# THERMAL AND ELECTROCHEMICAL STABILITY OF LCO AND LNCMO TYPE CATHODE MATERIALS


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# BATTERY CHEMISTRY RESEARCH TOPICS

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**Preparation of electrode materials**

-LCO, LFP, LTO, NMC, graphite
-Different methods applied

**Characterization of battery chemicals**

-Characterization of physical and chemical properties
-Electrochemical testing

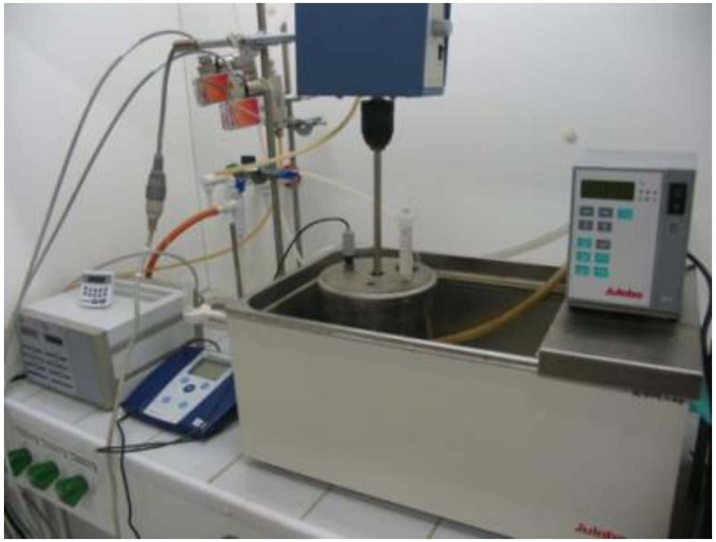
**Recovery of valuable metals**

-Metals recovery from process solutions, battery recycling, catalysts

# PREPARATION OF LITHIUM ION BATTERY CHEMICALS

Hydrothermal reaction:
Olivine materials
LFP and $LiCoPO_4$

Precipitation: Co- precursors



Heat treatment:
Co-precursors,
LFP, LCO, NCM

# Battery material characterization methods

- FESEM (Field Emission Scanninc Electron Microscope)
- XRD (X-ray diffraction)
- AAS ( Atomic absorption spectrometre)
- TOC (Total Carbon analyzer)
- Particle size analyzer
- Electrochemical tests (Coin cells, Pouchcells)
- DSC Differential scanning calorimetry

DSC device (Netzsch)


Tester for
Li-ion cells (Maccor)

## Comparison of $LiCoO_2$ (LCO) ($LiCoO_2$-OL) and $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (NCM) Electrochemical and thermal stability

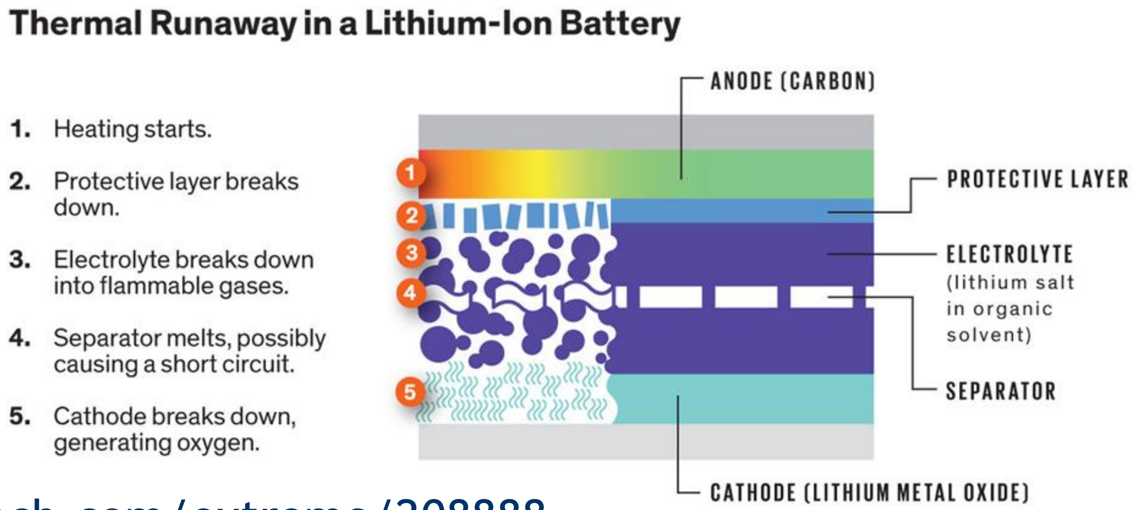
Electrode preparation

- Cathode: 2% Conductivity carbon (timcal), 3% PVDF (Kureha 1100)
- Anode: 4% Conductivity carbon (timcal), 4% PVDF (Kureha 9300)
- Two step mixing
- Drying in vacuum oven and calandering 3 times
- Activematerial loading 15mg/cm2
- Pouchcells 40 mAh (one electrode pair) and 400 mAh (5 pairs)
- Electrolyte EC, DEC, LiPF6 and additives
- Assempling in dry room (humidity -50 °C)

- Testing procedure 1063 cycles at different currents

# Thermal runaway in Li-ion battery

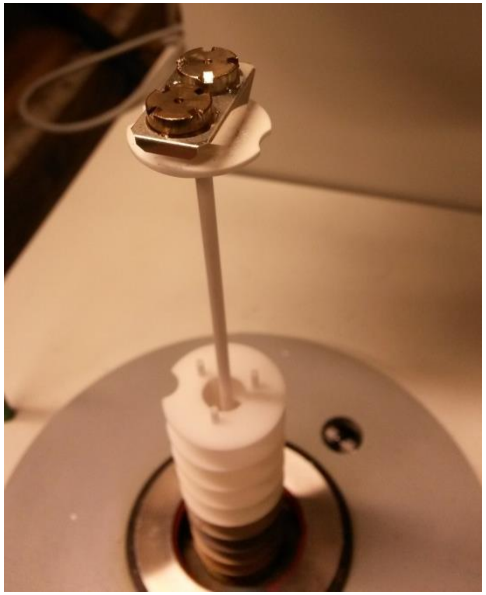
- The procession of reactions under thermal runaway is dependent on all the components and also the design of the battery pack itself. Heat generating reactions that are possible in abuse conditions:
- Heat production due to entropy changes, resistance or overpotential.
- **SEI decomposition on anode**
- Intercalated lithium reacting with electrolyte on the anode after SEI layer is gone (producing $Li_2CO_3$ and flammable gas) (100°C)
- Intercalated lithium reacting with fluorinated binder on anode
- Electrolyte decomposition (producing flammable gas)
- **Cathode material decomposition (producing oxygen if the cathode is a transition metal oxide) → Oxygen**




http://www.extremetech.com/extreme/208888-doping-lithium-ion-batteries-could-prevent-overheating-and-explosion

## Sample preparation for DSC measurements

- Charged pouchcells are opened carefully and washed three times with DMC before drying in vacuumoven
- 4mg of Cathode material and 2µl of electrolyte are closed in pressure DSC crucibles under Ar- atmosphere in clovebox



# LCO and NCM523 DSC results

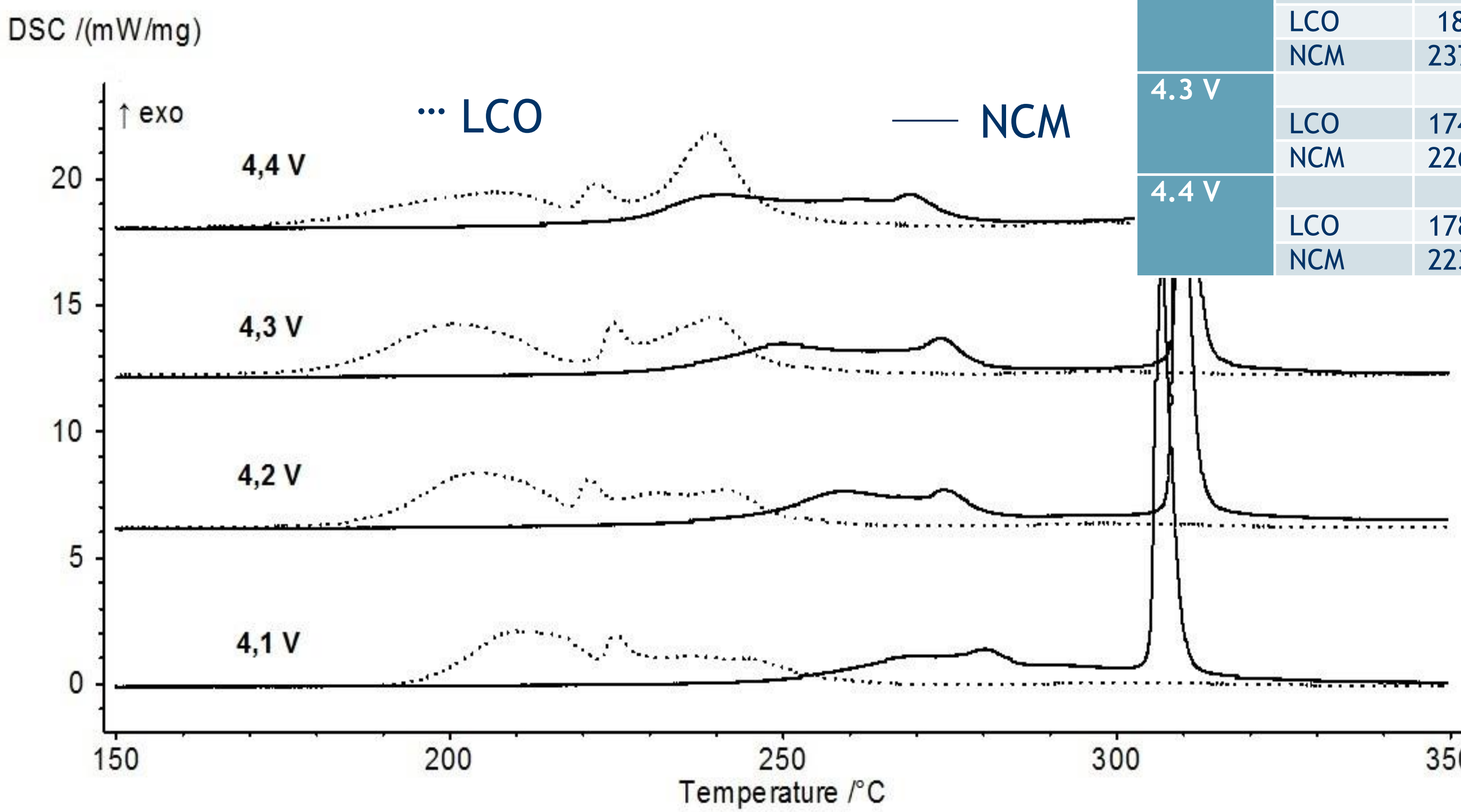
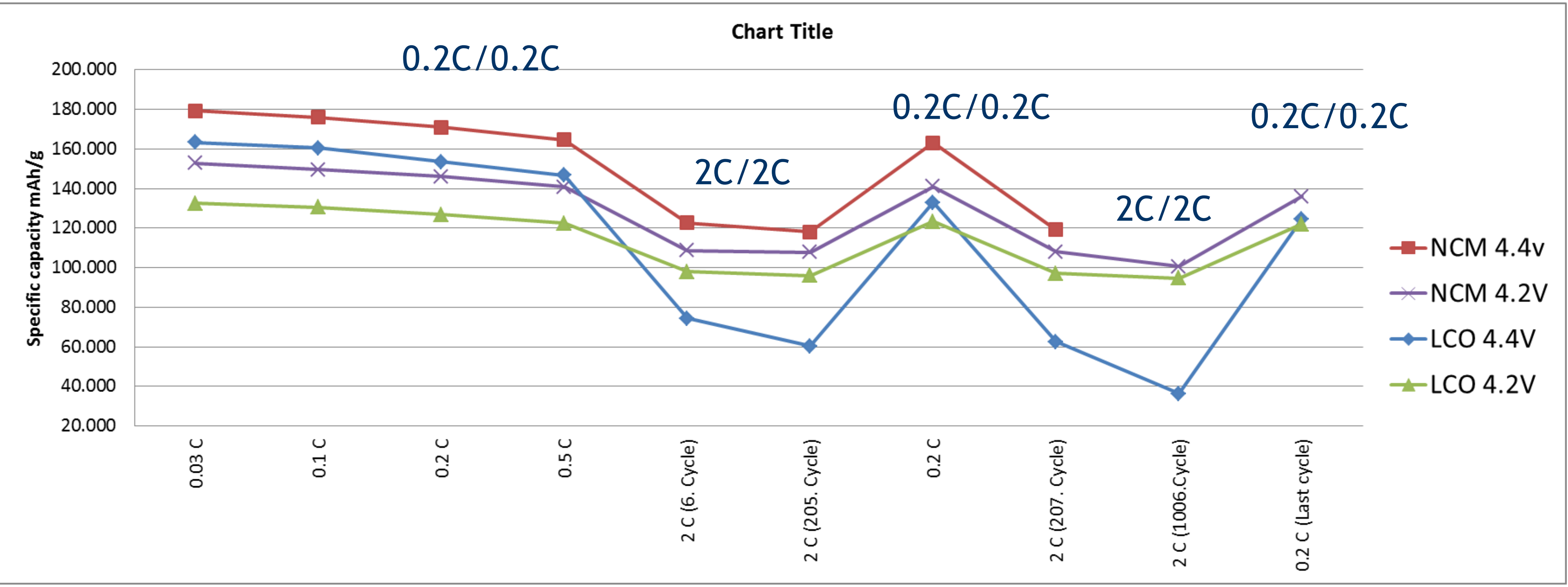


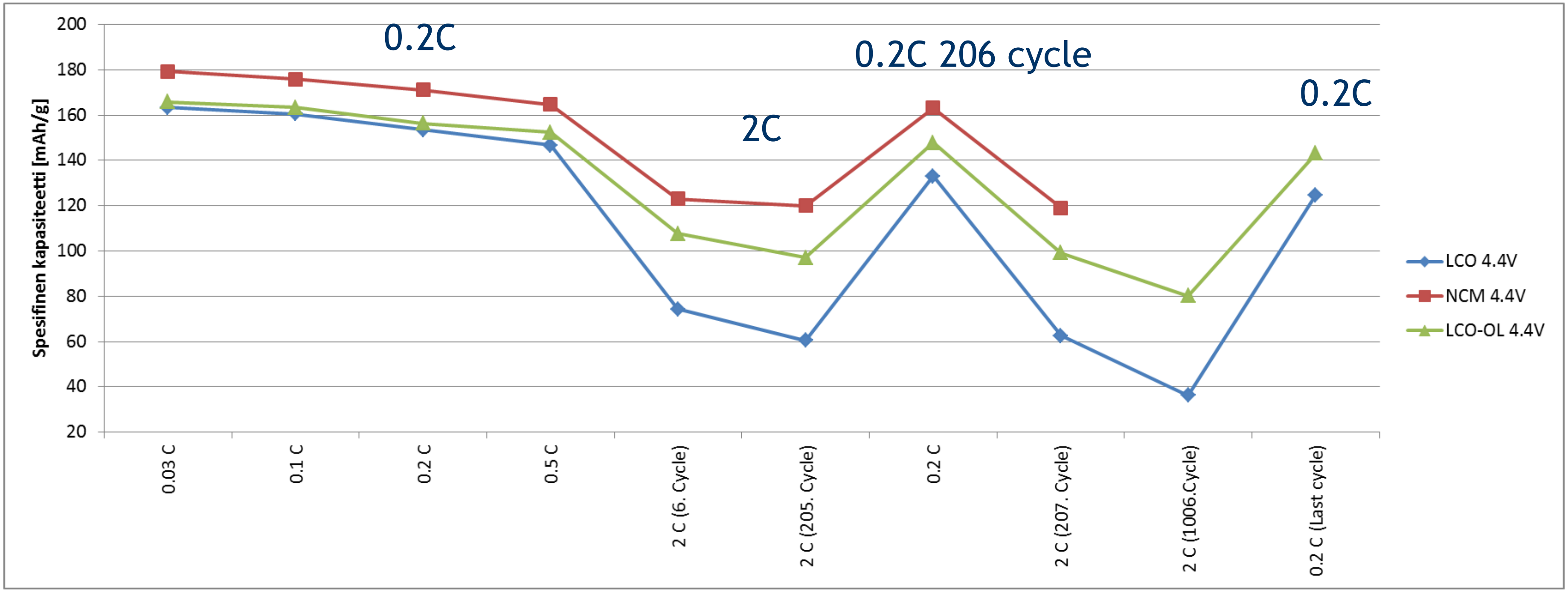

Table. onset temperatures and heat values for LCO and NCM samples represented in figure

| | | $T_0$ [a)] | ΔH [b)] |
|---|---|---|---|
| 4.1 V | | | |
| | LCO | 196 °C | 1010 J/g |
| | NCM | 242 °C | 937 J/g |
| 4.2 V | | | |
| | LCO | 189 °C | 1145 J/g |
| | NCM | 237 °C | 1095 J/g |
| 4.3 V | | | |
| | LCO | 174 °C | 1245 J/g |
| | NCM | 226 °C | 1148 J/g |
| 4.4 V | | | |
| | LCO | 178 °C | 1243 J/g |
| | NCM | 223 °C | 1240 J/g |

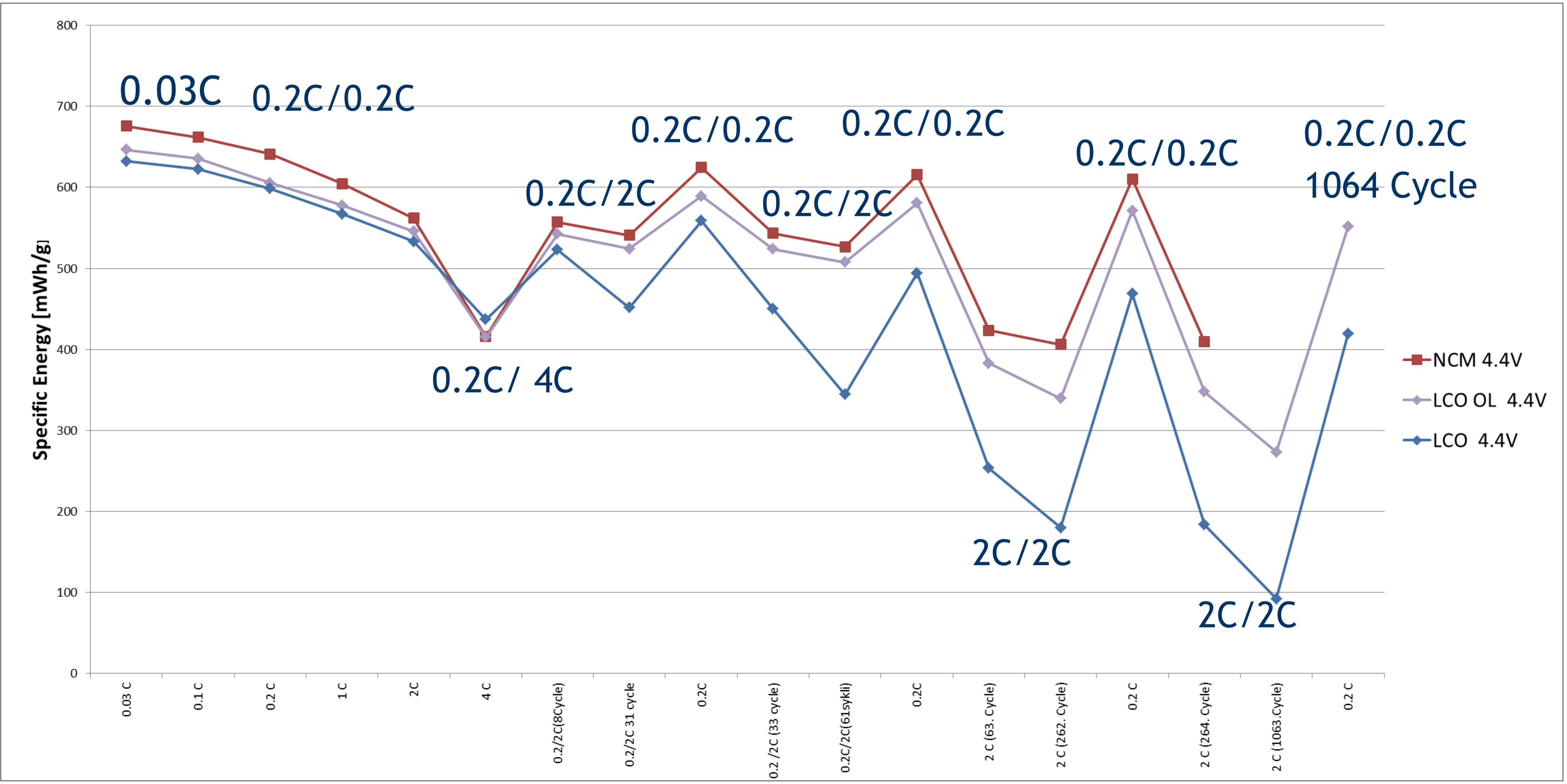
# Specific capacity Cutt-off voltages 4.2V and 4.4V, LCO and NCM



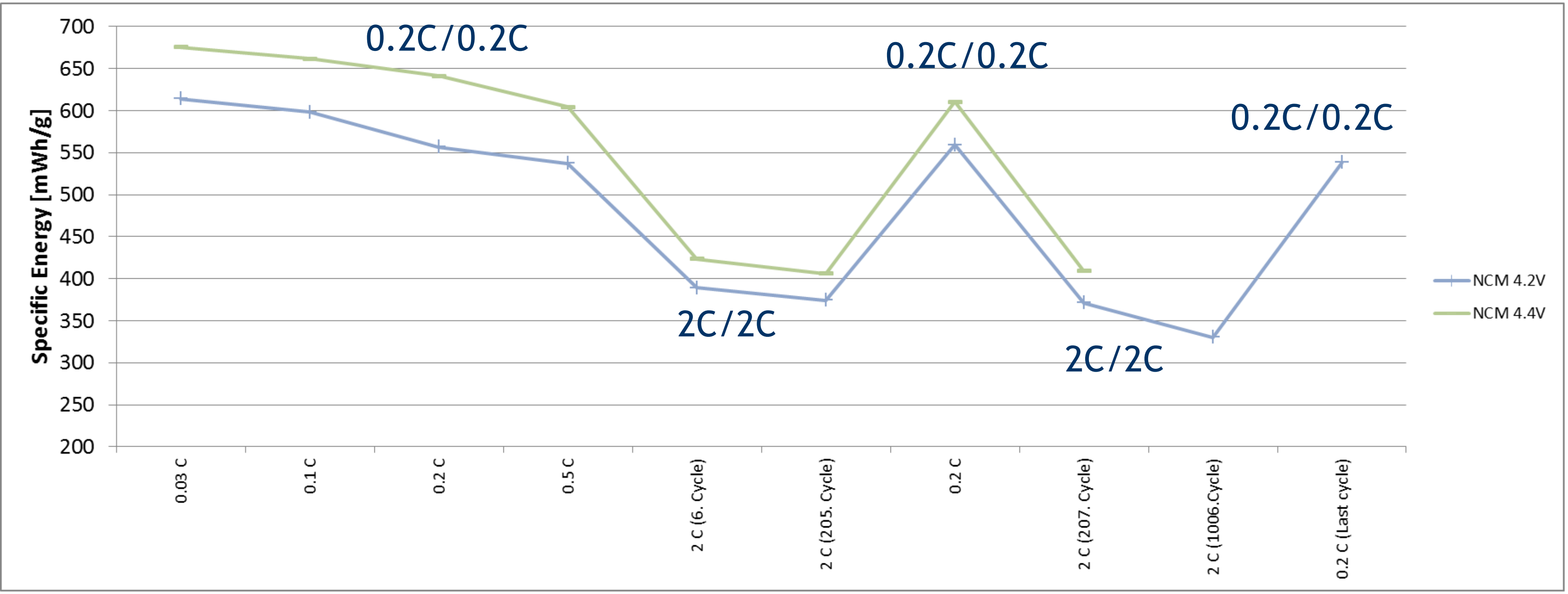
# Specific capacity 4.4 V, LCO, NCM and LCO-OL (over lithiated)



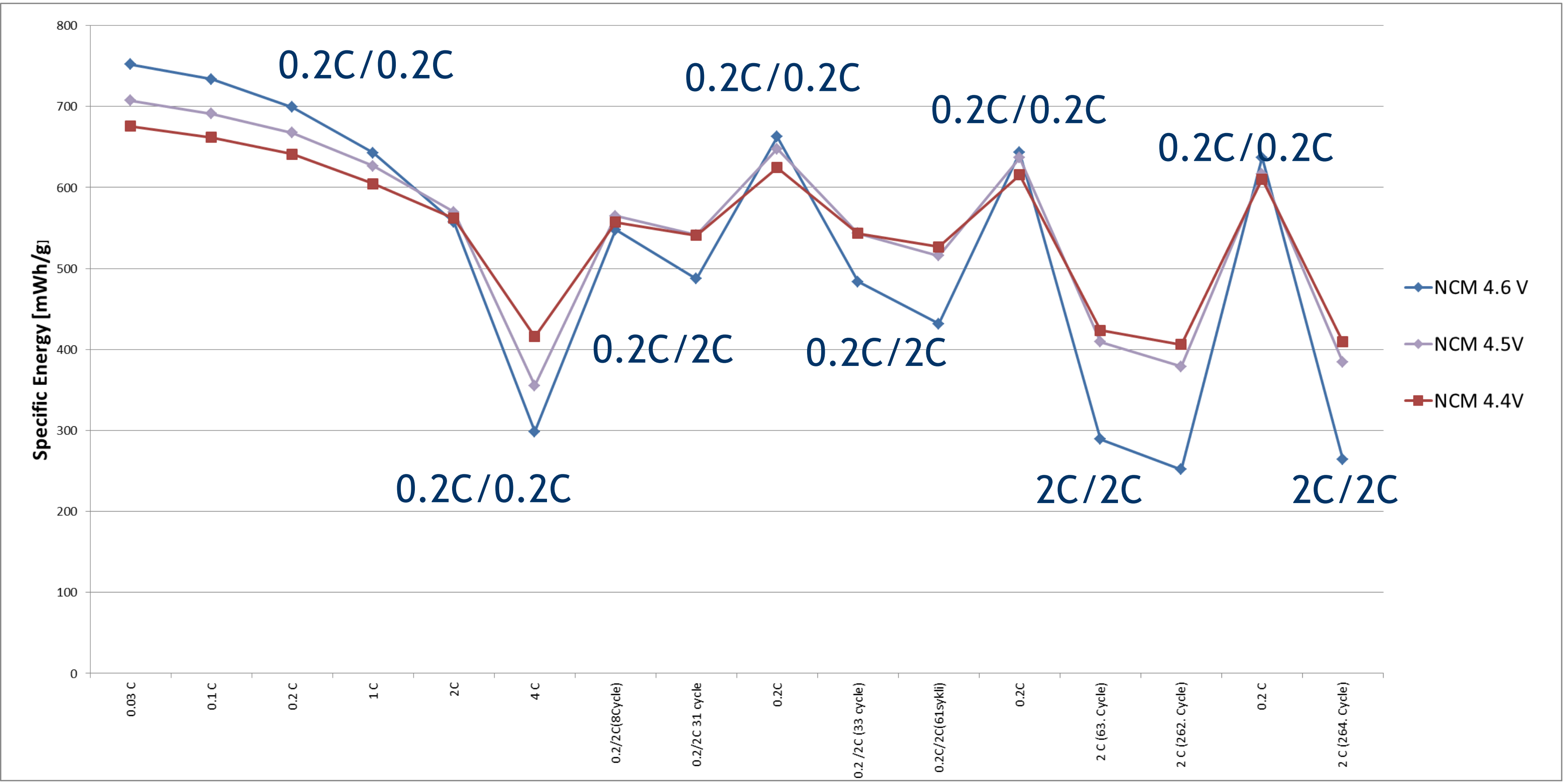
# Specific energy at different current, 1063 cycles 4.4V LCO, LCO-OL, NCM



# NCM cut off voltages 4.4V and 4.2V. 1007 cycles at different currents



# Specific energy 264 cycles at diffrent currents. Cut-off voltages 4.4V, 4.5V and 4.6V



# Conclusions

- LCO type materials release oxygen ''easier'' than NCM type materials.
- NCM type material resulted higher specific capacities than LCO when using 4.4 V cut-off voltages, however over lithiation seems to improve electrochemical properties of LCO
- Specific energies and capacities are almost similar for over lithiated LCO-OL and NCM

# Thank You for Your attention !

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