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PHY 312

Thermodynamics in Lead Acid Batteries

Like many other types of batteries, the lead acid battery consists of two electrodes submerged in a neutral electrolyte. The cathode consists of lead dioxide, and the anode consists of spongy lead, each connecting to their respective terminals. The battery holds the electrolyte in interconnected positive and negative cells, each surrounded by layers of different necessary plates. The innermost plate is a microporous separator to keep negative plate and negative cell from being in direct contact with each other. A negative plate is separated from an outer positive plate by an additional microporous separator. The grid plate caps the end of the battery.

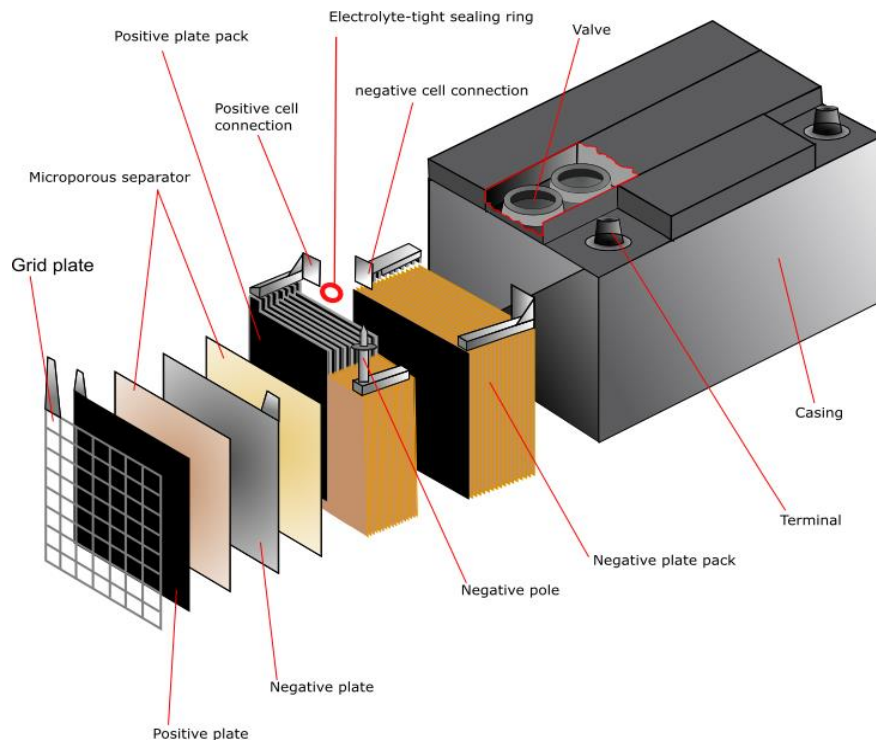


Figure 1. Physical representation of typical makeup of lead acid car battery

Lead acid batteries are commonly used in cars and other vehicles. They are typically protected by a cover of polypropylene to prevent structural damage. The positive and negative plates are essential for conducting a current between the terminals. For twelve volt batteries the case is divided into six cells. The cover is sealed at the end of production on top of this six cell grid, which consists of pure lead or an alloy of lead. A mixture of lead oxide, sulfuric acid, and water is applied to the grids. Expander material consisting of powdered sulfates is added to this mixture or paste to produce negative plates. The plates are separated by the microporous separator to prevent short circuits, while still allowing current flow through these pores. The two plates and separator make up an element. Each cell contains one element and is connected by conductive metal to other cells. The lead terminal is then welded on to the top of the cell's cover.

The purpose of a battery is to store charge for future use. The charge comes from a voltage created by chemical reactions from two oppositely charged materials. Each cell contributes approximately two volts of voltage for a total twelve volts. The terminals are themselves oppositely charged, and must in some way be put in series with each other via some device that will complete the circuit. By connecting the device requesting power to the battery, current is produced and flows into that device. At the same time however, the battery is always constantly charging and discharging simultaneously. This unique process is described as the cycling ability of the battery, and results from the fact that lead acid batteries can only be charged by feeding electrical current back into it, a product of the originally described discharge process.

The chemical reactions that take place during the discharging and charging of the battery is shown and described below.

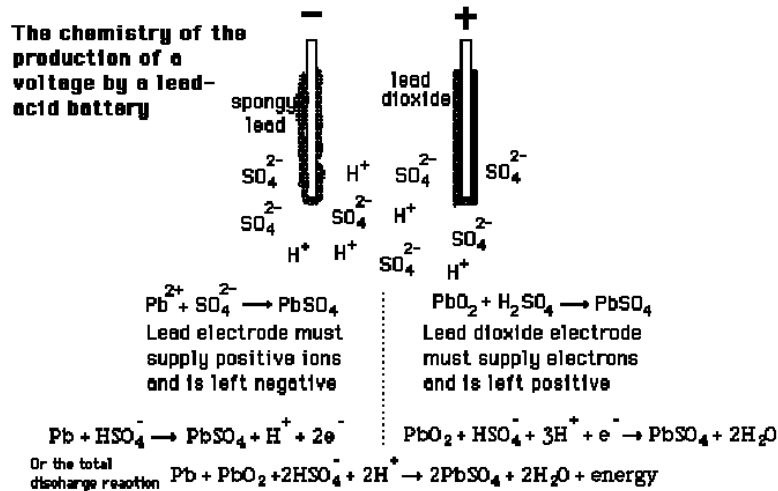


Figure 2. Reaction summary for Lead acid batteries. Cathode (lead oxide) and Anode (spongy lead) assumed to be submerged in electrolyte, resulting in reactions.

The cathode is described in the equation by PbO_2 , lead dioxide, and the anode consists simply of lead (Pb). Specifics of the reaction and functions of each substance are described by captions within Figure 2. The electrolyte solution can be separated into hydrogen and sulfate atoms, through the process of electrolysis with the aid of the electrical current running through the electrodes. Both substances within the electrodes or plates begin the reaction neutral, and do not hold their respective charges until a current induces the chemical reactions described. This means the more positive or negative an electrode is, the more charge can be stored in the battery at any different time.

Thermodynamics can be applied to any battery, including the lead acid battery. To show this, we should simplify the reactions into the following equations:



The overall reaction is given by:



Our change in standard free energy, ΔG° , is given by:

$$\Delta G^\circ = -nFE^\circ \quad (4)$$

$$\text{where } E^\circ \text{ is the standard cell potential} = E_C^\circ - E_A^\circ \quad (5)$$

If the battery is not in its most standard state, the energy of the battery is given by the equation:

$$E = E^\circ - \frac{RT}{ZF} \ln \frac{(aC)^c (aD)^d}{(aA)^a (aB)^b} \quad (6)$$

Where (aC) describes the activity of substance C (from initial reaction equations (1), (2), (3)) .

So, when we substitute for our standard cell potential,

$$\Delta G^\circ = -nFE^\circ - \frac{nRT}{F} \ln \frac{(aC)^c (aD)^d}{(aA)^a (aB)^b} \quad (7)$$

ΔG° describes the driving force for a battery, which enables it to deliver electrical energy to the vehicle. As we can see, this change in free energy has directly to do with the amount of electrons (n) included in the chemical reactions. As a result, more reactions lead to more electrons and therefore a greater change in free energy. The negative ions are only separated by the incoming current however, which is why the speed of this reaction for discharge is directly dependent on the rate of our charging process. We can substitute the components of the equations for lead acid battery charge and discharge from Figure 2 for these arbitrary components that make up our thermodynamic equations for free energy (7).

Our free energy can be directly applied quantitatively to the rate of the reaction by the with the following expression, the Arrhenius relationship:

$$\propto \exp\left(\frac{-\Delta G}{RT}\right) \quad (8)$$

Here, α is our rate constant, which varies from substance to substance. This equation can be applied to both the anode and the cathode. The cathode's rate is denoted k_c , and the anode's k_a . When we apply the Arrhenius relationship to each, the α is replaced by the product of z , the number of electrons in the given reaction, and the constant K , which we have seen in our equation for change in free energy. T represents the temperature of the system in Kelvin and R is our universal gas constant. The rate of reaction is then related to the current that flows through the battery, through the equation (for the anode):

$$\begin{aligned} i_o &= zFk_a \\ &= zFK \exp\left(\frac{-\Delta G}{RT}\right) \end{aligned} \quad (9)$$

If an overpotential is now applied in the anodic direction, the activation energy of the reaction is reduced to $(\Delta G - \alpha zF\eta)$, where α is now the “symmetry factor” of the electrical double layer, usually 0.5.

$$\begin{aligned} i_a &= zFK \exp\left(\frac{-(\Delta G - \alpha zF\eta)}{RT}\right) \\ &= zFK \exp\left(\frac{-\Delta G}{RT}\right) \exp\left(\frac{\alpha zF\eta}{RT}\right) \end{aligned} \quad (10)$$

$$\therefore i_a = i_o \exp\left(\frac{\alpha zF\eta}{RT}\right) \quad (11)$$

This is known as the *Tafel equation*.

This equation can be manipulated by substitution and taking the natural log of each side,

$$\ln(i_a) = \ln(i_o) + (E - E^o) \left(\frac{\alpha zF}{RT} \right) \quad (12)$$

and then applied graphically to the energy of the system:

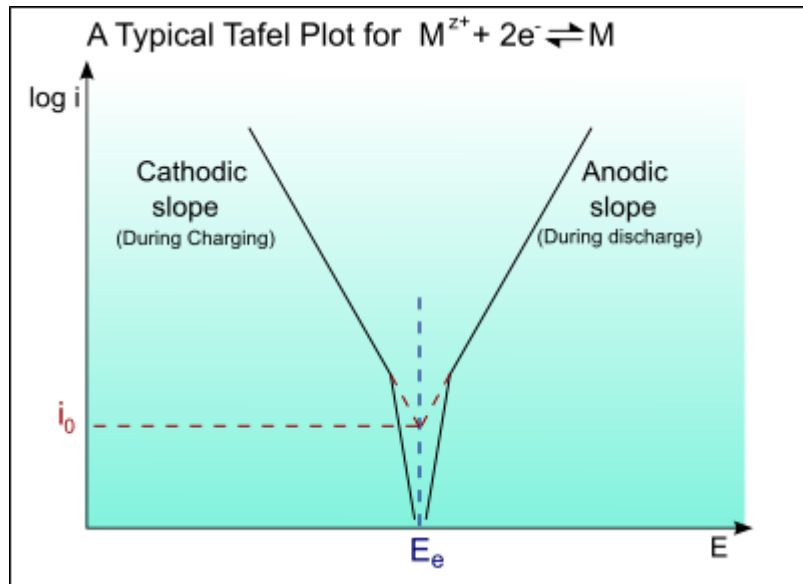


Figure 3. Graphical representation for relationship between the natural log of current ($\log i$) and energy (E). Tafel plot for reactions within battery where two electrons transferred per chemical reaction

Because Figure 3 can be applied to any reaction consisting of a transfer of two electrons between the electrodes and the electrolyte, it can be applied to our Lead Acid battery discharge reaction. We can use the convergence pattern of these slopes to locate the current through the battery (i_0), as shown. At high currents the Cathodic slope will behave like that of a graph sloped by the inverse of the square of the given value (E).

Bibliography

- Bode, H. "Lead-acid Batteries (Book) | SciTech Connect." *Lead-acid Batteries (Book) | SciTech Connect*. John Wiley and Sons, Inc., New York, NY, n.d. Web. 27 Apr. 2016.
- "DoITPoMS." *Cambridge University- TLP Library Batteries*. N.p., n.d. Web. 27 Apr. 2016.
- "Lead Acid Batteries." *Wayne.edu*. N.p., n.d. Web.
- "Lead Batteries." *My Website What Is a Lead Battery?* N.p., n.d. Web. 27 Apr. 2016.