Lead-Acid Batteries

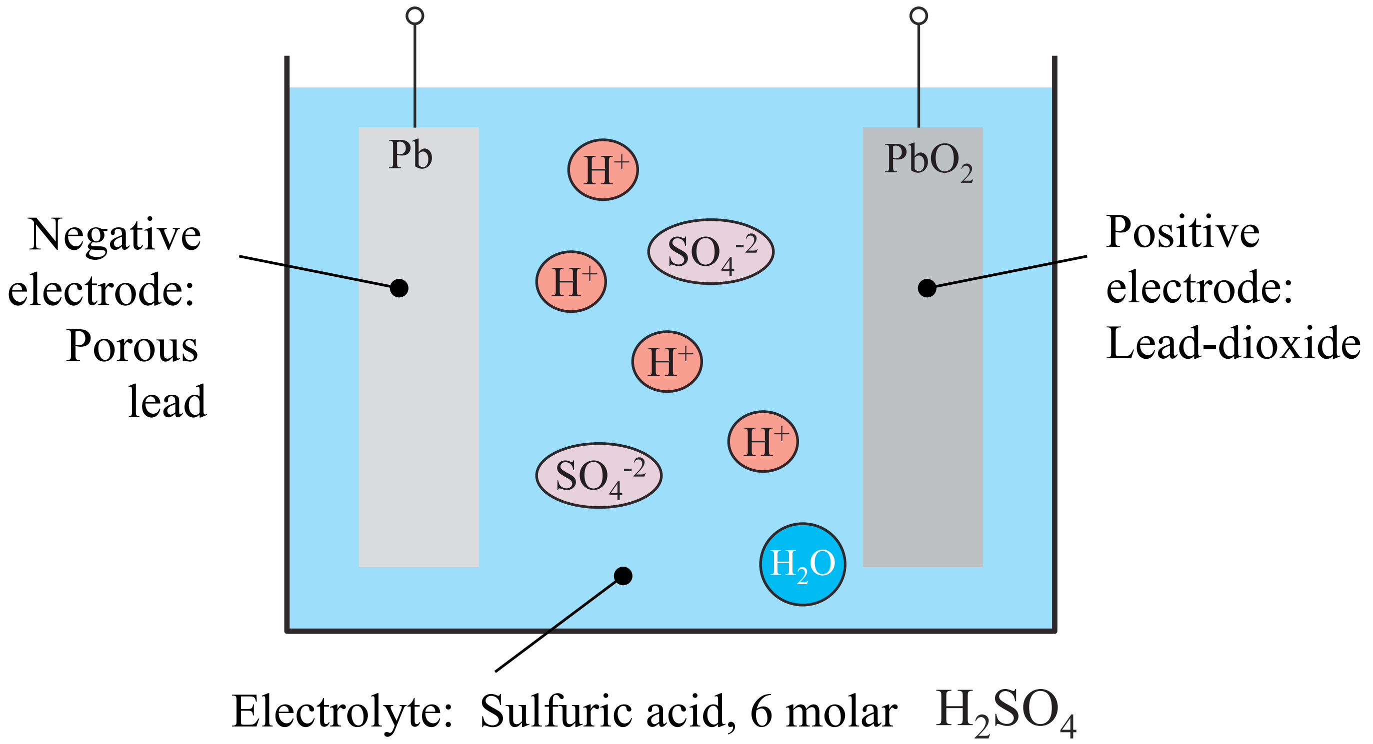
Lecture Outline

Lead-Acid Batteries
  - Basic Chemistry
  - Charging, discharging, and state of charge

Key equations and models
  - The Nernst equation: voltage vs. ion concentration
  - Battery equivalent circuit 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: cell chemistry



Negative electrode: Porous lead

Positive electrode: Lead-dioxide

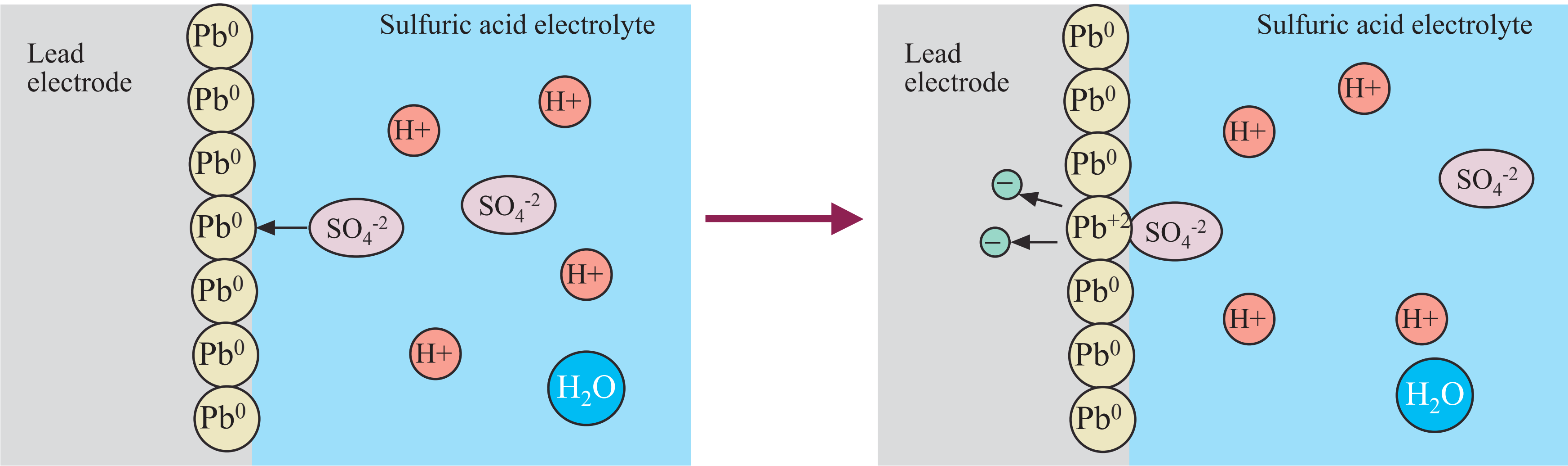
Electrolyte: Sulfuric acid, 6 molar H_2SO_4

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

Reaction at Negative (Pb) Electrode

Charged sulfate ion approaches uncharged lead electrode surface, dipole attraction kicks in on close approach

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



$$\underset{\text{solid}}{Pb} + \underset{\text{aqueous}}{SO_4^{-2}} \longrightarrow \underset{\text{solid}}{PbSO_4} + \underset{\text{in conductor}}{2e^-}$$

This reaction releases net energy

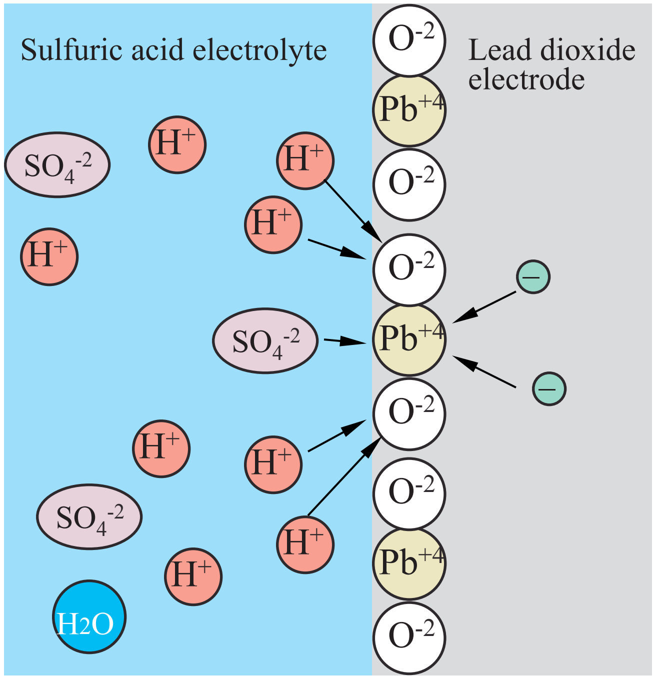
$$E^0 = 0.356 \text{ eV}$$

under standard conditions
(T = 298˚K, 1 molar concentration)

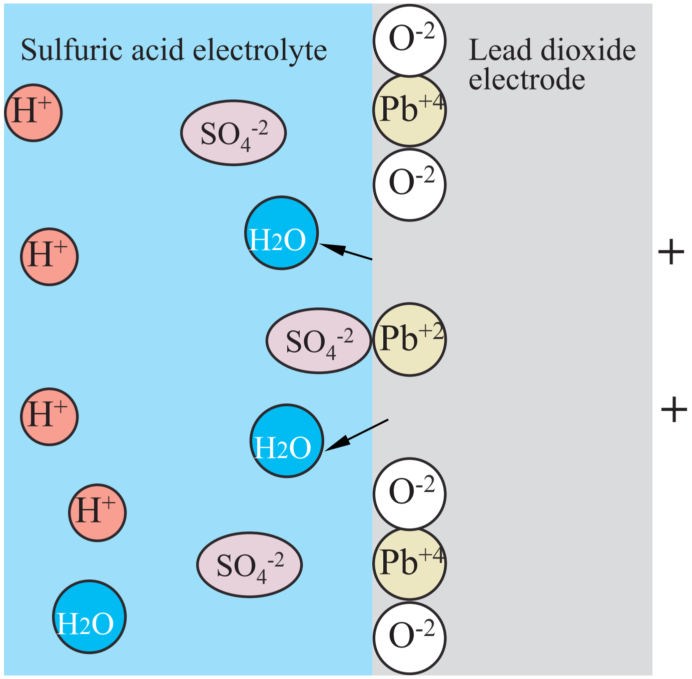
- **Release of two conducting electrons gives lead electrode a net negative charge**
- **As electrons accumulate they create an electric field which attracts hydrogen ions and repels sulfate ions, leading to a double-layer near the surface. The hydrogen ions screen the charged electrode from the solution which limits further reactions unless charge is allowed to flow out of electrode.**

Reaction at Positive (PbO_2) 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



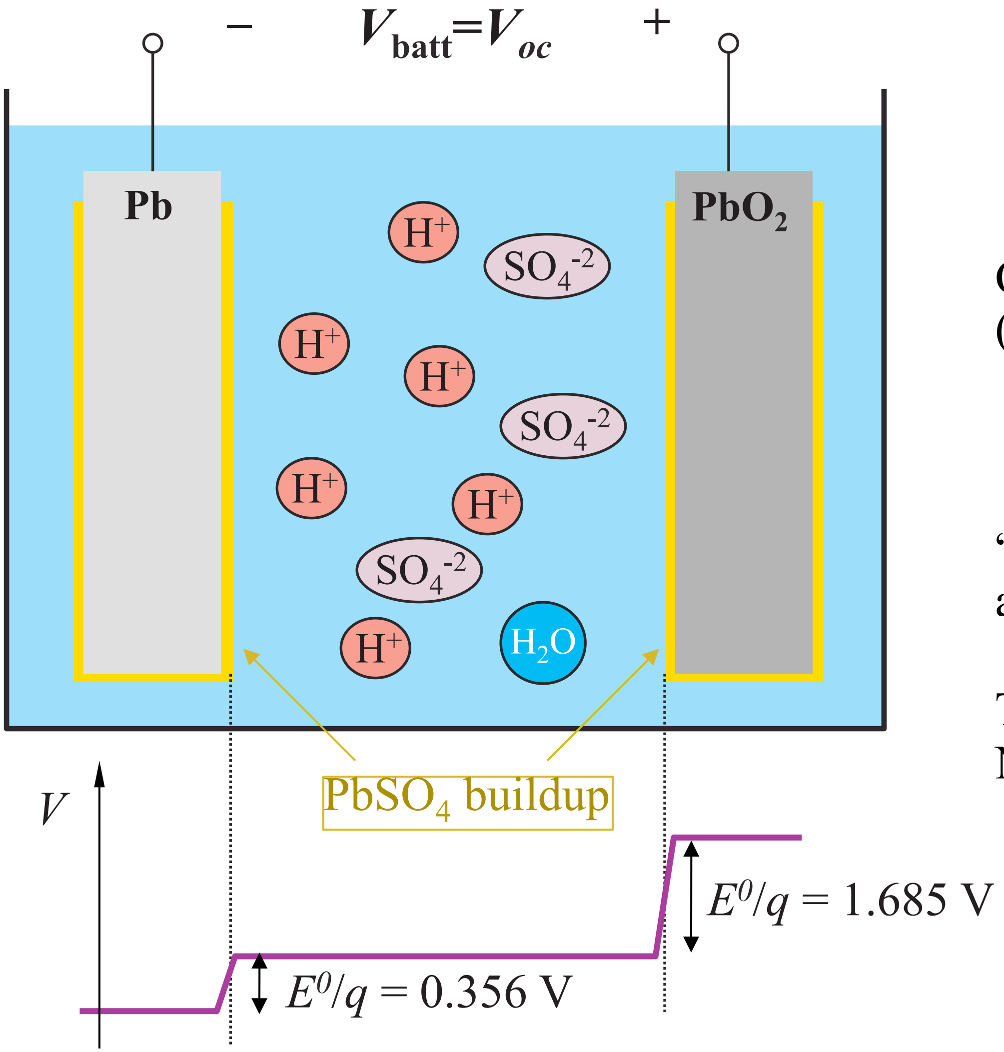
$$\underset{\text{solid}}{PbO_2} + \underset{\text{aqueous}}{SO_4^{-2}} + \underset{\text{aqueous}}{4H^+} + \underset{\text{in conductor}}{2e^-} \longrightarrow \underset{\text{solid}}{PbSO_4} + \underset{\text{liquid}}{2H_2O}$$

This reaction releases net energy

$E^0 = 1.685$ eV

- **As positive charge accumulates an electric field is created which will attract sulfate ions and repel hydrogen ions (charge screening) limiting further reaction unless charge is allowed to flow out of electrode.**
- **Note: Both half reactions cause the electrodes to become coated with lead sulfate (a poor conductor) and reduce the concentration of the acid electrolyte**

Battery Voltage at Zero Current (equilibrium)



As described in earlier slides, reactions at electrodes lead to opposite charge buildup on electrodes and hence a voltage difference

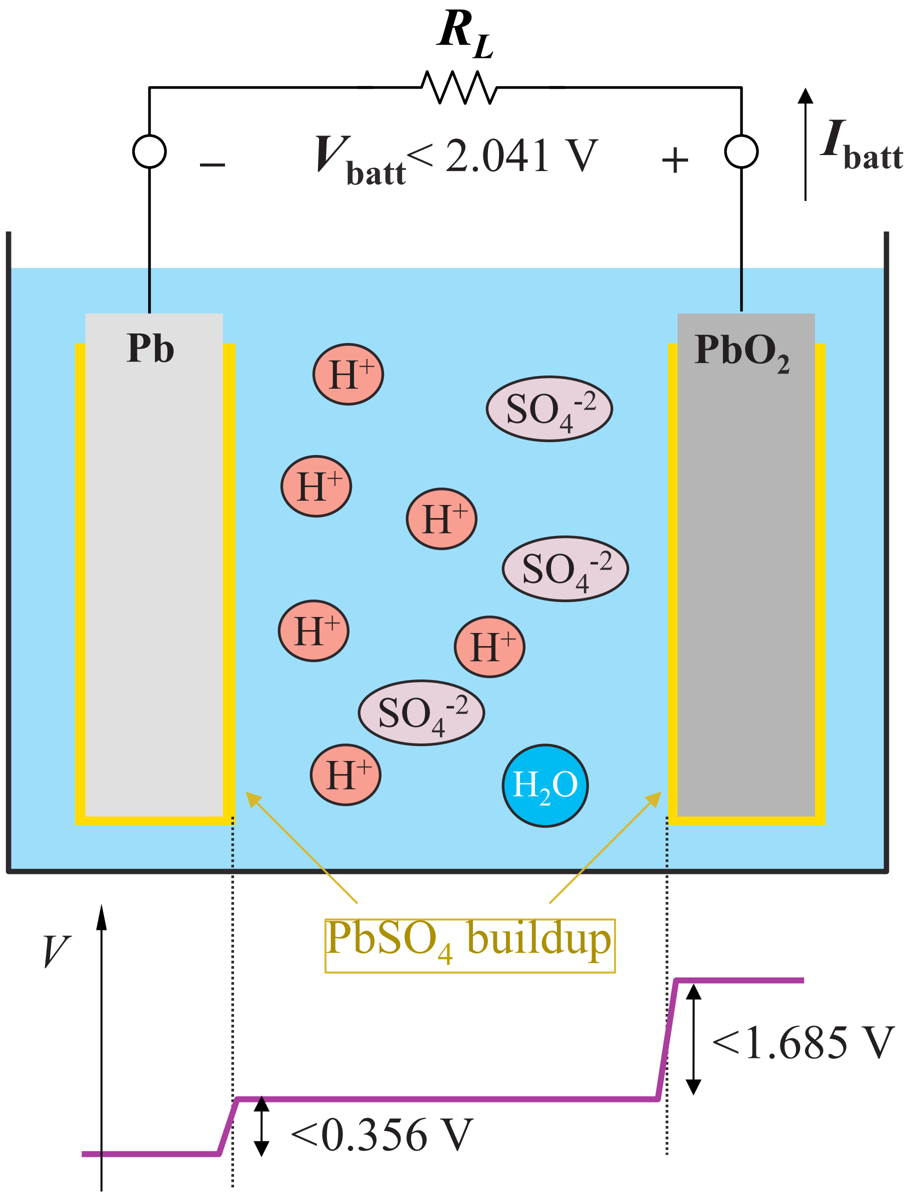
Open-circuit voltage under standard conditions ($T = 298^\circ$K and 1 molar acid electrolyte) is

$$V_{oc} = 0.356 + 1.685 = 2.041 \text{ V}$$

“Sulfation” of electrodes and double-layers at surfaces limits further reactions

Temperature plays an important role (see Nernst equation later)

Discharging through External Load



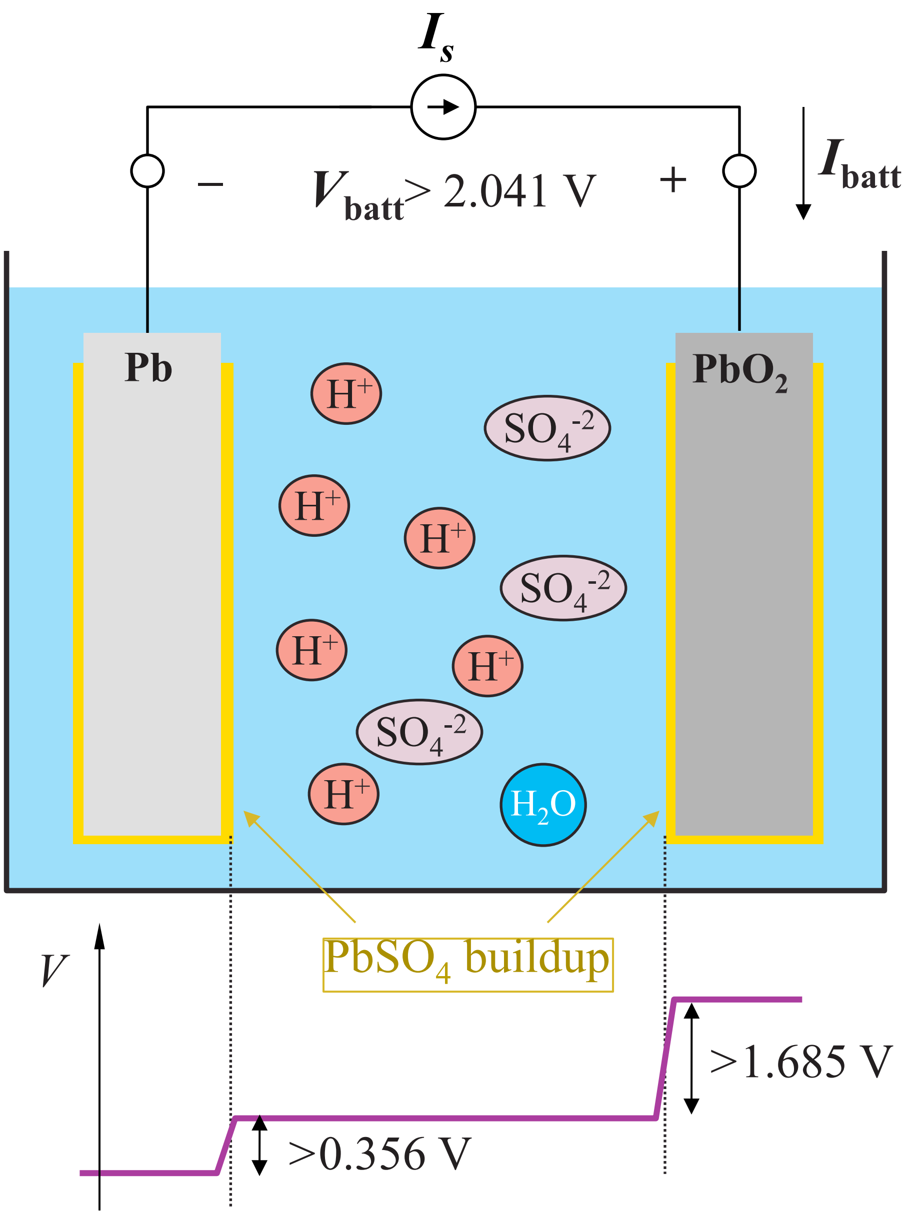
External load allows electrons to flow and chemical reactions to proceed

As battery is discharged, additional sulfation of electrodes occurs and acid electrolyte becomes weaker, lowering the terminal voltage

Note that current must flow through electrolyte to complete the circuit (combination of drift & diffusion currents)

The conductivity of electrolyte and the contact resistance of sulfated electrodes contribute to internal resistance of battery. Strong function of temperature and the state-of-charge of the system

Charging from External Source



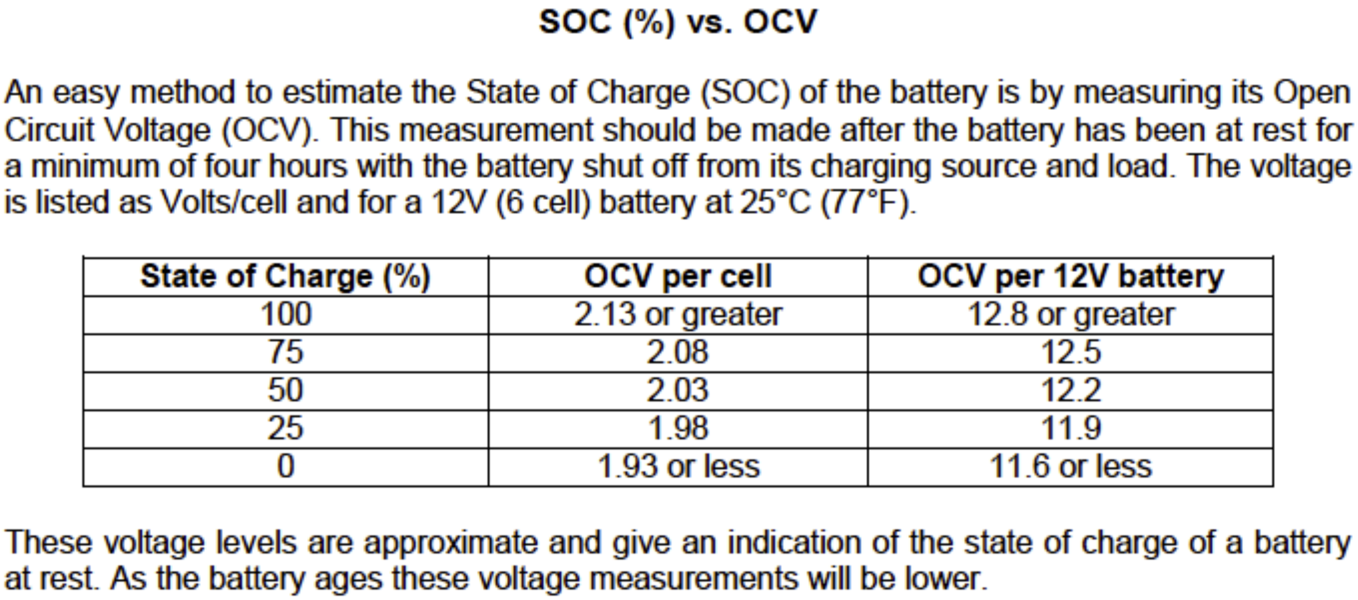
External source forces electrons to flow from positive to negative terminals

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)

	Full Charged	**Completely Discharged**
State of charge (SOC)	100%	0%
Depth of discharge (DOD)	0%	100%
Electrolyte concentration, Q	~6 molar	~2 molar
Electrolyte specific gravity	~1.3	~1.1
No-load voltage, $V_{oc,}$ @ 25C	12.7 (2.12V/cell)	11.7 (1.95 V/cell)



SOC (%) vs. OCV

An easy method to estimate the State of Charge (SOC) of the battery is by measuring its Open Circuit Voltage (OCV). This measurement should be made after the battery has been at rest for a minimum of four hours with the battery shut off from its charging source and load. The voltage is listed as Volts/cell and for a 12V (6 cell) battery at 25°C (77°F).

State of Charge (%)	OCV per cell	OCV per 12V battery
100	2.13 or greater	12.8 or greater
75	2.08	12.5
50	2.03	12.2
25	1.98	11.9
0	1.93 or less	11.6 or less

These voltage levels are approximate and give an indication of the state of charge of a battery at rest. As the battery ages these voltage measurements will be lower.

Voltage vs. Electrolyte concentration

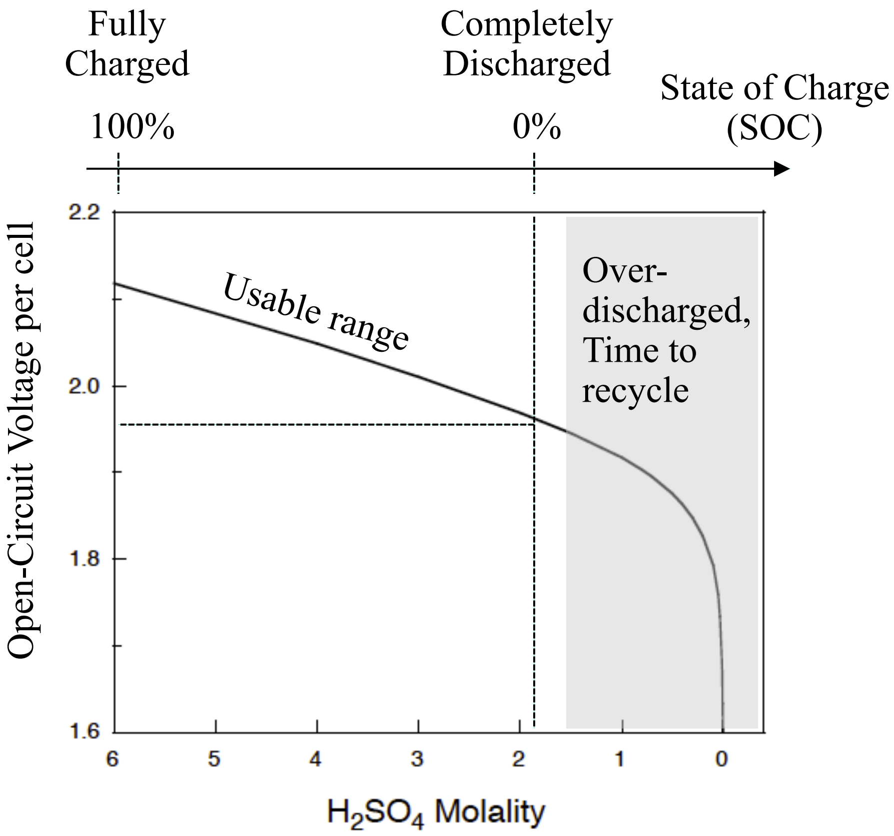
The Nernst equation relates the chemical reaction energy to electrolyte energy:

$$E = E^0 + \frac{kT}{q} \ln Q$$

where:
E = energy at a given concentration
E^0 = energy at standard 1 molar concentration
Q = molar concentration
kT/q = 26 mV at 298 ˚K

This is just an approximation for a real cell but gives some useful insight:

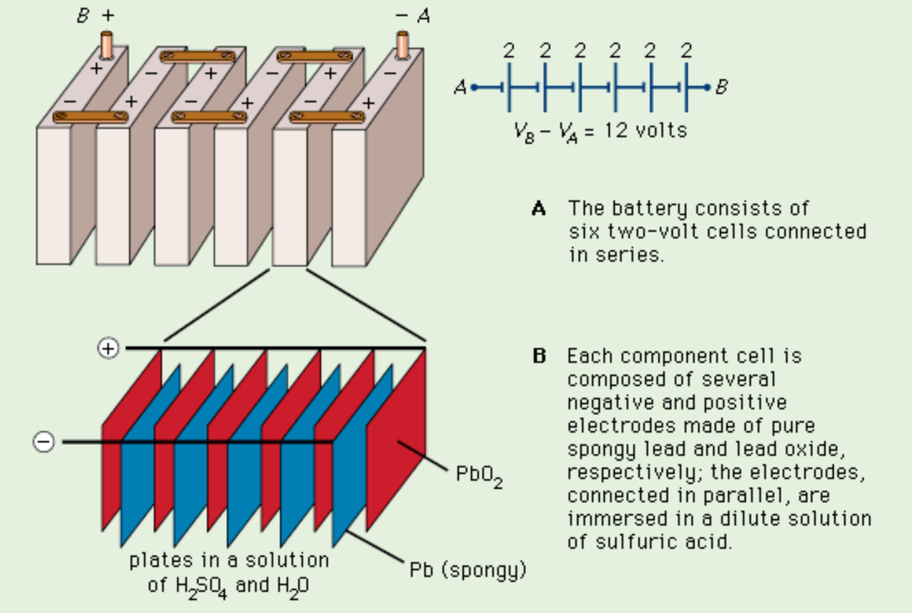
- At fully charged state (>6 molar), the cell voltage is a higher than E^0/q under standard conditions (1 molar)
- As the cell is discharged, the H_2SO_4 molality decreases so the open-circuit voltage decreases
- Voltage is temperature dependent (!)



At some point of discharge the electrode sulfation builds to a point where it becomes difficult to recharge the battery. This "over-discharge" regime should be avoided. Battery manufacturers will specify "complete discharge" at some cell voltage

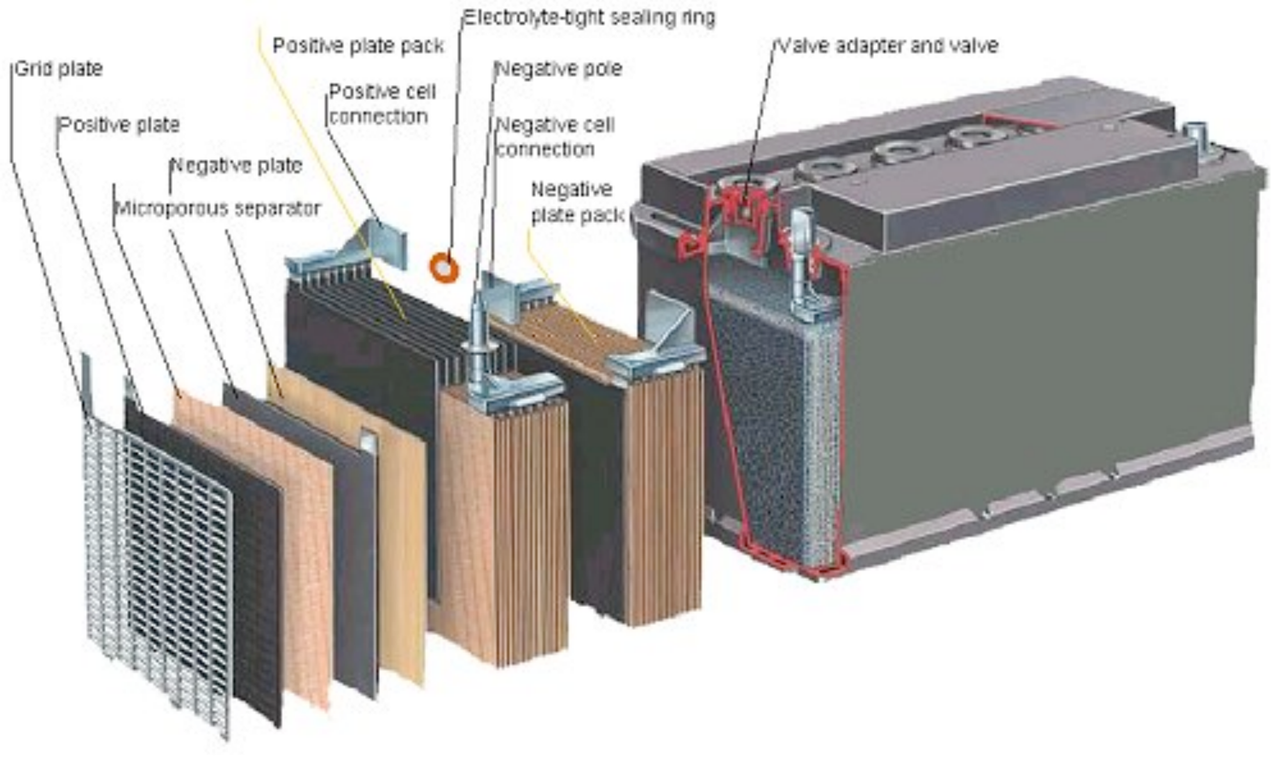
R. S. Treptow, "The lead-acid battery: its voltage in theory and practice," *J. Chem. Educ.*, vol. 79 no. 3, Mar. 2002

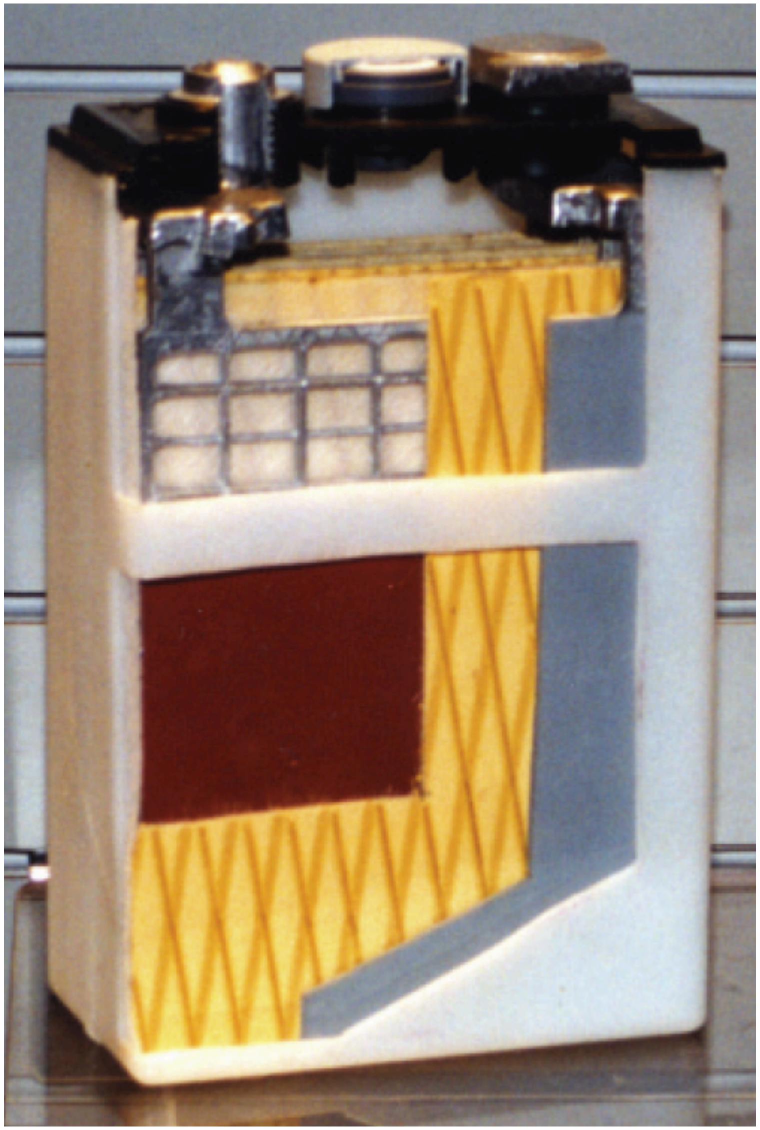
12V Lead-Acid Battery Construction



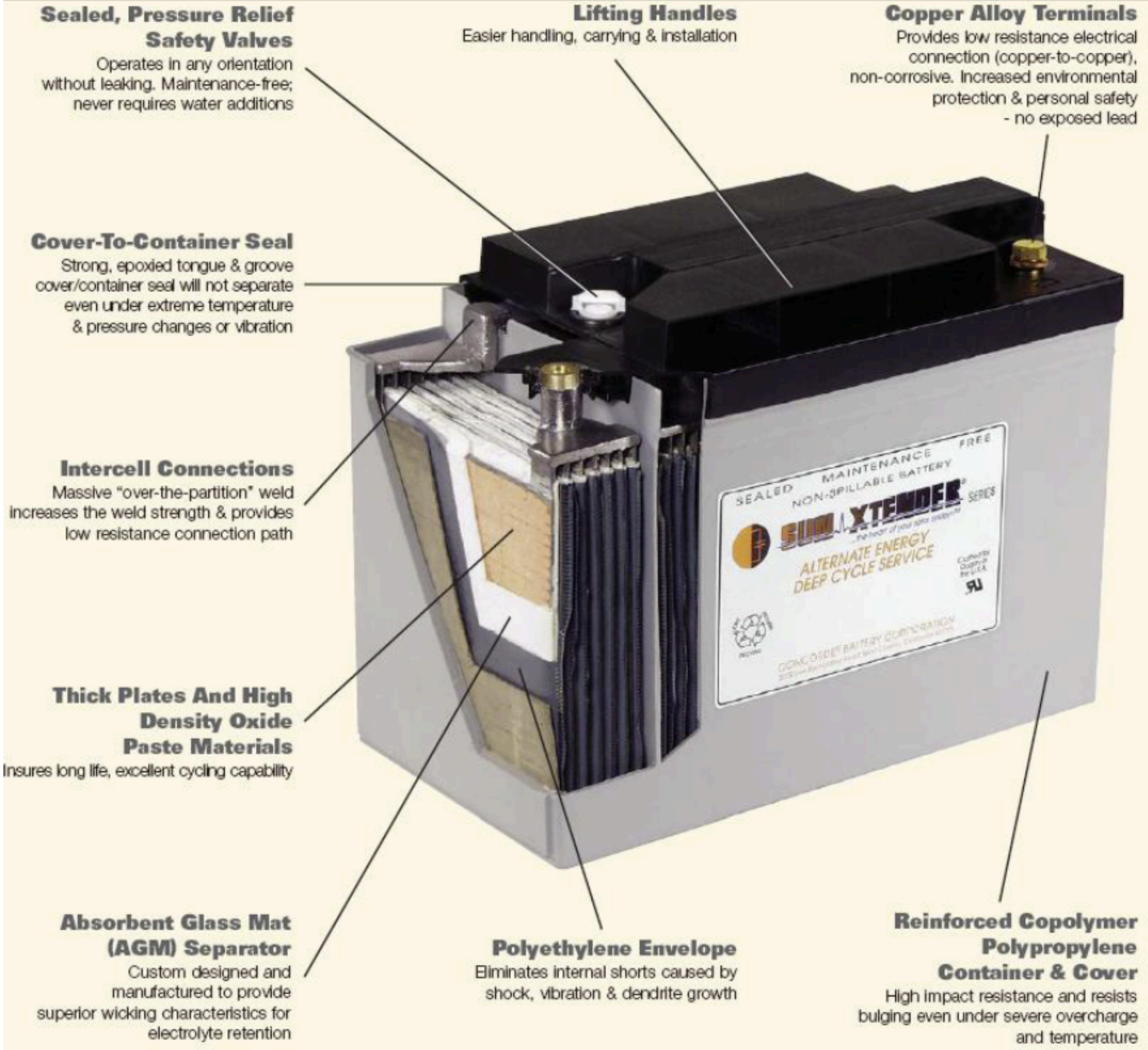
A The battery consists of six two-volt cells connected in series.

B Each component cell is composed of several negative and positive electrodes made of pure spongy lead and lead oxide, respectively; the electrodes, connected in parallel, are immersed in a dilute solution of sulfuric acid.





Concorde Sun Xtender Series



Sealed, Pressure Relief Safety Valves
Operates in any orientation without leaking. Maintenance-free; never requires water additions

Lifting Handles
Easier handling, carrying & installation

Copper Alloy Terminals
Provides low resistance electrical connection (copper-to-copper), non-corrosive. Increased environmental protection & personal safety - no exposed lead

Cover-To-Container Seal
Strong, epoxied tongue & groove cover/container seal will not separate even under extreme temperature & pressure changes or vibration

Intercell Connections
Massive "over-the-partition" weld increases the weld strength & provides low resistance connection path

Thick Plates And High Density Oxide Paste Materials
Insures long life, excellent cycling capability

Absorbent Glass Mat (AGM) Separator
Custom designed and manufactured to provide superior wicking characteristics for electrolyte retention

Polyethylene Envelope
Eliminates internal shorts caused by shock, vibration & dendrite growth

Reinforced Copolymer Polypropylene Container & Cover
High impact resistance and resists bulging even under severe overcharge and temperature

	Size	Weight		Capacity Amp-hrs	
Part #	L x W x H in (mm)	lbs	kgs	C	C_{120}
PVX-340T	7.7 x 5.2 x 6.9 (196 X 132 X 175)	25	11	21	38
PVX-420T	7.71 x 5.2 x 8.1 (196 x 132 x 204)	30	14	26	45
PVX-490T	9 x 5.5 x 8.8 (228 x 138 x 224)	36	16	31	55
PVX-560T	9 x 5.5 x 8.8 (228 x 138 x 224)	40	18	36	63
PVX-690T	10.22 x 6.6 x 8.9 (260 x 168 x 227)	51	23	42	79
PVX-840T	10.22 x 6.6 x 8.9 (260 x 168 x 227)	57	26	52	97
PVX-890T	12.9 x 6.8 x 9 (328 x 172 x 228)	62	28	55	102
PVX-1040HT	13.1 x 6.6 x 8.9 (333 x 168 x 227)	63	29	65	120
PVX-1040T	12. X 6.6 x 8.9 (305 x 168 x 227)	63	29	65	120
PVX-1080T	12.9 x 6.8 x 9 (328 x 172 x 228)	65	30	68	126
PVX-1180T	12.9 x 6.8 x 9 (328 x 172 x 228)	72	33	72	137
PVX-1290T	12.9 x 6.8 x 9 (328 x 172 x 228)	75	34	79	149
PVX-1530T	13.5 x 6.8 x 12 (342 x 172 x 304)	97	44	95	179
PVX-2120L	20.8 x 8.7 x 9.8 (527 x 221 x 248)	127	58	136	253
PVX-2580L	20.8 x 10.9 x 9.8 (527 x 277 x 248)	159	72	165	305

Battery capacity (C-factor)

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 (Note units confusion: C is a current in Amps but also used to characterize capacity in Amp-hrs)

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: $C_p = I^k t$

Relationship between C and C_p: $C_p = C^k$

This gives the Amp-hr capacity as: $It = Ct^{1-1/k}$

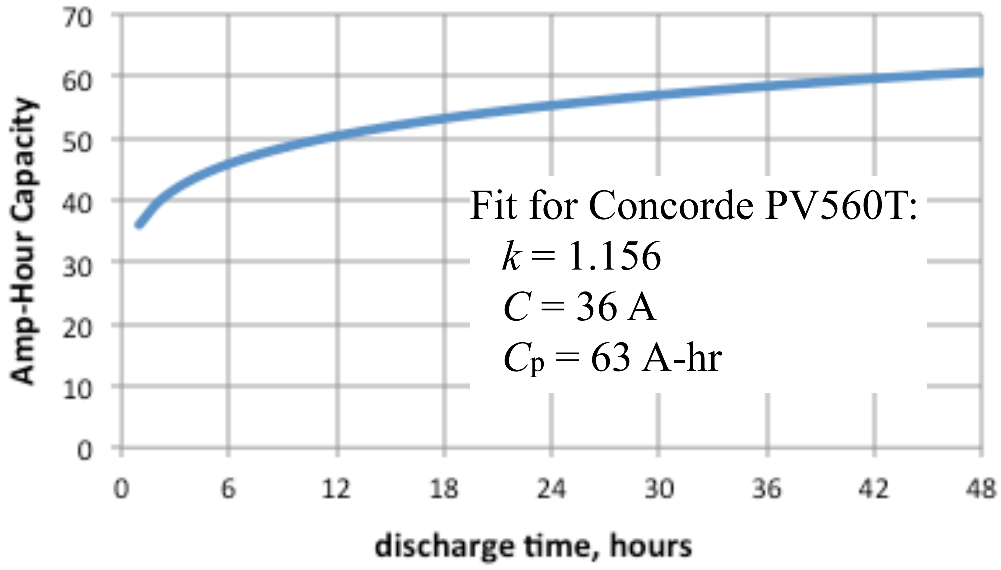
C_p is the ***amp-hour capacity at a 1 A discharge rate***

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

Usually the data sheet will give information about the A-hr capacity for a certain discharge rate or time period that can be used to determine C from above



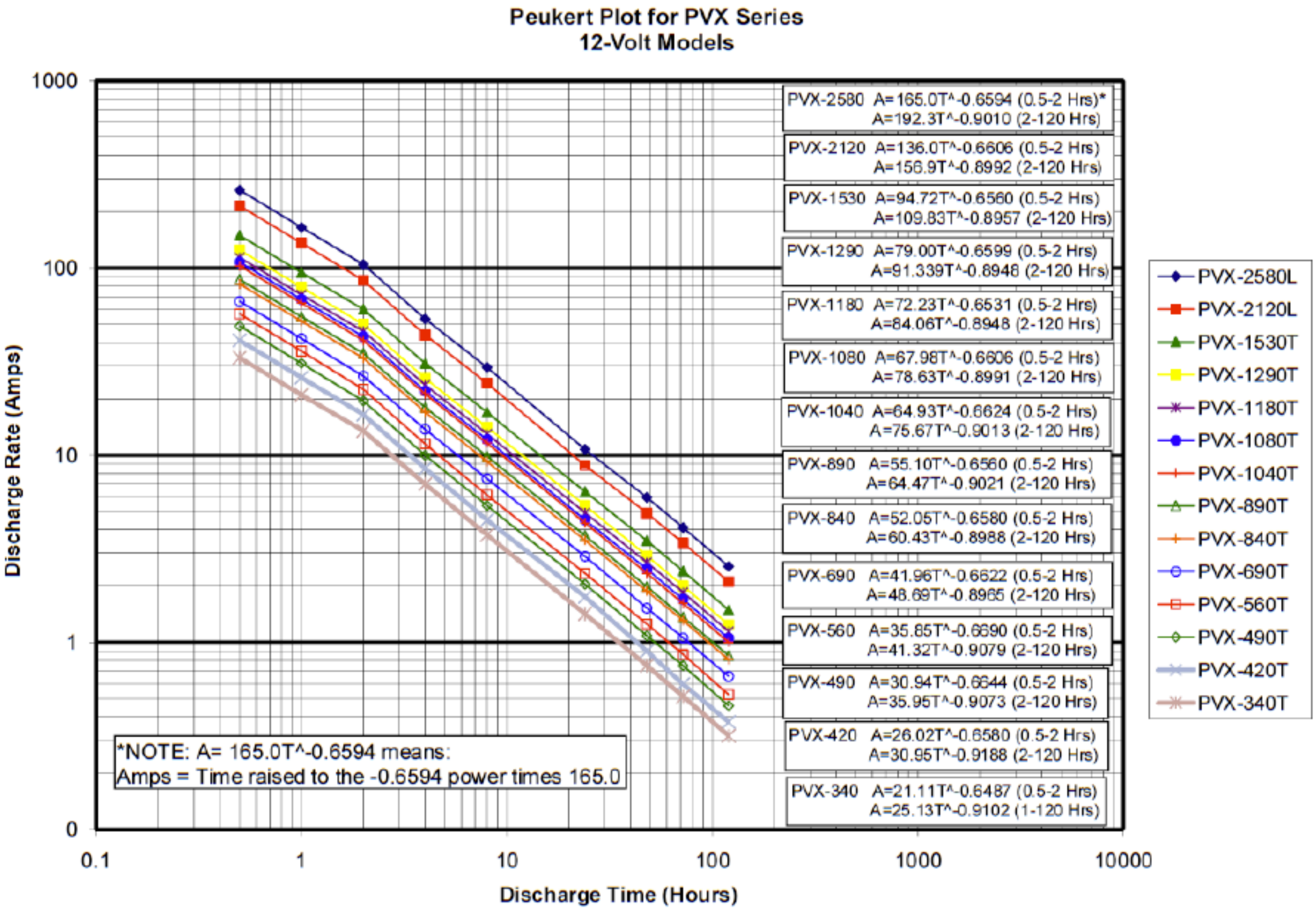
Fit for Concorde PV560T:
$k = 1.156$
$C = 36$ A
$C_p = 63$ A-hr

Concorde Sun Xtender PV560T
Manufacturer Data Sheet:

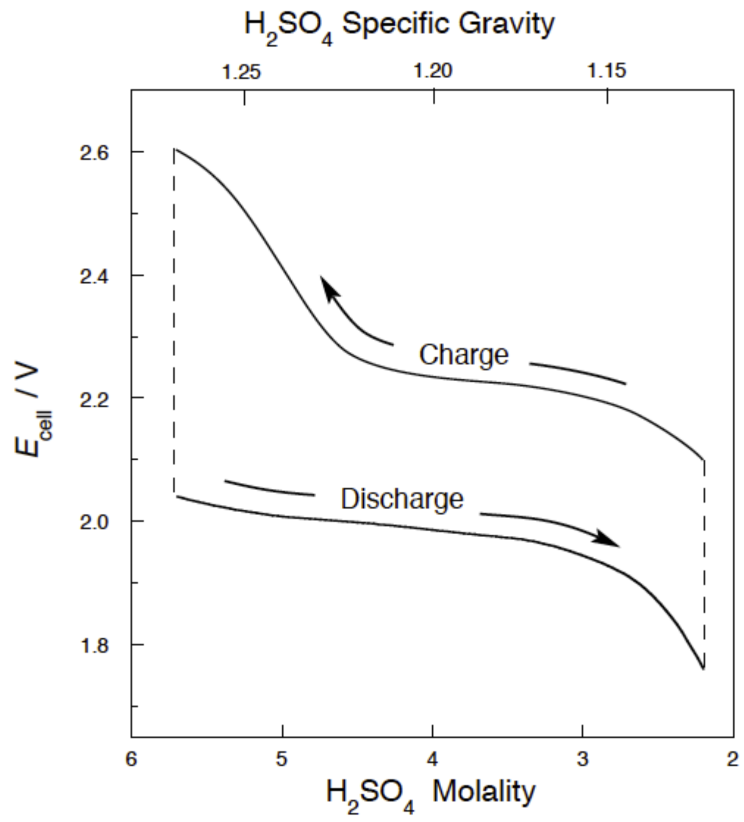
Nominal capacity: A-hrs @ 25C down to 1.75/cell						
Discharge time, hr	1	2	4	8	24	48
Capacity, A-hr	36	45	46	49	56	60
Discharge current, A	36	22.5	11.5	6.13	2.33	1.25

http://www.sunxtender.com/xtender_main.php

Concorde Sun Xtender Peukert Plots



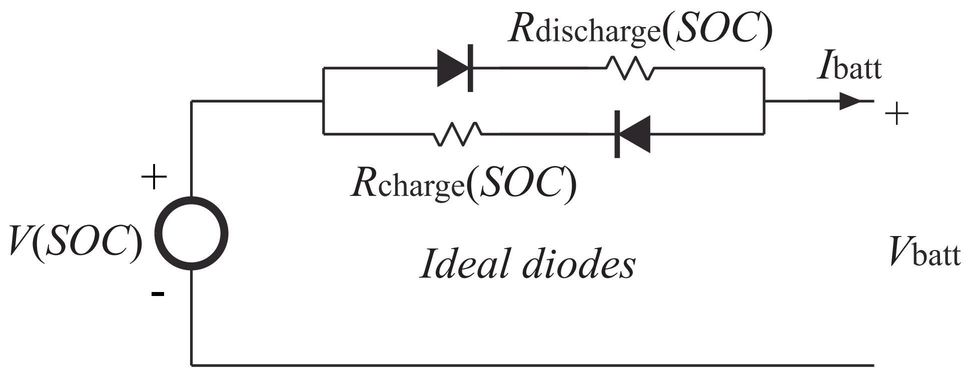
Battery Equivalent Circuit



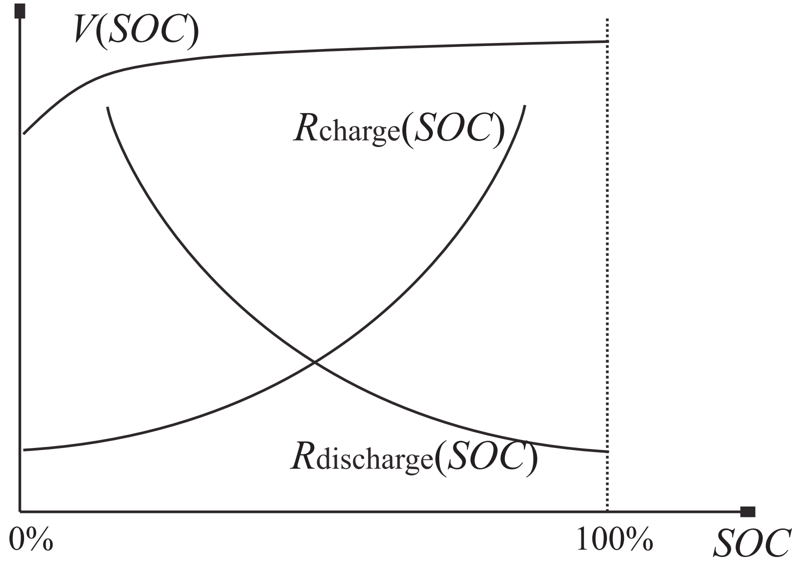
During discharge, ohmic losses in electrolyte and contacts lower voltage. Internal impedance increases due to lowering electrolyte concentration and electrode sulfation

During charging, effective resistance is low while sulfate buildup on electrodes is removed, resistance increases once electrolyte concentration is restored. Continued charging beyond this point leads to electrolysis of water and "gassing"

Basic model



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

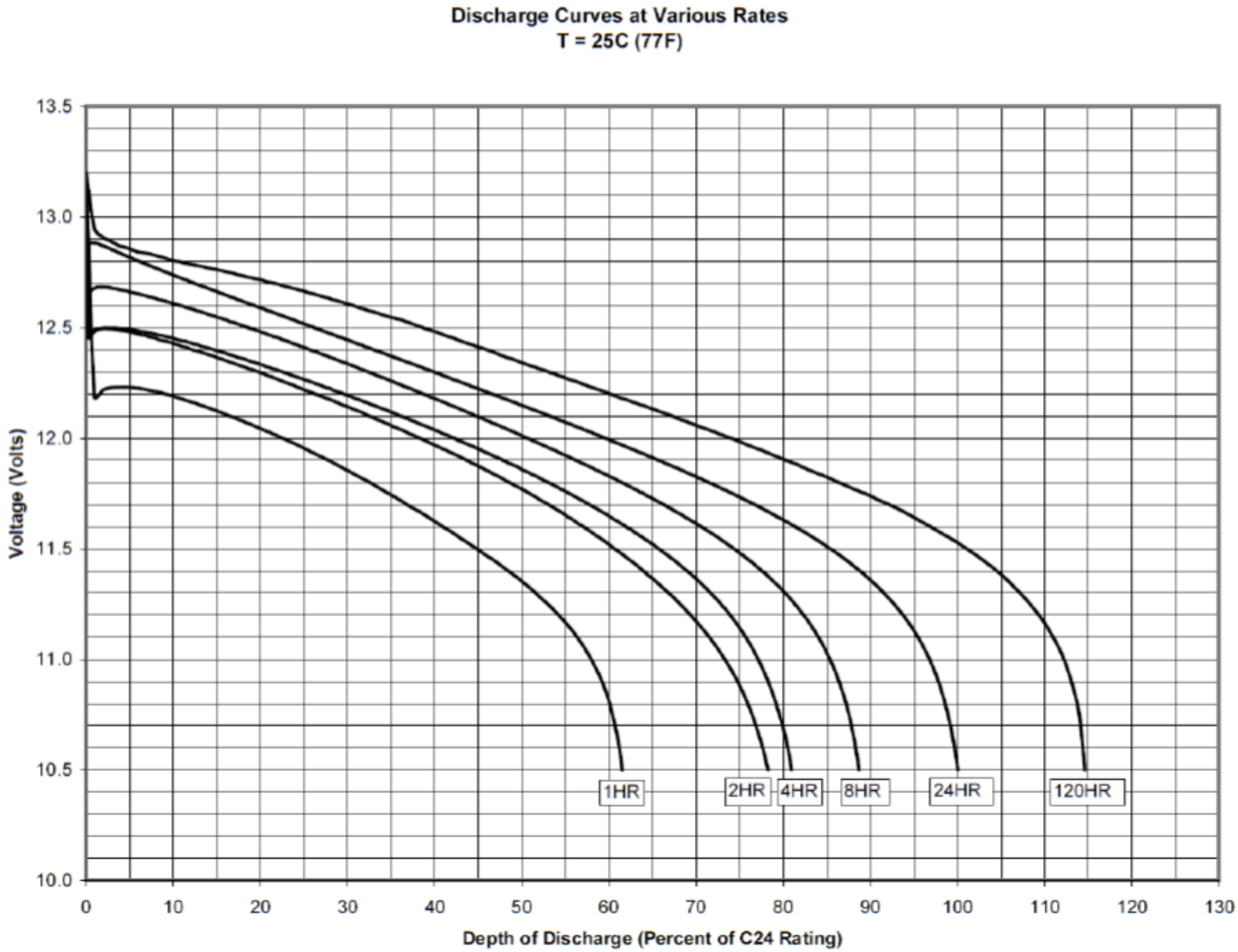


Concorde Sun Xtender Discharge Curves

Discharge at faster rate means greater voltage drop across internal resistances

Over-discharging leads to excessive sulfation and the battery could be ruined. The chemical reactions become irreversible when the size of the lead-sulfate formations become too large

Here the manufacturer recommends terminating discharge at 10.5V, at which point the battery is declared at 0% SOC, or 100% DOD

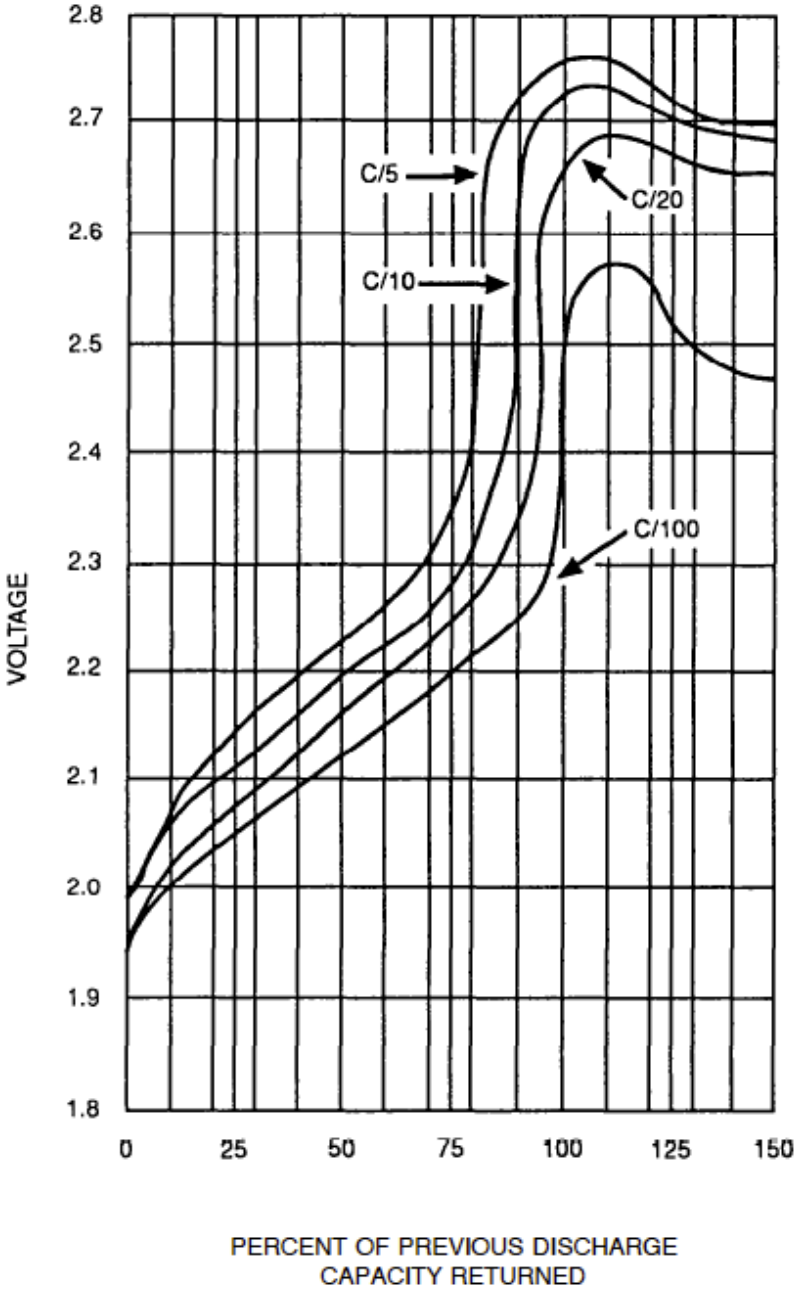


Influence of Charging Rate

Increased charging rate (current) is desirable to reduce charging time.

However, overcharging causes other undesirable reactions to occur ("gassing")

- 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



Source: John O'Conner, "A simple Lead-Acid Battery Charger", TI App note slua055 (originally Unitrode app note U-131)

Energy efficiency

Efficiency $= E_D/E_C$

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

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

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

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

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

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

At beginning of charge cycle, coulomb efficiency is near 100%

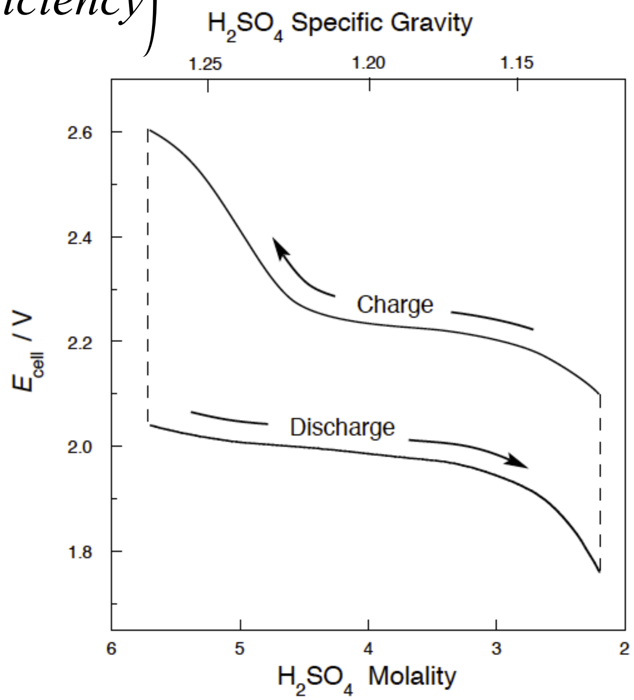
Near end of charge cycle, electrolysis of water reduces coulomb efficiency. Can improve this efficiency by reducing charge rate (taper charging)

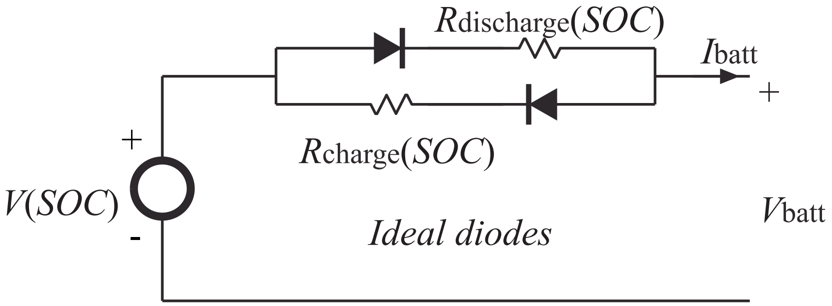
Typical net coulomb efficiency: 90%

Approximate voltage efficiency: (2V)/(2.3V) = 87%

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

Commonly quoted estimate: 75%





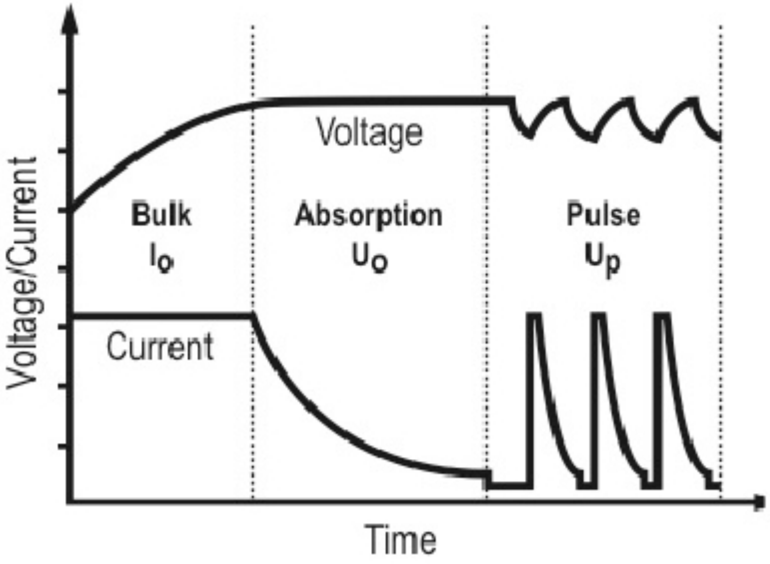
Charge Profile for Battery Charging

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

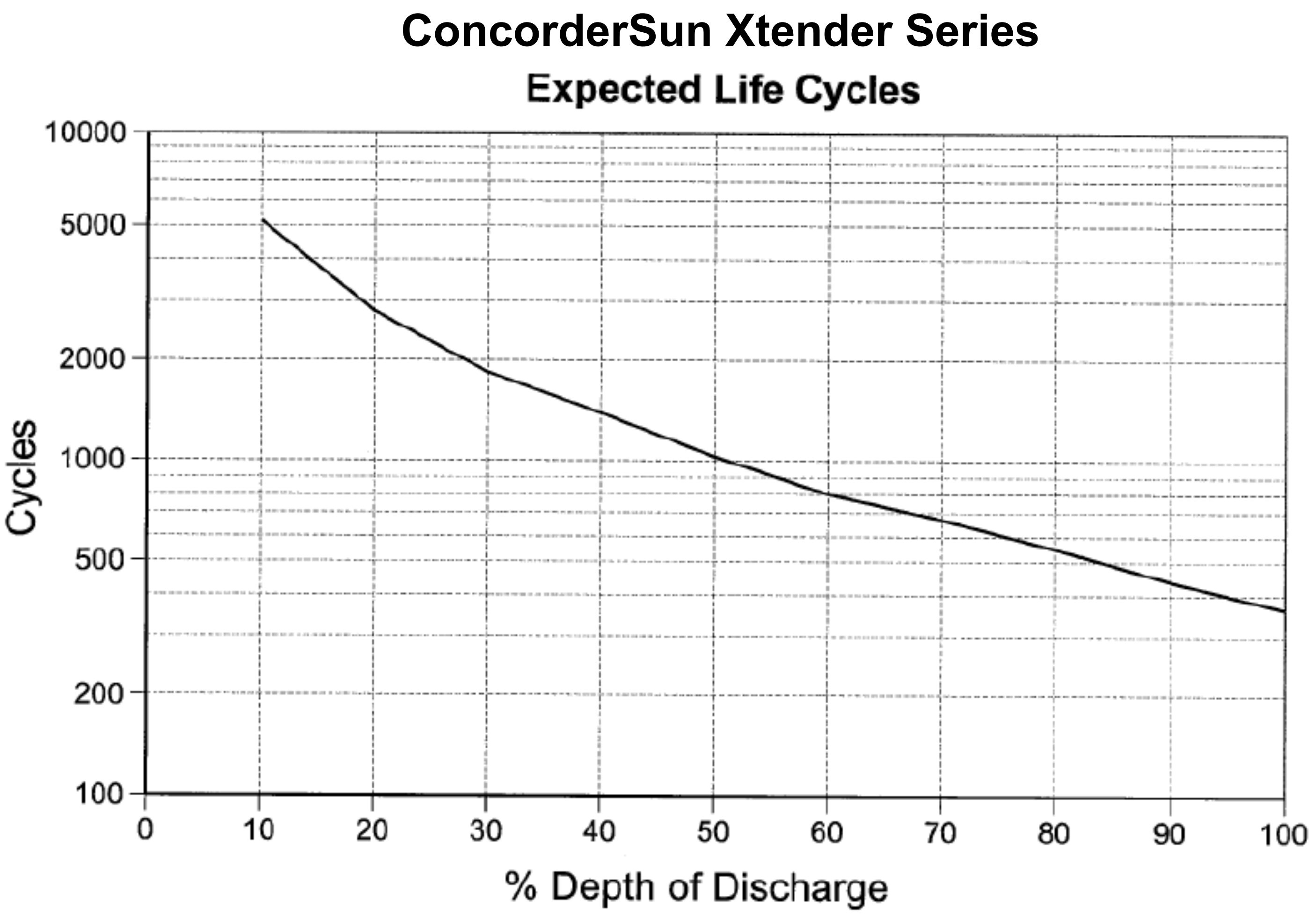
- Equalizes the charge on series-connected
  cells without significant gassing
- Prevents discharging of battery by
  leakage currents
- Occasional pulsing helps reverse sulfation
  of electrodes



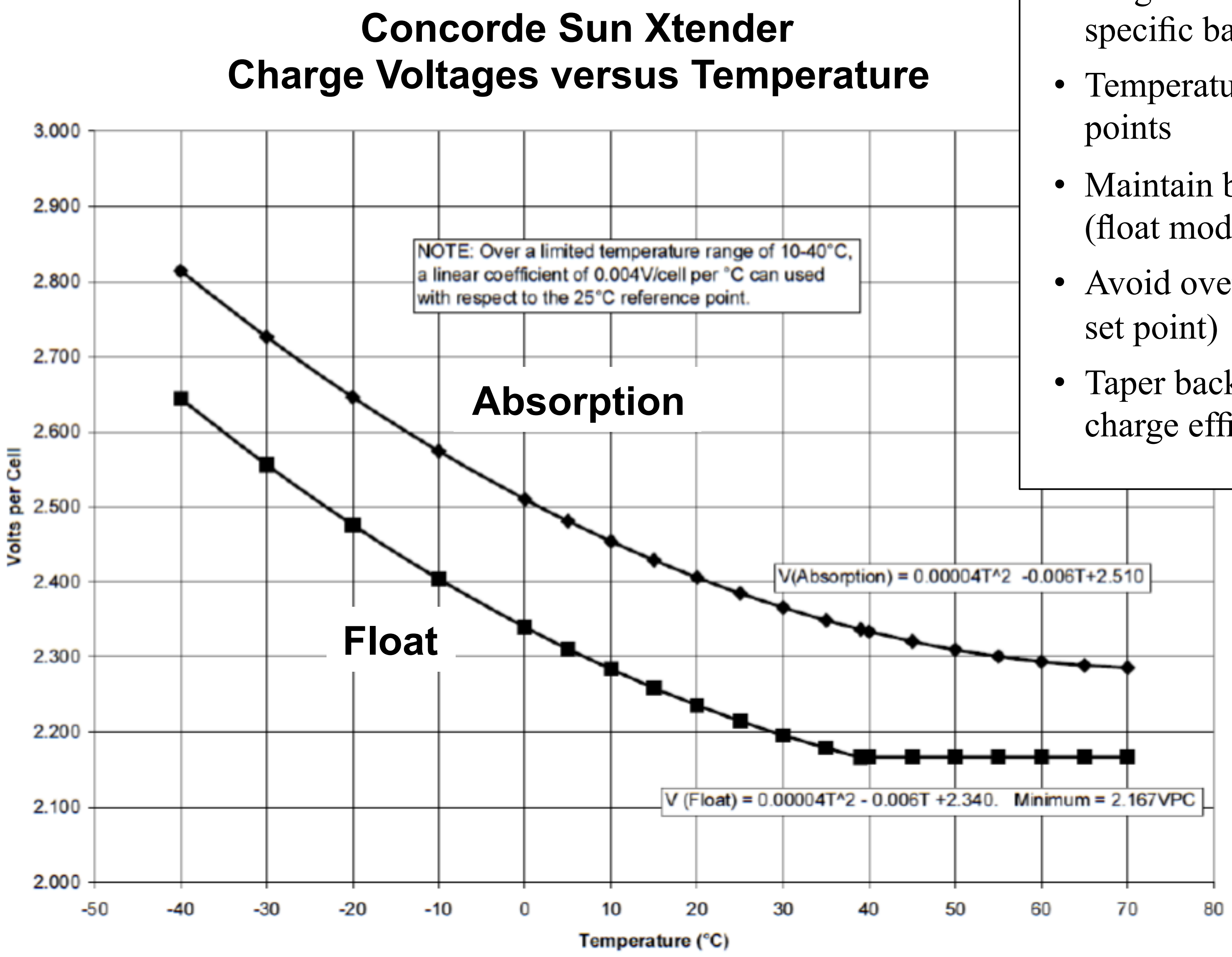
Battery life vs. Depth of Discharge

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 and float voltages



Concorde Sun Xtender
Charge Voltages versus Temperature

NOTE: Over a limited temperature range of 10-40°C, a linear coefficient of 0.004V/cell per °C can used with respect to the 25°C reference point.

V(Absorption) = 0.00004T^2 -0.006T+2.510

V (Float) = 0.00004T^2 - 0.006T +2.340. Minimum = 2.167VPC

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

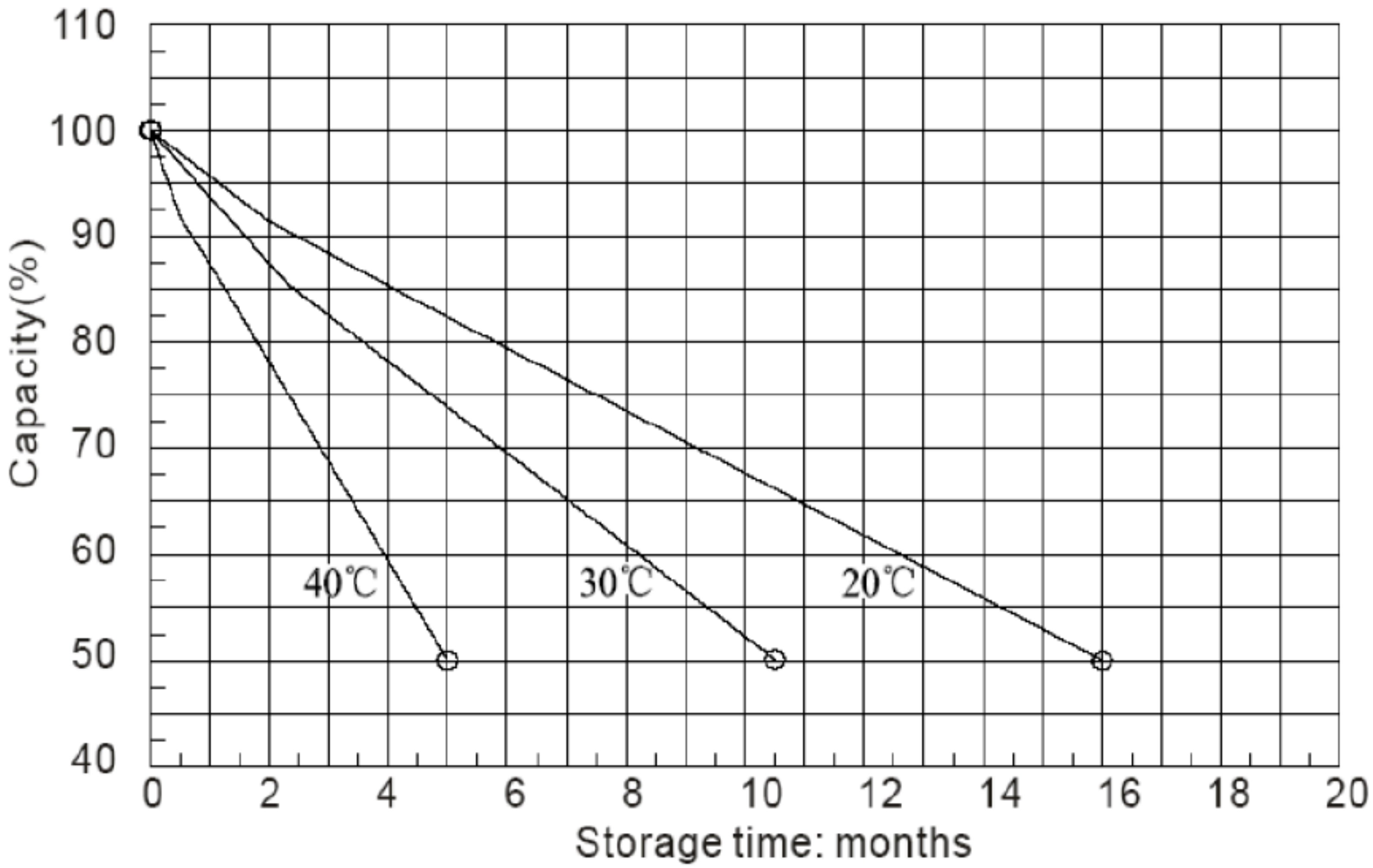
Some Types of lead-acid batteries

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
- 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

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

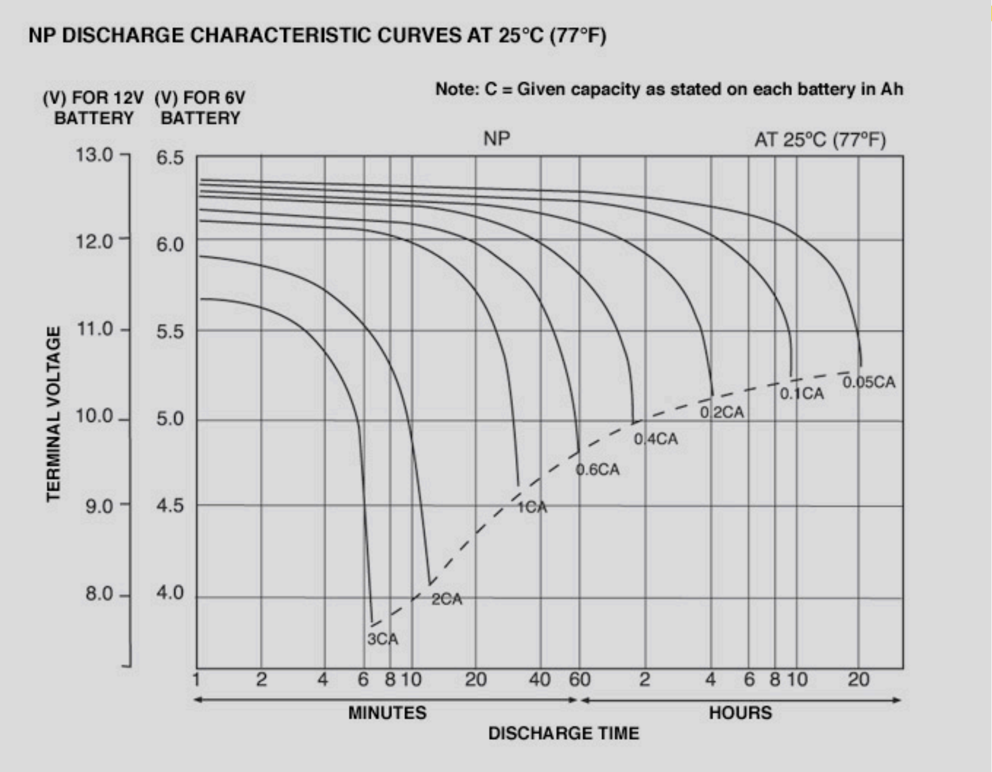
Self-Discharge

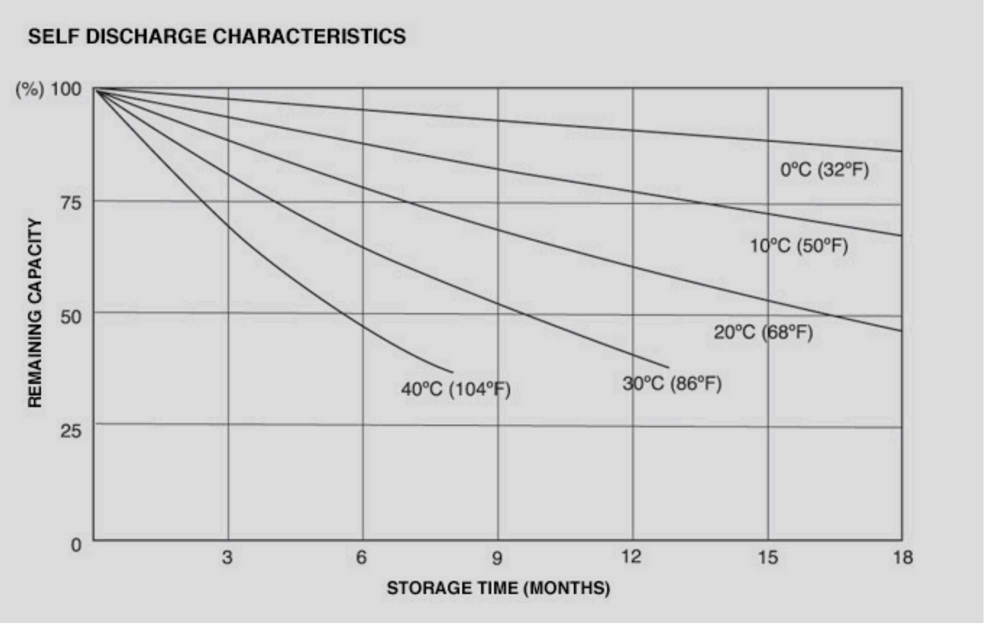


Self Discharge Characteristics

Concorde Sun Xtender Series

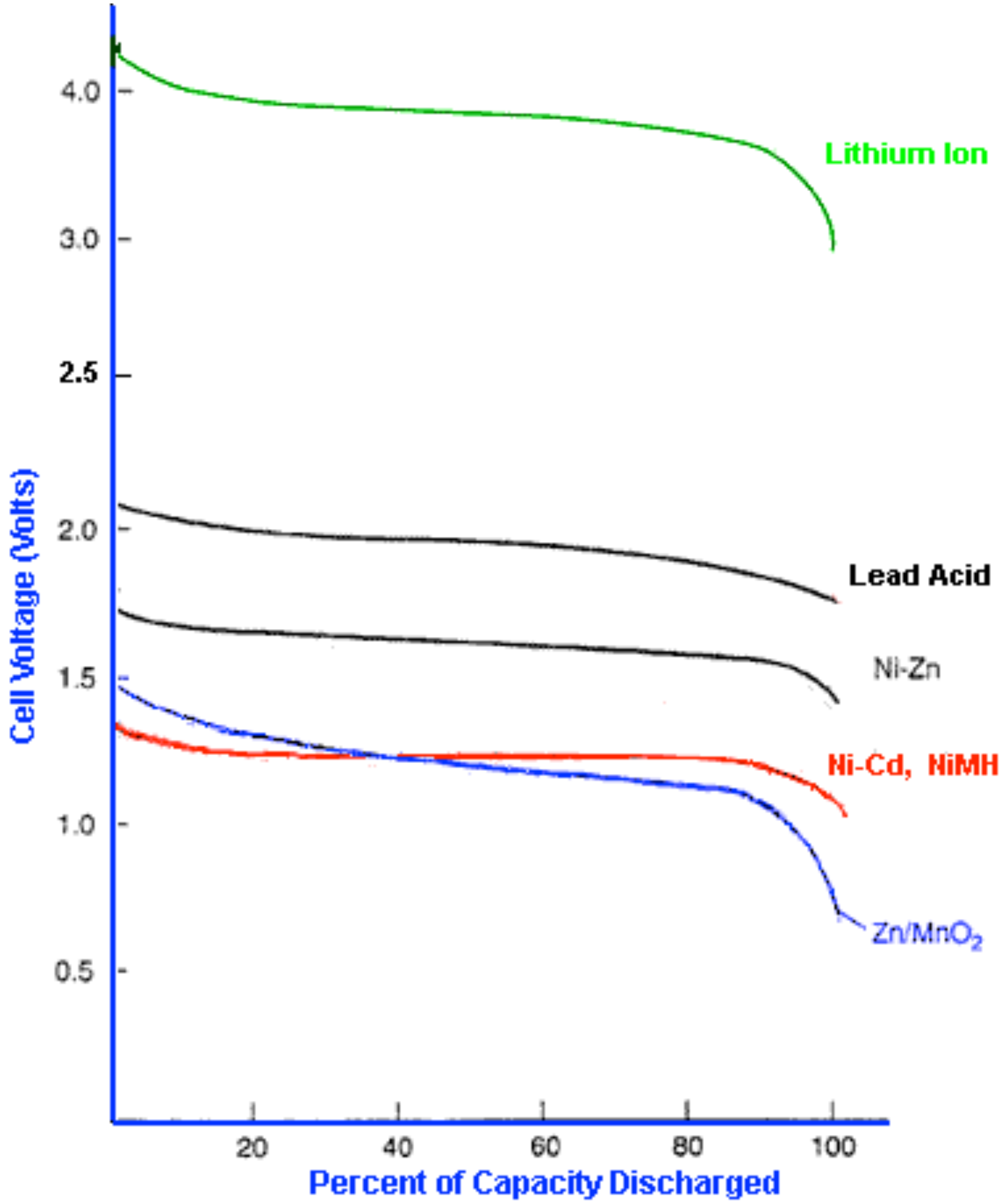
Example


NP DISCHARGE CHARACTERISTIC CURVES AT 25°C (77°F)


SELF DISCHARGE CHARACTERISTICS

Other Battery Types

Discharge Characteristics



Self-Discharge

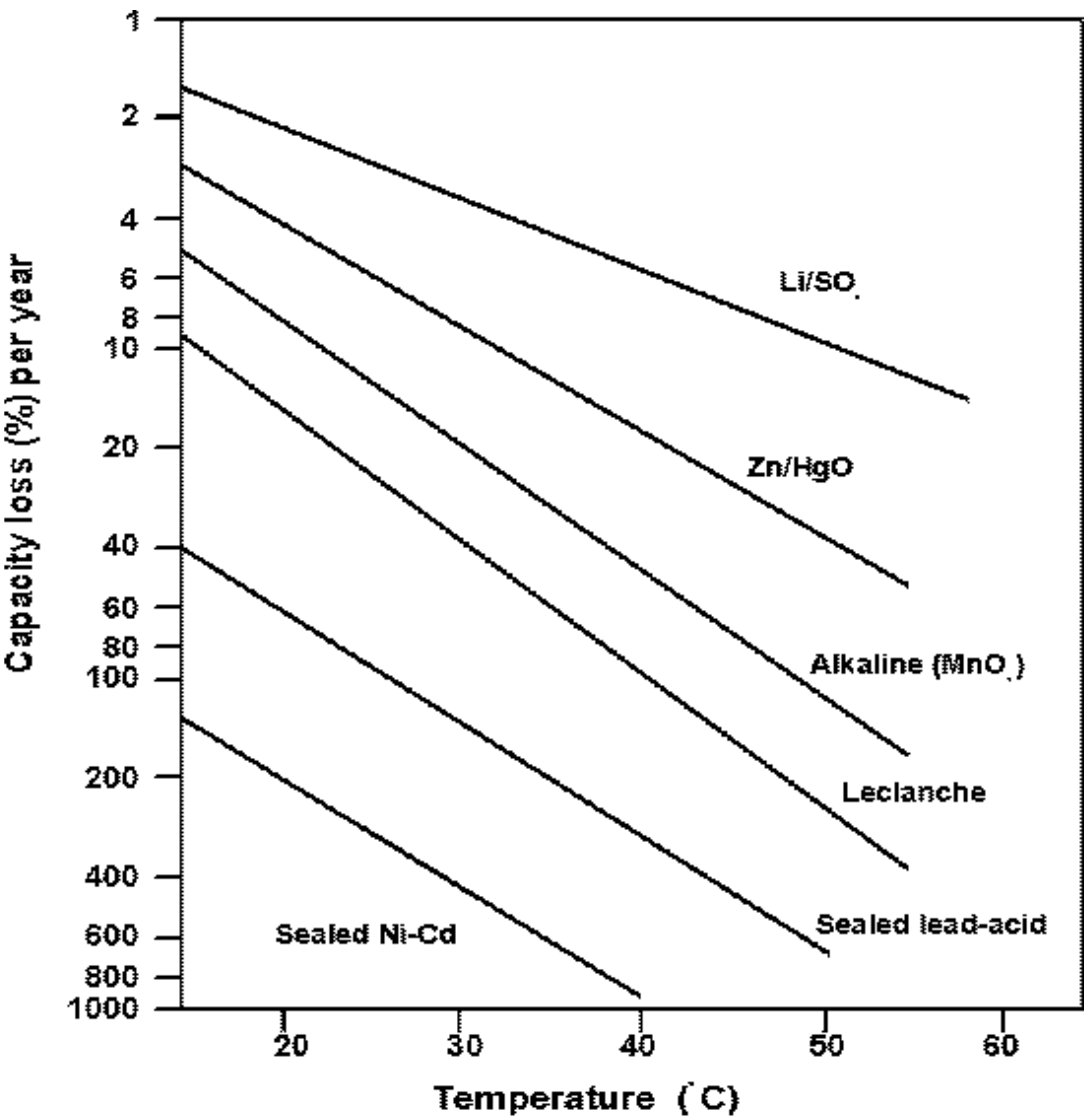
Self-discharge is the electrical capacity that is lost when the cell simply sits on the shelf. Self-discharge is caused by electrochemical processes within the cell and is equivalent to the application of a small external load.

Li-ion cells typically lose 8% of their capacity for the first month and then 2% for subsequent months. In many cases the rate of loss may decline after a time due, for instance, to the build-up of a passivation film on lithium anodes. In order to reduce self-discharge, it is recommended to store cells and batteries at lower temperatures.

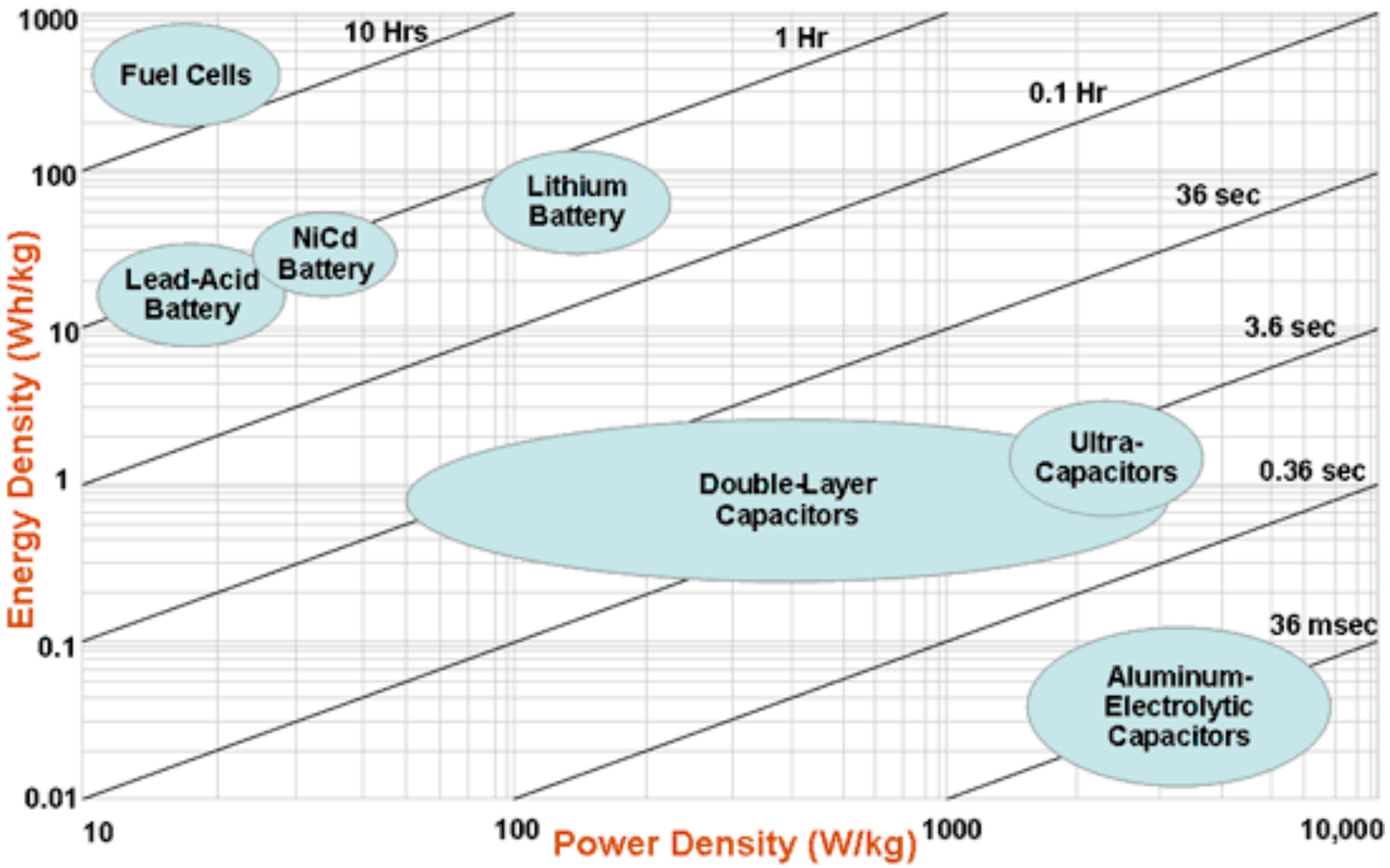
Typically Ni/Cd and Ni/MH cells suffer self-discharge rates as high as 25% per month. This presents the user with a major logistical problem since charging is normally always required before Ni/Cd batteries are used in the field.

Lead-acid and nickel-cadmium batteries lose their charge very quickly. For example, a lead-acid battery stored at 30°C would lose half its initial charge in about 3 or 4 months while, for nickel-cadmium, this would only take about 6 weeks. In normal use, this might present no real problem, as these types of battery can be recharged, but such batteries are clearly unsuitable for "fitting and forgetting".

Alkaline batteries hold their charge better than zinc-carbon unless they corrode badly, but lithium primary batteries have particularly good storage characteristics, due to the passivation layer that forms on the anode surface at open circuit. In most cases it is best to store batteries in a cool place and to warm them before use.



http://corrosion-doctors.org/Batteries/images/Fig29.gif



Source US Defence Logistics Agency

http://www.mpoweruk.com/images/ragone3.gif