

## New Insights using Isothermal Calorimetry and High Precision Cycling

In-operando isothermal calorimetry is a powerful tool for the study of active materials for energy storage. It has been used to study positive<sup>1-3</sup> and negative<sup>4-7</sup> electrode materials in half cells, as well as in symmetrical<sup>4,5</sup> and full cells.<sup>8-15</sup> Calorimetry can be used to quantify parasitic reactions enabling lifetime predictions but also identify structural and entropy changes in materials. This presentation will cover recent developments in both of these areas.

### Parasitics and Lifetime Predictions in Commercial Cells

High precision calorimetry is now possible on large format cells such as 18650s. High precision calorimetry and coulometry was performed at various temperatures on commercial 18650s allowing a quantification of the temperature dependence of coulombic efficiency and parasitics. Identical commercial cells underwent long term cycling. The comparison of parasitics to long term cycling at various temperatures establishes the applicability of isothermal calorimetry as a technique for commercial cell development or evaluation of commercial cells for a given application.

### Calorimetric Signature of Structural Changes in Silicon<sup>16</sup>

Silicon remains a promising material for increasing the energy density of Li-ion cells via addition to the negative electrode. Unlike graphite, the structural evolution of Si during lithiation and delithiation is uniquely dependent on the cycling conditions and can show either reversible or path dependent behavior. However, the calorimetric signature of this path dependence had never been characterized. In this presentation, metallurgical Si is cycled to exhibit both reversible and path dependent cycling while in-operando calorimetry is performed with a high

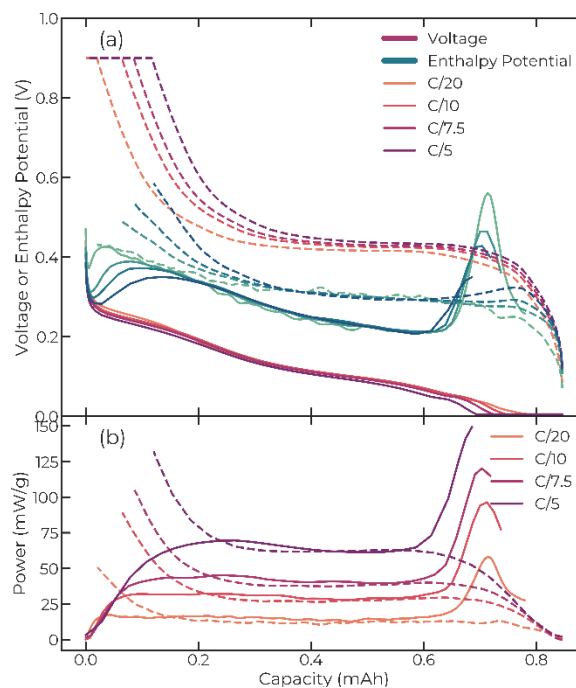


Figure 1. (a) Voltage, enthalpy potential and (b) thermal power for Si cycled between 5 mV and 0.9 V at various currents. (solid curves lithiation; dashed curves delithiation).

precision isothermal calorimeter. Figure 1 shows the voltage, calorimeter power and enthalpy potential of Si and the large exothermic signature of the crystallization to  $\text{Li}_{15}\text{Si}_4$  at full lithiation allowing the first quantification of the enthalpy of crystallization of  $\text{Li}_{15}\text{Si}_4$ . The voltage dependence of the parasitics in Si are also quantified. The results of this in depth calorimetric study of metallurgical Si provides valuable insights into the heat production and energy efficiency of Si as a negative electrode material in Li-ion batteries.

## References

1. M. M. Huie et al., *J. Phys. Chem. C*, **122**, 10316–10326 (2018) <https://pubs.acs.org/doi/10.1021/acs.jpcc.8b01681>.
2. M. M. Huie et al., *ACS Appl. Mater. Interfaces*, **11**, 7074–7086 (2019) <https://pubs.acs.org/doi/10.1021/acsami.8b20636>.
3. D. Chalise, W. Lu, V. Srinivasan, and R. Prasher, *J. Electrochem. Soc.*, **167**, 090560 (2020).
4. L. J. Krause, L. D. Jensen, and J. R. Dahn, *J. Electrochem. Soc.*, **159**, A937–A943 (2012) <http://jes.ecsdl.org/content/159/7/A937.abstract>.
5. V. L. Chevrier et al., *J. Electrochem. Soc.*, **161**, A783–A791 (2014) <http://jes.ecsdl.org/cgi/doi/10.1149/2.066405jes>.
6. L. M. Housel et al., *ACS Appl. Mater. Interfaces*, **11**, 37567–37577 (2019).
7. W. Li, M. N. Vila, E. S. Takeuchi, K. J. Takeuchi, and A. C. Marschilok, *MRS Adv.*, 1–10 (2020) [https://www.cambridge.org/core/product/identifier/S2059852120003126/type/journal\\_article](https://www.cambridge.org/core/product/identifier/S2059852120003126/type/journal_article).
8. L. E. Downie, K. J. Nelson, R. Petibon, V. L. Chevrier, and J. R. Dahn, *ECS Electrochem. Lett.*, **2**, A106–A109 (2013) <http://eel.ecsdl.org/cgi/doi/10.1149/2.010310eel>.
9. L. E. Downie and J. R. Dahn, *J. Electrochem. Soc.*, **161**, A1782–A1787 (2014) <http://jes.ecsdl.org/cgi/doi/10.1149/2.0301412jes>.
10. L. E. Downie, S. R. Hyatt, A. T. B. Wright, and J. R. Dahn, *J. Phys. Chem. C*, **118**, 29533–29541 (2014) <http://pubs.acs.org/doi/10.1021/jp508912z>.
11. L. E. Downie, S. R. Hyatt, and J. R. Dahn, *J. Electrochem. Soc.*, **163**, A35–A42 (2016) <https://iopscience.iop.org/article/10.1149/2.0081602jes>.
12. D. S. Hall, S. L. Glazier, and J. R. Dahn, *Phys. Chem. Chem. Phys.*, **18**, 11383–11390 (2016) <http://xlink.rsc.org/?DOI=C6CP01309K>.
13. L. J. Krause, L. D. Jensen, and V. L. Chevrier, *J. Electrochem. Soc.*, **164**, A889–A896 (2017) <http://dx.doi.org/10.1149/2.1651704jes>.
14. L. J. Krause, T. Brandt, V. L. Chevrier, and L. D. Jensen, *J. Electrochem. Soc.*, **164**, A2277–A2282 (2017) <http://jes.ecsdl.org/lookup/doi/10.1149/2.0501712jes>.
15. L. J. Krause, V. L. Chevrier, L. D. Jensen, and T. Brandt, *J. Electrochem. Soc.*, **164**, A2527–A2533 (2017) <http://jes.ecsdl.org/lookup/doi/10.1149/2.1121712jes>.
16. V. L. Chevrier, Z. Yan, S. L. Glazier, M. N. Obrovac, and L. J. Krause, *J. Electrochem. Soc.*, **168**, 030504 (2021) <https://iopscience.iop.org/article/10.1149/1945-7111/abe16a>.