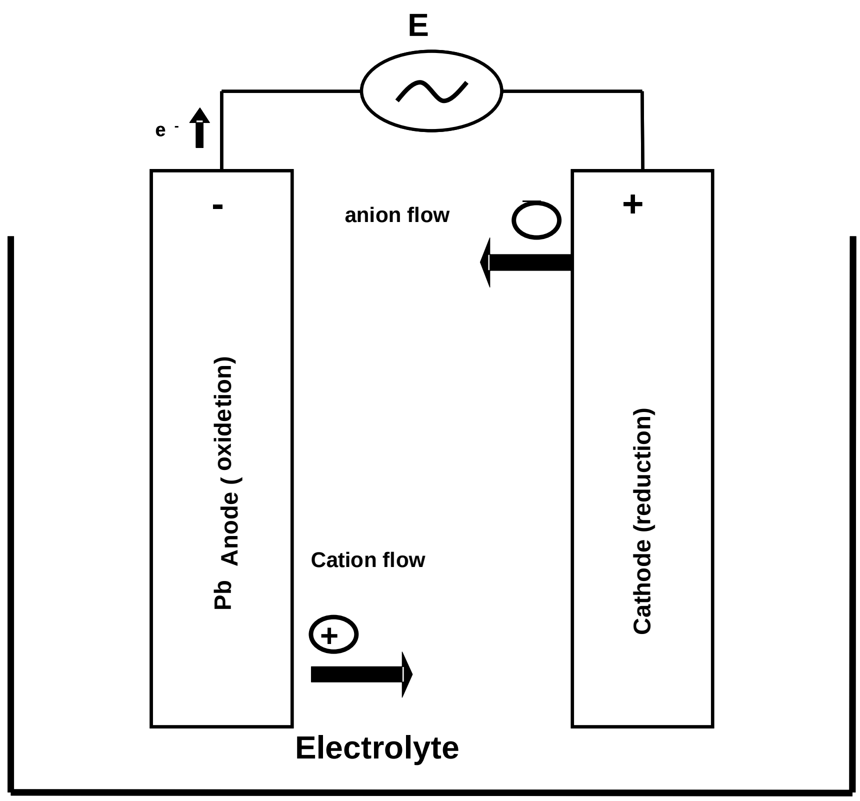
ELECTROLYTE: Sulfuric Acid (96%) from Mallinckrodt

INSTRUMENTS:

Multimeter, Hewlett Packard, 3457 A
Omega, Type-K (Chromel- Alumel) Thermocouple and digital meter
Digital hotplate and stirrer, VWR 575

EXPERIMENT:

Assemble a lead-acid cell in a 600 mL beaker with a cap to support the electrodes and a thermocouple. Connect the Pb anode (black-gray) to the negative terminal of the digital multimeter, and the lead oxide cathode (brown-red) to the positive terminal of the multimeter as shown in the figure below. In this configuration, a positive value is recorded for the measured cell potential, E. Fill the beaker with the desired concentration of sulfuric acid to approximately, 250 mL level.
Note: The maximum concentration of acid, 3.0M used here, is lower than the nominal concentrations, 4.5 – 6.0 M reported for auto batteries. The 3.0 M acid cell produces a potential above 2.0 volts, and is adequate for demonstrating our objectives.



1. Measure cell potential as a function of temperature.
   Acid concentration: 3.0 M
   Temperature range: ambient to 60˚ C

2. Measure cell potential as a function of electrolyte concentration.

   Acid concentrations: 0.01 M, 0.1 M, 0.5 M, 1.0 M, 2.0 M, 3.0 M
   Temperature: ambient
   Equilibrate the electrodes in each concentration for 20 minutes.

3. Measure cell potential for various combination of electrodes, to examine the effect of electrode composition on the cell potential.
   Pb electrode vs. Pb
   Pb electrode vs. Sn
   Pb electrode vs. Pb-Sn (50% by mass)
   Pb-Sn vs. Lead Oxide electrode
   Sn vs. Lead Oxide electrode

   Acid concentration: 1.0 M
   Temperature: ambient

ANALYSIS:

1. Demonstrate the validity of Nernst equation for the lead-acid cell used in this experiment.

   - Plot a graph of Cell Potential vs. Temperature
     Find the activity, a $_{H2SO4}$ of H^+ and SO_4^{2-} ions in 3.0 M sulfuric acid.

   - Plot a graph of Cell Potential vs. Molar concentration of sulfuric acid.

   - Plot a graph of Cell Potential vs. log (a $_{H2SO4}$).

2. Demonstrate the relationship between the Gibbs Free Energy and the Cell Potential.

   - Calculate the Gibbs free energy changes from the measured cell potential at ambient temperature for various concentrations of sulfuric acid.

   * Plot a graph of Gibbs Free Energy vs. Electrode Potential measured for various concentration of sulfuric acid.

   Is the cell discharge process, a spontaneous or non-spontaneous reaction?

3. Tabulate the cell potentials for the various combination of electrodes to demonstrate the effect of electrode composition on the cell potential.

REFERENCES:

1. http://www.4unique.com/battery/battery_tutorial.htm, access date, October 2003.

2. Handbook of Chemistry and Physics, WEAST, CRC PRESS, 61st edition, 1980 – 1981.

3. An introduction to Physical Science, by Shipman, Wilson and Todd, 7th edition, D. C. Heath and company, 1993. [Handed out]

4. “Handbook of Batteries”, 3rd edition, editors: David Linden, Thomas B. Reddy, McGraw Hill New York, 2002. [Handed out]

5. “Corrosion and Corrosion Control”, H. H . Uhlig, 2nd edition, page 18-21, Wiley, New York, 1971. [Handed out]