

Peltier heats of lithium-ion battery electrodes

Astrid Fagertun Gunnarshaug^a, Signe Kjelstrup^a, Dick Bedeaux^a and Odne Burheim^b

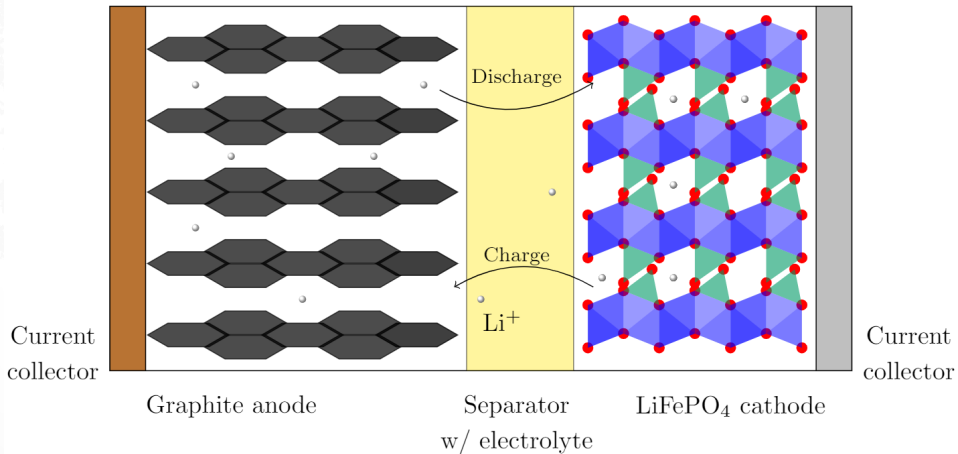
^aPoreLab, Department of Chemistry, NTNU, Trondheim, Norway

^bENERSENSE, Department of Energy and Process Engineering, NTNU, Trondheim,
Norway

30. August 2019



Li-ion batteries





Heat sources in Li-ion batteries

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



Heat sources in Li-ion batteries

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



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

$$\pi^s = - \left(\frac{J_q'^i - J_q'^o}{j/F} \right)_{T^s=T^i=T^o} \quad (1)$$

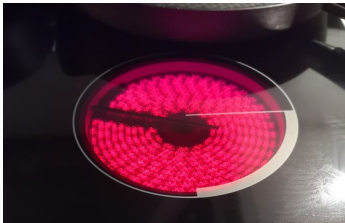
- Reports scarce in literature
- Entropy changes in Li-ion batteries have been reported for many cells
- Only the Peltier heats give information on what happens locally at the electrode surface
- Why are local heat sources important?



Peltier heats in Li-ion batteries

$$\pi^s = - \left(\frac{J_q^i - J_q^o}{j/F} \right)_{T^s=T^i=T^o} \quad (1)$$

- 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?

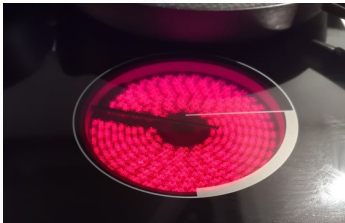




Peltier heats in Li-ion batteries

$$\pi^s = - \left(\frac{J_q^i - J_q^o}{j/F} \right)_{T^s=T^i=T^o} \quad (1)$$

- 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?



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:

$$\pi = -T \left(\frac{\Delta\phi}{\Delta T} \right)_{j=0} \quad (2)$$

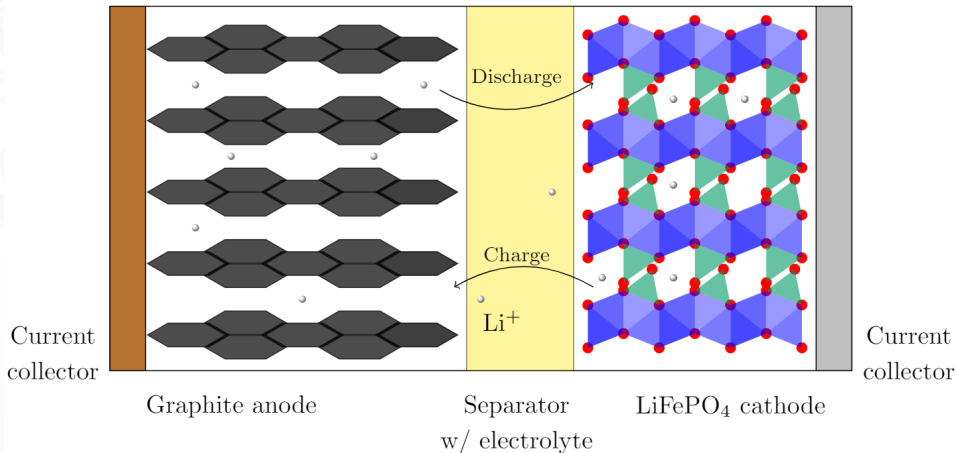
- $\left(\frac{\Delta\phi}{\Delta T} \right)_{j=0}$ is the Seebeck coefficient of a symmetric cell made from the same materials as the two bulk phases associated with the interface ³. $j = 0$ means open circuit conditions.

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

³Richter, Frank and Gunnarshaug, Astrid and Burheim, Odne Stokke and Vie, Preben J. S. and Kjelstrup, Signe, Single Electrode Entropy Change for LiCoO₂ Electrodes, ECS Trans., 2017, vol. 80, 10, 219-238.

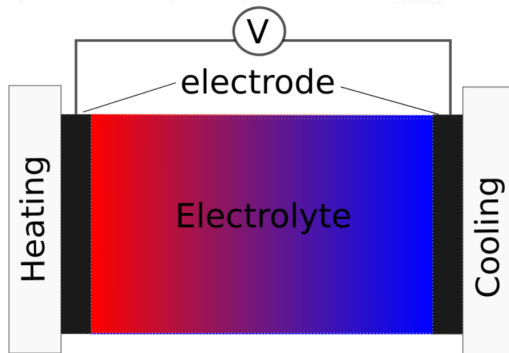
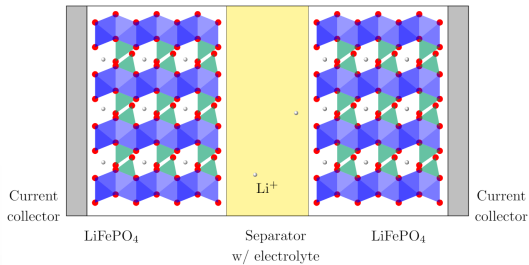


How to measure Peltier heats





How to measure Peltier heats



Peltier heats of lithium-ion battery electrodes

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

$$\pi = -TS_{\text{Li}-\theta} - TS_{\text{e}^-}^* + TS_{\text{Li}^+}^* + \sum_{i=1}^n t_i q_i^* \quad (3)$$

$S_{\text{Li}-\theta}$ - entropy liberated from the reaction

$S_{\text{e}^-}^*$ - entropy transported by the charge carrier in the electrodes

$S_{\text{Li}^+}^*$ - 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

Peltier heats of lithium-ion battery electrodes

For an interface between an $\text{Li-}\theta$ electrode and LiX salt/ n -carbonate components (uniform) electrolyte:

$$\pi = -TS_{\text{Li-}\theta} - TS_{\text{e-}}^* + TS_{\text{Li}^+}^* + \sum_{i=1}^n t_i q_i^* \quad (4)$$

$S_{\text{Li-}\theta}$ - entropy liberated from the reaction - **will be different for different electrodes and different lithiated states (state of charge of the electrode)**

$S_{\text{e-}}^*$ - entropy transported by the charge carrier in the electrodes

$S_{\text{Li}^+}^*$ - 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

Peltier heats of lithium-ion battery electrodes

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

$$\pi = -TS_{\text{Li}-\theta} - TS_{\text{e}^-}^* + TS_{\text{Li}^+}^* + \sum_{i=1}^n t_i q_i^* \quad (5)$$

$S_{\text{Li}-\theta}$ - entropy liberated from the reaction - will be different for different electrodes and different lithiated states (state of charge of the electrode)

$S_{\text{e}^-}^*$ - entropy transported by the charge carrier in the electrodes - will be different for different electrodes

$S_{\text{Li}^+}^*$ - 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

Peltier heats of lithium-ion battery electrodes

For an interface between an $\text{Li}-\theta$ electrode and LiX salt/ n -carbonate components (uniform) electrolyte:

$$\pi = -TS_{\text{Li}-\theta} - TS_{\text{e}^-}^* + TS_{\text{Li}^+}^* + \sum_{i=1}^n t_i q_i^* \quad (6)$$

$S_{\text{Li}-\theta}$ - entropy liberated from the reaction - will be different for different electrodes and different lithiated states (state of charge of the electrode)

$S_{\text{e}^-}^*$ - entropy transported by the charge carrier in the electrodes - will be different for different electrodes

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

t_i - transference coefficient of component i

q_i^* - heat of transport of component i in the electrolyte

Peltier heats of lithium-ion battery electrodes

For an interface between an $\text{Li}-\theta$ electrode and LiX salt/ n -carbonate components (uniform) electrolyte:

$$\pi = -TS_{\text{Li}-\theta} - TS_{\text{e}^-}^* + TS_{\text{Li}^+}^* + \sum_{i=1}^n t_i q_i^* \quad (7)$$

$S_{\text{Li}-\theta}$ - entropy liberated from the reaction - will be different for different electrodes and different lithiated states (state of charge of the electrode)

$S_{\text{e}^-}^*$ - entropy transported by the charge carrier in the electrodes - will be different for different electrodes

$S_{\text{Li}^+}^*$ - 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

Peltier heats of lithium-ion battery electrodes

For an interface between an $\text{Li-}\theta$ electrode and LiX salt/ n -organic carbonate components (uniform) electrolyte:

$$\pi = -TS_{\text{Li-}\theta} - TS_{\text{e-}}^* + TS_{\text{Li+}}^* + \sum_{i=1}^n t_i q_i^* \quad (8)$$

$S_{\text{Li-}\theta}$ - entropy liberated from the reaction - will be different for different electrodes and different lithiated states (state of charge of the electrode)

$S_{\text{e-}}^*$ - entropy transported by the charge carrier in the electrodes - will be different for different electrodes

$S_{\text{Li+}}^*$ - 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

Peltier heat of lithium-ion battery electrodes

If we assume that $S_{\theta_1-e^-}^* \approx S_{\theta_2-e^-}^*$ and close to isothermal conditions:

$$\pi_1 - \pi_2 = T \Delta S_{Li} \quad (9)$$

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 ΔS for the full cell is known.



Summary

- Safety and ageing in Li-ion batteries are temperature dependent



Summary

- Safety and ageing in Li-ion batteries are temperature dependent
- Heat sources include irreversible and reversible effects



Summary

- Safety and ageing in Li-ion batteries are temperature dependent
- Heat sources include irreversible and reversible effects
- The Peltier heats are the reversible effects local to the electrode surface

Summary

- Safety and ageing in Li-ion batteries are temperature dependent
- Heat sources include irreversible and reversible effects
- 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

Summary

- Safety and ageing in Li-ion batteries are temperature dependent
- Heat sources include irreversible and reversible effects
- 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

Thank you!

Thanks to the Norwegian Research Council for their the Research Council of Norway through its Centres of Excellence funding scheme, project number 262644, PoreLab, and project no. 228739 SafeLiLife as well as to ENERSENSE, NTNU.