CHARGED LEAD-ACID CELL

DISCHARGED LEAD-ACID CELL

$$PbO_2 + Pb + 2H_2SO_4 \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} 2PbSO_4 + 2H_2O$$
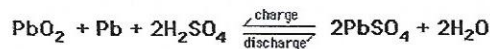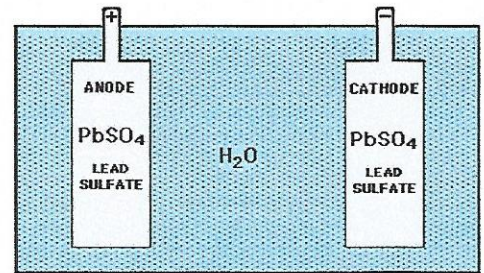
Charge Reactions

The charging process is the reverse of the discharging process. During the charging process, a current (flow of electrons) is forced through the cell in the opposite direction by the application of voltage across the cell's anode and cathode. The reversal of the electronic flow within the cell causes the chemical bond between the lead and the sulfate ions to be broken, and the sulfate ions are released into the electrolyte solution. The charge equations for the lead-acid cell are as follows:

Charge

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

Cathode: $PbSO_4 + 2e^- \rightarrow Pb + SO_4^=$
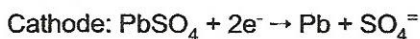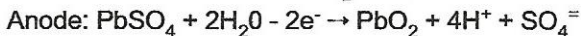
When all the sulfate ions have been removed from the plates and are in solution with the electrolyte, the cell is said to be charged. In actual practice, all of the ions cannot really be removed from the plates. Some continue to remain bonded to the plates in the form of lead sulfate. The inability of the charging process to remove all the sulfate ions bonded to the plates is one cause of the cell's finite lifetime. In time, the plate area available for reaction becomes smaller and smaller as more and more sulfate ions cannot be kicked free of the plates. Such a cell is said to be "sulfated" and suffers from "sulfation."

Sulfation

The longer the sulfate ions stay bonded to the lead plates, the more difficult they are to dislodge with the normal recharging process. The equalizing charge insures that the inevitable process of sulfation is delayed as long as possible. An equalization charge is a controlled overcharge of an already fully recharged cell. The usual equalization charge rate is C/20 (the capacity of the cell in Ampere-hours divided by 20 yields the equalization charge rate in Amperes).

The active material of both electrodes is a highly porous, three-dimensional structure that has a very

large surface area. When the cell is discharged, a layer of microcrystalline lead sulfate coats the surface of the electrodes. Normally, this layer is so thin (only a few molecules thick) that it does not seriously increase the electrical resistance of the cell. The highly porous electrodes still have a very large surface area. However, things don't stay this way. Although lead sulfate is "insoluble", it dissolves in water to a very small extent. An equilibrium exists between precipitate and dissolved material, so that a small amount of lead sulfate is continually dissolving and an equal amount recrystallizing. The recrystallizing process results in crystal growth, with microcrystals merging together to form larger crystals with a smaller total surface area. The result is an electrode surface with a higher electrical resistance, a lower power density (resulting in more rapid voltage changes during charge and discharge), and a lower energy storage capacity. It doesn't take a lot of recrystallizing to reduce the active area of the electrodes by half. Finally, there has been enough crystalline rearrangement that the original plate surface is clogged with sulfate crystals. The effective surface area of the electrodes has been reduced by a factor of 100 or even 1000. The cell's electrical resistance is now so high that it may take over 20 Volts to move even a small amount of current through a cell that once was recharged easily with 2.6 Volts.

The most common cause (over 80%) of lost storage capacity in lead-acid cells is sulfation caused by chronic undercharging. The longer a lead sulfate ion stays bonded to the electrode, the more likely it is to form larger crystals and deeply coat the electrodes. This is why it is so important to fully, regularly, and completely, recharge lead-acid cells.

Equalization Charges

If the loss in cell capacity is due to sulfation, then a repeated series of equalizing charges can break most of the sulfate bonds. If your lead-acid cells have lost capacity, then a regime of equalizing charges is the first