Understanding the Lead-Acid Cell

Richard Perez and Conrad Heins

All batteries are chemical engines. An understanding of the electrochemical reactions taking place within the lead-acid cell will help you to use your battery more efficiently. An understanding of sulfation, which kills over 80% of all lead-acid cells, will help you make your battery last longer. The processes are simple and understandable to anyone who managed to stay awake during high school chemistry or physics.

Chemical Composition of Lead-acid Cells

The positive plates (anodes) within the lead-acid cell are made of lead dioxide (PbO_2). The negative plates (cathodes) are constructed of lead (Pb). The electrolyte is a dilute solution (≈25%) of sulfuric acid (H_2SO_4) and water. In the charged state, the electrolyte exists as ions, charged molecules. This is because sulfuric acid, when it dissolves in water, dissociates to form two hydrogen ions ($2H^+$) and a sulfate ion ($SO_4^=$). Both electrodes of the cell are completely immersed in this electrolyte. The reversible chemical reaction between the plates and the electrolyte allows the storage and retrieval of energy from the cell.

Lead-acid cells differ from most electrochemical cells because the electrolyte actually participates in the chemical reaction, plating out on the electrodes. In alkaline cells (nickel-cadmium and nickel iron), the electrolyte changes chemical compostion during charge and discharge of the cell. In a lead-acid cell the concentration of sulfuric acid in the electrolyte gradually decreases as the cell is discharged. If the cell is fully charged, then the electrolyte is rich in sulfuric acid. If the cell is fully discharged, then the electrolyte is depleted of sulfate ions and contains mostly water. This change in electrolyte chemical composition allows a rough measurement of the cell's state of charge with a hydrometer.

The voltage produced across a single lead-acid cell is a function of the electrochemical reaction between the active materials in the cell. All lead-sulfuric acid reactions proceed at about 2 Volts. This is a given factor. If more voltage is needed, then more cells must be added in series. The physical size of the cell is variable and determines the amount of current, at 2 Volts, available from the cell. In other words, the more massive the cell, the greater its capacity in Ampere-hours. No matter how large the single cell is, its voltage still will be around 2 Volts.

Discharge Reactions

When a lead-acid cell is being discharged, the active materials of both electrodes are changed into lead sulfate ($PbSO_4$). The sulfuric acid is gradually consumed from the electrolyte. The discharge chemical equations for the anode and cathode follow:

Discharge

Anode: $PbO_2 + 4H^+ + SO_4^= + 2e^- \rightarrow PbSO_4 + 2H_2O$

Cathode: $Pb + SO_4^= - 2e^- \rightarrow PbSO_4$

As the cell is discharged, all the electrodes gradually become plated with lead sulfate ($PbSO_4$). $PbSO_4$ is an electrical insulator; it will not conduct current. The $SO_4^=$ (sulfate) ions are gradually consumed from the electrolyte and are bonded to the plates to form $PbSO_4$ (lead sulfate). This reaction releases two electrons at the cathode for every $SO_4^=$ radical which is bonded to the plates. This release of free electrons at the cathode is the source of the cell's electric power.

During discharge, the area of the plates available for reaction decreases as the surface of the plates becomes covered with the insulative lead sulfate crystals. This decrease in the active area results in a rise of the cell's internal resistance and a drop in the cell's voltage. Eventually the plates have no more area available for chemical reaction and the sulfate ions are consumed from the electrolyte. It is not possible to remove any more energy from the cell. At this point the cell is said to be fully discharged.

Actually, the process of discharging is terminated before all of the sulfate ions are consumed from the electrolyte. The ratings of battery manufacturers are based on the actual usable energy, which is much lower than the calculated energy of the battery using the masses of the reactants as a basis. This is because only the exterior portion of the electrode is exposed to the electrolyte. Commercially available batteries are rated between 15% and 40% of their theoretical electrochemical capacity.