Institute of Engineering Thermodynamics

Thermal stability studies of lithium-intercalated electrode materials with accelerating rate calorimetry (ARC)

Andreas M. Dreizler, Sina Klostermann, Maximilian Wolf, Norbert Wagner and K. Andreas Friedrich

German Aerospace Center (DLR), Pfaffenwaldring 38-40, D-70569 Stuttgart, Germany; andreas.dreizler@dlr.de

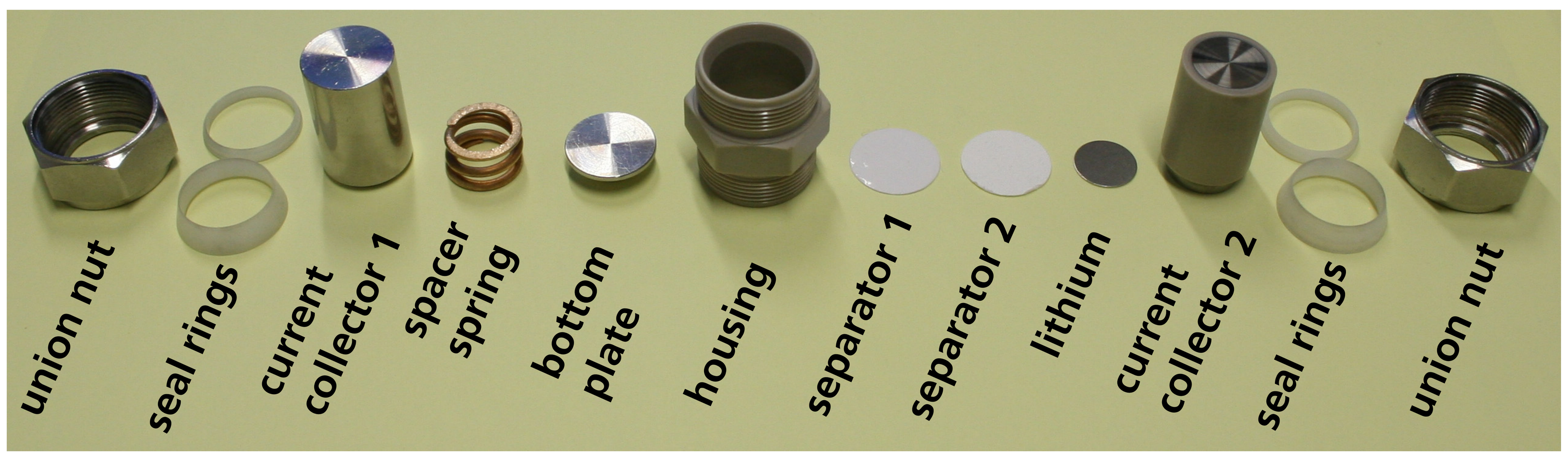
Introduction:

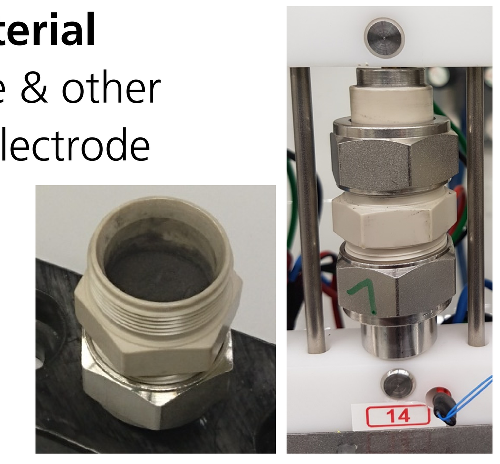
Lithium-ion battery cells for portable electronic and automotive applications have to be carefully designed and engineered to be safe under different thermal and electrical abuse conditions. Some electrode materials will approach market introduction soon, while others still require some basic groundwork in materials research. In order to produce market readiness battery materials and cells, it is necessary to improve their safety characteristics.

In general, it is extremely challenging to design large lithium-ion cells which pass the same safety test criteria that are applied for smaller lab-sized cells. There is often a big lack between research results on smaller lab-sized and large-sized battery cells or even stacks since the thermal behavior can differ fundamentally due to the various cell housings. Therefore, our goal is to provide a method to test the reactivity of samples that containing small amount of electrode material in electrolyte to make quantitative predictions about the safety of larger and more application-oriented lithium-ion battery cells subjected to thermal or electrical abuse.

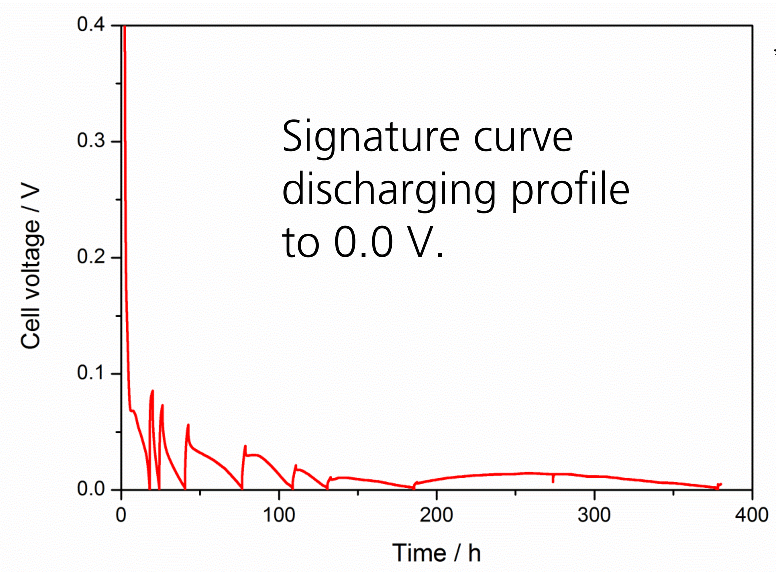
An accelerating rate calorimeter (ARC), which is an adiabatic calorimeter, is a very advantageous device for such studies. In this work, an ARC is used to measure the thermal stability of lithiated electrode materials in standard electrolytes under adiabatic conditions. In this context, the lithium content is varied in a wide range in order to represent different states of charge in the battery. Measurements are carried out to determine the effects of the lithium content of the electrode as well as the initial heating temperature on thermal stability. In the first instance, the study concentrates on anode materials, in particular graphite and silicon-graphite composite electrodes. First results show that the self-heating rate depends strongly on the amount of intercalated lithium in the electrode material, whereby the reactivity increases with increasing lithium content.

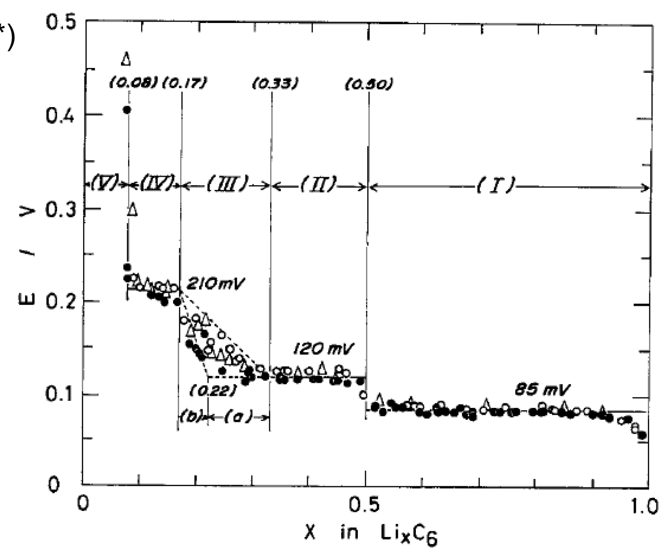
Lithiation of graphite material: self-made "Swagelok" cell





- Self-made **"Swagelok" cell** for **lithiation** of **graphite material**
- Possible **Powder materials:** graphite, NCM, Si/C composite & other
- **Lithium metal** (negative electrode): Li source & reference electrode
- **Separator: Celgard® 2320** & **fiberglass** (Ø 22 mm)
- **Standard electrolyte: EC/DEC 50:50 (v/v)** and **1 M $LiPF_6$** conducting salt
- Cell assembling in **glovebox** under argon atmosphere





*) Figure taken from reference [1]; natural graphite

- **Stepwise lithiation** of electrode materials via **battery test system "BaSyTec"** → maximum 12 V, 16 A, 200 W and 16 channels in parallel
- **Reversible cell potential** depends on the **Li-content x** of the graphite material Li_xC_6
- **Target potentials** of **lithiated mesocarbon microbead** (MCMB) material [2]: a) 0.0 V → $Li_{0.8}C_6$; b) 0.089 V → $Li_{0.45}C_6$; c) 0.127 V → $Li_{0.2}C_6$

ARC sample preparation: outline of necessary steps

1) Pre-assembling Swagelok cell
2) Fill in dry electrode active material (graphite)
3) Glovebox: add Li & electrolyte; Finish cell assembling
4) Signature curve discharge to the appropriate voltage
5) Remove cell from charger; Open cell & recover pellet
6) Grind pellet lightly and pour into sample tube
7) Add excess electrolyte; Stick tube and cap together
8) Mount tube in the calorimeter chamber
9) Measure thermal stability of sample in the ARC

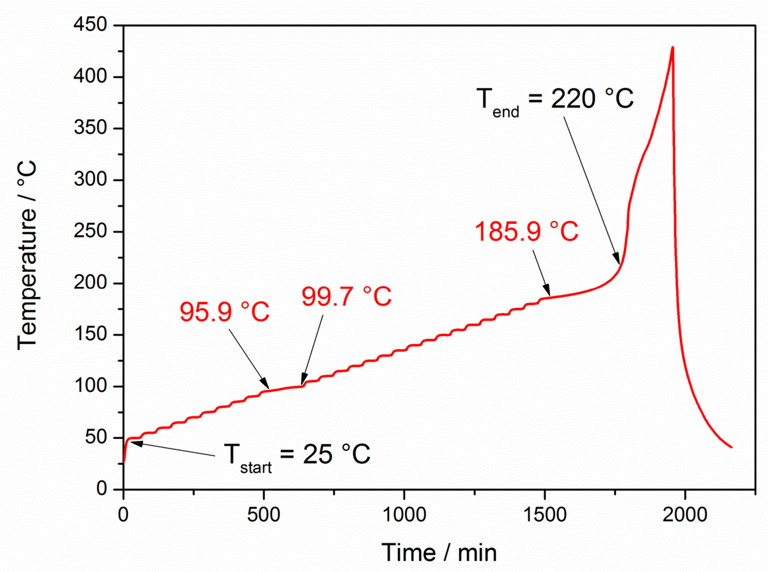
Accelerating rate calorimetry (ARC): thermal stability tests

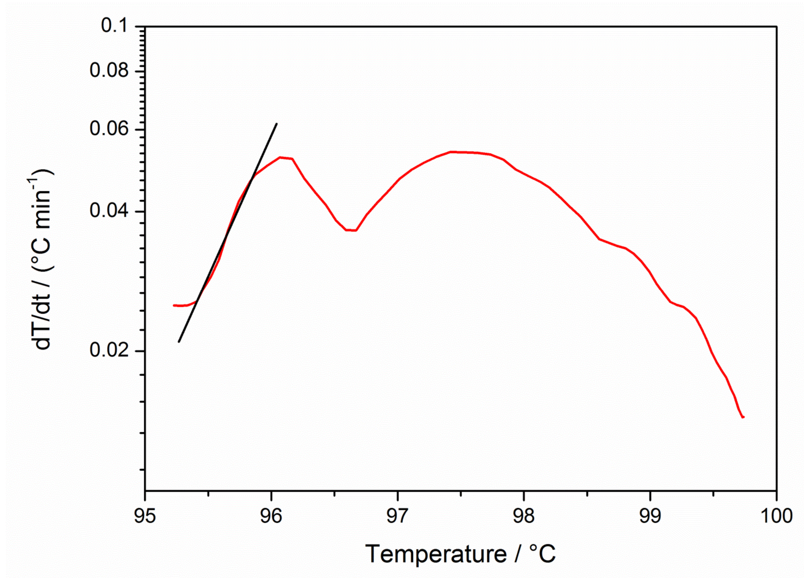
Battery lab test equipment:

- Accelerating Rate Calorimeter "NETZSCH ARC® 254"
- Impedance test system "ZAHNER-Elektrik IM6"
- Battery test system "BaSyTec"

Goal of thermal stability tests:

→ **Thermal runaway predictions** of **battery cells** on the basis of ARC materials investigation.





ARC measurement of lithiated graphite

- **Heat-Wait-Search** mode: ΔT = 5 °C
- Temperature range: **50–220 °C**
- 80 % Li-content: **$Li_{0.8}C_6$**
- **Exothermic reaction: 95.9–99.7 °C** → **conversion** of **metastable solid electrolyte interface (SEI)** to **stable SEI**

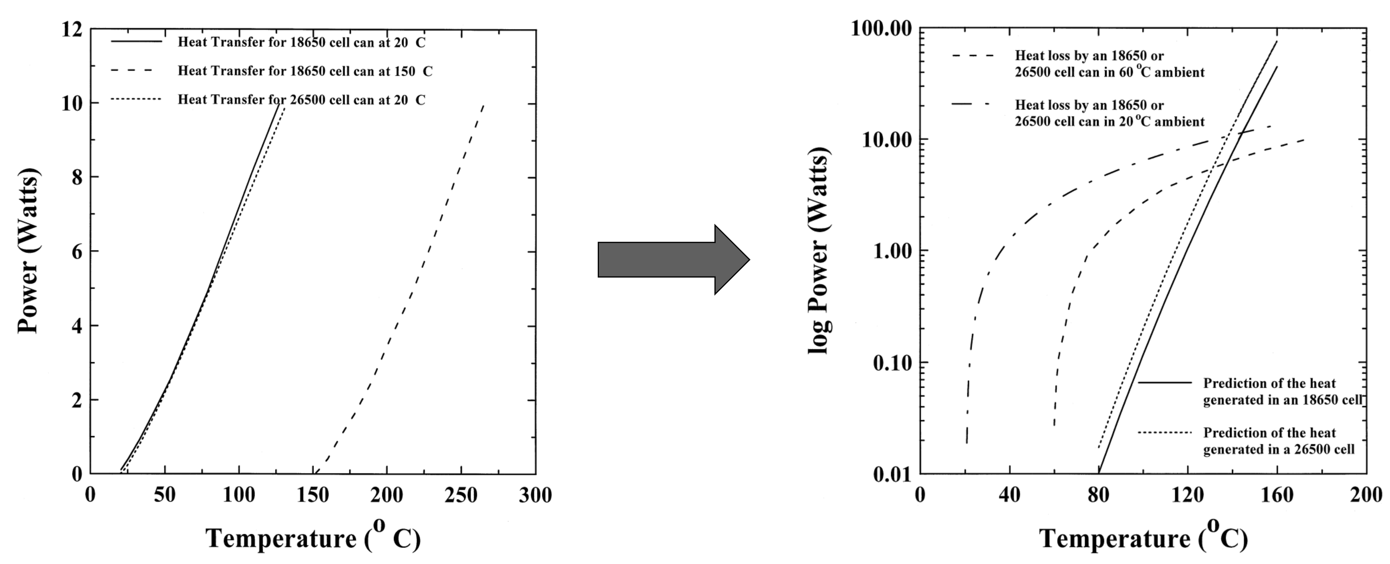
Initial self-heating rate (SHR) profile:

- Dependency on **initial start temperature** in ARC experiment
- Calculation of **activation energy** for exothermic reaction → different ARC start temperatures → **Arrhenius**-like plot

$$\ln(dT/dt) \approx \ln(A\Delta T) - E/(k_B T)$$

Upscaling of ARC results: thermal behavior of battery cells

Goal: Prediction of thermal (runaway) behavior of different battery cells.



*) Figures taken from reference [3]

Upscaling requirements:

- **Heat dissipation** of **cell housing** has to be known.
- **Existing** heat dissipation **data** for **cylindrical cells 18650** and **26500** from literature [3].
- **Further heat dissipation data** for other cells (e.g. pouch bags) via **oven experiments**.

$$P_{ARC} = c_{ARC} \cdot m_{ARC} \frac{dT}{dt}$$

$$P_{battery} = P_{ARC} \frac{m_{battery}}{m_{ARC}}$$

References:

[1] T. Ohzuku, Y. Iwakoshi, K. Sawai, J. Electrochem. Soc., **140** (1993) 2490–2498.
[2] M. N. Richard, J. R. Dahn, J. Electrochem. Soc., **146** (1999) 2068–2077.
[3] M.N. Richard, J.R. Dahn, Journal of Power Source, 79 (1999) 135-142.

Acknowledgments:

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