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Safer Sodium Battery: Thermal and electrochemical studies of Na-ion based batteries

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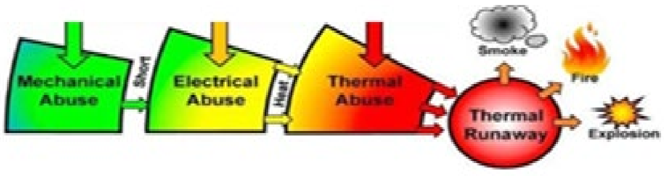
Content:

- Motivation
- Thermophysical characterization of P2-type structure $Na_{0.53}MnO_2$ cathode material
- Electrochemical performance of Half cell & Full cell
- Full cell assembly and electrochemical investigation
- Heat generation test by means of Tian-Calvet MS80 calorimeter –Half & Full cells
- Conclusions and Outlook

Safety Aspects

Safety is a prerequisite for scaling-up and market acceptance of new battery technologies



Identification of guiding principles for the safe combination of materials and for safe cell operation. involving improvement of safety by cell design

- Holistic safety assessment of Post-Li systems
- Investigation of thermal behavior and reaction mechanisms
- Novel combined electrochemical-calorimetric characterization techniques
- Fast feedback for cell producers for safe cell upscaling

Thermophysical Characterization:

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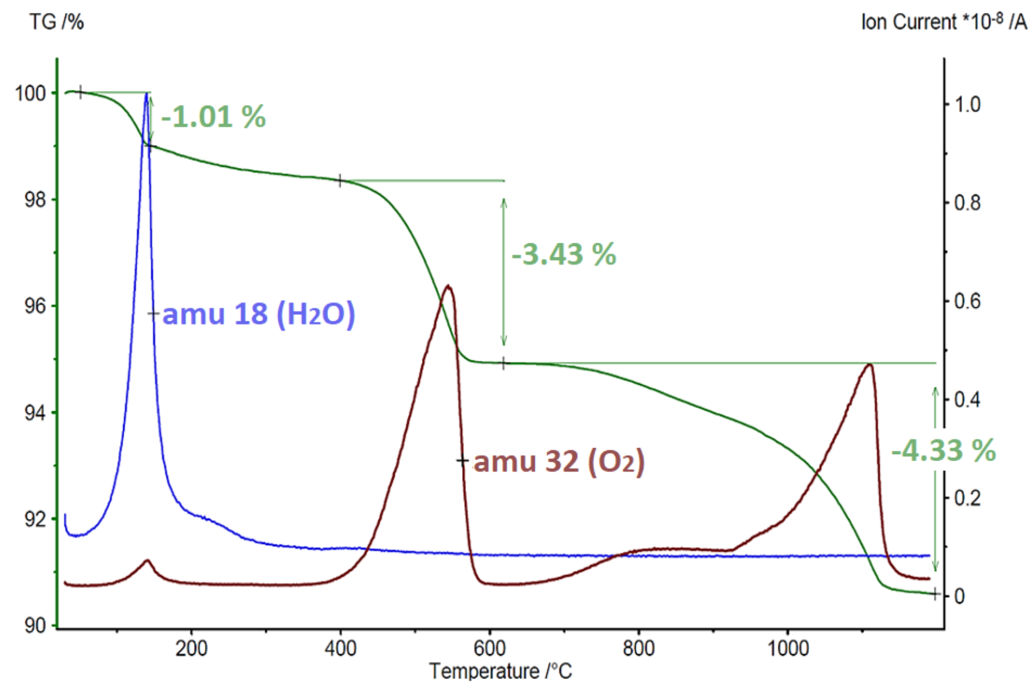
Test run profile (TGA-MS):
$Na_{0.53}MnO_2$ powder material under Ar atmosphere (50 ml/min) with heating rate of 10 K/min up to 1200°C.

1st mass loss/change:
represents the presence of water/moisture, sharp H_2O peak was observed at 100 °C.

2nd & 3rd mass loss/change:
at onset temperature of 400°C shows the thermal decomposition of the compound by evolving O_2 molecules and followed by further evolving of O_2 at high temperature.

Sodium manganese oxide ($Na_{0.53}MnO_2$) decomposes into $Na_{0.53}Mn_2O_3$ and $Na_{0.53}Mn_3O_4$ species as reported in literature



K. Terayama and M. Ikeda, Study on Thermal Decomposition of MnO_2 and Mn_2O_3 by Thermal Analysis, Trans. Of Japan Inst. Of Metals, Vol. 24 (11), (1983), pp 754-758

Thermophysical Characterization:

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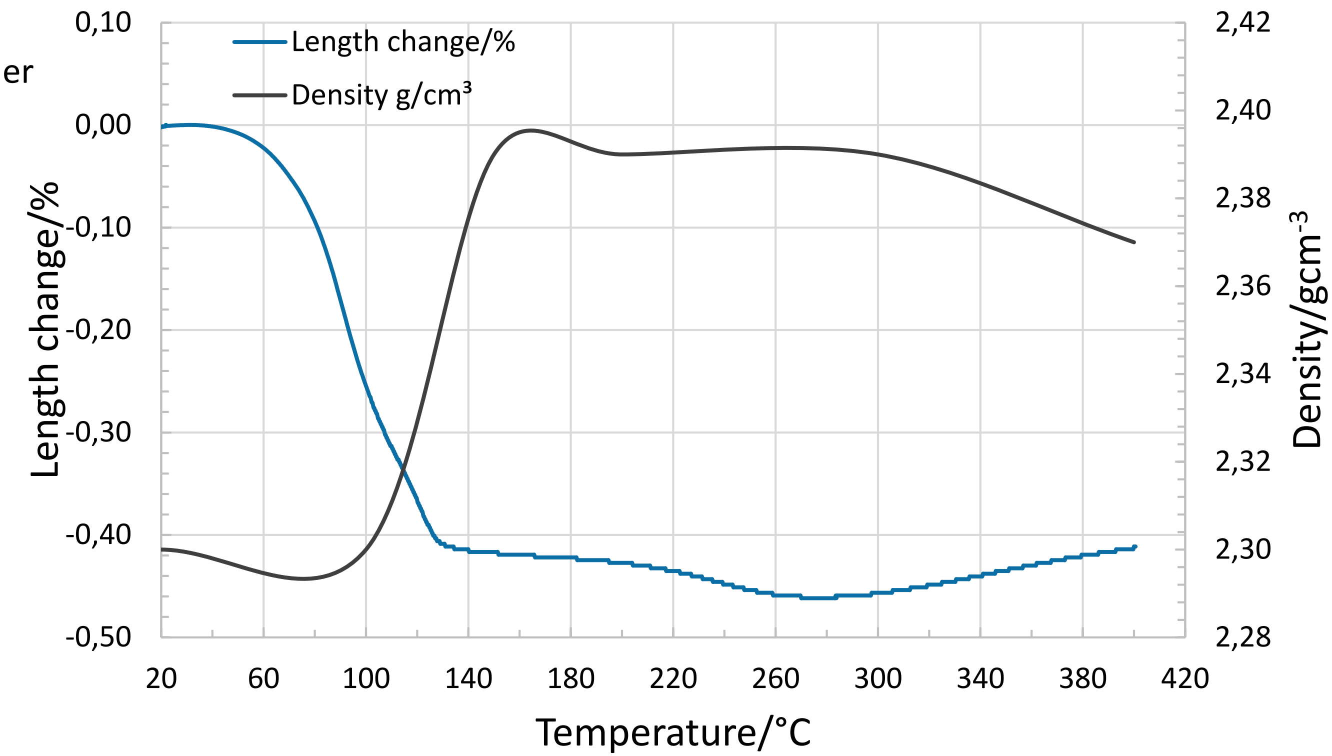
Test run profile (Dilatometry):
Pressed pellet (6 mm diameter) $Na_{0.53}MnO_2$ powder material under He atmosphere (50 ml/min) with heating rate of 2.5 K/min up to 400°C.



Density increases until 150°C, which is the result of water evaporation. After water evaporation, density was more or less constant and from 300°C specimen started to expand by evolving of little O2, subsequently a slight decrease in density can be seen.

Thermophysical Characterization:

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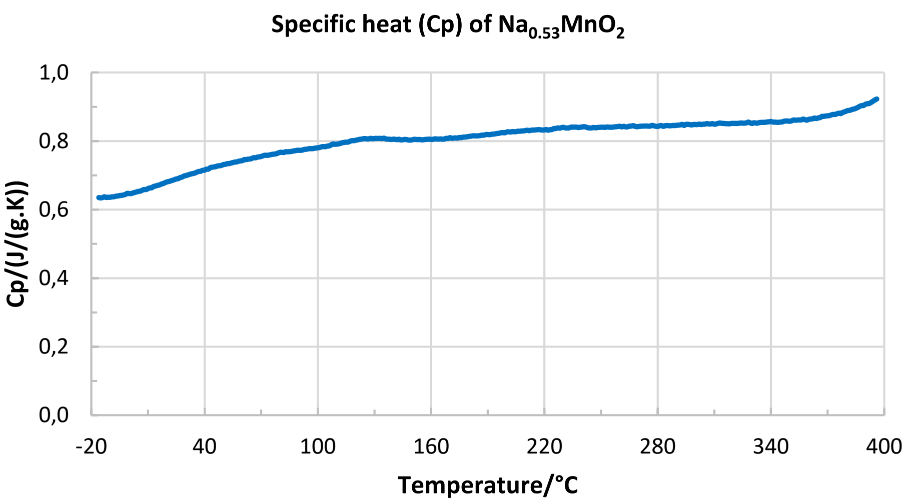
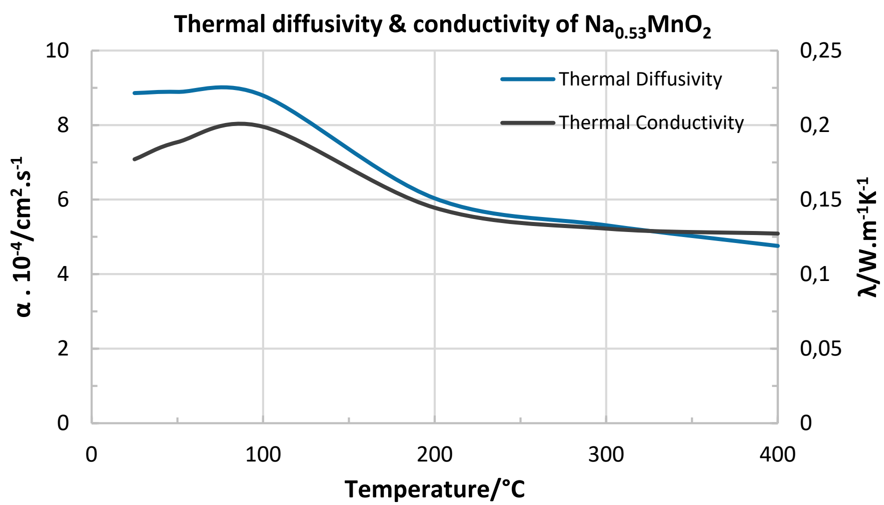
Test run profile (DSC):
Specific heat (Cp): $Na_{0.53}MnO_2$ powder material under Ar atmosphere (100 ml/min) with heating rate of 10 K/min

Test run profile (LFA):
Thermal diffusivity: $Na_{0.53}MnO_2$ powder material under vacuum with heating rate of 10 K/min





Thermal conductivity of cathode material was calculated corresponding to measured thermal diffusivity, specific heat and density. Such data are highly relevant and important for thermal simulation studies of thermal management and thermal runaway in all type of batteries, because the allow the determination of the released heat of the materials both under normal use and abuse conditions.

Half cell $Na_{0.53}MnO_2$:

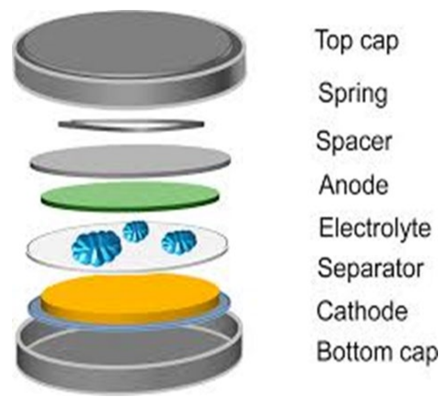
Assembling of the Coin cell

Coin cell CR2032

Cathode

90 wt% $Na_{0.53}MnO_2$
5 wt% PVDF
5 wt% Carbon Black

Active mass: approx. 6.9 mg /(13mm Ø)



Anode

Pure Na Metal
Electrolyte: 1M NaClO4
[EC:DMC:EMC (vol. 1:1:1) 2% FEC]

Separator GFA (Whatman)

Electrochemical investigation of Half cell $Na_{0.53}MnO_2$:

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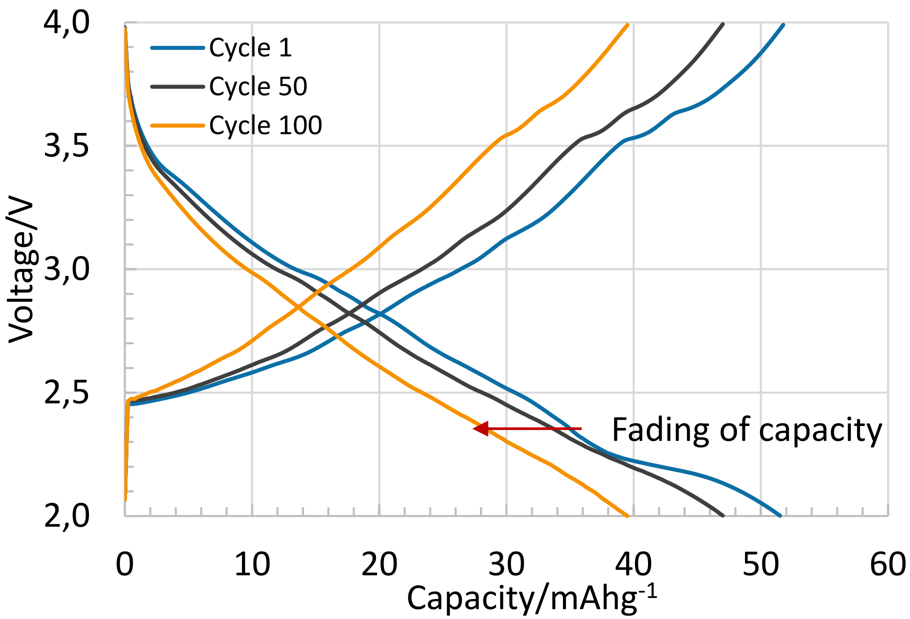
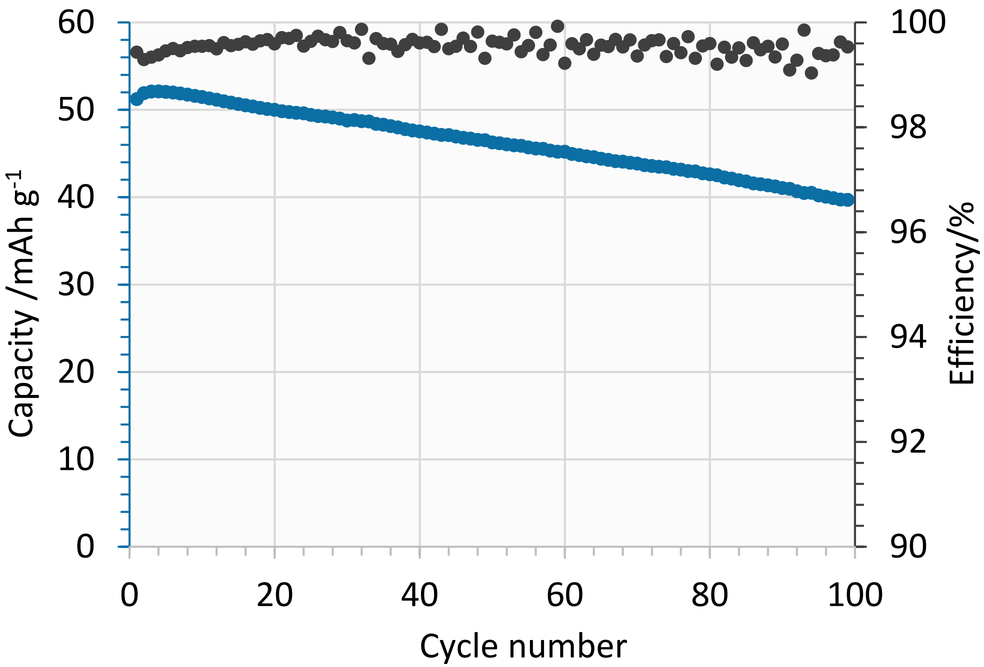
Cyclability **(0.5C rate-100 cycles)**





Coulombic efficiency > 99.50 %
Capacity depletion after 100 cycles ~ 20%

CR2032 half coin cell:

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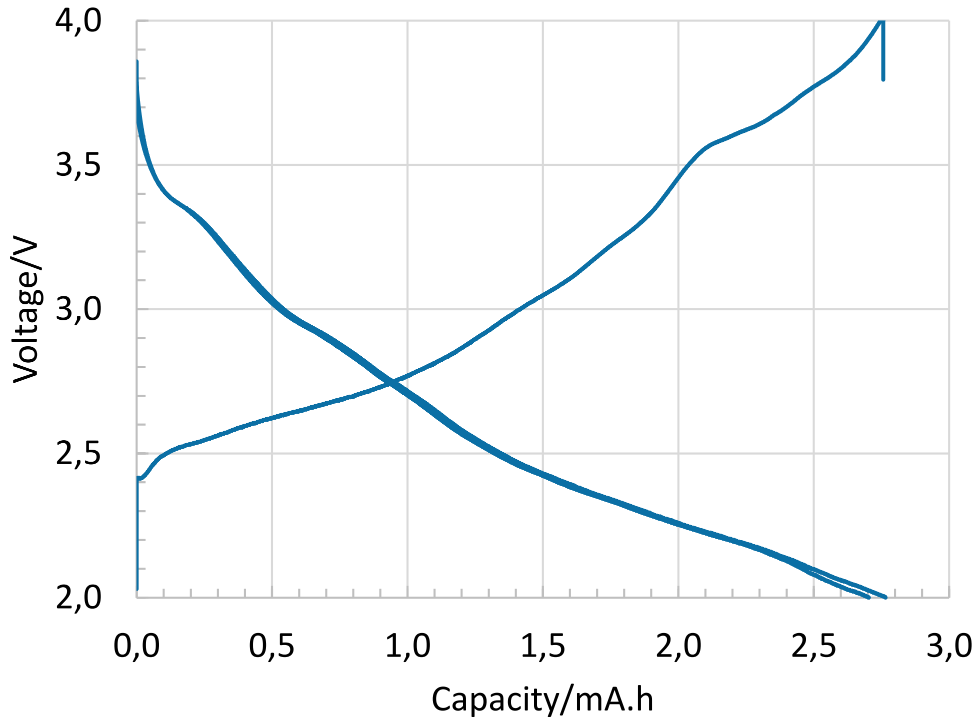

Half cell	Capacity/mA.h
$Na_{0.53}MnO_2$	2.8

Cathode material loading = 27 - 28 mg/cc

Heat generation test in Half cell $Na_{0.53}MnO_2$:

MS80 3D Calvet calorimeter (Setaram Instrumentation)

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Test Run Profile:

Charge parameter

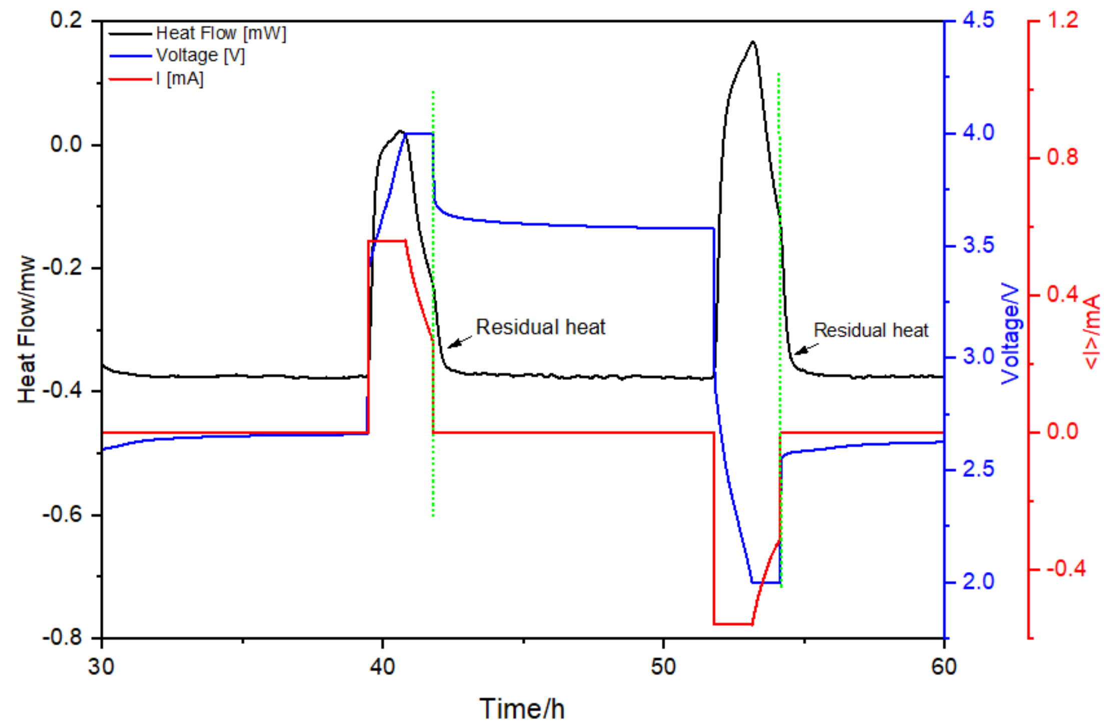
Constant Current, Constant Voltage (CCCV) Profile at 25°C, CV-Step at 4.0 V (I < C/20 or t > 60min)

V_{max} = 4.0

Discharge parameter

Constant Current, Constant Voltage (CCCV) Profile at 25°C, CV-Step at 2.0 V (I < C/20 or t > 60min)

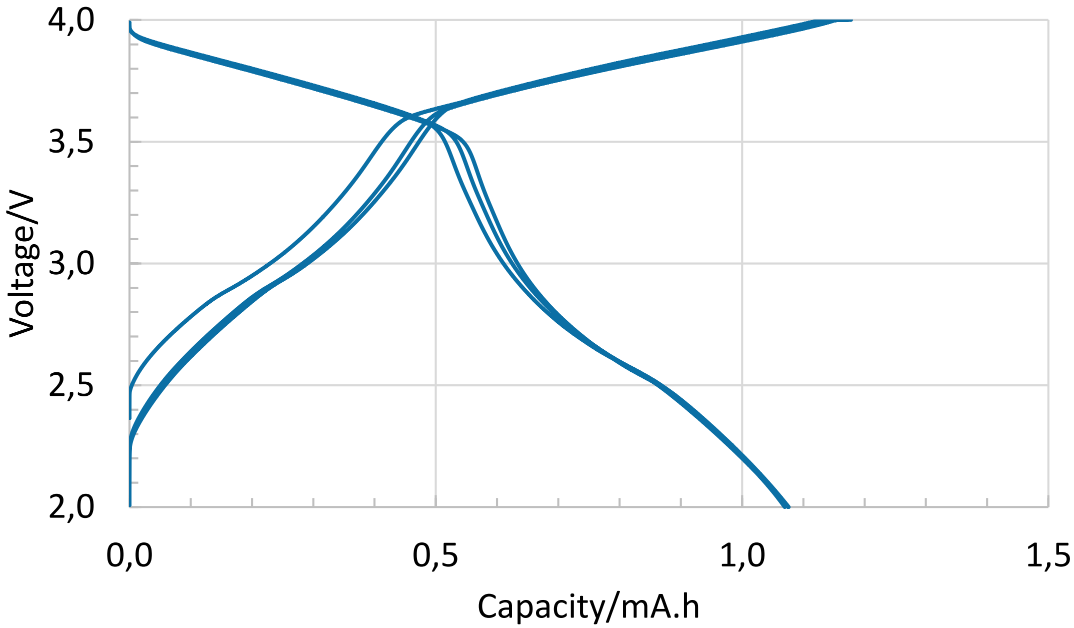
V_{min} = 2.0



Vessel Ø: 32 mm

Current Flow (2.8 mAh)	Capacity mA.h	Heat generation charge (J)	Heat generation discharge (J)
0.2 C	1.16±0.01	2.65 ±0.03	3.70 ±0.03

CR2032 full coin cell



Full cell	Discharge capacity /mA.h
$Na_{0.53}MnO_2$	1.15

Cathode material loading = 27-28 mg/cc
Anode HC loading = 13 - 14 mg/cc

Heat generation test in full cell $Na_{0.53}MnO_2$/HC:

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MS80 3D Calvet calorimeter (Setaram Instrumentation)

Test Run Profile:

Charge parameter

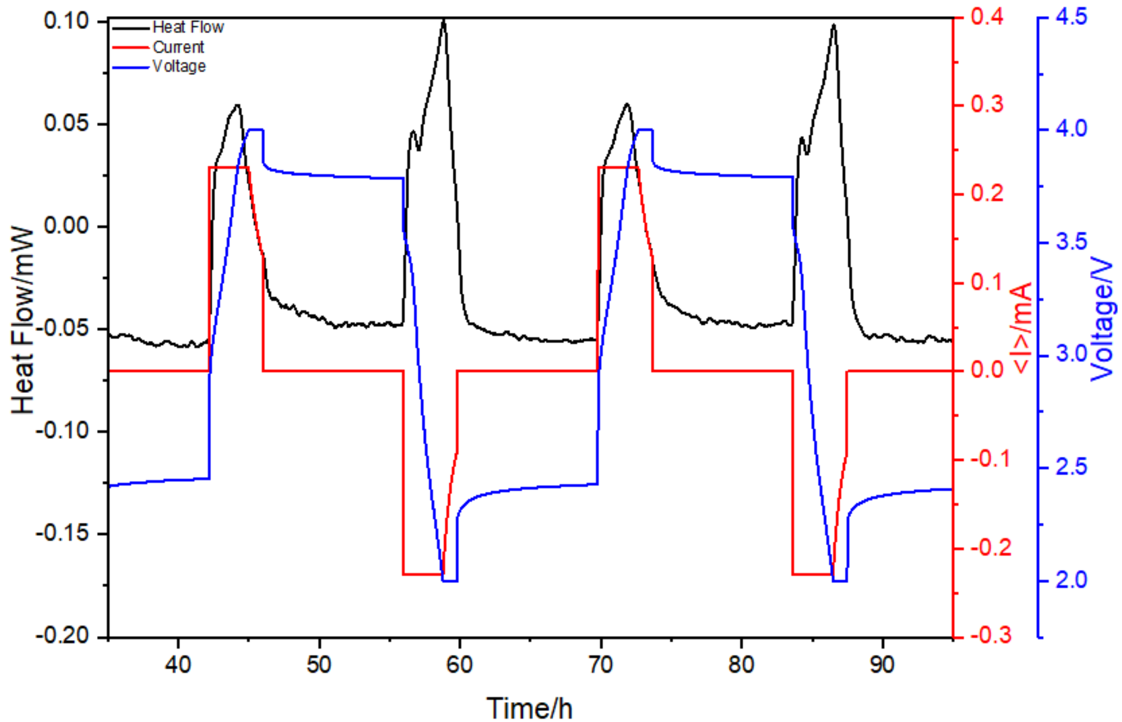
Constant Current, Constant Voltage (CCCV) Profile at 25°C, CV-Step at 4.0 V (I < C/20 or t > 60min)

V_{max} = 4.0

Discharge parameter

Constant Current, Constant Voltage (CCCV) Profile at 25°C, CV-Step at 2.0 V (I < C/20 or t > 60min)

V_{min} = 2.0



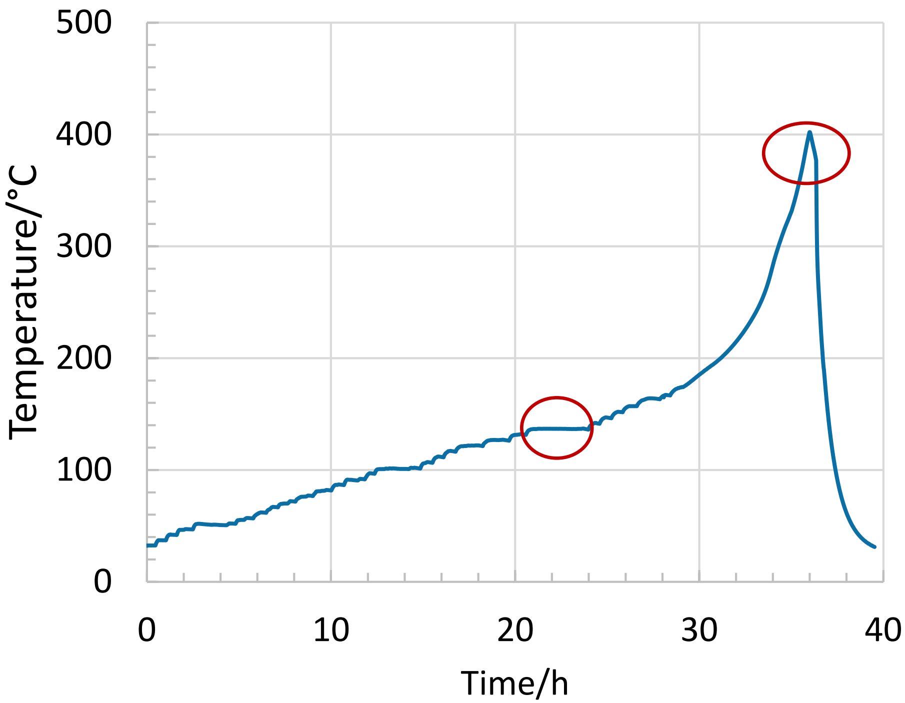
Vessel Ø: 32 mm

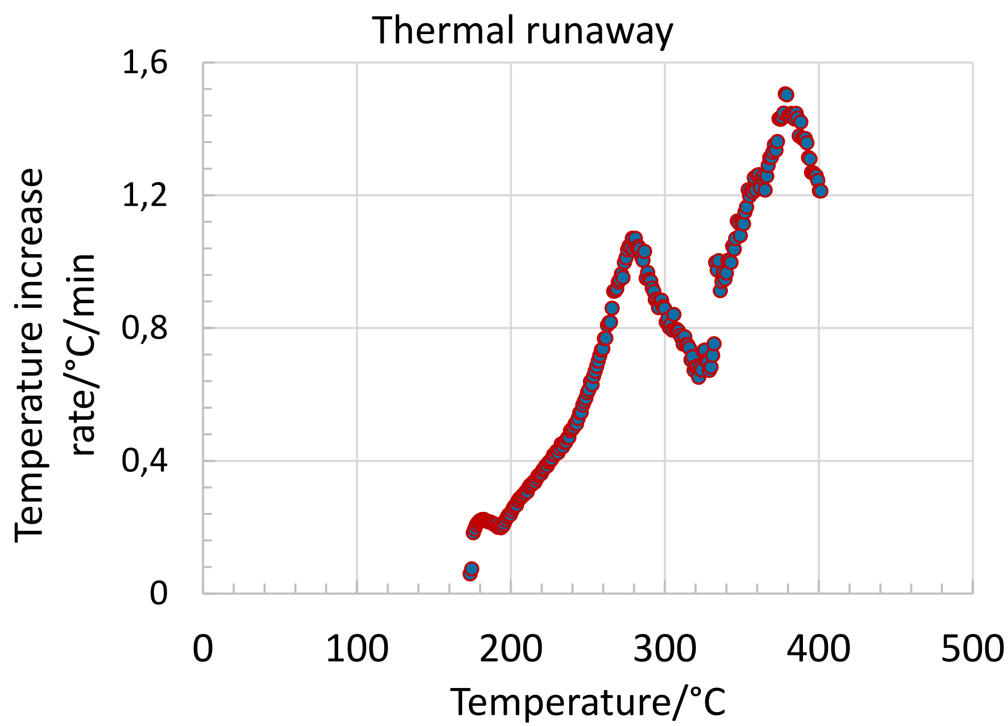
Current Flow (1.15 mAh)	Capacity mA.h	Heat generation charge (J)	Heat generation discharge (J)
0.2 C	0.82±0.04	1.31 ±0.03	1.49 ±0.01

Safety Test:

Accelerating Rate Calorimetry (ARC):

- Heat-Wait-Seek (HWS) test $Na_{0.53}MnO_2$/HC
  - Set temperature range 30 - 450°C
  - Heating up with 5°C
  - Threshold sensitivity 0.02 °C/min
  - Waiting time 15 min





- >100 °C decomposition of SEI layer
- >160 °C exothermic reactions between the electrolyte and the cathode
- >200 °C decomposition of the electrolyte.

The thermal runaway events of fully charged coin cells can reach 400 °C with a temperature rate of 1.5 °C/min.

Electrolyte $NaClO_4$ (EC:DMC:EMC 1:1:1) + 2% vol. FEC

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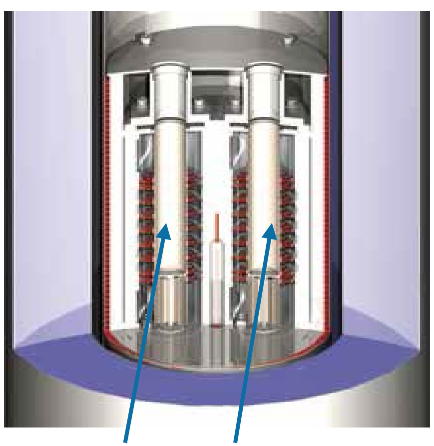
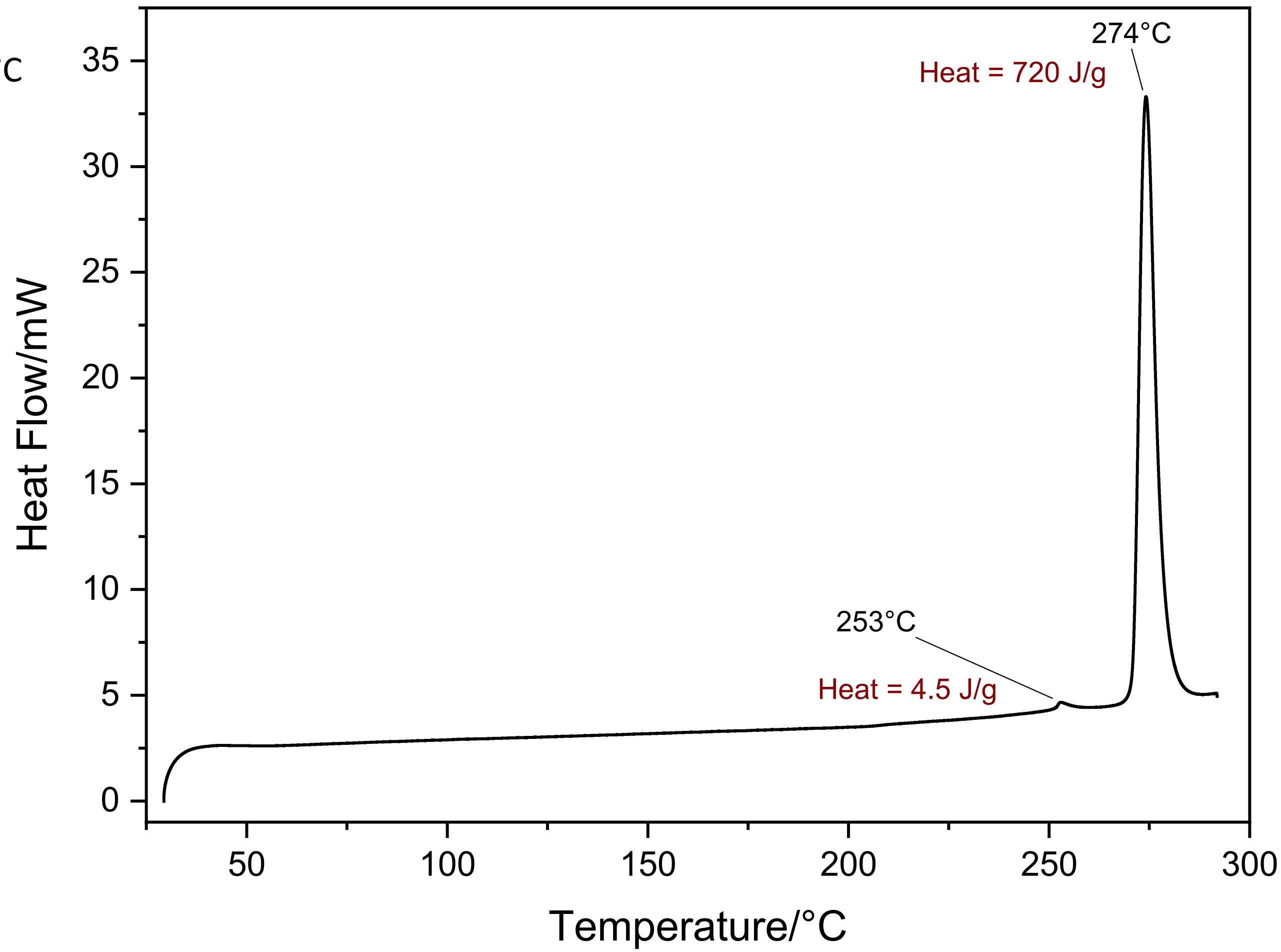
C80 3D Calvet Calorimeter (Setaram Instrumentation)

- Set temperature range 30 - 300°C
- Heating up with 0.5 K/min
- Under sealed container in Ar atmosphere



Vessel Ø: 15 mm



Conclusions:

- Cathode material is thermally not stable at high temperature; decomposition starts at 400°C
- Thermophysical properties of selected material was measured and thermal data were generated.
- Half and Full coin cells were investigated and showed good electrochemical performance.
- Heat generation during charge/discharge in Half & full coin cells were measured.
- Thermal runaway test (Heat-Wait-Seek) of Half cell and Full coin cell were executed and exothermic reactions were identified.

Outlook:

- Heat generation test of individual components. cathode, anode & electrolyte
- Outgasing analysis during thermal runaway test and pressure measurement.

Acknowledgement:

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