# Introduction of Lithium Ion Rechargeable Battery

September 2011

**EVB Technology (HK) Limited**

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# DEFINITION OF TERMS

# Definition

**Nominal Voltage** = 3.2V (LFP)

**Ri**: Internal impedance

**ACRi** – conductivity test, measure the electrochemical characteristic of a battery

**DCRi** – internal battery resistance, measure the voltage drop

# Definition

- **Capacity:** Amount of electrical energy that can be given out by cell, unit: Ah
- **C-rate:** Relative rate used in cell, i.e. current (A) / nominal capacity (Ah)
- **Self-discharge:** Loss of capacity by cell during storage
- **Cycle Life:** No. of cycle a cell can run while still delivering the min. capacity

# Relation of V, I, R, P

$$V = I \times R$$

P (Power) = I x V

Unit: W

E (Energy) = V x Ah

Unit: Wh

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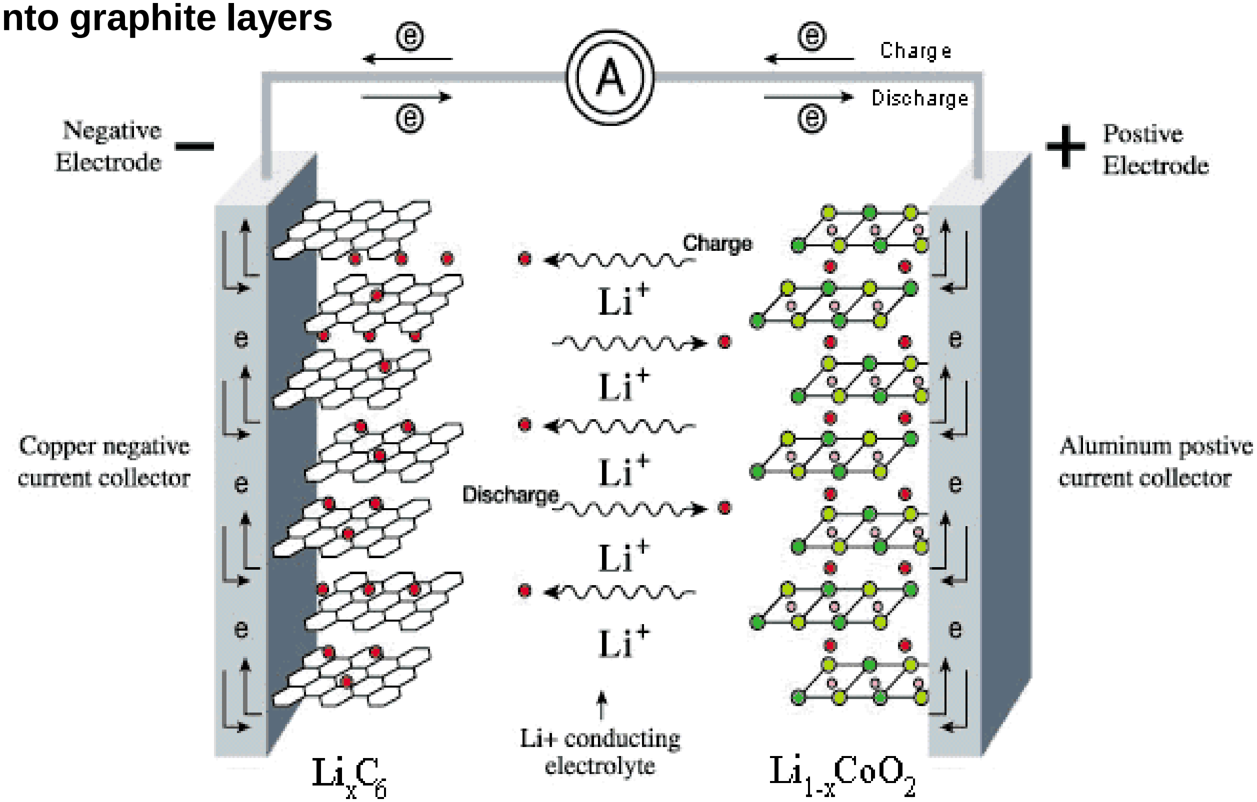
# CHEMISTRY

# Lithium Ion Batteries

- **Standard Lithium Ion Batteries**
- Electrodes: Graphite Anode and LiMOx Lithium-Metalloxide Cathode
- Electrolyte: organic solvent with Lithium salt (eg. LiPF6)
- Separator: microporous PolyEthylene, PolyPropylene
- **Battery charging**: **Removal of Li+ from the Metal-oxide and intercalation into graphite layers**



# Lithium Ion Batteries

- **Lithium Ion Cell is a thermodynamically instable system**
- **In charged state the lithiated graphite reacts with electrolyte under formation of an solid-electrolyte-interface SEI. Only the SEI enables the cell functionality: permeable for lithium ions but not for electrons (ideally)**
- **In charged state, because of un-occupied lattice sites, the de-lithiated metal oxide is instable towards structural disordering, dissolving in the electrolyte and oxygen release**

# Failing Mechanism - Anode

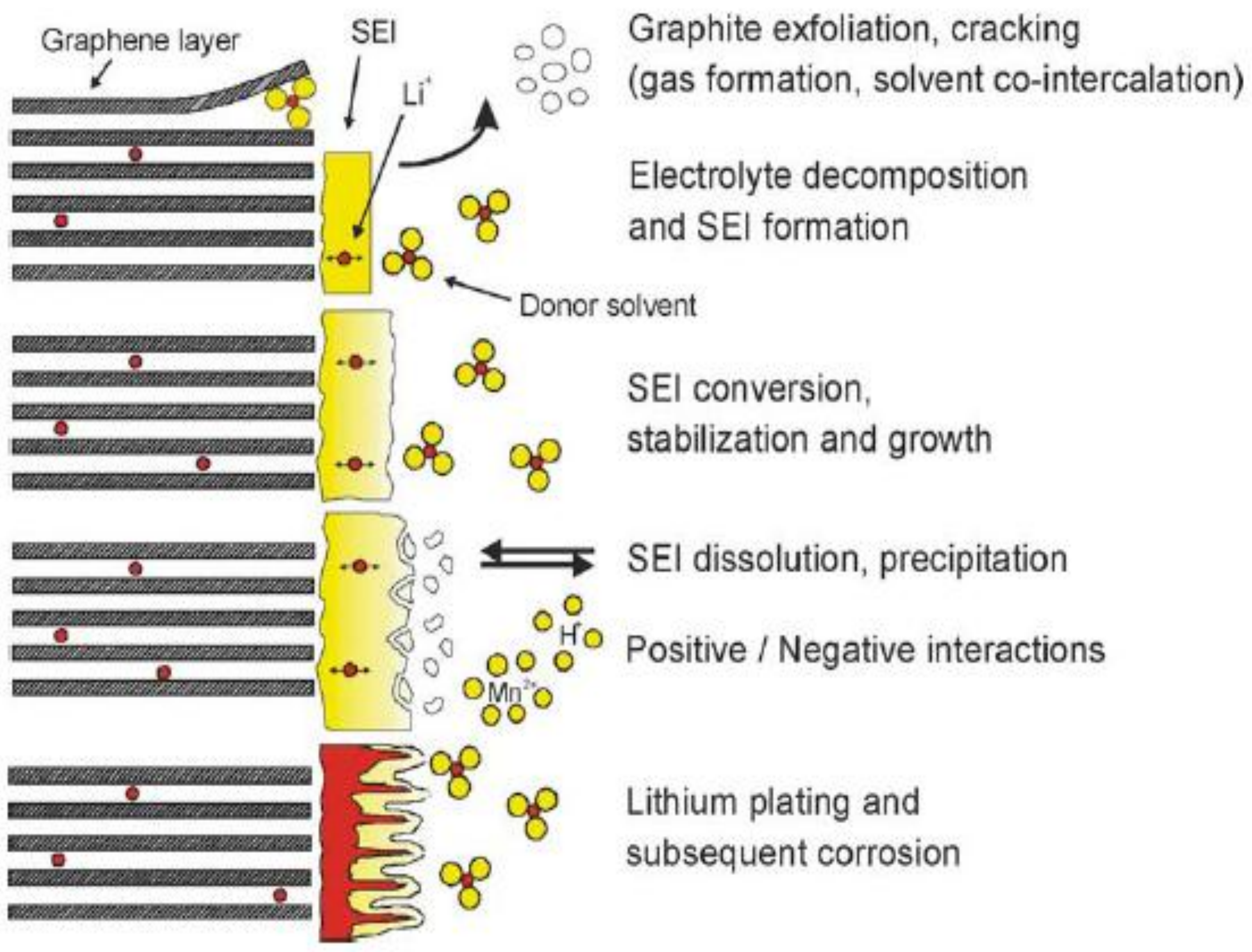



Fig. 1. Changes at the anode/electrolyte interface.

# Failing Mechanism - Cathode

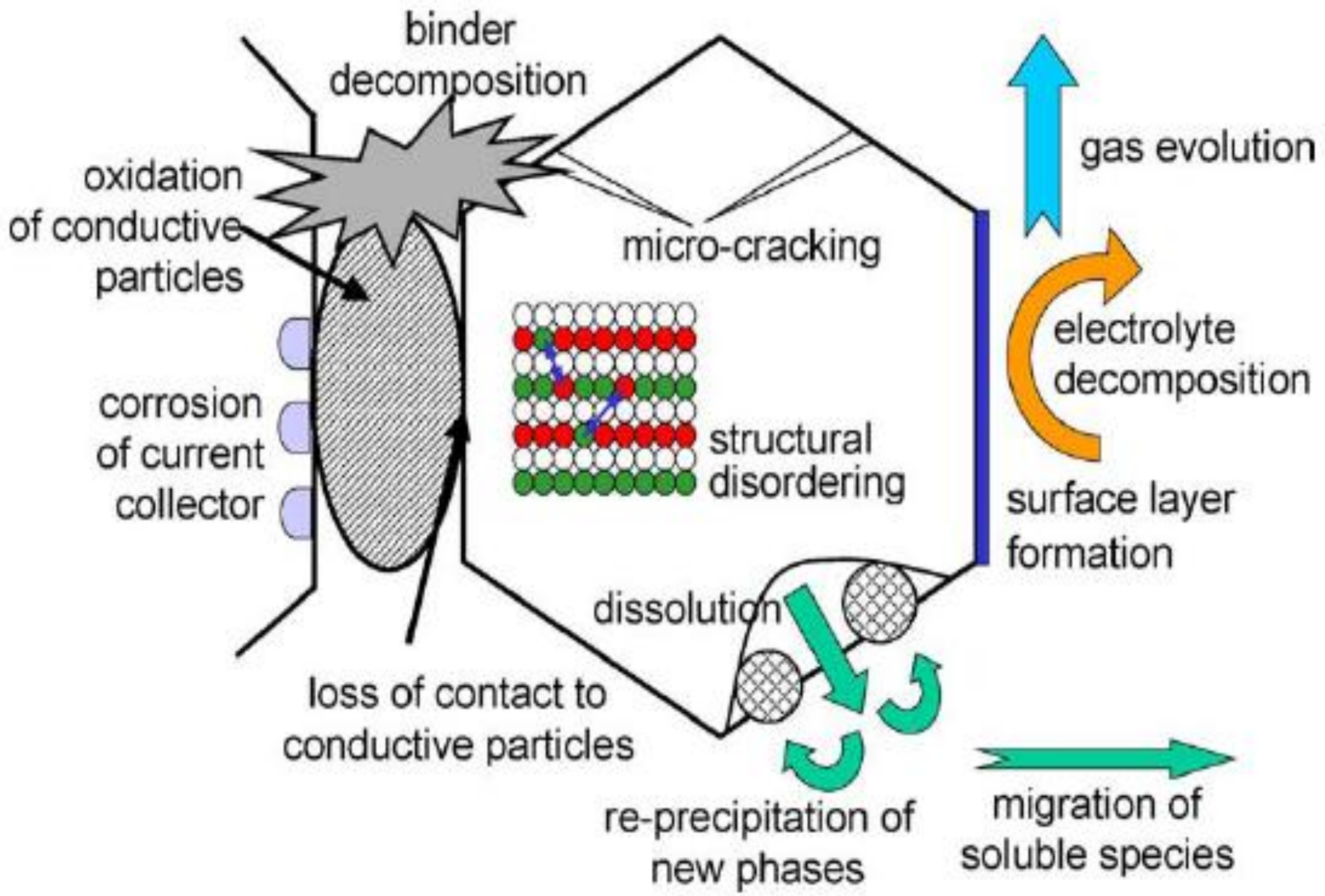



Fig. 2. Overview on basic ageing mechanisms of cathode materials.

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# BATTERY COMPONENTS

# Main Components

**Chemical**

- Positive Electrode
- Negative Electrode
- Separator
- Electrolyte

**Mechanical**

- Casing
- LID
- Connection joint and etc,

# Positive

**Substrate for +ve electrode**

- Aluminum Foil

# Positive

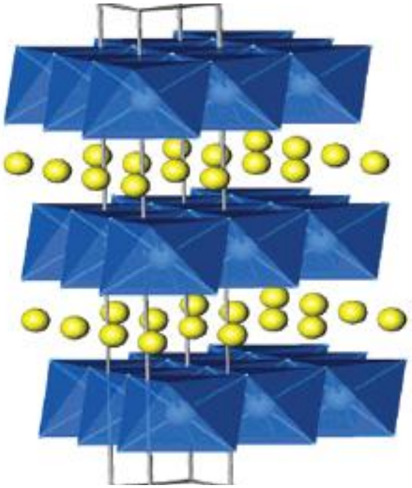
- **Cathode:**
  - **LiCoO2 (LCO):** capacity 140 -170 mAh/g, high cost Co, instability towards overcharge, toxic, main cathode for consumer batteries (China, Japan Korea)
  - **LiNi0.8Co0.15Al0.05O2 (NCA**): capacity 180 -200 mAh/g, Ni has been cheaper than Co, structure shows slightly higher stability due to Al, toxic, cathode for high end batteries (SAFT, GAIA, Toyota)
  - **LiNi0.33Co0.33Mn0.33O2 (333**): capacity 160 mAh/g, Mn cheaper than Ni, Co, structure shows slightly higher stability by Mn, toxic, cathode for high end batteries (ENAX, Hitachi, Panasonic, Sanyo)
  - **LiMn2O4** (Manganese Spinel): capacity 120 -125 mAh/g, some use, low cost Mn, non-toxic, higher stability towards thermal runaway, high power, Mn2+ dissolves auto-catalytically in electrolyte (GS Yuasa, LG Chem, NEC Lamilion, Samsung)
  - **LiFePO4** (phosphate): capacity 150 – 160 mAh/g, emerging, carbon coated to improve electronic conductivity, no thermal runaway, lower cell voltage/specific energy, inexpensive, non-toxic, cathode for high power application (A123, PiHsiang, Sanyo, SAFT)
  - **LiMnPO4** (phosphate): capacity 120-135 mAh/g, 20% more cell voltage than Fe, same properties as **LiFePO4** , possible cathode for low power application (HPL / Toyota)

# Characteristic of Cathode Material of Lithium Ion:

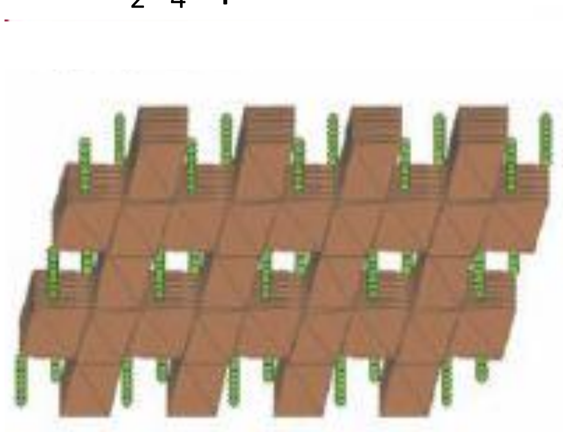
| | LiCoO2 | Li(NiMnCo)O2 | LiMn2O4 | LiFePO4 |
|---|---|---|---|---|
| Voltage (V) | 3.7 | 3.6 | 3.8 | 3.2 |
| Density(g/cm 3) | 5.1 | 4.4-4.6 | 4.3 | 3.5 |
| Specific capacity (Ah/kg) | 145 | 150-160 | 110 | 130-150 |
| Energy density (Wh/kg) | 537 | 540-576 | 418 | 416-480 |
| Cycle life (Score) | 8 | 9 | 6 | 10 |
| Safety (Score) | 7 | 9 | 10 | 10 |
| Price attractivenes s (Score) | 5 | 8 | 10 | 7 |

# Positive

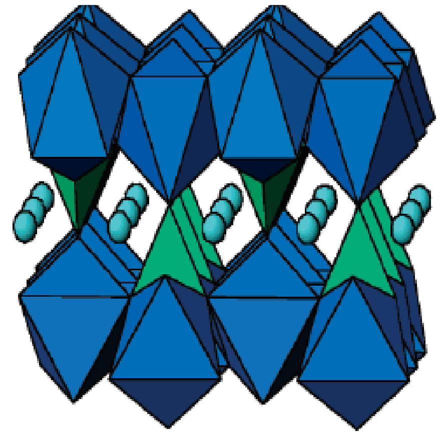
$LiCo0_2$ Layered structure



$LiMn_20_4$ Spinel structure



$LiFeP0_4$ Divine structure



**Cathode properties are structure related**

**Phosphates do not undergo structural disordering and oxygen release while de-lithiated**

$LiFePO_4$

Triphylite

„discharged“

$FePO_4$

Heterosite

„charged“

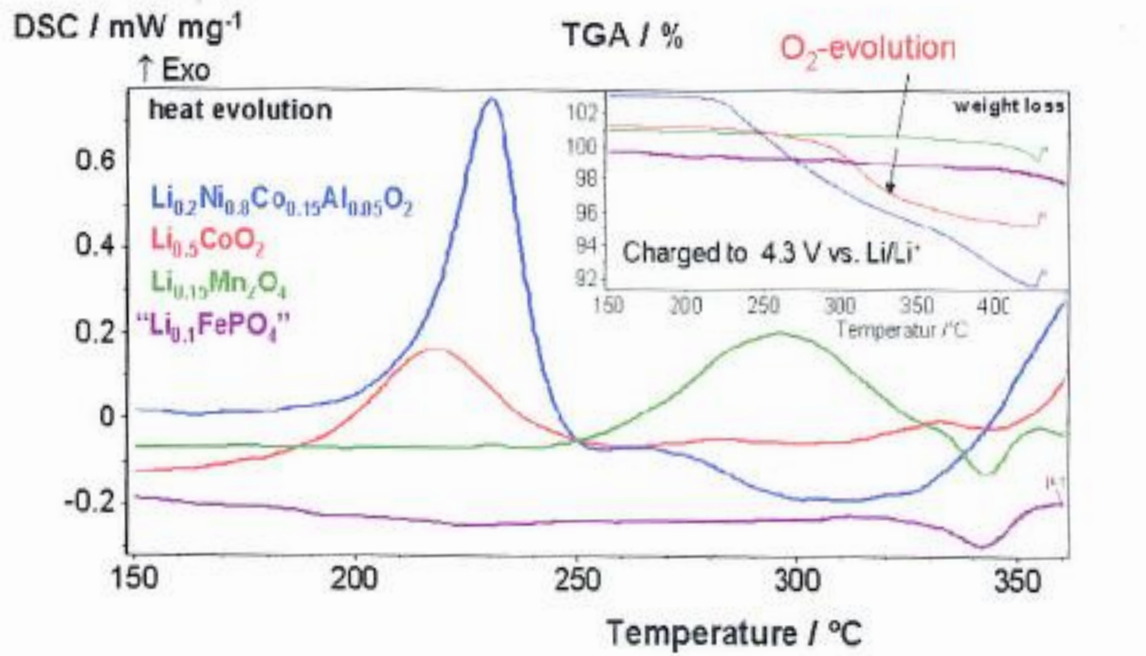
Li-Ion Battery

# Thermal Stability Reference

## Thermal Stability of Charged Cathode Materials*

Differential Scanning Calorimetry (DSC) and Thermal Gravimetry Analysis (TGA):

Heat development and oxygen loss during gradual temperature increase




*Courtesy of M. Wohlfahrt-Mehrens (ZSW)

# Negative

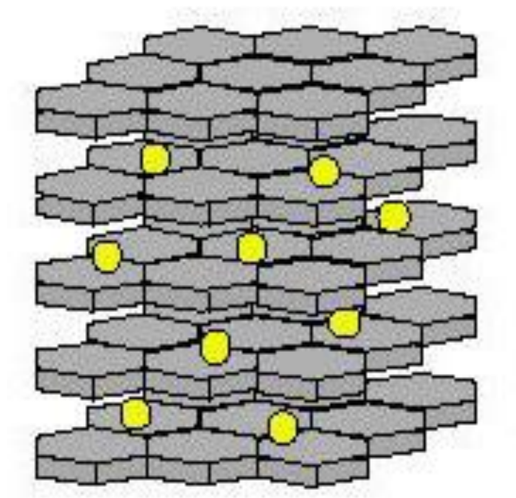
**Substrate for -ve electrode**

- Copper Foil

# Negative

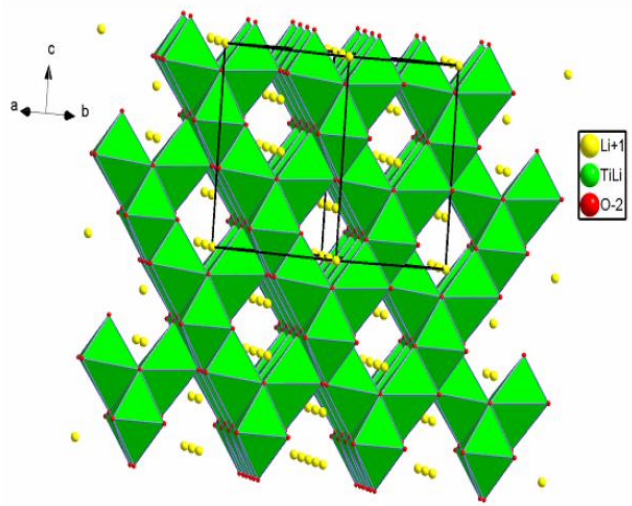
- **Anode:**
  - **$LiC_6$**: capacity 300 – 370 Ah/kg, pure graphite used for production, high cell voltage, potential close to $Li/Li^+$ enables risk of lithium plating, low temperature charging causes lithium plating on graphite (-20°C), SEI breakdown at T > 80°C followed by thermal runaway, volume change by lithium intercalation during cycling, main anode for lithium ion batteries
  - **$Li_4Ti_5O_{12}$** capacity 167 Ah/kg, potential distant from $Li/Li^+$, no risk of lithium plating, no reductive interactions with electrolyte, no SEI formation and decay, stable crystal lattice in lithiated state, zero strain material, no thermal runaway, lower cell voltage/specific energy, cold cranking capable anode for high power and long life batteries (Altairnano, EnerDel, leclanche)

# Structural Comparison



The anode half reaction

$$x\mathrm{Li}^+ + x\mathrm{e}^- + 6\mathrm{C} \leftrightarrows \mathrm{Li_xC_6}$$




- $Li[Li_{1/3}Ti_{5/3}]O_4$
- defect spinel structure
- „zero-strain“ material

$$\mathrm{Li_4Ti_5O_{12}} + 6\,\mathrm{LiCoO_2} \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftarrows}} \mathrm{Li_7Ti_5O_{12}} + 6\,\mathrm{Li_{0,5}CoO_2}$$

**Graphite anode functionality is entangled with ageing and safety issues**

**Titanate anode does not show such ageing and safety phenomena**

GPB

# Electrolyte

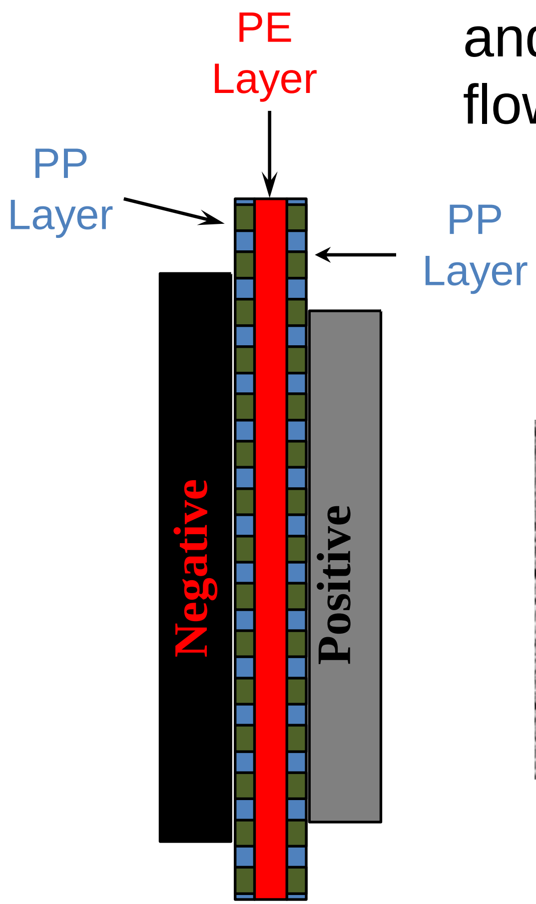
- Propylencarbonate (PC), Ethylencarbonate (EC), Dimethylcarbonate (DMC), Diethylcarbonate (DEC) mixtures to ensure high dielectric constant and low viscosity; with dissolved LiPF6 ( some use of LiBF4, LiClO4) as lithium salts; safety issues due to low flame point and low boiling point (91 -126°C ), toxic, electrolyte decomposition at cell voltage, stabilised by proprietary additives, moisture causes HF formation with fluorides, HF dissolves cathode material (Mn, Fe)

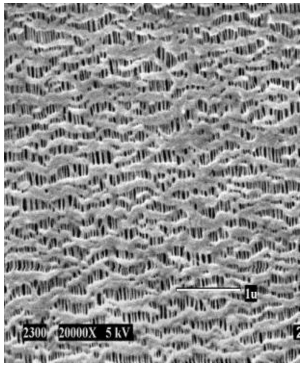
**HF evolution in electrolyte:**

$$LiPF_6 + 4H_2O \rightarrow 5HF + LiF + H_3PO_4$$

# Separator

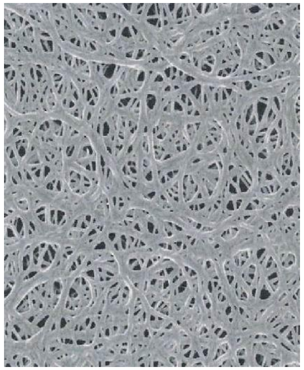
- If temperature is over 135 to 140 ºC,
- PE layer melt down, close the pore and stops Ion, respectively, current flow.




Tri-Layer Separator PP/PE/PP

*Thickness Below 25 µm Change to*



PE Separator

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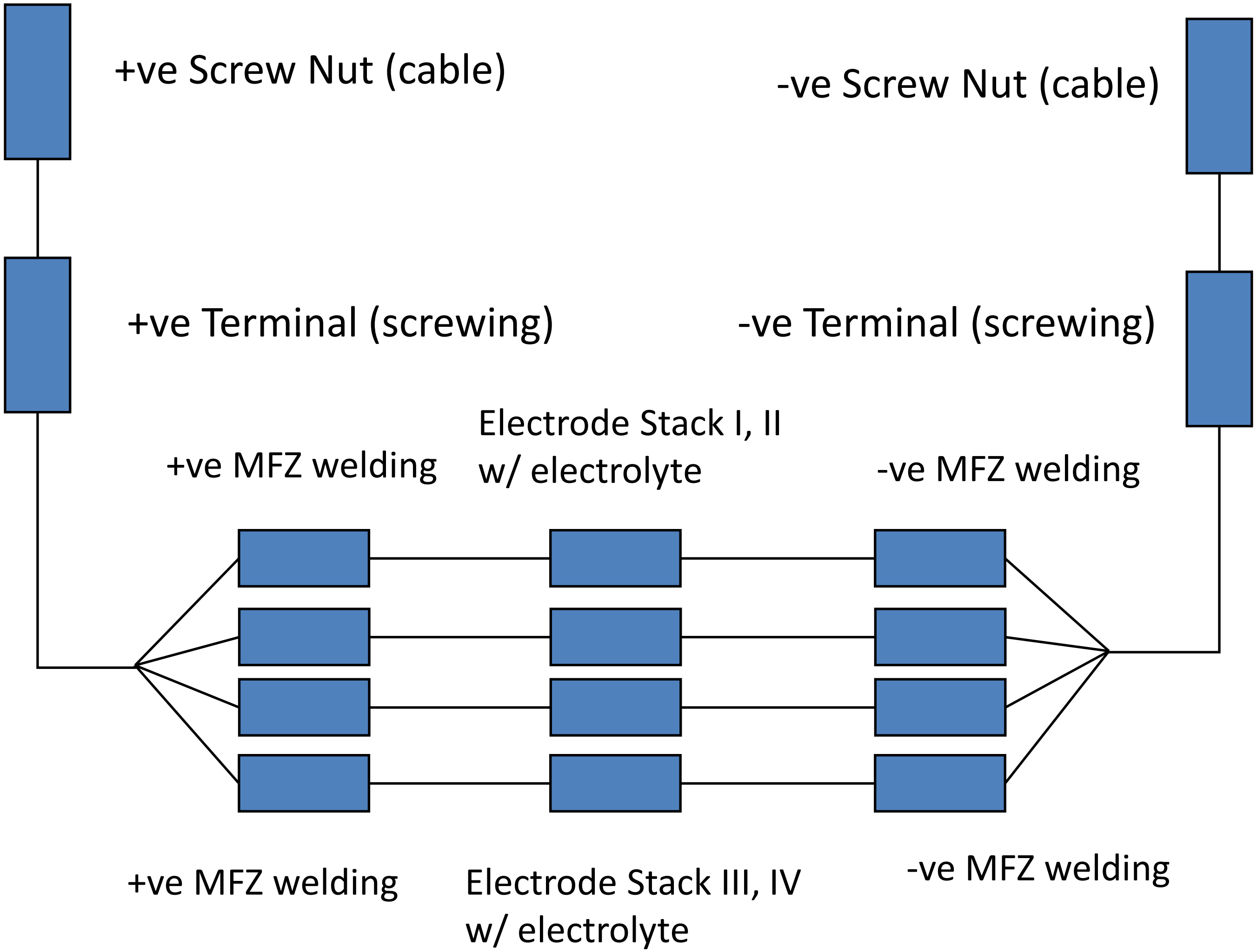
# RI CONTRIBUTION

# Ri Contribution



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# CHARGING & DISCHARGING METHODOLOGY

# Charging Methodology

- **Stage 1 :** Apply charging current limit until the voltage limit per cell is reached.
- **Stage 2 :** Apply maximum voltage per cell limit until the current declines below 1-3% of rated charge current.
- **Stage 3 :** Balancing

# Balancing Technology

- Balancing can be **active** or **passive**
- In passive balancing, energy is drawn from the most charged cell and is wasted it as heat, usually through resistors
- In active balancing, energy is drawn from the most charged cell and transferred to the least charged cells, usually through DC-DC converters
- Active balancing is usually more efficient than passive balancing

# Discharging Methodology

- **Different discharge modes**

  - *Constant Current*: A battery discharge regime whereby the current drawn during the discharge remains constant

  - *Constant Power*: the amount of current will increase as the battery discharges electricity in order to maintain constant power

  - *Constant Resistance*: A battery discharge regime whereby the resistance of the equipment load remains constant throughout discharge

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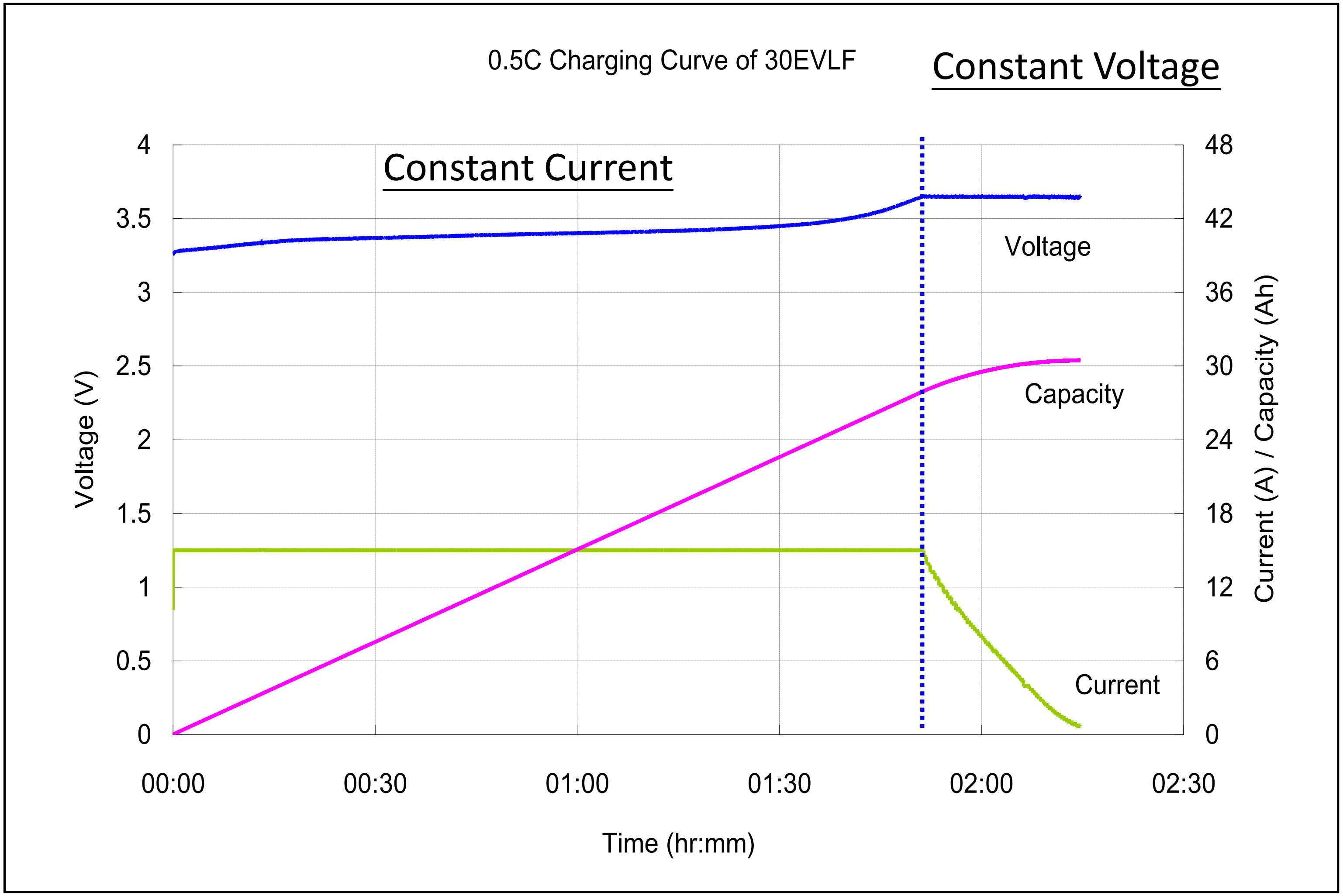
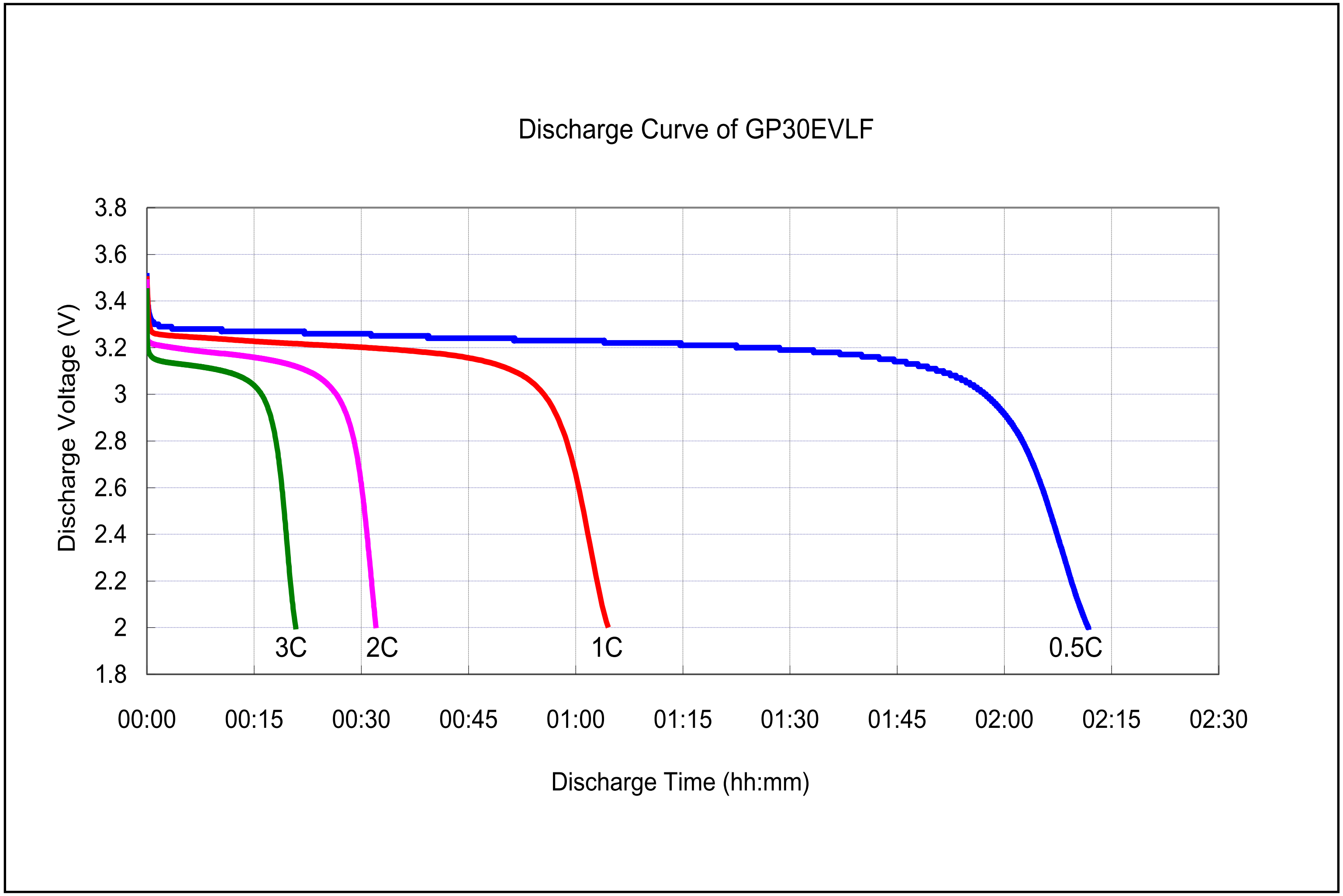
# ELECTRICAL PERFORMANCE – GP30EVLF EXAMPLE

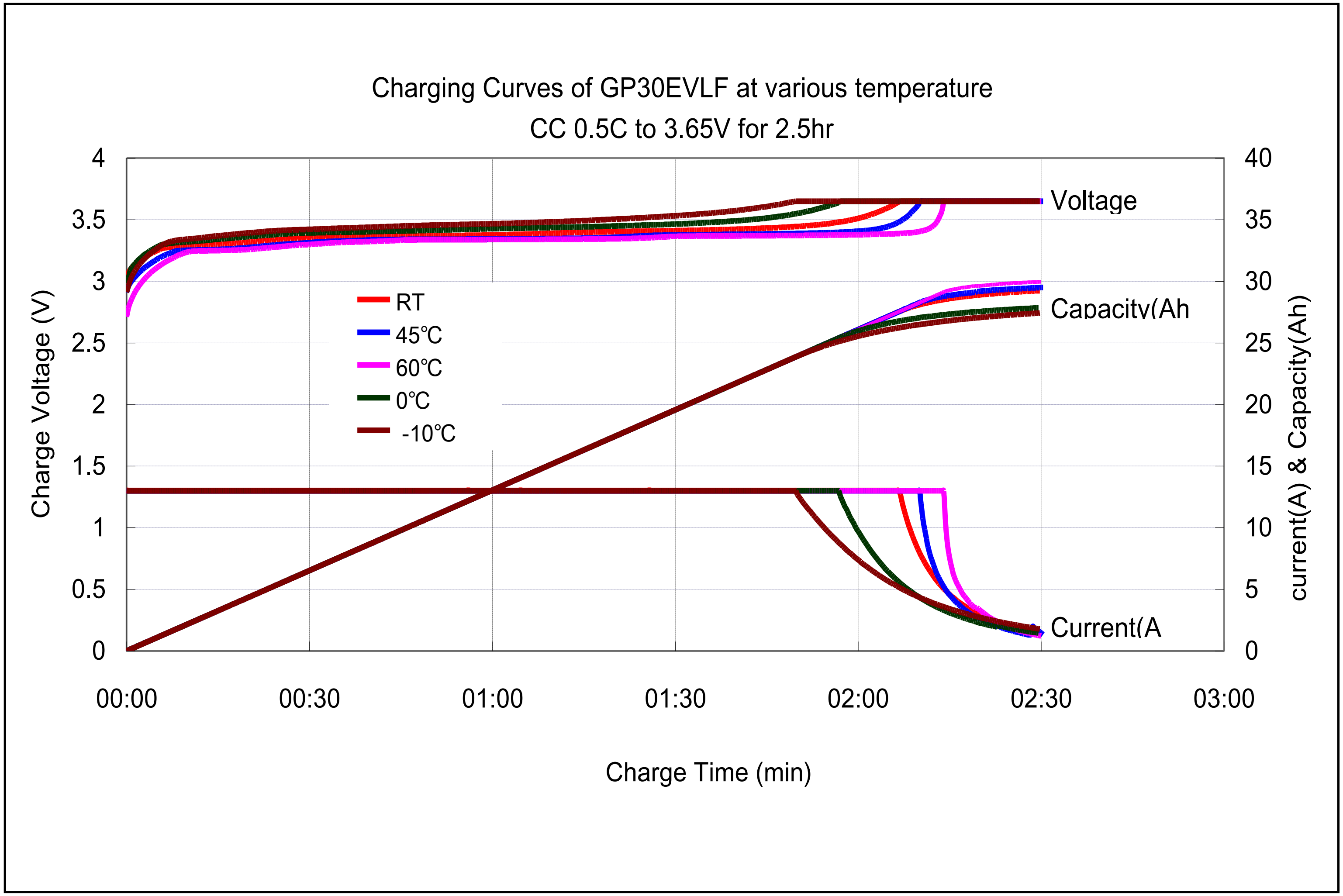
# Charge Characteristic of 30EVLF



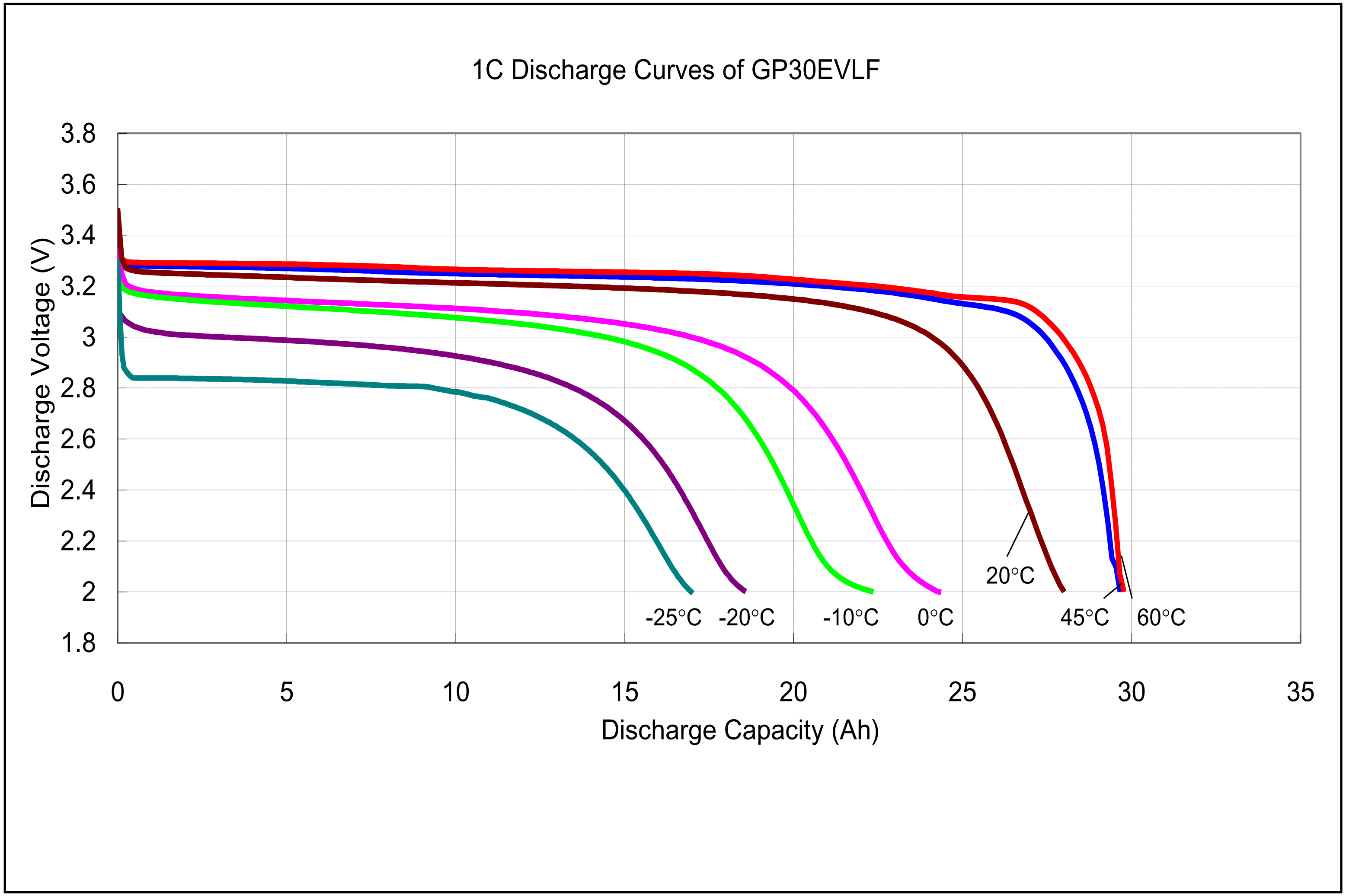
# Discharge Characteristic of 30EVLF



# Temperature Effect - Charging



# Temperature Effect - Discharging



# Contact Information

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