Influence of Cathode Material Surface Area on Thermal Stability of Li-Ion Batteries

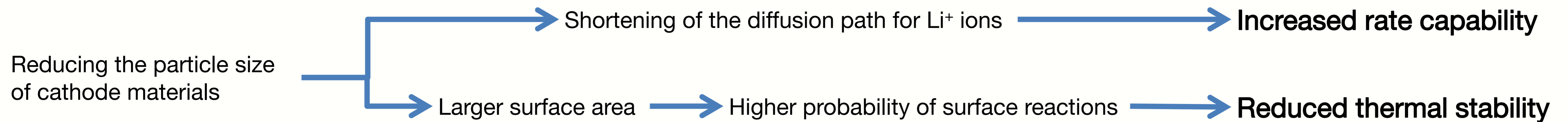Jan Geder[1], Harry Hoster[1], Andreas Jossen[3], Denis Y.W. Yu[1,2]

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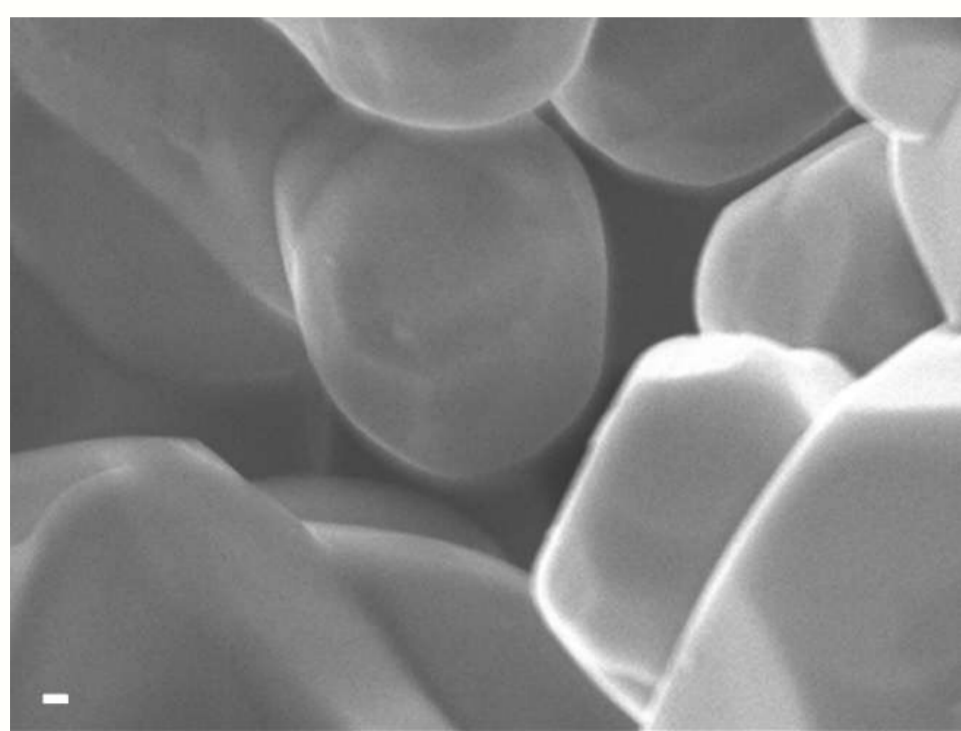
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Motivation

Reducing the particle size of cathode materials
- → Shortening of the diffusion path for Li+ ions → **Increased rate capability**
- → Larger surface area → Higher probability of surface reactions → **Reduced thermal stability**
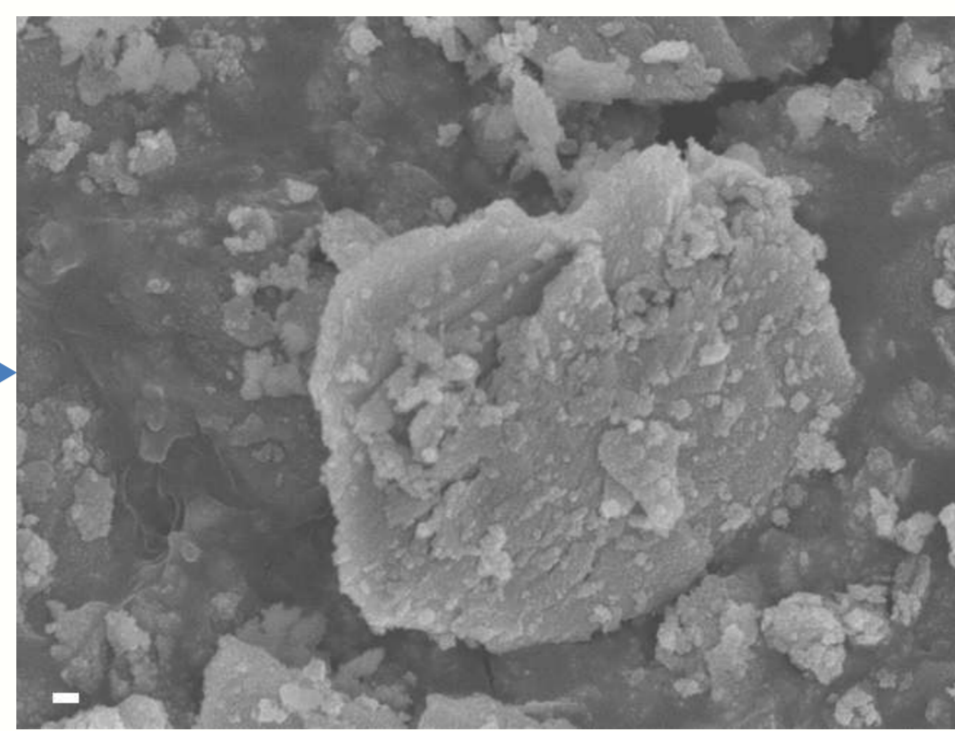
Methodology

Bulk commercial $LiCoO_2$

Ball milling, 0-5 h at 500 rpm in acetone

No change in crystal structure or composition detected by XRD

Ball milled $LiCoO_2$

FESEM image of pristine (left) and 5 h ball-milled (right) material under 33,000x magnification

| Milling time	BET surface area
0 h	0.4 m²/g
1 h	4.6 m²/g
2 h	14.4 m²/g
3 h	16.0 m²/g
5 h	18.3 m²/g

Charging / de-lithiation

Electrochemical
- Coating of cathode with LiCoO2 (80%), acetylene black (10%) and PVDF (binder, 10%)
- Assembly into a $LiCoO_2$ | Li half-cell
- Delithiation by charging to equivalent of $Li_{0.5}CoO_2$

Chemical:
- $LiCoO_2 + \frac{1}{4}K_2S_2O_8 \rightarrow Li_{0.5}CoO_2 + \frac{1}{4}K_2SO_4 + \frac{1}{4}Li_2SO_4$
- Stirring at 60°C in $K_2S_2O_8$ solution for 48 h

Cathode Thermal Stability

Thermogravimetric analysis (TGA) of charged cathode – 25 to 400°C at 5 K/min, held 1 h at 400°C. Performed under Argon atmosphere. Evolved gases were analysed by mass spectroscopy
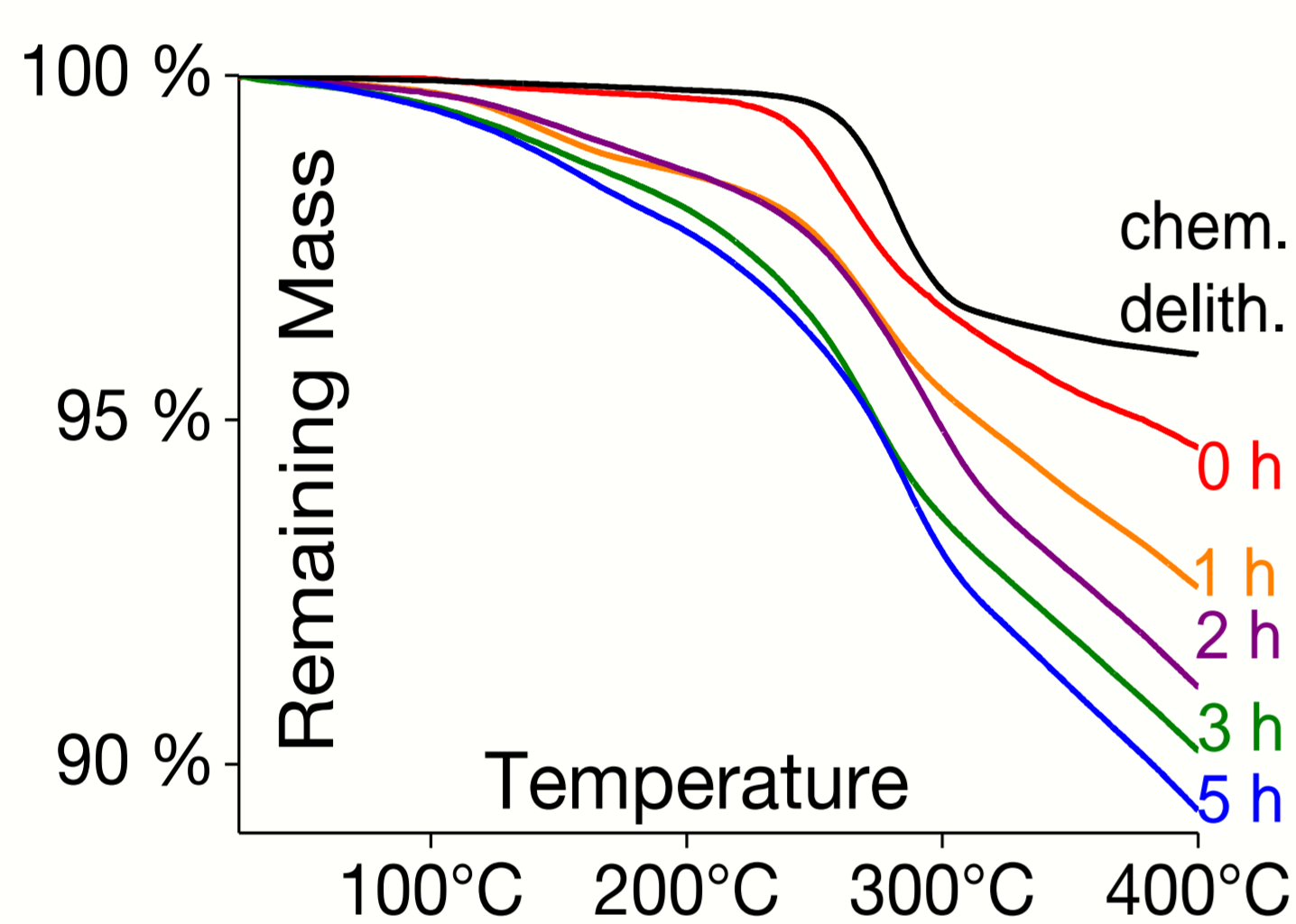
Material	Onset	Total mass loss
Chemically delithiated	260°C	4.22%
Pristine	225°C	8.59%
1 h milled	224°C	10.24%
2 h milled	222°C	11.80%
3 h milled	194°C	12.37%
5 h milled	194°C	13.54%

- Higher surface area leads to lower onset temperature
- Total amount of decomposed mass increases with surface area
- Oxygen followed by carbon dioxide detected from decomposition of pristine cathode
- O_2 reacts with acetylene black in cathode
- No oxygen from milled particle cathodes, earlier detection of CO_2
- Mass loss higher than theoretical, therefore binder decomposes too
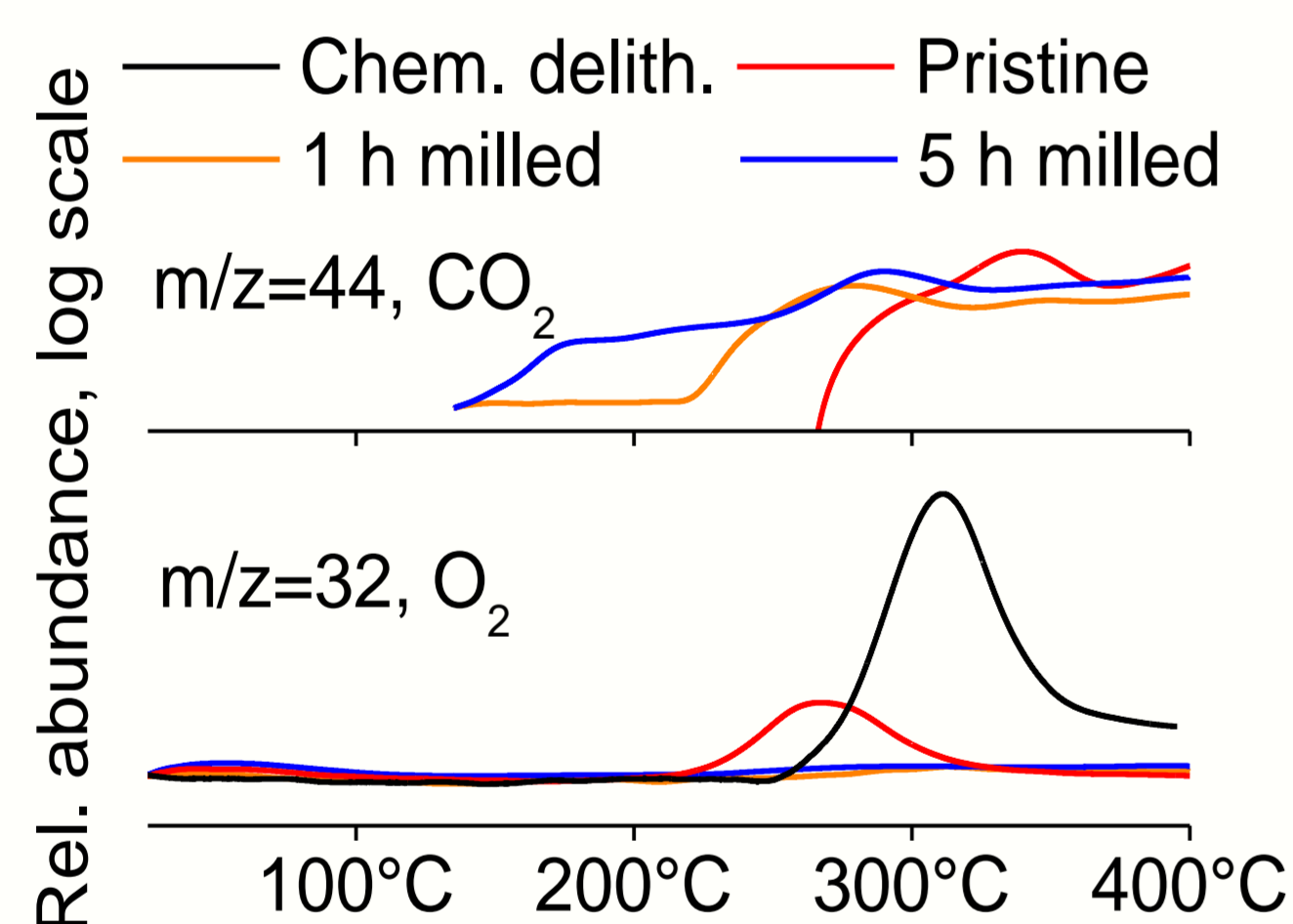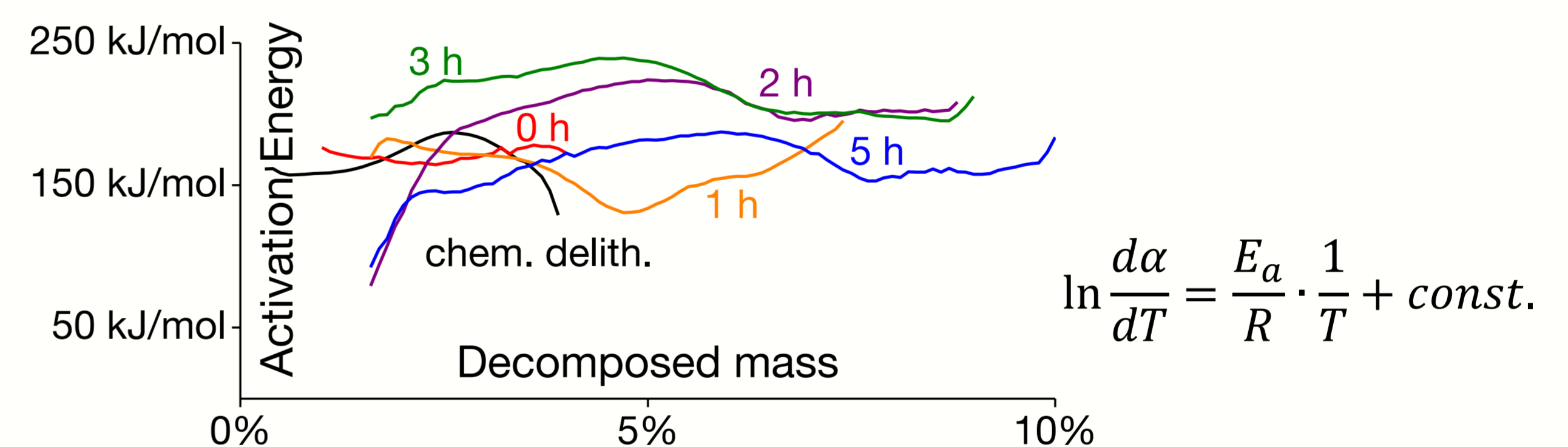
Cathode Decomposition Kinetics

Assumed reactions:
- Decomposition: $Li_{0.5}CoO_2 \rightarrow \frac{1}{2}LiCoO_2 + \frac{1}{6} Co_3O_4 + \frac{1}{6} O_2$
- Burning of acetylene black: $C + O_2 \rightarrow CO_2$
- Binder decomposition (not known exactly)

Conversion (α) is proportional to mass loss ($\Delta m/m_0$)

Reaction rate equation:

$$\frac{d\alpha}{dt} = k \cdot f(\alpha) \rightarrow \beta \cdot \frac{d\alpha}{dT} = k_0 \cdot \exp(E_a/RT)$$

- TGA at different rates (β = 1,3,5,7,9 K/min) yields same conversion at different temperatures
- Activation energy (E_a) can be calculated at various values of conversion
- Calculation independent from reaction model ($f(\alpha)$)

$$\ln\frac{d\alpha}{dT} = \frac{E_a}{R} \cdot \frac{1}{T} + const.$$

Activation energy as function of decomposed mass fraction

- No dependance of reaction kinetics on surface area can be ssen

Stability of Cathode-Electrolyte System

Accelerating Rate Calorimetry (ARC) of 32 mg charged cathode + 16 µl electrolyte (1M $LiPF_6$ in 1:1 EC/DMC)

Material	Onset	Max rate	Time to max rate
Pristine	306°C	3.2°C/min	6 min 36 s
5 h milled	240°C	1.9°C/min	2 s
	300°C	3.2°C/min	1 min 35 s
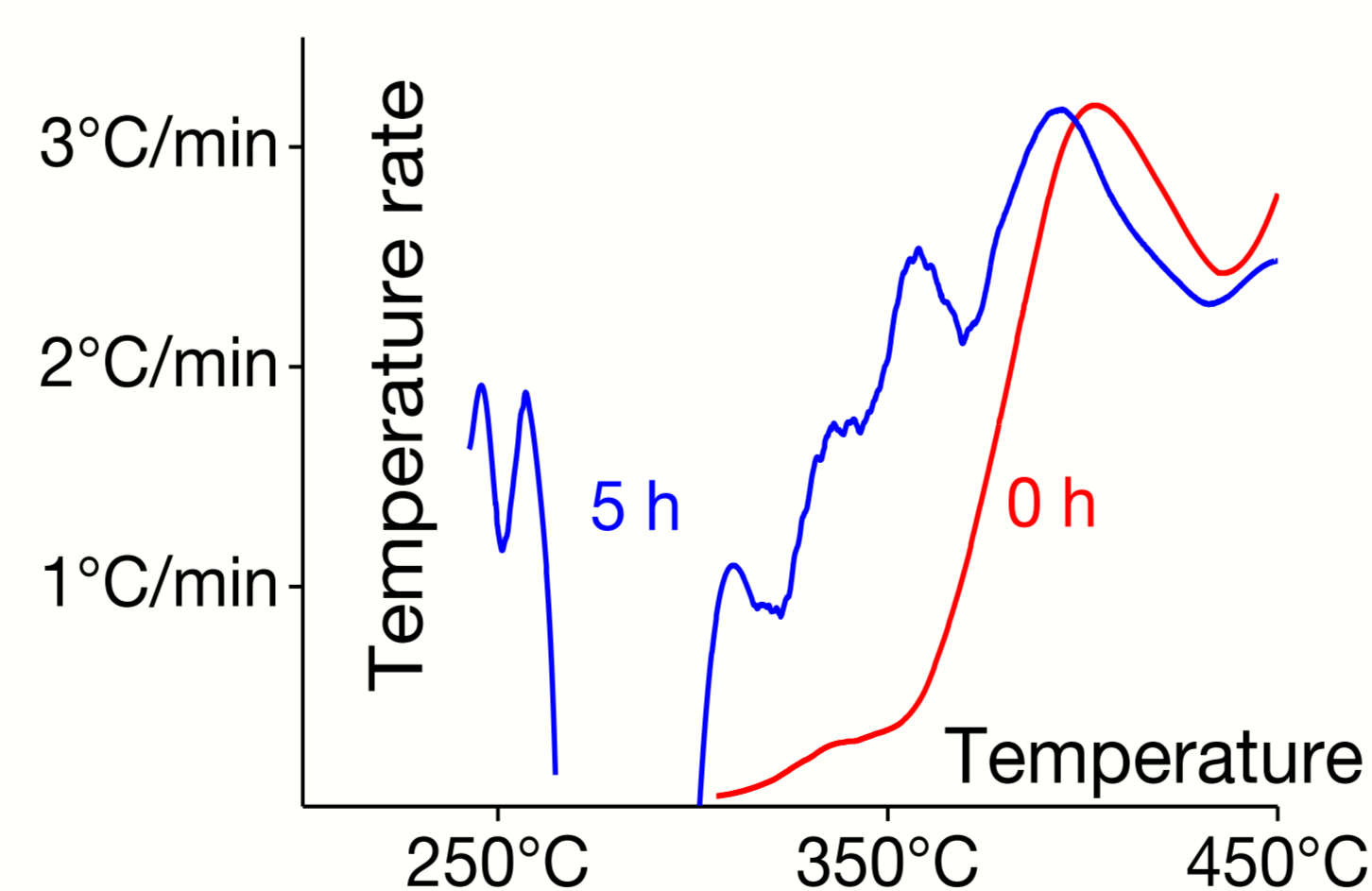
- Single exotherm with slow onset for pristine cathode
- Very steep reaction onset for cathode of milled particles
- Two reaction exotherms in case of milled LiCoO2

Conclusions

- Higher surface area reduces thermal stability of $LiCoO_2$ cathode
- In case of milled particles, all released O_2 reacts in the cathode to form CO2
- Cathode-electrolyte system is thermally less stable with higher $LiCoO_2$ surface area

Prospects

- Alternative ways of surface area increase (synthesis from precursors)
- Comparison with other cathode materials, electrolytes and additives
- Investigation of anode materials