清華大學

Test of Li-ion battery for self-heating & lifetime Evaluation

US-China Electric Vehicle and Battery Technology Workshop
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Tsinghua University

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Self heating

Self heating effects

1. In order to provide sufficient capacity, a large-scale lithium-ion battery generally consists of many individual cells that are connected in parallel. This configuration inherently increases the thermal resistance of a battery, so thermal management becomes critical for operation.

2. Choose two LiFePO4 batteries and two LiMn2O4 batteries which are typically representative.

Self heating

Temperature effects on equilibrium potential

- ✓ Temperature effects on kinetic processes and relative parameters
- ✓ Temperature effects on diffusion processes and relative parameters
- ✓ Dynamic thermal energy balance.
  - ➢ The temperature of the battery should be solved dynamically so that it can be used to predict the effects of temperature on equilibrium potential, kinetic and diffusion processes.
  - ➢ The effects of ohmic heating, heat generation due to entropy change, phase change, heat capacity change, mixing processes, as well as heat exchange to surroundings will be considered and compared to see which heat effects can be neglected to simplify the evaluation.

Evaluation formulations

- **Transient balance equations of equivalent circuit**

$$\left.\begin{aligned} V_{\mathrm{ohm}}(t) &= i(t)R_{\mathrm{ohm}} \\ C_{\mathrm{k}}\frac{\mathrm{d}V_{\mathrm{k}}(t)}{\mathrm{d}t} + \frac{V_{\mathrm{k}}(t)}{R_{\mathrm{k}}} &= i(t) \\ C_{\mathrm{d}}\frac{\mathrm{d}V_{\mathrm{d}}(t)}{\mathrm{d}t} + \frac{V_{\mathrm{d}}(t)}{R_{\mathrm{d}}} &= i(t) \end{aligned}\right\} \Rightarrow \boxed{V(t) = \mathrm{OCV} - V_{\mathrm{ohm}}(t) - V_{\mathrm{k}}(t) - V_{\mathrm{d}}(t)}$$

- Dynamic energy balance equation

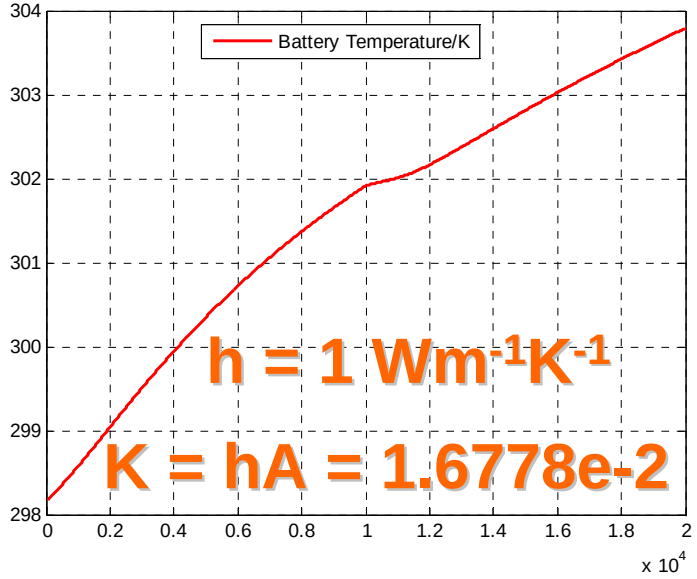
$$mc_{\mathrm{p}}\frac{dT(t)}{t} = Q - \underbrace{h_{\mathrm{c}}A\left(T(t) - T_{\mathrm{amb}}\right)}_{\text{Convective heat transfer}}$$

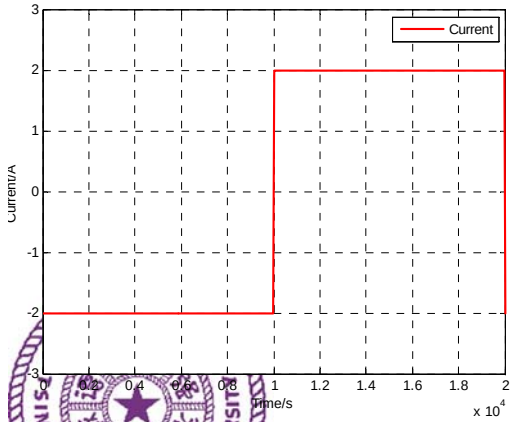
Heat source term

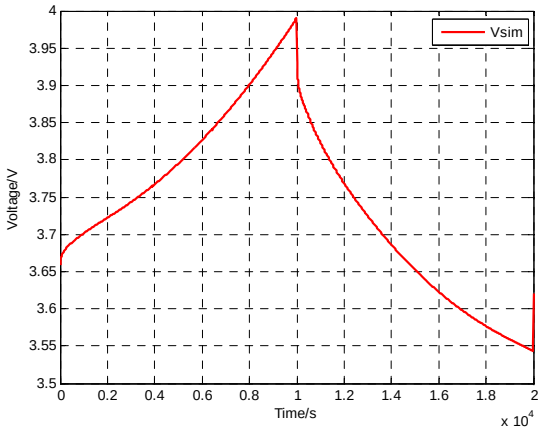
$$Q = \underbrace{\frac{V_{\mathrm{ohm}}(t)^2}{R_{\mathrm{ohm}}}}_{\text{Ohmic heat}} + \underbrace{\frac{V_{\mathrm{k}}(t)^2}{R_{\mathrm{k}}}}_{\text{Kinetic polarization heat}} + \underbrace{\frac{V_{\mathrm{d}}(t)^2}{R_{\mathrm{d}}}}_{\text{Diffusion polarization heat}}$$

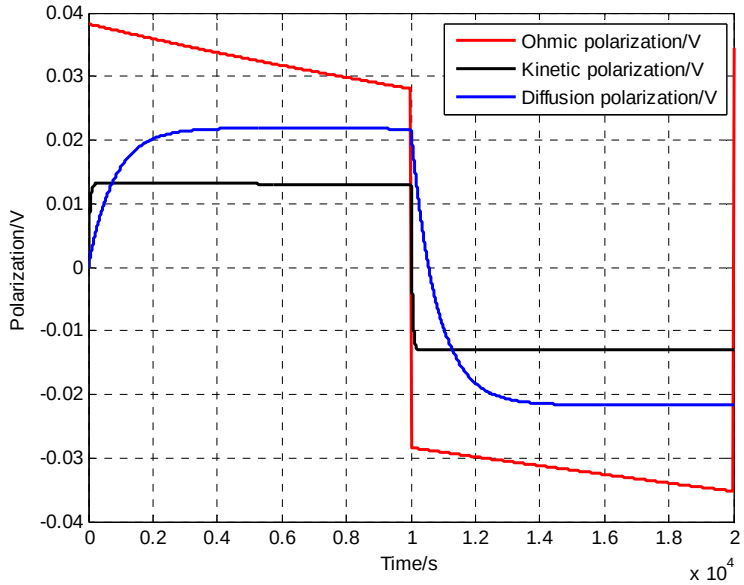
parameters

Parameter	Unit	Electrode material	
		$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$	$LiFePO_4$
High	**mm**	**67**	**104**
Width	**mm**	**70**	**70**
Thickness	**mm**	**27**	**27**
Weight	**kg**	**~0.275**	**~0.410**
Capacity	**Ah**	**~10**	**~11.5**
Surface area	**m^2**	**16.778e-3**	**23.956e-3**
Heat capacity	**$J.kg^{-1}K^{-1}$**	**925**	**925**
Ambient temperature	**°C**	**25**	**25**

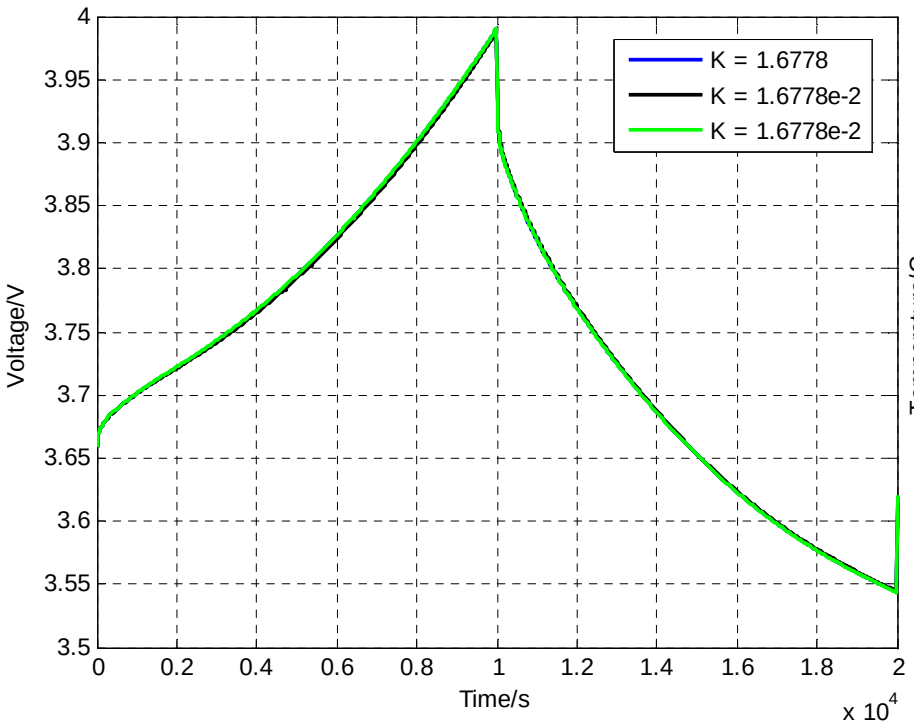


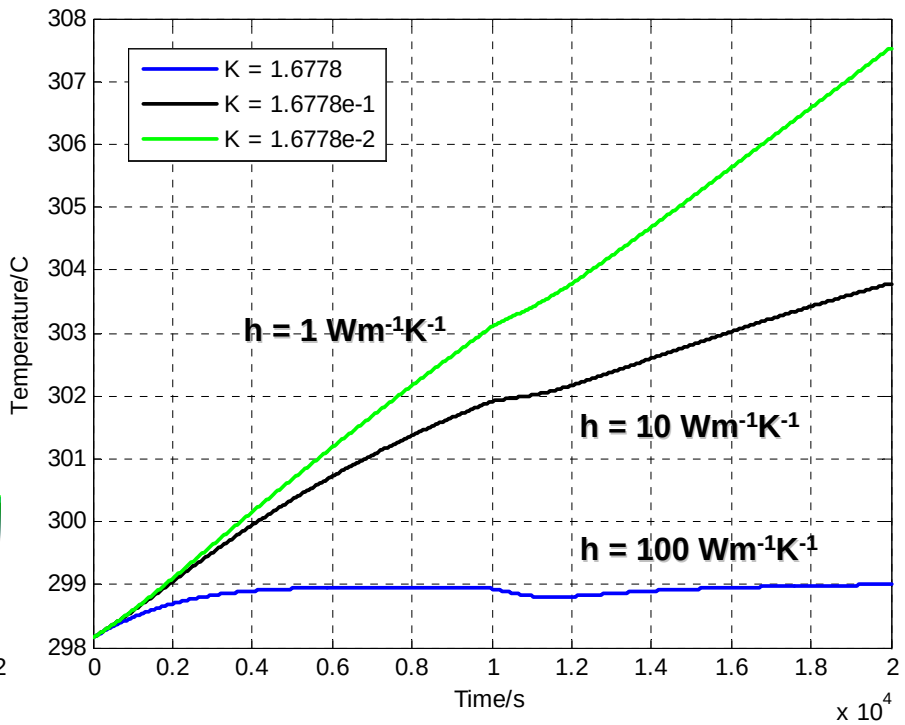






Effects of parameter K = hA



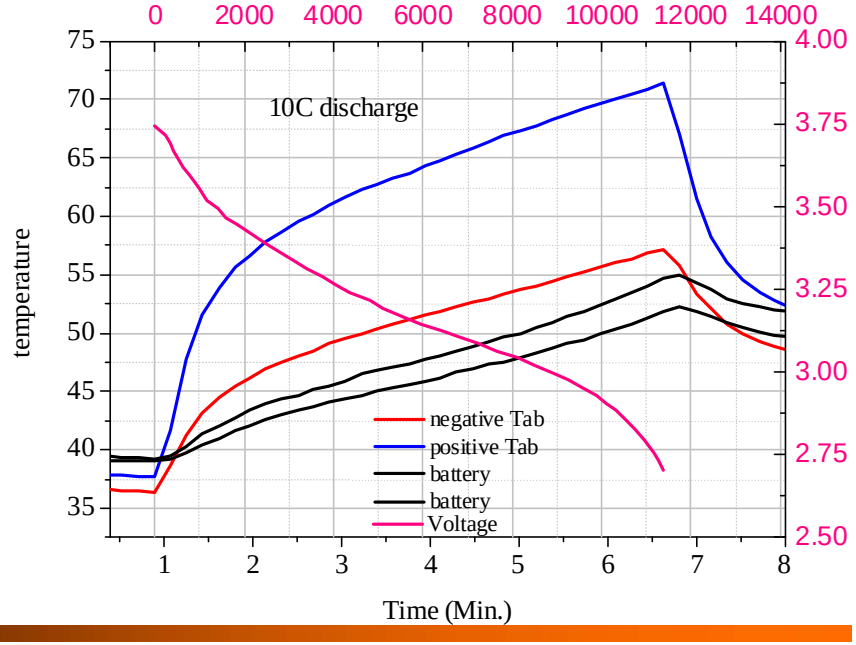


- K value affect the performance and temperature much especially when K value is relatively small.
- Cruicial for battery geometry deisign and cooling system design

Battery temperature prediction

Summary

1. **Battery temperature can be simply predicted during operation with acceptable error.**
2. **The most important factor is the cooling & Radiating .**
3. **The battery self heating evaluation is helpful for the battery design and battery pack design.**



Life time evaluation

Considering (1) self discharge (2) SEI film growth

- The effects of SEI growth was represented in additional resistance of ohmic resistance and kinetic polarization resistance.
- The self discharging process will be represented as a parallel resistance.

Experimental methodology

✓ Cycle life evaluation : Choose 10Ah-rated LiFePO4 batteries and 10Ah-rated LMO batteries which are typical. Testing duration is ~1 year.

✓ Calendar life evaluation : Choose 10Ah-rated LiFePO4 batteries and 10Ah-rated LMO batteries. These two kinds of batteries shall go fifty-fifty on shelfing at room temperature and on shelfing at 55℃in constant temperature box during day time. The 1C rate current charging-discharging capacities of batteries will be measured every half month. OCV of batteries will be measured every day. The duration is ~1 year.

Self Discharging

$$R_{\text{selfdischarging}} = R_{\text{S,rev}} + R_{\text{S,irr}}$$

Treated as constant

$$R_{\text{S_irr}} = k_{\text{S,irr}} \exp\left(-\frac{A_{\text{S,irr}}}{T} + B_{\text{S,irr}} \right) \int_0^t \left| i(t) \right| dt$$

Function of temperature and delivered capacity during self discharging

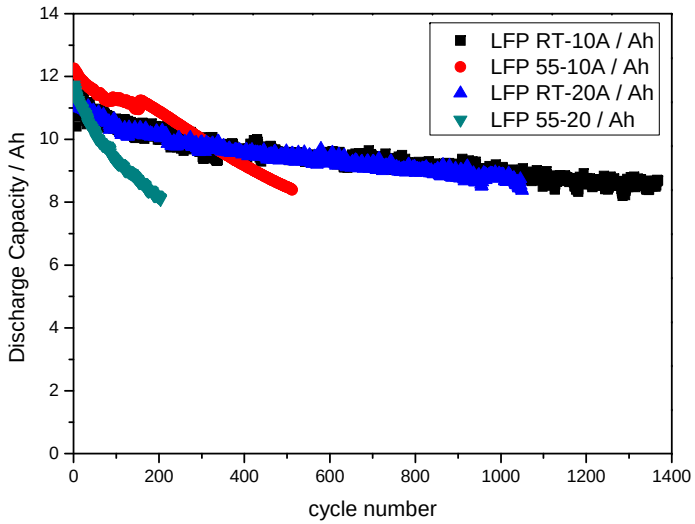
SEI film (resistance) growth

- Assuming newly increased SEI film thickness is proportional to the delivered capacity
- Side reaction rate can be formulated as Arrhenius dependence on temperature

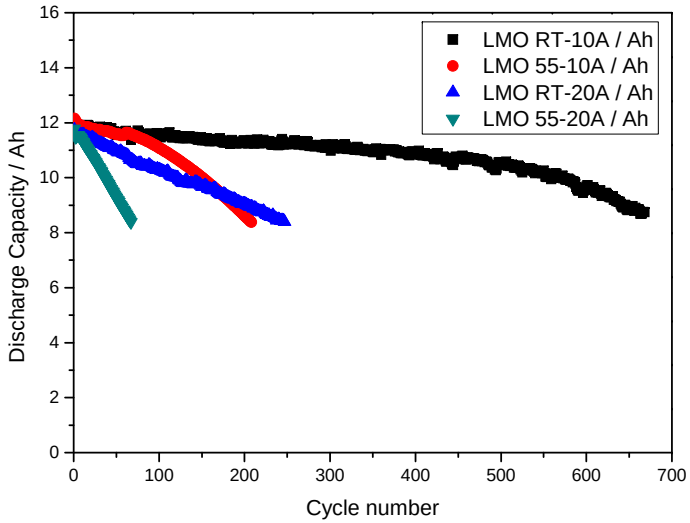
$$R_{\text{ohm_degradation}} = k_{\text{SEI,ohm}} \exp\left(-\frac{A_{\text{SEI,ohm}}}{T} + B_{\text{SEI,ohm}}\right)\int_0^t \left|i(t)\right| dt$$

$$R_{\text{k_degradation}} = k_{\text{SEI,k}} \exp\left(-\frac{A_{\text{SEI,k}}}{T} + B_{\text{SEI,k}}\right)\int_0^t \left|i(t)\right| dt$$

Cycle Life of LFP Batteries and LMO Batteries

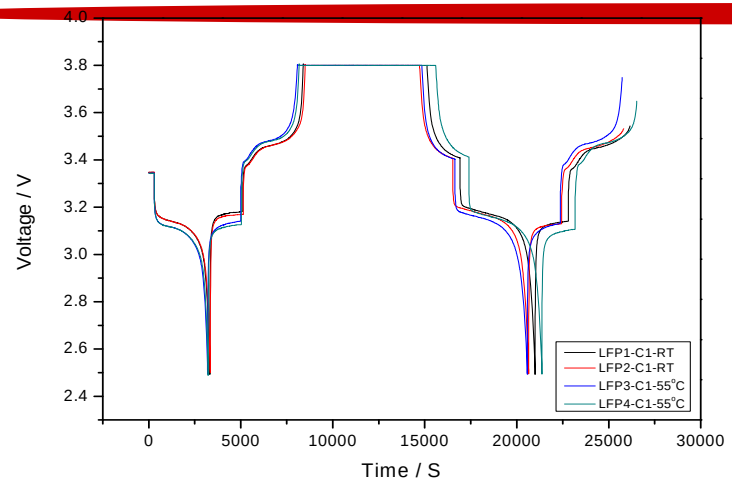


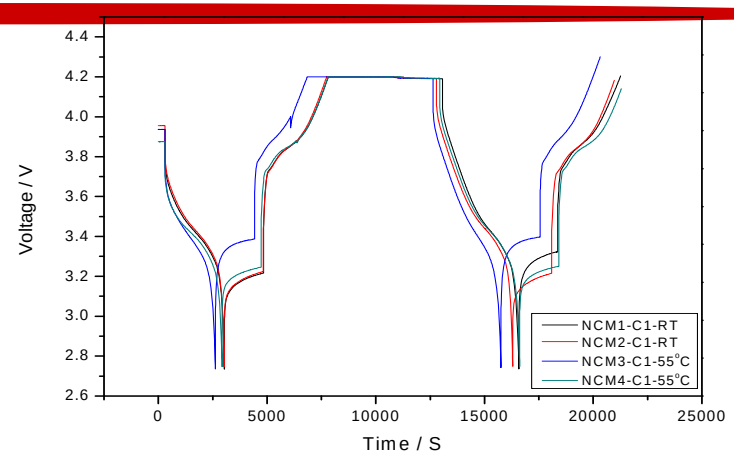
The variation of discharged capacity for lithium ion batteries based on LFP cathode materials with cycle number at 10A charge/discharge current & room temperature (RT) and at 20A charge/discharge current & 55 ^{o}C

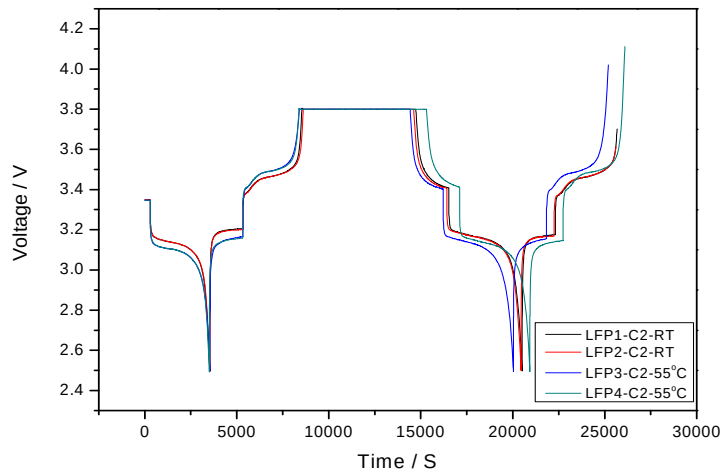


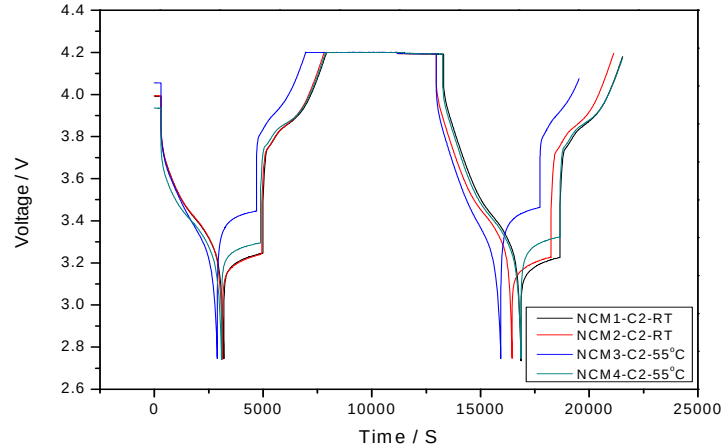
The variation of discharged capacity for lithium ion batteries based on LMO cathode materials with cycle number at 10A charge/discharge current & room temperature (RT) and at 20A charge/discharge current & 55 ^{o}C

Calendar Life









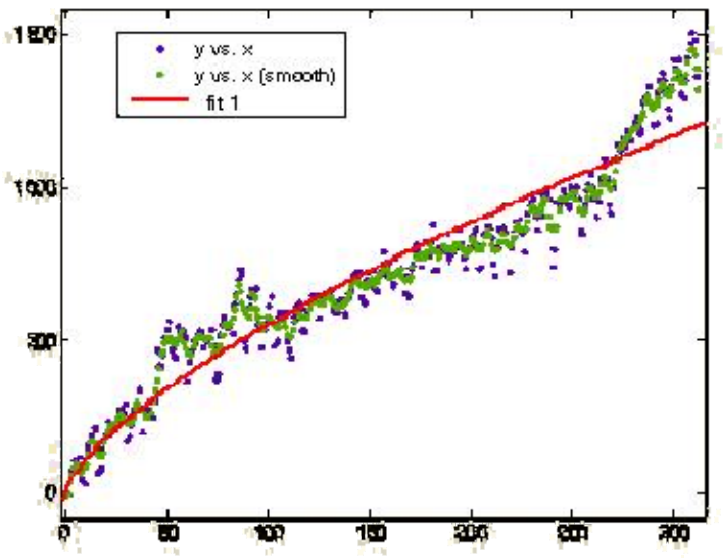
Charge/discharge profiles of LFP batteries at 10A charge/discharge current. RT means the battery was stored in room temperature. 55°C means the battery was stored at 55°C.

Charge/discharge profiles of LMO batteries at 10A charge/discharge current. RT means the battery was stored in room temperature. 55°C means the battery was stored at 55°C.

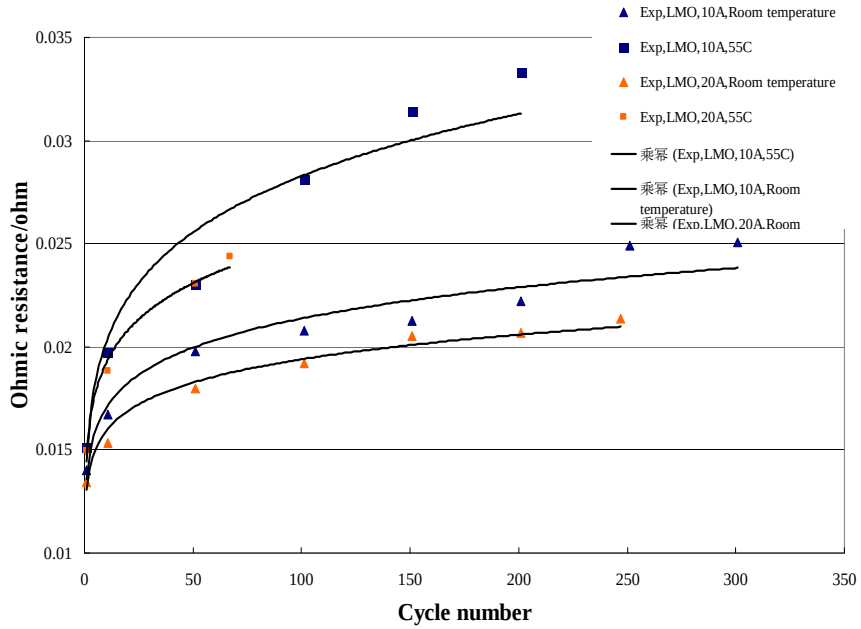
Simplified Evaluation of Capacity Fading and Ohmic resistance increasing

$$\frac{dC}{dt} = f(I)e^{-\Delta G/RT}dt$$

$$C = C_{\text{full}} - f(I)e^{-\Delta G/RT}(t - t_0)$$



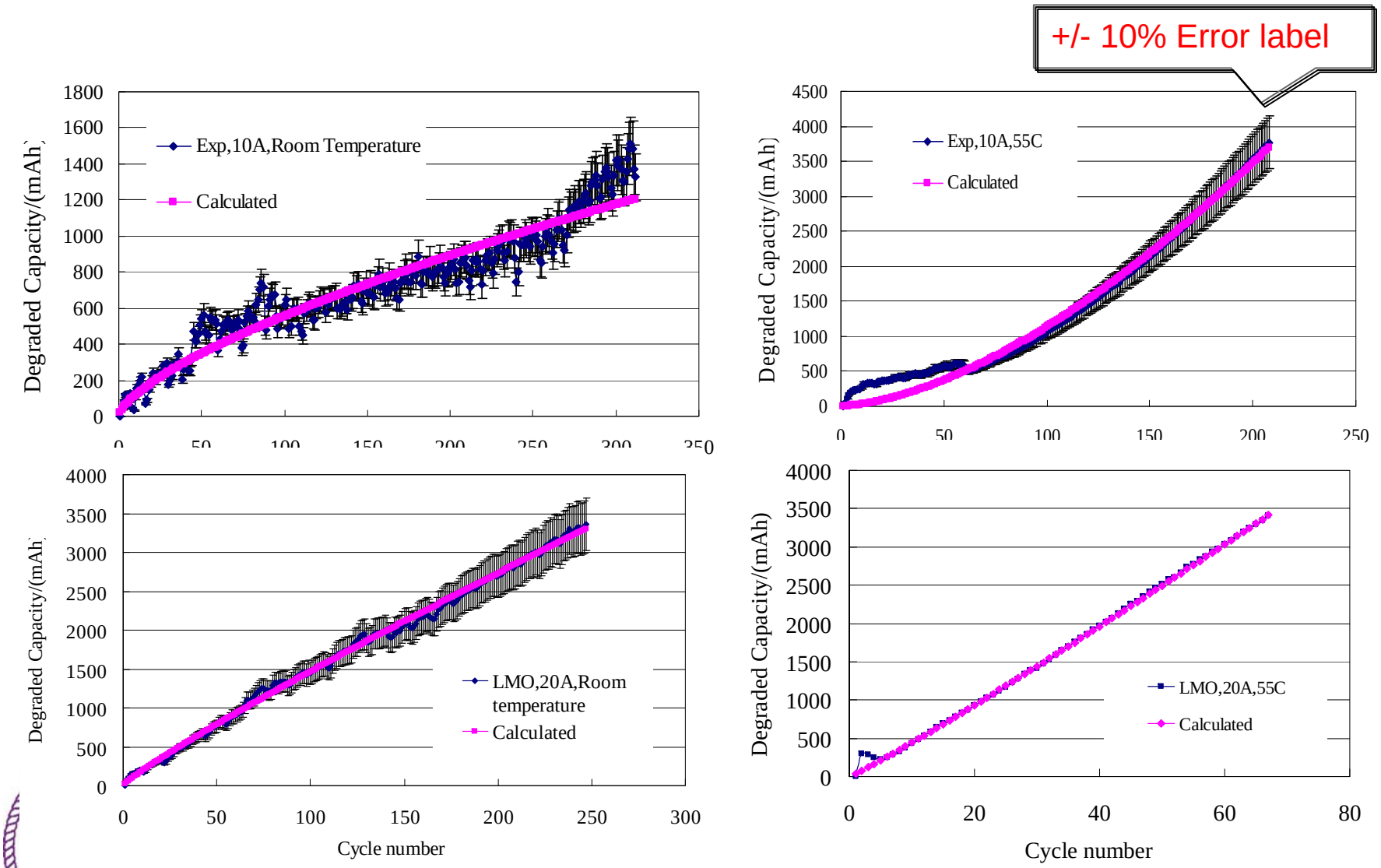
$$R_{\text{ohm_degradation}} = k_{\text{SEI,ohm}} \exp\left(-\frac{A_{\text{SEI,ohm}}}{T}\right)\int_0^t |i(t)|\,dt$$



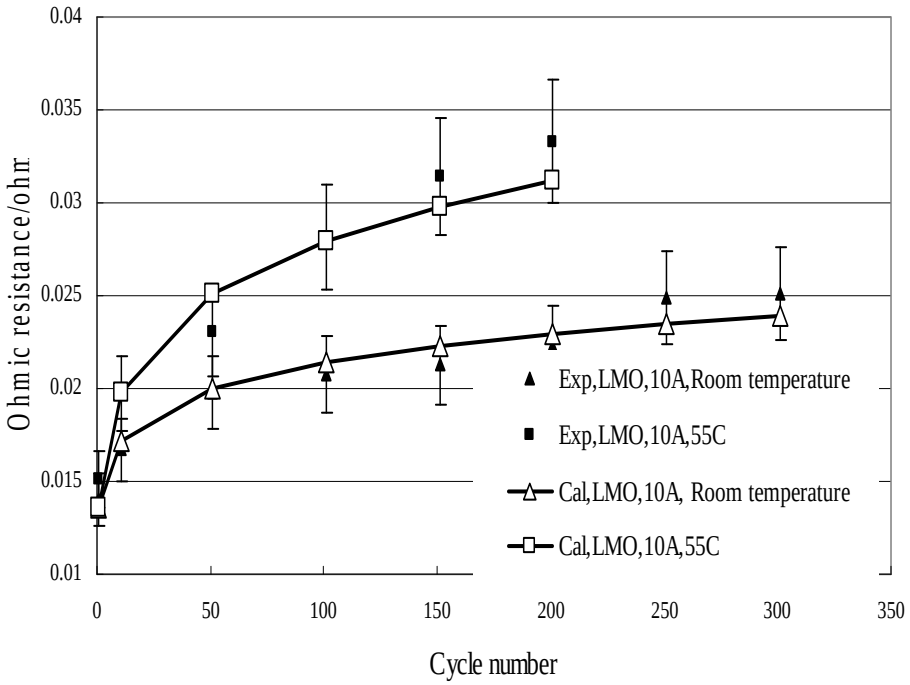
$$C = C_{\text{full}} - A(I,T)n^{B(I,T)}$$

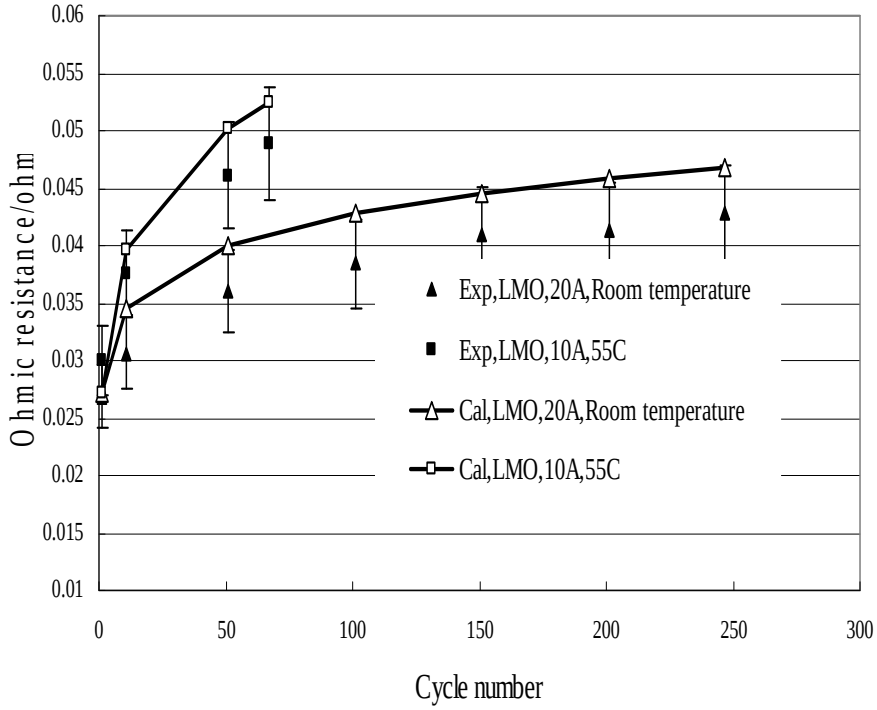
$$R_{\text{ohm_degradation}} = An^{B\exp\left(C\left(\frac{1}{T_0}-\frac{1}{T_1}\right)\right)}$$

Capacity Fading prediction



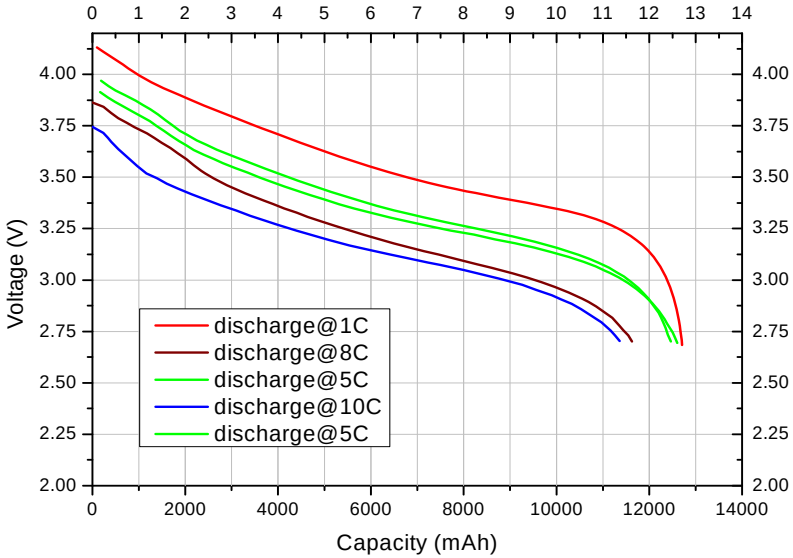
Ohmic Resistance Increasing prediction

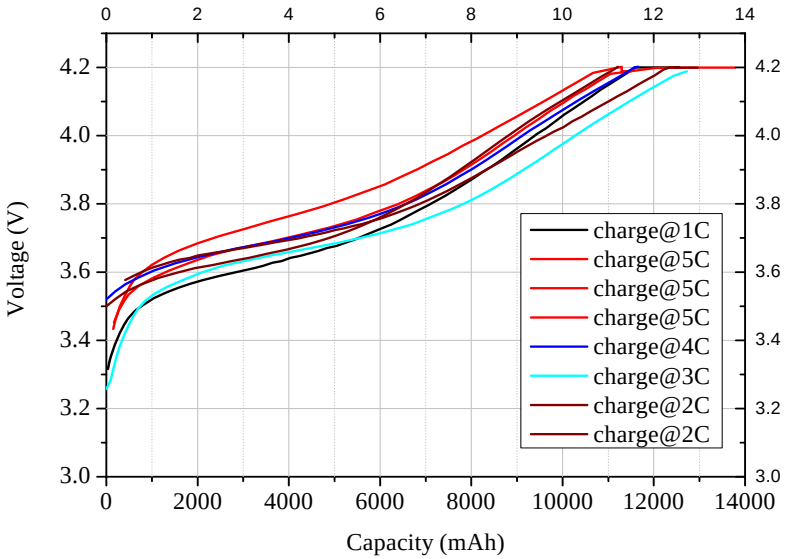


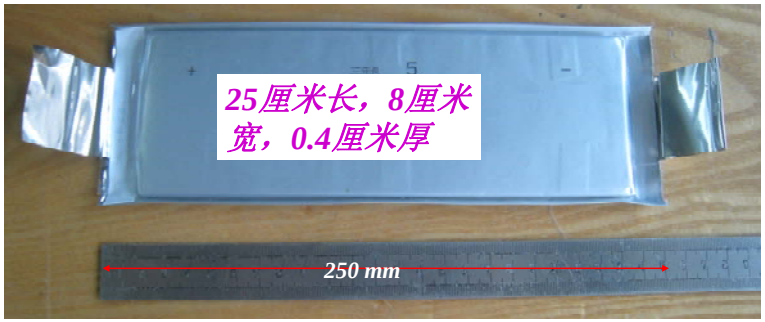


- Model can well predict the ohmic resistance increasing during the battery cycle operation with the relative error falling into the range of +/-10%.

12Ah NCM batteries



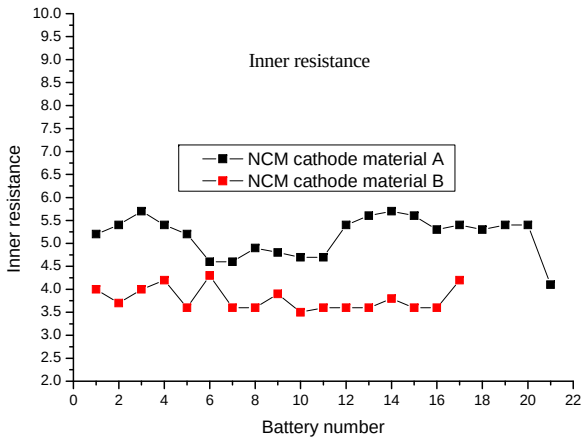


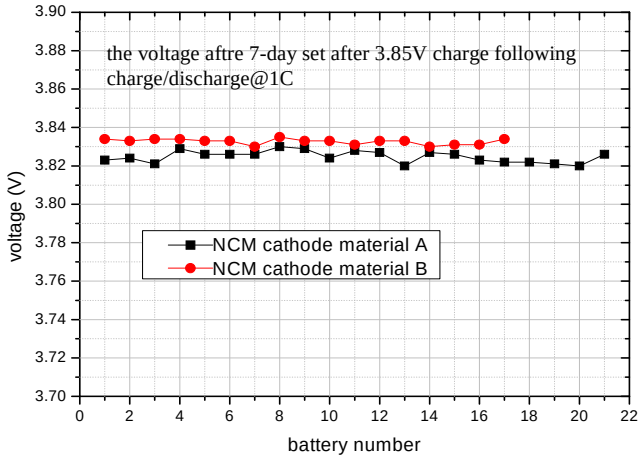


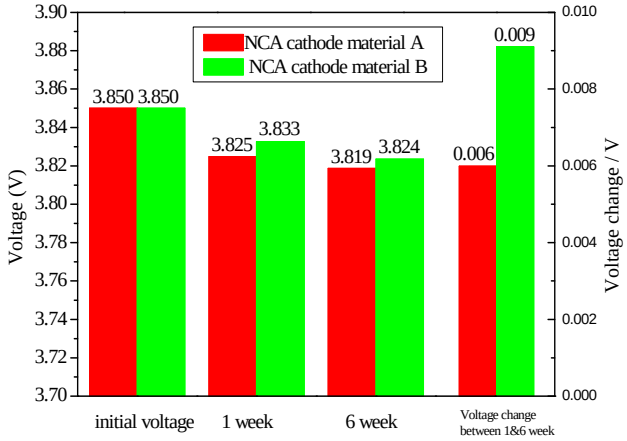
- **12Ah batteries**
- **Batteries based on two NCM cathode materials (A and B)**
- **The performance of battery A and B show the same.**

NCM cathode material evaluation

- **12Ah batteries**
- **5 cycles@1C， charge to 3.85V， rest for 1 week，**
- **Batteries based on two NCM cathode materials (A and B)**





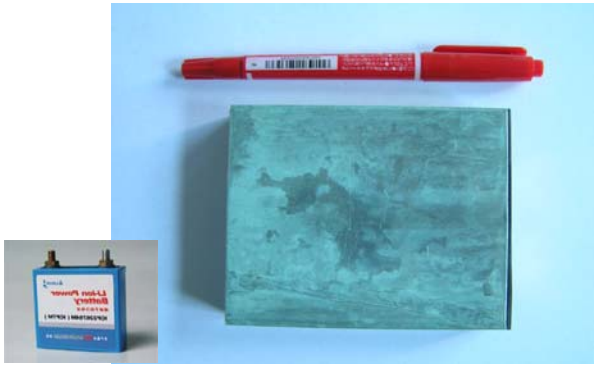


- **12Ah batteries**
- **Batteries based on two NCM cathode materials (A and B)**
- **The performance of battery A and B show the same.**
- **They show different self discharge and lifetime characteristics.**

Battery Life time evaluation

Summary

1. **Battery life time can be simply predicted based on experimental results with acceptable error.**
2. **The evaluation can give out the comment of battery quality from different company.**

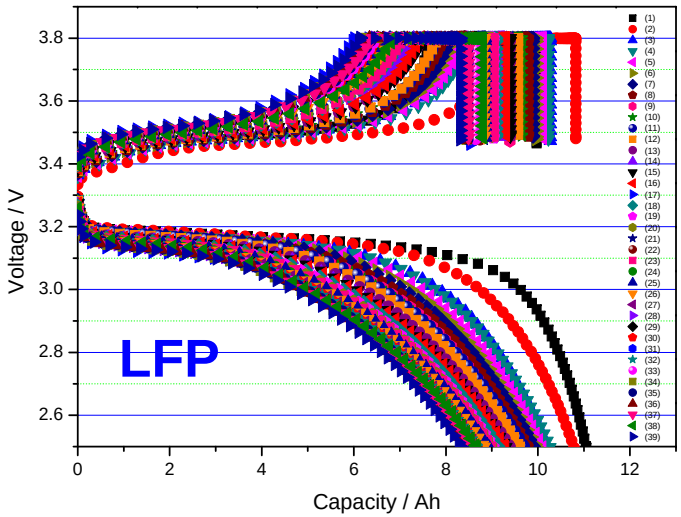


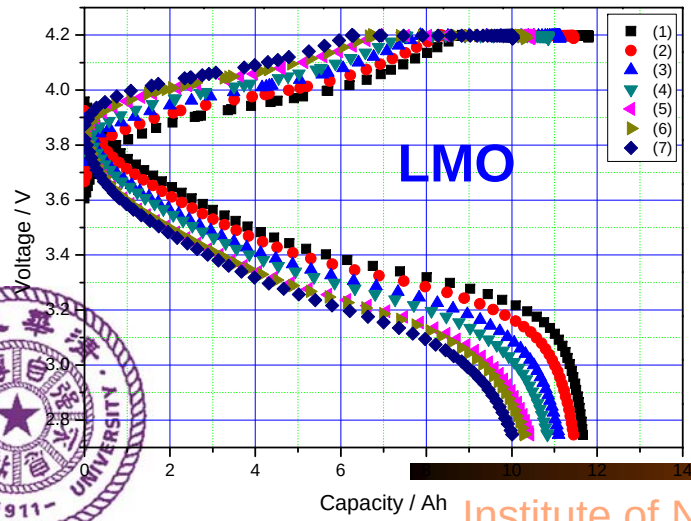
Battery SOH evaluation

- The battery-powered products have problems in cost and reliability for unknown battery replacement time
  - Early replacement causes replacement cost
  - Late replacement causes product reliability declining by reducing battery performance

- The estimation of battery SOH (State Of Health) is needed, but detection of SOH is difficult

Evaluation of SOH





Focus on:

- ✓ Internal resistance degradation (especially considered)
- ✓ Capacity degradation
- ✓ Change of battery temperature

1. Voltage difference between the voltage at charge process of 40% SOC and the voltage at discharge process of 40% SOC
2. The voltage difference increase can be used to evaluate the SOH.
3. When it reaches a certain value, the battery can be considered to be needed for replacement.

More needs to be done

Thanks for your attention!