Evaluating Contributions of Pitch-Carbon Coating to Improved Stability of Si Anodes through Voltage-Resolved Multi-Phase Characterization

Kae Fink, National Renewable Energy Laboratory

Experimental Team (NREL):

Kae Fink, Jack Palmer, Christof Zwiefel, Maxwell Schulze, Gerard M. Carroll, Sarah Frisco, Glenn Teeter, Chaiwat Engtrakul, Sang-Don Han, Nathan R. Neale, Bertrand Tremolet de Villers

Continuum Modeling Team (NREL):

Peter Weddle, Ankit Verma, Andrew Colclasure

Atomistic Modeling Team (LBNL):

Evan Spotte-Smith, Sudarshan Vijay, Kristin Persson

Transport Modeling & Experimental Teams (ORNL):

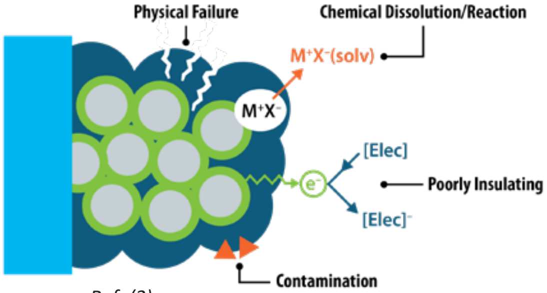
Lorena Alzate Vargas, Jean-Luc Fattebert, Gabriel Veith

242nd ECS Meeting
October 9, 2022

Motivation: Promise and Challenges of Si Anodes

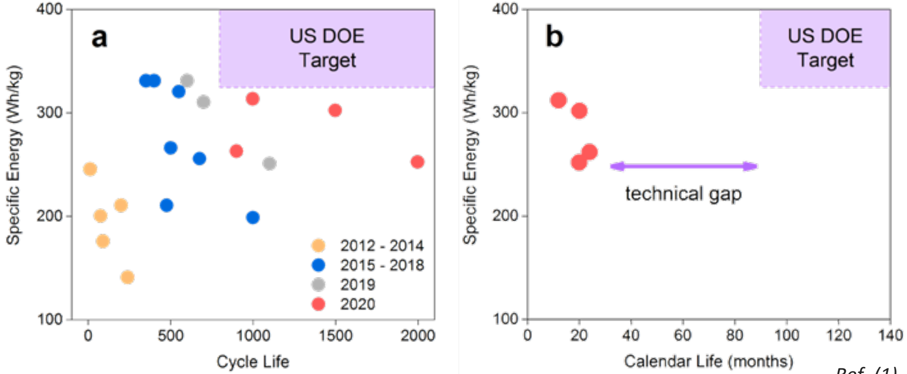
Expansion of renewable technologies and electrification of the transportation sector contributes to a growing demand for **next-generation battery materials** to provide:

- ❖ High energy density
- ❖ High power density
- ❖ Long cycle life
- ➢ Long calendar life



Ref. (2)

Silicon is a promising next-generation anode candidate, offering an ideal theoretical capacity ~10x that of graphite.



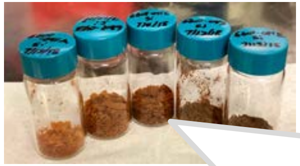
Ref. (1)

Leading Si anode battery demonstrations are approaching target metrics for cycle life, but complex modes of reactivity and degradation result in *reduced calendar life*. **Understanding and deconvoluting these processes is critical for viable Si anodes.**

(1) McBrayer, J.D. , M-T.F. Rodrigues, M.C. Schulze, D.P. Abraham, C.A. Apblett, I. Bloom, G.M. Carroll, A.M. Colclasure, C. Fang, K.L. Harrison, G. Liu, S.D. Minteer, N.R. Neale, G.M. Veith, C.S. Johnson, J.T. Vaughey, A.K. Burrell, B. Cunningham. 2021. *Nature Energy* 6: 866–872; (2) R. Kostecki. Annual Merit Review Presentation. 2022, Washington, DC.

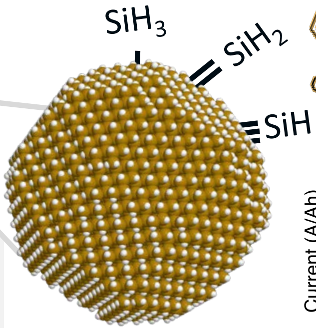
Introduction: Surface-Functionalized PECVD Si

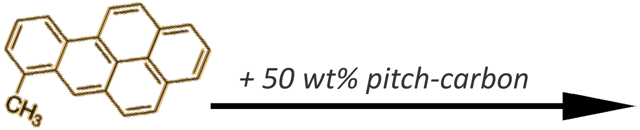
- **PECVD Si** (~6 nm) is a strong candidate to meet energy density targets for next-generation Si anodes.
- Nanosized Si suffers from high reactive surface area in native (unfunctionalized) form.
- Surface functionalization reduces overall reactivity, but influences the properties of the SEI (and thus performance stability, calendar life) in ways that are not fully understood.



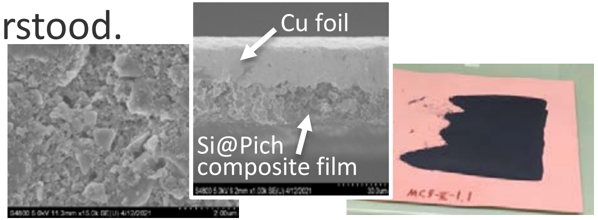
Nano-scale PECVD Si

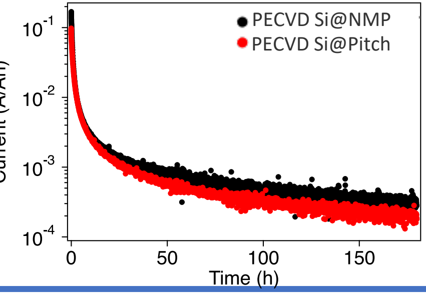
More details: Poster A04-0491 (M. Schulze)

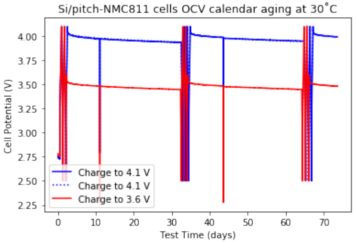


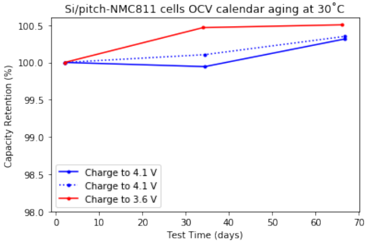


+ 50 wt% pitch-carbon









Data collected by M.C. Schulze (NREL)

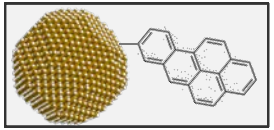
Optimal surface functionalization strategy(ies) for nano-Si should:

1) Promote pathways that contribute to stable calendar life
2) Disrupt pathways that contribute to unstable calendar life

Goal: *Evaluate how Si surface functionalization impacts the progression & favorability of specific reaction pathways associated with improved performance and calendar life.*

Materials Specifications & Experimental Approach

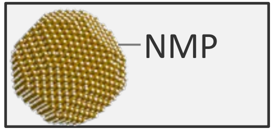
Pitch-Coated PECVD Si (Si@Pitch)



M.C. Schulze, NREL

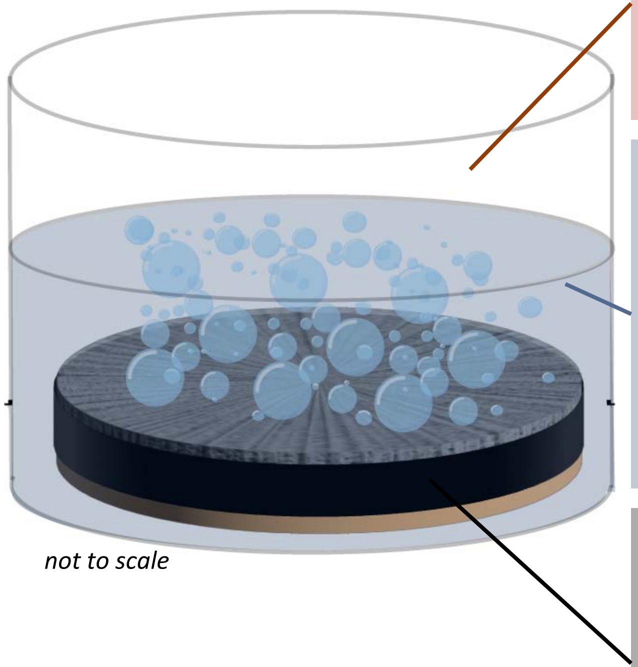
- (50% Si + 50% pitch):C45:P84 = 8:1:1
- Powder: Annealed at 700 °C
- Electrode: Dried at 150 °C
- Approx. loading: ~2.2 mg/cm^2

Uncoated PECVD Si (Si@NMP)



G.M. Carroll, NREL

- Si:C45:P84 = 6:2:2
- Powder: Unannealed
- Electrode: Dried at 420 °C
- Approx. loading: ~1.1 mg/cm^2



not to scale

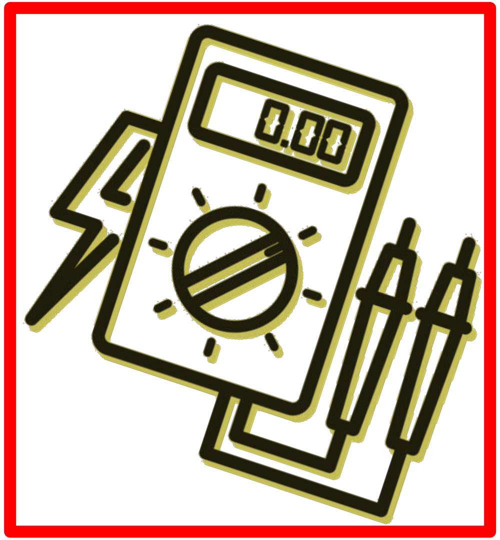
Gas-Phase Reactions:
In situ ID & quantification of gaseous headspace (*in situ; GC-MS-FID*)

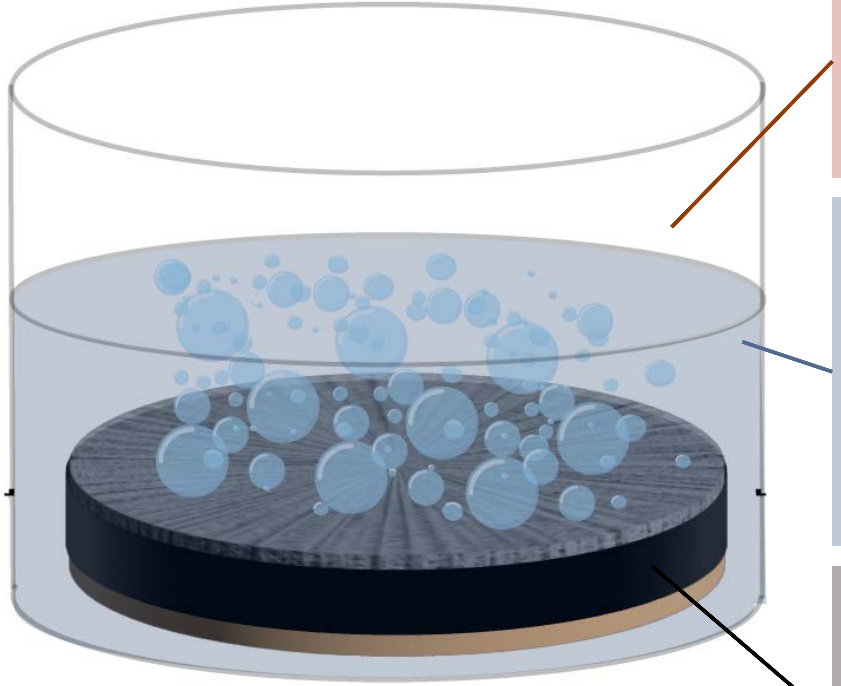
Liquid-Phase Reactions:
ID & semi-quantitative tracking of electrolyte & soluble SEI components (*ex situ/post-mortem; SPME-GC-MS*)

Solid-Phase Reactions:
Analyze evolution of anode SEI (*ex situ/post-mortem; FT-IR + XPS*)

We have coupled multi-modal and multi-phase in situ/ex situ/post-mortem techniques to holistically probe contributions of pitch coating to SEI evolution and interfacial stability.

Electrochemical Analysis Approach





Gas-Phase Reactions:
In situ ID & quantification of gaseous headspace (*in situ; GC-MS-FID*)

Liquid-Phase Reactions:
ID & semi-quantitative tracking of electrolyte & soluble SEI components (*ex situ/post-mortem; SPME-GC-MS*)

Solid-Phase Reactions:
Analyze evolution of anode SEI (*ex situ/post-mortem*; *FT-IR + XPS*)

Electrochemical Analysis Approach

Reaction pathways associated with SEI growth are multi-phase *and voltage-dependent.*

Voltage Holds @1st Lithiation (180 hr)

- OCV → Pure chemical reactivity
- 1.5V → Salt decomposition; *linear carbonate decomposition*?
- 0.8V → Below FEC reduction potential
- 0.4V → Below EC reduction potential
- 0.05V → Lithiation

Voltage Holds @1st Delithiation (180 hr)

- 0.75V & 1.5V →Re-solubilization of solid SEI?

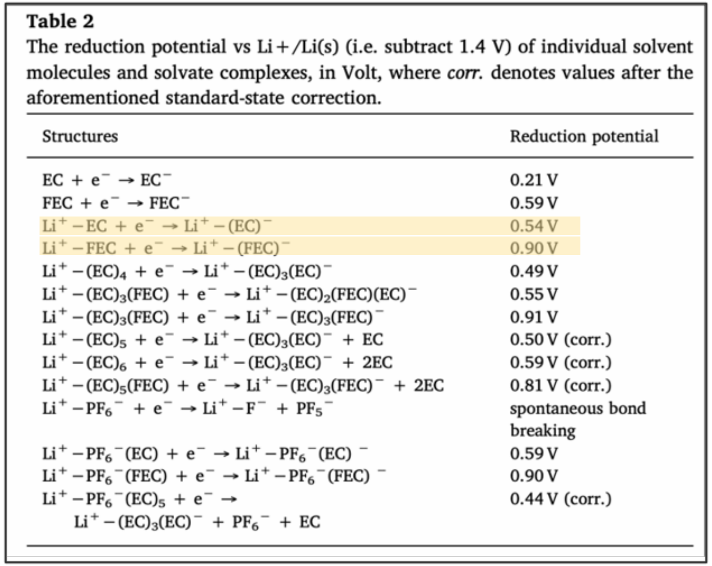
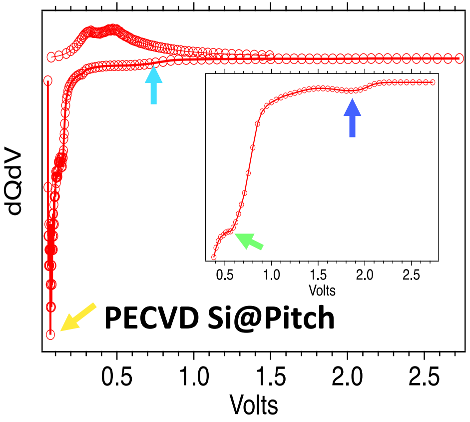
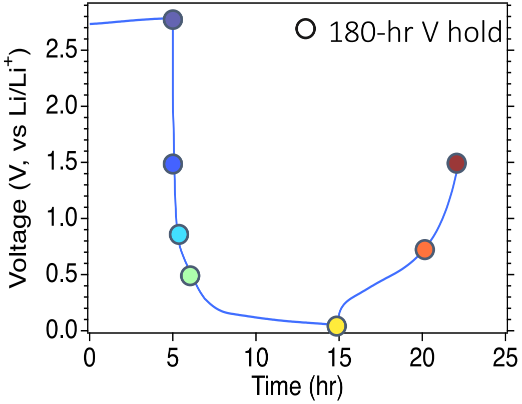


Table 2
The reduction potential vs Li+/Li(s) (i.e. subtract 1.4 V) of individual solvent molecules and solvate complexes, in Volt, where *corr.* denotes values after the aforementioned standard-state correction.

Structures	Reduction potential
$EC + e^- \rightarrow EC^-$	0.21 V
$FEC + e^- \rightarrow FEC^-$	0.59 V
$Li^+-EC + e^- \rightarrow Li^+-(EC)^-$	0.54 V
$Li^+-FEC + e^- \rightarrow Li^+-(FEC)^-$	0.90 V
$Li^+-(EC)_4 + e^- \rightarrow Li^+-(EC)_3(EC)^-$	0.49 V
$Li^+-(EC)_3(FEC) + e^- \rightarrow Li^+-(EC)_2(FEC)(EC)^-$	0.55 V
$Li^+-(EC)_3(FEC) + e^- \rightarrow Li^+-(EC)_3(FEC)^-$	0.91 V
$Li^+-(EC)_5 + e^- \rightarrow Li^+-(EC)_3(EC)^- + EC$	0.50 V (corr.)
$Li^+-(EC)_6 + e^- \rightarrow Li^+-(EC)_3(EC)^- + 2EC$	0.59 V (corr.)
$Li^+-(EC)_5(FEC) + e^- \rightarrow Li^+-(EC)_3(FEC)^- + 2EC$	0.81 V (corr.)
$Li^+-PF_6^- + e^- \rightarrow Li^+-F^- + PF_5^-$	spontaneous bond breaking
$Li^+-PF_6^-(EC) + e^- \rightarrow Li^+-PF_6^-(EC)^-$	0.59 V
$Li^+-PF_6^-(FEC) + e^- \rightarrow Li^+-PF_6^-(FEC)^-$	0.90 V
$Li^+-PF_6^-(EC)_5 + e^- \rightarrow Li^+-(EC)_3(EC)^- + PF_6^- + EC$	0.44 V (corr.)

Hou, T., G. Yang, N. N. Rajput, J. Self, S.-W. Park, J. Nanda, and K. A. Persson. 2019. Nano Energy *64: 103881.*





Voltage holds at reduction potentials of interest allows us to decouple specific (electro)chemical reactions tied to interfacial stability.

***Approach adapted from** Hasa, I., A. M. Haregewoin, L. Zhang, W.-Y. Tsai, J. Guo, G. M. Veith, P. N. Ross, R. Kostecki. 2020.* ACS Appl. Mater. Interf. *12: 40879-40890.*

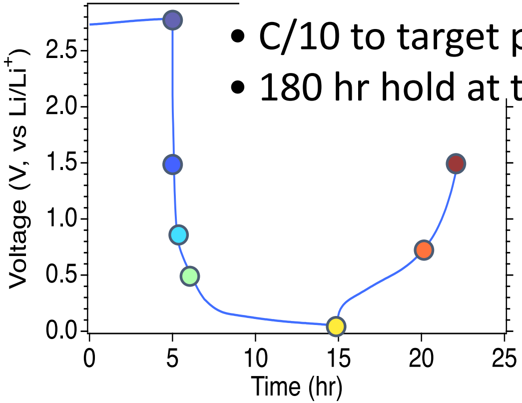
Electrochemical Analysis:

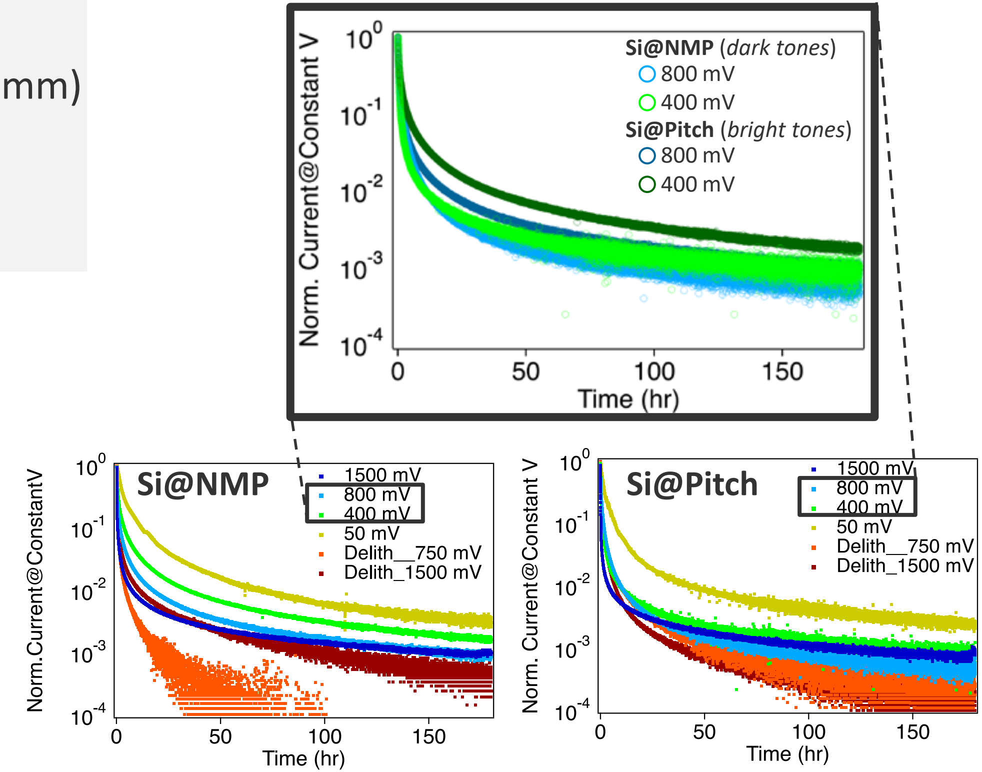
Electrochemical Analysis: Half Cells

- Working Electrodes: **Si@NMP** or **Si@Pitch** (14 mm)
- Counter Electrode: Li^0 (15 mm)
- Celgard 2325 separator (16 mm)
- GenF electrolyte (Gen 2 + 10 wt% FEC; 40 µL)

Voltage Hold Protocol:

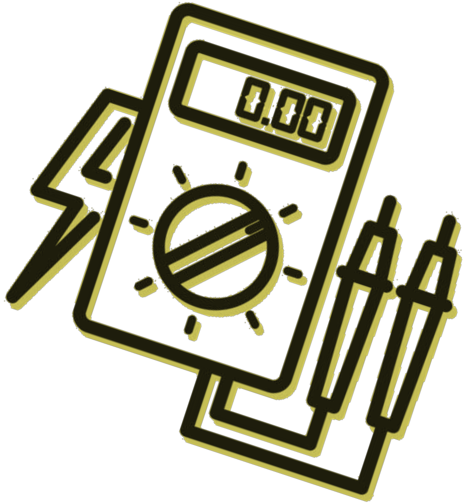
- 5 hr initial OCV rest
- C/10 to target potential
- 180 hr hold at target potential

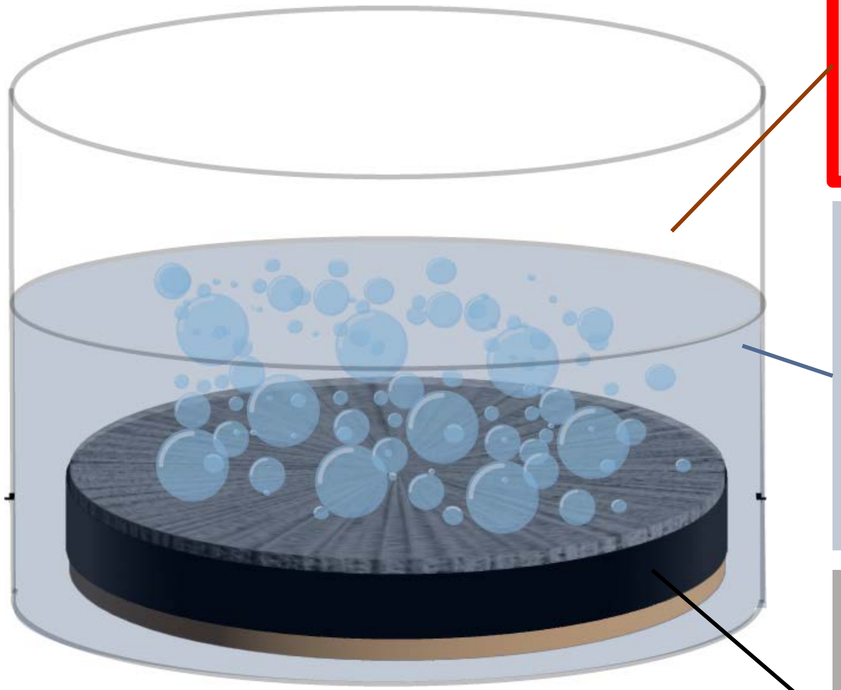




Pitch coating appears to suppress continuous electrochemical reactivity:
Lower & more stable current decay for Si@Pitch vs Si@NMP, particularly <800 mV

Gas-Phase Reactions





<u>Gas-Phase Reactions</u>:
In situ ID & quantification of gaseous headspace (*in situ; GC-MS-FID*)

<u>Liquid-Phase Reactions</u>:
ID & semi-quantitative tracking of electrolyte & soluble SEI components (*ex situ/post-mortem; SPME-GC-MS*)

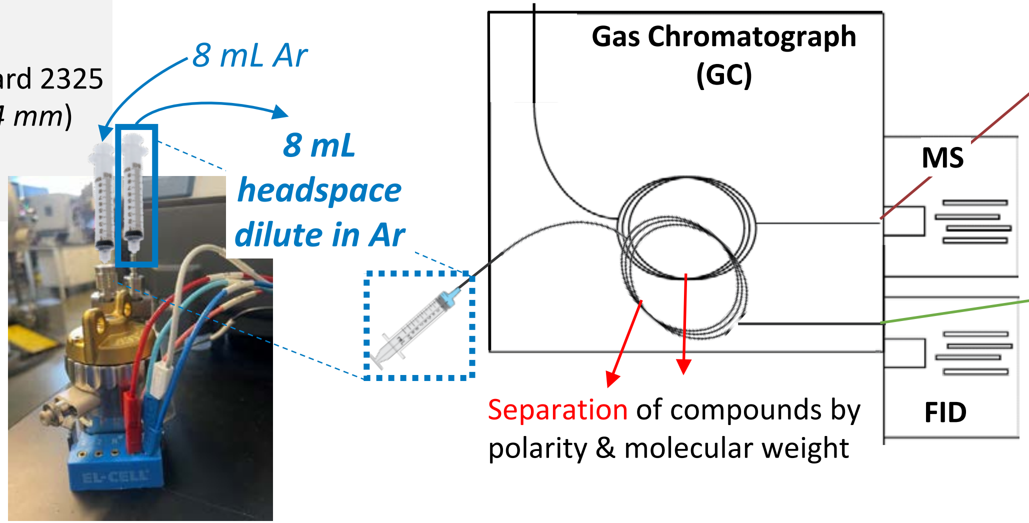
<u>Solid-Phase Reactions:</u>
Analyze evolution of anode SEI (*ex situ/post-mortem*; *FT-IR + XPS*)

Experimental Setup & Analysis Methods

Upper plunger
Li metal (*15 mm*)
Insulation sleeve w/ Celgard 2325
Si electrode on Cu foil (*14 mm*)
Lower plunger (flow field)
+ 200 µL GenF (10 wt% FEC)

<u>El Cell:</u> Coin-type half cell; enables sampling directly from cell headspace (*in situ*)

* Analysis methods optimized quantification of oxide & HC gases



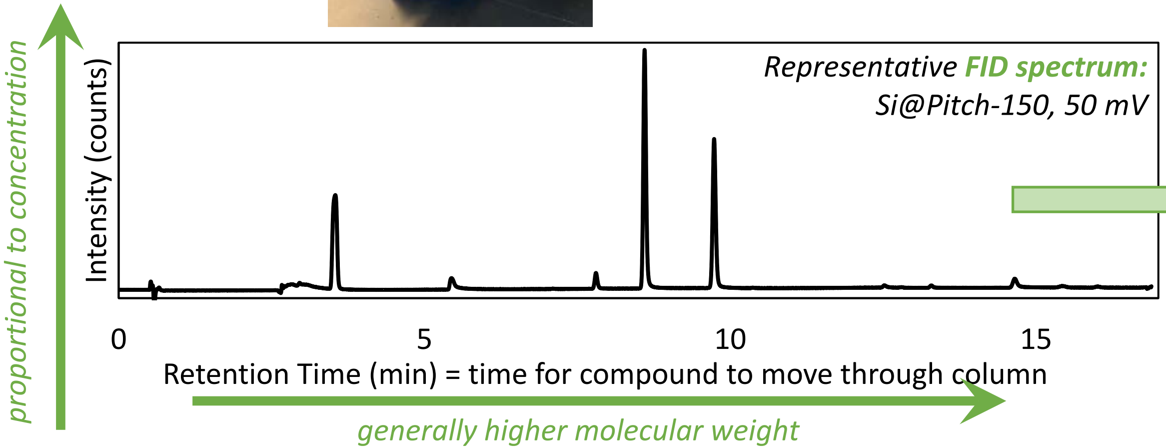
Separation of compounds by polarity & molecular weight

Electron ionization (compound fragmentation)

Mass spectrometer (MS): qualitative ID + signal quantification

Flame ionization (combustion)

Flame Ionization Detector (FID): signal quantification only

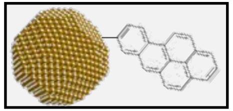


*Representative **FID spectrum:***
Si@Pitch-150, 50 mV

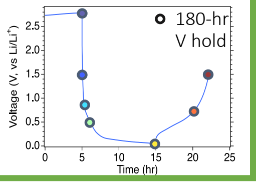
Calibration with standards:
- -Qualitative ID of chemical species
- -Quantification of gas concentration

Gas-Phase Behavior: Si@Pitch

Si@Pitch

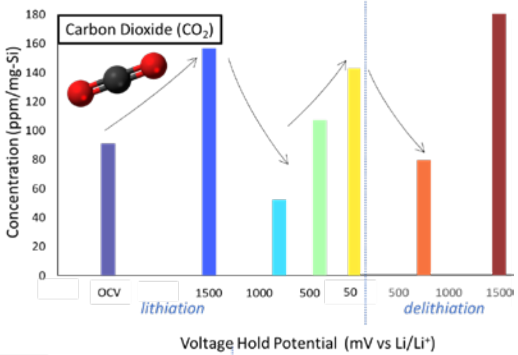


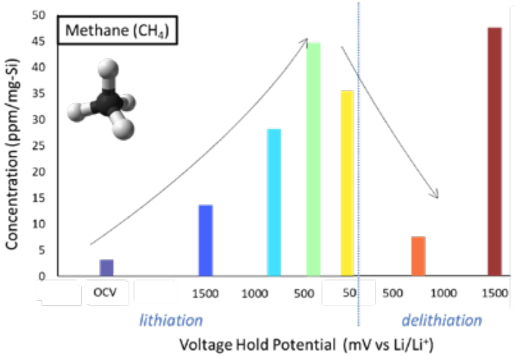
Gas sampled after 180 hr hold at each reported voltage

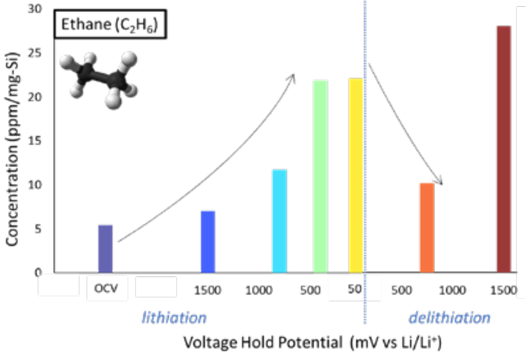


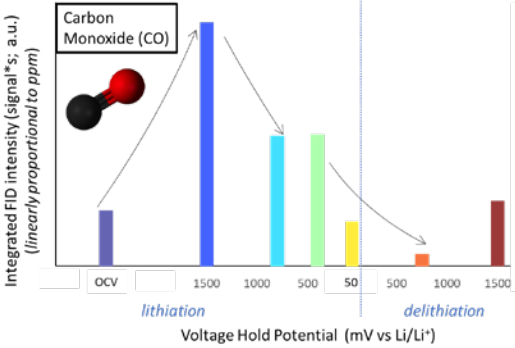
Tracking evolution of 7 gas-phase species across 7 potentials:

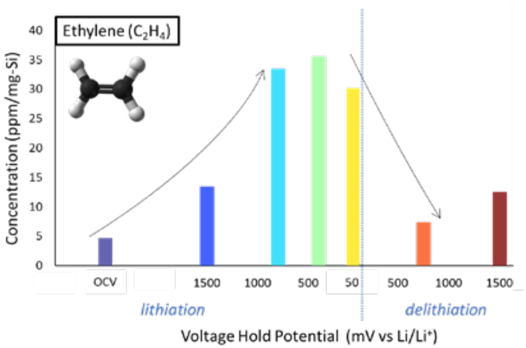
Non-monotonic reactive behavior observed for each gas-phase species.

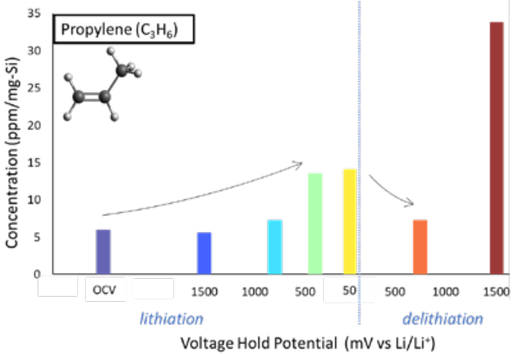


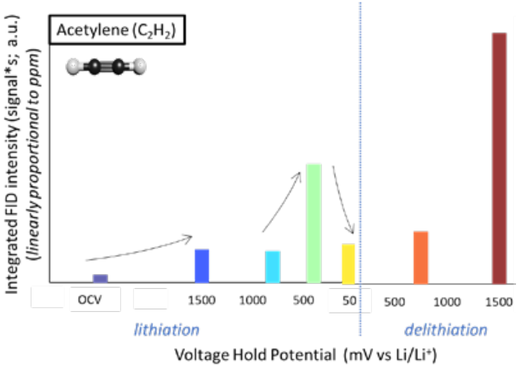






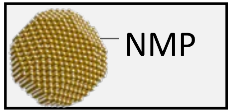




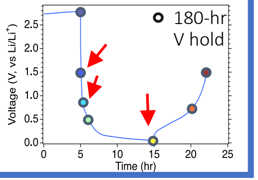


Gas-Phase Behavior: Si@NMP

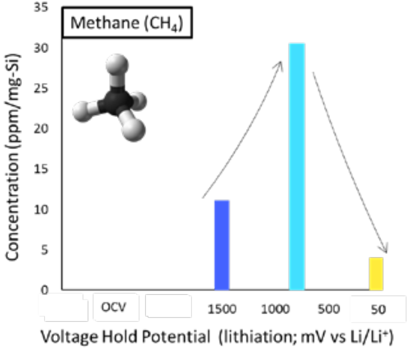
Si@NMP

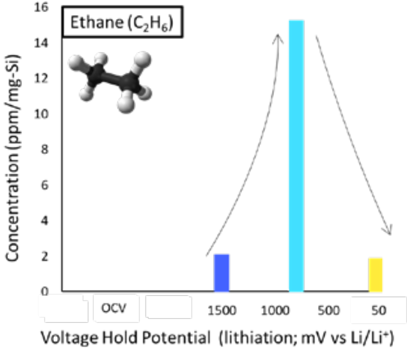


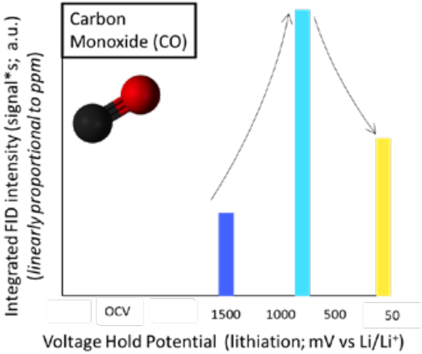
Gas sampled after 180 hr hold at each reported voltage

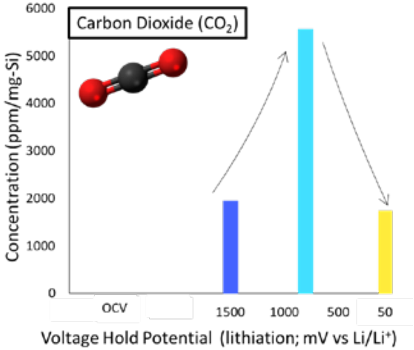


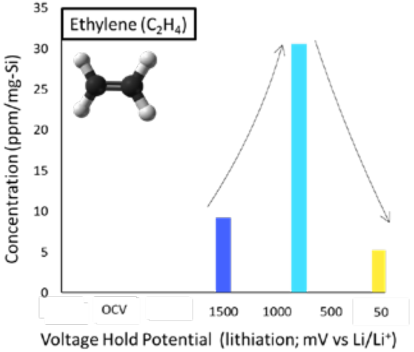
Tracking evolution of 7 gas-phase species across a subset of potentials for reference comparison with Si@Pitch.
Consistent trend in voltage-resolved reactivity across all gases

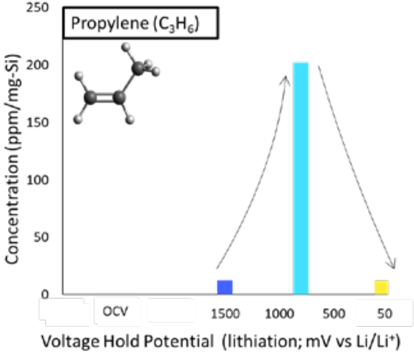


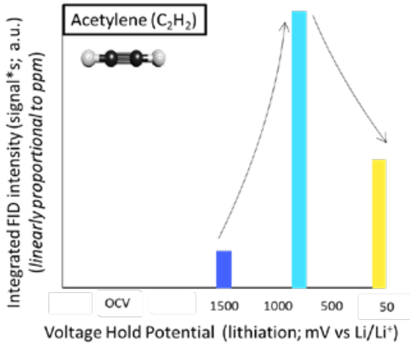












…so what?

2 Si compositions x ***7 gas species*** x ***7 measurement potentials*** = **a lot of convoluted data!**

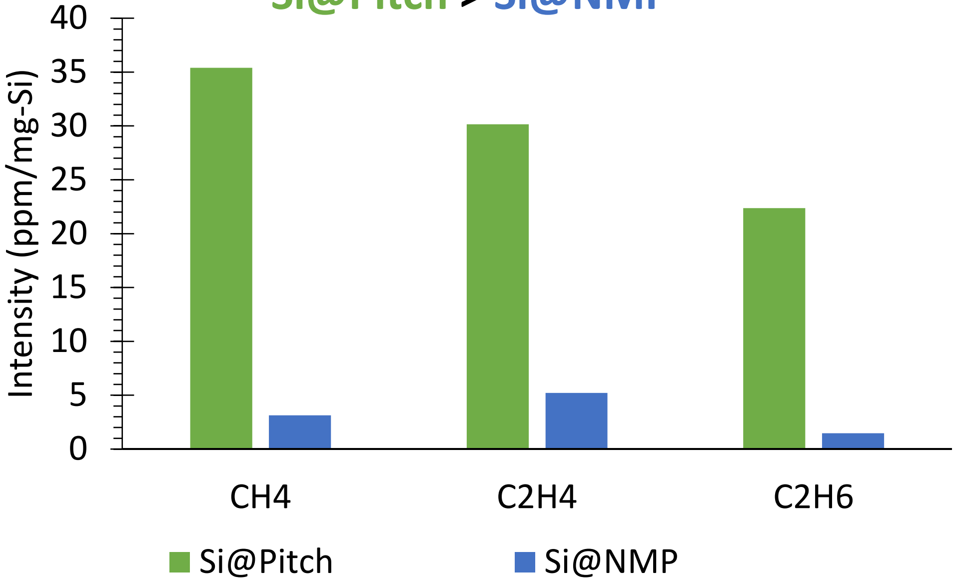
Questions driving analysis:

1) Which pathways produce these gases – and how are these pathways associated with SEI formation?
2) Which of these gases are “good” vs “bad” for calendar life stability?
3) How can varying Si surface properties (e.g., through PECVD Si functionalization) promote or suppress desirable pathways?

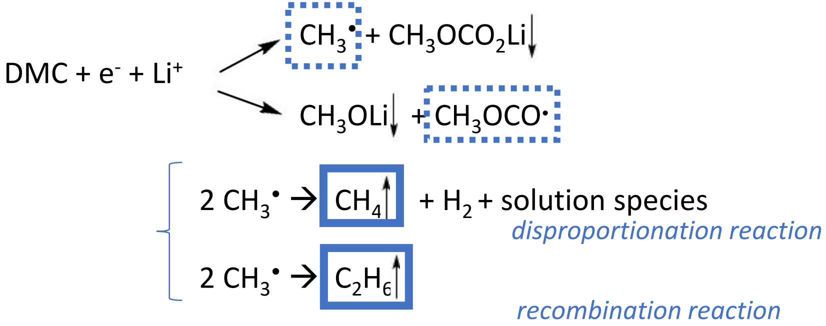
CH_4 / C_2H_6 / C_2H_4: “Simple” Carbonate Reduction

For CH_4, C_2H_4, & C_2H_6 at selected analysis potential (<u>50 mV</u>):

Si@Pitch > Si@NMP



Linear carbonate reduction pathway to form CH_4 and C_2H_6:



$$\mathrm{DMC} + e^- + Li^+ \rightarrow \boxed{CH_3^\bullet} + CH_3OCO_2Li\downarrow$$

$$\mathrm{DMC} + e^- + Li^+ \rightarrow CH_3OLi\downarrow + \boxed{CH_3OCO^\bullet}$$

$$2\,CH_3^\bullet \rightarrow \boxed{CH_4\uparrow} + H_2 + \text{solution species}$$

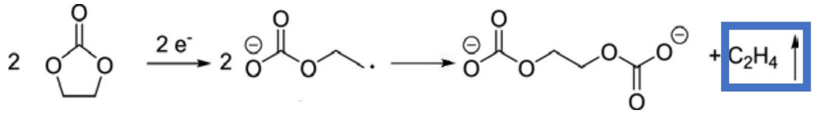
disproportionation reaction

$$2\,CH_3^\bullet \rightarrow \boxed{C_2H_6\uparrow}$$

recombination reaction

D. Aurbach. 2000. J. Power Sources, *89 (2): 206–218.*

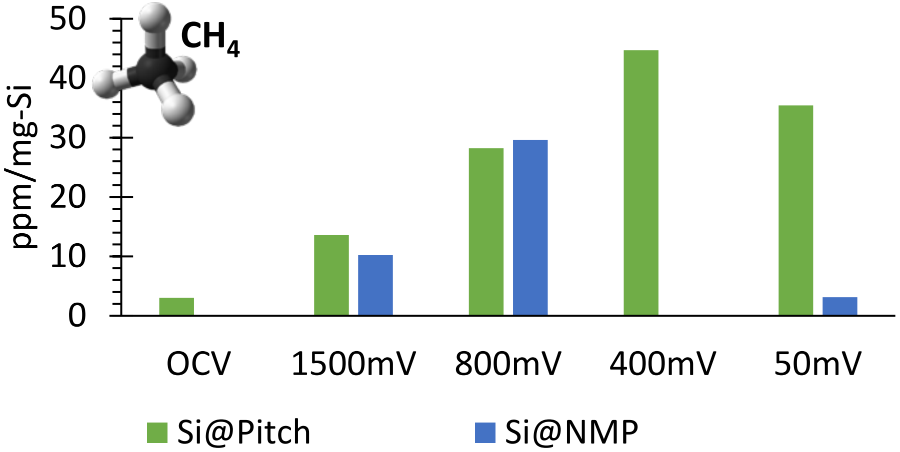
EC reduction pathway to form C_2H_4:

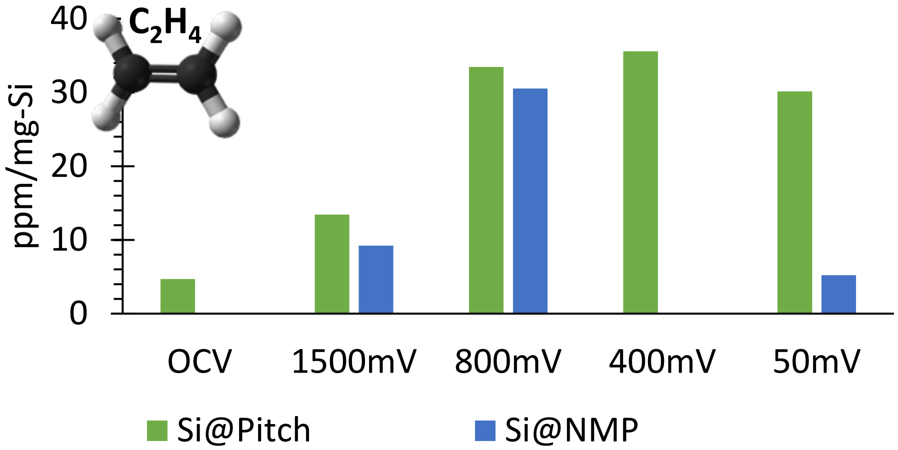


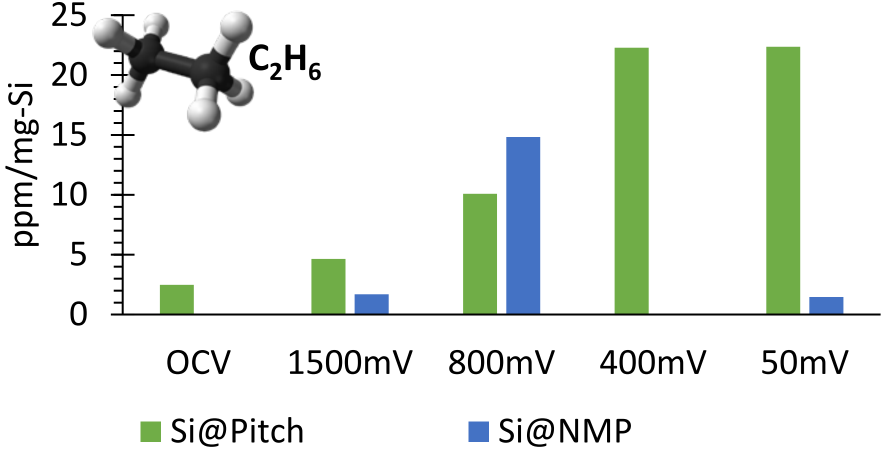
Han, B., C. Liao, F. Dogan, S.E. Trask, S.H. Lapidus, J.T. Vaughey, B. Key. 2019. ACS Appl. Mater. Interfaces, *11 (33): 29780–29790.*

The conjugated carbon rings in pitch coating provides supplemental e^- density, which we anticipate to enhance these carbonate reduction pathways.

CH_4 / C_2H_4 / C_2H_6: “Simple” Carbonate Reduction?







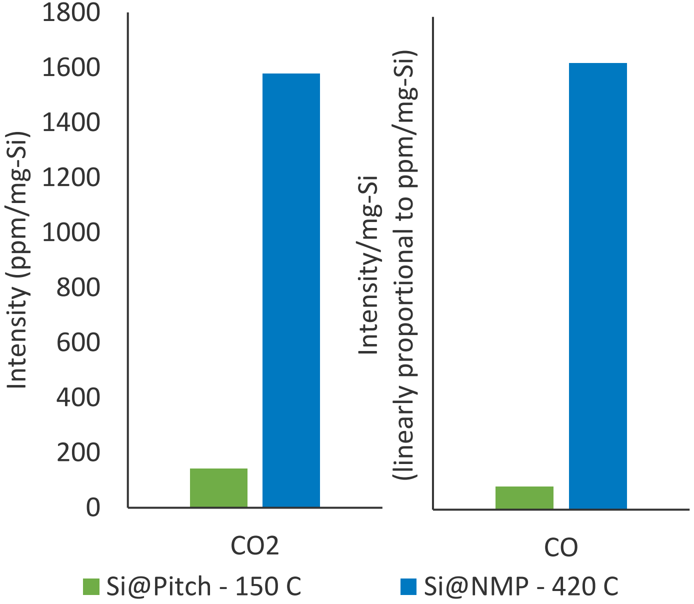
- Si@Pitch shows *increased* production of major hydrocarbon gases (CH_4, C_2H_4, C_2H_6) relative to Si@NMP at 1500 & 50 mV
- Linear carbonate reduction products (CH_4, C_2H_6) are *lower* for Si@Pitch at 800 mV – competition w/ FEC reduction pathway
- Electrochemical benefit of Si@Pitch over Si@NMP (lower residual current; improved cycling and calendar stability) suggests Si@Pitch has more passivating surface

** These results are not necessarily contradictory!*
Evolution of certain first-cycle gases may be tied to a “better” and more stable SEI…we aim to identify which ones

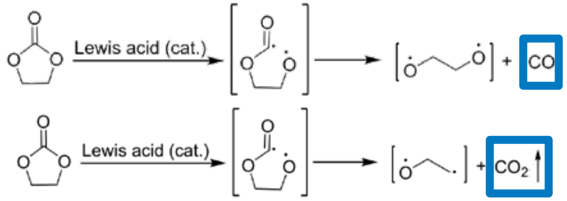
CO, CO_2: Convoluted Reactive Pathways!

For CO_2 and CO at selected analysis potential (<u>50 mV</u>):

Si@Pitch – 150 °C > Si@NMP – 350 °C

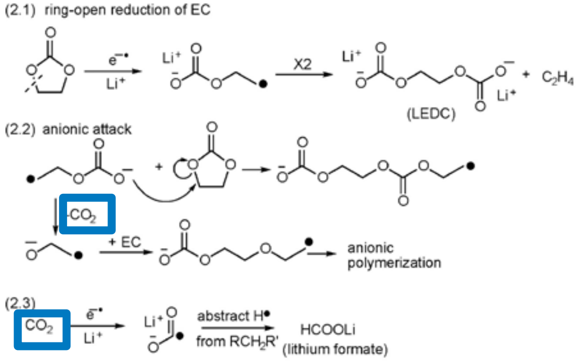


EC reduction pathway to form CO & CO_2:



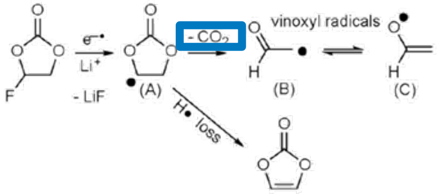
Seitzinger, C.L., R.L. Sacci, J.E. Coyle, C.A. Apblett, K.A. Hays, R.R. Armstrong, A.M. Rogers, B.L. Armstrong, T.H. Bennett, N.R. Neale, G.M Veith. 2020. Chem. Mater., *32 (1): 3199–3210.*

EC reduction pathway to form CO_2:



Jin, Y., N.-J.H. Kneusels, P.C.M.M. Magusin, G. Kim, E. Castillo-Martinez, L.E. Marbella, R.N. Kerber, D.J. Howe, S. Paul, T. Liu, C.P. Grey. 2017. J. Am. Chem. Soc., *139: 14992-15004.*

FEC reduction pathway to form CO_2:



Jin, Y., N.-J.H. Kneusels, P.C.M.M. Magusin, G. Kim, E. Castillo-Martinez, L.E. Marbella, R.N. Kerber, D.J. Howe, S. Paul, T. Liu, C.P. Grey. 2017. J. Am. Chem. Soc., *139: 14992-15004.*

HF production & subsequent reaction to form CO_2:

$PF_5 + H_2O \rightarrow PF_3O + 2HF$

$Li_2CO_3 + 2HF \rightarrow \boxed{CO_2\uparrow} + 2LiF\downarrow + H_2O$

D. Aurbach. 2000. J. Power Sources, *89 (2): 206–218.*

CO forming CO_2 in the presence of unpassivated Si:

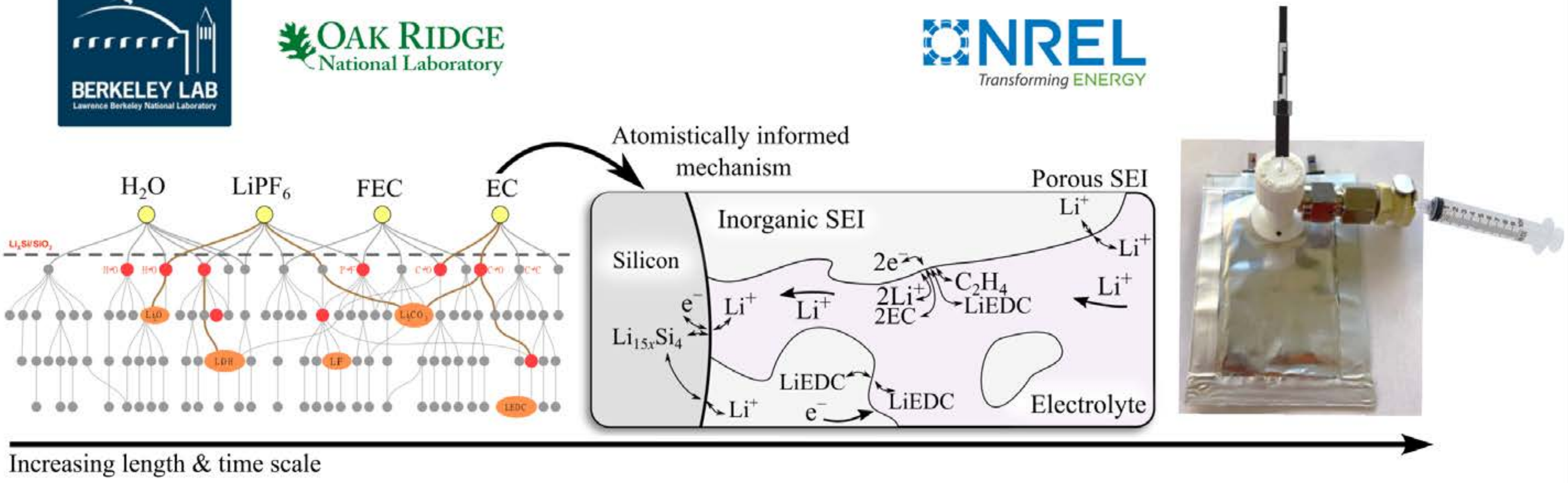
$Si^0 + 2CO_2 \rightarrow SiO_2 + \boxed{2CO\uparrow}$

C.L. Seitzinger, R.L. Sacci, J.E. Coyle, C.A. Apblett, K.A. Hays, R.R. Armstrong, A.M. Rogers, B.L. Armstrong, T.H. Bennett, N.R. Neale, G.M Veith, Chem. Mater. 2020, 32, 1, 3199–3210.

- Lower CO, CO_2 production for Si@pitch relative to Si@NMP: runs counter to HC gas trends
- CO- and CO_2- producing pathways are convoluted – involve both production and consumption

How to determine (and predict) favorability of multiple competing mechanisms for gas production & SEI evolution?

Collaboration: Multi-Scale Modeling Teams



Atomistic modeling & machine learning

- Identify SEI reaction mechanisms
- Predict thermodynamic properties
- Estimates kinetic rates
- Predict initial SEI formation (MD)
- Predict transport properties (MD)

Continuum-level modeling

- Incorporates reaction mechanism
- Predicts long time- & length- scales
- Apt for experimental validation
- Identify strategies for stable SEI growth

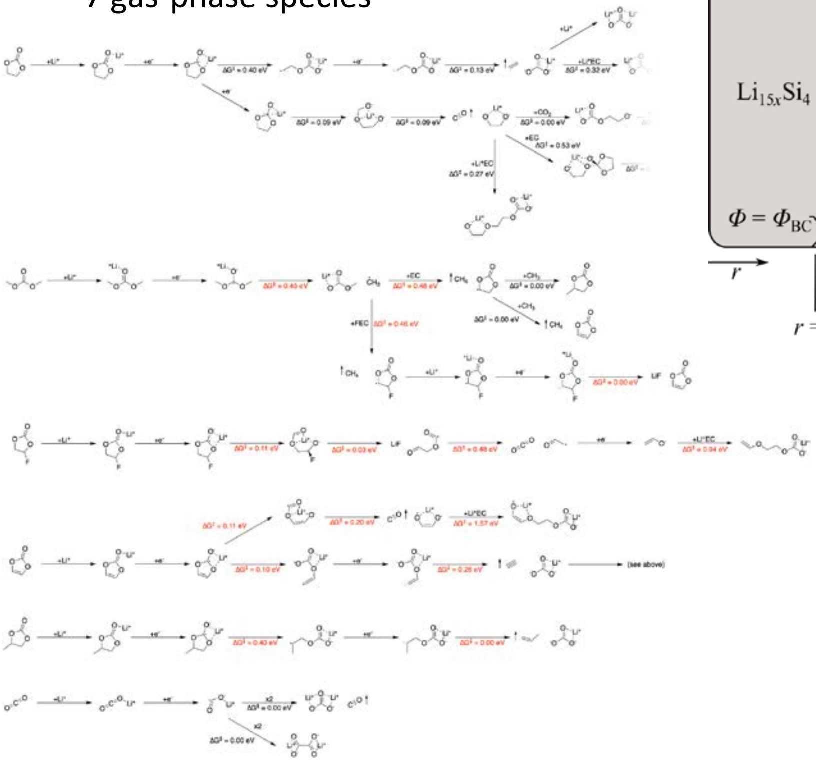
Gas-phase detection

- Quantitative in situ species concentrations
- Extracted after 180 hr V-hold
- Find Si-sensitive gas-phase byproducts
- Postulate reaction pathways

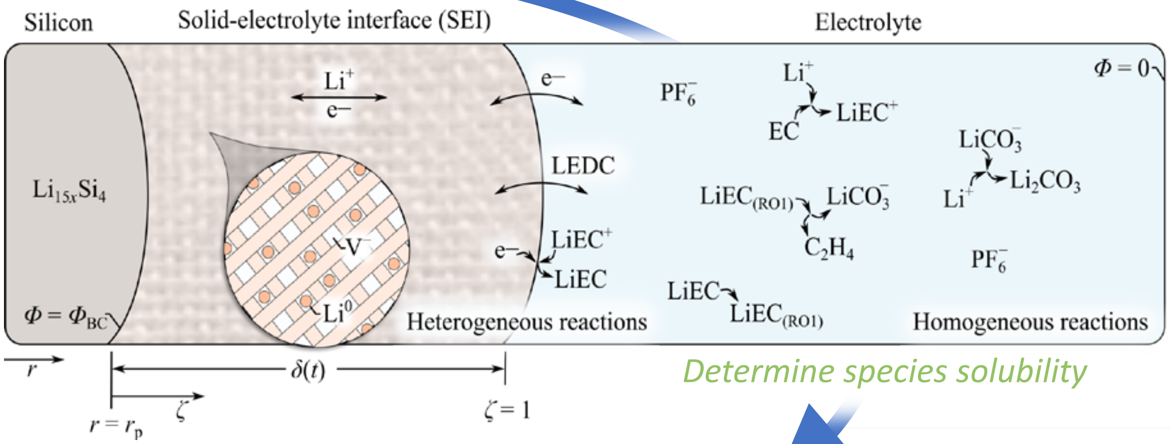
Collaboration: Multi-Scale Modeling Teams

Reaction mechanism

- 7 SEI species
- 57 electrolyte species
- 7 gas-phase species

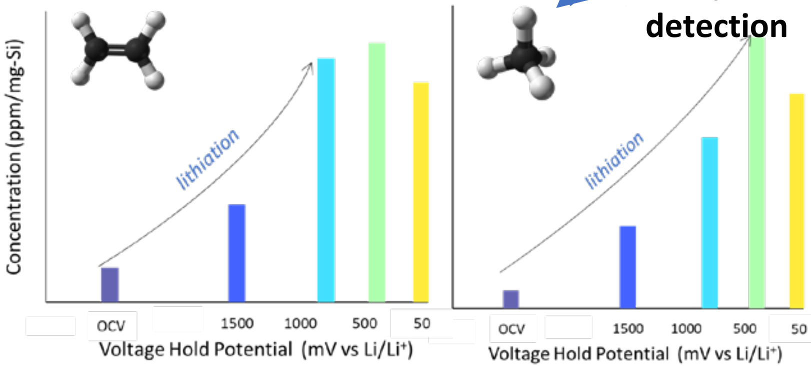


Continuum-level model



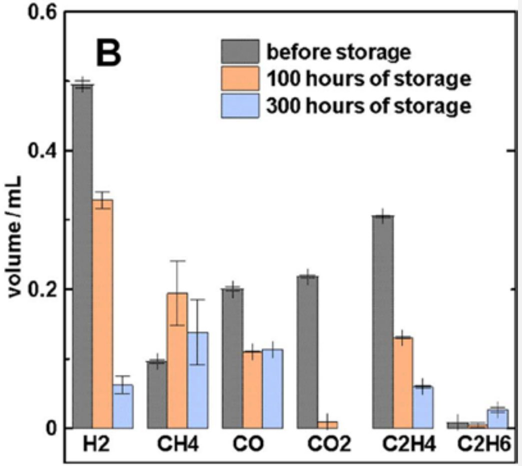
Determine species solubility

Gas-phase detection



Delving into Non-Monotonic Gas-Phase Behavior

OCV (chemical) reconsumption behavior of relevant gaseous species (*Gr vs NMC*)



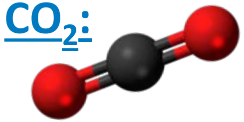
Ellis, L. D., J.P. Allen, L.M. Thompson, J.E. Harlow, W.J. Stone, I.G. Hill, J.R. Dahn. 2017. J. Electrochem. Soc. *164 (14): A3518-A3528.*

>40% of gas evolved in first charge cycle is reconsumed during the first 100 hr of storage

- **-Not** attributable to electrolyte solubility
- **-Not** attributable to diffusion through case
- **-Is** attributable to reaction!

Proposed Pathways for Gas Consumption:

CO_2:



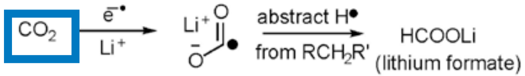
$2CO_2 + 2Li \rightarrow Li_2C_2O_4$

$2\ CO_2 + 2Li \rightarrow Li_2CO_3 + CO\uparrow$

Ellis, L. D., J.P. Allen, L.M. Thompson, J.E. Harlow, W.J. Stone, I.G. Hill, J.R. Dahn. 2017. J. Electrochem. Soc. *164 (14): A3518-A3528.*

$Si^0 + 2CO_2\uparrow \rightarrow SiO_2 + 2CO\uparrow$

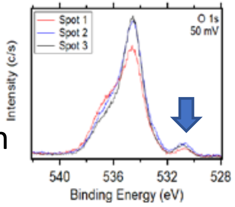
C.L. Seitzinger, R.L. Sacci, J.E. Coyle, C.A. Apblett, K.A. Hays, R.R. Armstrong, A.M. Rogers, B.L. Armstrong, T.H. Bennett, N.R. Neale, G.M Veith, Chem. Mater. 2020, 32, 1, 3199−3210.



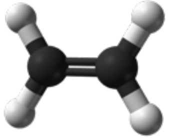
Y. Jin, N.-J.H. Kneusels, P.C.M.M. Magusin, G. Kim, E. Castillo-Martinez, L.E. Marbella, R.N. Kerber, D.J. Howe, S. Paul, T. Liu, C.P. Grey, J. Am. Chem. Soc. 2017, 139, 14992-15004.

Experimental Validation:

- -Quantitative pairing of CO_2 consumption/CO production
- -Further solid-state analysis (Li_2CO_3 vs SiO_2 vs $Li_2C_2O_4$ vs LiCOOH?)



C_2H_4:

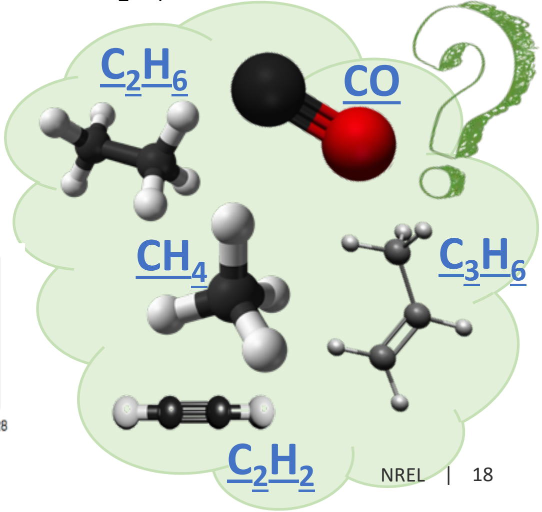


$nC_2H_4 + Li \rightarrow Li(C_2H_4)_n$ (n = 1,2,3)

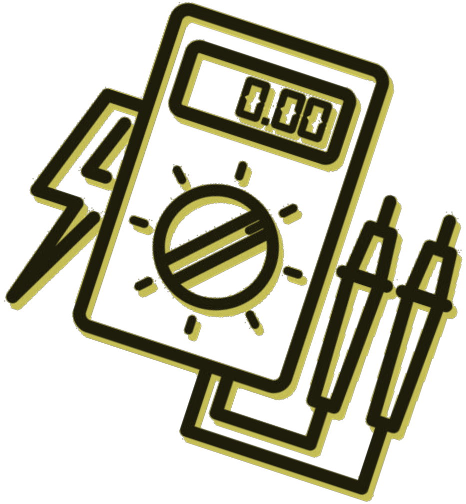
$Li(C_2H_4)_n + C_2H_4 \rightarrow (C_2H_4)_n$ (PE)

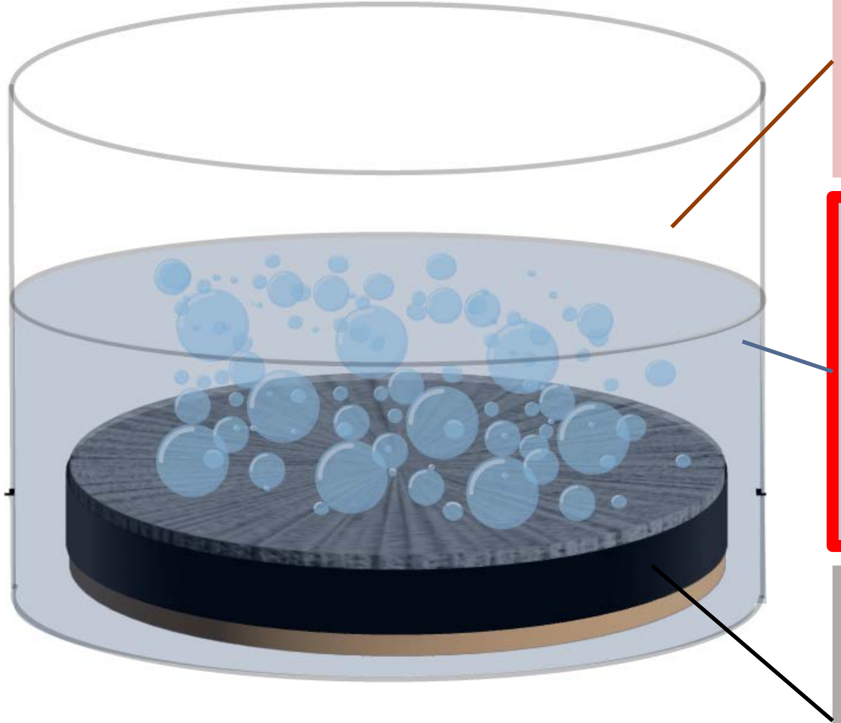
Experimental Validation:

-Growth of PE-rich SEI concurrent with C_2H_4 consumption?



Liquid-Phase Reactions





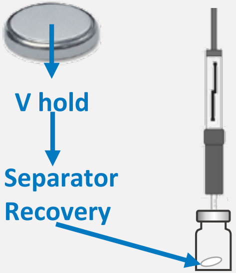
Gas-Phase Reactions:
In situ ID & quantification of gaseous headspace
(*in situ; GC-MS-FID*)

Liquid-Phase Reactions:
ID & semi-quantitative tracking of electrolyte & soluble SEI components
(*ex situ/post-mortem; SPME-GC-MS*)

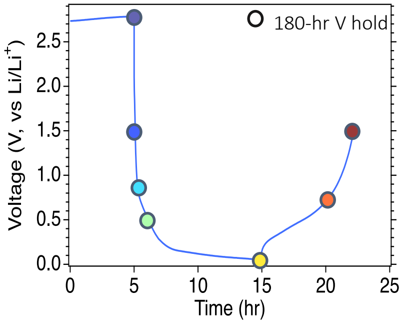
Solid-Phase Reactions:
Analyze evolution of anode SEI
(*ex situ/post-mortem*; *FT-IR + XPS*)

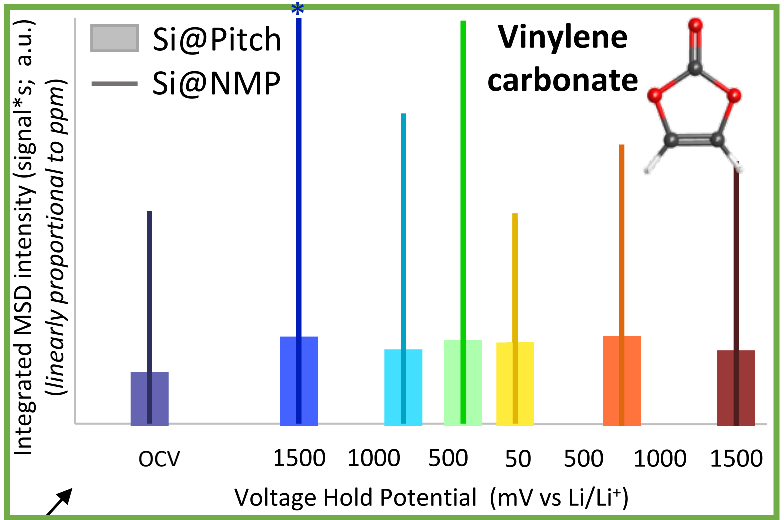
SPME: Tracking VC Pathways

Post-mortem analysis of Li^0 half-coin-cells via ***Solid-Phase Microextraction (SPME):***



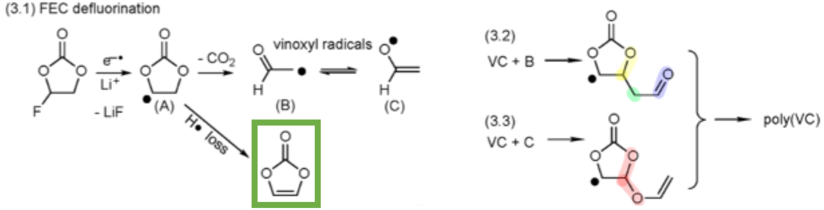
SPME fiber *preconcentrates volatile headspace analytes for improved detection of trace compounds*





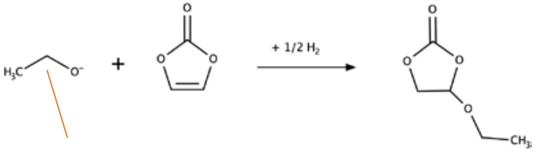
equal scale ~ equal conc.

VC: Reported FEC reduction product

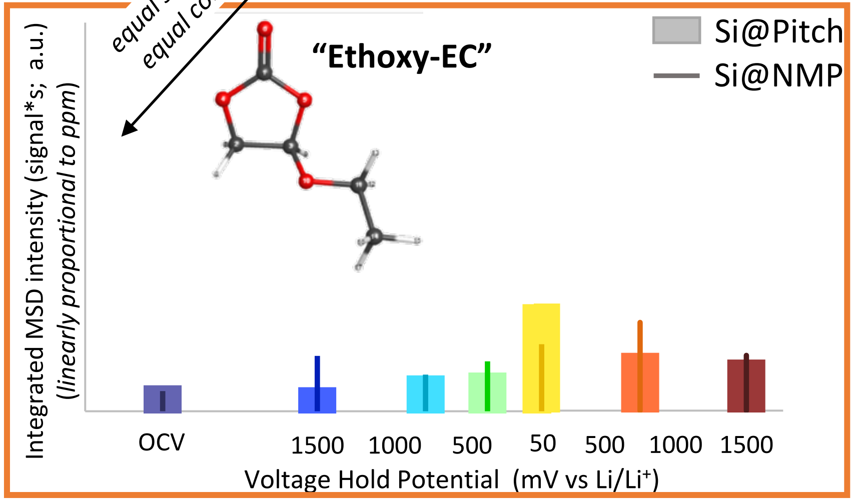


Jin, Y., N.-J. H. Kneusels, P. C. M. M. Magusin, G. Kim, E. Castillo-Martínez, L. E. Marbella, R. N. Kerber, D. J. Howe, S. Paul, T. Liu, C. P. Grey. 2017. **J.** Am. Chem. Soc., *139: 14992-15004.*

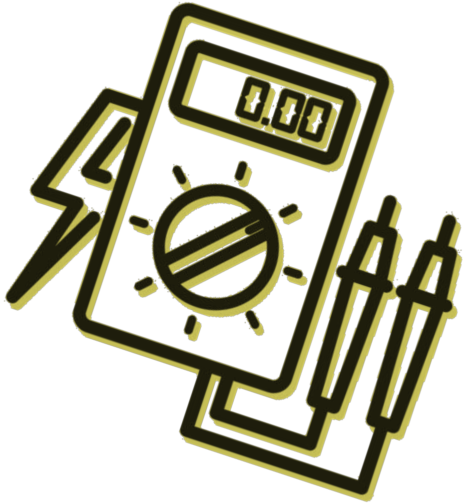
"Ethoxy-EC": Hypothesized VC reduction product

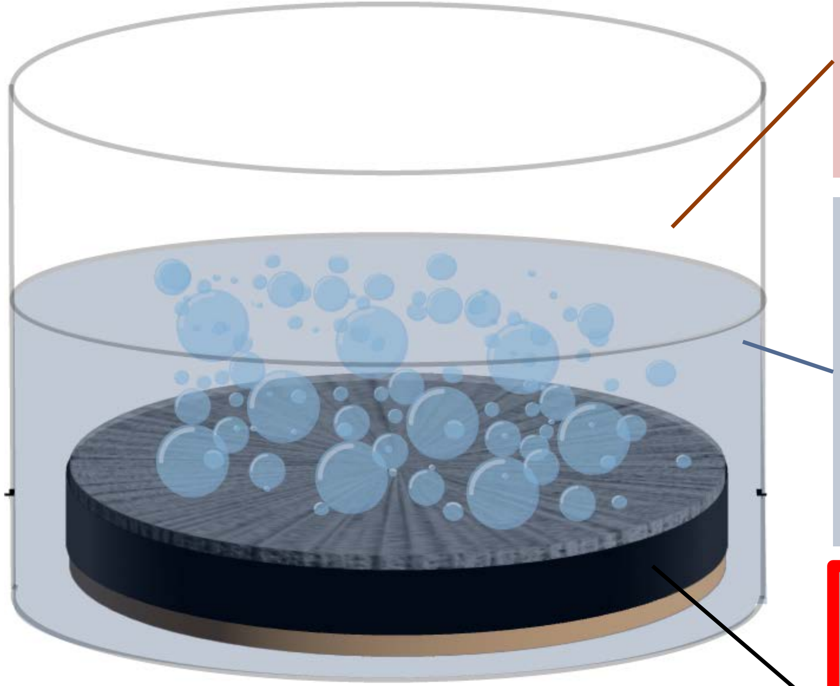


Alykoxy radical (from linear carbonates)



Solid-Phase Reactions





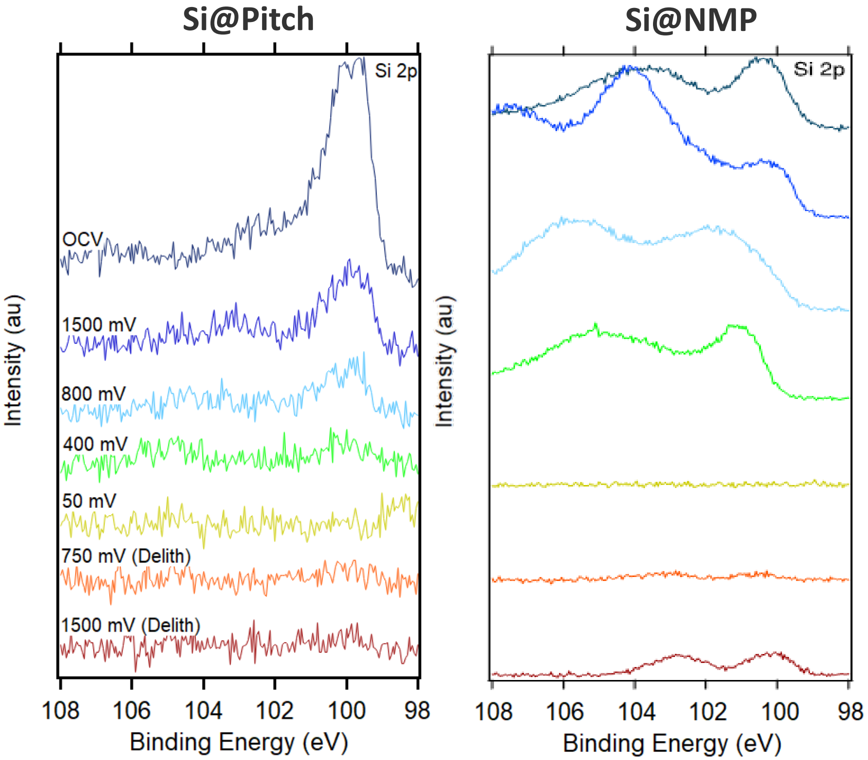
Gas-Phase Reactions:
In situ ID & quantification of gaseous headspace
(*in situ; GC-MS-FID*)

Liquid-Phase Reactions:
ID & semi-quantitative tracking of electrolyte & soluble SEI components
(*ex situ/post-mortem; SPME-GC-MS*)

Solid-Phase Reactions:
Analyze evolution of anode SEI
(*ex situ/post-mortem*; *FT-IR + XPS*)

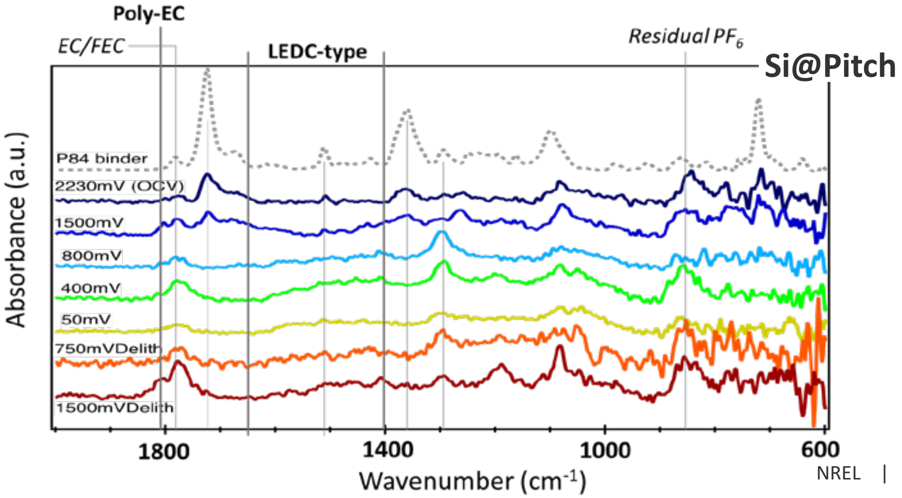
Solid-State Validation for Pathways of Passivation

- Si 2p signal is associated with surface-exposed Si
- Fade in Si 2p signal indicates surface passivation, attributable to SEI growth
- Passivation occurs at ~800 mV in Si@Pitch samples; not until 50 mV in Si@NMP samples
  - -Pitch favors FEC reductive pathway?
- XPS results consistent with FT-IR results for Si@Pitch (*SEI grow-in starting at 800 mV*)

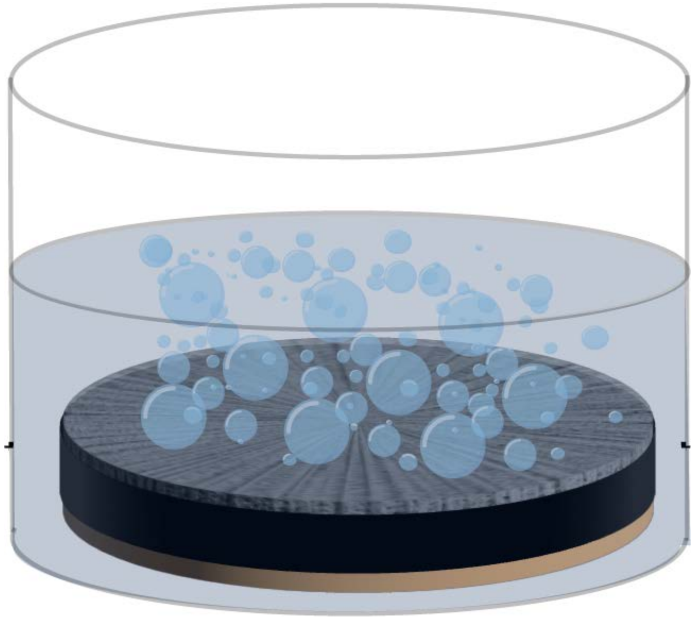


Data collected by S. Frisco and G. Teeter (NREL)

Samples recovered from disassembled cells following voltage hold; soaked in 1 mL DMC for 1 min



Summary & Ongoing Efforts



- Gas-phase products are of critical importance to holistically understand SEI formation, and influence dynamic SEI evolution through *non-monotonic* pathways
- Pitch-carbon coating on nanosized PECVD Si enhances first-cycle linear carbonate reduction
- Pitch coating may also favor FEC reduction, leading to surface passivation at higher potentials
- ID of 6 additional gas species drastically increases complexity (and accuracy) of atomistic models
- Ongoing collaboration with multiscale modeling teams to incorporate experimentally quantified gas-phase data
- Pairing comprehensive multi-phase data with robust models to achieve goal of identifying surface-modification strategies for stable SEI growth

Thank you! Questions?

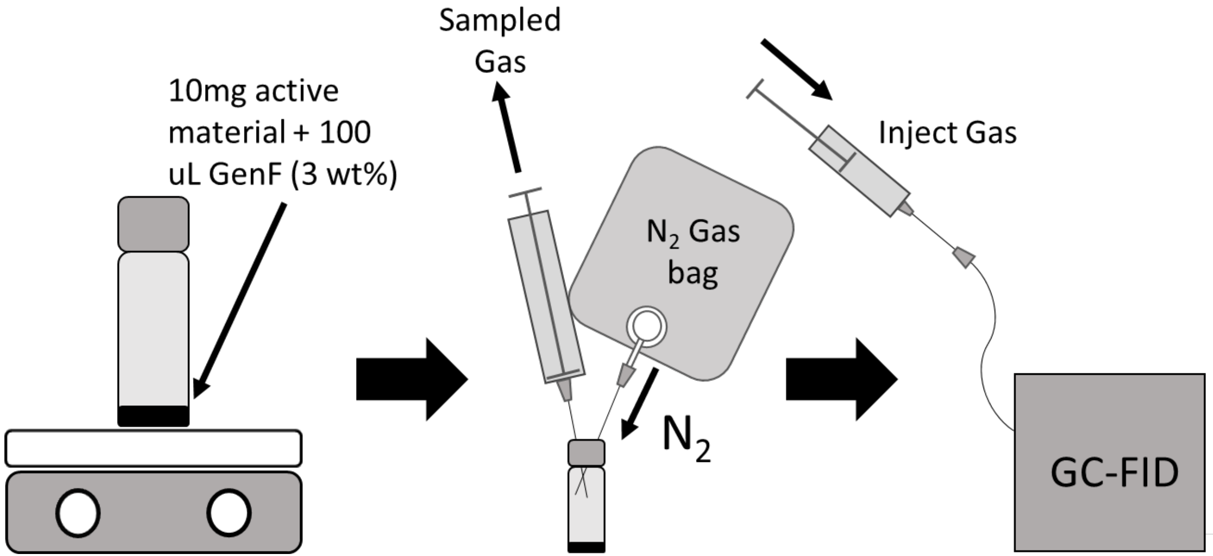
Kae.Fink@nrel.gov

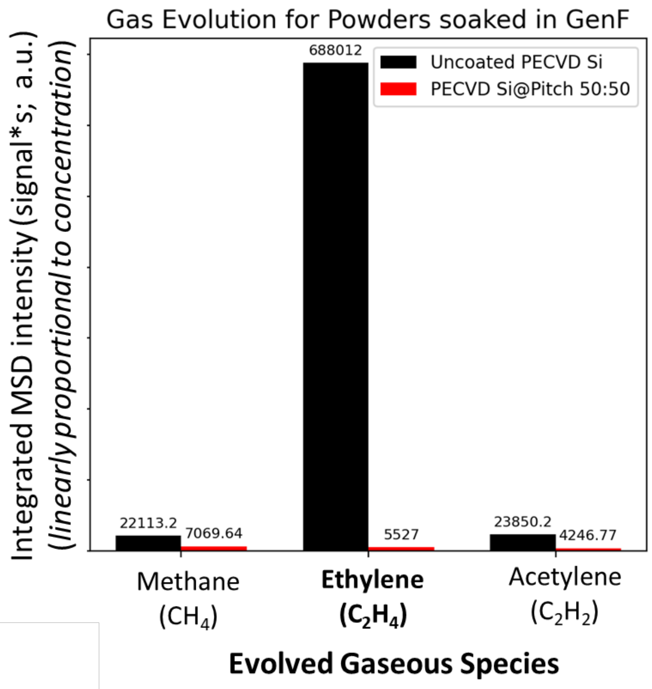
www.nrel.gov

NREL/PR-5700-83012

This work was authored by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. 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.

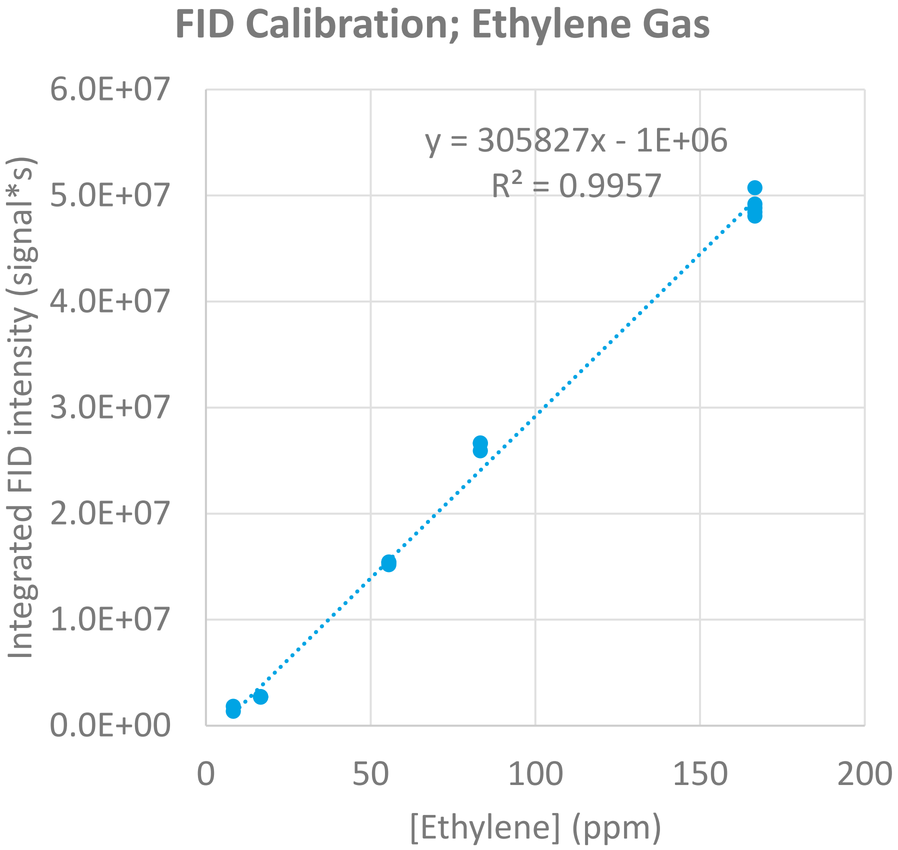
Supplemental: Powder Soaking Experiments

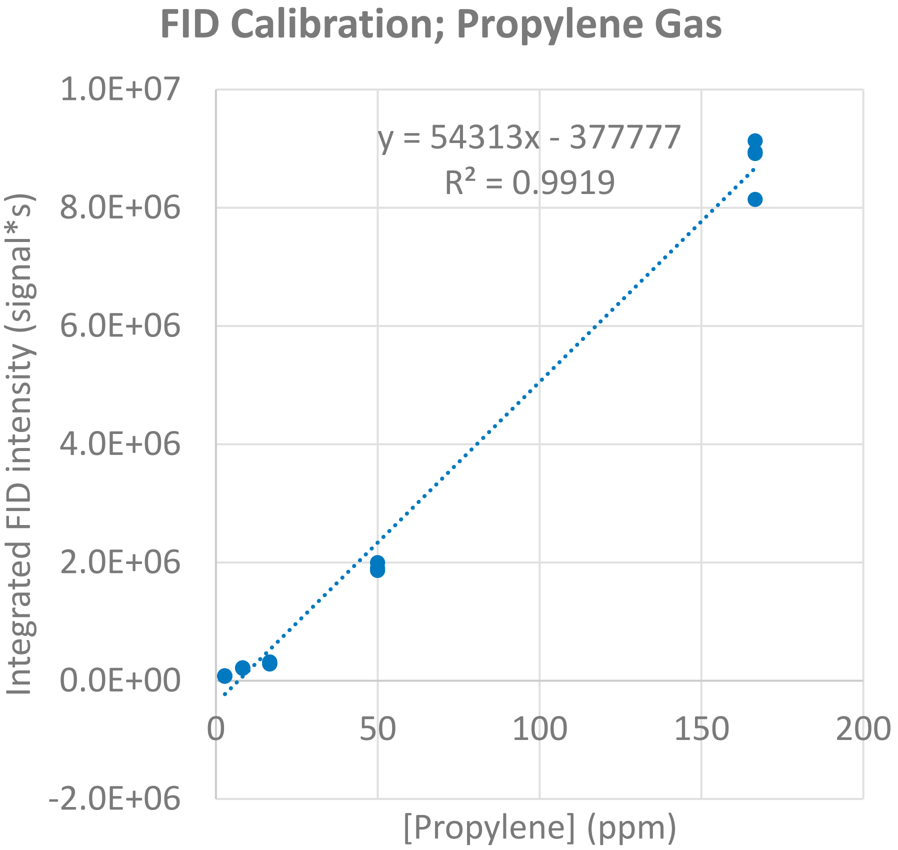




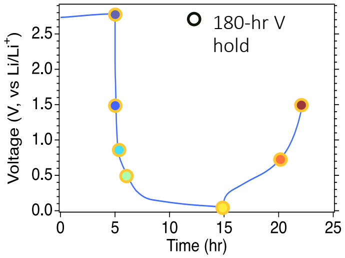
- Rapid screening test suggests that pitch-coated PECVD Si suppresses pure chemical reactivity, relative to uncoated PECVD Si (esp. evident for production of C_2H_4 gas).
- How to deconvolute impacts of pitch on *electro*chemical reactivity?

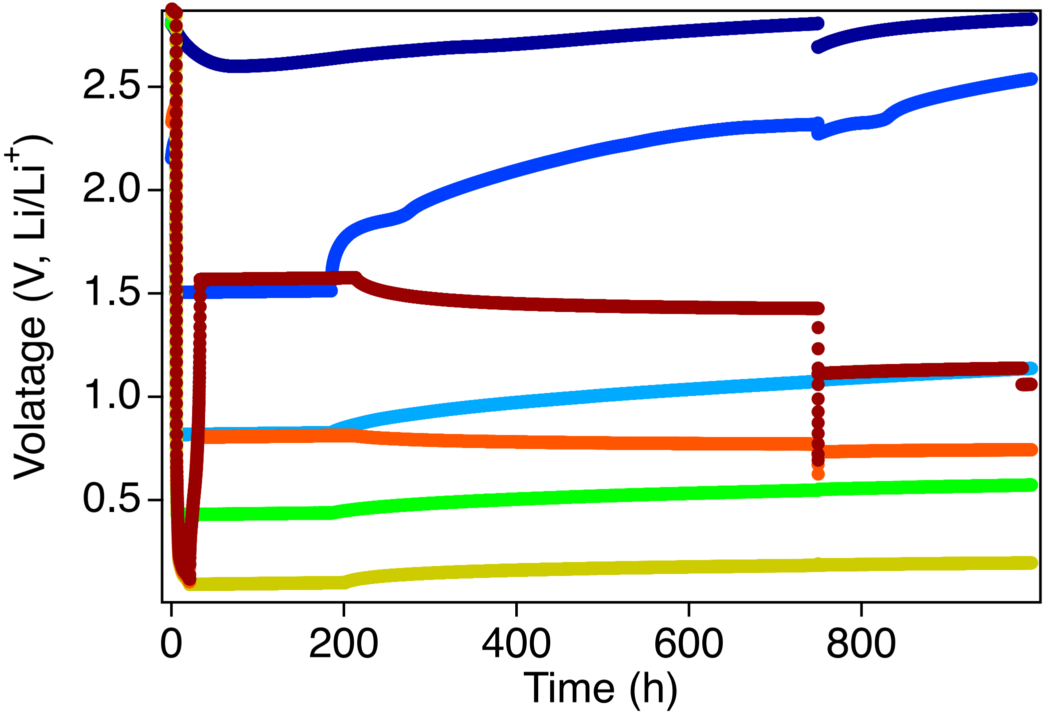
FID Calibration

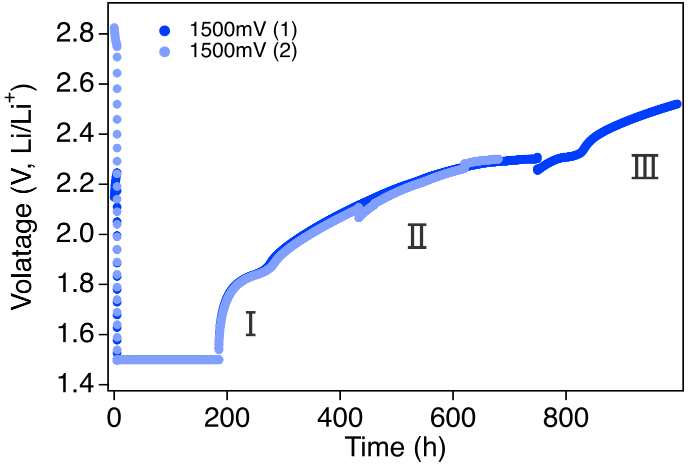




Coin Cell Voltage holds: Voltage relaxation

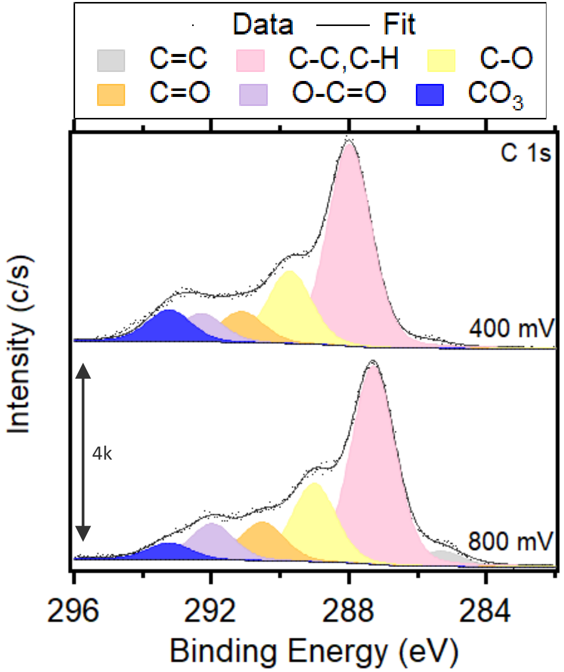


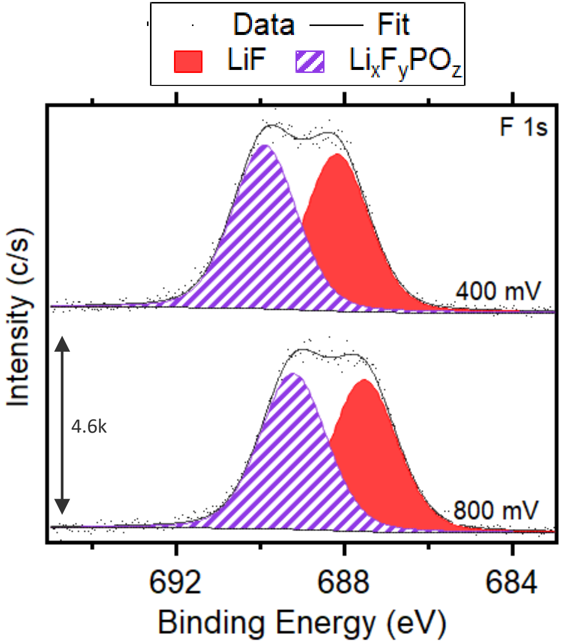




Impacts of pitch coating on solid-phase reactivity of PECVD Si

XPS & fittings conducted by Sarah Frisco





- Distribution of C binding environments indicates surface exposure of surface pitch + formation of organic outer SEI

  -C=C decline between 800- 400 mV: follows SEI growth trend

- LiF/Li_2CO_3 ratio tied to FEC/EC degradation predominance

  -Comparative analysis with uncoated PECVD Si will reveal any impacts of pitch on *preferential FEC reduction path*

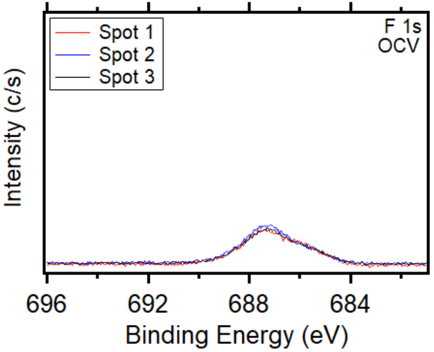
Hold Potential	LiF/total	LiF/F total	Li_2CO_3/total	Li_2CO_3/C total	LiF/Li_2CO_3
800 mV	0.14	0.49	0.11	0.04	1.33
400 mV	0.14	0.49	0.20	0.08	0.70

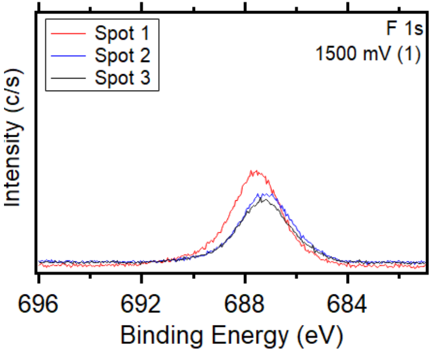
Impacts of pitch coating on solid-phase reactivity of PECVD Si

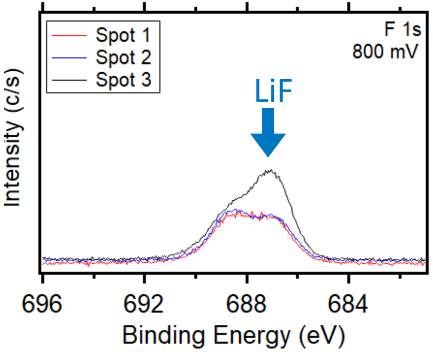
XPS & fittings conducted by Sarah Frisco

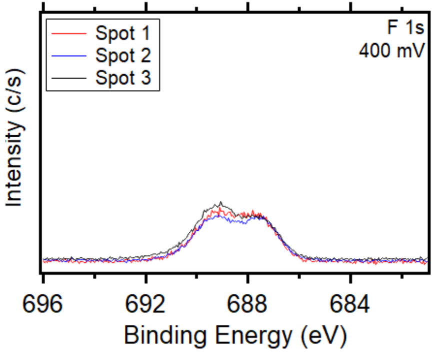
-Peak splitting indicates LiF formation: Evolves ~800 mV (FEC degradation)

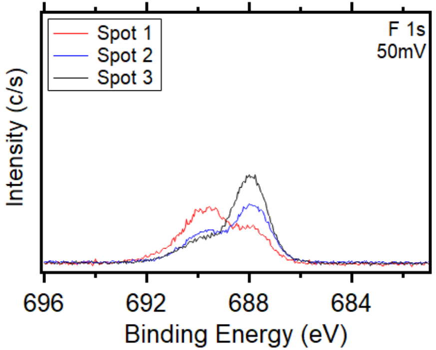
Intensity Scale: 20.1k

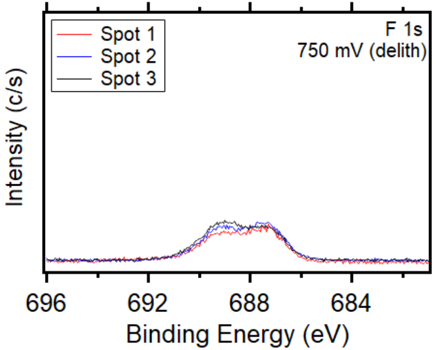


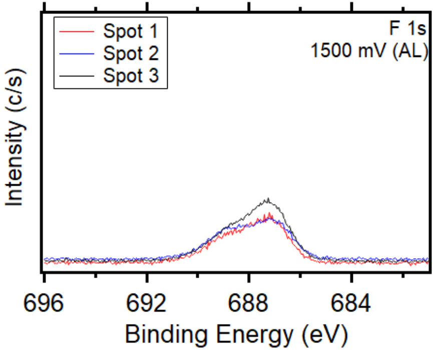










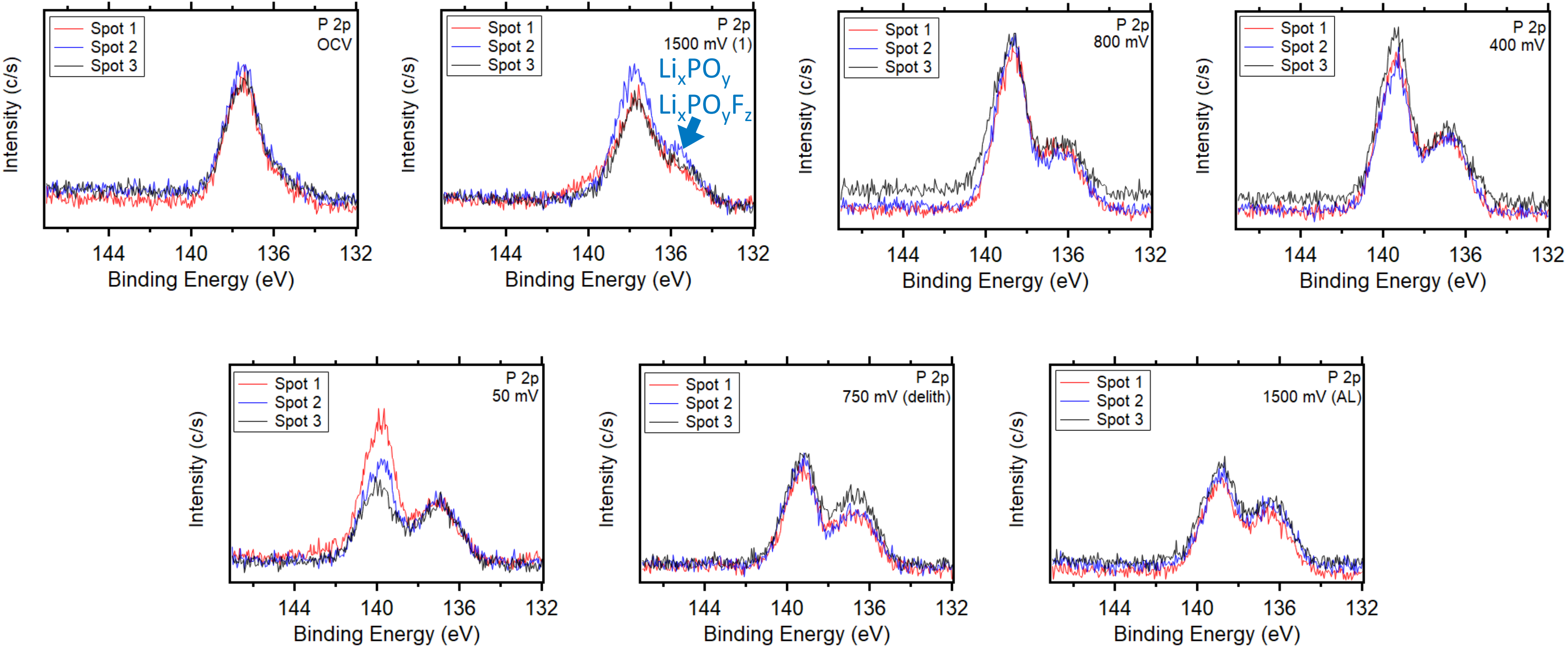


Impacts of pitch coating on solid-phase reactivity of PECVD Si

XPS & fittings conducted by Sarah Frisco

-Growth of lower-energy peak associated with $LiPF_6$ decomposition (Li_xPO_y or $Li_xPO_yF_z$)

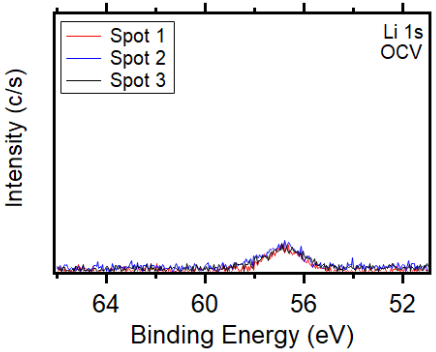
Intensity Scale: 370

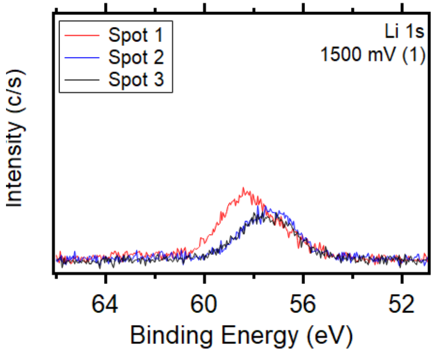


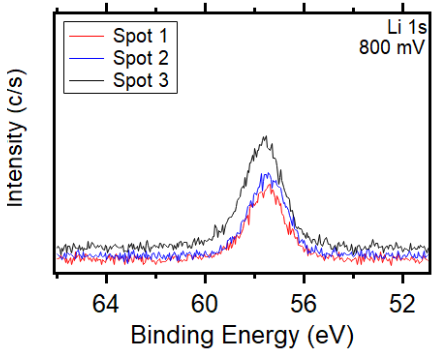
Impacts of pitch coating on solid-phase reactivity of PECVD Si

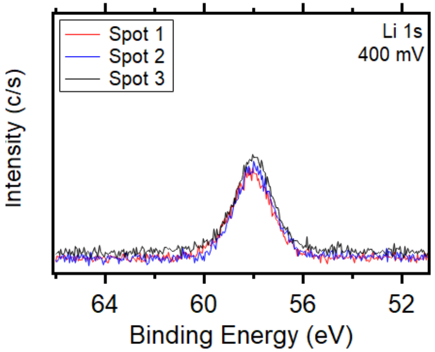
XPS & fittings conducted by Sarah Frisco

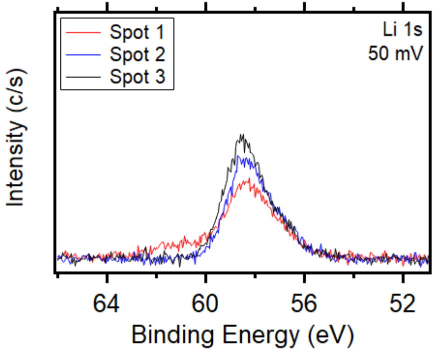
Intensity Scale: 610

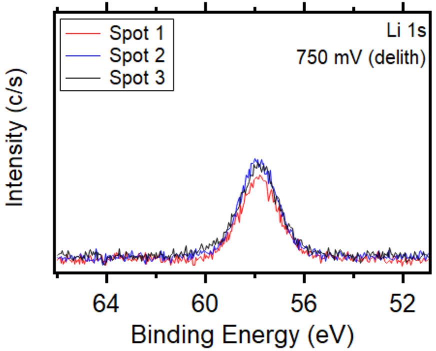


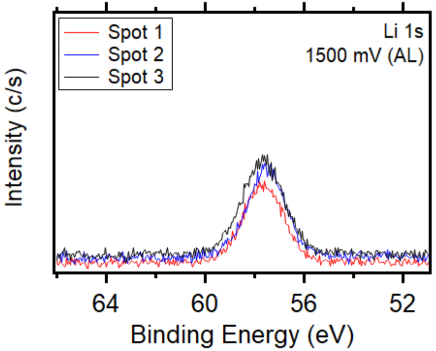












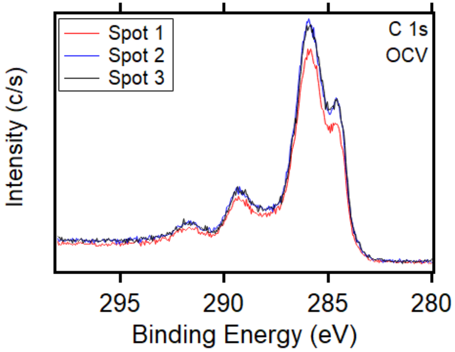
Impacts of pitch coating on solid-phase reactivity of PECVD Si

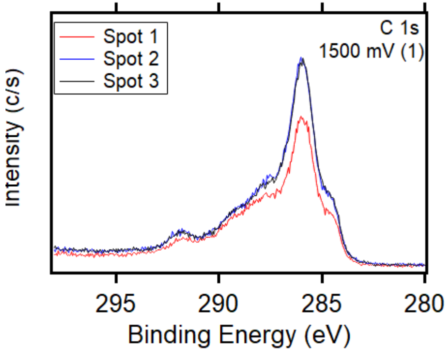
XPS & fittings conducted by Sarah Frisco

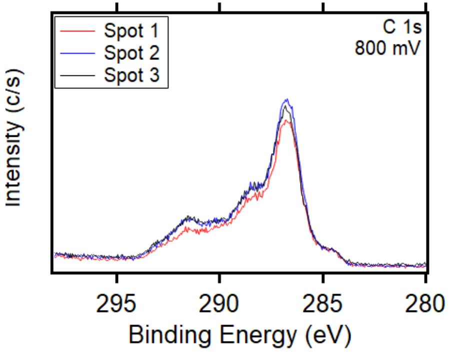
-Lower-energy peak (~286eV) from aliphatic carbon species

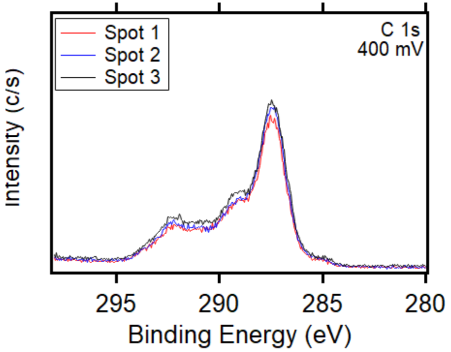
-Higher-energy peak (~292eV) from carbonate-type species

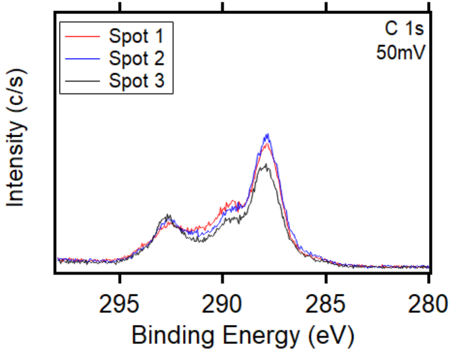
Intensity Scale: 6,500

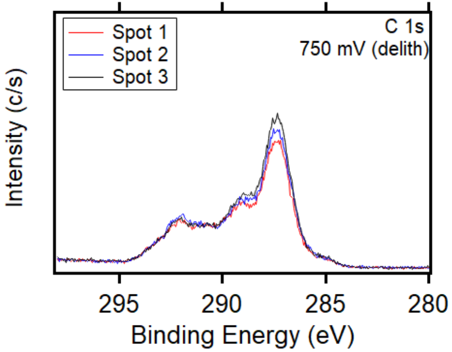


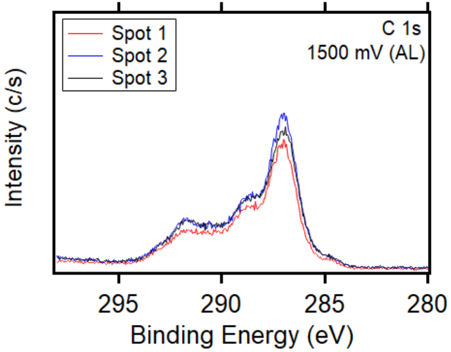












Impacts of pitch coating on solid-phase reactivity of PECVD Si

XPS & fittings conducted by Sarah Frisco

-Unique peak in 50 mV sample at ~531 eV (Li_2O_2 from EC? $Li_2C_2O_4$ from CO_2 reconsumption?)

Intensity Scale: 8.4k