SILICON ELECTROLYTE INTERFACE STABILIZATION (SEISTA): ELECTROCHEMICAL METHODS

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U.S. DEPARTMENT OF ENERGY
VEHICLE TECHNOLOGIES OFFICE
2020 ANNUAL MERIT REVIEW

Project ID BAT437

1 June 2020

OVERVIEW

Timeline

- October 1st 2016 – September 30st 2019.
- Percent complete: 80%

Barriers

- Development of PHEV and EV batteries that meet or exceed the DOE and USABC goals
  - Cost, Performance and Safety

Budget

- Funding for FY 20: $3800

Partners

- Six Laboratory Team lead by NREL:
  - Sandia National Laboratory
  - Argonne National Laboratory
  - Oak Ridge National Laboratory
  - Lawrence Berkeley National Laboratory
  - Pacific Northwest National Laboratory
- UC Berkeley, Colorado University Boulder, Colorado School of Mines, University of Rhode Island

RELEVANCE : OBJECTIVES

Si anodes exhibit ca. 3x higher volumetric energy density than graphite anodes

1. Si anodes have three major challenges to commercialization
   - Rapid capacity fade
   - Poor shelf life
   - Electrode formulation/manufacturability/stability
2. SEI formation in Si is much more complex than in graphite, and seems to be dependent on initial state and history
   - Inherently non-passivating in organic carbonate electrolytes
   - Large volume expansion on alloying
   - Extensive gas formation

Improve calendar life and understand initial stages of SEI formation by understanding intrinsic chemical reactivity of Si electrodes

APPROACH

Critical Questions:

- What are the unique basic properties of the Li_xSi/electrolyte interface?
- What is the mechanism of the SEI formation?
- How fast does the silicon SEI grow?
- Does it stop growing?
- Role of soluble components?
- What is the composition, structure and function of the surface film?
- How to stabilize SEI on silicon?

Team work:

- Close coordination with the Deep Dive Program
- Fundamental understanding is critical
- Multiple approaches on the same problem
- Well defined samples
- Standardized experimental protocols
- Reproducibility across the team (multiple labs)
- Rapid communication
  - All information is stored on BOX
  - Weekly team meetings (video)
  - Quarterly face to face
  - Multiple side phone meetings
  - Site visits by researchers to other labs

Sandia National Laboratories

OAK RIDGE National Laboratory

Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle Since 1965

NREL NATIONAL RENEWABLE ENERGY LABORATORY

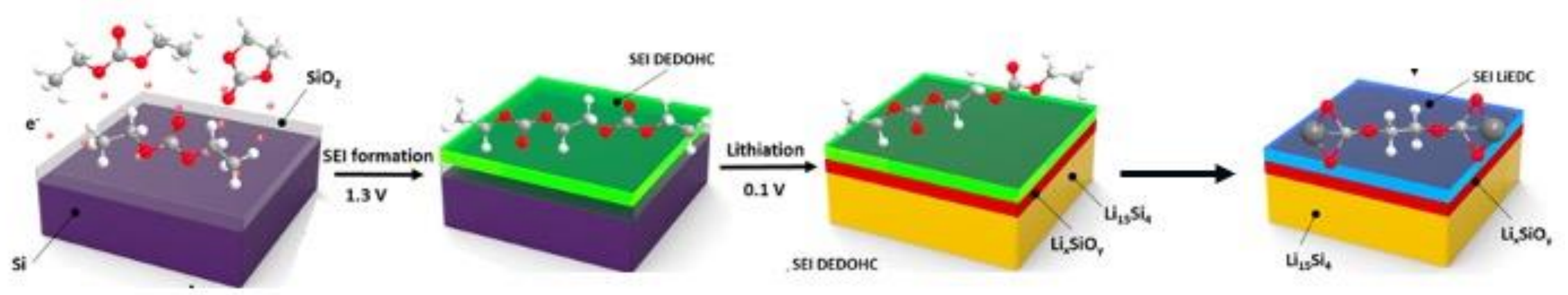
BERKELEY LAB

Argonne NATIONAL LABORATORY

MILESTONES IN FY20

1. Have demonstrated ability to make model electrodes of Mg-Si zintl compounds and compared SEI chemistry to silicon using XPS, STEM-EDS and FTIR/Raman. **Q1 Complete**
2. Have established experiments and protocols for understanding the factors that affect safety in silicon anodes, with a specific focus on highly exothermic reactions that occur at silicon electrodes. **Q1 Complete**
3. Have determined the affect that CO2 has on the stability of SEI formation on model electrodes, but examining the changes in the nature of the SEI (XPS, and FTIR/Raman and quantitate electrochemical measurement) as a function of CO2 concentration. **Q2 Complete**
4. Have determined zintl phase formation mechanism and its effect on SEI with model systems including Si NPs, Si wafer, a-Si thin film using XPS, AFM/SSRM, STEM-EDS and FTIR/Raman. **Q2 Complete**
5. **Go/NoGo** on production of tin-silicon alloys to be determined by the ability of the alloys to be prepared in 1g quantities and a demonstration that the alloys exhibit greater cyclic life than the pure metals alone. **Q2 Complete**
6. Have determined the chemistry and interfacial properties (e.g. nature of the chemical bonding at the surface of Si and the organic material) of LiPAA/Si interfaces as a function of charge (OCV, 0.8V, 0.4V, 0.15V, 0.05V) and drying temperature (100, 125, 150, 175, 200C). **Q3**
7. Have determined how binder changes the stress/strain on silicon electrodes as a function of state of charge by varying Si NP size and surface functionally utilizing both 2 or three dimensional model systems. **Q3**
8. Have implemented protocols that enable comparisons of safety responses in silicon anodes as a metric for improving safety in silicon cells. **Q3**
9. Have published a document that will enable other research and development groups to analyze stability of the SEI on a silicon-based anode, thus enabling developers or researchers to continually improve silicon cell stability (joint milestone with the Silicon Deep Dive). **Q4**
10. Have understood how the nature and amount of formed/soluble SEI species varies with electrolyte, binder, and Si anode (with surface functionalization) using GC-MS, (in-situ) FTIR/Raman and XPS. **Q4**

SEISTA – APPROACH AND OVERVIEW



J. Phys. Chem. C 2017, 121, 14476–14483

Overarching Mission: Develop a stable SEI layer for Silicon Anodes to enable the use of intermetallic anodes for lithium ion batteries. This is not a new challenge but we believe that the difficulties working with silicon have precluded a “quick fix” to long term stability of silicon electrodes.

We require a foundational understanding of the formation and evolution of the SEI on silicon

Understand first, fix later!

INTRODUCTION

Intrinsic non-passivating behavior of Si anodes in organic carbonate electrolytes

- SEI layer (electro)chemical instability leads to high “leakage” or “corrosion” current
- Surface composition of Li_xSi electrode is constantly changing during cycling
- Si particle decrepitation and fresh surface exposure during cycling

Three strategies to stabilize Si/electrolyte interface

Electrolyte Modification

Effect of CO_2 on SEI behavior

Saturate electrolyte with CO_2 (one of electrolyte reduction products) to alter formation of the SEI of the SEI and gain control over the SEI composition, structure and passivating behavior

Interface Modification

Si-Mg Zintl phase *in situ* formation

Modify *in situ* the surface of Si anode by electrochemical formation of Si-Mg Zintl phase to promote formation of stable SEI

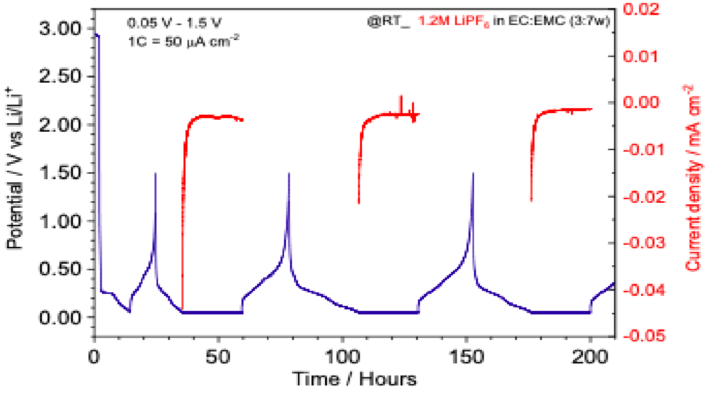
Advanced Materials Development

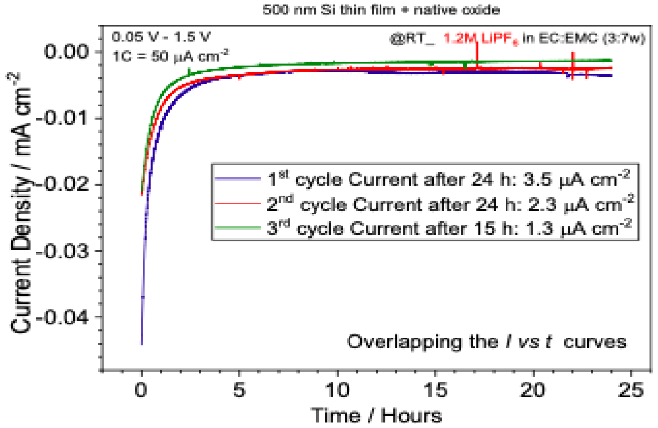
Si-based Amorphous Alloys

Synthesize a new class of Si-based amorphous electrode active materials with greatly improved interfacial and mechanical properties

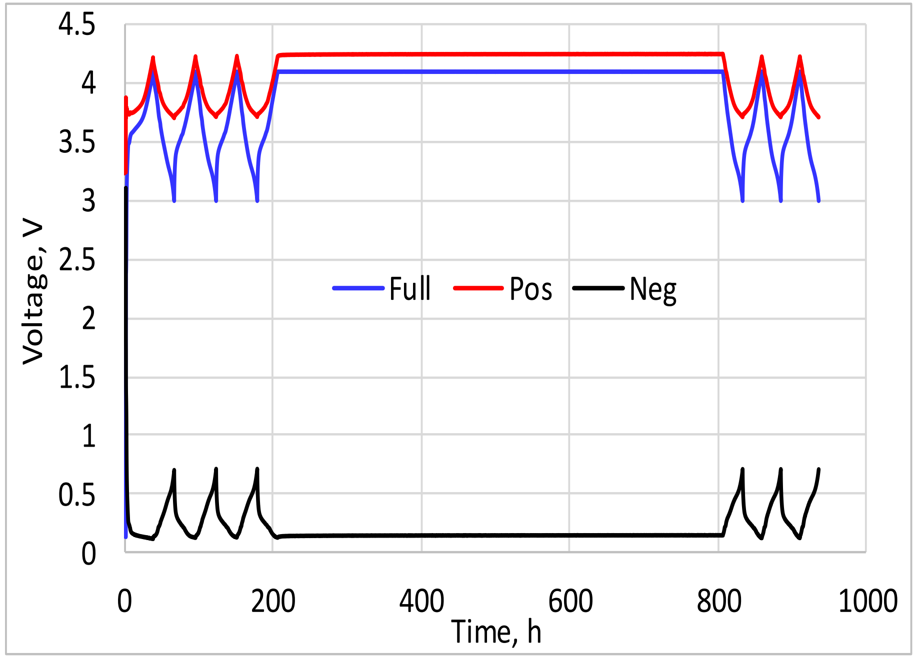
ORIGINS OF POOR PASSIVATING BEHAVIOR OF SI IN LI-ION CELLS

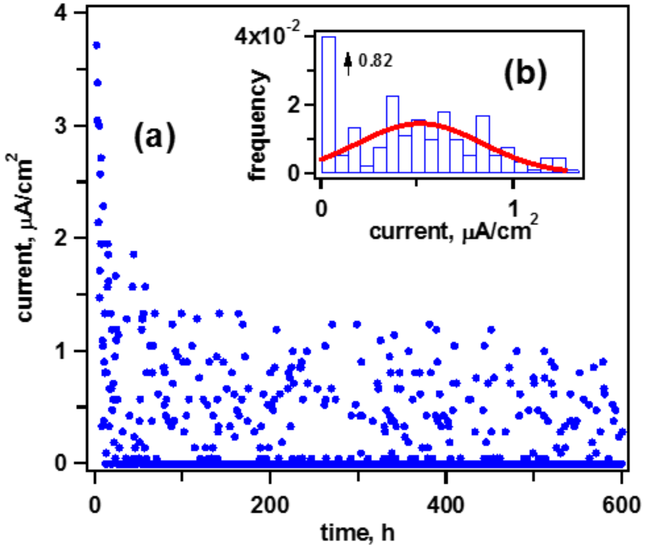
Li/Gen-2/Si 50 nm thin-film





NCM523/Gen2-10FEC/Si-Gr: 3.0-4.1 V 3x C/20, 600 h hold at 4.1 V, 3x C/20

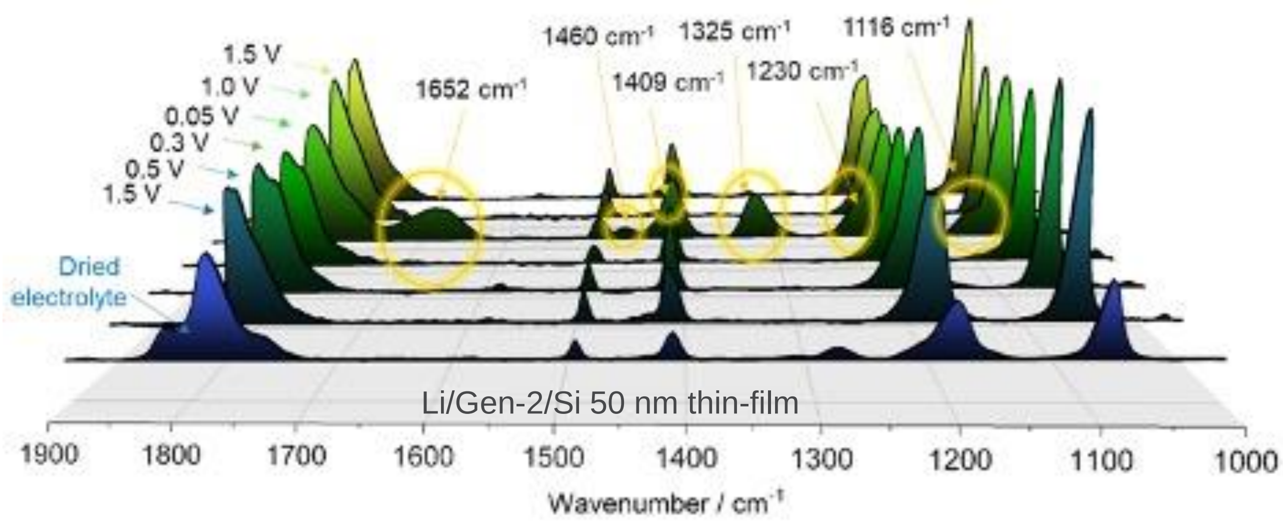




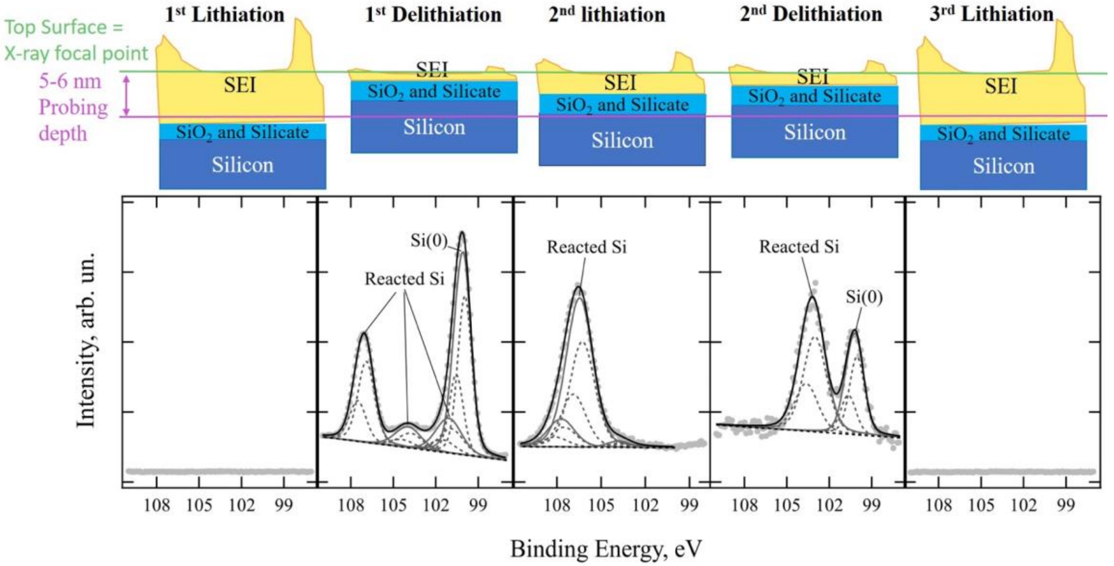
- Corrosion current measured for model Si thin-film electrodes corresponds exactly to the parasitic current from Si anode in full Li-ion cells under steady-state conditions
- Si interfacial instability is primarily responsible for the observed lithium inventory shift and capacity fade in Li-ion cells

ORIGINS OF POOR PASSIVATING BEHAVIOR OF SI IN LI-ION CELLS

Ex situ ATR FTIR Spectroscopy



Ex situ XPS Spectroscopy



- Dynamic growth and dissolution of the SEI layer on silicon during lithiation/de-lithiation, respectively
  - SEI layer “breathing effect” is directly related to formation of LiEDC and P-F and P-O-F containing compounds at low potentials and their disappearance upon de-lithiation
- SEI layer gets enriched with inorganic compounds, mainly LiF, during cycling

Overall composition and morphology of the film and its interactions with the Li_xSi electrode and electrolyte, appears to be strongly dependent on the electrolyte potential

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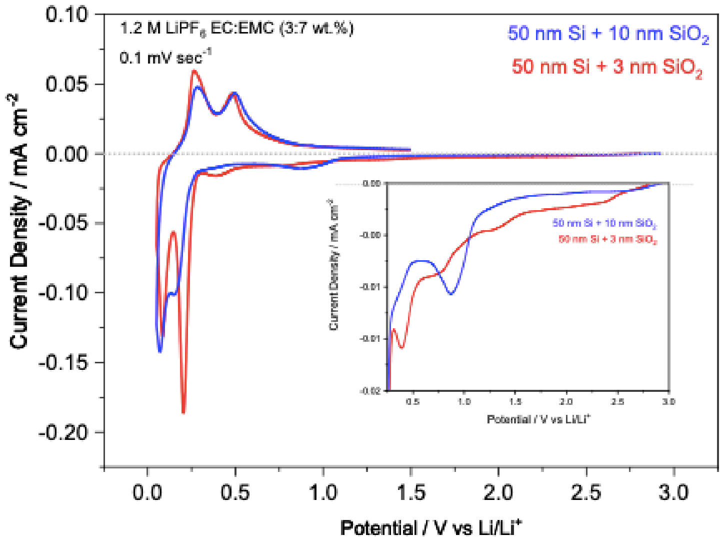
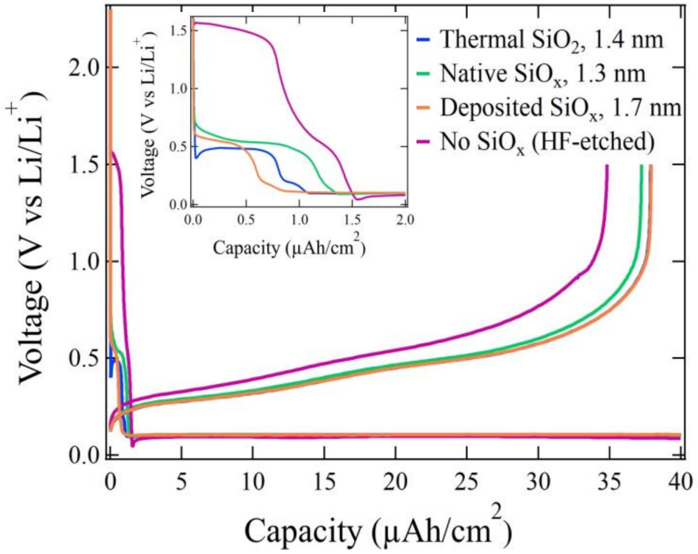
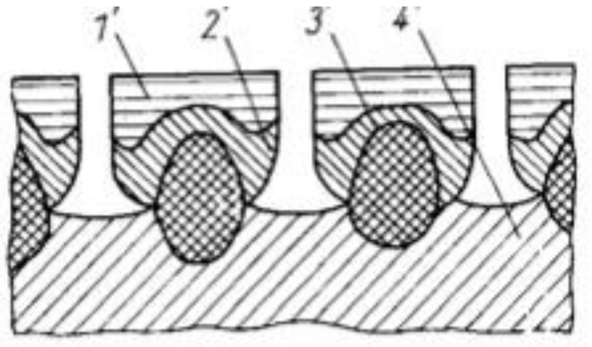
ROLE OF SiO_2 ON PASSIVATING BEHAVIOR OF SI IN LI-ION CELLS

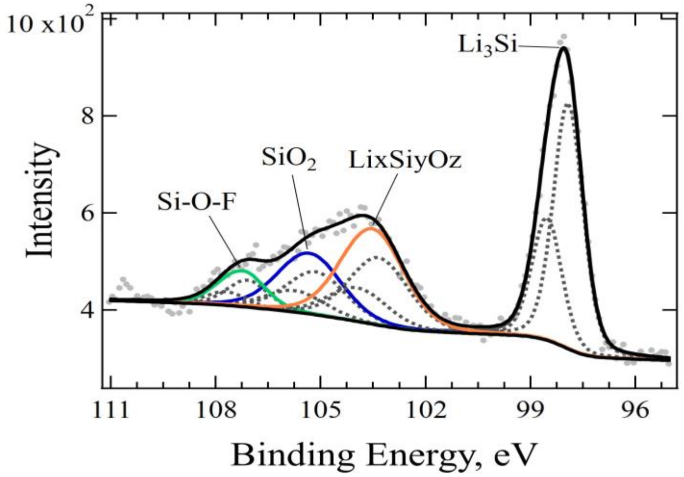






1- Amorphous
2- Cristobalite
3- Quartz
4- Silicon

Rumak et. al., Phys. Stat. Sol. (a) 86, 93 (1984)

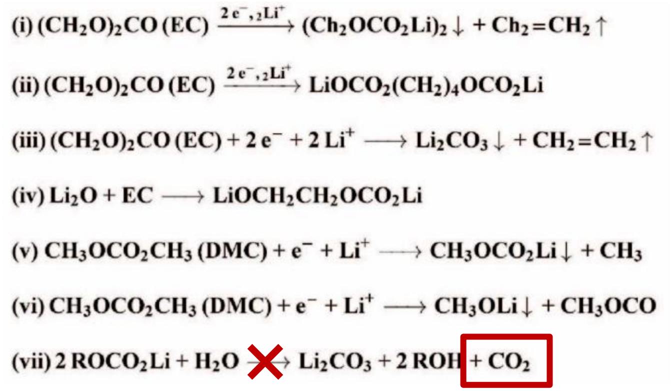


- SiO_2 is omnipresent on Si surface
- Effect of SiO_2 on interfacial properties of silicon varies with the film thickness, phase composition and morphology, which depend on film growth methods e.g., native, thermal, sputtered, etc.
- SiO_2 exhibits some activity toward Li^+ i.e., a fraction of the film may undergo physical and chemical changes during charge/discharge processes

SiO_2 film alone does not appear to help promote growth of a stable SEI layer on Si electrodes

THREE STRATEGIES TO STABILIZE SI/ELECTROLYTE INTERFACE

Electrolyte Modification



$(i)\ (CH_2O)_2CO\ (EC) \xrightarrow{2e^-,\,2Li^+} (Ch_2OCO_2Li)_2 \downarrow + Ch_2{=}CH_2 \uparrow$

$(ii)\ (CH_2O)_2CO\ (EC) \xrightarrow{2e^-,\,2Li^+} LiOCO_2(CH_2)_4OCO_2Li$

$(iii)\ (CH_2O)_2CO\ (EC) + 2e^- + 2Li^+ \longrightarrow Li_2CO_3 \downarrow + CH_2{=}CH_2 \uparrow$

$(iv)\ Li_2O + EC \longrightarrow LiOCH_2CH_2OCO_2Li$

$(v)\ CH_3OCO_2CH_3\ (DMC) + e^- + Li^+ \longrightarrow CH_3OCO_2Li \downarrow + CH_3$

$(vi)\ CH_3OCO_2CH_3\ (DMC) + e^- + Li^+ \longrightarrow CH_3OLi \downarrow + CH_3OCO$

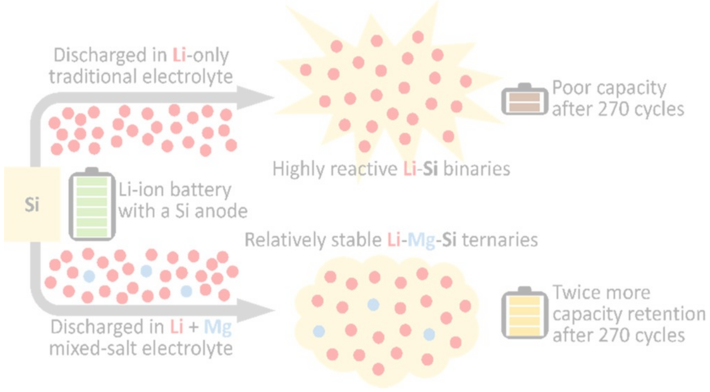
$(vii)\ 2\,ROCO_2Li + H_2O \cancel{\longrightarrow} Li_2CO_3 + 2\,ROH \boxed{+ CO_2}$

Aurbach et al.
J. Electrochem. Soc., Vol. 143, No. 12, December 1996

Effect of CO_2 on SEI behavior

Saturate electrolyte with CO_2 (one of electrolyte reduction products) to alter formation of the SEI of the SEI and gain control over the SEI composition, structure and passivating behavior

Interface Modification

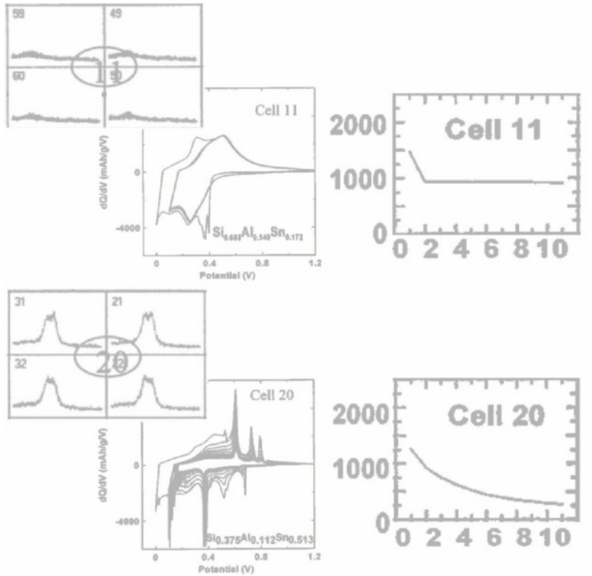


Baris *et al. ACS Appl. Mater. Interfaces* **2019**, *11*, 29780

Si-Mg Zintl phase *in situ* formation

Modify *in situ* the surface of Si anode by electrochemical formation of Si-Mg Zintl phase to promote formation of stable SEI

Advanced Materials Development



Hatchard et al., *Electrochem.Solid-State Lett*, **2003**, *6*, A129

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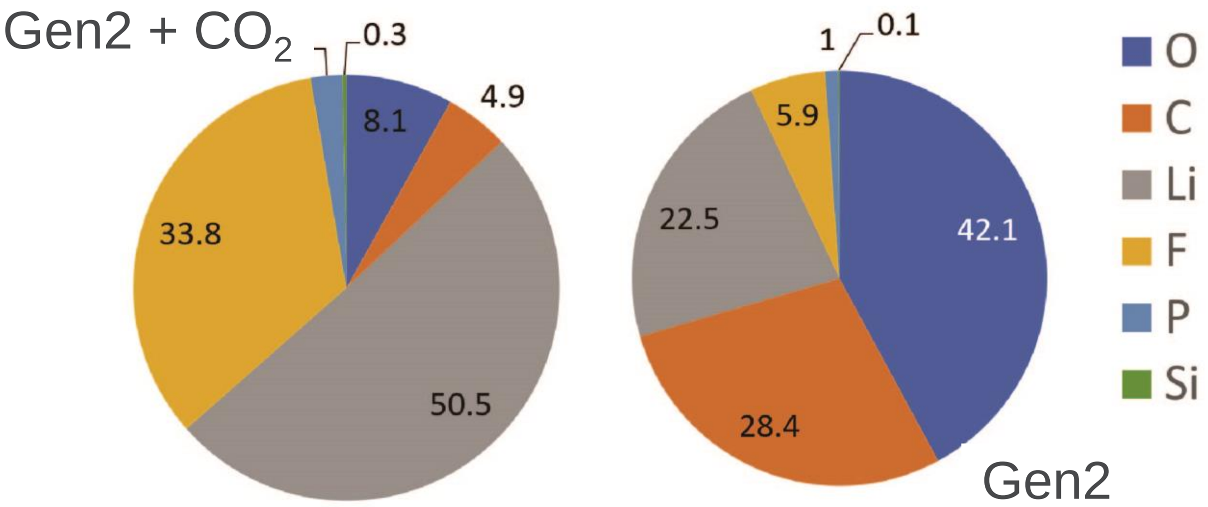
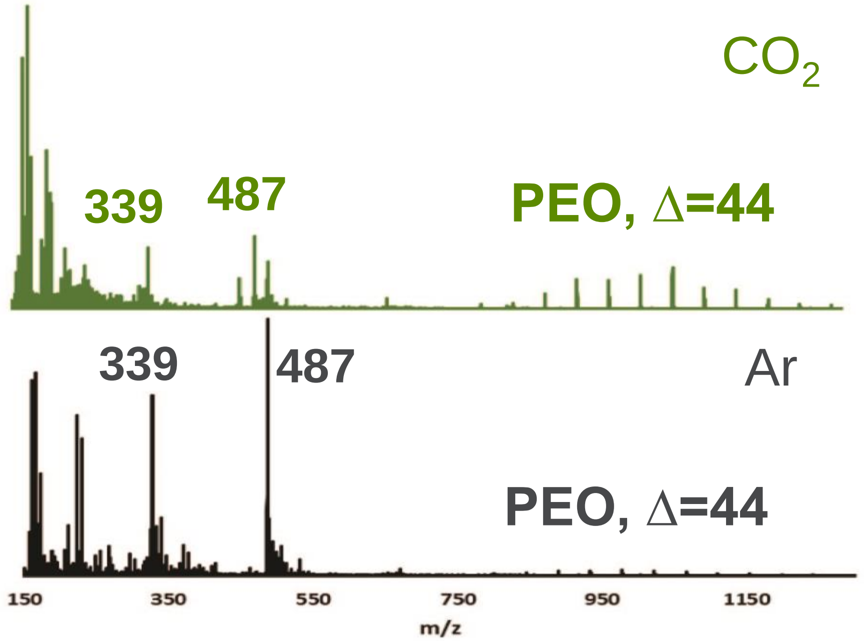
EFFECT OF CO_2 ON INTERFACIAL PROPERTIES OF SI ANODE

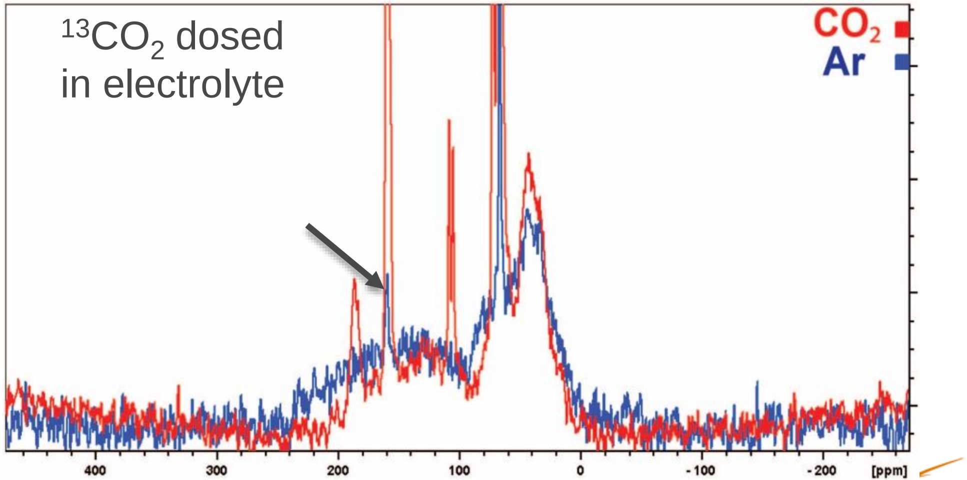
Ex situ XPS of Si/SEI



Ex situ ToF-MS of SEI on SI



Ex situ ^{13}C NMR



- Presence of CO_2 in Gen2 electrolyte substantially changes SEI composition on Si:
  - Promotes LiF and suppresses Li_2CO_3 formation
  - Promotes formation of aldehyde/ketone-like organic species and PEO oligomers

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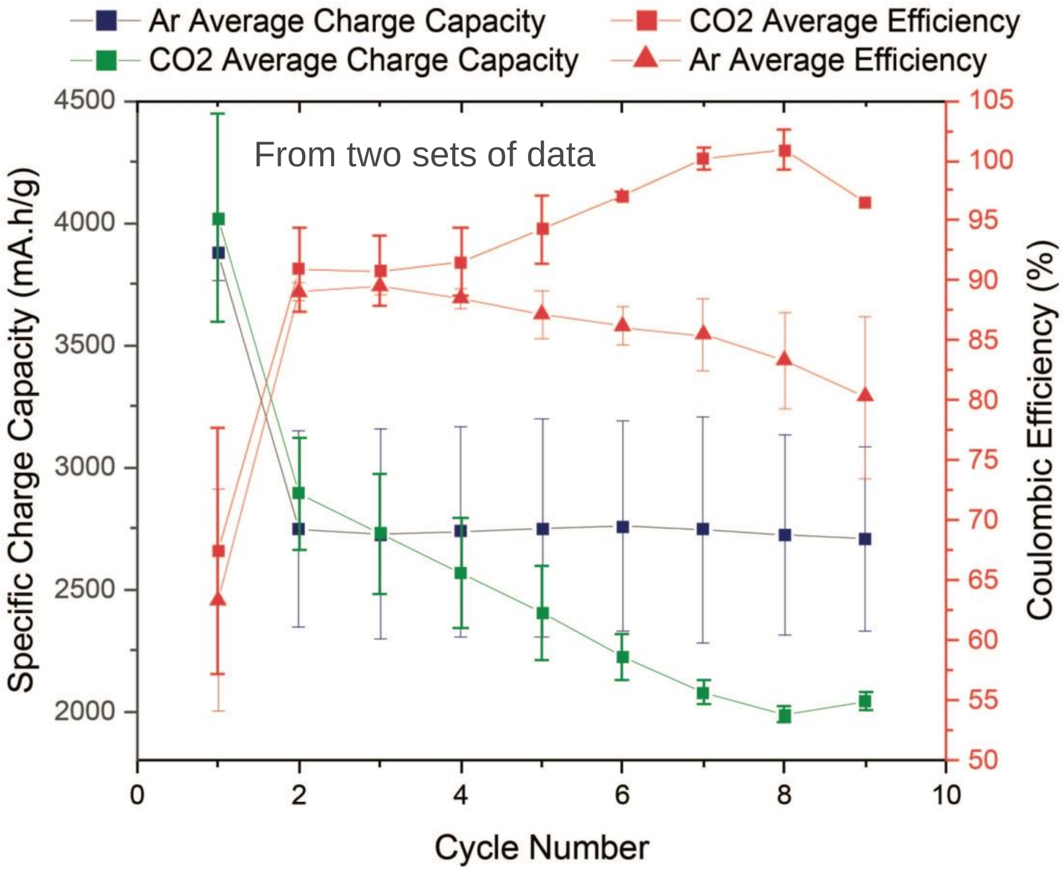
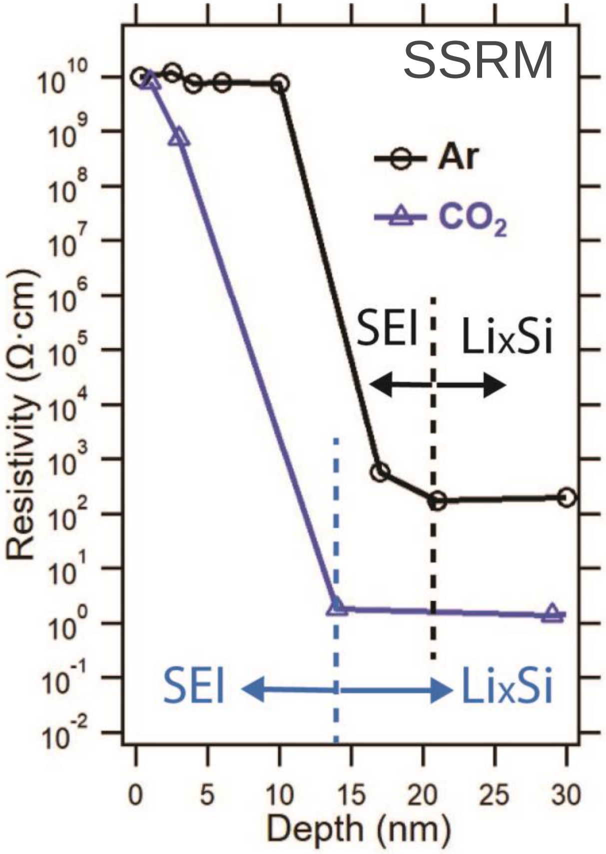


From two sets of data



- SEI film formed in the presence of CO_2 tends to be thinner and less electronically resistive
- CO_2–saturated Gen2 electrolyte does not improve Si cycling performance

THREE STRATEGIES TO STABILIZE SI/ELECTROLYTE INTERFACE

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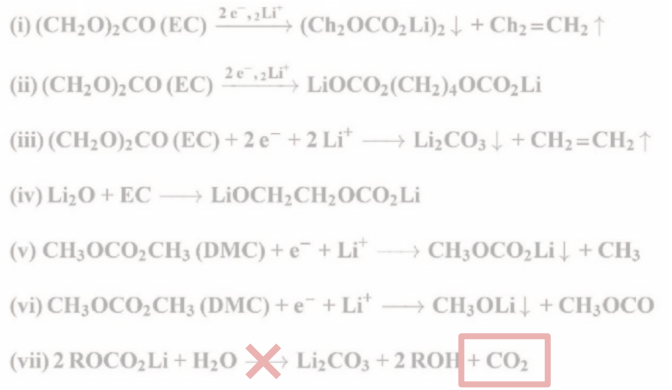

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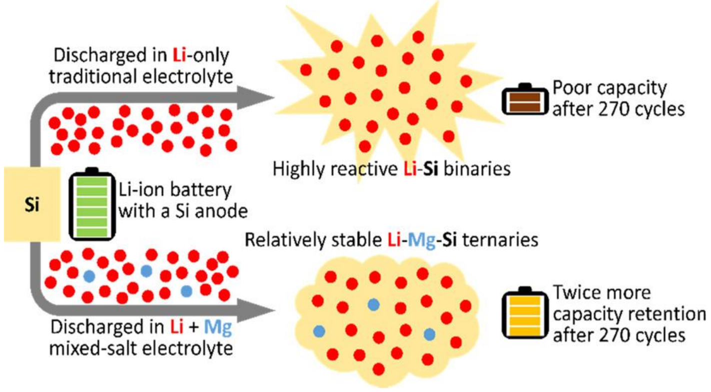
Interface Modification



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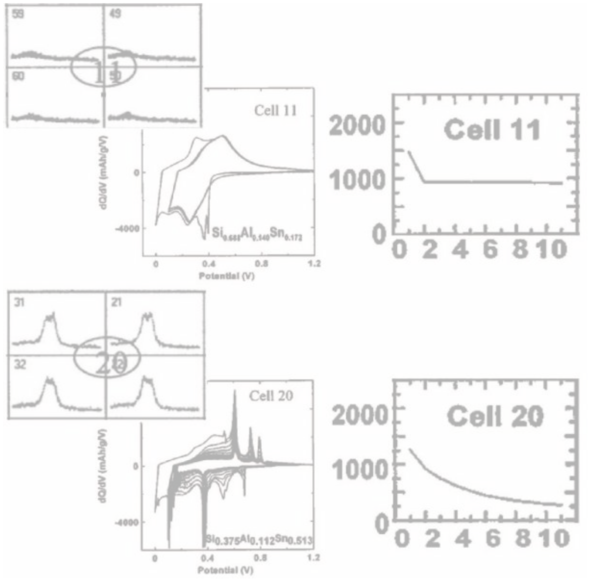

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Si-based Amorphous Alloys

Synthesize a new class of Si-based amorphous electrode active materials with greatly improved interfacial and mechanical properties

MECHANISM OF ZINTL PHASE FORMATION ON SI ANODE

$Mg(TFSI)_2$ electrolyte additive alters composition of the Si/electrolyte interface

Lithiation: 3 working hypotheses

1. Exchange:

$3.75Li + Si \rightarrow Li_{3.75}Si$

$Li_{3.75}Si + 0.1Mg^{2+} \rightarrow Li_{3.55}Mg_{0.1}Si + 0.2Li^+$

2. Co-alloying

$Li_{3.5}Si + Mg^{+2} \text{-->} Li_{3.5}Mg_{0.1}Si$

3. Co-insertion followed by equilibration:

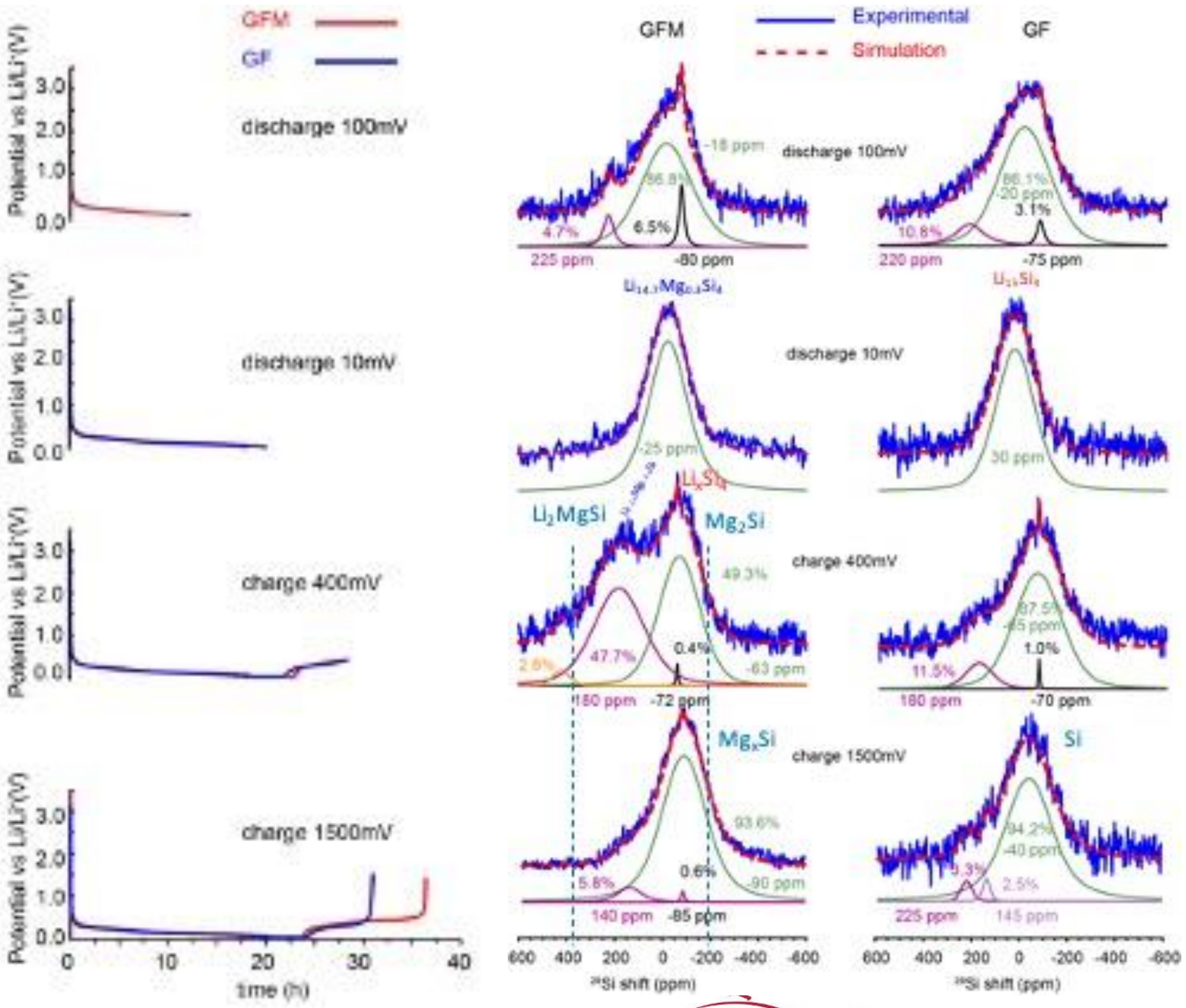
$Li_{3.75}Si + Mg^{+2} \text{-->} Li_{3.75}Mg_{0.1}Si$

$Li_{3.75}Mg_{0.1}Si \text{-->} Li_{3.5}Mg_{0.1}Si + 0.2\ Li^+$

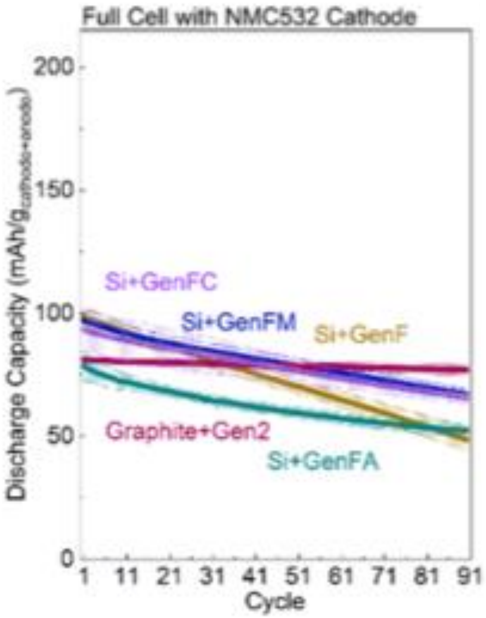
Delithiation:

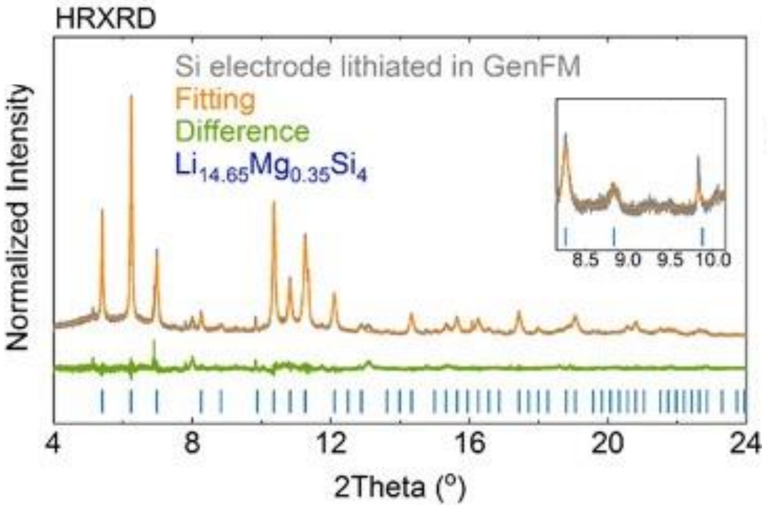
$Li_{3.75-2x}Mg_xSi \rightarrow Mg_xSi + (3.75-2x)Li$

NMR indicates no removal of Mg when delithiation is carried out in GENFM, consistent with Mg strong coordination to Si

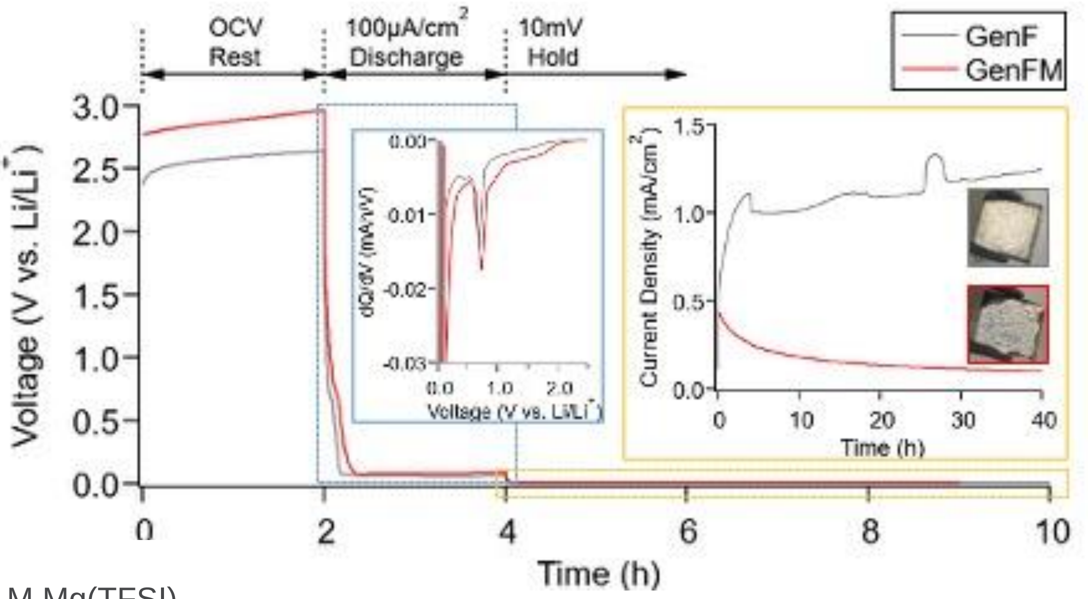


EFFECT OF ZINTL ON SI ANODE INTERAFCIAL BEHAVIOR





GENF:1.2 $LiPF_6$ EC:EMC (3:7 wt%) +10%FEC
GENFM: 1.2 $LiPF_6$ EC:EMC (3:7 wt%) +10%FEC + 0.1M $Mg(TFSI)_2$



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- Improved in Si electrode capacity retention in GenFM electrolyte
- Li_xMg_ySi phase formation on the electrode/electrolyte interface
- Lower parasitic current at 10 mV, indicating better passivating properties of the SEI on Si in presence of $Mg(TFSI)_2$

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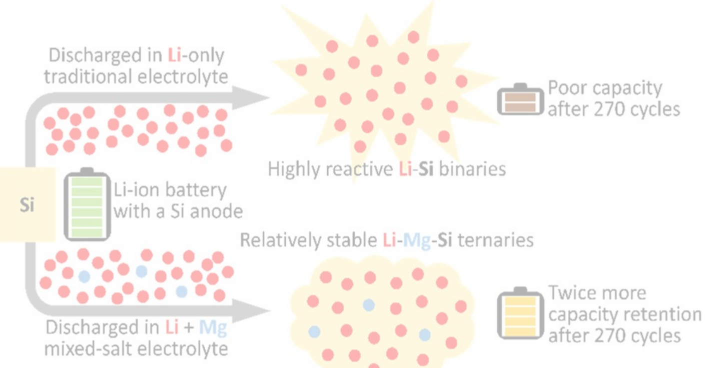

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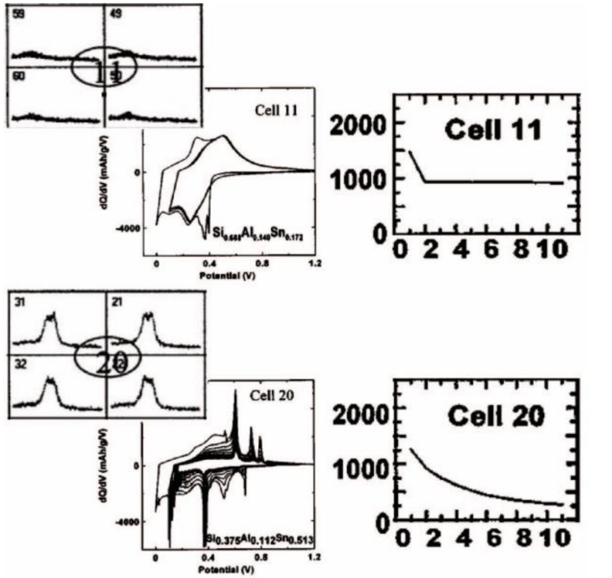

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Si-based Amorphous Alloys

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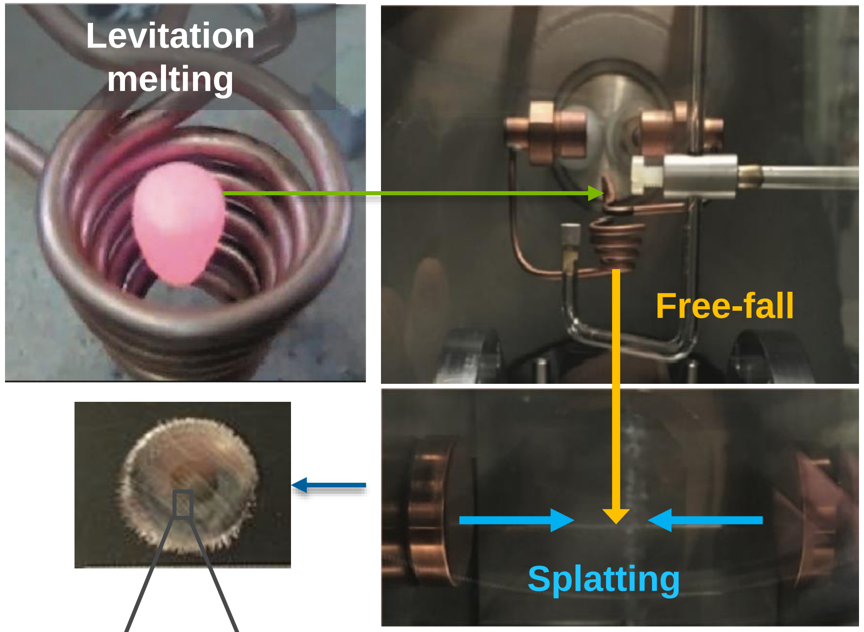
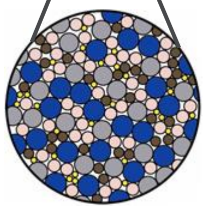
SI AMORPHOUS ALLOYS SYNTHESIS & CHARACTERIZATION

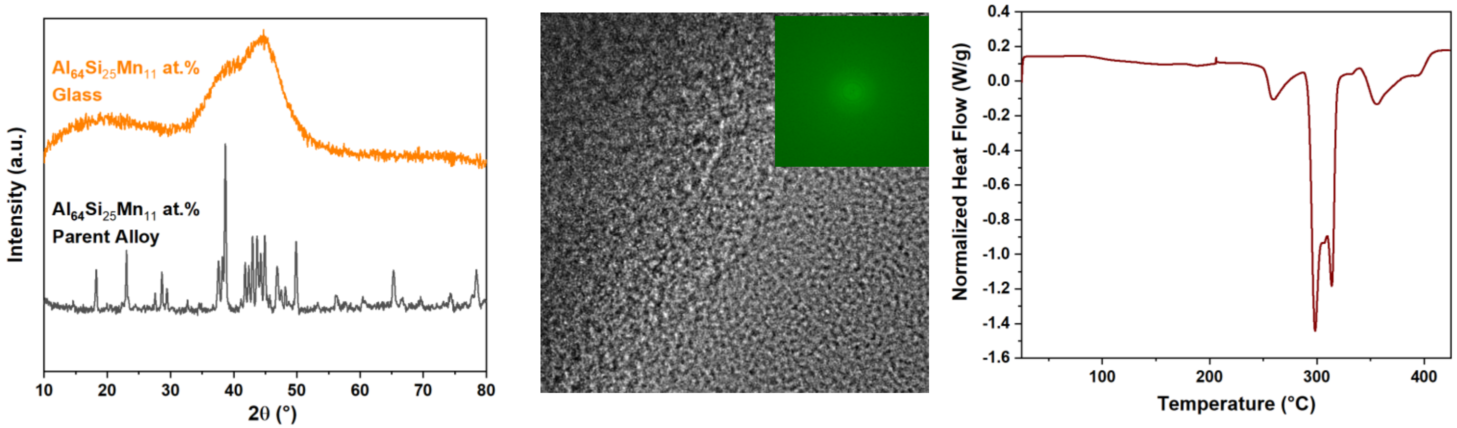
Splat quenching of a molten alloy droplet by splatting it with two cold metal surfaces at cooling rates of 10^5-10^6 K/s produces amorphous alloys





Lack of phase boundaries introduces new and unique materials properties

XRD, TEM and DSC results confirm successful fabrication of amorphous $Al_{64}Si_{25}Mn_{11}$ metallic glasses



Known Binary System (A_xB_y at.%)

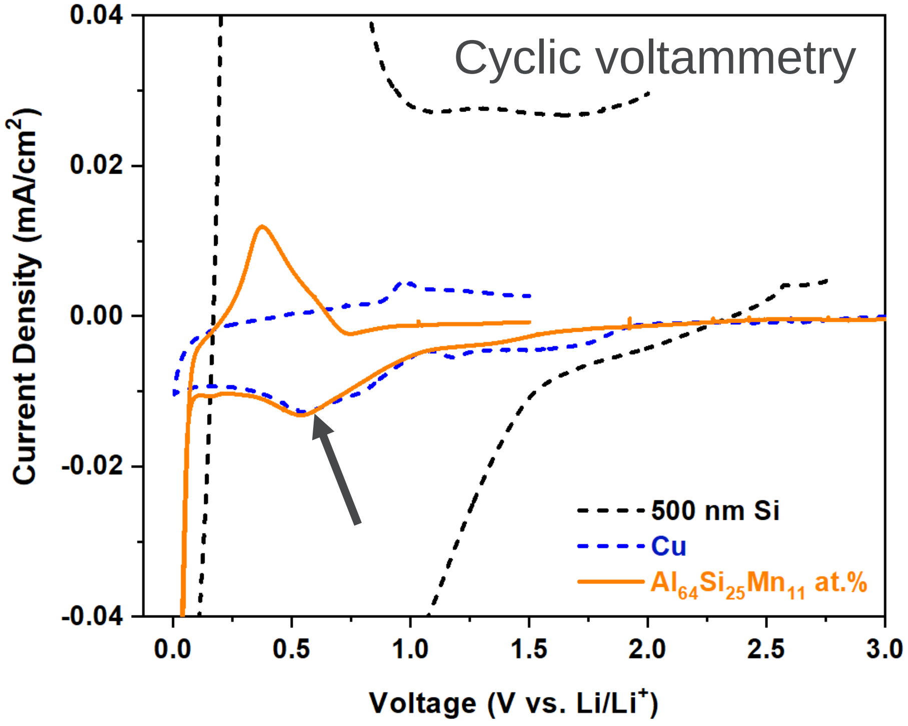
	$Ti_{0.84}Si_{0.16}$	$Ni_{0.75}Si_{0.25}$	$Zr_{0.8}Si_{0.2}$
Capacity	357 mAh/g	489 mAh/g	378 mAh/g

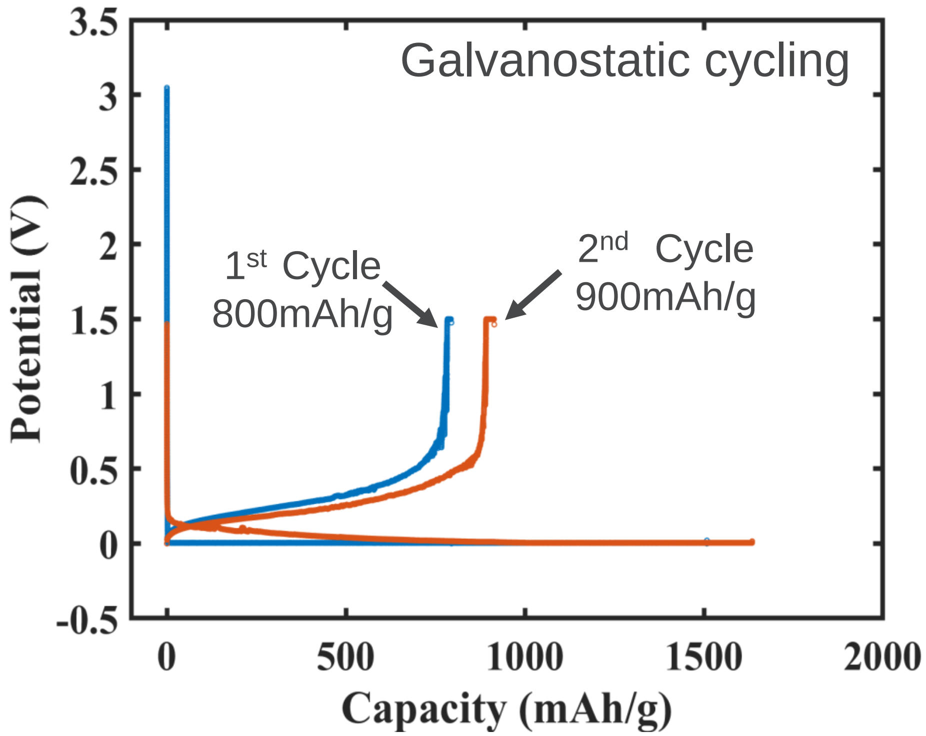
Ternary System ($A_xB_yC_z$ at.%)

	$Fe_{1-x-y}Si_xB_y$ $(x + y \;\; 25)$	$Ni_{1-x-y}Si_xB_y$ $(x + y \;\; 49)$	$Co_{1-x-y}Si_xB_y$ $(x + y \;\; 35)$
Capacity	266 - 523 mAh/g	374 - 1152 mAh/g	300 - 730 mAh/g

SI-BASED AMORPHOUS ALLOYS ELECTROCHEMICAL BEHAVIOR

Si-alloys retain volumetric energy density of Si and show much improved interfacial and mechanical stability





- SEI formation charge and current profile is comparable to copper
- Specific capacity ~900 mAh/g obtained for foil (2-4 μm) alloy sample. Higher values expected with properly engineered electrodes

SUMMARY

1. Inherent non-passivating behavior of Si in organic carbonate electrolytes confirmed and quantified
    - Corrosion/parasitic currents of 1 μA/cm^2 observed on model and composite Si electrodes
    - Gradual electrolyte consumption and lithium inventory shift in Si-based cells
    - SiO_2 film has to be carefully optimized to promote surface passivation
2. New routes to achieve interfacial stability of Si electrode explored and evaluated
    - SEI composition and structure can be altered by shifting reaction equilibria by soluble products of the electrolyte decomposition
    - ZINTL phase set s a new path for in situ modification of Si/electrode interface
3. Exploratory research of new Si-based high-energy electrode materials
    - A series of new Si-based binary and ternary amorphous alloys was synthesized and tested
    - Preliminary data show much improved interfacial behavior and mechanical properties

REMAINING CHALLENGES / FUTURE PLAN

Three Research Themes with Staggered Timelines

I. Use round robin electrodes for control and modification of physico-chemical properties
   - Characterize electrode surface reactivity, SEI layer composition and structure
   - Unveil hidden SEI layer components
   - Understand rthe mechanism of SEI layer operation and function

II. Correlate interfacial properties with electrochemical behavior
   - Formulate working hypothesis of the mass and charge transfer across the surface film
   - Develop methods to track Li^+ in the film and electrode active material
   - Use and investigate chemical spillover effects from active and passive electrode components

III. Design rational Si electrode design principles to address performance challenges
   - Correlate modifications to specific challenges, e.g. surface reactivity to electrolyte, volume change, “cracking, etc.
   - Design and study model electrodes with tailored interfaces to control the kinetics i.e., rate and selectivity of interfacial processes.

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