Lecture: Lead-acid batteries
ECEN 4517/5517

How batteries work
- Conduction mechanisms
- Development of voltage at plates
- Charging, discharging, and state of charge

Key equations and models
- The Nernst equation: voltage vs. ion concentration
- Battery model
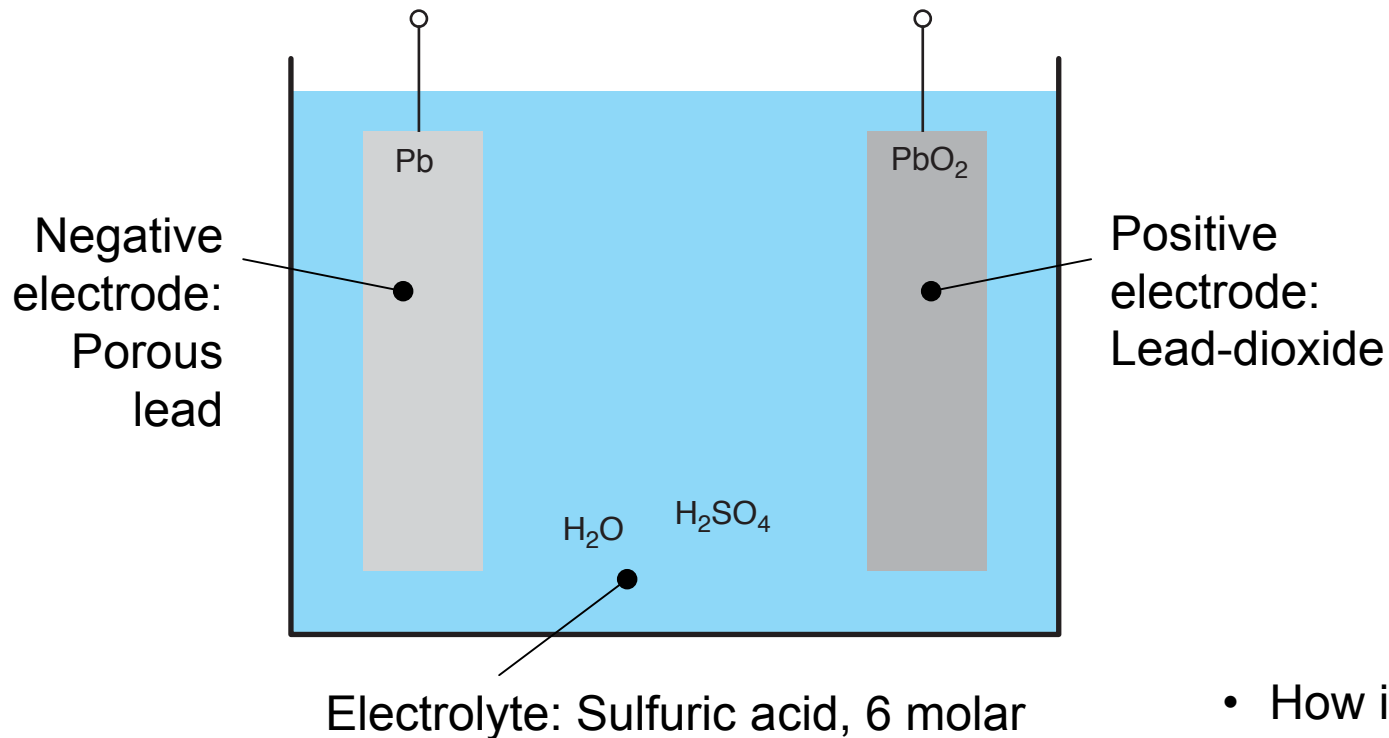- Battery capacity and Peukert's law

Energy efficiency, battery life, and charge profiles
- Coulomb efficiency, voltage drops, and round-trip efficiency
- Battery life vs. depth of discharge
- Charging strategies and battery charge controllers

Lead-acid battery: construction

Pb

PbO$_2$

Negative
electrode:
Porous
lead

Positive
electrode:
Lead-dioxide

H$_2$O   H$_2$SO$_4$

Electrolyte: Sulfuric acid, 6 molar

- How it works
- Characteristics and models
- Charge controllers

Electrical conduction mechanisms

Lead and lead-dioxide are good electrical conductors. The conduction mechanism is via electrons jumping between atoms.

The electrolyte contains aqueous ions (H^+ and SO_4^{-2}). The conduction mechanism within the electrolyte is via migration of ions via diffusion or drift.
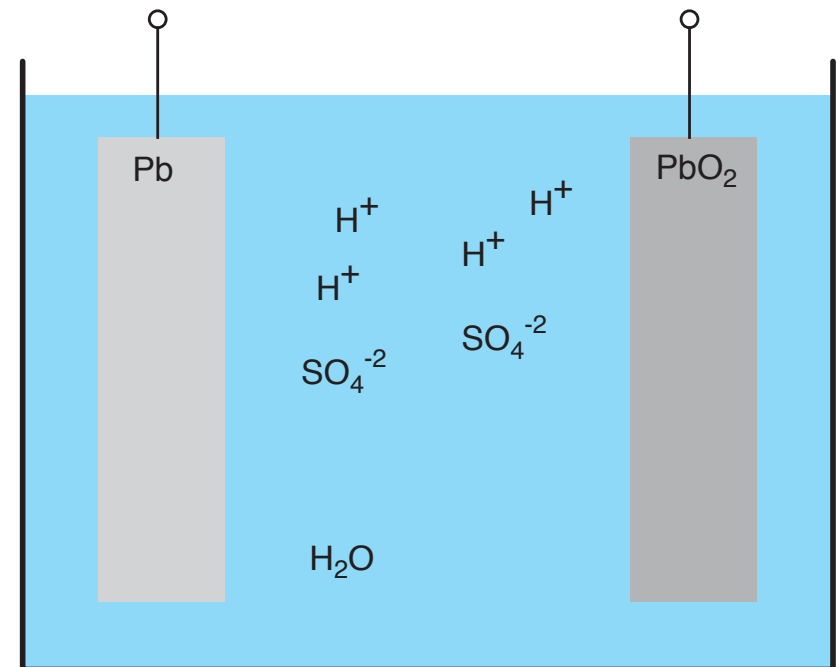

Q: What are the physical mechanisms of conduction in the complete path from one terminal, through an electrode, into the electrolyte, onto the other electrode, and out the other terminal?

Conduction mechanism
# at the surface of the electrode

Oxidation-reduction (Redox) reaction transfers charge from ions in solution
to conducting electrons in the electrode

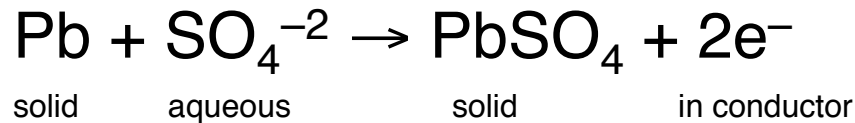<u>At the surface of the lead (negative) electrode:</u>

Charged sulfate ion approaches uncharged lead atom on surface of electrode
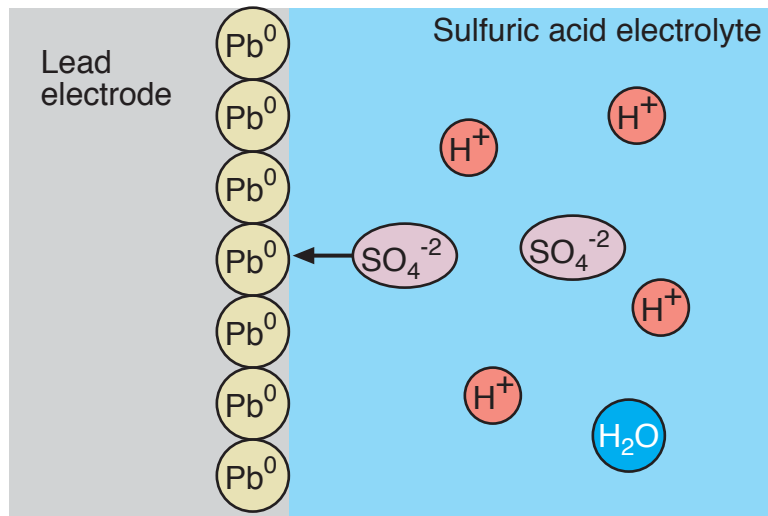
Lead atom becomes ionized and forms ionic bond with sulfate ion. Two electrons are released into lead electrode
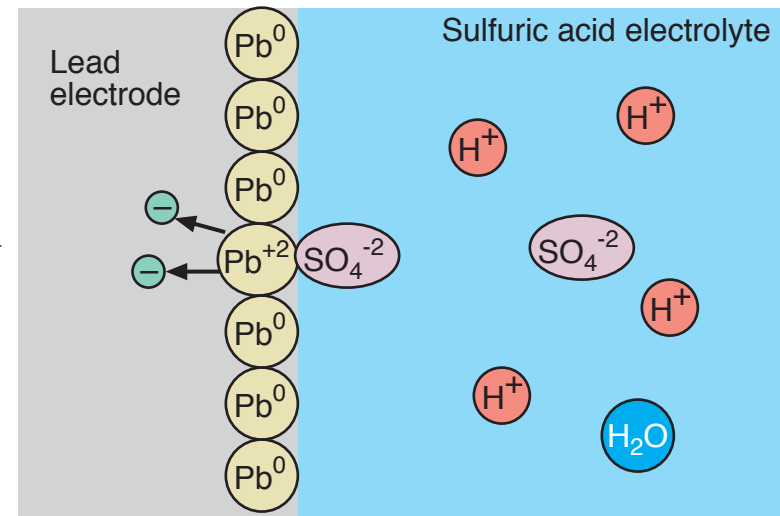
The chemical reaction ("half reaction") at the lead electrode

$$Pb + SO_4^{-2} \rightarrow PbSO_4 + 2e^-$$

solid   aqueous   solid   in conductor

This reaction releases net energy

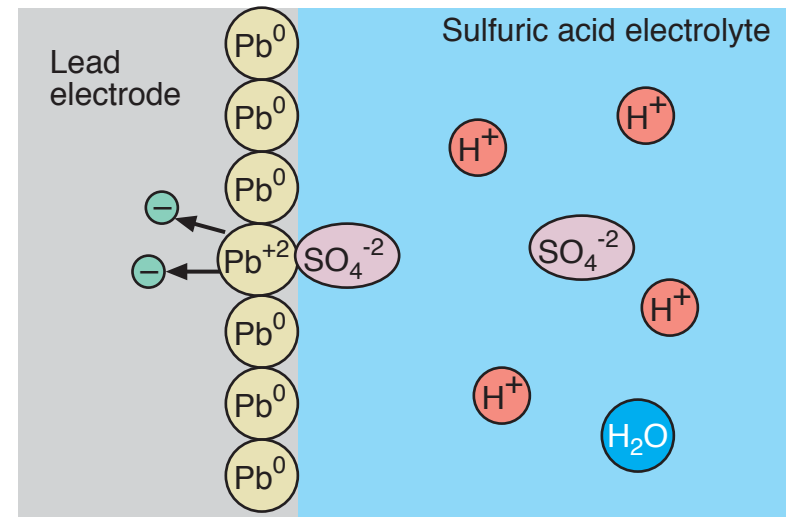$E^0 = 0.356$ eV

— the "Gibbs free energy", under standard conditions ($T = 298°K$, concentration = 1 molar)


Units: Energy = (charge)(voltage)

Energy in eV = (charge of electron)(1 V)

So the charge of the aqueous sulfate ion is transferred to two conducting electrons within the lead electrode, and energy is released.
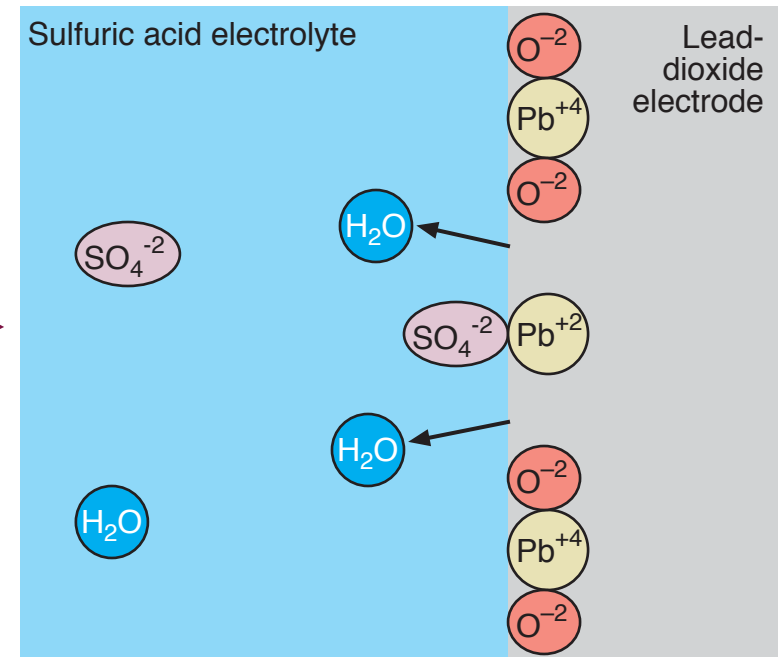
Conduction mechanism
at the surface of the positive electrode

Charged sulfate and hydrogen ions approach lead-dioxide molecule (net uncharged) on surface of electrode
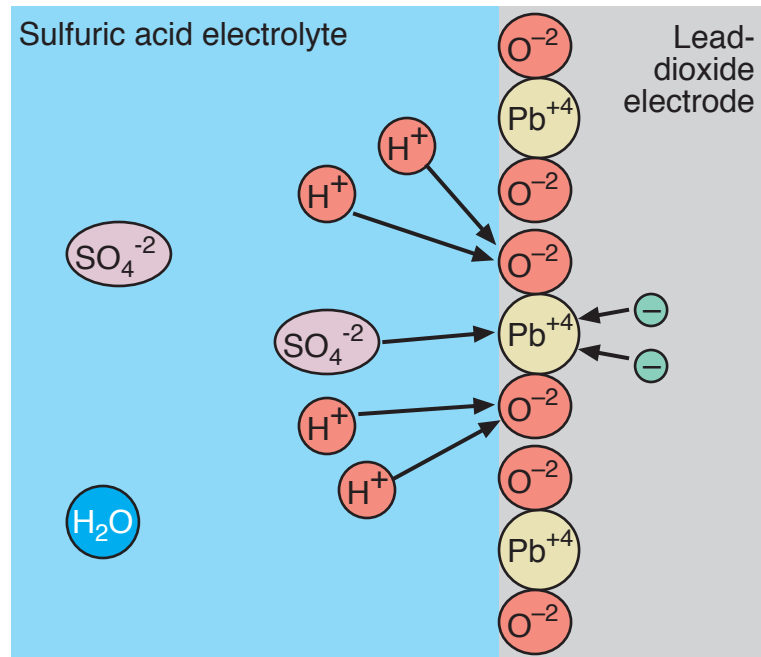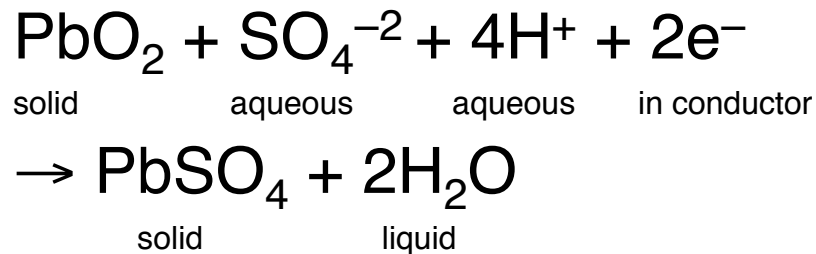
Lead atom changes ionization and forms ionic bond with sulfate ion. Two water molecules are released into solution

- *Lead changes oxidation state from +4 to +2*
- *Two electrons are removed from conduction band in electrode*

The chemical reaction ("half reaction") at the lead-dioxide electrode

$$PbO_2 + SO_4^{-2} + 4H^+ + 2e^-$$

solid ⁣ ⁣ ⁣ ⁣ ⁣ ⁣ ⁣ ⁣ ⁣aqueous ⁣ ⁣ ⁣ ⁣ ⁣ ⁣ ⁣ ⁣aqueous ⁣ ⁣ ⁣ ⁣in conductor

$$\rightarrow PbSO_4 + 2H_2O$$

 ⁣ ⁣ ⁣ ⁣ ⁣ ⁣solid ⁣ ⁣ ⁣ ⁣ ⁣ ⁣ ⁣ ⁣ ⁣ ⁣ ⁣liquid
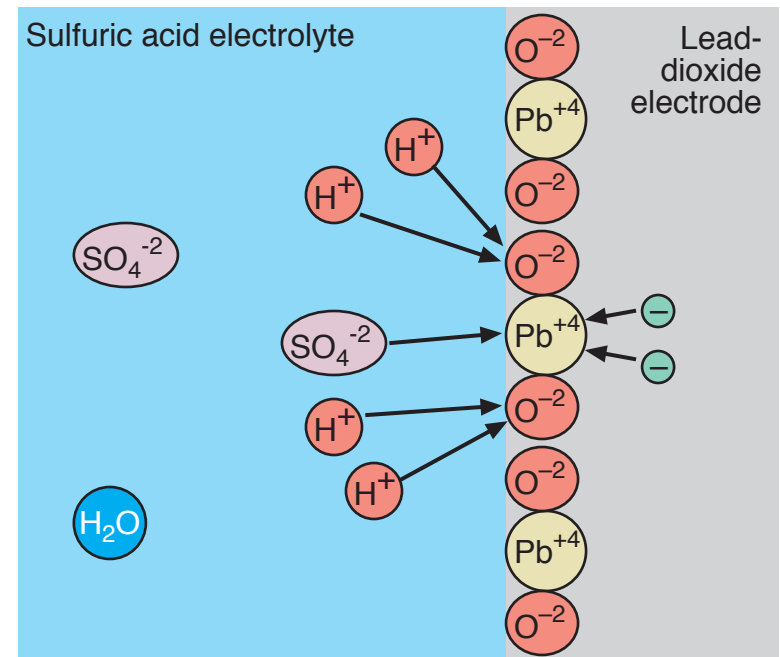
This reaction releases net energy

$E^0 = 1.685$ eV

Net charge of two electrons is transferred from the electrode into the electrolyte
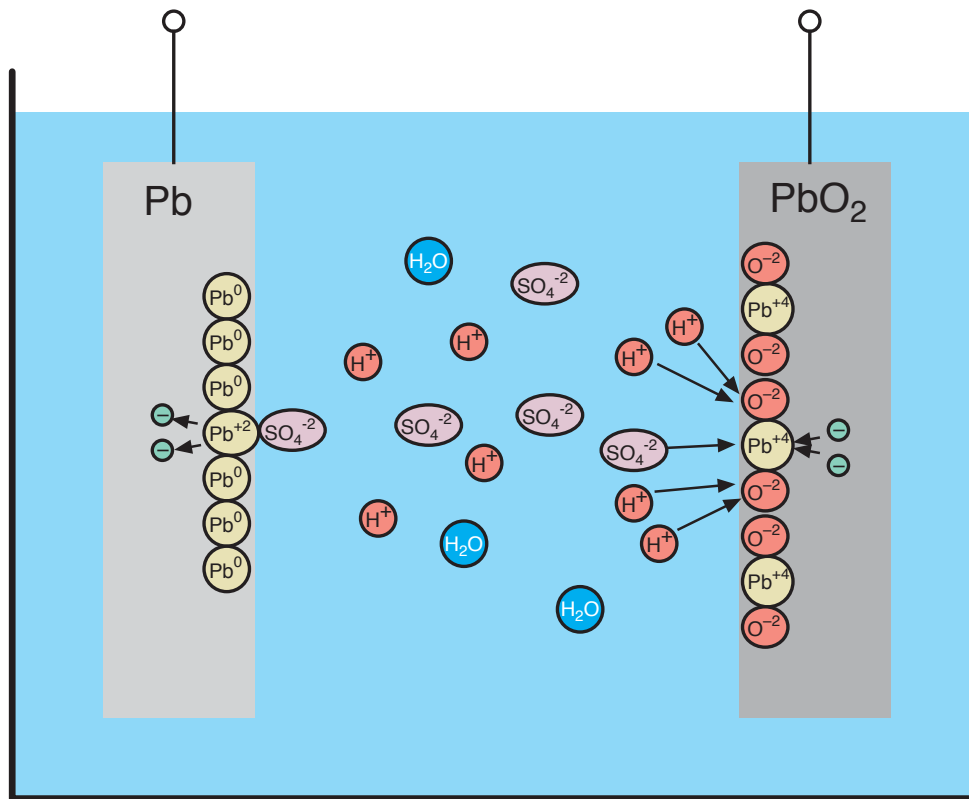
Both half reactions cause the electrodes to become coated with lead sulfate (a poor conductor) and reduce the concentration of the acid electrolyte

How the battery develops voltage

Consider the following experiment:

New electrodes are placed inside electrolyte, with no external electrical circuit connected


- The reactions start to occur

- They use up aqueous ions near electrodes

- Diffusion within electrolyte replenishes ions near electrodes

- Excess electrons are created in lead electrode, and electron deficit is created in lead-dioxide electrode

- Electric field is generated at electrode surfaces. This electric field opposes the flow of ions.

Battery voltage at zero current
Energy barriers at electrode surface
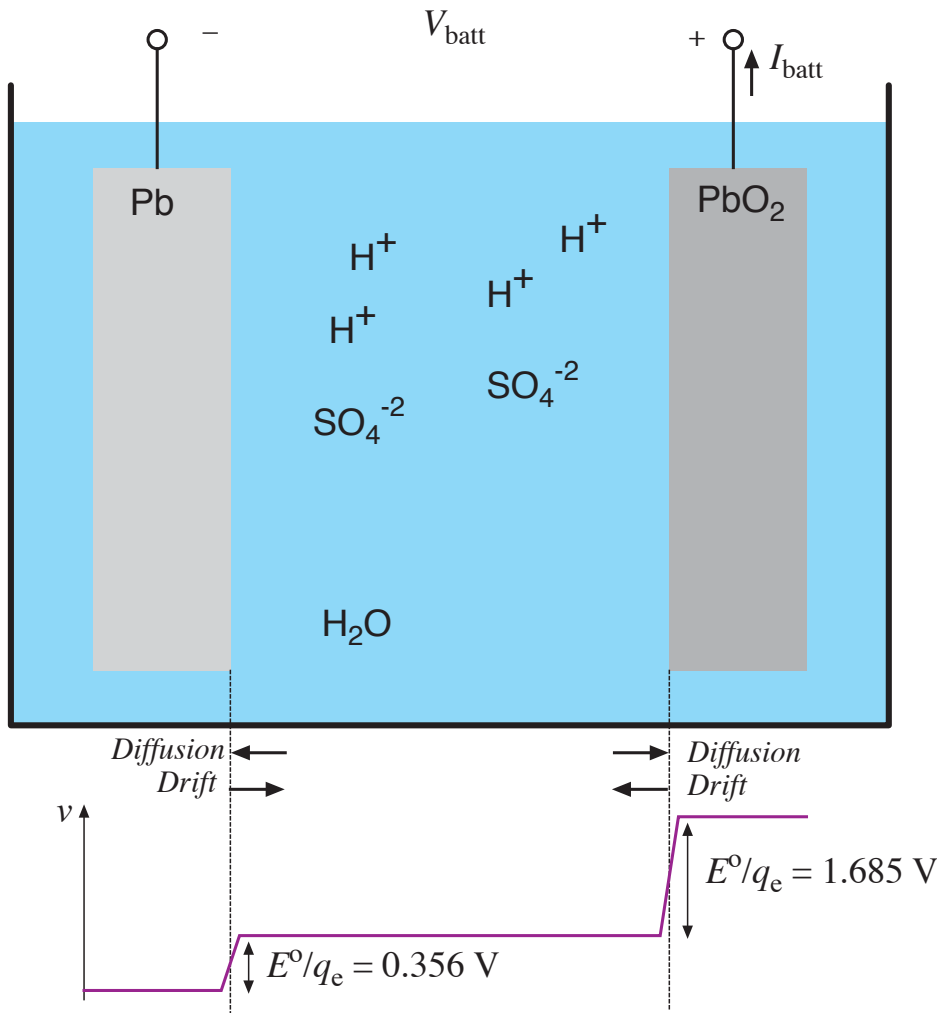
The chemical reactions at the electrode surfaces introduce electrons into the Pb electrode, and create a deficit of electrons in the PbO_2 electrode

These charges change the voltages of the electrodes

The system reaches equilibrium when the energy required to deposit or remove an electron equals the energy generated by the reaction

Total voltage (at $T = 298°K$ and 1 molar acid electrolyte) is $V_{batt} = 0.356 + 1.685 = 2.041$ V

Discharging
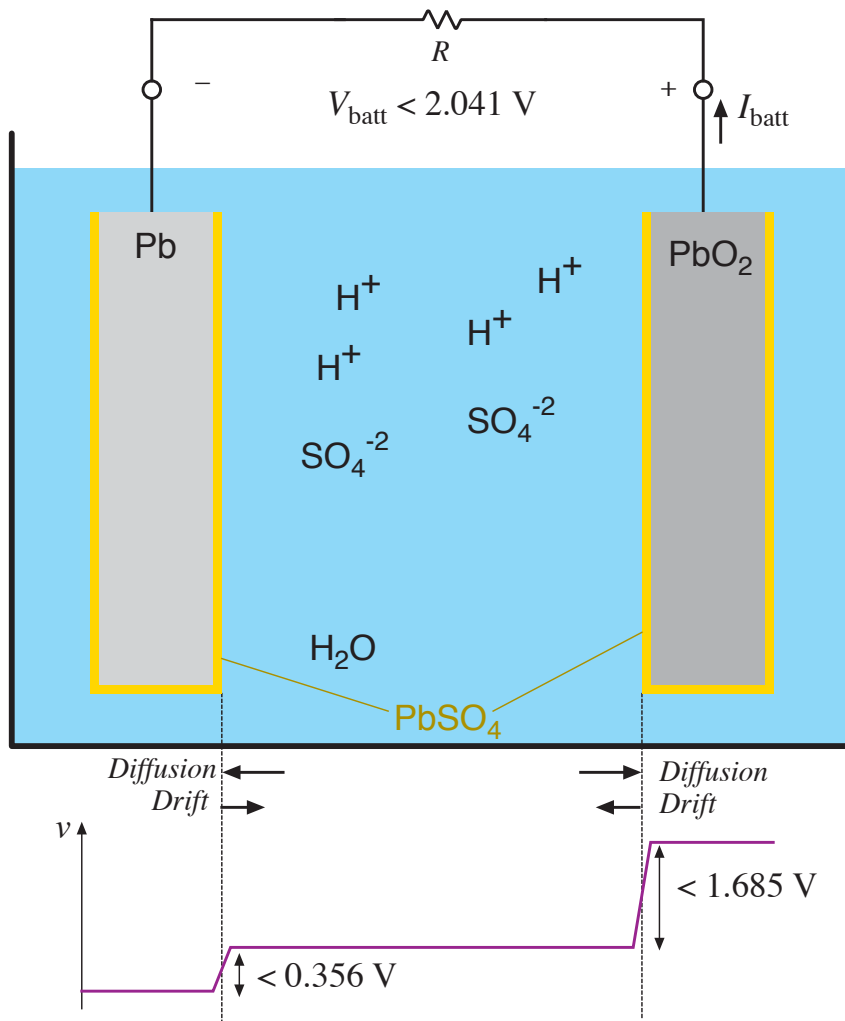
Connection of an electrical load allows electrons to flow from negative to positive terminals

This reduces the charge and the voltages at the electrodes

The chemical reactions are able to proceed, generating new electrons and generating the power that is converted to electrical form to drive the external electrical load

As the battery is discharged, the electrodes become coated with lead sulfate and the acid electrolyte becomes weaker

Charging

External source of electrical power

$V_{batt} > 2.041$ V

I_{batt}

Pb

PbO$_2$

H$^+$ H$^+$ H$^+$ H$^+$

SO$_4^{-2}$ SO$_4^{-2}$

H$_2$O

PbSO$_4$

Diffusion   Diffusion
Drift   Drift

v

> 1.685 V

> 0.356 V
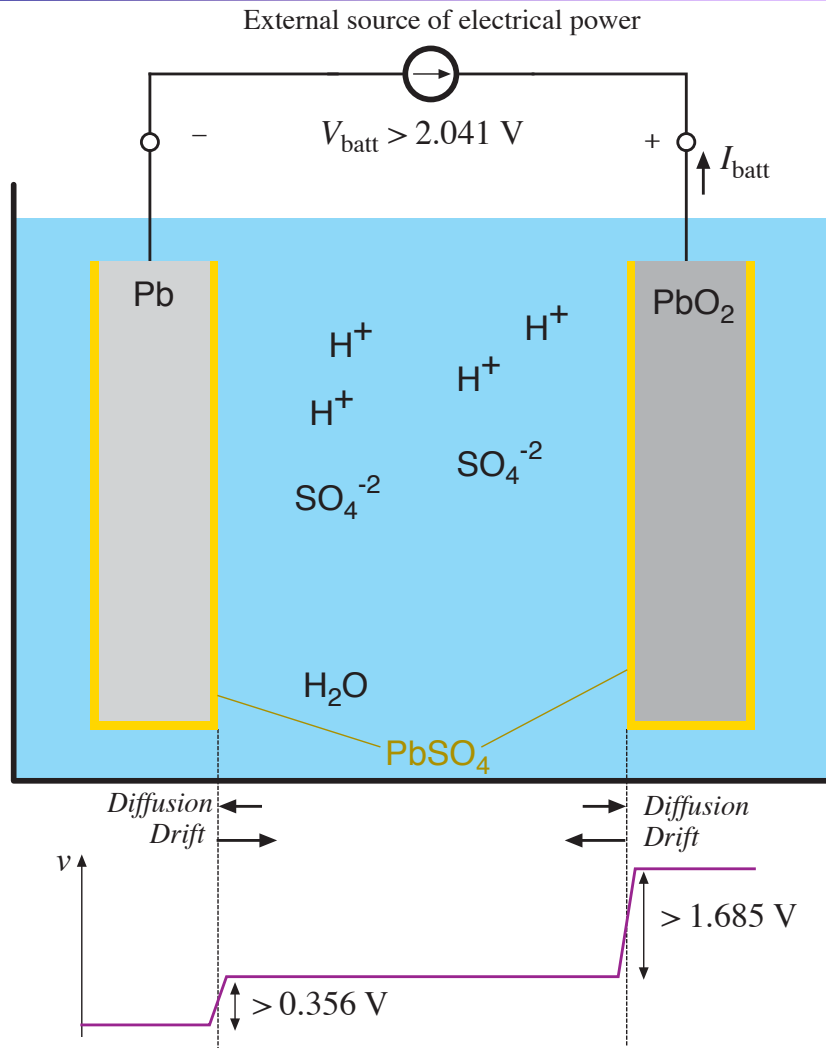
Connection of an electrical power source forces electrons to flow from positive to negative terminals

This increases the charge and the voltages at the electrodes

The chemical reactions are driven in the reverse direction, converting electrical energy into stored chemical energy

As the battery is charged, the lead sulfate coating on the electrodes is removed, and the acid electrolyte becomes stronger

Battery state of charge (SOC)

	Fully Charged	Completely Discharged
State of charge:	100%	0%
Depth of discharge:	0%	100%
Electrolyte concentration:	~6 molar	~2 molar
Electrolyte specific gravity:	~1.3	~1.1
No-load voltage:	12.7 V	11.7 V

(specific battery types may vary)

Battery voltage vs. electrolyte concentration

The *Nernst* equation relates the chemical reaction energy to electrolyte energy:

$$E = E^0 + (kT/q_e) \ln [(\textit{electrolyte concentration})/(1 \text{ molar})]$$

(idealized)

with

E = energy at a given concentration

E^0 = energy at standard 1 molar concentration
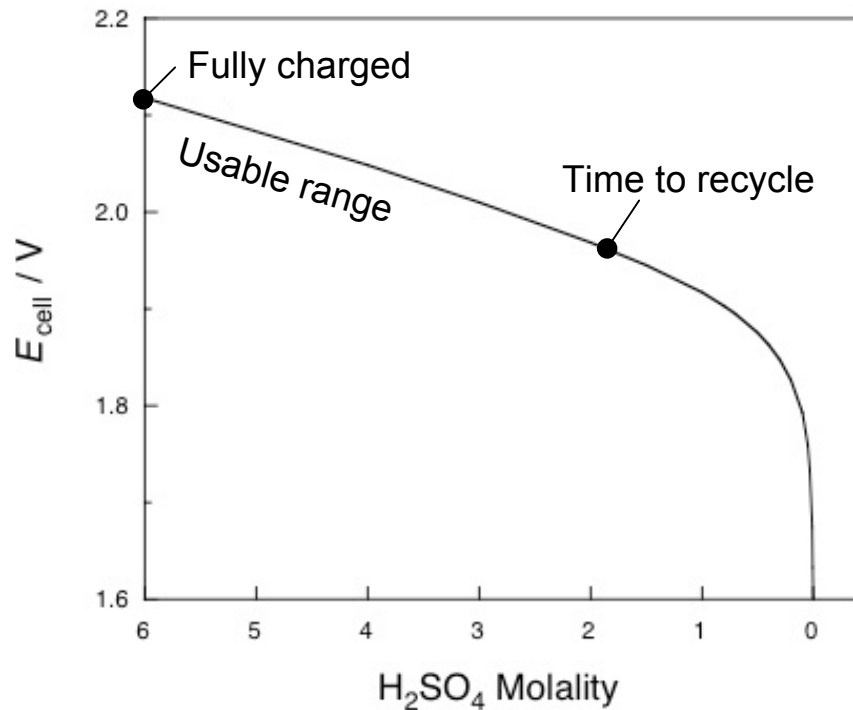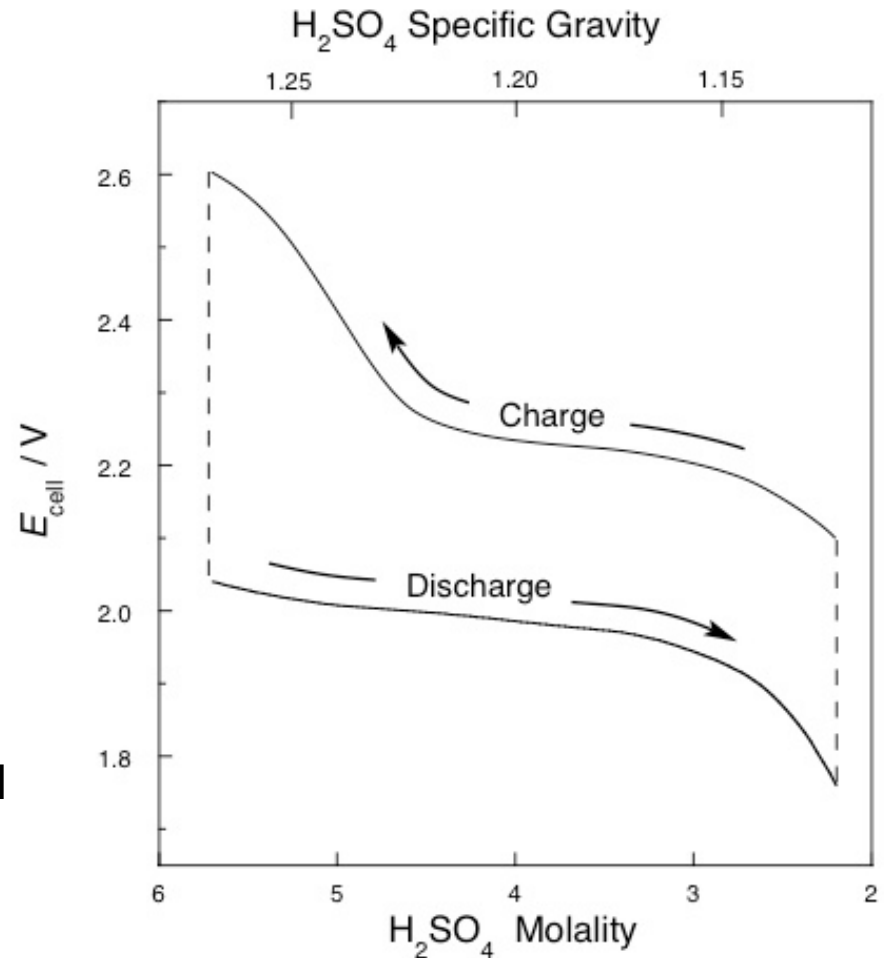
kT/q_e = 26 mV at 298 ˚K

Implications:

At fully charged state (6 molar), the cell voltage is a little higher than E^0/q_e

As the cell is discharged, the voltage decreases

Voltage vs. electrolyte concentration

Voltage of lead-acid electrochemical cell vs. electrolyte concentration, as predicted by Nernst equation

R. S. Treptow, "The lead-acid battery: its voltage in theory and practice," *J. Chem. Educ.*, vol. 79 no. 3, Mar. 2002

Mechanisms that affect terminal voltage

1. Equilibrium voltage changes with electrolyte concentration (as described above – Nernst equation)

2. With current flow, there are resistive drops in electrodes, especially in surface lead-sulfate

3. With current flow, there is an electrolyte concentration gradient near the electrodes. Hence lower concentration at electrode surface; Nernst equation then predicts lower voltage

4. Additional surface chemistry issues: activation energies of surface chemistry, energy needed for movement of reacting species through electrodes

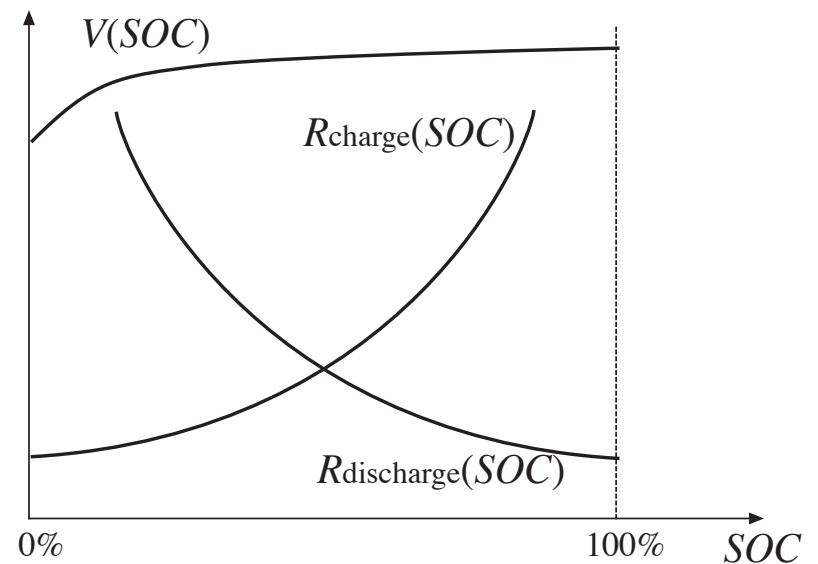5. Physical resistance to movement of ions through electrodes

(2) - (5) can be modeled electrically as resistances

A basic battery model

Basic model
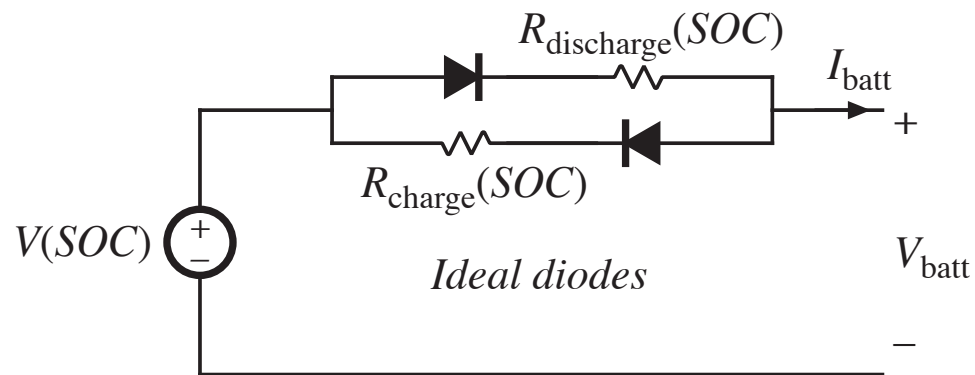
Dependence of model parameters on battery state of charge (SOC)

Types of lead-acid batteries

1. Car battery
    "SLI" - starter lighting ignition
    Designed to provide short burst of high current
        Maybe 500 A to crank engine
    Cannot handle "deep discharge" applications
        Typical lifetime of 500 cycles at 20% depth of discharge

2. Deep discharge battery
    We have these in power lab carts
    More rugged construction
    - Bigger, thicker electrodes
    - Calcium (and others) alloy: stronger plates while maintaining low leakage current
    - More space below electrodes for accumulation of debris before plates are shorted
    Ours are
    - Sealed, valve regulated, absorbent glass mat
    - Rated 56 A-hr at 2.33A (24 hr) discharge rate

Types of lead-acid batteries

3. "Golf cart" or "forklift" batteries

    Similar to #2

    Bigger, very rugged

    Low cost — established industry

    Antimony alloy

- Strong big electrodes
- But more leakage current than #2

    Can last 10-20 years

Manufacturer's specifications for our power lab batteries:

Nominal capacity: A-hrs @ 25˚C to 1.75 V/cell				
1 hr	2 hr	4 hr	8 hr	24 hr
36 A-hr	45 A-hr	46 A-hr	49 A-hr	56 A-hr

Battery capacity

The quantity C is defined as the current that discharges the battery in 1 hour, so that the battery capacity can be said to be C Ampere-hours (units confusion)

If we discharge the battery more slowly, say at a current of $C/10$, then we might expect that the battery would run longer (10 hours) before becoming discharged. In practice, the relationship between battery capacity and discharge current is not linear, and less energy is recovered at faster discharge rates.

Peukert's Law relates battery capacity to discharge rate:

$$C_\mathrm{p} = I^k\ t$$

where C_p is the amp-hour capacity at a 1 A discharge rate

       I is the discharge current in Amperes

       t is the discharge time, in hours

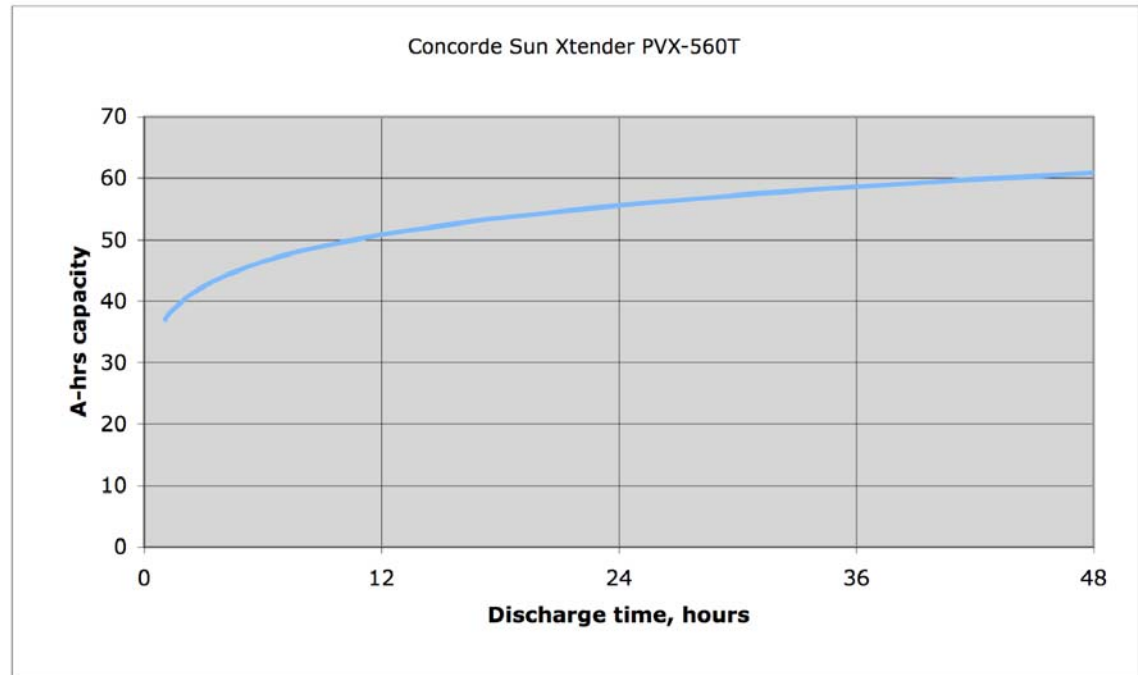 k is the Peukert coefficient, typically 1.1 to 1.3

Example

Our lab batteries

$k = 1.15$

$C = 36$ A

$C_\mathrm{p} = 63$ A-hr

Prediction of Peukert
equation is plotted at left

Concorde Sun Xtender PVX-560T

What the manufacturer's
data sheet specified:

| Nominal capacity: A-hrs @ 25˚C to 1.75 V/cell				
1 hr	2 hr	4 hr	8 hr	24 hr
36 A-hr	45 A-hr	46 A-hr	49 A-hr	56 A-hr

Energy efficiency

Efficiency $\eta = E_D/E_C$

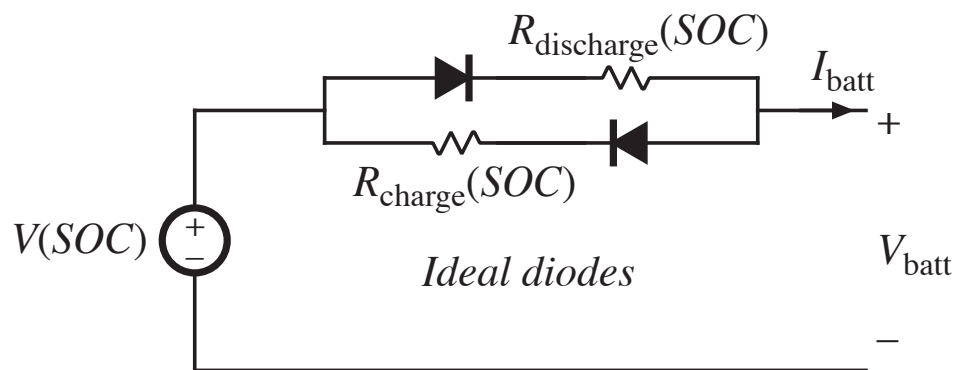E_C = Total energy during charging = $\int v_{\text{batt}} (-i_{\text{batt}}) \, dt \approx V_C I_C T_C$

E_D = Total energy during discharging = $\int v_{\text{batt}} \, i_{\text{batt}} \, dt \approx V_D I_D T_D$

$$Energy \; efficiency \; = \left(\frac{V_D}{V_C}\right)\left(\frac{I_D T_D}{I_C T_C}\right) = \left(voltage \; efficiency\right)\left(coulomb \; efficiency\right)$$

Coulomb efficiency = (discharge A-hrs)/(charge A-hrs)

Voltage efficiency = (discharge voltage)/(charge voltage)
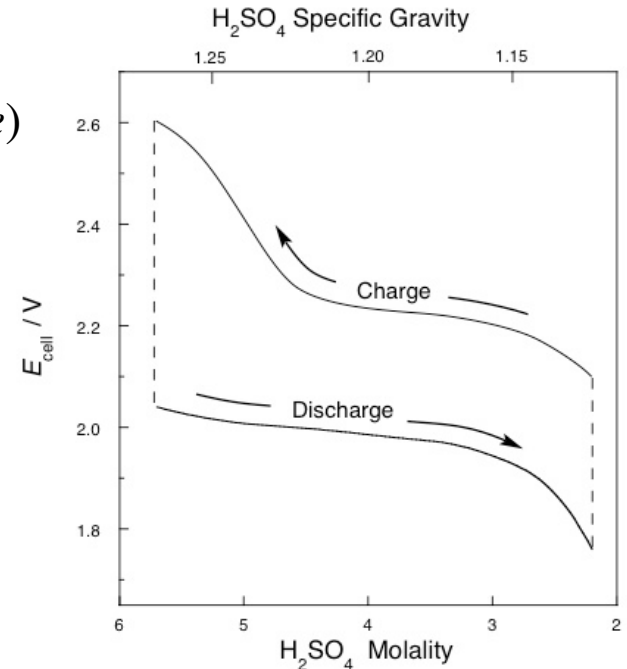
Energy efficiency

Energy is lost during charging when reactions other than reversal of sulfation occur

At beginning of charge cycle, coulomb efficiency is near 100%
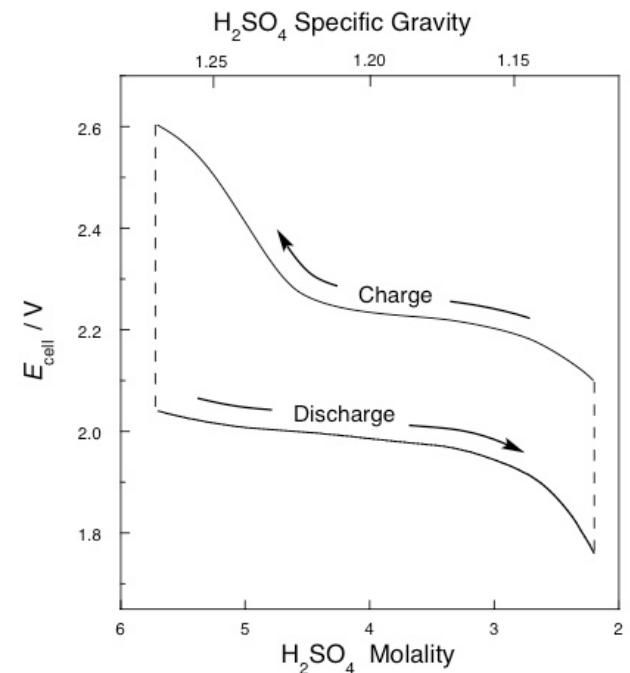
Near end of charge cycle, electrolysis of water reduces coulomb efficiency. Can improve this efficiency by reducing charge rate (taper charging)

Typical net coulomb efficiency: 90%
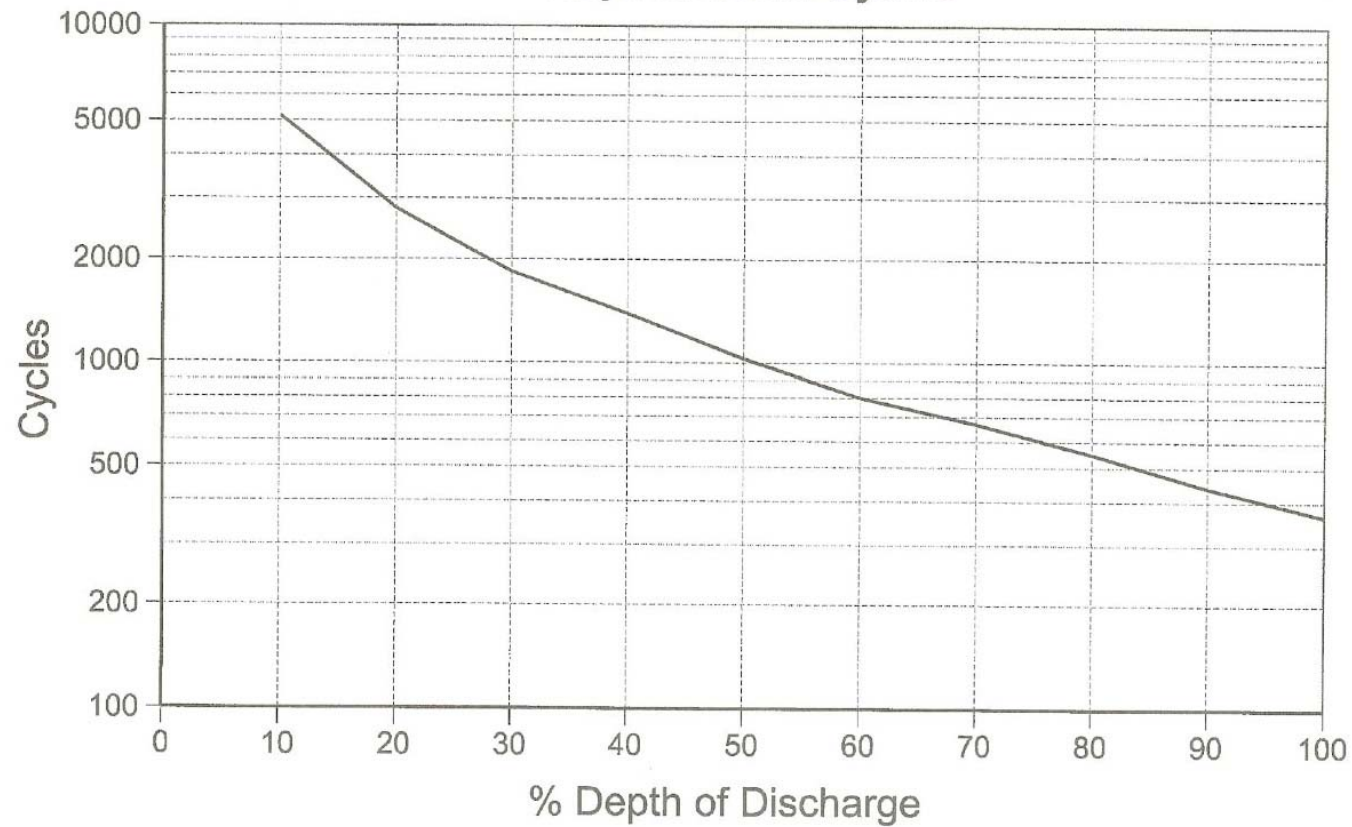
Approximate voltage efficiency: (2V)/(2.3V) = 87%

Energy efficiency = (87%)(90%) = 78%

Commonly quoted estimate: 75%

Battery life

Concorde AGM Battery
Expected Life Cycles

Test Conditions:
1. Discharge Voltage=1.75 Volts/Cell 2. Charge Voltage=2.40 Volts/Cell 3. DOD=100 % 4. Battery Temperature=25°C 5. End of Life=80 % of Capacity

0306 Concorde Battery Corporation, 2009 San Bernardino Rd, West Covina, CA, 91790   www.concordebattery.com   Phone: 626-813-1234

Charge management

Over-discharge leads to "sulfation" and the battery is ruined. The reaction becomes irreversible when the size of the lead-sulfate formations become too large

Overcharging causes other undesirable reactions to occur

Electrolysis of water and generation of hydrogen gas

Electrolysis of other compounds in electrodes and electrolyte, which can generate poisonous gasses

Bulging and deformation of cases of sealed batteries

Battery charge management to extend life of battery:

Limit depth of discharge

When charged but not used, employ "float" mode to prevent leakage currents from discharging battery

Pulsing to break up chunks of lead sulfate

Trickle charging to equalize charges of series-connected cells