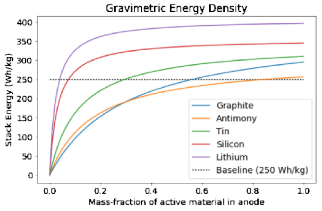
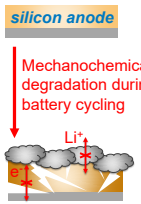
A04-0491 - Reduced electrolyte reactivity of pitch-carbon coated Si nanoparticles for Li-ion battery anodes

Maxwell C. Schulze, Kae Fink, Jack Palmer, Gerard M. Carroll, Nikita Dutta, Christof Zwiefel, Chaiwat Engtrakul, Sang-Don Han, Nathan R. Neale, Bertrand Tremolet de Villers
DOE VTO Silicon Consortium Project

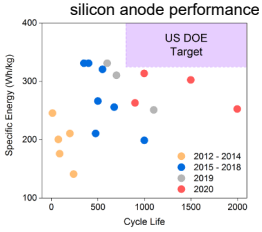
Silicon as an Anode in Li-ion Batteries

$C_{6\ (graphite)} + Li^+ + e^- \longleftrightarrow LiC_6$ vs. $4\ Si + 15\ Li^+ + 15\ e^- \longleftrightarrow Li_{15}Si_4$

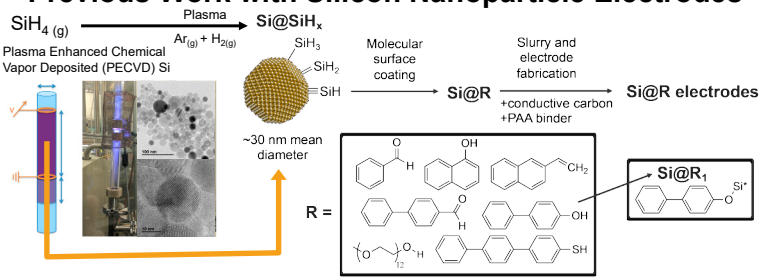


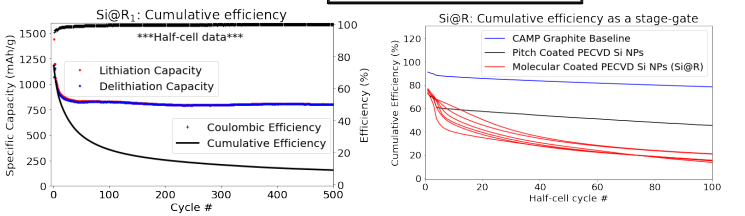


Recent improvements in silicon anode performance



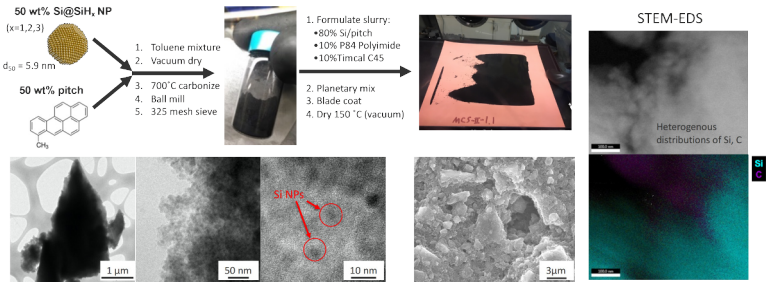
Previous Work with Silicon Nanoparticle Electrodes





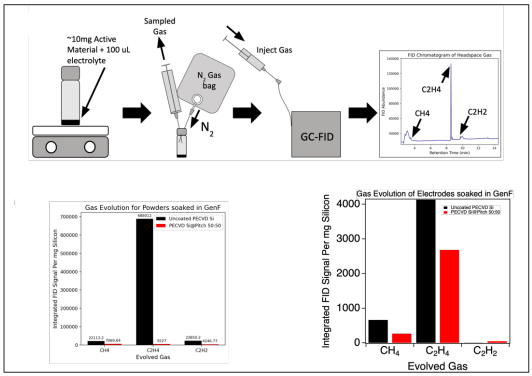
Half-cell cycling is promising, but cumulative coulombic efficiency suggests molecular coated PECVD Si nanoparticles will not have long cycle lifetimes in full-cells where the Li-inventory is limited.

Synthesis of Si/pitch Composite Electrodes



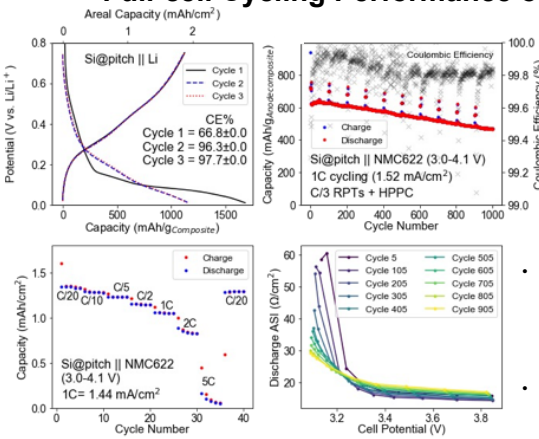
Synthesis of Si/pitch composite material by carbonizing a mixture of pitch and the PECVD Si NPs forms micron sized secondary particles comprising <10 nm Si NPs embedded in a conducting carbon matrix.

Si/Pitch Minimizes Chemical Reactivity with Electrolyte



- Si-containing anodes can have high chemical reactivities with electrolytes containing $LiPF_6$ in carbonate solvents
- Uncoated PECVD Si reacts with 1.2 M LiPF6 in EC:EMC (3:7) + 3% FEC to form significant amounts CH_4, C_2H_4, and C_2H_2 gasses
- Si/pitch protects Si surface from reacting with electrolytes as evidenced by significantly less gas produced

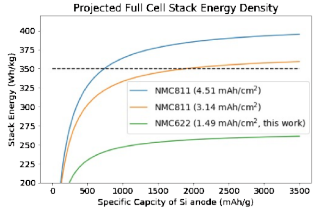
Full-cell Cycling Performance of Si/Pitch

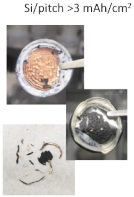


- Despite lower reactivity with electrolyte, Si/pitch electrodes still require prelithiation in a half-cell to account for low 1st cycle efficiency of ~67%
- Si/pitch reassembled into a full-cell vs. an NMC622 cathode with N/P≈1.3, exhibits ~75% capacity retention after 1000 cycles
- Si/pitch electrode delivers >1 mAh/cm² up to 1C cycling rate; capacity utilization falls off at a 2C rate with minimal delivered capacity at a 5C rate
- Area specific impedance (ASI) for the Si/pitch-NMC622 full-cell has negligible increase over 1000 cycles

Future Challenges

- The Si/pitch electrodes tested in this work are comparatively low loadings (< 2 mAh/cm²)
- Higher loading electrodes (>3 mAh/cm²) are needed to improve energy density of Si/pitch
- Higher loading Si/pitch electrodes exhibit severe macro-mechanical stresses that shred Cu foil





References

1. J. D. McBrayer, M. T. F. Rodrigues, M. C. Schulze et al., *Nat. Energy*, **6**, 866–872 (2021).
2. M. C. Schulze and N. R. Neale, *ACS Energy Lett.*, **6**, 1082–1086 (2021).
3. M. C. Schulze, Kae Fink, Jack Palmer, et al., *JECS*, in preparation (2022).

This research was supported by the U.S. Department of Energy's Vehicle Technologies Office under the Silicon Consortium Project, directed by Brian Cunningham, and managed by Anthony Burrell. This work was conducted in part by the Alliance for Sustainable Energy, LLC, the manager and operator of the National Renewable Energy Laboratory for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.

242nd Electrochemical Society Meeting
Atlanta, GA
October 9-13, 2022

NREL/PO-5700-84240