Analysis and Measurement of Heat Sources of Lithium-Ion Polymer Battery Using Electrochemical Thermal Model and Calorimeter

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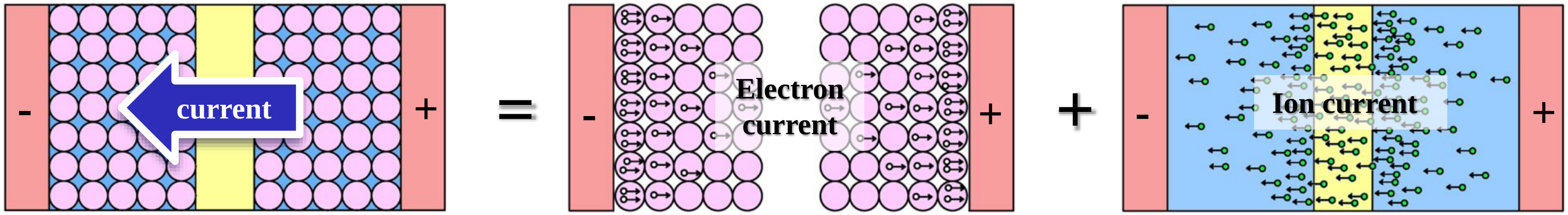
Introduction



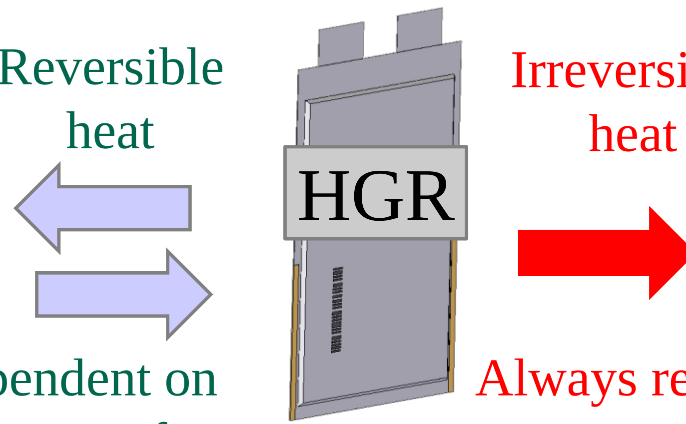
Energy equation for temperature of lumped battery model

$$\rho C_P \frac{\partial T}{\partial t} = \dot{Q}_{gen} - \dot{Q}_{trnasfer}$$

$$\dot{Q}_{gen} = f\left(I, T, SOC, aging, location, \cdots\right)$$

Reversible heat

Irreversible heat



Dependent on direction of process

Always release heat

✓ HGR : Heat Generation Rate

- Identification of causes of temperature rise is important particularly at high C rate and low temperature.
- Estimation and measurement of HGR is important.
- Optimal design of coolant system.

Lack of current thermal model and measurement

HGR

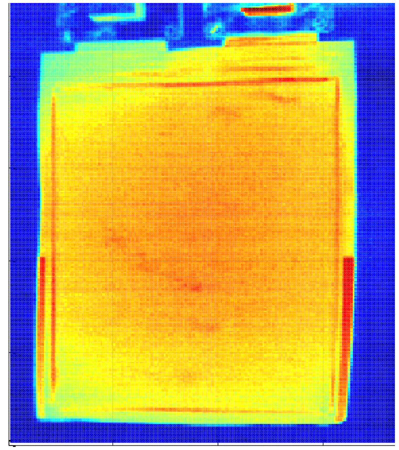
✓ HGR : Heat Generation Rate

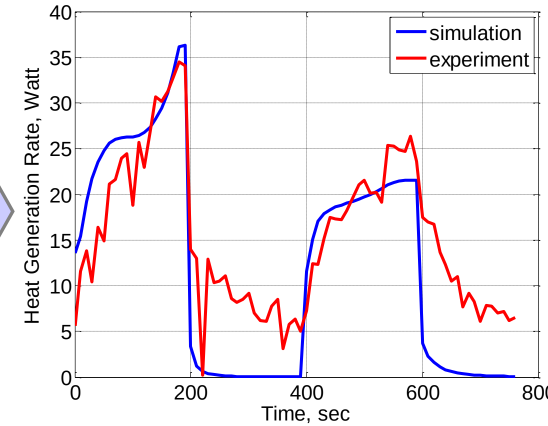
Irreversible

$$I\left(U_{OCV}-V_t\right)$$

Reversible

$$-IT\frac{dU_{OCV}}{dT}$$





Classical equation for HGR	Measurement of HGR
• Only for lumped model. • No detail information for HGR • No heat of mixing	• Not accurate measurement of HGR • Temperature control using thermal chamber – not able to control temperature accurately

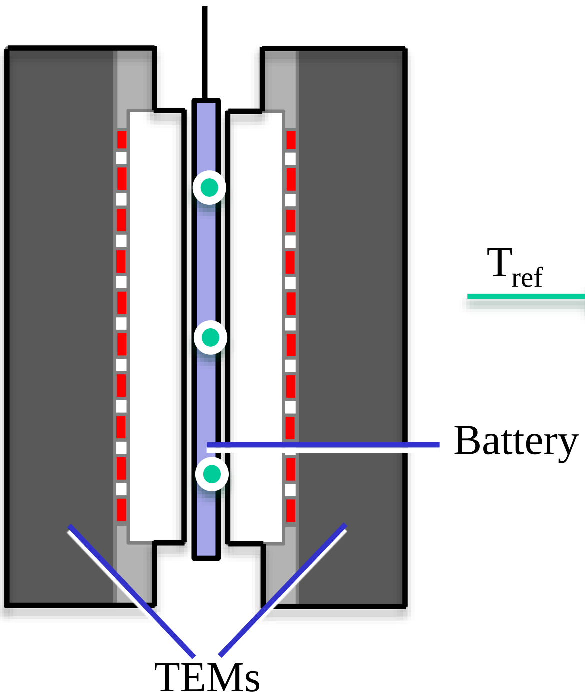
- Thermal model for physic based electrochemical model
- Accurate measurement of heat generation rate and control of temperature

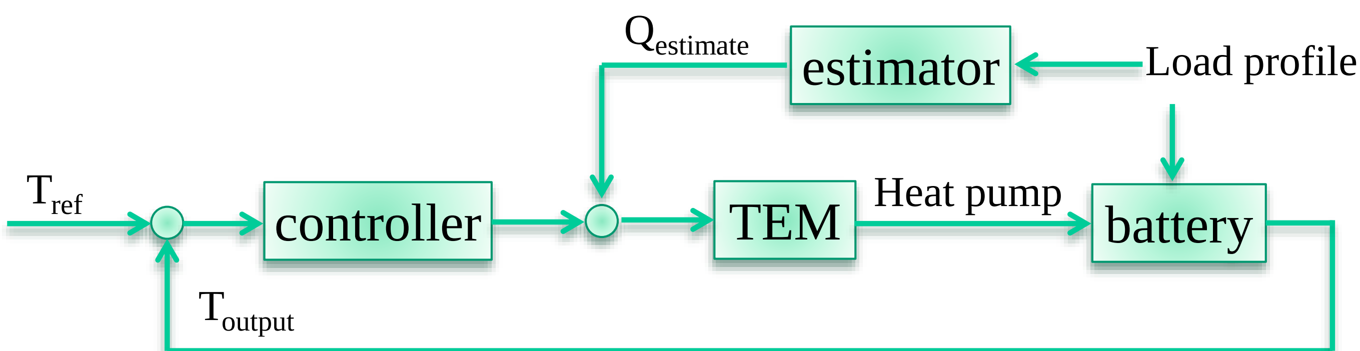
Measurement of heat generation rate
design of calorimeter

Principle of calorimeter

Requirement of new experiment method

1. Accurate regulation and tracking control of temperature.
2. Accurate measurement of heat generation rate.





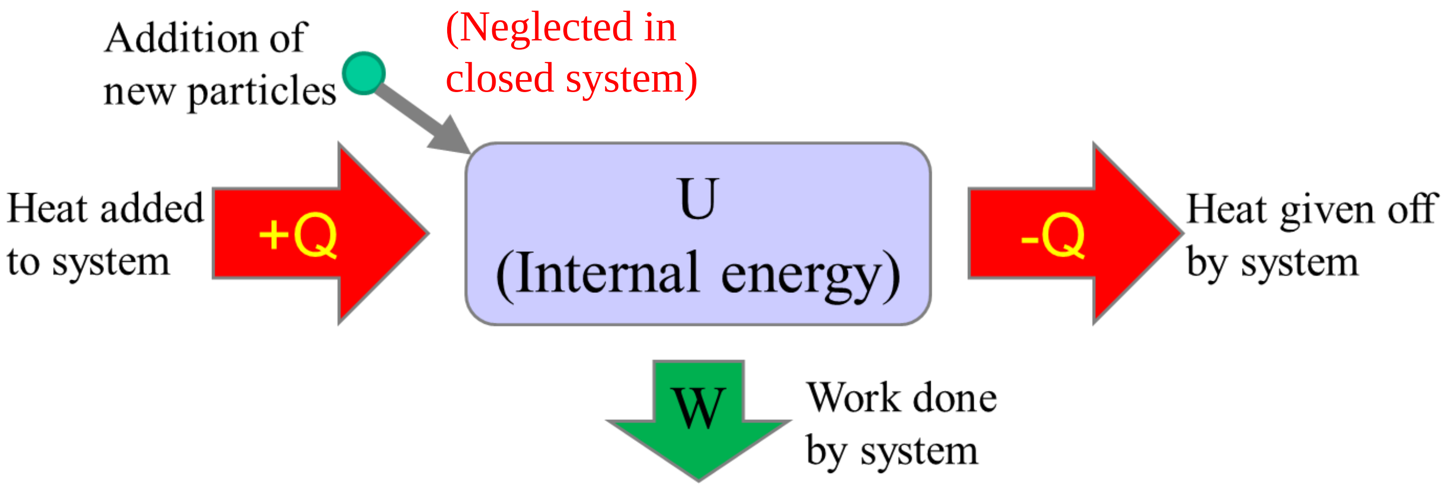
Accurate T control from feedback loop

$$\rho C_P \frac{\partial T}{\partial t} = \dot{Q}_{gen} - \dot{Q}_{transfer}$$ In isothermal system, dT/dt=0 ⇒ $$\dot{Q}_{gen} = \dot{Q}_{transfer}$$

Theory of heat generation rate

Reformulation of heat source terms

The first law of thermodynamics in closed system $dU = dQ - dW$

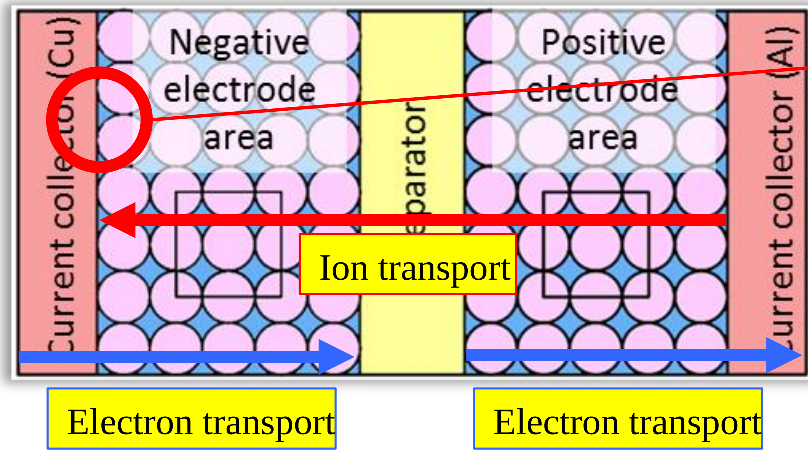


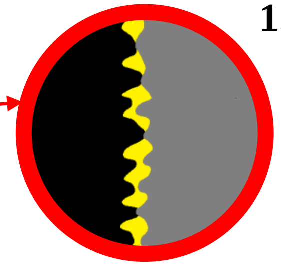
Enthalpy $H = U + PV$

- Defined as internal energy plus product of pressure and volume.
- Given battery volume, change of enthalpy is equal to the change of internal energy.
- Change of enthalpy consists of
    1. Enthalpy reaction change
    2. Change of temperature
    3. Heat of mixing

$$\frac{dH}{dt} = IT^2 \frac{d\frac{U_{OCV}}{T}}{dT} + C_p \frac{dT}{dt} + \int \left(\bar{H} - \bar{H}^{ave} \right) \frac{\partial c}{\partial t} dv$$

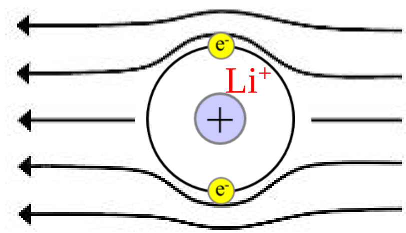
Charging process considering internal behavior





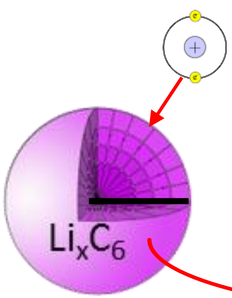
1. Transport of electrons

- Migration
- Ohmic overpotential from contact resistance



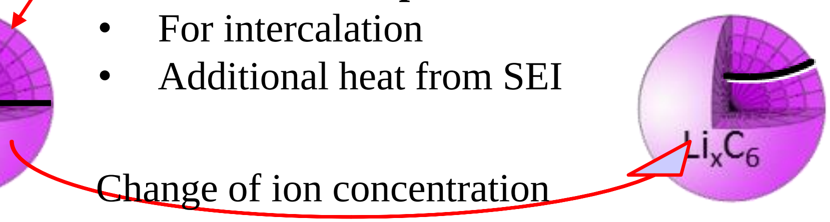
2. Transport of ions

- Migration (larger)
- Diffusion (neglected)
- Concentration overpotential decreases potential gradient



3. Activation overpotential

- For intercalation
- Additional heat from SEI



4. Actual work to battery

- Change surface ion concentration

5. Useful chemical energy

- From averaged ion concentration

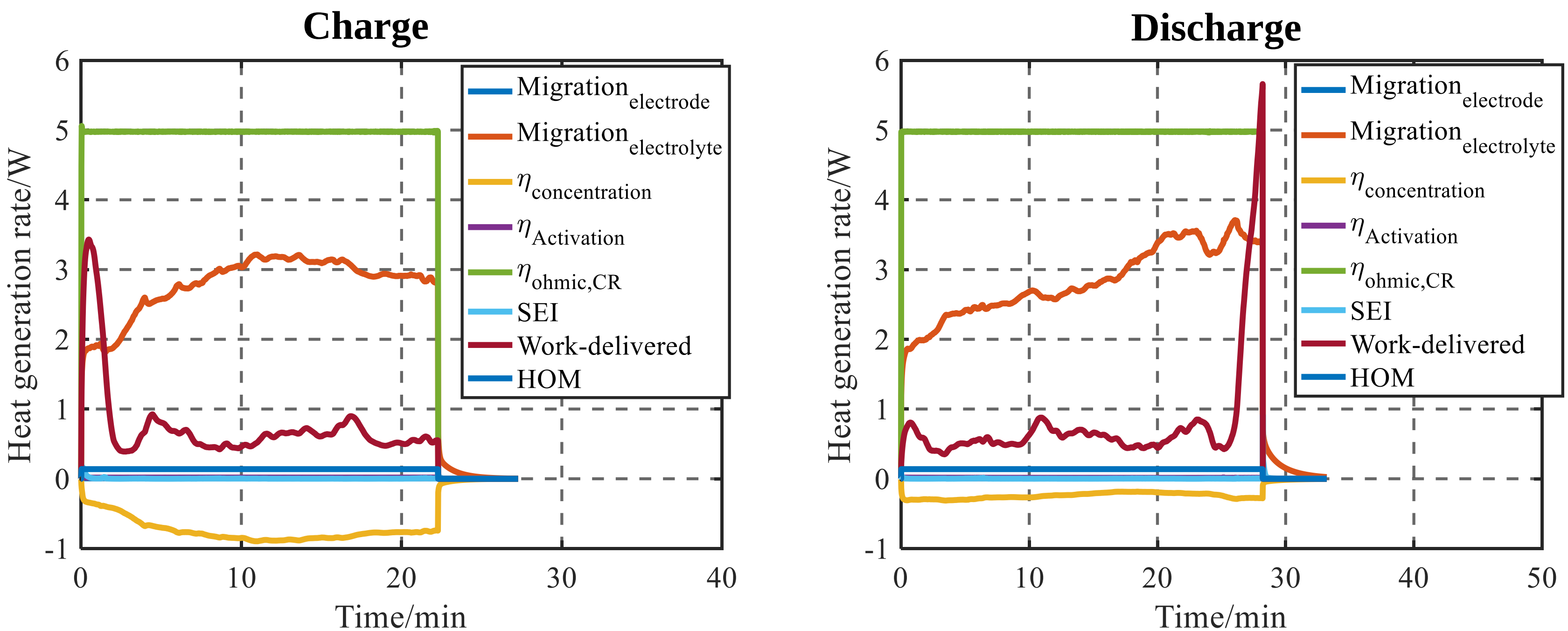
6. Change of enthalpy

- Change of entropy
- Change of battery temperature
- Heat of mixing

$$\frac{dH}{dt} = IT^2 \frac{d\frac{U_{OCV}}{T}}{dT} + C_p \frac{dT}{dt} + \int \left(\bar{H} - \bar{H}^{ave} \right) \frac{\partial c}{\partial t} dv$$

Irreversible heat source terms

❖ Simulation results of 2C CC charging / discharging from physic based electrochemical model.



❖ Dominant heat sources: migration in electrolyte, contact resistance, work – delivered energy.

❖ Negligible sources: migration in electrode, heat of mixing, SEI at BoL.

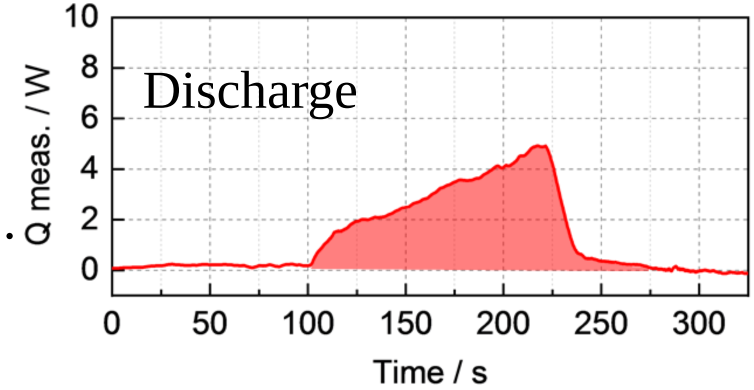
❖ Negative heat from concentration overpotential in electrolyte phase.

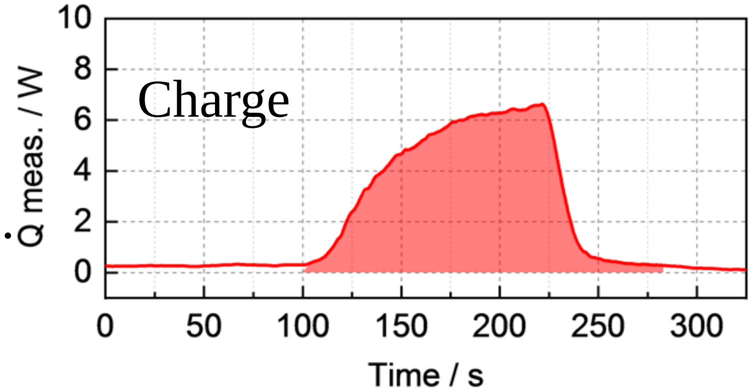
❖ Remaining heat can be estimated using designed thermal model.

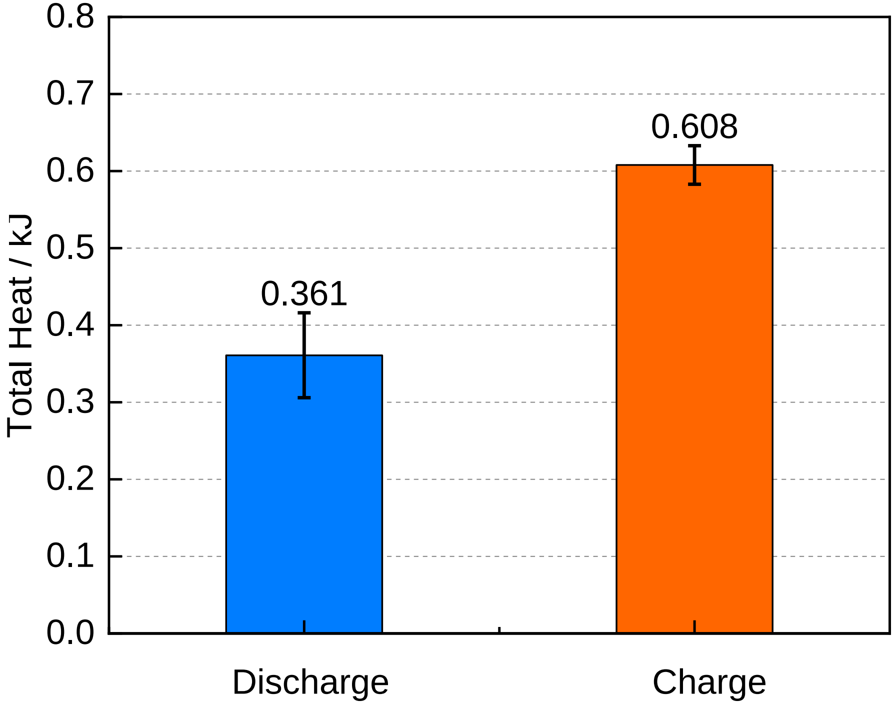
Heat source – reversible heat source

Pulse test analysis (50% SOC)

Comparison of the heat during pulse discharge and charge test.





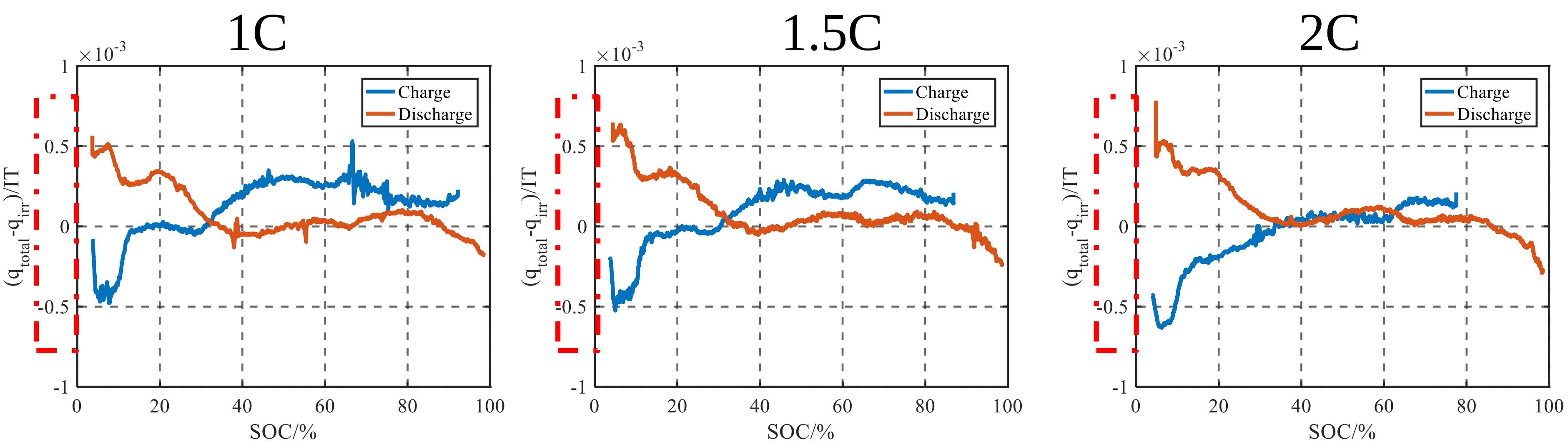


At 50% SOC, the total heat generated during discharge is smaller than that during charge.

Empirical equation for reversible heat

Empirical equation for reversible heat

- Measured HGR – estimated irreversible HGR at different C rate

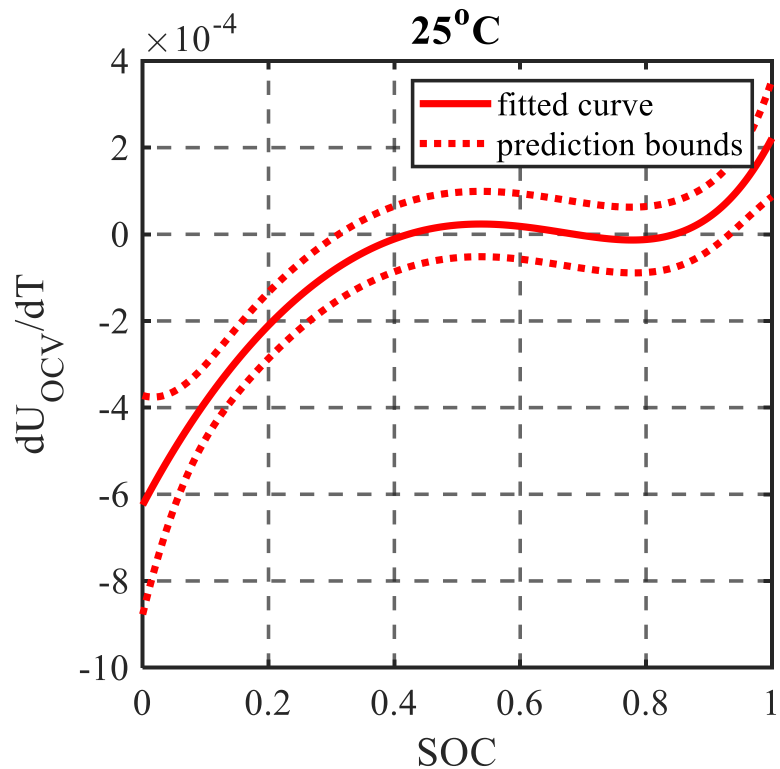


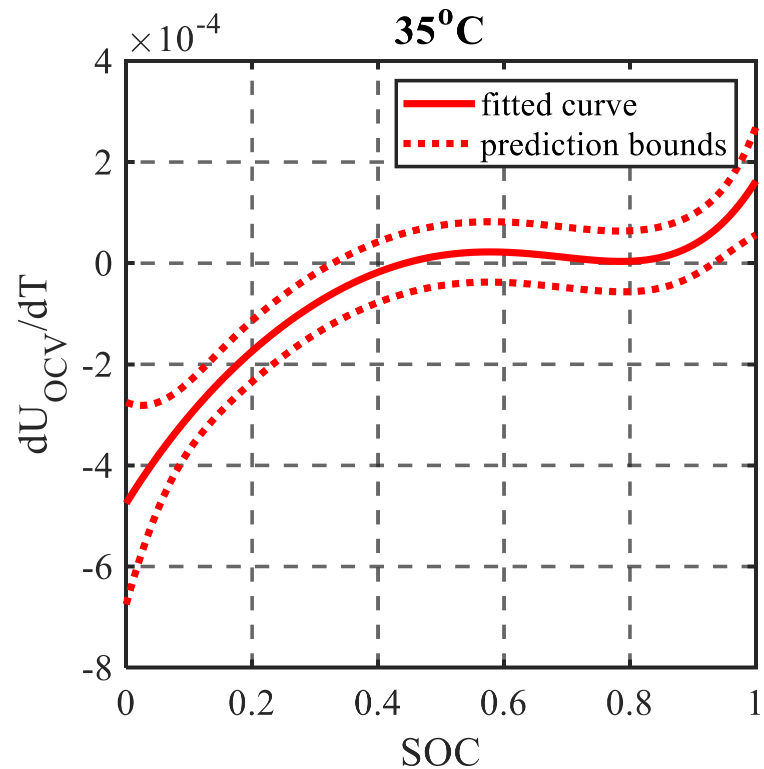
- Similar tendency and mirrored behavior from charging and discharging.
- Assume no heat of mixing, $\dot{Q}_{total} = \dot{Q}_{irr} - IT\frac{dU_{OCV}}{dT}$
  - $\frac{dU_{OCV}}{dT} = \frac{\dot{Q}_{irr} - \dot{Q}_{total}}{IT}$
- Obtain entropy coefficient as a function of SOC and temperature from least square estimation

Empirical equation for entropy coefficient

- ❖ Obtain entropy coefficient as a function of SOC from least square estimation.
- ❖ Based on 2C measurement.

❖ 95% of confidence level for the bounds





- ❖ One equation for other temperature ranges.
- ❖ Dominant at low SOC range.

Reversible heat source term – measurement of entropy coefficient

Measurement method of entropy coefficient

$$\dot{Q}_{rev} = -IT\frac{dU_{OCV}}{dT}$$

- I, T : directly measureable during experiment
- dU_{OCV}/dT : entropy coefficient, a function of temperature, SOC

How to measure the entropy coefficient?

Fix temperature and varies SOC. Compares at different temperature.	Fix SOC and varies temperature. Compares at different SOC.
OCV varies nonlinearly with SOC. Less accurate.	OCV varies linearly with temperature around room temperature. More accurate.
Find OCV-SOC relationship at different temperature. Less time consuming.	Select the number of SOC points and varies temperature. The accuracy is directly related to the number of SOC points. More time consuming.

Measurement of dU_{OCV}/dT

Measure U_{OCV} by varying T at a fixed SOC

Charge/discharge the cell to target SOC: ($I = 0.1C$)

↓

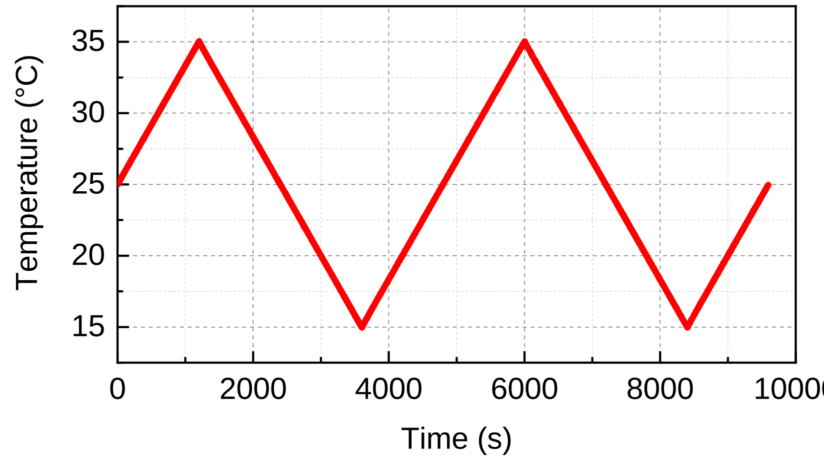
Rest 10 hours to reach equilibrium state

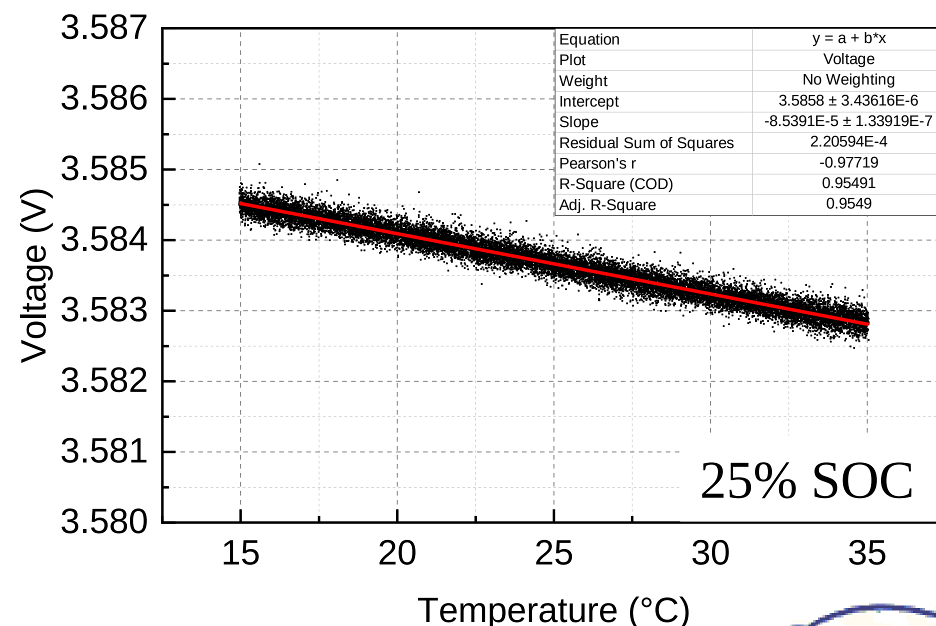
↓

Temperature excitation:
ΔT=10°C,
Temp.Rise Rate = 0.5°C/min)

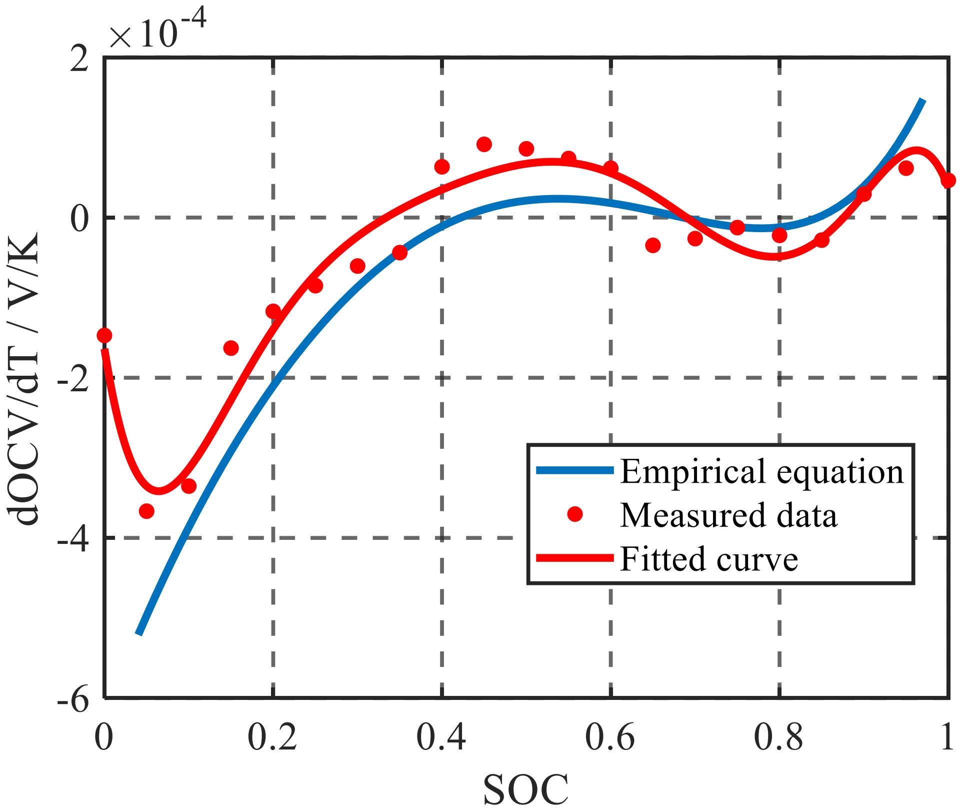
↓

Linearly fitting the $U_{OCV}=f(T)$ and calculate the slope: dU_{OCV}/dT





Comparison of measured entropy coeff. with empirical equation



- Measurement of dOCV/dT;
  - A fixed SOC, but temperature change at the every 5% of SOC interval.
- Good agreement of measured entropy coefficient with empirical equation.
- Negative at low SOC range, the reason for the negative peak of heat generation rate during charging.
- One fitted curve for all temperature ranges from -30˚C to 45˚C.

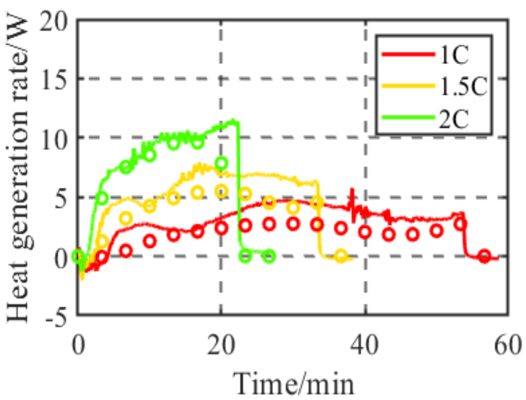
Model validation – comparison of HGR

Validation of HGR

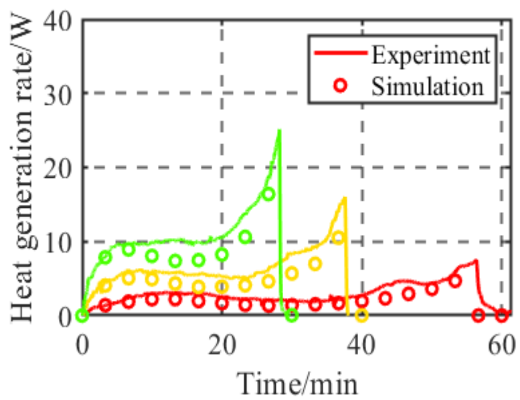
- Validation results from 25˚C, 2 upper temperature (35˚C and 45˚C), and 2 lower temperature (-15˚C and -30˚C).
- Results using a pouch type NMC 622 cell (26Ah)

Results at 25˚C

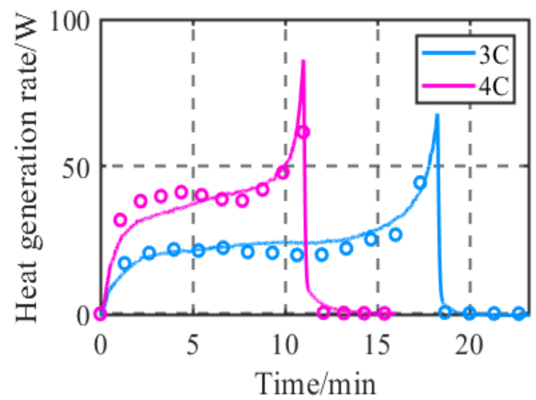
Charge



Discharge



Discharge



❖ HGR validation using physic based electrochemical model.

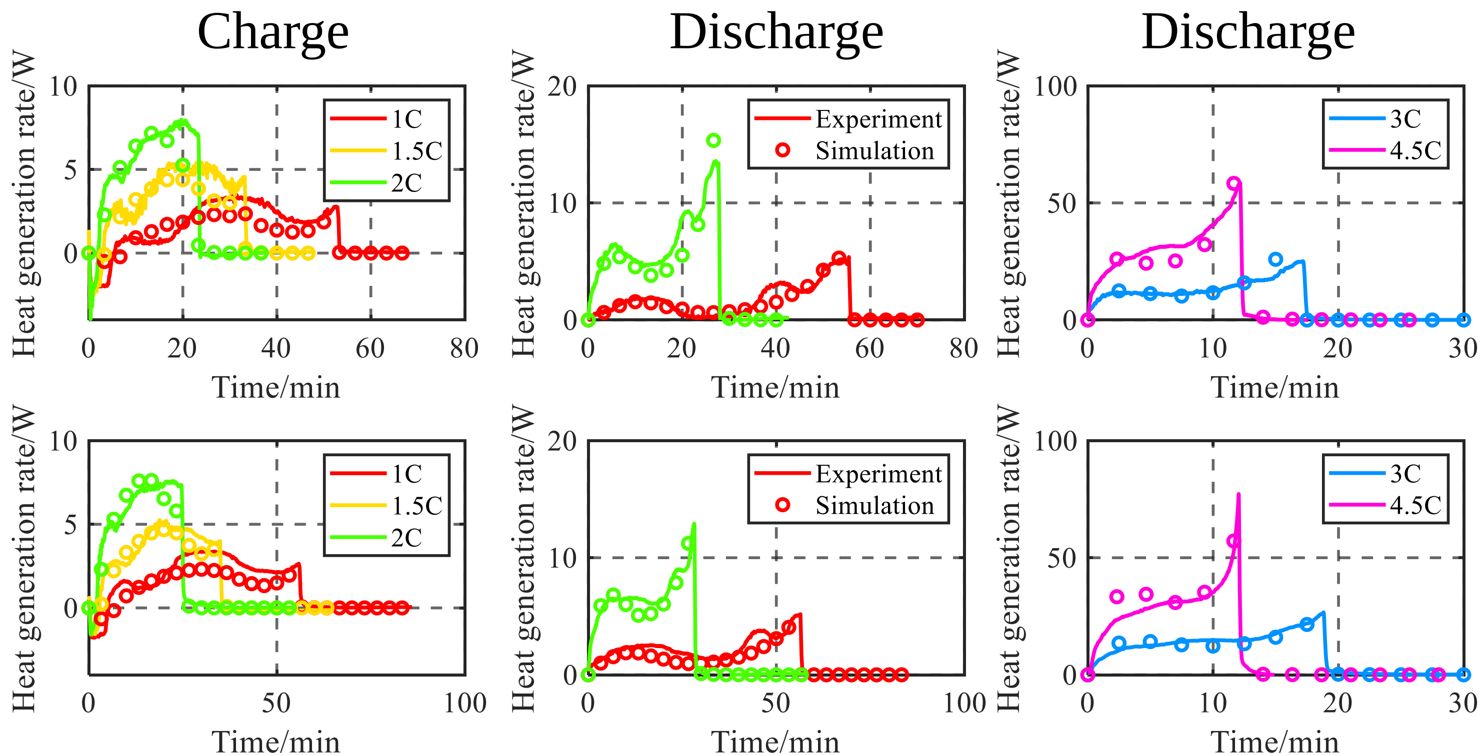
❖ Heat generation rate can be accurately estimated from 1C to 4C.

Validation of HGR

- Results using a pouch type NMC 622 cell (26Ah)

45°C

35°C

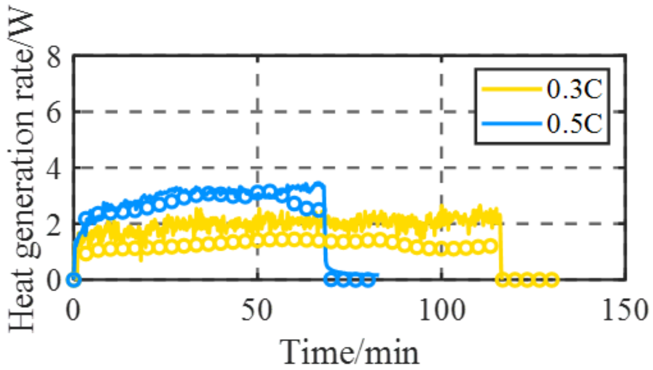


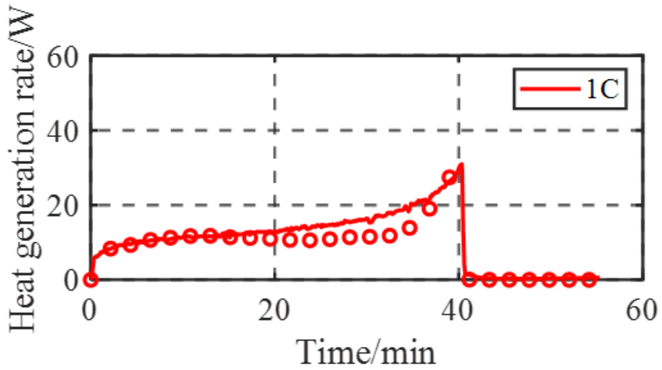
- HGR validation using physic based electrochemical model.
- Heat generation rate can be accurately estimated from 1C to 4.5C.
- Negative peak at low SOC during charging is due to reversible heat.

Validation of HGR

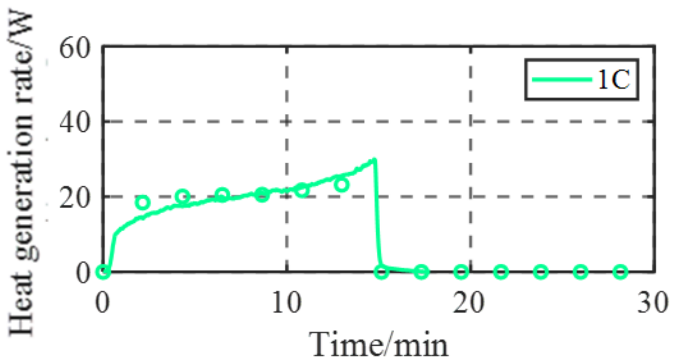
- Results using a pouch type NMC 622 cell (26Ah)

-15°C





-30°C

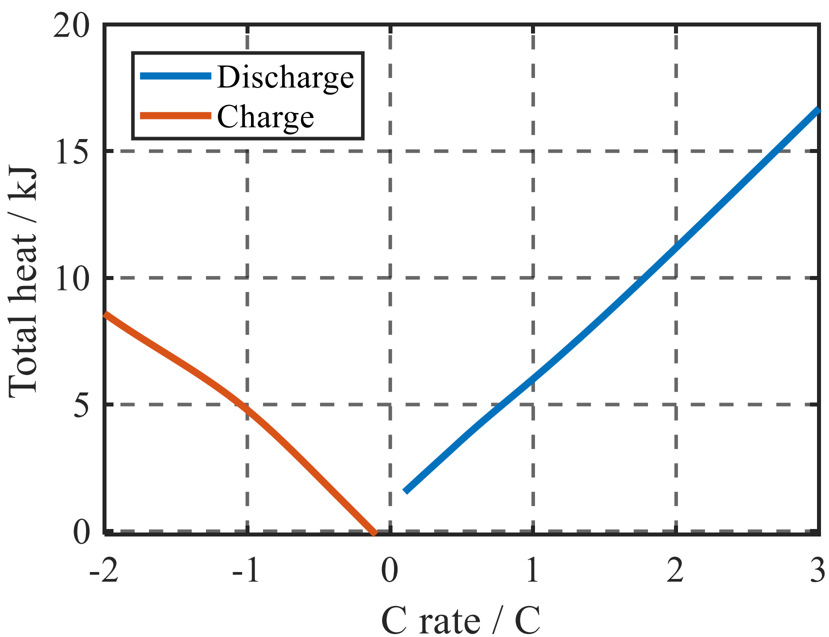


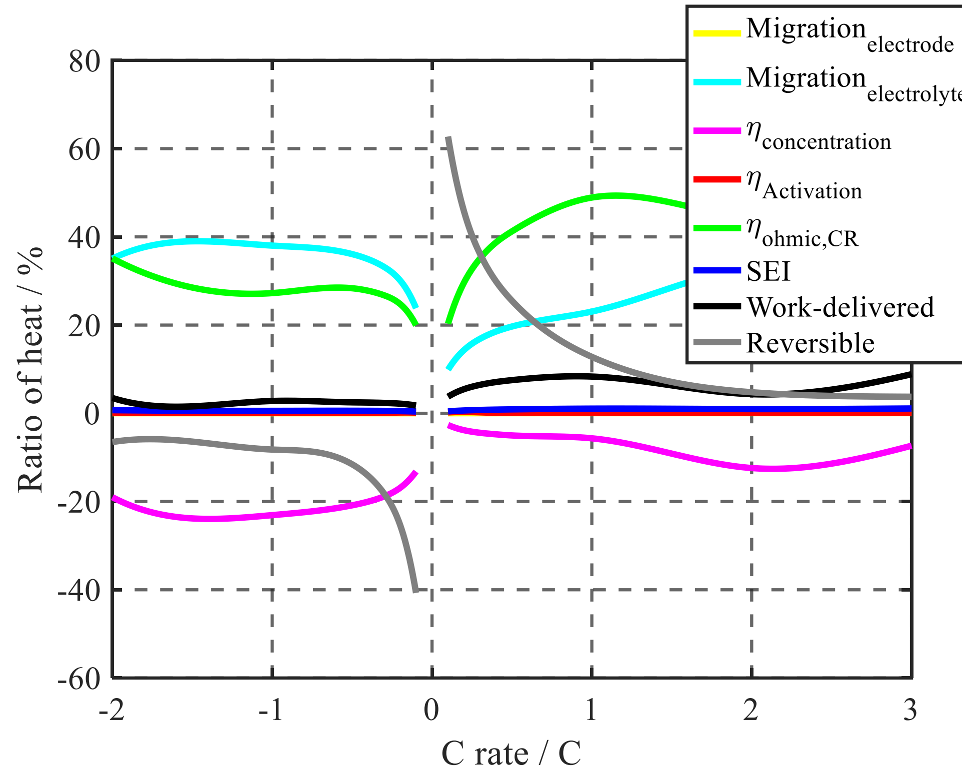
❖ Due to extremely low temperature, current is limited and no charging is recommended at -30°C

Heat source analysis – effect of C rate on HGR

Heat source analysis – effect of charging current

❖ Based on the validation results at 35˚C.





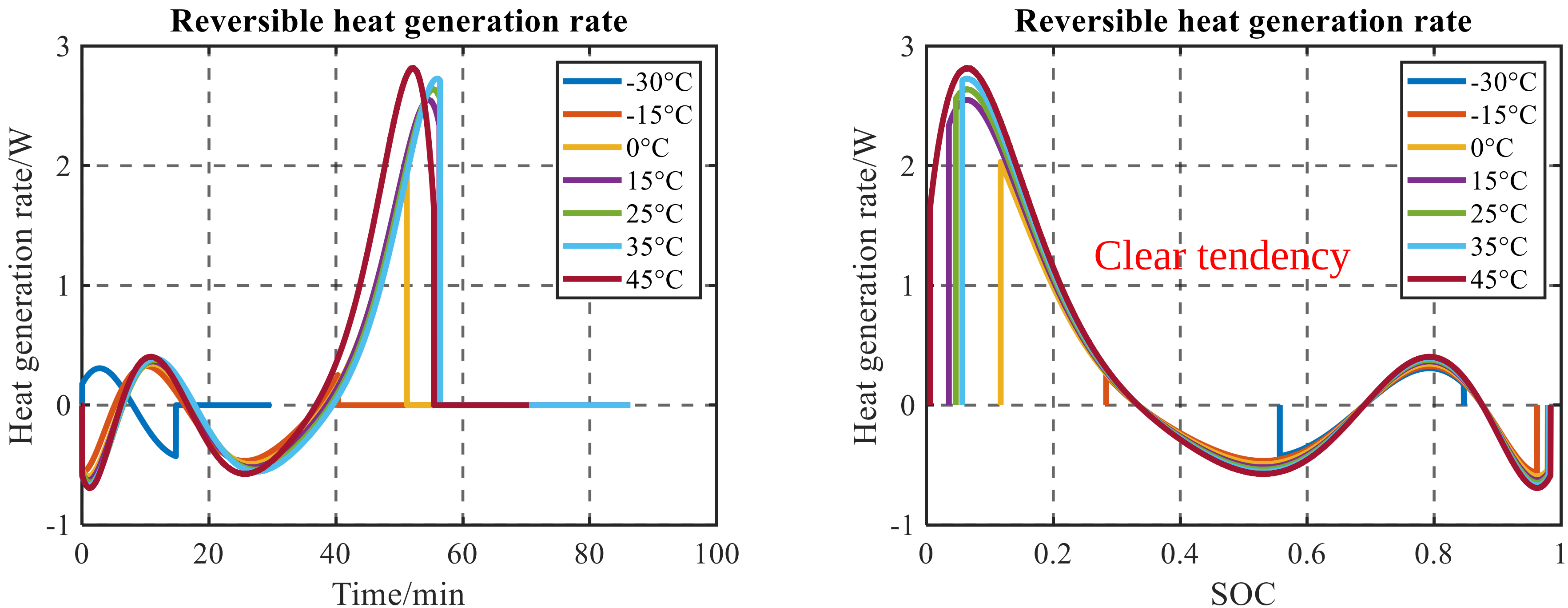
- ❖ Proportional relationship of Joule heating and square of current.
- ❖ Reduction of charging time with C rate.
- ❖ Linearly increasing total heat.
- ❖ Less total heat from charging.

- ❖ Less total heat from charging caused by negative reversible heat.
- ❖ At low C rate, reversible heat is dominant.
- ❖ At high C rate, irreversible heat is dominant.

Heat source analysis – effect of temperature on HGR

Reversible heat generation rate at different temperature

- The reversible heat generation rate over time and SOC (1C CC discharge).

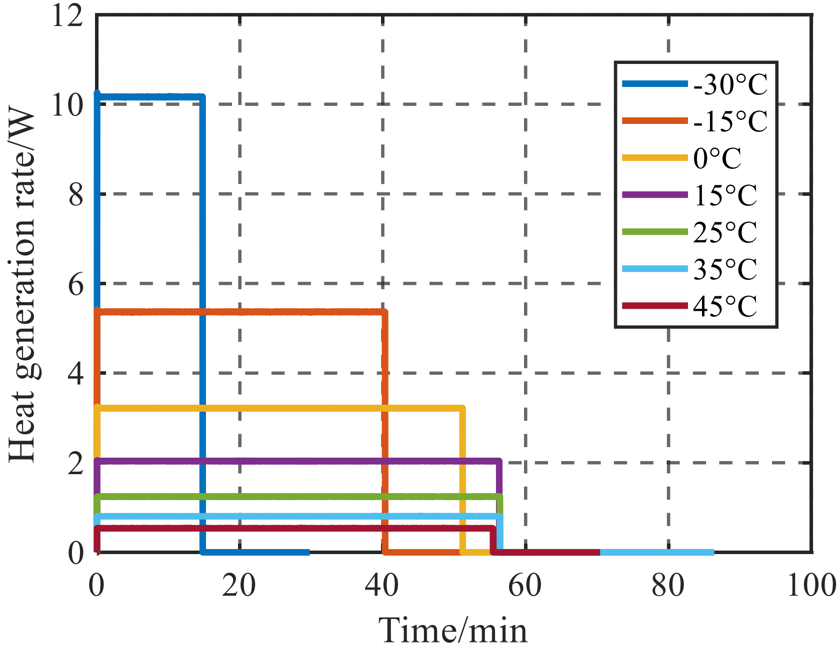


- ❖ Most dominant factor for low C rate.
- ❖ Same shapes regardless of operating temperature (more dependent on SOC), but slight increase at elevated temperature.
- ❖ Mirrored behavior at charging that causes a negative peak at the beginning of charging.

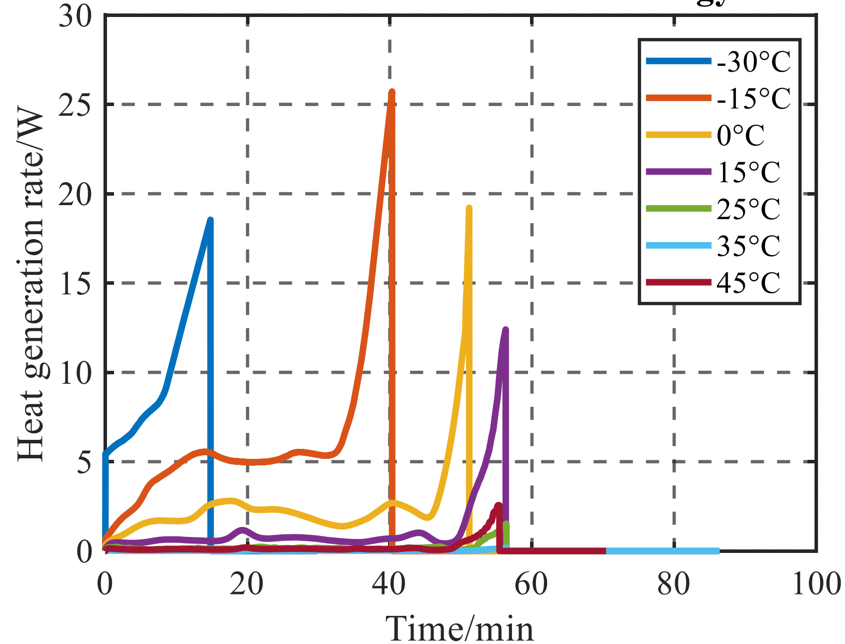
Irreversible heat – Joule heating

- The irreversible heat during 1C CC discharge.

From contact resistance



Heat from work-delivered energy



❖ Overall magnitude.

❖ The similar profile to that of the applied current profile.

❖ Peak of HGR.

❖ -30˚C: reduced HGR due to short discharging time.

Conclusion and future work

Achievement

- Accurately validated new thermal model from physic based model.
- New experimental method that control temperature and measure HGR accurately.
- Analysis of heat sources based on new thermal model.

Future work

$$\dot{Q}_{gen} = f\left(I, T, SOC, aging, location, \cdots\right)$$

1. Effect of aging (side reaction and lithium plating) on heat generation rate.
2. Estimation of heat generation rate and temperature distribution on 3D model.

Thank you!

