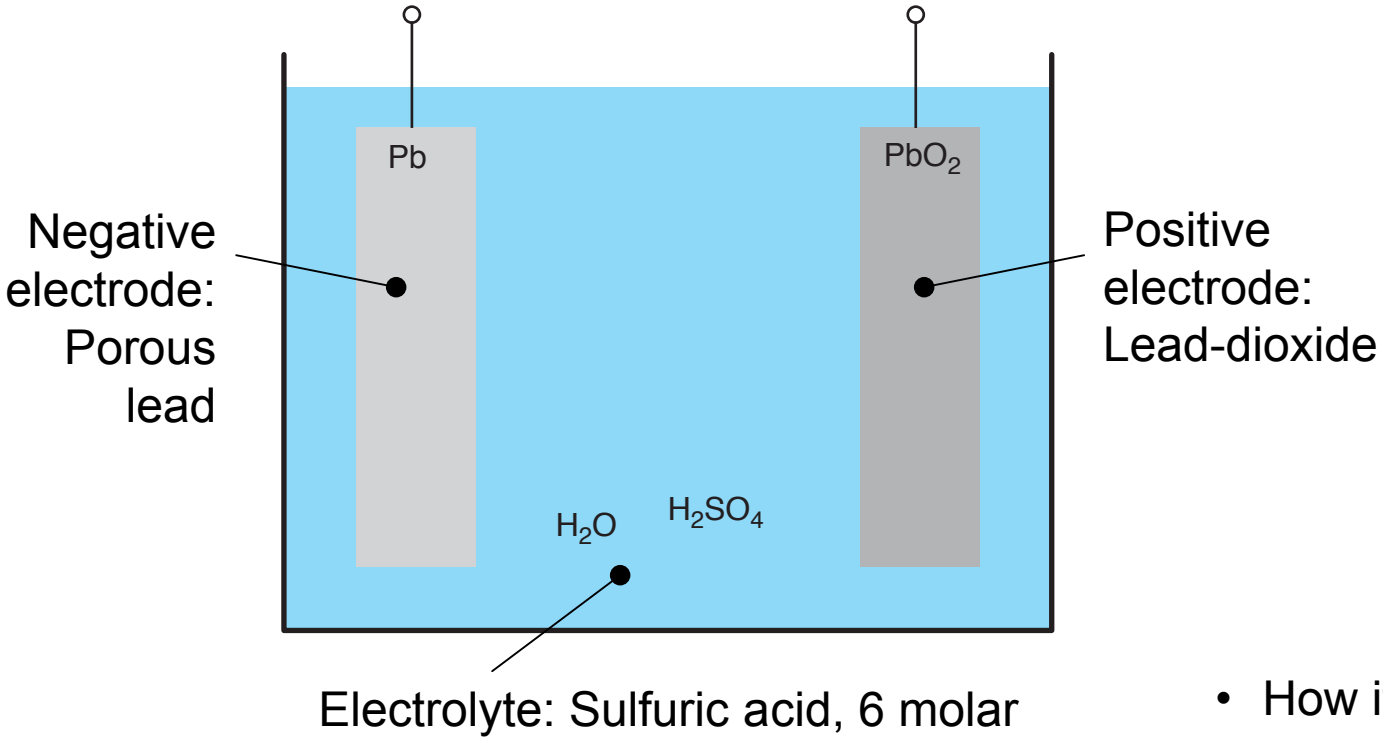
Lecture: Lead-acid batteries

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

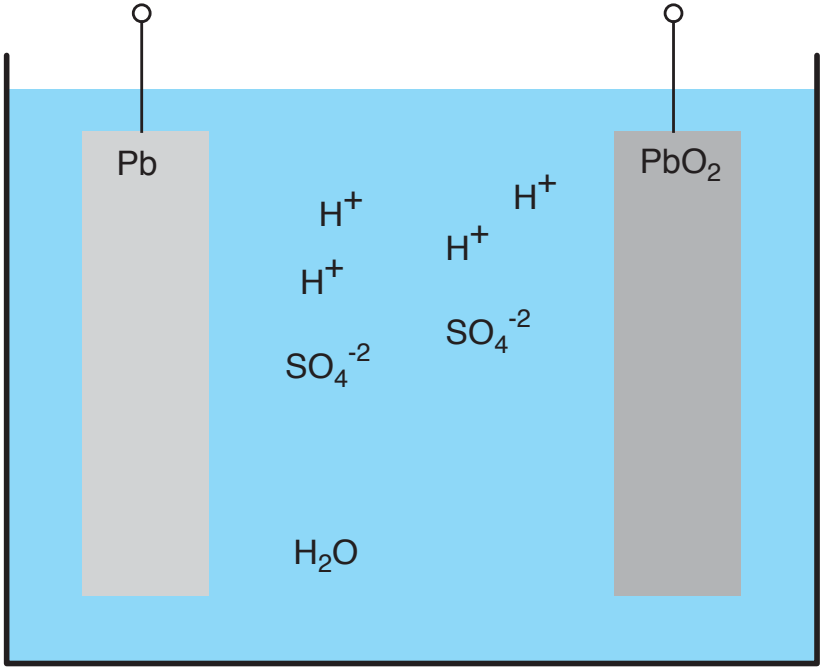


- How it works
- Characteristics and models
- Charge controllers

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?

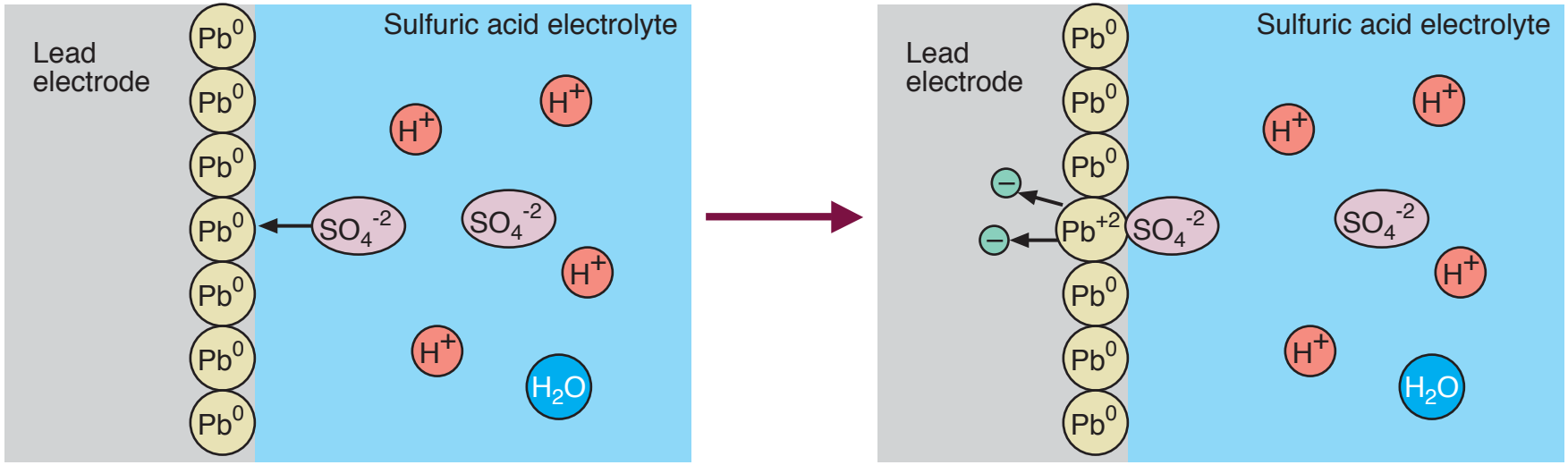
Conduction mechanism at the surface of the electrode

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

At the surface of the lead (negative) electrode:

Charged sulfate ion approaches uncharged lead atom on surface of electrode

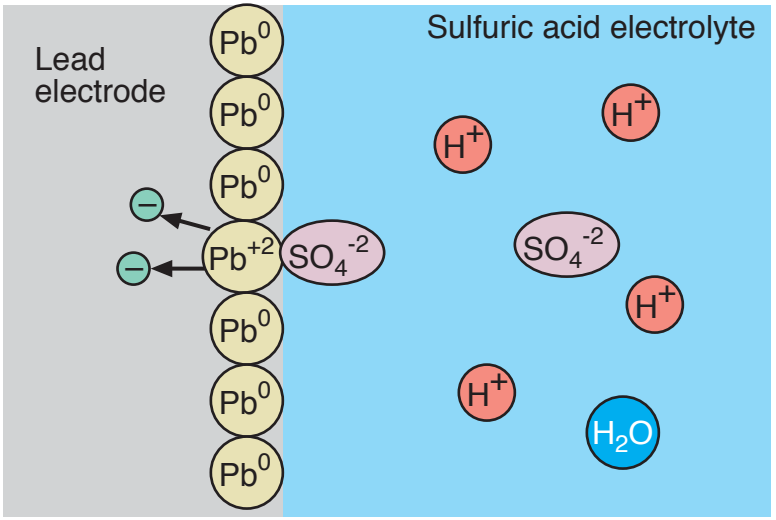
Lead atom becomes ionized and forms ionic bond with sulfate ion. Two electrons are released into lead electrode



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 ($T = 298^\circ$K, concentration = 1 molar)

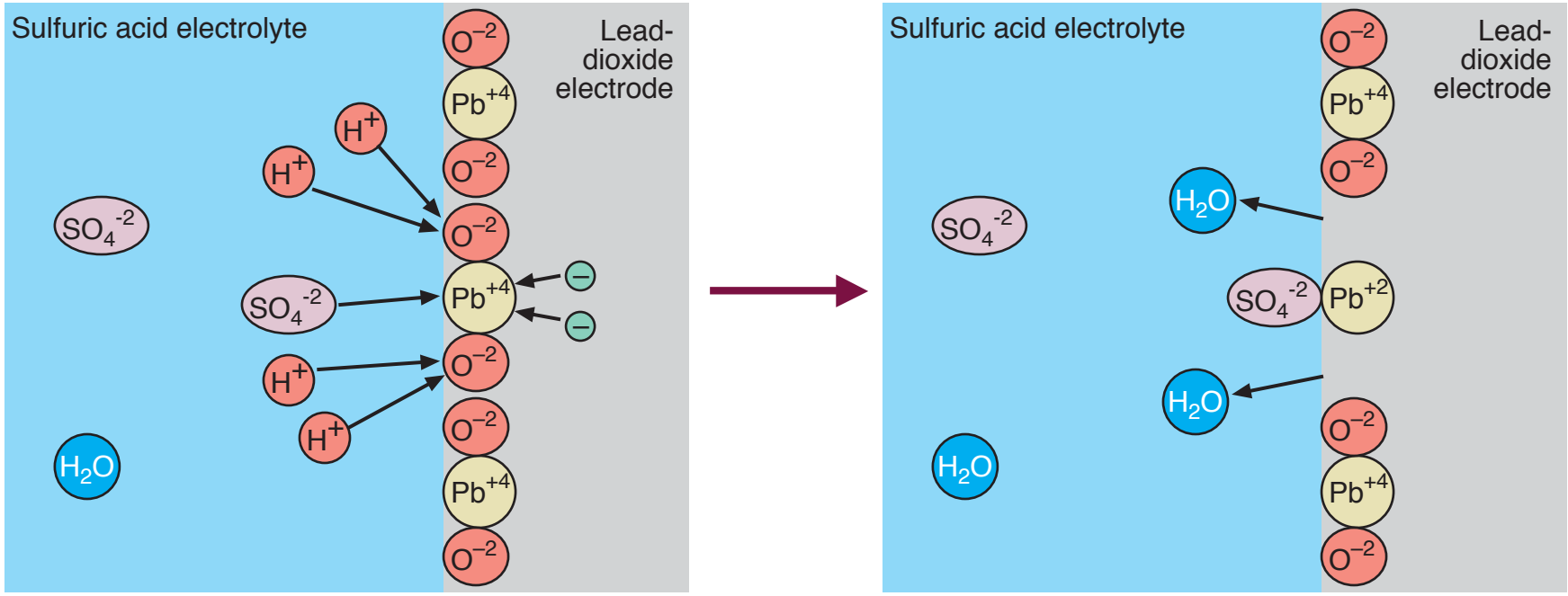
Units: Energy = (charge)(voltage)
Energy in eV = (charge of electron)(1 V)

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

$$\rightarrow PbSO_4 + 2H_2O$$

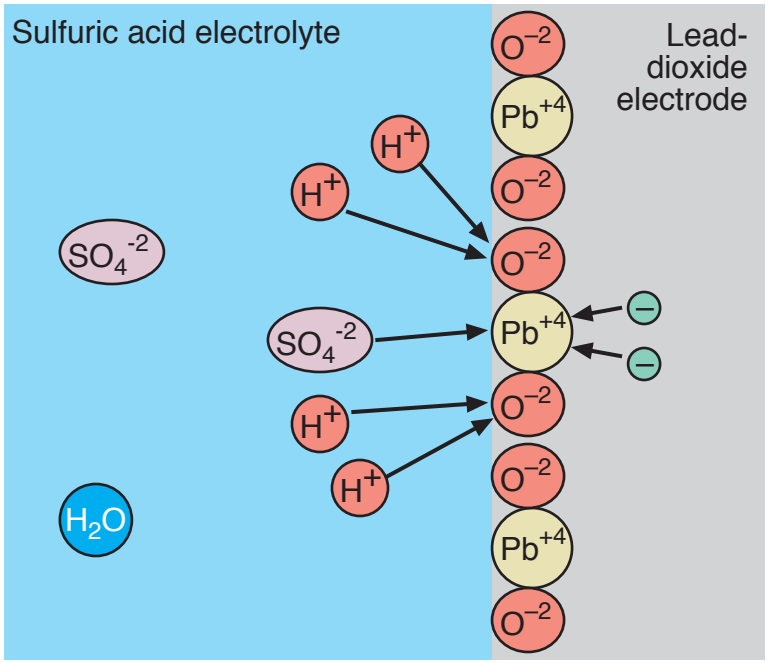
solid liquid

This reaction releases net energy

$E^0 = 1.685$ eV

Net charge of two electrons is transferred from the electrode into the electrolyte

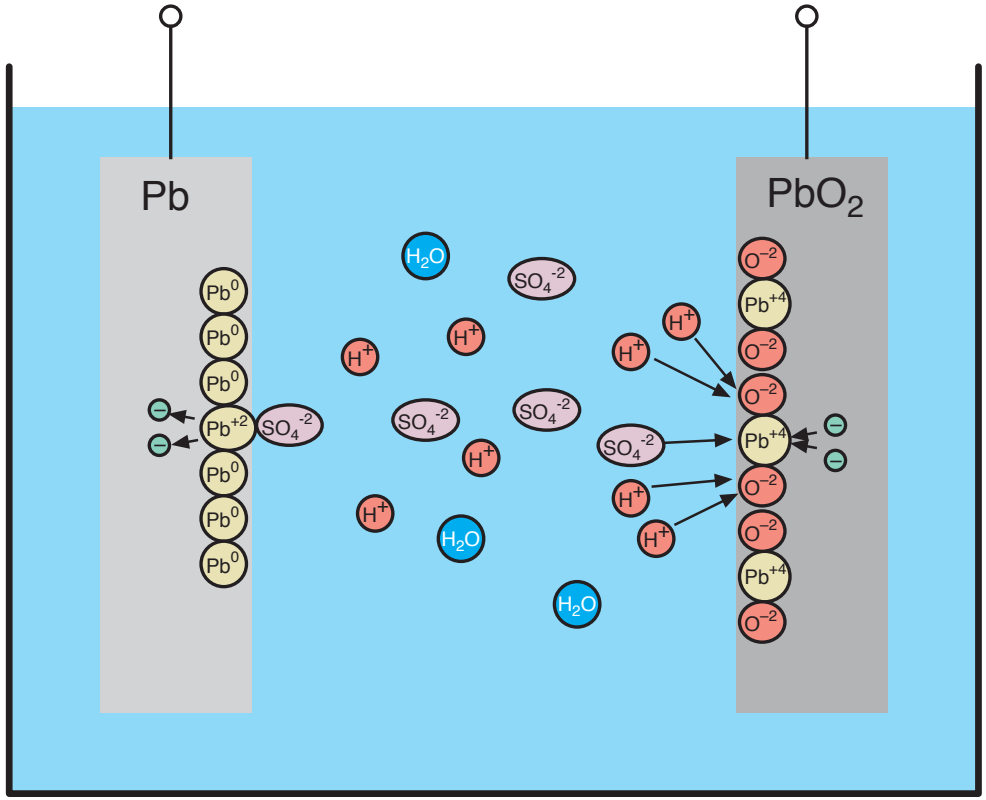
Both half reactions cause the electrodes to become coated with lead sulfate (a poor conductor) and reduce the concentration of the acid electrolyte



How the battery develops voltage

Consider the following experiment:

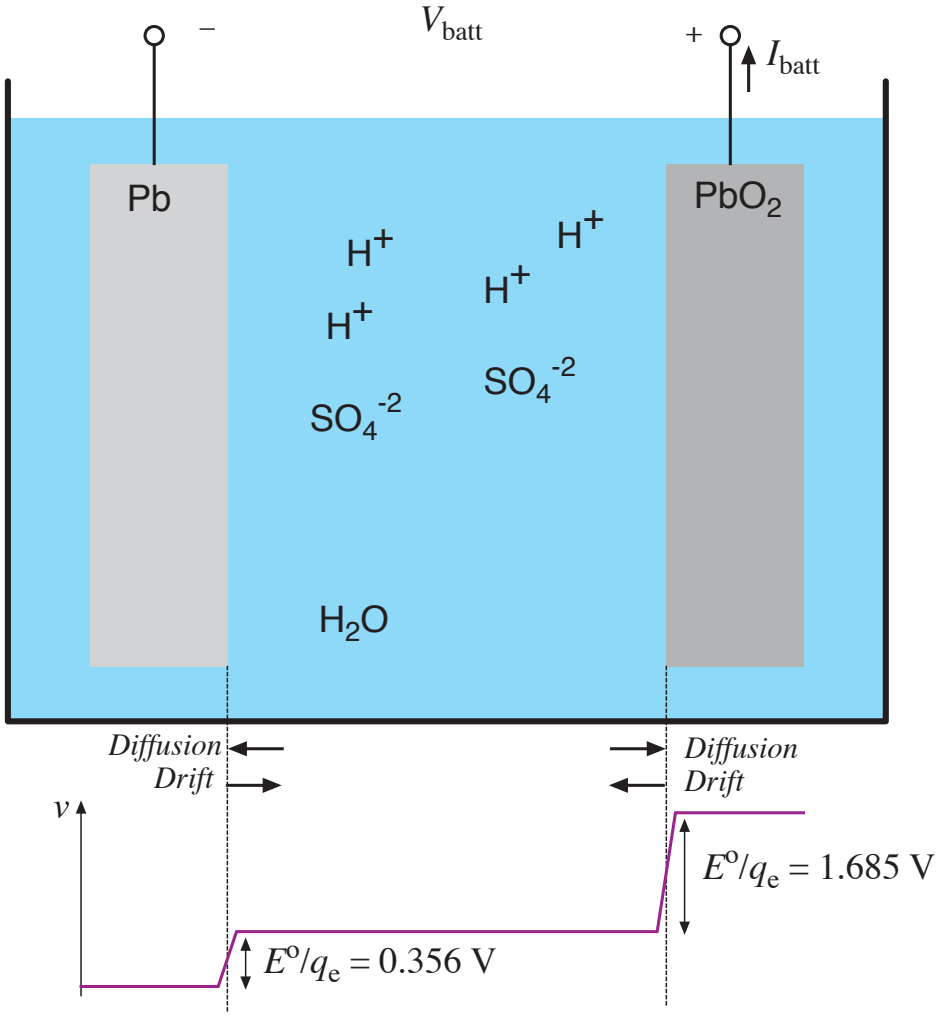
New electrodes are placed inside electrolyte, with no external electrical circuit connected



- 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.

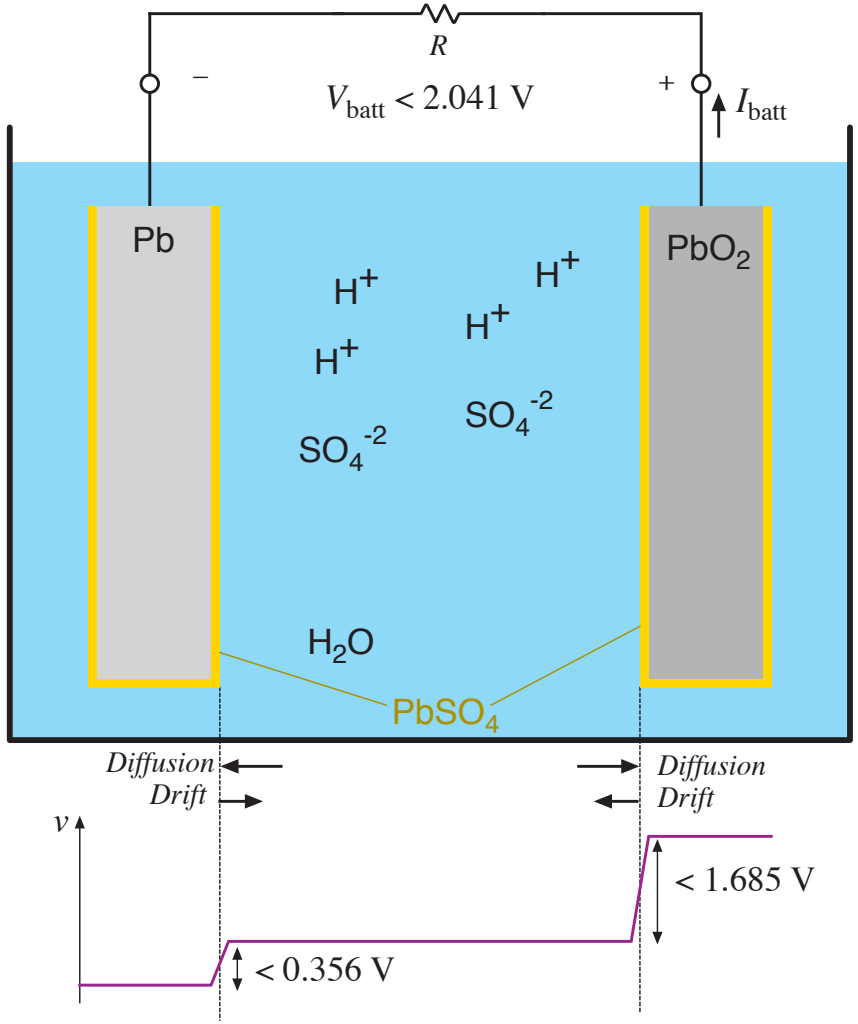
Battery voltage at zero current

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



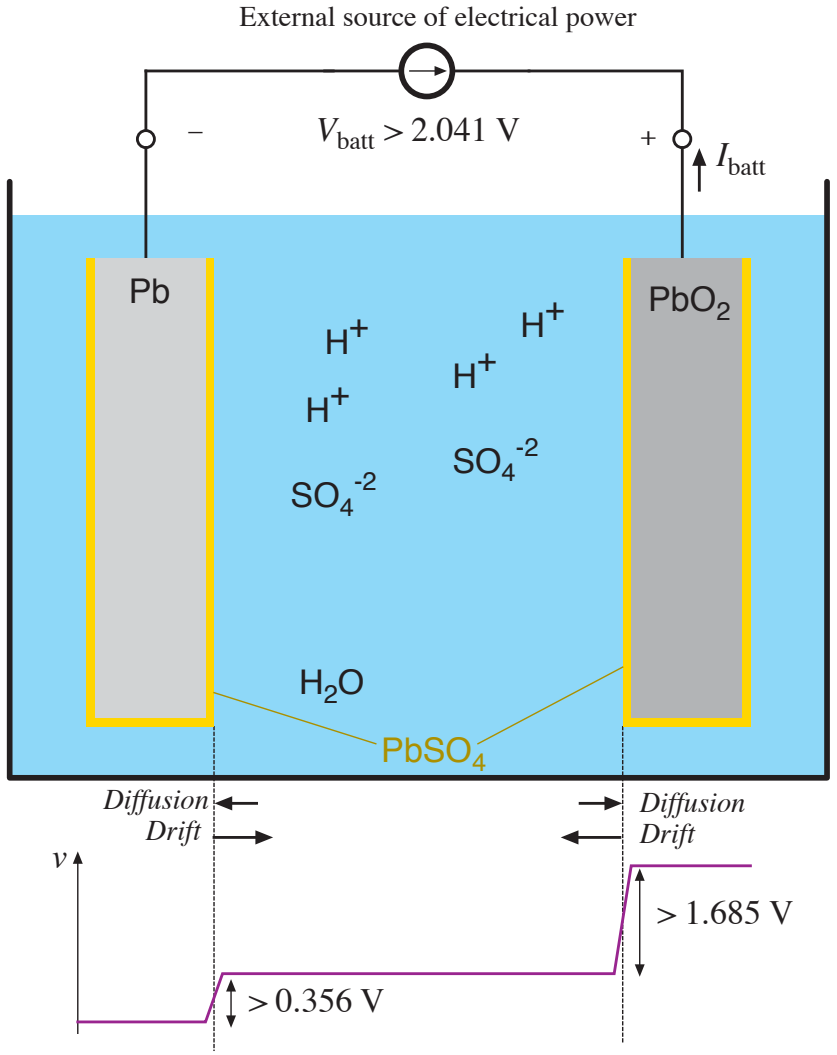
Connection of an electrical load allows electrons to flow from negative to positive terminals

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



- 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

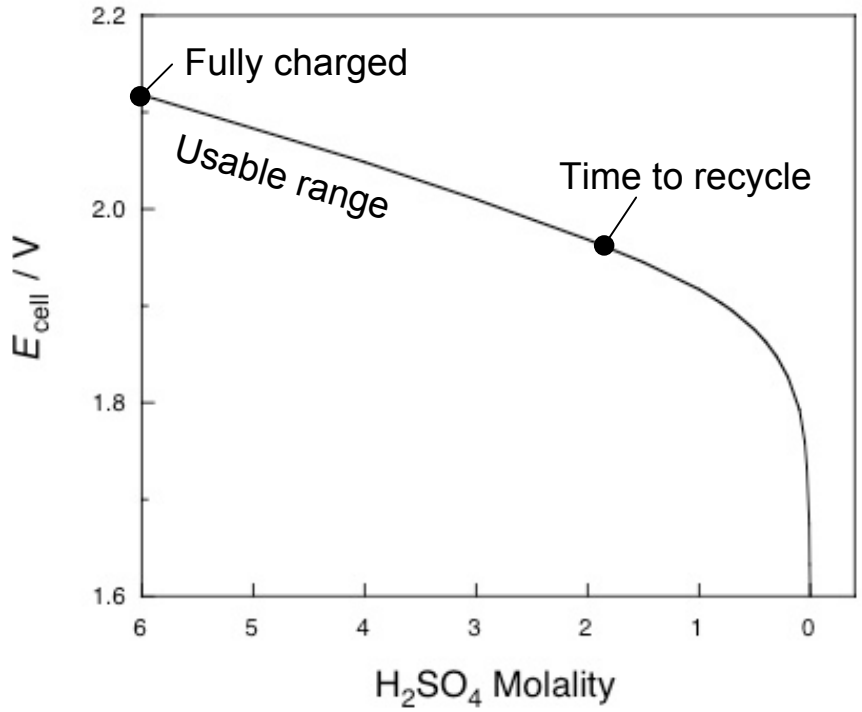
kT/q_e = 26 mV at 298 ˚K

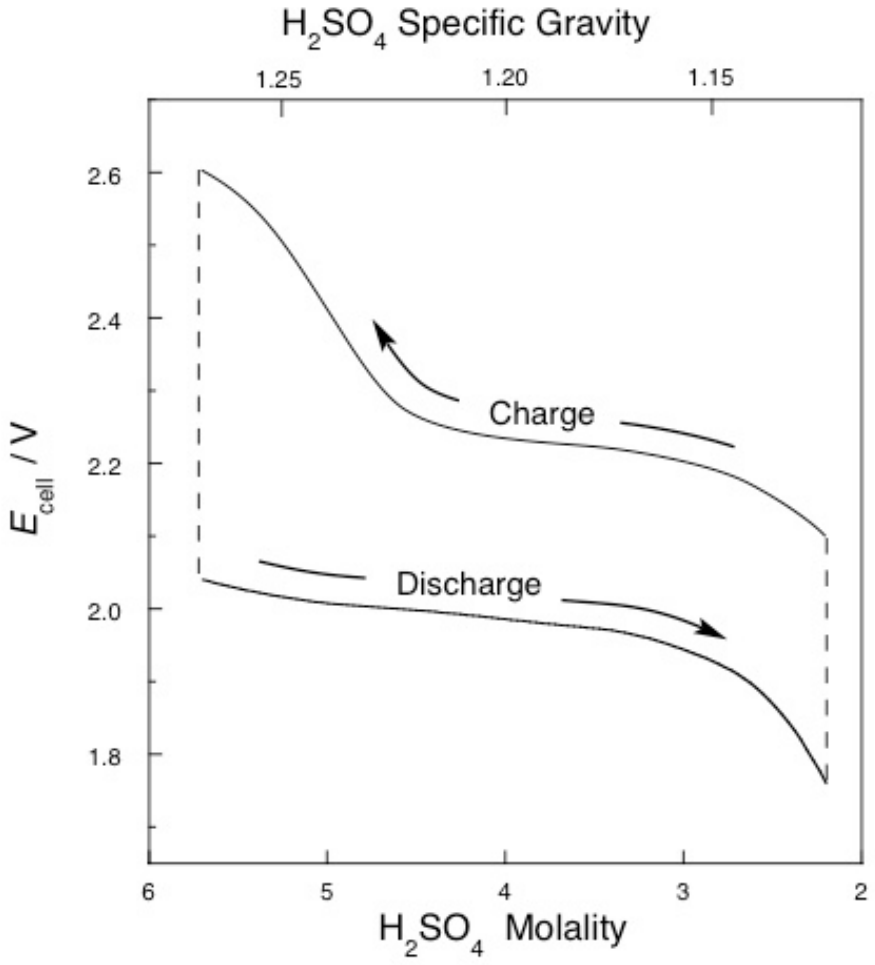
Implications:

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

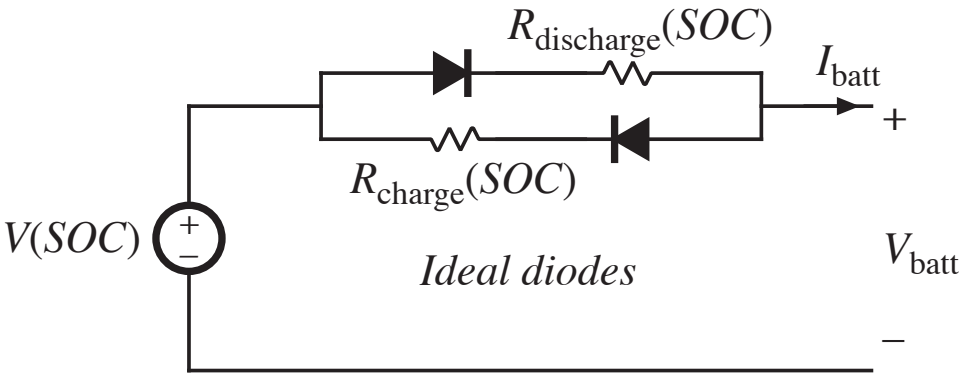
Mechanisms that affect terminal voltage

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

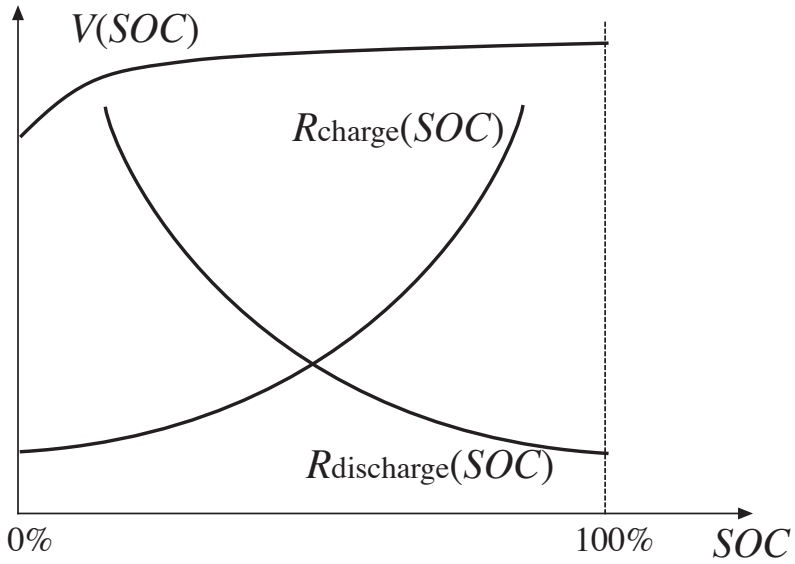
(2) - (5) can be modeled electrically as resistances

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

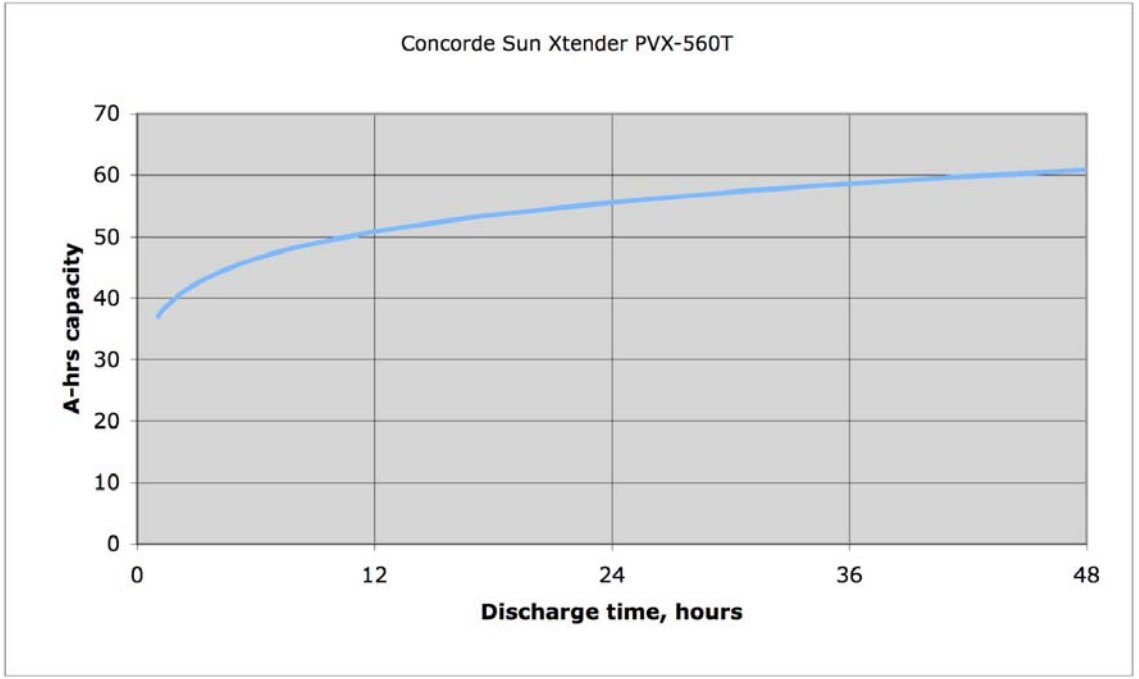
Our lab batteries

k = 1.15

C = 36 A

C_p = 63 A-hr

Prediction of Peukert equation is plotted at left



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 $\eta = E_D/E_C$

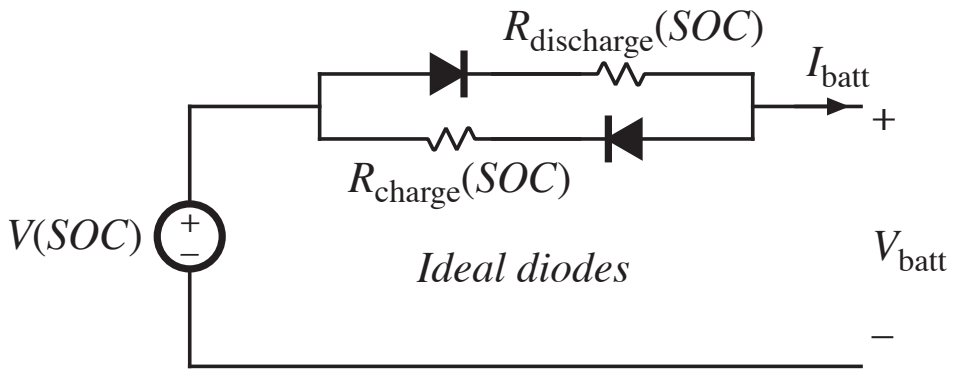
E_C = Total energy during charging = $\int v_{batt}\,(-i_{batt})\,dt \approx V_C I_C T_C$

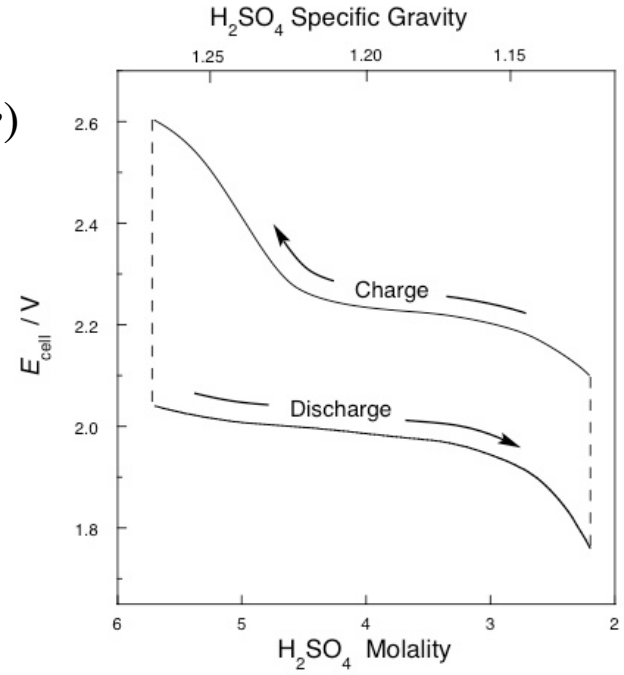
E_D = Total energy during discharging = $\int v_{batt}\,i_{batt}\,dt \approx V_D I_D T_D$

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

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

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





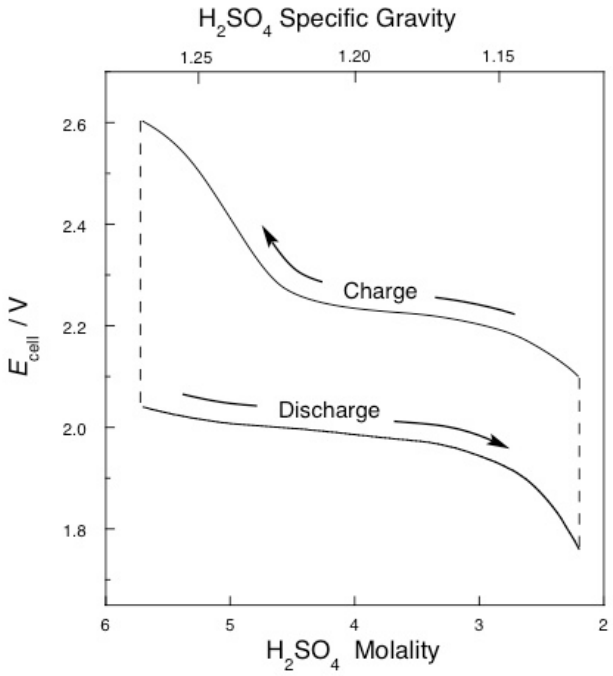
Energy efficiency

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

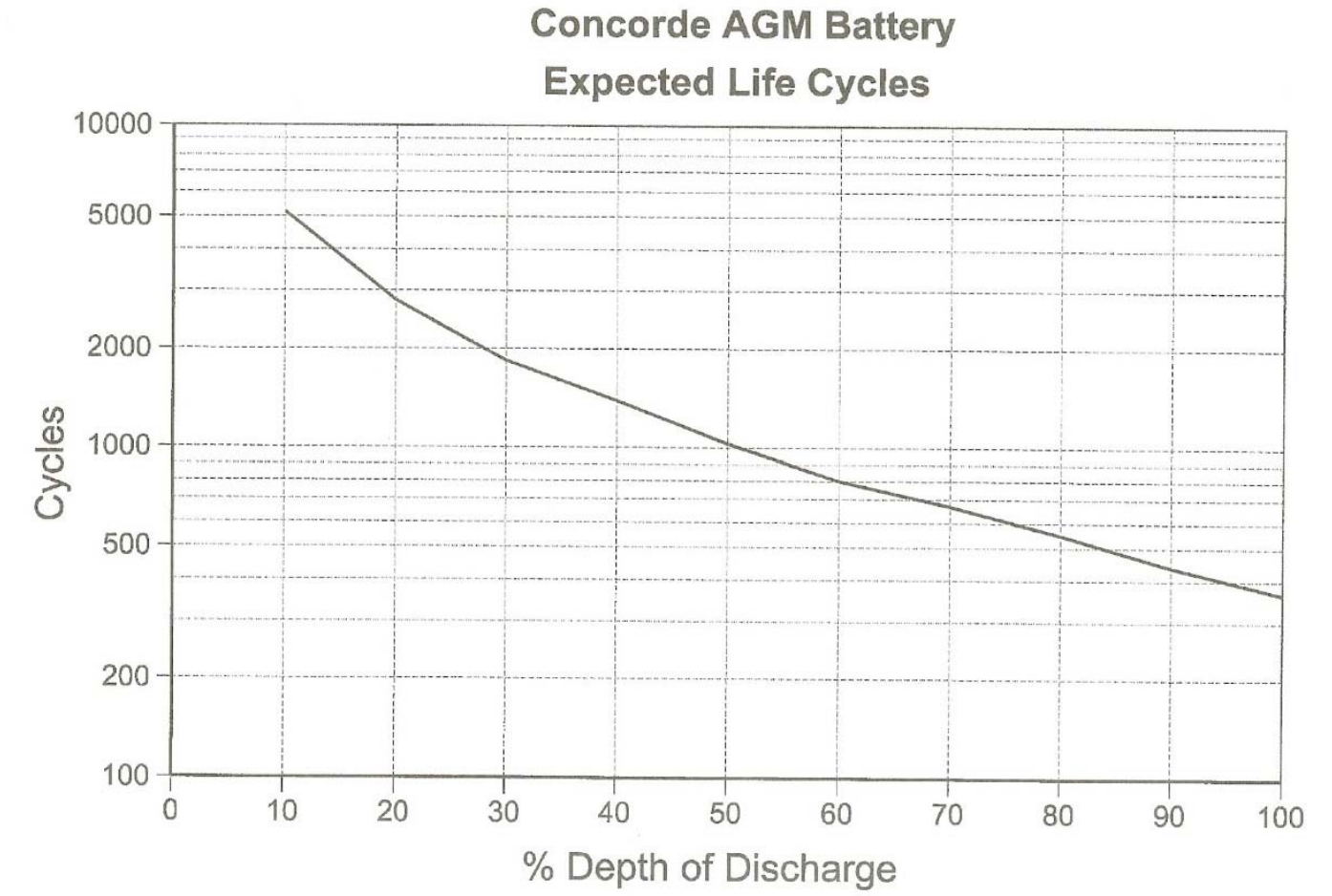
- At beginning of charge cycle, coulomb efficiency is near 100%
- Near end of charge cycle, electrolysis of water reduces coulomb efficiency. Can improve this efficiency by reducing charge rate (taper charging)
- Typical net coulomb efficiency: 90%
- Approximate voltage efficiency: (2V)/(2.3V) = 87%

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

Commonly quoted estimate: 75%



Battery life



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

Charge profile

A typical good charge profile:

Bulk charging at maximum power

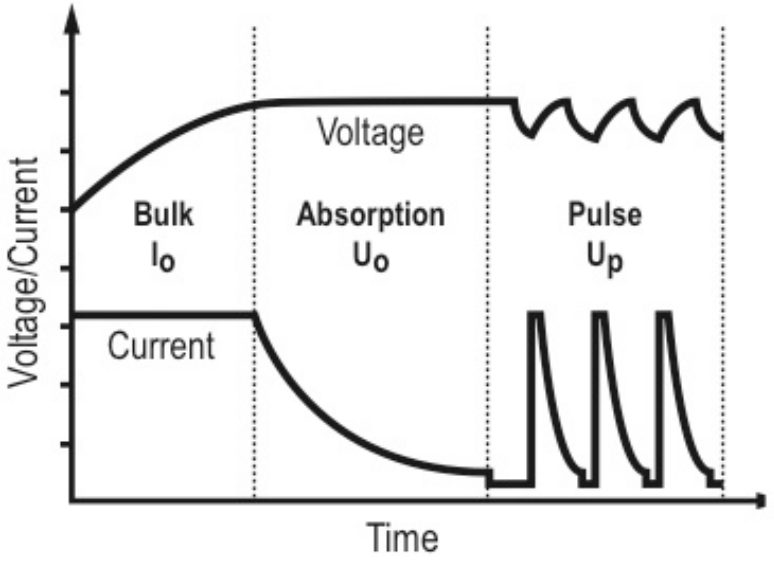
- Terminate when battery is 80% charged (when a voltage set point is reached)

Charging at constant voltage

- The current will decrease
- This reduces gassing and improves charge efficiency
- "Absorption" or "taper charging"

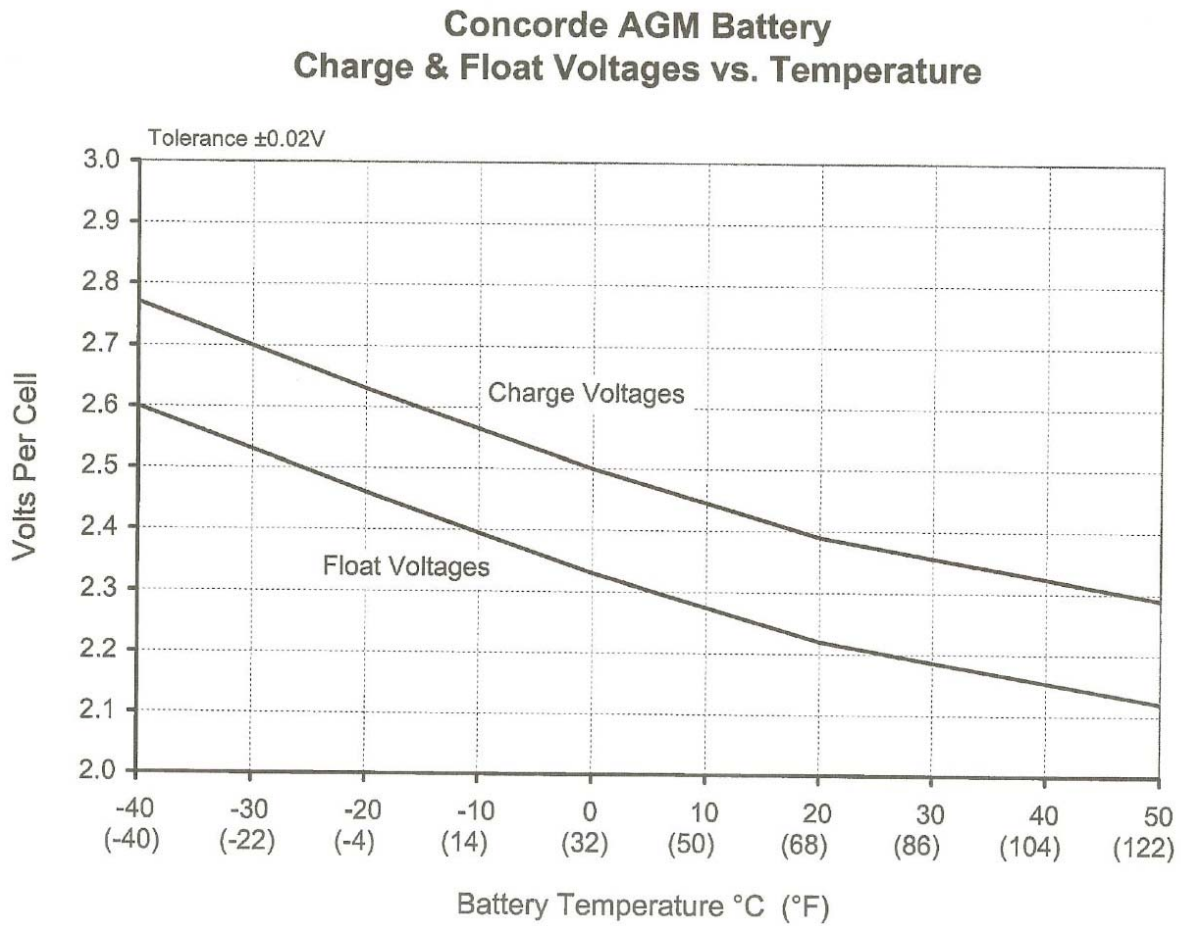
Trickle charging / float mode

- Equalizes the charge on series-connected cells without significant gassing
- Prevents discharging of battery by leakage currents
- Occasional pulsing helps reverse sulfation of electrodes



The three-step charge profile used by the chargers in our power lab

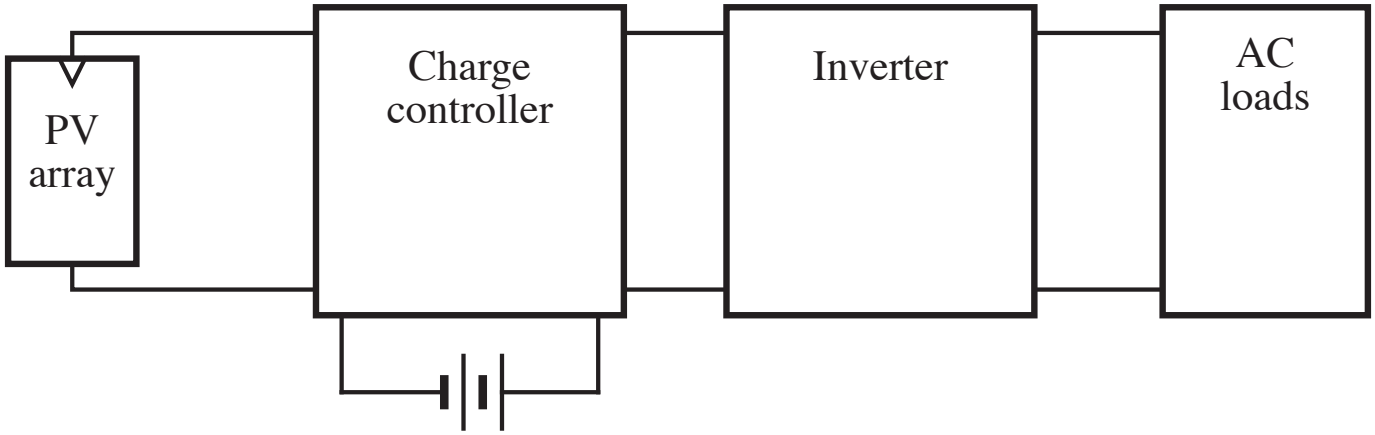
Charge and float voltages



Good chargers can:

- Program charge/float voltages to needs of specific battery type
- Temperature-compensate the voltage set points
- Maintain battery in fully charged state (float mode) when in storage
- Avoid overcharging battery (charge voltage set point)
- Taper back charging current to improve charge efficiency and reduce outgassing

Battery charge controller



- Prevent sulfation of battery
  - Low SOC disconnect
  - Float or trickle charge mode
- Control charge profile
  - Multi-mode charging, set points
- Nightime disconnect of PV panel

Direct energy transfer

Charge battery by direct connection to PV array

MPPT

Connect dc-dc converter between PV array and battery; control this converter with a maximum power point tracker