Synthesis and Characterization of Silicon Clathrates for Anode Applications in Lithium-Ion Batteries

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Project ES149

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BATT Batteries for Advanced Transportation Technologies

Overview

Timeline

- Program Start: January 2011
- Program End: December 2014

Budget

- DOE Share: $1.15M
- Funding Received in FY12: $299K
- Funding for FY13: $296K

Barriers

- (A) - Cost
- (C) - Performance
- (E) - Life

Targets

Specific Energy (W·h/kg)	Specific Power (W/kg)	Cycle-Life	Calendar Life (yr)
200 (EV)	316	1000	15
96 (PHEV)	316	3000 (40 mi equiv.)	15

Baseline Systems: Conoco Phillips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

Collaborators

- Arizona State Univ. (Candace Chan)
- Arizona State University (Xihong Peng)
- Florida International Univ. (Jiuhua Chen)

Objectives - Relevance

Overall

- Theoretically and experimentally assess the intrinsic physicochemical, mechanical and electronic advantages of Type I silicon clathrate (Si_{46}) over conventional (diamond) silicon (Si_4) as a high-performance anode material for Li^+ batteries.

- Demonstrate improved life and abuse tolerance of Li^+ batteries using Si_{46} and its metal-silicon framework analogues ($A_x@M_ySi_{46-y}$) as anode materials.

M = Metallic Framework Atom
A = Metallic Guest Atom

Current

- Employ first principles computations to: (a) predict Li^+ occupancy and lattice expansion potential of Type I silicon and metal-silicon clathrate alloys ($A_x@M_ySi_{46-y}$); and, (b) identify possible reaction pathways for the formation of the corresponding lithiated species [$Li_n@Si_{46}$ and $Li_n@(A_x@M_ySi_{46-y})$].

- Synthesize and characterize batch-scale quantities (200 g) of Type I silicon clathrates (Si_{46}) and/or Type I metal-silicon clathrate alloys ($A_x@M_ySi_{46-y}$) – either empty or containing guest atoms.

- Experimentally assess the capacity and cyclability of clathrate anodes as a function of electrolyte/additive formulations and formation techniques.

Milestones

Target Date	Milestone	Status
06/2012	Identify possible reaction pathways for the formation of empty clathrates $\Box Si_{46}$, $Li_n@Si_{46}$, $Li_{15}Si_4$, and $Li_n@(A_x@M_ySi_{46-y})$	Complete
09/2012	Synthesize 100-200 g of Type I silicon clathrate (Si_{46}) and/or metal-silicon Type I clathrate alloys with complementary determination of structural purity $\Rightarrow$ 200 g of $Ba_8@Al_8Si_{38}$ synthesized	50% Complete
01/2013	Construct and evaluate several electrochemical half-cells using anode materials synthesized in Year 2, combined with best-case additives and electrolyte formulations	Complete
04/2013	Characterize electrochemical properties of silicon clathrate anodes made from Year 2 materials	Pending
07/2013	Identify structural and mechanical states of silicon clathrate anodes during lithiation and delithiation processes and validate against theoretical calculations	Pending
09/2013	Achieve reversible capacity of 400 mAh/g after 50 cycles at C/15 for either Si_{46} or $A_8@M_ySi_{46-y}$ (A = Ba, Na; M = Al, Cu)	Pending

Strategy

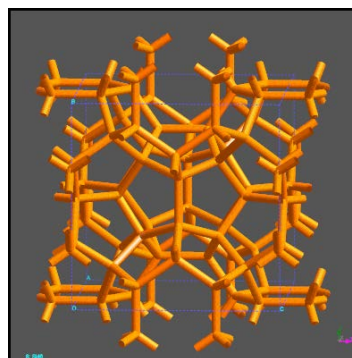*Asses the structural and electronic attributes of Type I clathrate Si_{46} versus conventional Si_4*

Allotropic Transformation →

Synthesize Clathrate Allotrope
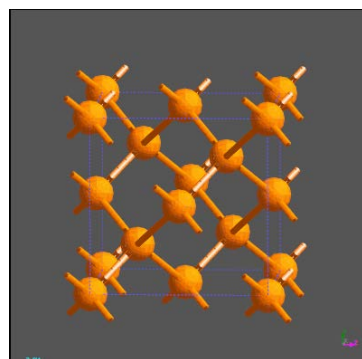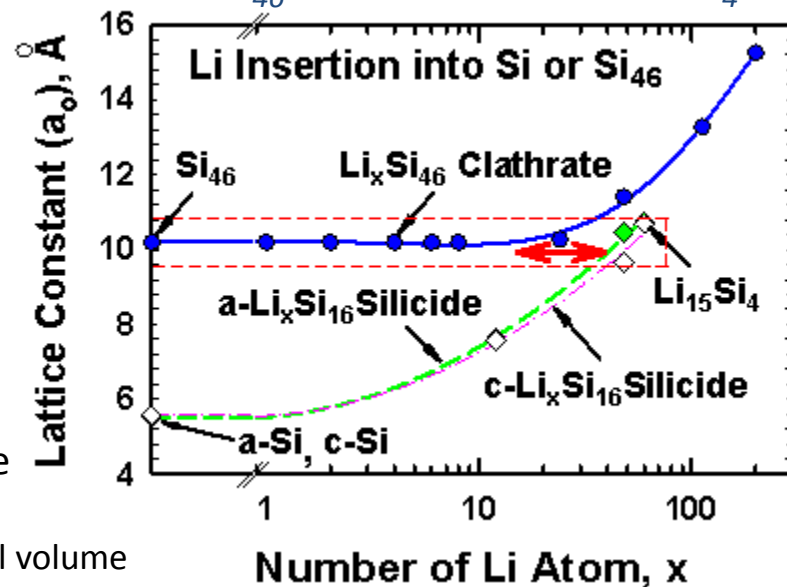
Si_4 $[Fd\overline{3}m]$
Diamond Structure

Si_{46} $[Pm\overline{3}n]$
Clathrate Type I Structure

- Undergoes large volume changes (> 300%) on charging/discharging
- Mechanically unstable
- Capacity loss

- Computations indicate small volume change in Si_{46} compared to a-Si or c-Si
- $Li_x@Si_{46}$ and $Li_{15}Si_4$ have similar lattice constants
- Specific grav. capacity of 478 mA·h/g

Validate theoretical predictions by synthesizing silicon clathrates and measuring electrochemical capacity

Structure	Space Group	Lattice Constant (Å)	Predicted Equilibrium Volumes (Å³/u.c.)				No of Li⁺	Specific Grav. Capacity (mA·h/g)
			Total Cell	Available	Occupiable	Accessible		
Si_{46} (Type I)	$Pm\overline{3}n$	10.355	1110	169.51	47.76	43	23	478
Si_4 (diamond)	$Fd\overline{3}m$	5.456	1191	549.9	112.83	110	15	4000
C (graphite)	$P6_3/mmc$	2.460	35.64	4.25	1.89	0.78	1	372

Overview of Approach

Experiment

Theory

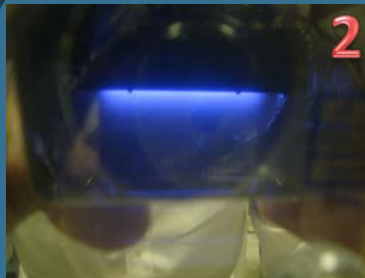**Synthesis of Si_{46} and $A_x@(M_ySi_{46-y})$ via parallel paths:**

1 Vacuum arc melting from elemental powders to form $A_x@M_ySi_{46-y}$

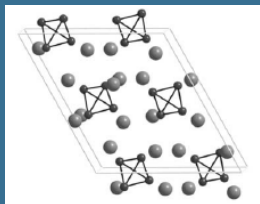**2** Vacuum PEMS onto ionic liquid (IL)

3 Heterogeneous batch synthesis in solution via Hofmann-type elimination-oxidation reaction

$$4[R'-CH_2-NR_3]^+ + Si_4^{4-} \xrightarrow{\sim 300°C} 9Si^0 \text{ [Clathrate I]} + 4[R'=CH_2] + 4NR_3 + 2H_2$$
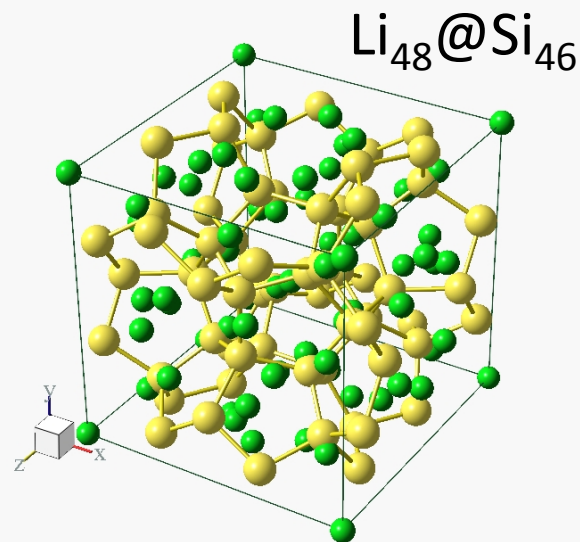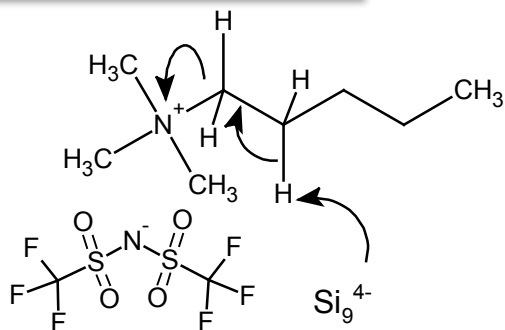
Zintl Phase Formation

First principles predictions of:

- Lithiation pathways
- Thermodynamic and kinetic constraints
- Transformation of allotropic states
- Mechanical stability

$Li_{48}@Si_{46}$

Approach - Synthesis

Solution Synthesis of Si_{46} ✓

Trial 5
$BaSi_2$ + DTMAC-BTFMSI → Si_{46}

Completed: Product confirmed by PXRD and Raman; removed byproducts; performed EC measurements; yield may be improved with NaSi.
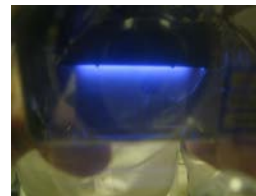
Trial 6
$NaSi_{1.5}$ + DTMAC-BTFMSI → Si_{46}

Completed: Vigorous reaction, though impure product yield. Purity may be improved with pure Zintl phase of NaSi

Precursor Modification
400 – 750°C
$NaSi_{1.5}$ + NaH (excess) → NaSi (Zintl)

Underway: PXRD results indicate partial formation of Zintl phase

Plasma Mag. Synthesis of Si_{46} in IL

Trial 3
d-Si + Proprietary IL → Yield of Unknown Particle Size

✗

Completed: Raman evidence of □Si_{46}; particles isolated and imaged; low product yield.

New Approach

Trial 4: Plasma Enhanced Magnetron Sputtering (PEMS)

d-Si → Deposition of Si_{46} directly onto copper electrode

Underway

✓ = Selected for further development

Approach – Synthesis (Cont.)

Vacuum Arc-Melting Synthesis of $A_x@M_ySi_{46-y}$ Alloys ✓

Trial 6
$38\ d\text{-Si} + 8\ Al + 8\ Ba \rightarrow$
$Ba_8@Al_8Si_{38}$

Completed: Products confirmed by PXRD and Raman; performed EC measurements at two labs; high structural purity; some chemical impurities remain; high yield technique.

Scale-Up
$38\ d\text{-Si} + 8\ Al + 8\ Ba \rightarrow$
$Ba_8@Al_8Si_{38}$ [200 g]

Completed: Products confirmed by PXRD and Raman; achieved higher structural purity than in previous trials.

**Milling**
$Ba_8@Al_8Si_{38}$ [200 g] $\rightarrow$ < 250 nm

Completed: Particle sizes < 250 nm without compromising structural purity.

**Measurement of Anode Capacity & Cyclability vs. Preparation Technique**

Underway

Approach - Computations

- Compute energies of formation and stabilization using DFT and Carr-Parrinello Molecular Dynamics (CPMD) levels of theory for various Type I clathrate compositions.

- Predict the excess stability and lattice expansion effected by different ratios of Ba guests and Al framework atoms in $Ba_x@Al_ySi_{46-y}$ clathrate (Type I) when lithium atoms are intercalated to yield $Li_n@(Ba_x@Al_ySi_{46-y})$.

- Predict the excess stability and lattice expansion effected by intercalation of Na and Li guest atoms into silicon clathrate (Si_{46}) and Al_ySi_{46-y} to yield $Na_n@(Li_x@Si_{46})$ and $Na_n@(Li_x@Al_ySi_{46-Y})$.
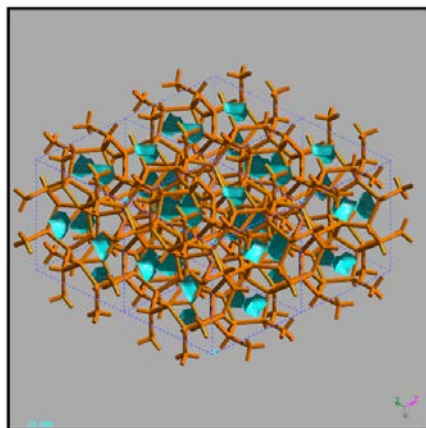
Prediction of Accessible Volume for Li^+ Occupation

6d

Tetrakaidecahedron

2a

Pentagonal dodecahedron
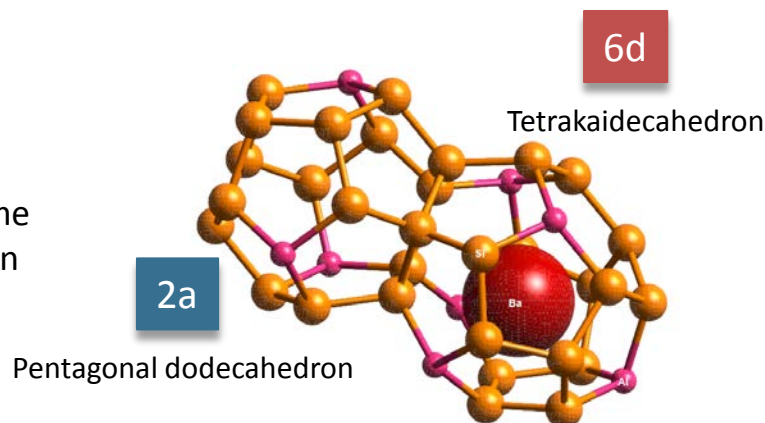
Accomplishments - Vacuum Arc-Melt Synthesis

Scale-Up Synthesis of Metal-Substituted Type I Silicon Clathrate via Arc Melting

- Framework-substituted Type I clathrate $Ba_8@Al_8Si_{38}$ successfully synthesized in bulk (200 g).
- Employed large-volume vacuum arc melter.
- Arc-melting process yielded material of higher structural purity than previous small-scale batches without secondary phase formation of Type II clathrates or d-Si.
- Scale-up synthesis of this clathrate material enabled ball milling techniques to be employed for formation and evaluation of prototype anode.
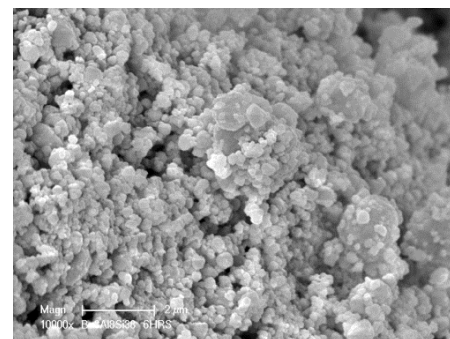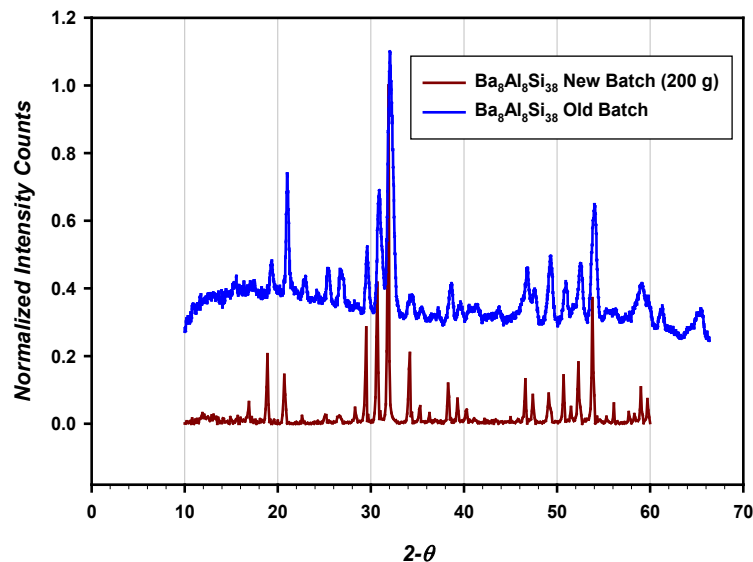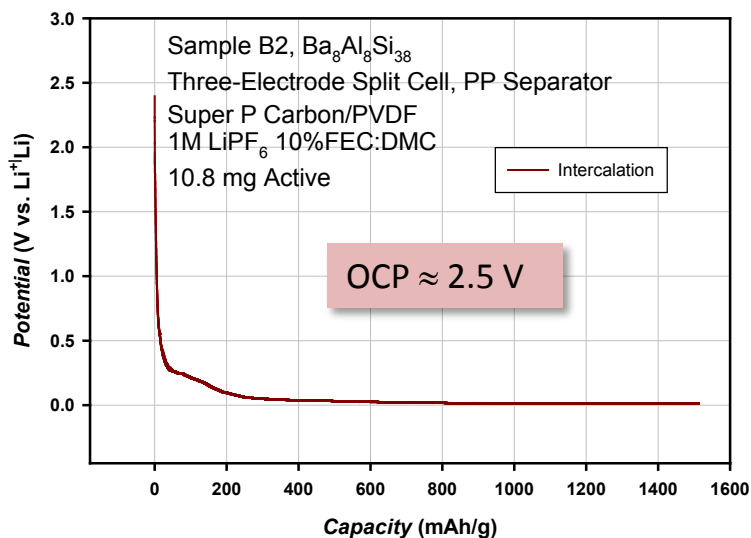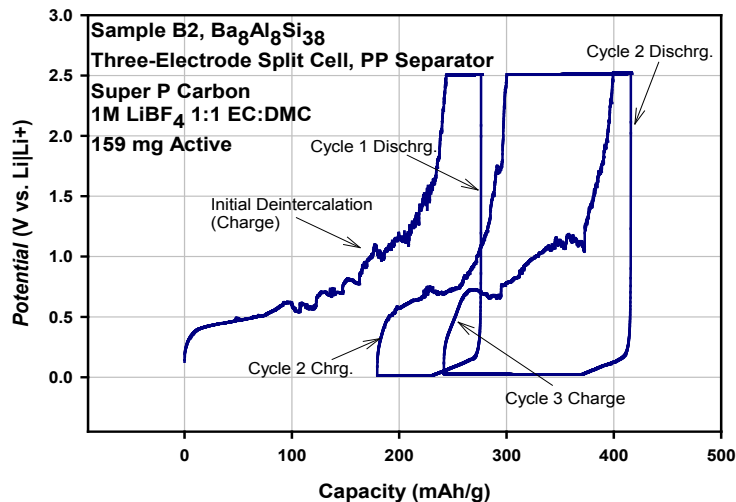

Particle morphology of ball-milled $Ba_8@Al_8Si_{38}$ powder for prototype anode

Accomplishments - Vacuum Arc-Melt Synthesis

## *Electrochemical Half-Cell Measurements: Capacity & Cyclability of Compounded Anode*

Sample B2, $Ba_8Al_8Si_{38}$
Three-Electrode Split Cell, PP Separator

Super P Carbon
1M $LiBF_4$ 1:1 EC:DMC
159 mg Active

Cycle 2 Dischrg.
Cycle 1 Dischrg.
Initial Deintercalation (Charge)
Cycle 2 Chrg.
Cycle 3 Charge

Sample B2, $Ba_8Al_8Si_{38}$
Three-Electrode Split Cell, PP Separator
Super P Carbon/PVDF
1M $LiPF_6$ 10%FEC:DMC
10.8 mg Active

— Intercalation

OCP $\approx$ 2.5 V

- Compounded anode of $Ba_8@Al_8Si_{38}$ without binder (top) formed by mechanical compression into free-standing disks (1 cm diam. $\times$ 3 µm thick).
- Anodes as prepared tend to be diffusionally constrained at rates $\geq$ C/14.
- Li^+ intercalate into lattice guest sites even while Ba guest atoms are tightly bound.
- First-cycle net (irreversible) loss for this un-optimized anode is 24% of the theoretical capacity (259 mA·h/g).
- Potential and/or current fluctuations point to instabilities in SEI formation that persist beyond second cycle.
- Anode formed by thin-casting slurry composed of $Ba_8@Al_8Si_{38}$, carbon additive, and binder (bottom) extended capacity beyond theoretical limit: 1500 mA·h/g based on 10.8 mg of active material.

Accomplishments - Vacuum Arc-Melt Synthesis

*Electrochemical Half-Cell Measurements: Ball-Milled Anode Material*
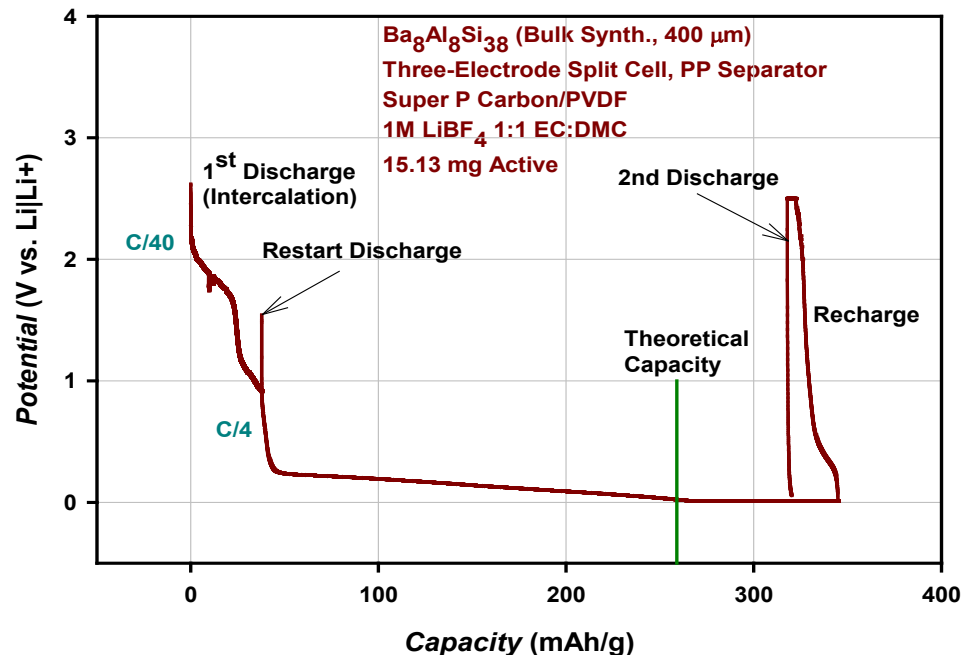
- Time required to attain a stable OCP (2.7 V) is significantly shortened for prototype anode incorporating ball-milled (< 250 nm) $Ba_8@Al_8Si_{38}$.
- Intercalation kinetics are notably faster: a 10-fold increase in C-rate is achievable, while surpassing the theoretical capacity as noted.

Additional studies needed to understand root cause of first-cycle capacity loss and make necessary changes to anode composition

Accomplishments - Computations

Comparisons of Computed Lattice Constant and Energy Change as a Function of Li Insertion in $A_x@M_ySi_{46-y}$ vs. Si_{46} vs. Si_4
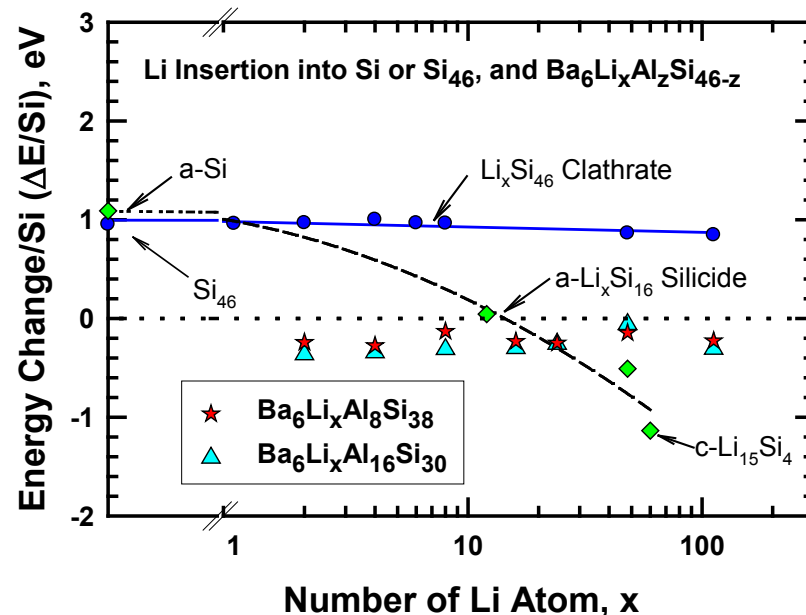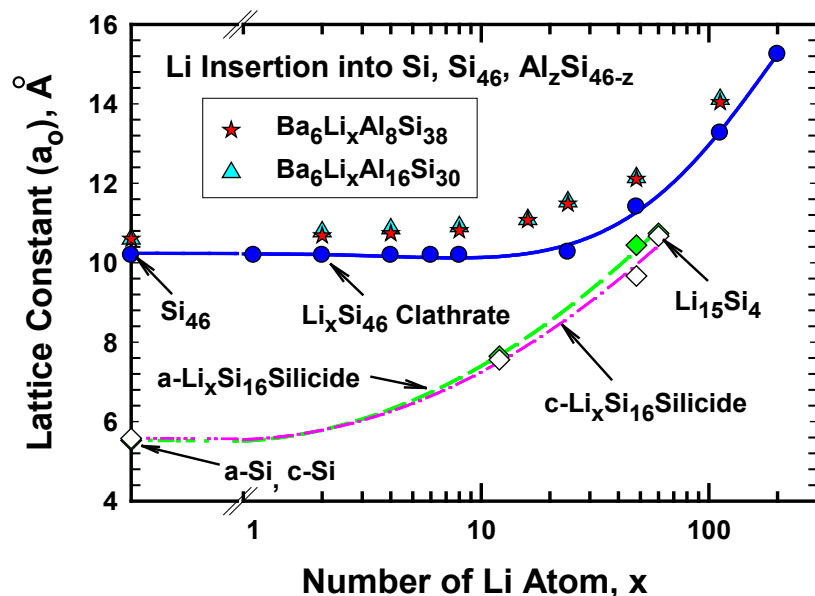

- Optimum ratios of Ba guests and Al framework atoms required to attain a stable alloyed Si clathrate structure with limited volume expansion during Li intercalation have been determined.
- $Li_n@(Ba_6@Al_8Si_{38})$ and $Li_n@(Ba_6@Al_{16}Si_{30})$ both allow insertion of up to 24 Li atoms without Ba removal, without significant increase in lattice constant

Accomplishments - Computations

Intercalation and Stabilization of Silicon Clathrate Structures Using Sodium Atoms
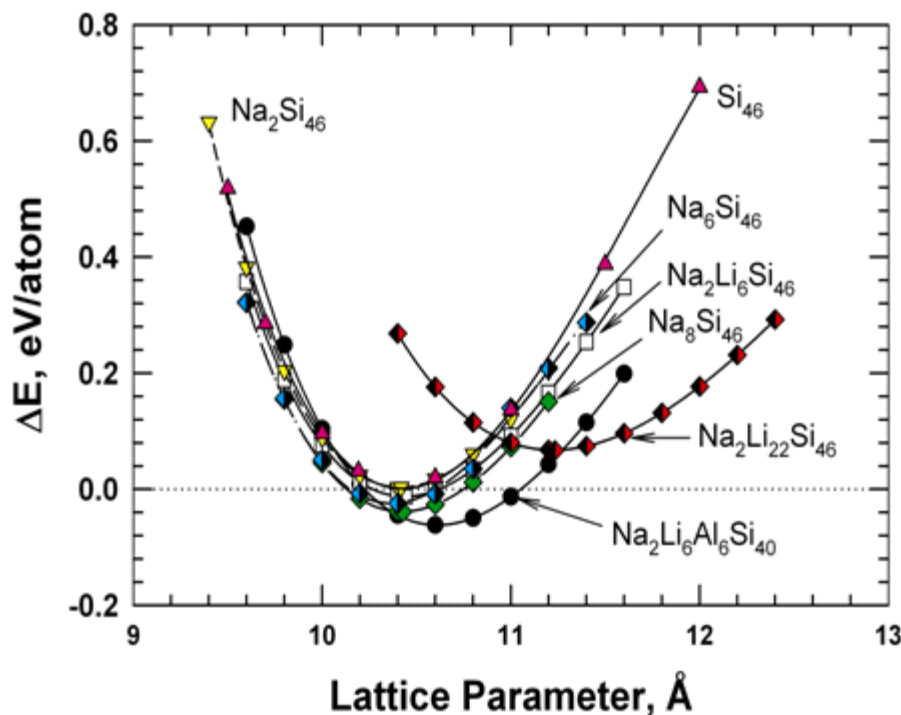

- CPMD computations indicate that Na guest atoms tend to stabilize silicon clathrate structures and their framework alloys $\Rightarrow$ Energy of formation falls < 0.

- Intercalation of Li atoms further reduces energy of formation below zero without a volume expansion.

- Energy of formation becomes positive again when ≥ 22 Li atoms are inserted, accompanied by 8% increase in unit cell volume.

Results suggest that Li intercalation into Na-stabilized Si_{46} is energetically favored over empty silicon clathrate structures.

Accomplishments - Computations

Computed Energies of Formation for Na and Li Insertion in Al-substituted Type I Clathrate Compositions
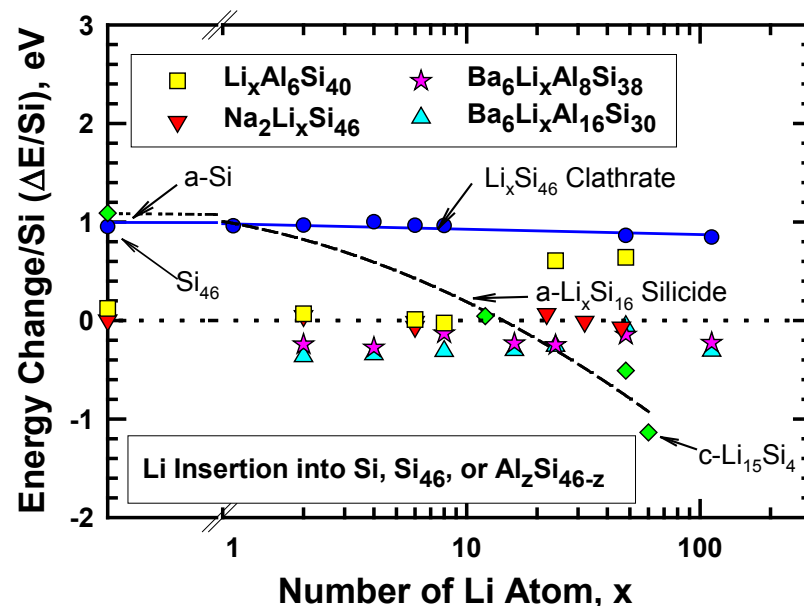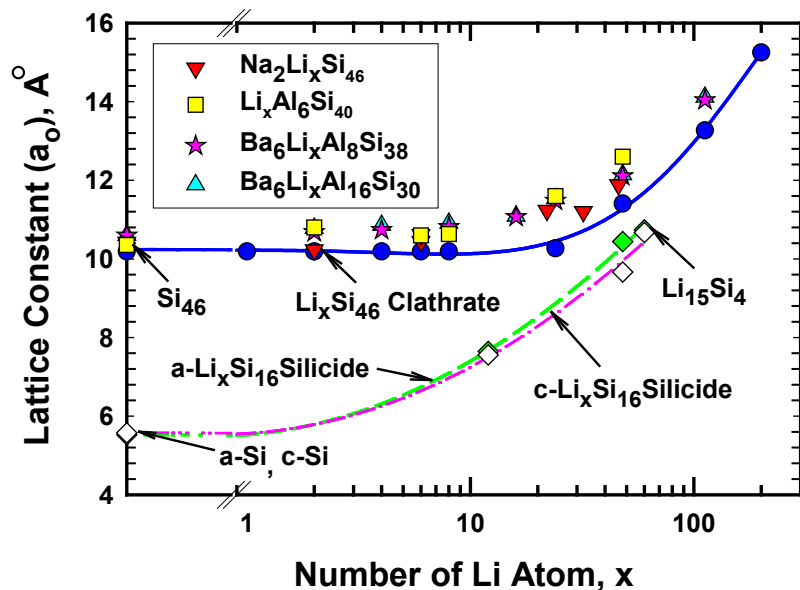
Identified compositions of Na-stabilized or Al-substituted Si clathrates that can be lithiated to form stable compounds comparable to a-Li_xSi or c-Li_xSi

Collaborations

- Dr. Candace K. Chan, Assistant Professor, Materials Science & Engineering, Arizona State University, Tempe, AZ: Providing materials, process expertise, and initial EC data on arc-melt synthesis of metal-substituted silicon clathrates; co-inventor

- Dr. Jiuhua Chen, Assoc. Professor, Assoc. Director of the *Center for the Study of Matter at Extreme Conditions* (CeSMEC), Mechanical and Materials Engineering Department, Florida International University, Miami, FL: Provided laboratory services and technical expertise on multi-anvil synthesis

- Dr. Xihong Peng, Assistant Professor, Department of Applied Science and Mathematics, College of Technology and Innovation, Arizona State University at the Polytechnic Campus, Mesa, AZ; Providing first-principles computation expertise and DFT computations using the VASP code for comparisons against CPMD results.

Future Work

- Characterize electrochemical properties of silicon clathrate anodes made from Year 2 materials (arc-melt $Ba_8@Al_8Si_{38}$) with Graphenol® (graphene) as conductive additive.

- Solution synthesis of empty Si_{46} using converted NaSi (Zintl phase).

- Perform post-mortem analyses of clathrate anodes to map the structural and mechanical states at various lithiation levels using a suite of characterization techniques (CP-MAS-NMR, Raman, XRD, Neutron Diffraction).

- Perform first-principles computations to compare with experimental observations and to verify lithiation pathways and products.

- Submit sample to LBNL (Vince Battaglia) for half-cell testing and independent validation.

Summary

- Synthesized empty and Al-substituted silicon clathrates via several methods; down-selected to arc-melting and direct-solution synthesis method based on scalability.

- Synthesized 200 g of $Ba_8@Al_8Si_{38}$ by an industrial vacuum arc-melt technique.

- Predicted the Li^+ occupancy and lattice expansion potential of Type I metal-silicon clathrate alloys using classical and *ab initio* calculations.

- Identified possible reaction pathways for the formation of empty clathrates $\square Si_{46}$, $Li_x@Si_{46}$, $Li_{15}Si_4$, and $Li_x@M_ySi_{46-y}$.

- Performed electrochemical characterization of $Ba_8@Al_8Si_{38}$ anodes at several C-rates for limited cycles.

Project Team

Carol A. Ellis-Terrell, M.S., Research Scientist: *material synthesis, EC measurements*

Wuwei Liang, Ph.D., Sr. Research Engineer: *DFT and CPMD computations*

Thomas L. Booker, Engineering Technologist: *engineering design and measurements*