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Peltier heats of lithium-ion battery electrodes

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Li-ion batteries

Heat sources in Li-ion batteries

- When charging or discharging a battery, heat is released (or absorbed).
- Why is this important?

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Heat sources in Li-ion batteries

- When charging or discharging a battery, heat is released (or absorbed).
- Why is this important? Safety, ageing [1]
- The main heat effects are:
  - Irreversible heat effects: Ohmic resistance in the bulk phases and at the interfaces
  - Reversible heat effect: related to the entropy change of the cell (if the cell is assumed to be isothermal)

The electrode reaction occurs at two separate locations in the battery; the anode and the cathode. The reversible heat effect is therefore actually two local effects, the Peltier heat of the interfaces.

Peltier heats in Li-ion batteries

$$ {}^{s} = \left. \frac{J_q^{0i} \quad J_q^{0o}}{j/F} \right!_{T^s = T^i = T^o} \qquad (1)$$

- Reports scarce in literature
- Entropy changes in Li-ion batteries have been reported for many cells
- Only the Peltier heats give information on what happens locally at the electrode surface
- Why are local heat sources important?

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How to measure the Peltier heats

- Peltier heats are difficult to measure because it is an incremental change at the interface
- There are two heat sources at the interface; resistance and Peltier heat
- Through non-equilibrium thermodynamics we have [2]:

$$ = T \left(\frac{}{T} \right)_{j=0} \tag{2}$$

- $\left(\frac{}{T} \right)_{j=0}$ is the Seebeck coefficient of a symmetric cell made from the same materials as the two bulk phases associated with the interface [3]. $j = 0$ means open circuit conditions.

[2] K.S. Førland, T. Førland and S.K. Ratkje,Irreversible thermodynamics: theory and applications, John Wiley & Sons Inc,1988

[3] Richter, Frank and Gunnarshaug, Astrid and Burheim, Odne Stokke and Vie, Preben J. S. and Kjelstrup, Signe, Single Electrode Entropy Change for $LiCoO_2$ Electrodes, ECS Trans., 2017, vol. 80, 10, 219-238.

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How to measure Peltier heats

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How to measure Peltier heats

Peltier heats of lithium-ion battery electrodes

For an interface between an Li- electrode and LiX salt/n-carbonate component (uniform) electrolyte:

$$= \quad TS_{\mathrm{Li}} \qquad TS_{\mathrm{e}} + TS_{\mathrm{Li}^+} + \sum_{i=1} t_i q_i \tag{3}$$

S_{Li} - entropy liberated from the reaction
S_{e} - entropy transported by the charge carrier in the electrodes
S_{Li^+} - entropy transported from the interface to the electrolyte by Li^+
t_i - transference coefficient of component i
q_i - heat of transport of component i in the electrolyte

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Peltier heats of lithium-ion battery electrodes

For an interface between an Li- electrode and LiX salt/n-organic carbonate components (uniform) electrolyte:

$$= \quad T S_{\mathrm{Li}} \qquad T S_{\mathrm{e}} + T S_{\mathrm{Li}^+} + \sum_{i=1}^{n} t_i q_i \tag{8}$$

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S_{e} - entropy transported by the charge carrier in the electrodes - will be different for different electrodes

S_{Li^+} - entropy transported from the interface to the electrolyte by Li^+ - will be different for different electrolytes

t_i - transference coefficient of component i - will be different for different electrolytes

q_i - heat of transport of component i in the electrolyte - will be different for different electrolytes

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Peltier heat of lithium-ion battery electrodes

If we assume that $S_{1}\ \mathrm{e}$ $S_{2}\ \mathrm{e}$ and close to isothermal conditions:

$$_{1} \quad _{2} = T \quad S_{Li} \tag{9}$$

This is the reversible heat production for the full cell per faraday of charge.

We only need to measure the Peltier heats of one electrode if S for the full cell is known.

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Summary

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- The Peltier heats are the reversible effects local to the electrode surface
- The Peltier heats of one electrode will depend on the composition of the electrodes and electrolyte (and the composition of the electrodes change when discharging/charging the battery) - we need a lot of measurements
- If the entropy change of a full cell is known we need only measure the Peltier heats of one of electrodes

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