New Insights using Isothermal Calorimetry and High Precision Cycling

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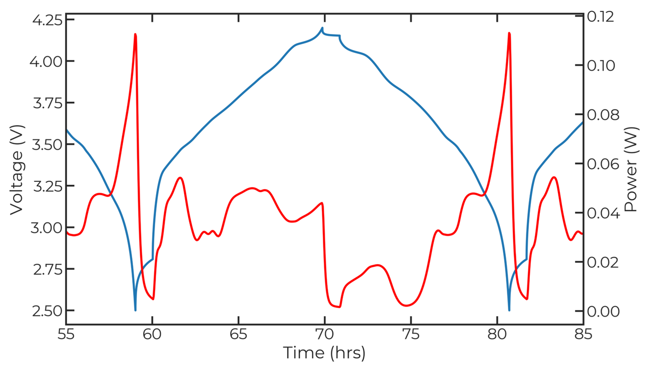
Isothermal Evaluation of Commercial 18650

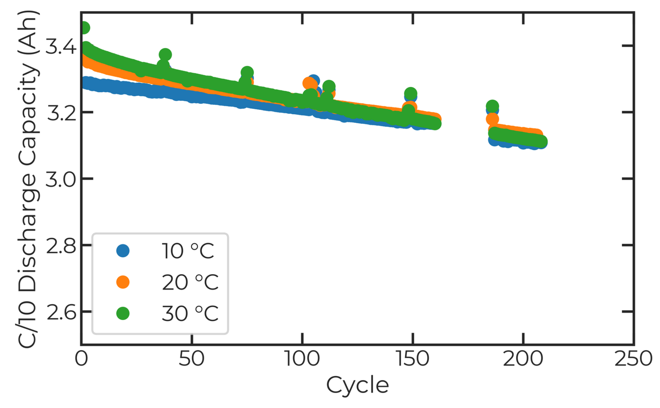
National Research Council Canada | Conseil national de recherches Canada

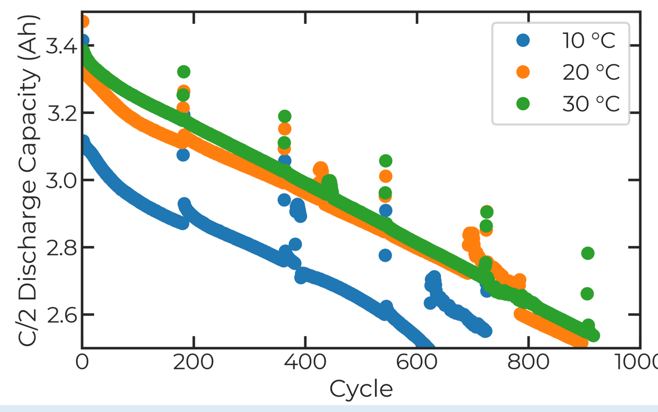
Moli high energy density 18650s (NCA | SiGr) were studied by long term cycling at constant temperature (NRC) and by *in-operando* isothermal calorimetry in a TA Instruments TAMIV MicroXL (Cyclikal)



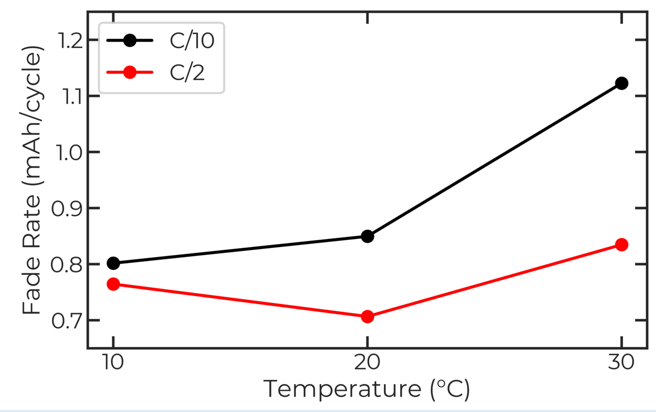
The heat flow is defined as

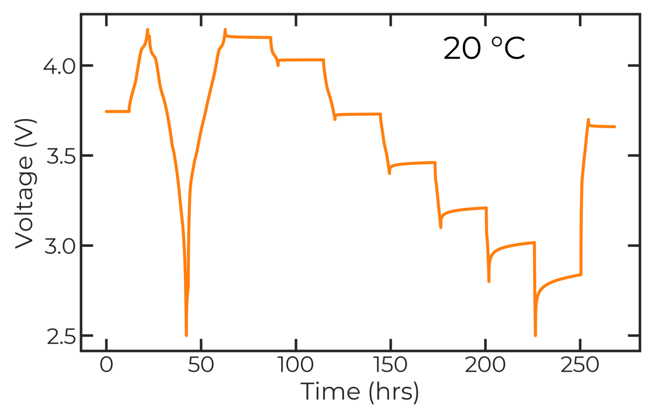
$$\dot{q} = \underbrace{I\eta}_{\text{hysteresis}} + \underbrace{\frac{IT}{nF}\frac{dS}{dx}}_{\text{entropy}} + \underbrace{\dot{q}_p}_{\text{parasitics}}$$



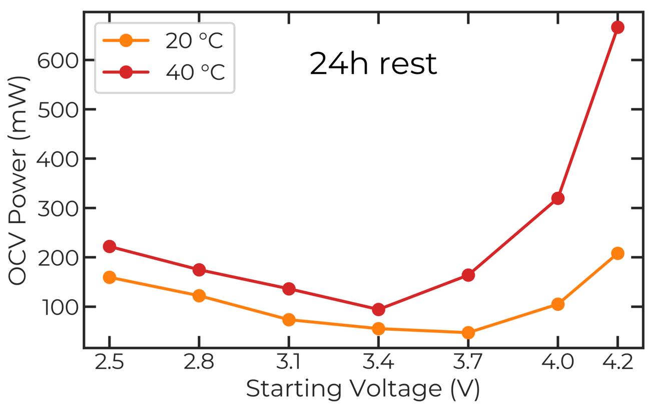


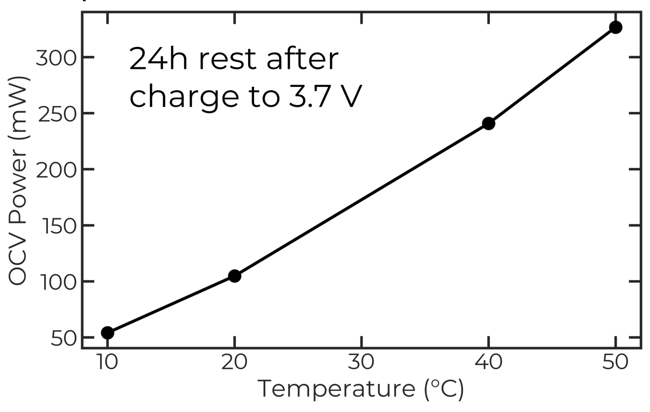
- Long term cycling shows fade rate dependence on cycling rate and temperature.
- Fade rate decreases with increasing cycling rate.
- New failure mode starts below 20°C.

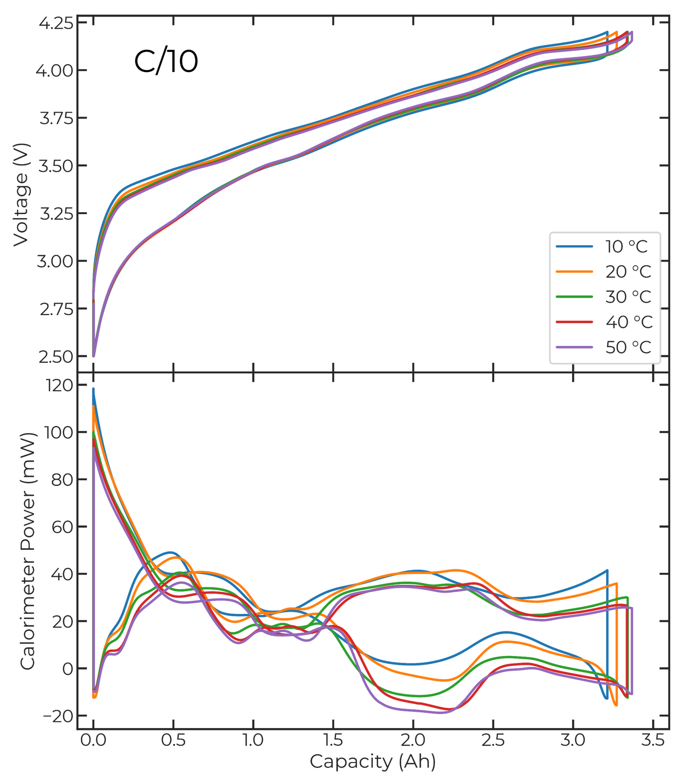




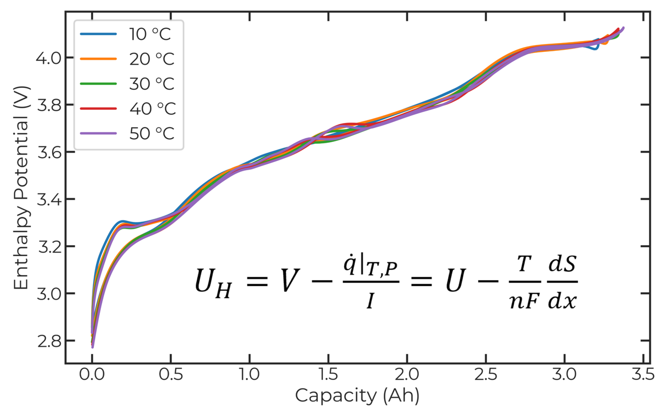
- Stepped discharge with 24h open circuit heat flow measurements.
- Parasitics strongly depend on temperature at high voltage but much less at low voltage
- Parasitics increase with temperature, parasitics are not responsible for increased fade rate at low temperature.







- *In-operando* heat flow measured in a broad range of temperatures.
- Enthalpy potential (U_H) shows reversibility (except in Si region) and very weakly influenced by entropy.
- Enthalpy potential can be used to predict heat flow for broad range of temperatures: $\dot{q} = I(V - U_H)$



$$U_H = V - \frac{\dot{q}|_{T,P}}{I} = U - \frac{T}{nF}\frac{dS}{dx}$$

Calorimetric Signature of Structural Changes in Silicon

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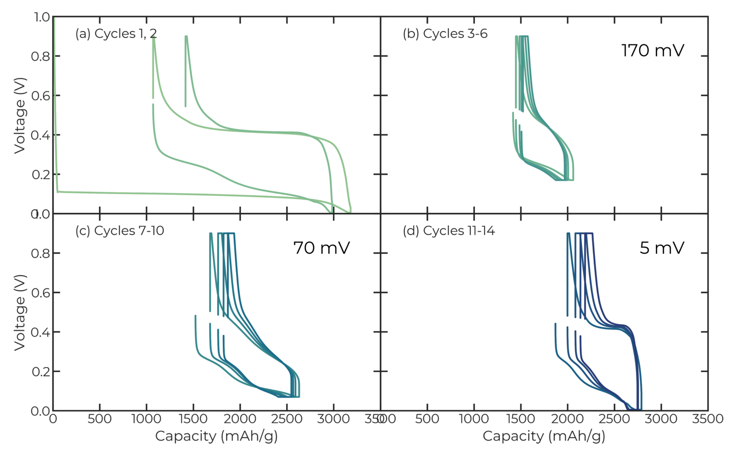
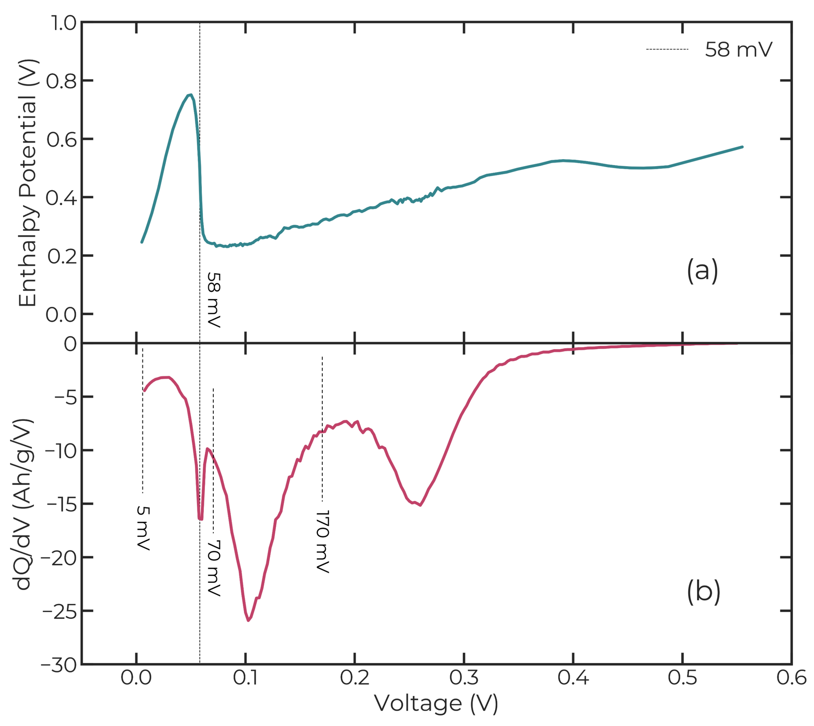
Silicon has unique, voltage dependent, electrochemical behaviors, such as $Li_{15}Si_4$ crystallization. For the first time these behaviors are carefully characterized with isothermal calorimetry.

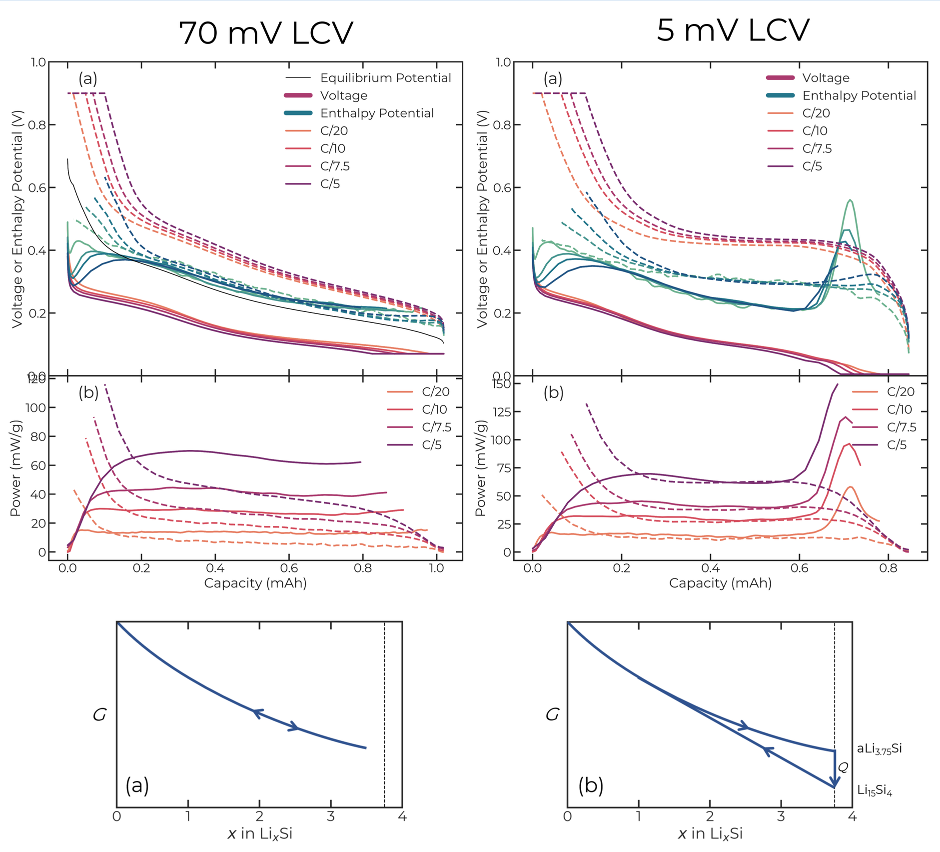
- Metallurgical silicon half cells for pure silicon behavior (Dalhousie)
- In-operando isothermal calorimetry in a TA Instruments TAMIII with 20 mL calorimeters (Cyclikal)
- Figure shows impact of lower voltage cutoff (LCV).



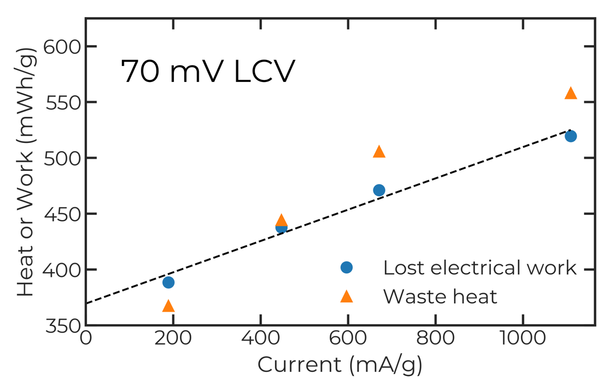
- Different cutoffs correspond to different regions of the dQ/dV curve.
- **The crystallization of $Li_{15}Si_4$ has a very small feature in the dQ/dV but a very large exotherm in the isothermal calorimetry!**
- The lithiation in the amorphous Li_xSi region is featureless and consistent with solid thermodynamics.

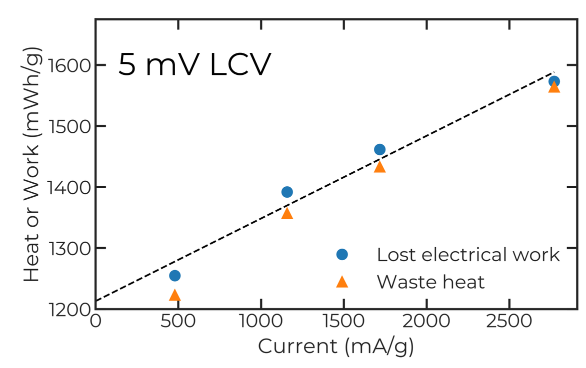


- 70 mV LCV shows no crystallization exotherm, and an enthalpy potential which is identical on lithiation and delithiation indicating a reversible process.
- 5 mV LCV shows a crystallization exotherm, and different enthalpy potential on lithiation and delithiation indicating thermodynamic path dependence.



- The lost electrical work (voltage curve hysteresis) is consistent with the waste heat (calorimeter) at all currents.
- Substantial heat is predicted at zero currents for all LCVs, showing current independent hysteresis.
- Significantly larger heat is produced if the Si crystallizes, showing the importance of the Si structure in real world applications for thermal management and efficiency.





V. L. Chevrier, Z. Yan, S. L. Glazier, M. N. Obrovac, and L. J. Krause, *J. Electrochem. Soc.*, **168**, 030504 (2021)

Contact Cyclikal for cell characterization services and consulting.
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