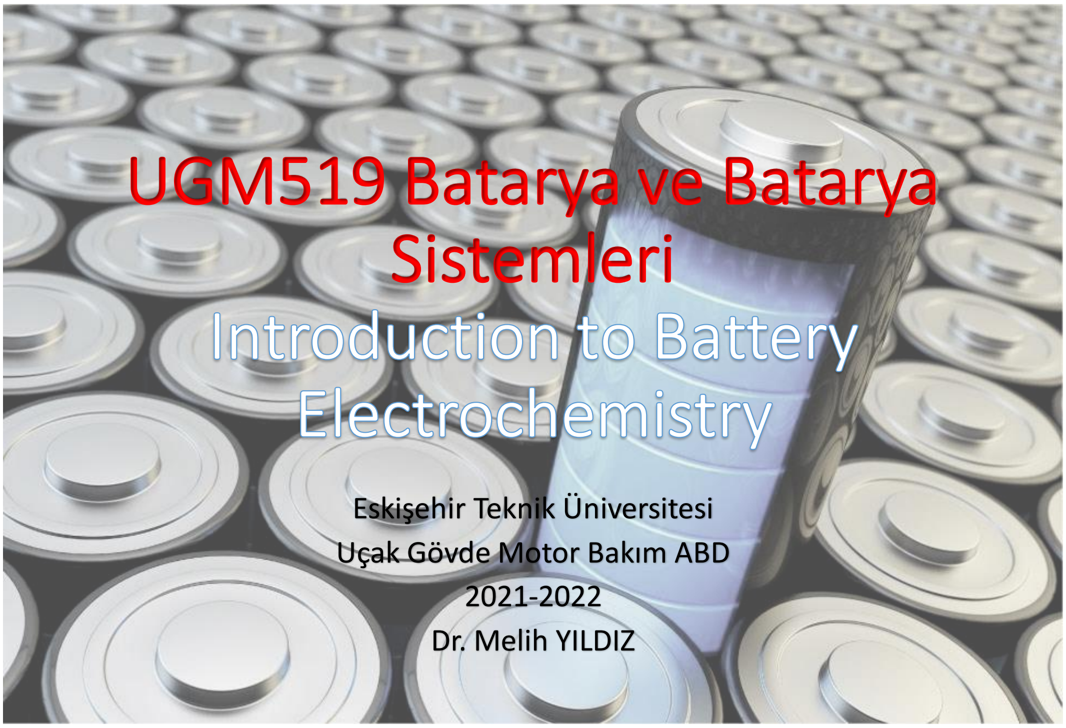

UGM519 Batarya ve Batarya Sistemleri

Introduction to Battery Electrochemistry

Eskişehir Teknik Üniversitesi
Uçak Gövde Motor Bakım ABD
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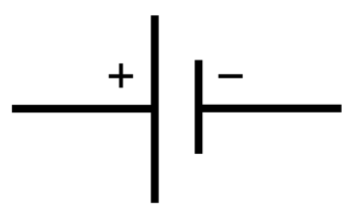
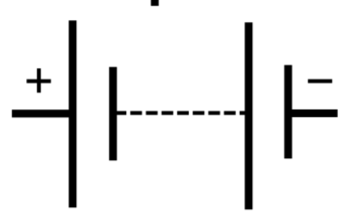
What is a battery?

- **Cell**: a combination of two electrodes arranged so that an overall oxidation-reduction reaction produces an electromotive force.



- **Battery**: a umber of connected electric cells that produce a direct current through the conversion of chemical energy into electrical energy.



Types of batteries

- Primary Battery/Cell
  - A cell which an irreversible chemical reaction generates electricity; a cell that can not be recharged.
    - Example: alkaline manganese cell
- Reserve Battery
  - A battery which is inert until an operation is performed which brings all the cell components into the proper state and location to become active.
    - Example: missile or life vest batteries
- Secondary Battery/Cell
  - A rechargeable electric cell that converts chemical energy into electrical energy by a reversible chemical reaction.
    - Example: lead-acid, lithium-ion

Batteries used in transportation

- Single use (primary):
  - Memory backup for telematics and infotainment
- Multiple use (rechargeable):
  - Power back-up
  - Motive traction
  - Load leveling

Common units of measure

- Voltage (Volts - V)
  - Voltage (electromotive force –E) is a measure of energy per unit charge
- Current – I (Amperes – A)
  - A measure of the transfer of electric charge (coulombs per second)
- Power (Watts – W)
  - A function of both current and voltage: P (W) = E (V) x I (A)
- Capacity – C (Ampere-hours – Ah)
  - A measure of total electrical charge (equivalent to coulombs)
- Energy (Watt-hours – Wh)
  - A function of both capacity and voltage: E (Wh) = E (V) x C (Ah)

- State of Charge (SoC - %)
  - The fraction, usually expressed as a percentage, of the total electrical energy stored in a battery by charging **that is still available** for discharging at a certain point of time.
- Depth of Discharge (DoD - %)
  - The fraction, usually expressed as a percentage, of the total electrical energy stored in a battery **that was recovered by** discharging at a certain time.
  - **SoC and DoD, while often used interchangeably, are rarely the same values**.
    - The SoC is how much gas in the tank, while DoD is how much gas has been removed.
      - There may be some unusable fuel left over!

Common figures of merit

- Energy Density (Wh/l)
  - A measure of battery energy, as a function of battery volume
- Specific Energy (Wh/kg)
  - A measure of battery energy, as a function of battery mass
- Power Density (W/l)
  - A function of battery power, as a function of volume
- Specific Power (W/kg)
  - A measure of battery power, as a function of mass

Electrochemistry

- Comparison of energies: what do I need to travel 1 mile in a vehicle?
  - 80 kg CNG
  - 96g gasoline
  - 200g chocolate
  - 1600 g of a lithium-ion cell
  - 6900 g of a lead-acid cell
  - 20 g of lithium metal

These utilize thermal process (80 kg CNG, 96g gasoline, 200g chocolate)

These utilize electrochemical process (1600 g of a lithium-ion cell, 6900 g of a lead-acid cell, 20 g of lithium metal)

- Liquid and solid fuels remain considerably more dense than those used in electrochemical reactions
- A battery is an active energy source, requiring conversion of its electrochemical potential energy into other form (mechanical, thermal, etc) in order to be removed from the device
- A liquid fuel is a passive energy source, which can be removed or transferred without conversion.

Voltage and Potential Energy

- Chemical and electrochemical energy are forms of potential energy.
- Chemical energy is normally released through heat of reaction.
- Electrochemical energy is released through the exchange of electrons, and resulting in Joule heating.
- Voltage (Electromotive Force) is a measure of energy per unit charge.
- Every electrochemical reaction has a standard potential:

$$\Delta G^{\circ}=-nFE^{\circ}$$

- F=Faraday constant (=96,500 Coulombs, or 26,.5 Ah)
- n= number of electrons involved in reaction
- E°=standard potential (volts)

Reduction and Oxidation

- **Reduction**:
  - A chemical reaction in which an atom or ion gains electrons, thus undergoing a decrease in valence.
    - The lead-acid battery positive electrode (**cathode**):

$$PbO_{2(s)} + 4H^{+}_{(aq)} + SO_4^{2-}{}_{(aq)} + 2e^{-} \rightarrow PbSO_{4(s)} + 2H_2O_{(L)}$$

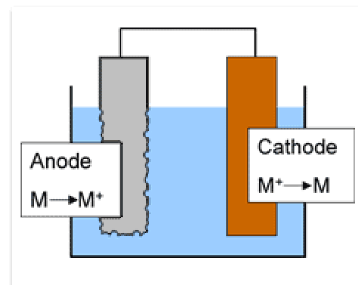
- **Oxidation**:
  - A chemical reaction in which a material gives up electrons, as when the material combines with oxygen.
    - The lead-acid battery negative electrode (**anode**):

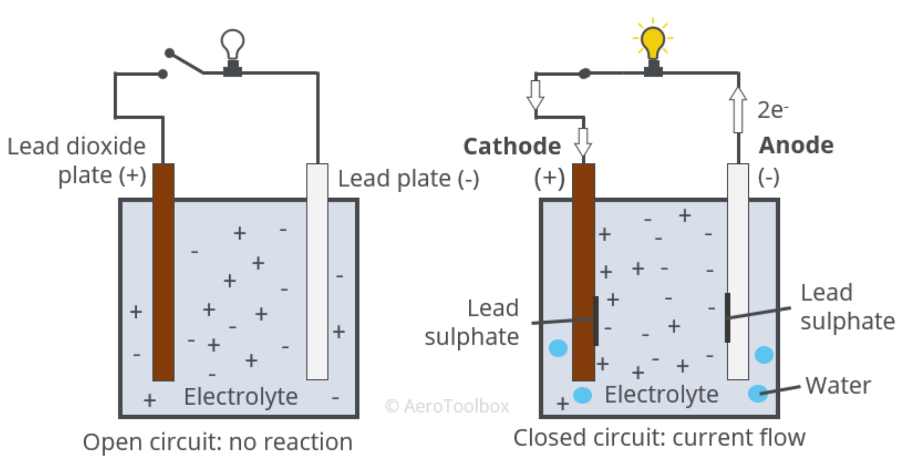
$$Pb_{(s)} + SO_4^{2-}{}_{(aq)} \rightarrow PbSO_{4(s)} + 2e^{-}$$

- A chemical or electrochemical reaction that combines a reduction and oxidation reaction is called a **Redox Reaction**.

The Single electrode reaction

- Reduction (cathode)
  - Electrons are received, allowing material to deposit from electrolyte solution
- Oxidation (anode)
  - Material dissolves into electrolyte solution, and electrons are liberated.
- The application of a potential (voltage) can accelerate or reverse the process.





Reduction potentials and electrochemical couples

- A list of example reduction reactions are given
- These reduction reactions are known as **half-cell reactions**.
- Since these are reduction reactions, all are shown as accepting electrons.
- Each reaction requires a potential (relative to hydrogen) in order to proceed
- A complete cell can be prepared by matching two reactions with differing potentials. This is known as an **electrochemical couple**.

Standard Reduction Potentials at 298K, 1M, 1atm

strong oxidizing agents ↑

HALF-REACTION	$E°$ (V)
$F_{2(g)} + 2e^- \rightarrow 2F^-_{(aq)}$	+2.87
$O_{3(g)} + 2H^+_{(aq)} + 2e^- \rightarrow O_{2(g)} + H_2O_{(l)}$	+2.07
$Co^{3+}_{(aq)} + e^- \rightarrow Co^{2+}_{(aq)}$	+1.82
$H_2O_{2(aq)} + 2H^+_{(aq)} + 2e^- \rightarrow 2H_2O_{(l)}$	+1.77
$PbO_{2(s)} + 4H^+_{(aq)} + SO_4^{2-}{}_{(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(l)}$	+1.70
$Ce^{4+}_{(aq)} + e^- \rightarrow Ce^{3+}_{(aq)}$	+1.61
$MnO_4^-{}_{(aq)} + 8H^+_{(aq)} + 5e^- \rightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)}$	+1.51
$Au^{3+}_{(aq)} + 3e^- \rightarrow Au_{(s)}$	+1.50
$Cl_{2(g)} + 2e^- \rightarrow 2Cl^-_{(aq)}$	+1.36
$Cr_2O_7^{2-}{}_{(aq)} + 14H^+_{(aq)} + 6e^- \rightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$	+1.33
$MnO_{2(s)} + 4H^+_{(aq)} + 2e^- \rightarrow Mn^{2+}_{(aq)} + 2H_2O_{(l)}$	+1.23
$O_{2(g)} + 4H^+_{(aq)} + 4e^- \rightarrow 2H_2O_{(l)}$	+1.23
$Br_{2(l)} + 2e^- \rightarrow 2Br^-_{(aq)}$	+1.07
$NO_3^-{}_{(aq)} + 4H+_{(aq)} + 3e^- \rightarrow NO_{(g)} + 2H_2O_{(l)}$	+0.96
$2Hg^{2+}_{(aq)} + 2e^- \rightarrow Hg_2^{2+}{}_{(aq)}$	+0.92
$Hg_2^{2+} + 2e^- \rightarrow 2Hg_{(l)}$	+0.85
$Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$	+0.80
$Fe^{3+}_{(aq)} + e^- \rightarrow Fe^{2+}_{(aq)}$	+0.77
$O_{2(g)} + 2H^+_{(aq)}\ 2e^- \rightarrow H_2O_{2(aq)}$	+0.68
$MnO_4^-{}_{(aq)} + 2H_2O_{(l)} + 3e^- \rightarrow MnO_{2(s)} + 4OH^-_{(aq)}$	+0.59
$I_{2(s)} + 2e^- \rightarrow 2I^-_{(aq)}$	+0.53
$O_{2(g)} + 2H_2O + 4e^- \rightarrow 4OH^-_{(aq)}$	+0.40
$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$	+0.34
$AgCl_{(s)} + e^- \rightarrow Ag_{(s)} + Cl^-_{(aq)}$	+0.22
$SO_4^{2-}{}_{(aq)} + 4H^+_{(aq)} + 2e^- \rightarrow SO_{2(g)} + 2H_2O_{(l)}$	+0.20
$Cu^{2+}_{(aq)} + e^- \rightarrow Cu^+_{(aq)}$	+0.15
$Sn^{4+}_{(aq)} + 2e^- \rightarrow Sn^{2+}_{(aq)}$	+0.13
$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$	0.00
$Pb^{2+}_{(aq)} + 2e^- \rightarrow Pb_{(s)}$	-0.13
$Sn^{2+}_{(aq)} + 2e^- \rightarrow Sn_{(s)}$	-0.14
$Ni^{2+}_{(aq)} + 2e^- \rightarrow Ni_{(s)}$	-0.25
$Co^{2+}_{(aq)} + 2e^- \rightarrow Co_{(s)}$	-0.28
$PbSO_{4(s)} + 2e^- \rightarrow Pb_{(s)} + SO_4^{2-}{}_{(aq)}$	-0.31
$Cd^{2+}_{(aq)} + 2e^- \rightarrow Cd_{(s)}$	-0.40
$Fe^{2+}_{(aq)} + 2e^- \rightarrow Fe_{(s)}$	-0.44
$Cr^{3+}_{(aq)} + 3e^- \rightarrow Cr_{(s)}$	-0.74
$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$	-0.76
$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$	-0.83
$Mn^{2+}_{(aq)} + 2e^- \rightarrow Mn_{(s)}$	-1.18
$Al^{3+}_{(aq)} + 3e^- \rightarrow Al_{(s)}$	-1.66
$Be^{2+}_{(aq)} + 2e^- \rightarrow Be_{(s)}$	-1.85
$Mg^{2+}_{(aq)} + 2e^- \rightarrow Mg_{(s)}$	-2.37
$Na^+_{(aq)} + e^- \rightarrow Na_{(s)}$	-2.71
$Ca^{2+}_{(aq)} + 2e^- \rightarrow Ca_{(s)}$	-2.87
$Sr^{2+}_{(aq)} + 2e^- \rightarrow Sr_{(s)}$	-2.89
$Ba^{2+}_{(aq)} + 2e^- \rightarrow Ba_{(s)}$	-2.90
$K^+_{(aq)} + e^- \rightarrow K_{(s)}$	-2.93
$Li^+_{(aq)} + e^- \rightarrow Li_{(s)}$	-3.05

strong reducing agents ↓

Electrochemical cell – putting it all together

- An electrochemical cell uses an electrochemical couple to produce a voltage, and uses that voltage to drive a redox reaction, thereby delivering power.
- The cell voltage for the lead acid example is as follows:

Cell Reaction Of Lead Acid Battery

❖**Discharging**

(+) electrode: $PbO_{2(s)} + 4H^+_{(aq)} + SO_4^{2-}_{(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(L)}$ E˚=1.70 V

(−) electrode: $Pb_{(s)} + SO_4^{2-}_{(aq)} \rightarrow PbSO_{4(s)} + 2e^-$ E˚=-(-0.31) V

E˚= 2.01 V

❖**Charging**

(+) electrode: $PbSO_{4(s)} + 2H_2O_{(L)} \rightarrow PbO_{2(s)} + 4H^+_{(aq)} + SO_4^{2-}_{(aq)} + 2e^-$

(+) electrode: $PbSO_{4(s)} + 2e^- \rightarrow Pb_{(s)} + SO_4^{2-}_{(aq)}$

Specific Capacity

- A material's performance is measured by its specific capacity.
- Specific capacity is the measure of amount of electric charge per unit mass.
- C_s= (N x F)/m
  - N= valence of reaction
  - F = Faraday constant
  - m=Atomic weight

	Atomic No	Atomic weight	Valence	Specific capacity (mAh/g)
H/H(+)	1	1.0	1	26588
Li/Li(+)	3	6.9	1	3861
Na/Na(+)	11	23.0	1	1166
Mg/Mg(2+)	12	24.3	2	2205
Al/Al(3+)	13	27.0	3	2980
K/K(+)	19	39.1	1	685
Ca/Ca(2+)	20	40.1	2	1337
Zn/Zn(2+)	30	65.4	2	820
Pb/Pb(2+)	82	207.2	2	259

Fuel cells

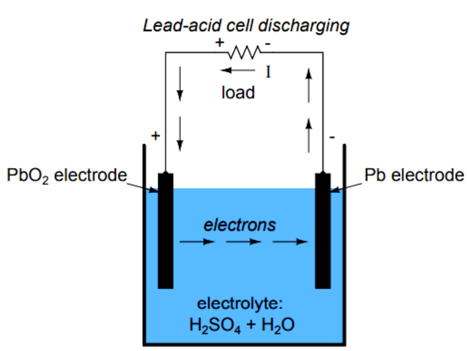
+3 interesting

Major battery elements

- The primary elements of a cell are the Anode, cathode, separator, current collectors, electrolyte, and enclosure hardware.
  - The anode (negative electrode) is the source of the oxidation reaction (during discharge)
  - The cathode (positive electrode) is the source of the reduction reaction (during discharge)
    - Both electrodes contain the active materials for the electrochemical reaction
  - The separator is an insulating divider, which physically seperates the electrodes (to prevent electrical shorting), and facilitates ion flow fromone electrode to the other

- The current collectors reside within each electrode, acting as a physical support for the electrode materials, and conduct electrons to and from the active materials, within the external electrical circuit.
- The electrolyte provides the ions necessary to support the electrochemical reaction
- The enclosure hardware contains the electrodes, separator, current collectors and electrolyte, and both protects all components from the external environment, and users from the internal componets, and isolates cells.

An example of the lead-acid cell



At (+) electrode: $Pb(IV)O_2 + 3H^+ + HSO_4^- + 2e^- \rightarrow Pb(II)SO_4 + 2H_2O$

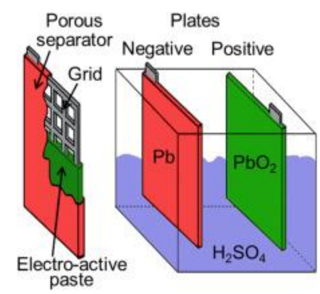
At (-) electrode: $Pb + HSO_4^- \rightarrow Pb(II)SO_4 + H^+ + 2e^-$

Overall cell: $PbO_2 + Pb + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$

The reactions shown are for discharge. Charging reverses these reactions.

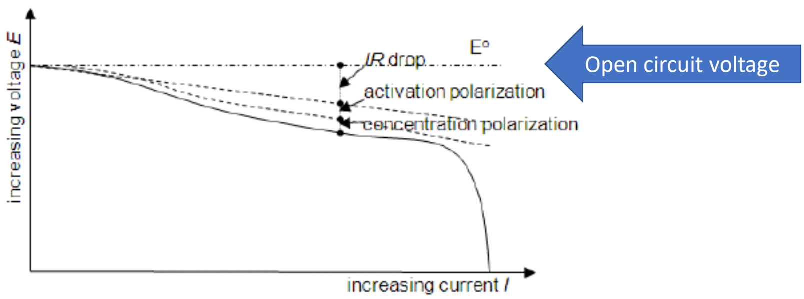
Electrode design

- An electrode is typically a porous structure, created by the compounding of powders, comprised by the active media, a conductive media (typically a carbon), and a binder.
- The electrode is formed onto a current collector, often a metallic substrate.
- Key design parameters include porosity, electrode thickness, and sheet resistance.
  - Higher energy but lower power from reduced porosity and increased thickness.

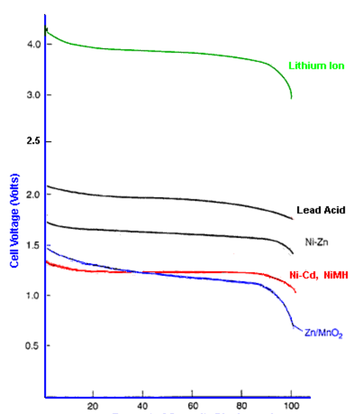


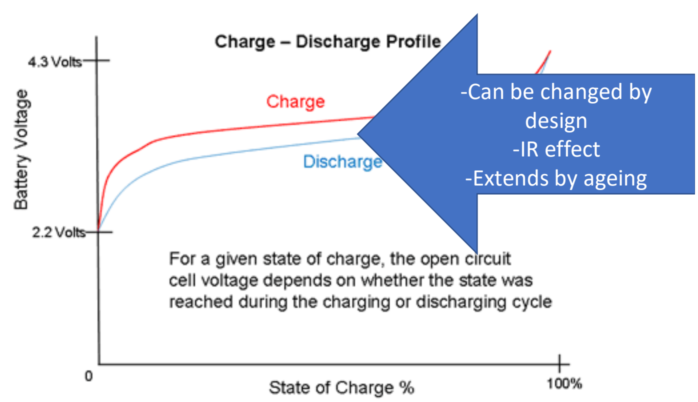
Resistance and polarization

- Cell voltage is rarely identical. An electrochemical cell will have a defined internal resistance, dependent upon the rate that charge is removed or provided (the electric current)
- IR Polarization (ohmic loss)
  - The internal resistance of the cell, determined by the electrical conductivity of the discrete components.
- Activation Polarization
  - Over-voltage at electrodes, required to initiate the transfer of electric charge.
- Concentration Polarization
  - Resistance as a function of the diffusion rate of the active species at the electrode surface.

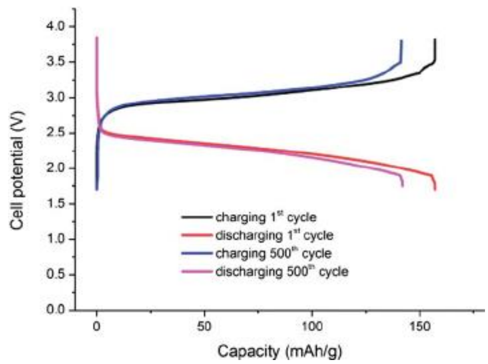


Charging and Discharging

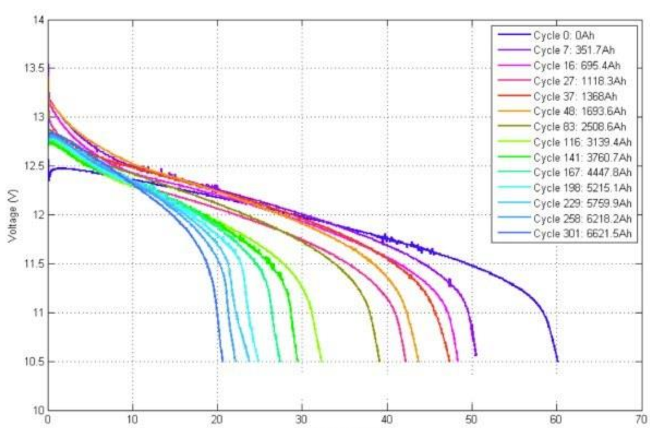




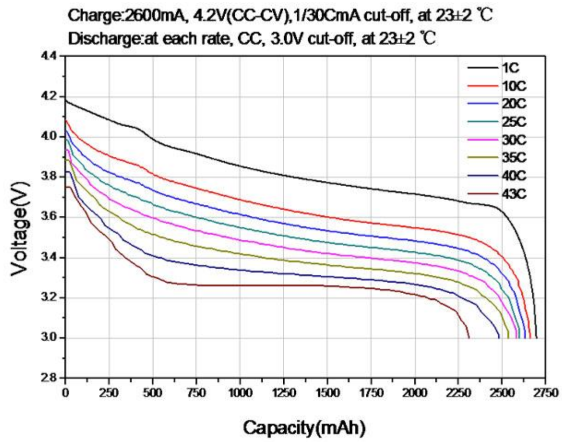
- Cell voltage will vary between its upper and lower voltage limits, as a function of chemistry, state-of-charge, and rate.

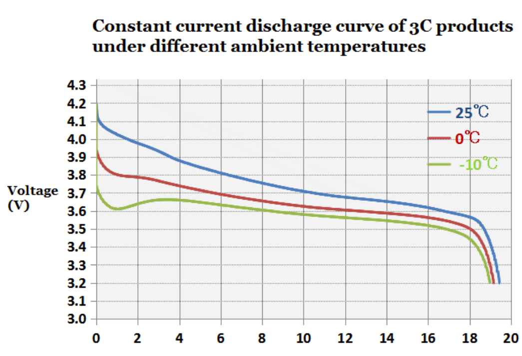


Cell potential (V)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
50
100
150
Capacity (mAh/g)
charging 1st cycle
discharging 1st cycle
charging 500th cycle
discharging 500th cycle



Voltage (V)
14
13.5
13
12.5
12
11.5
11
10.5
10
0
10
20
30
40
50
60
70
Capacity (Ah)
Cycle 0: 0Ah
Cycle 7: 351.7Ah
Cycle 16: 695.4Ah
Cycle 27: 1118.3Ah
Cycle 37: 1368Ah
Cycle 48: 1693.6Ah
Cycle 83: 2508.6Ah
Cycle 116: 3139.4Ah
Cycle 141: 3760.7Ah
Cycle 167: 4447.8Ah
Cycle 198: 5215.1Ah
Cycle 229: 5759.9Ah
Cycle 258: 6218.2Ah
Cycle 301: 6621.5Ah


Charge:2600mA, 4.2V(CC-CV),1/30CmA cut-off, at 23±2 ℃
Discharge:at each rate, CC, 3.0V cut-off, at 23±2 ℃
Voltage(V)
Capacity(mAh)
1C
10C
20C
25C
30C
35C
40C
43C
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
0
250
500
750
1000
1250
1500
1750
2000
2250
2500
2750


Constant current discharge curve of 3C products under different ambient temperatures
Voltage (V)
Discharge period (mins)
25℃
0℃
-10℃
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
3.0
0
2
4
6
8
10
12
14
16
18
20

Ders içeriği

Konular
Giriş
Enerji depolama metodları
Batarya elektrokimyalarına giriş
Kurşun asit bataryalar
Lithium ion bataryalar
Süper kapasitörler
Nikel Metal Hydrid bataryalar
Batarya sistem entegrasyonu
Otomotiv batarya uygulamaları
Şebekeye bağlı enerji depolama sistemleri ve uygulamaları
Havacılık uygulamaları
Bataryaların modelleme ve simülasyonu
Gelecek elektrik enerjisi depolama uygulamaları

Ders içeriği -2

Konular
Enerji depolama sistemleri araştırmaları
Bataryaların ölçümü, tahmini ve korunması
Şarj üniteleri
Batarya geri dönüşümü
Batarya standartları ve testleri
Süper kapasitörler

- **Sorular ??**