Performance of multifunctional calorimeter for thermal characterization of lithium ion battery

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  - Pressure and temperature gradient
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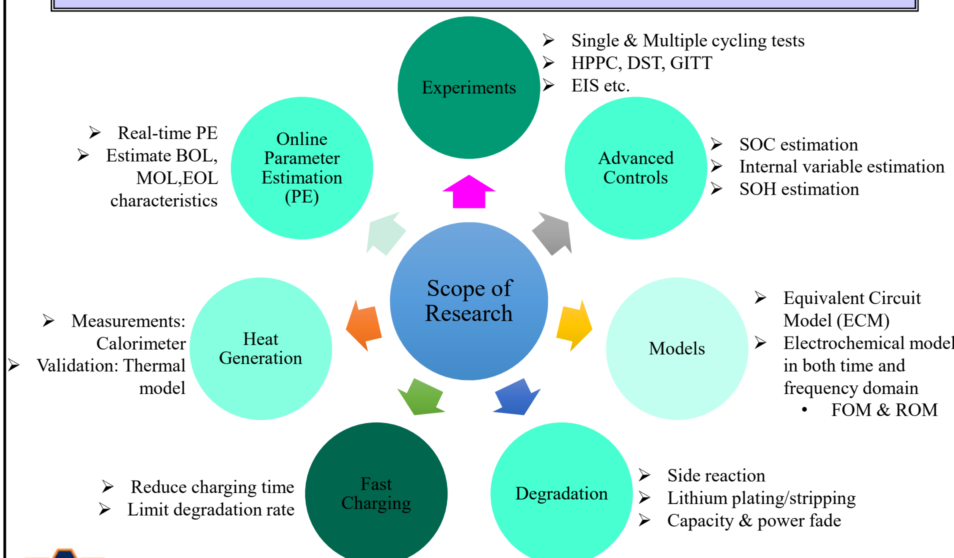
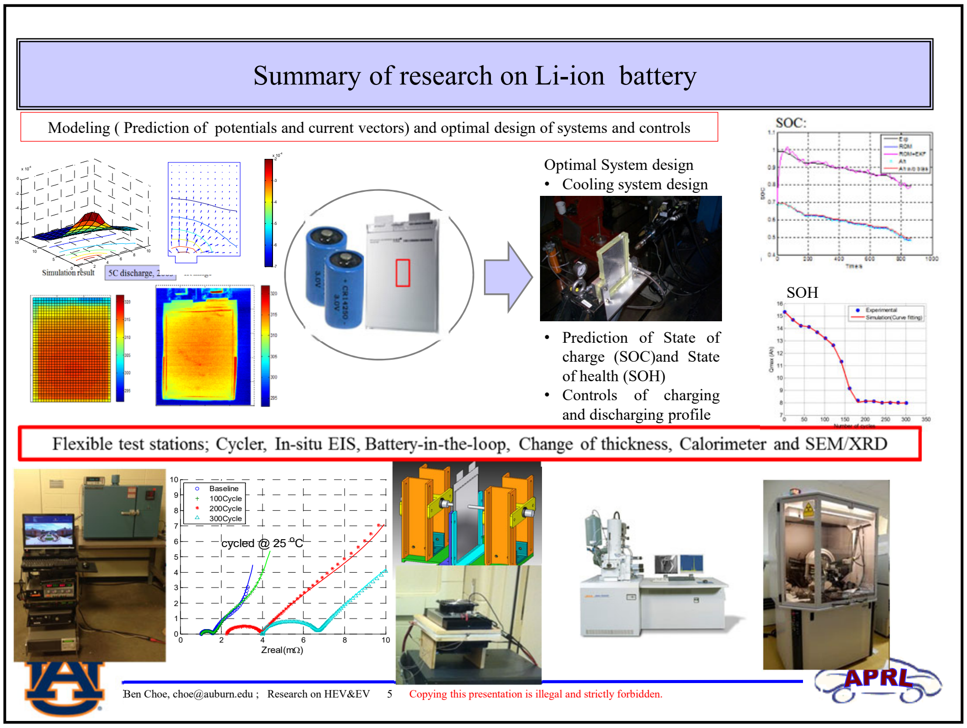
Background and introduction

Overview of AU R&D





Summary of research on Li-ion battery
Modeling (Prediction of potentials and current vectors) and optimal design of systems and controls
Simulation result
5C discharge
Optimal System design
• Cooling system design
• Prediction of State of charge (SOC)and State of health (SOH)
• Controls of charging and discharging profile
SOC:
SOH
Flexible test stations; Cycler, In-situ EIS, Battery-in-the-loop, Change of thickness, Calorimeter and SEM/XRD
Baseline
100Cycle
200Cycle
300Cycle
cycled @ 25 °C
Zreal(mΩ)
APRL
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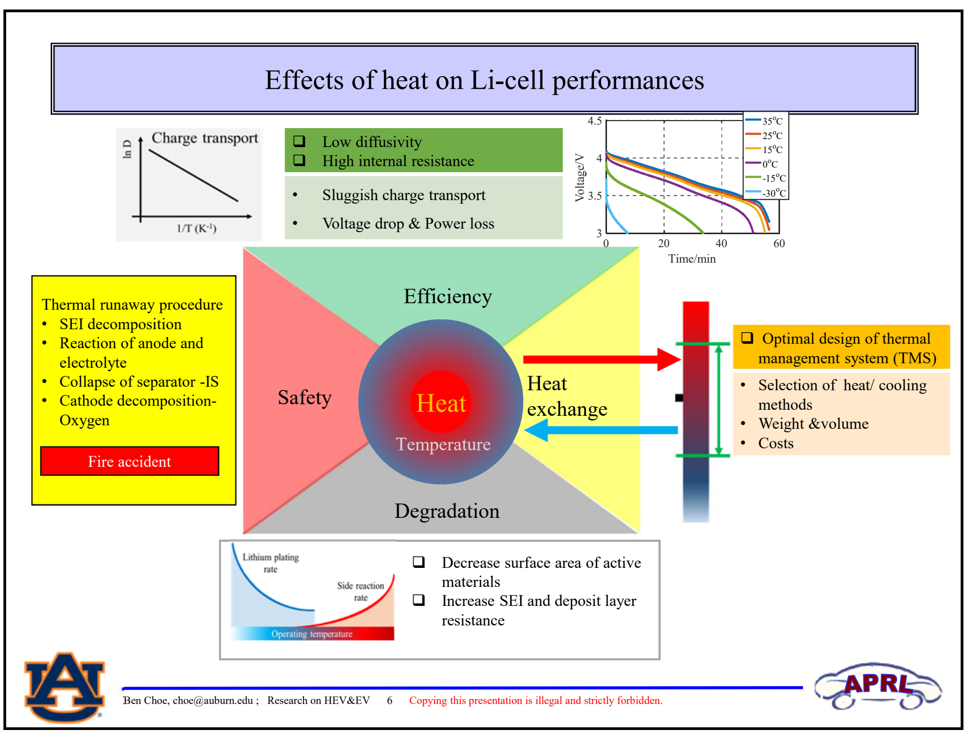

Effects of heat on Li-cell performances
Charge transport
ln D
1/T (K⁻¹)
Low diffusivity
High internal resistance
• Sluggish charge transport
• Voltage drop & Power loss
Voltage/V
Time/min
35°C
25°C
15°C
0°C
-15°C
-30°C
Thermal runaway procedure
• SEI decomposition
• Reaction of anode and electrolyte
• Collapse of separator -IS
• Cathode decomposition-Oxygen
Fire accident
Efficiency
Safety
Heat
Temperature
Heat exchange
Degradation
Optimal design of thermal management system (TMS)
• Selection of heat/ cooling methods
• Weight &volume
• Costs
Lithium plating rate
Side reaction rate
Operating temperature
Decrease surface area of active materials
Increase SEI and deposit layer resistance
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Background

In a control volume, the energy equation

$$\rho C_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(k_X \frac{\partial T}{\partial x}\right) + \frac{\partial}{\partial y}\left(k_Y \frac{\partial T}{\partial y}\right) + \frac{\partial}{\partial z}\left(k_Z \frac{\partial T}{\partial z}\right) + \dot{Q} + \dot{Q}_{conv}$$

CV	Control volume
k	Thermal conductivity
ρ	Density
C_p	Heat capacity
$\dot{Q}$	Heat generation rate
conv	Convection

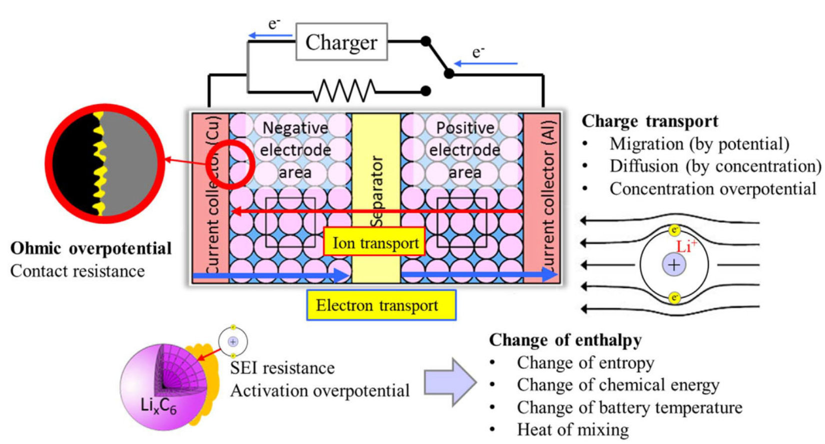
In rechargeable batteries, the heat generation rate (HGR) is a sum of irreversible and reversible one

$$\dot{Q} = I \cdot (U_{OCV} - V_{Terminal}) - I \cdot T \cdot \frac{dU_{OCV}}{dT}$$

Heat Generation ($\dot{Q}$), Current (I), Equilibrium Potential (U_{OCV}), Terminal Voltage ($V_{Terminal}$), Temperature (T), Entropy Coefficient ($\frac{dU_{OCV}}{dT}$)

*M. Song, Y. Hu, S-Y Choe, and T. R. Garrick. 2020 *J. Electrochem. Soc.* **167** 120503

Principle of Heat generation



*M. Song, Y. Hu, S-Y Choe, and T. R. Garrick. 2020 *J. Electrochem. Soc.* **167** 120503

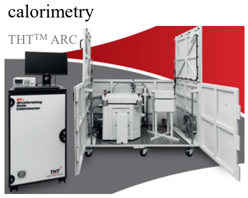
Background

- Increased size of the cells and associated design of TMS
  - Uniform or non-uniform temperature gradients
  - Uniform or non-uniform compression
  - Operando characterization of thermal properties during charging and discharging

❑ Commercial calorimeters for measurements of heat generation:

Accelerated rate calorimetry

THT™ ARC



Differential scanning calorimeters

NETZSCH™ DSC

Isothermal titration calorimeter

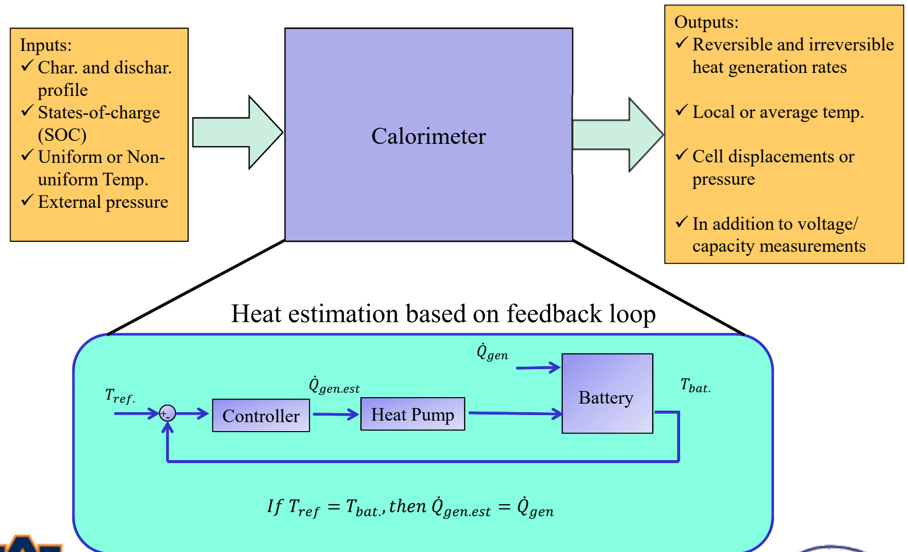
Affinity™ ITC

- ✓ High accuracy and dynamic response
- ✖ Limited space size for large format cells
- ✖ Very expensive
- ✖ No pressures

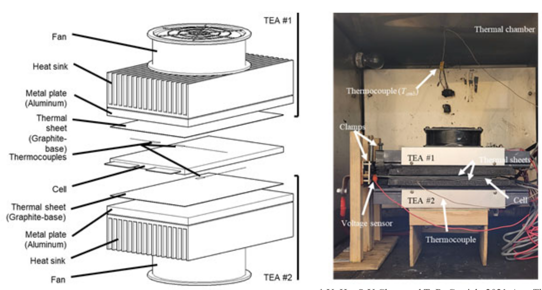
Design of multifunctional calorimeters

(varies based on type of the cell)

Concept of developed multifunctional calorimeter (Patented)

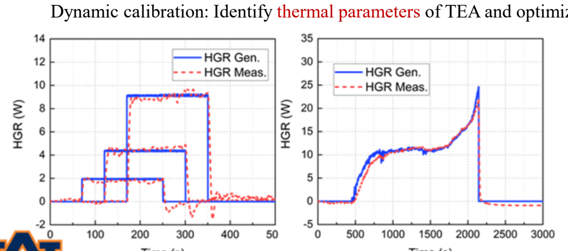


Calibration for lumped HGR measurement



* Y. Hu, S-Y Choe, and T. R. Garrick. 2021 *App. Thermal Eng.* **189** 116709

Dynamic calibration: Identify thermal parameters of TEA and optimize the covariance values of Kalman filter



❑ Performance analysis:

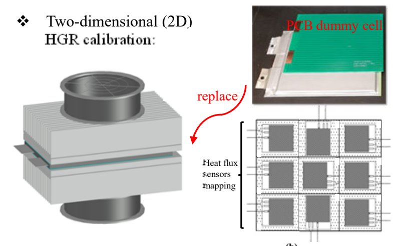
Maximum measurable HGR: 100W

Average measurement error = 0.67W

Response time < 10s

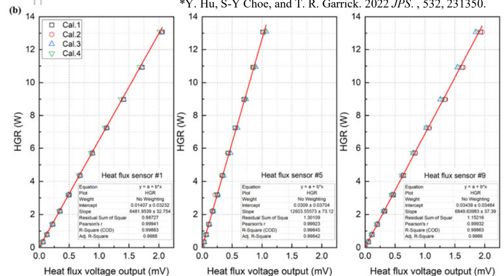
Calibration for 2D HGR measurement

- Static calibration:
  - Two-dimensional (2D) HGR calibration:



$\dot{Q}_{pump} \approx fitting(HF\ output)$

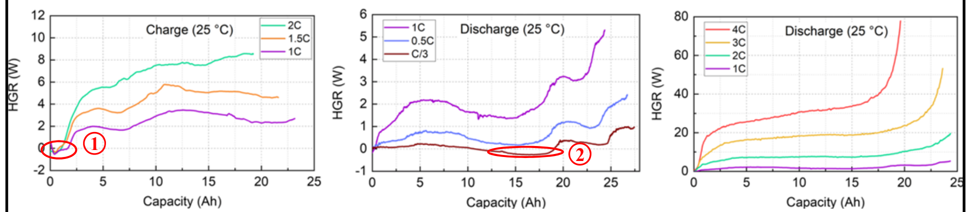
*Y. Hu, S-Y Choe, and T. R. Garrick. 2022 *JPS.* , 532, 231350.



9 heat flux sensors are placed in the order of 3 × 3 matrix to simultaneously measure the heat flux and temperature

Measurement of entropy coefficient

Reversible heat generation – C-rate effects



① Endothermic region at the beginning of charging due to the reversible heat

② Reversible heat affects the discharging HGR profile

$$\dot{Q} = I \cdot (U_{OCV} - V_{Terminal}) - I \cdot T \cdot \frac{dU_{OCV}}{dT}$$

$$I \cdot (U_{OCV} - V_{Terminal}) \approx I^2 R$$

As current I increases, irreversible heat becomes more dominant

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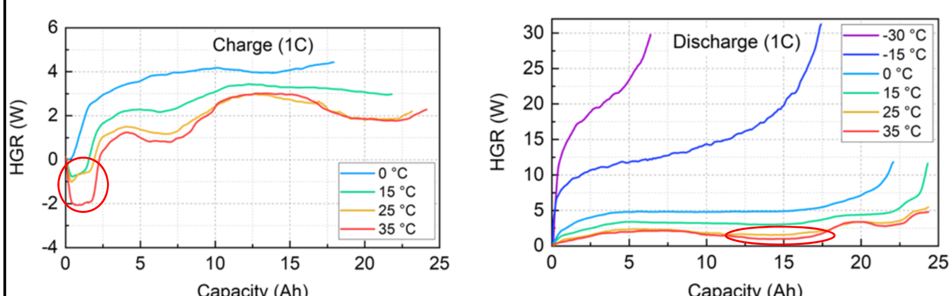
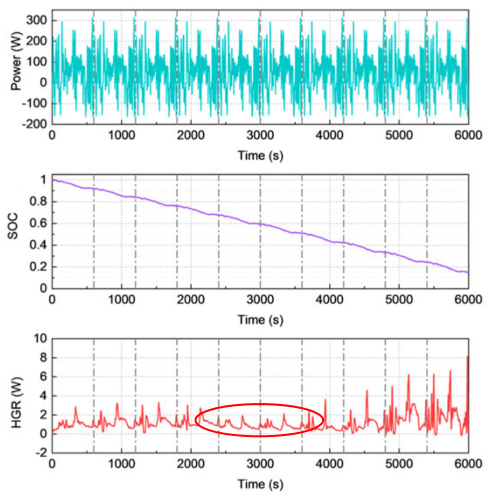
Reversible heat generation – Temperature effects



- ❑ As temperature increases, the internal resistance decreases, so the reversible heat becomes more dominant
- ❑ Quantification of reversible heat is needed for better validation of HGR measurement

Heat Generation Measurement Dynamic Response



- ❑ Need for reversible heat quantification appears during dynamic operation as well
- ❑ Reversible heat (entropy coefficient) is a function of SOC

Motivation: Characterization of heat sources

Total HGR
- Reversible heat - Entropy change during the electrochemical reaction
- Irreversible heat - Internal resistances (R)

❑ Characterization of heat source terms:

- Reversible heat:
  - **Potentiometric** method: measure open circuit voltage change at varied temperature
    - ✓ High accuracy
    - ▪ Long testing time: equilibrium state
  - **Calorimetric** method: measure difference of total heat generation at charge/discharge
    - ✓ Fast measurement time
    - ✓ Need calorimeter
    - ▪ Average value in certain SOC range
- Irreversible heat: V-I characteristics, EIS technique
  - ▪ Long testing time: equilibrium state

❑ Improved method:

Improved experimental method

- o Background correction
- o Electrothermal impedance spectroscopy (ETIS)

Model based estimation

Estimate reversible and irreversible heat by a battery thermal model.

Measurement of Entropy Coefficient

$$\dot{Q} = \boxed{I \cdot (U_{OCV} - V_{Terminal})} - \boxed{I \cdot T \cdot \frac{dU_{OCV}}{dT}}$$

Irreversible Reversible

- Potentiometric method

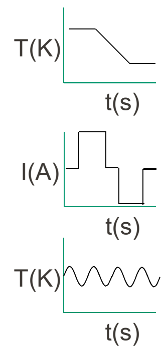
$$\frac{dU_{OCV}}{dT} = \frac{V_F - V_I}{T_F - T_I}$$

- Calorimetric method

$$\frac{dU_{OCV}}{dT} = \frac{Q_{discharge} - Q_{charge}}{-2I_0 T t_0}$$

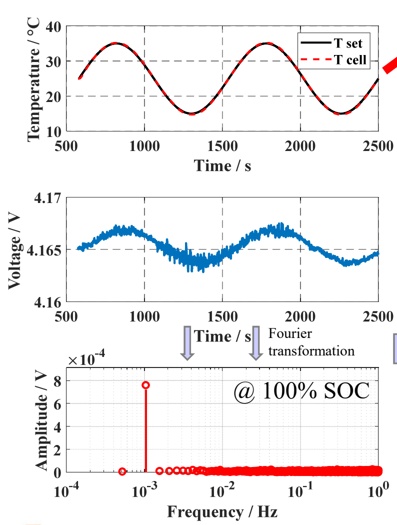
- Hybridized Time-Frequency Domain Analysis (HTFDA)

$$\frac{dU_{OCV}}{dT} = -sgn[\angle PA(f_i)] \left|\frac{2}{\Delta T} P(f_i)\right|$$

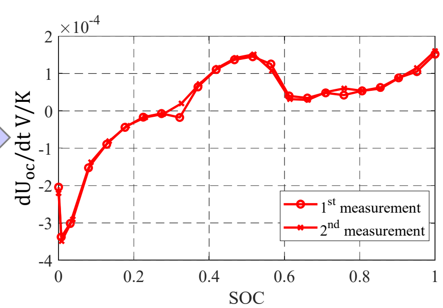


HTFDA method significantly reduces the time for EC measurement, while maintaining the accuracy

Measurement entropy coefficient



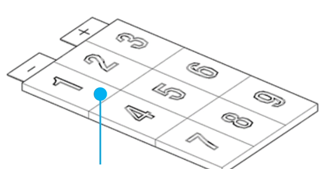
- Accurate temperature control allows the measurement of entropy coefficient
- Measurement using hybrid time-frequency domain analysis (HTFDA*)
- 21 measurements with 5% SOC intervals



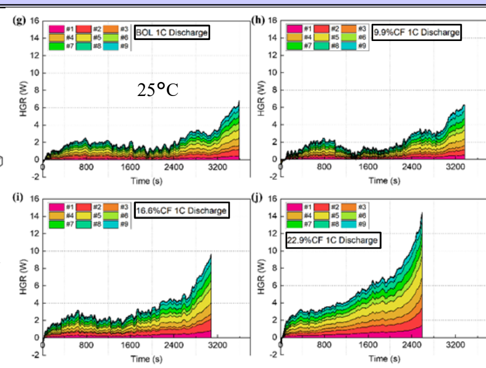
*Y. Hu, S.Y. Choe, T.R. Garrick. *Electrochimica Acta*. 2020 Dec 1;362:137124.

Measurement results from the multifunctional calorimeters

Measurement of 2D HGR under aging conditions



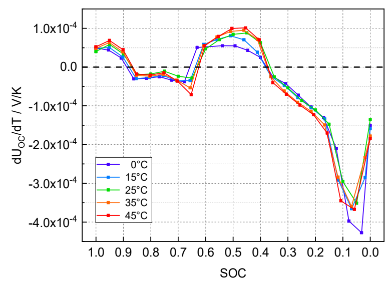
Non-uniform HGR:
- Inhomogeneous current distribution
- Complex heat transfer process



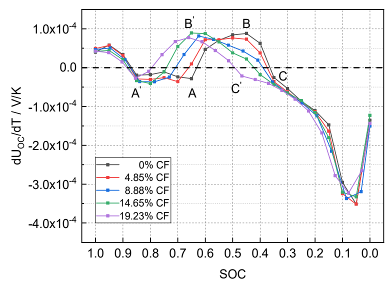
- ❑ HGR at the center of the cell (#5) is the highest
- ❑ HGR gradient from the center to the edge of the cell
- ❑ The 2D HGR increase during aging, while the internal resistance of the cell increases

Measurement of EC under different temperature and aging conditions

- EC at different temperatures



- EC at different aging conditions



- ❑ HTFDA reduction of measurement time: ~ 25 hours (~294 hours conventional potentiometric method)
- ❑ The shape of EC are similar within 0-45°C
- ❑ As the cell aged, the peak value of the EC shifted towards higher SOC

* Y. Hu, S.Y. Choe, T.R. Garrick. *Electrochimica Acta*. 2020 Dec 1;362:137124

Conclusion and future work

Achievement

- Design of a multifunctional calorimeter suitable for various types and operating conditions of the cell
- The development of HTFDA significantly reduces the time of EC measurement
- Measured HGRs are validated with theoretical equation

Future work

1. Understanding the physic reasons that the HGR varies as a function of pressure, temperature gradient, aging, 2D …
2. Validation using the physic equations on electrochemical model

Thank you!