



Engineering Approaches to Dendrite-Free Lithium Metal Anodes

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Project ID #BAT327

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Overview

Timeline

- Project start date:
 - October 1, 2016
- Project end date:
 - September 30, 2019
- Percent complete: 75%

Budget

- Total project funding
 - DOE share: \$1,250,000
 - Contractor share: \$0
- Funding received in FY 2018: \$416,982
- Funding for FY 2019: \$431,960

Barriers

- Barriers addressed
 - Limited Cycle life
 - High cost
 - Low Energy Density

Partners

- Interactions/collaborations
 - UPitt (D. K. Achary)
 - Malvern Panalytical (S. Speakman)
 - Kurt J. Lesker Co. (KJL)
 - Complete Solutions

Relevance/Objectives

- Basic understandings of the **fundamental mechanisms and mitigation strategies** for planar/non-planar growth of Li metal anode during cycling.
- Develop multicomponent alloys (MCA) and structurally isomorphous alloys (SIA) as an effective current collector exhibiting **high Gibbs Thomson parameter and interfacial energy of adhesion (resistance to perturbation)** with Li metal to **inhibit “non-planar interface”** (e.g. cellular structure and dendrites).
- **Surface modification** of traditional copper current collector by coating with non Li ion reactive (inert) interface engineered (IE) materials to increase **the Gibbs Thomson parameter and adhesion energy**.
- Develop highly stable, long cycle life (≥ 300) dendrite free anodes with areal capacity $\geq 4\text{mAh/cm}^2$ in Li metal batteries (LMBs) along with $\geq 99.5\%$ coulombic efficiency.

Any proposed future work is subject to change based on funding levels

Milestones-FY 2018 and FY-2019

Date	Description	Type	Status
March 2018	Surface modification of Li metal electrode for preferential and controlled nucleation and growth to inhibit mossy and dendritic growth	Milestone	completed
March 2018	Synthesis and testing of effective SIA electrodes: Zero nucleation overpotential; inhibit the rapid crystal growth to form non planar interface (cellular and dendritic structure). Specific capacity (≥ 4 mAh/cm ²), >300 cycles, growth overpotential $\leq 0.01\%$ per cycle, CE: $\geq 99.5\%$	Milestone	completed
June 2018	Synthesis and testing of suitable LIC; Li ion conductivity (≥ 10 mS/cm)	Milestone	completed
October 2018	Generate multicomponent alloys (MCA) and interface engineered (IE) electrode; Specific capacity ($\geq 4-8$ mAh/cm ²), >500 cycles, growth overpotential $\leq 0.01\%$, CE: $\geq 99.5\%$	Milestone	completed
March 2019	Optimize MCAs, SIA and IE electrodes to improve the capacity and stability for scaling: Specific capacity (≥ 4 mAh/cm ²), cyclability (>1000 cycles) Growth potential $\leq 0.001\%$, CE: $\sim 99.5\%$	Go/No-Go	On-going
July 2019	Determine and analyze the cost of the MCA, SIA and IE electrodes, electrolytes, separators, binders, and related processes: Cost target: \$75/kWh from current \$200-300/kWh or 75% reduction in cost to the end-user	Milestones	On-going
September 2019	Utilizing the Li coated MCA, SIA and interface engineered electrode to study Li-S pouch cell configuration to achieve the DOE target \$200-300/kWh	Milestones	On-going

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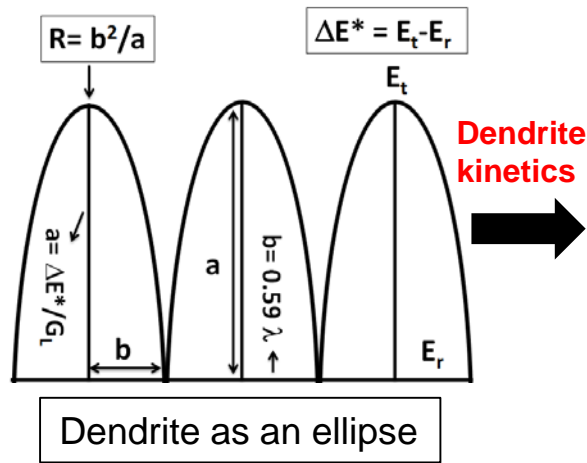
Approaches

- Detailed study of **mass and charge transfer kinetics** to understand the fundamental mechanisms of dendrite formation, and **determine the operating conditions (e.g. current density) and electrolyte properties (e.g. diffusivity constant)** for interface stability.
- Detailed perturbation and kinetic studies of dendrite formation to obtain correlation between **dendrite tip radius, primary arm spacing and marginal stable wavelength** with operating conditions (e.g. current density), current collector properties (e.g. **Gibbs Thomson parameter**) and electrolyte properties.
- **Multicomponent alloys (MCA)** exhibiting **bcc structure** has been synthesized by melt casting, high energy ball milling (including low-temperature cryo-milling) and solid state methods.
- Develop effective structurally isomorphous alloys (SIA) forming solid solution with Li metal and **inhibit rapid Li crystal growth** creating “**non-planar interface**” (non-dendritic structures).
- Surface coating onto copper current collector with **Li-ion non-reacting interface engineered (IE) materials** to improve the adhesion energy and eliminating dendrite formation
- Investigate the **nucleation and growth mechanism of dendrite** and their impact on the solid electrolyte interphase (SEI) layers combined with the cycle life.
- Design electrodes to achieve maximum plating/stripping of Li metal by maintaining the targeted performance ($\sim 4 \text{ mAh/cm}^2$).

Technical Accomplishments and Progress

Basic understandings on how battery cycling conditions, electrolyte properties and the current collector properties influence the microstructure

Perturbation Analysis and Dendrite Kinetics: **Minimum unstable wavelength (λ_i), tip radius of cell/dendrite (R) and primary dendrite arm spacing (λ_1) of deposited Li metal**



$$LR^2 = \frac{4\pi^2 \Gamma D_L F}{\Delta E (1 - t_+) \Omega}$$

$$\lambda_i = 2\pi \sqrt{\frac{\Gamma \cdot D_L F}{\Delta E \cdot L (1 - t_+) \Omega}}$$

$$\lambda_1 = \frac{4.34}{L^{0.25} G_L^{0.5}} \left(\frac{\Delta E^* D_L \Gamma F}{(1 - t_+) \Omega} \right)^{0.25}$$

λ_i : minimum unstable wavelength (cm)
 D_L : Li ion diffusivity constant (cm²/sec)
 L : current density (A/cm²)
 ΔE : $RT/F (\ln C_o/C_i)$ (V)
 t_+ : transference number
 Γ : Gibb's Thomson parameter (V.cm)
 R : dendrite tip radius (cm)
 λ_1 : primary dendrite arm spacing (cm)
 ΔE^* : potential difference of dendrite tip and root
 F : Faraday constant (96500 Coulomb/mole)
 Ω : molar volume of Li metal (cm³/mole)

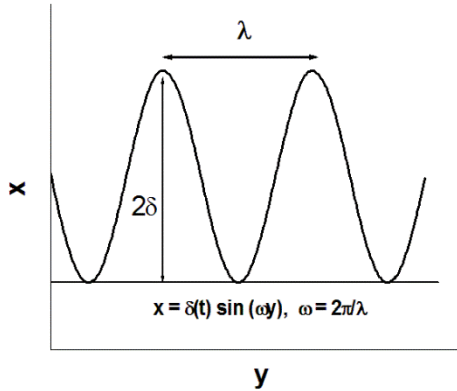
Criteria for improving battery cycle life:

- **Increase** in minimum unstable wavelength (λ_i), tip radius of cell/dendrite (R), and primary dendrite arm spacing (λ_1)
- **Electrolyte properties:** Increase in **Diffusivity**, D_L , and **transference number** t_+
- **Current collector properties:** Improve the **Gibbs Thomson parameter**, Γ (**resisting perturbation**)
- **Battery operating condition:** decrease the **Current density**, L , **charge density** or ΔE

Present study: **Effect of Gibbs Thomson Parameter (resisting perturbation) on the cycling stability**

Technical Accomplishments and Progress

Effect of Gibbs Thomson parameter (Γ) on the stability of planar interface



Dendrite:
Sinusoidal deformation
 $x = \delta(t) \sin(\omega y)$

Perturbation analysis

$$\left(\frac{\delta}{\delta}\right) = \left(\frac{D_L}{\Delta E}\right) \left\{ b - \frac{L(1-t_+)\Omega}{D_L F} \right\} (-\omega^2 \Gamma - G_L + mG_c) \rightarrow$$

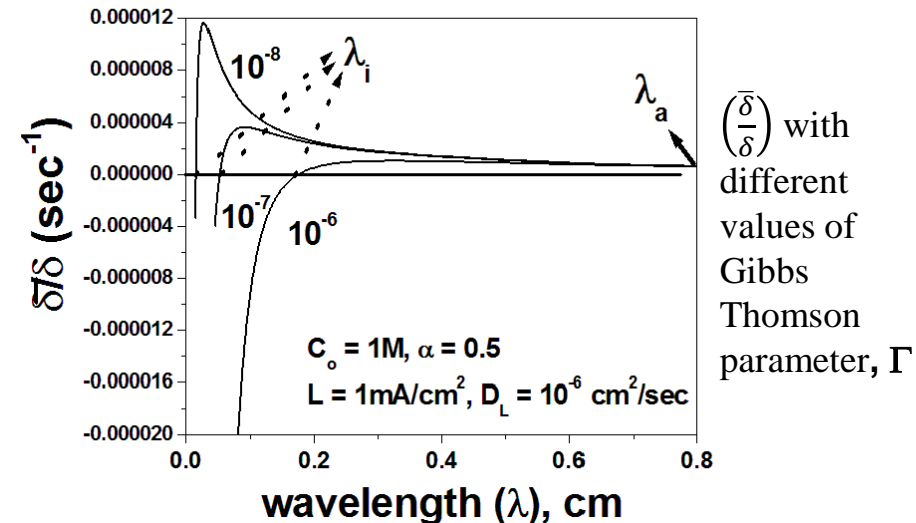
$\bar{\delta} = \frac{d\delta}{dt}$ = rates of change of amplitude with time

$$\Gamma = \frac{2\gamma\Omega \cos\theta}{F} \rightarrow \text{Resistance to perturbation}$$

$$(mG_c - G_L) \rightarrow \text{Driving force for perturbation}$$

$$\lambda_i = 2\pi \left(\frac{\Gamma}{mG_c - G_L} \right)^{0.5}$$

Γ : Gibb's Thomson parameter (V.cm)
 γ : interfacial/surface energy (J/m²)
 θ : wetting angle
 δ : amplitude
 ω : wavenumber
 λ : wave length
 α : transference number
 G_L : Electrolyte potential gradient
 G_c : concentration gradient
 mG_c : potential gradient at the interface



Γ ($10^{-8} - 10^{-6}$ V.cm with $\gamma = 10^{-4} - 10^{-2}$ Jcm⁻² and $\theta = 0$)

- The minimum unstable wavelength λ_i increases with increase in Γ and rate of change of amplitude decreases with increasing Γ
- Resistance to perturbation of the planar interface increases with increase in Gibbs Thomson parameter

Technical Accomplishments and Progress

Modified Gibbs Thomson Parameter and adhesion energy for inhibiting the growth of Li dendrite during cycling

$$\Gamma = \frac{2\gamma\Omega \cos\theta}{F} \xrightarrow{\text{Modified Gibbs Thomson}} \Gamma = \frac{2\Delta\gamma^{ad}\Omega \cos\theta}{F}$$

$$\Delta\gamma_{Li-ep-M}^{adhesion} = -(\gamma_{Li} + \gamma_M) + \gamma_{Li-M}^{inter} \text{ (epitaxial interface)}$$

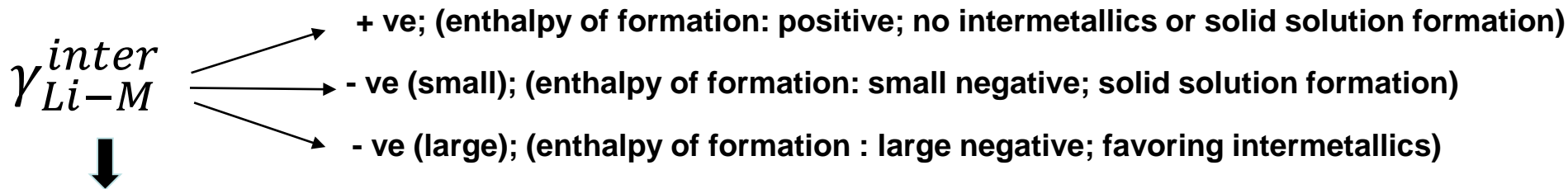
$$\Delta\gamma_{Li-M}^{adhesion} = -0.85(\gamma_{Li} + \gamma_M) + \gamma_{Li-M}^{inter} \text{ (non-epitaxial interface)}$$

High interfacial energy of adhesion:

- **better adhesion between Li metal and the current collector**
- **Higher resistance to perturbation**

Element	Surface energy (mJ/m ²)	Interfacial energy (kJ/mole)
Li	525	
Sn	675	-56
Si	1250	-46
Mg	760	-1
Al	1160	-13
Zn	990	-26
Fe	2475	+94
Mn	1600	+76
Ni	2450	+3
Co	2550	+30
Ti	2100	+130
Cu	1825	+110

Effect of interfacial energy on phase formation



$$\gamma_{Li-M}^{inter} = \left\{ \frac{V_{Li}^{2/3}}{\eta_{ws}^{1/3}} \right\} \left[P ((\Delta\phi^*))^2 + Q (\eta_{ws}^{1/3})^2 \right]$$

V_{Li} = molar volume of Li, $P = 14.2, Q = 113.5$
 $\eta_{ws}^{1/3}$ = mean value of the electron density at the boundary of Wigner-Seitz cell
 $\Delta\phi^*$ = difference between work function of Li and M

Any proposed future work is subject to change based on funding levels

Technical Accomplishments and Progress

Criteria determined from growth kinetics analysis for achieving dendrite free substrates as anodes

- Modified Gibbs Thomson parameter ($\geq 10^{-6}$ V.cm)
- Interfacial energy (kJ/mole)
 - ✓ $\cong 0$ kJ/mole to bypass the formation of intermetallics
 - ✓ Small negative to form structurally isomorphous alloy
- Surface energy ($\gamma \sim$ large negative value e.g. 10^{-2} J/m²)
- Lattice registry ($\theta \leq 30^\circ$)

$G_{cr(het)}$: activation barrier for nucleation
 D_L : Diffusivity
 θ : wetting angle (lattice registry)
 ΔG_V : change of chemical potential
 r_{cr} : critical cluster size
 a : jump distance
 C_a : concentration of critical cluster

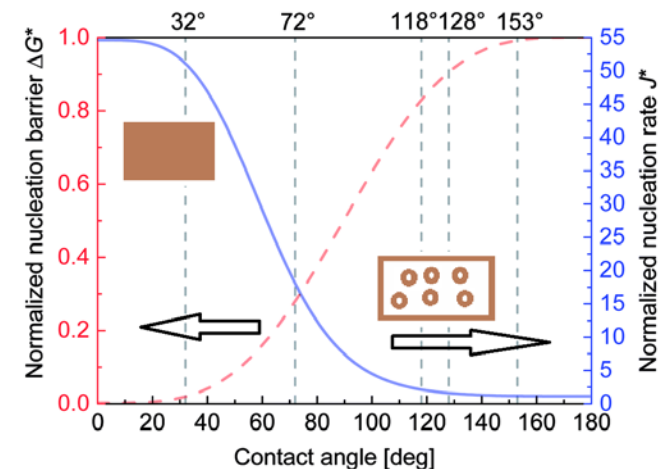
Effect of the above determined conditions on nucleation kinetics

Nucleation barrier:

$$G_{cr(het)} = \left(\frac{16\sigma_{LS}^3 D_L}{3\Delta G_V^2} \right) \left(\frac{2 - 3\cos\theta + \cos^3\theta}{4} \right)$$

Nucleation rate:

$$J_{het} = \left(\frac{D_L}{a^2} \right) \left(\frac{2r_{cr}^2 (1 - \cos\theta)}{a^2} \right) C_a \exp \left[\left(-\frac{G_{cr(hom)}}{kT} \right) f(\theta) \right]$$



Wetting angle/lattice registry ($\theta \leq 30^\circ$)

Low nucleation barrier and high nucleation rate

Low nucleation underpotential; smooth homogeneous surface

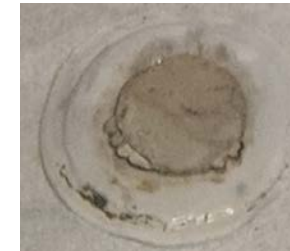
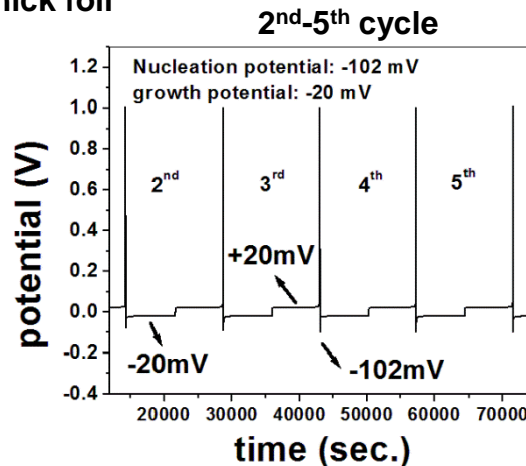
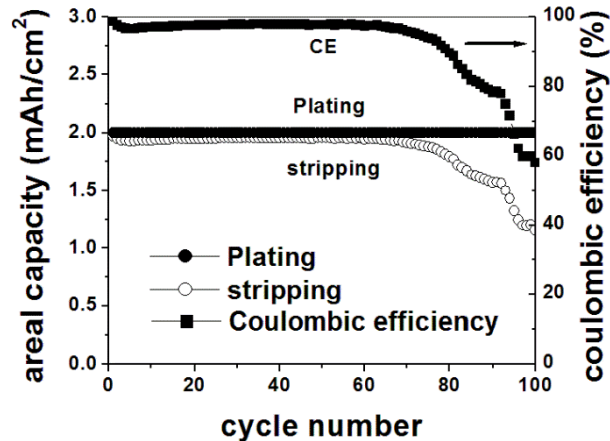
Prevention of dendrites

Any proposed future work is subject to change based on funding levels

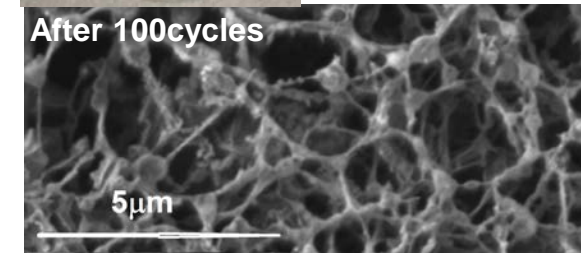
Technical Accomplishments and Progress

Effect of positive interfacial energy, low Gibbs Thomson parameter, Γ and positive adhesion energy on the cycle life of Li metal anode

Charging condition: 1mA/cm² for 2h, charge capacity: 2mAh/cm²
Electrolyte: 1.8M LiTFSI + 0.1M LiNO₃ in DOL:DME (1:1 v/v)
Electrode: 12 mm diameter 0.1 mm thick foil



After 100cycles



After 100cycles

- Poor cycle life after 60 cycles
- Excellent CE at 1st cycle (~99.8%) (non reactive substrate)

- No intermetallic or solid solution formation
- Only plating (-20mV) and stripping (+20mV)
- High nucleation underpotential

- Detachment of plated Li from substrate (100 cycles)
- Non-planar microstructure

Advantages of the substrate: No significant side reaction with electrolyte (Excellent 1st cycle CE)

➤ No intermetallics/solid solution formation

Disadvantages: poor cycle life due to low Gibbs Thomson parameter between Li and substrate

➤ Low interfacial adhesion (inferior resistance to perturbation)

SUMMARY:

✓ Not preferred

✓ Alloy design needed to improve cycle life by altering the modified Gibbs Thomson parameter, and modifying Interfacial adhesion

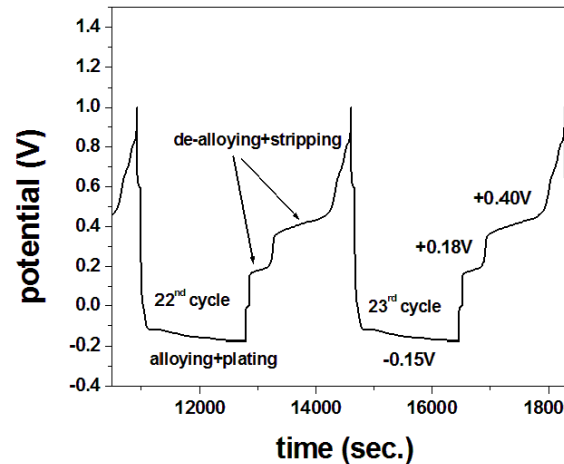
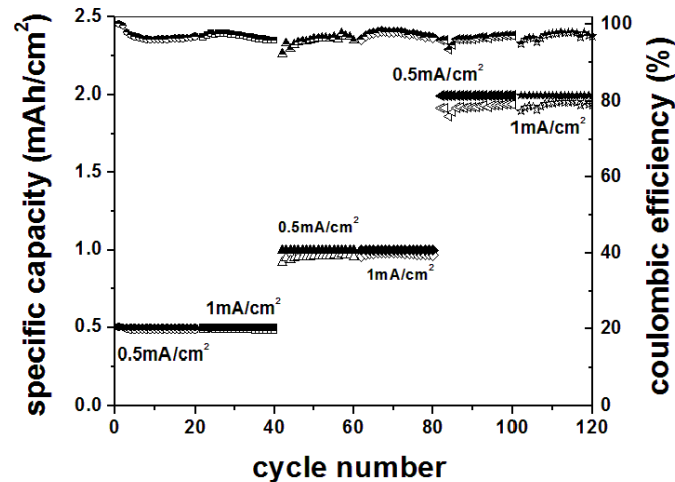
Any proposed future work is subject to change based on funding levels

Technical Accomplishments and Progress

Effect of large negative interfacial Energy (high enthalpy of formation of intermetallics) and high adhesion energy on the cycling stability

Electrode : 12mm diameter 0.1 mm thick foil
Cycled at 0.5mA/cm² and 1mA/cm²

Electrolyte: 1.8M LiTFSI + 0.1M LiNO₃ in DOL:DME (1:1 v/v)



22nd and 23rd cycle;
0.5mAh/cm²

- Improved cycle life
- Exhibit excellent CE: ~96-98%

Zero Nucleation under potential
Growth potential : -150mV; formation of intermetallics
Dealloying potential: +0.18V and +0.4V
Formation of Intermetallics: volume expansion and contraction

Current collector with negative interfacial energy:

Advantage: High interfacial adhesion with Li metal, good wetting, zero nucleation underpotential

Disadvantage: **Formation of Intermetallics**, Change in crystal structure (**pulverization expected during long term cycling**), Dealloying at higher potential ($\geq 0.2-1V$)

SUMMARY

- ✓ Not preferred
- ✓ Need for alloying to control the interfacial energy to inhibit the formation of intermetallics

Technical Accomplishments and Progress

Three Novel Strategies Followed

Control of interfacial energy, Gibbs Thomson Parameter and lattice registry

- ✓ Novel multicomponent alloys (MCA)
- ✓ Structurally isomorphous alloys (SIA)
- ✓ Interface Engineering (IE)

Interfacial energy calculation of MCA, SIA and IE materials of composition: $\text{Li}_x\text{B}_y\text{C}_{1-x-y}$

$$\gamma_{\text{LiBC}}^{\text{int}} = x f_B^{\text{Li}} \gamma_{\text{Li in B}}^{\text{int}} + x f_C^{\text{Li}} \gamma_{\text{Li in C}}^{\text{int}} + y f_C^{\text{B}} \gamma_{\text{B in C}}^{\text{int}}$$

Goals:

- Synthesize theoretically predicted MCA of bcc structure of similar lattice parameter with Li metal and $\gamma_{\text{LiBC}}^{\text{int}} \sim 0$ kJ/mole
- Synthesize SIA of similar lattice registry with Li metal with $\gamma_{\text{LiBC}}^{\text{int}}$ small negative (e.g. -(1-2) kJ/mole)
- Synthesize non Li ion reacting (inert) IE materials coatings on Cu foil with high adhesion energy (2-5 J/m²)

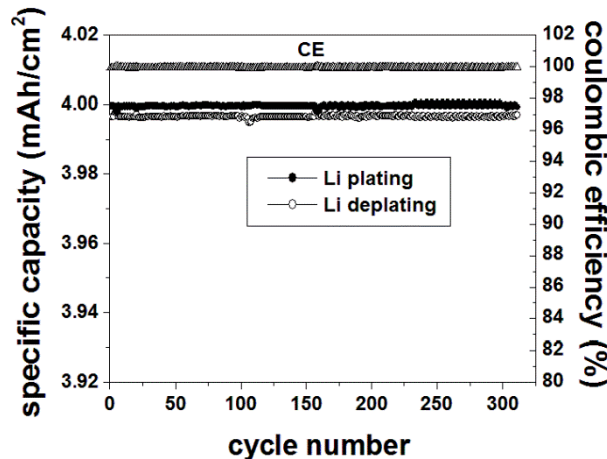
Technical Accomplishments and Progress

Novel Multicomponent Alloy (bcc structure) substrate as an anode

Tested at 4mAh/cm² charge density: 1mA/cm² current density

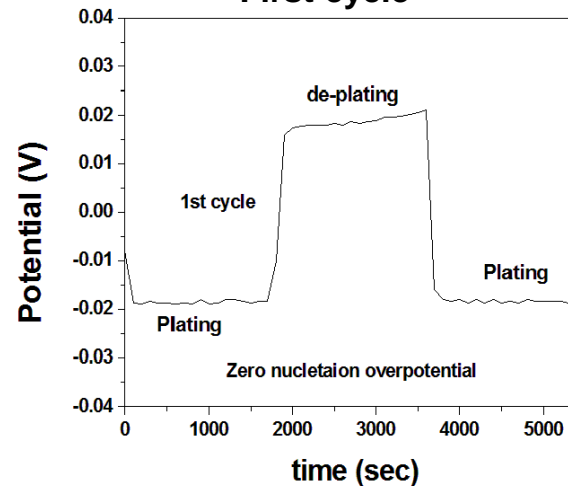
Electrolyte: 1.8M LiTFSI + 0.1M LiNO₃ in DOL:DME (1:1 v/v)

Electrode: 13mm diameter 1mm thick MCA pellet



Excellent CE (~99.9%)
and excellent cycle life

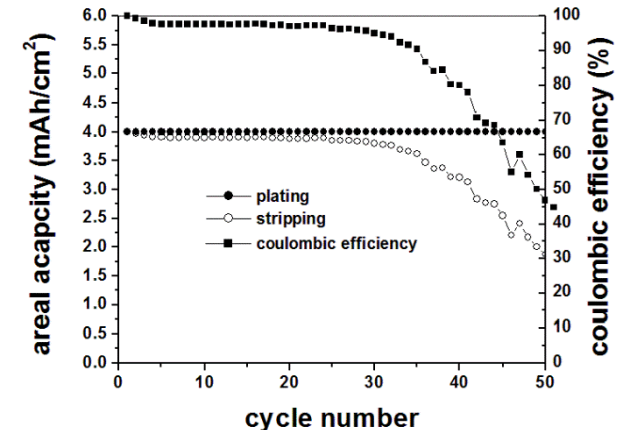
First cycle



Zero nucleation underpotential

Base metal

12mm diameter 0.1 mm thick foil



Poor cycle life of positive
interfacial energy base metal

- Zero nucleation overpotential
- **CE at 1st cycle:** High coulombic efficiency at 1st cycle (~99.9%) even with EC:DEC based carbonate electrolyte
- **CE:** Excellent CE (~99.9%) up to 300 cycles
- **Cyclability:** Excellent cyclability, No significant change in the plating and deplating growth underpotential ($\leq 0.01\%$ increases per cycle) with cycle numbers

Future work: Use of 20-40 μ m Li metal coating on the substrate and full cell testing for Li-S system

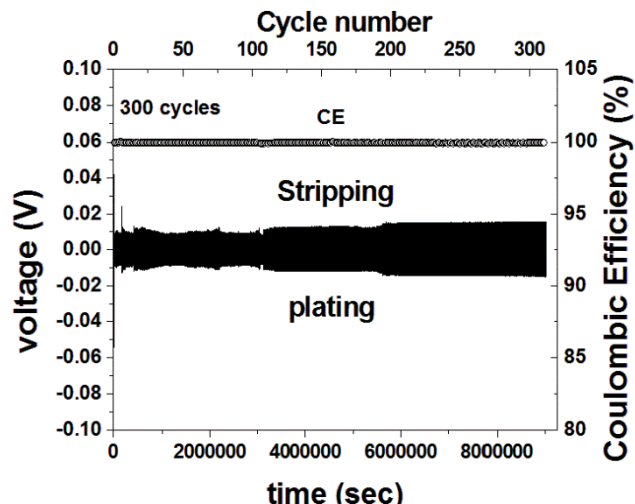
Technical Accomplishments and Progress

Novel Multicomponent Alloy (bcc structure) substrate as anode

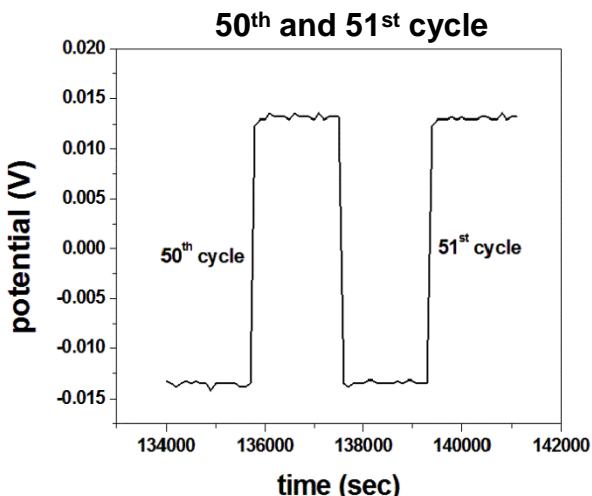
Tested at 4mAh/cm² charge density: 1mA/cm² current density

Electrolyte: 1.8M LiTFSI + 0.1M LiNO₃ in DOL:DME (1:1 v/v)

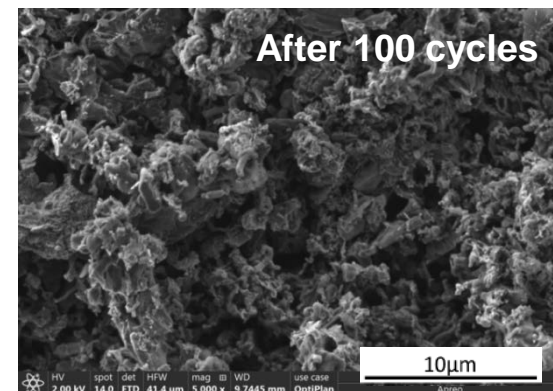
Electrode : 13mm diameter 1mm thick pellet



- Growth potential remains invariant with time



Excellent reversibility with no intermetallics formation



Dendrite free morphology after 100 cycles

- Growth potential remains invariant with time
- **CE:** Excellent CE (~99.9%) up to 300 cycles
- **Cyclability:** Excellent cyclability, No significant change in the plating and deplating growth overpotential ($\leq 0.01\%$ increases per cycle) with cycle numbers
- No cellular structure or dendrite formation

Future work: Use of 20-40μm Li metal coating on the substrate and full cell testing for Li-S system

Any proposed future work is subject to change based on funding levels

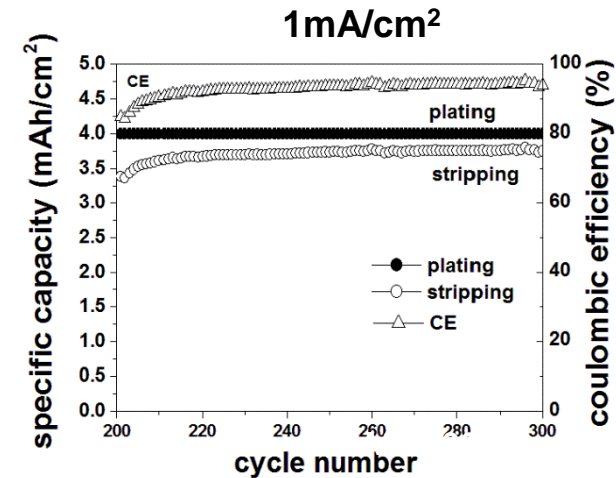
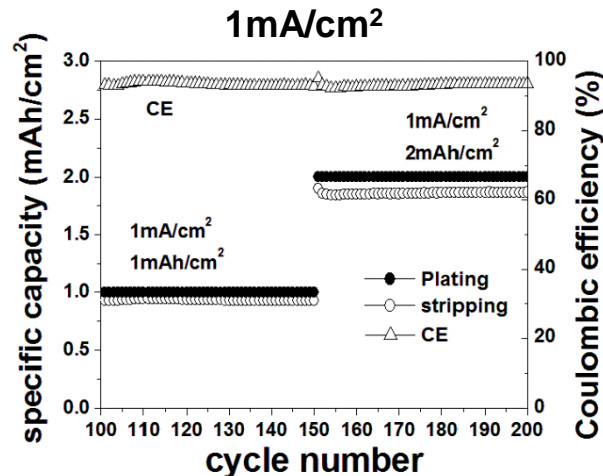
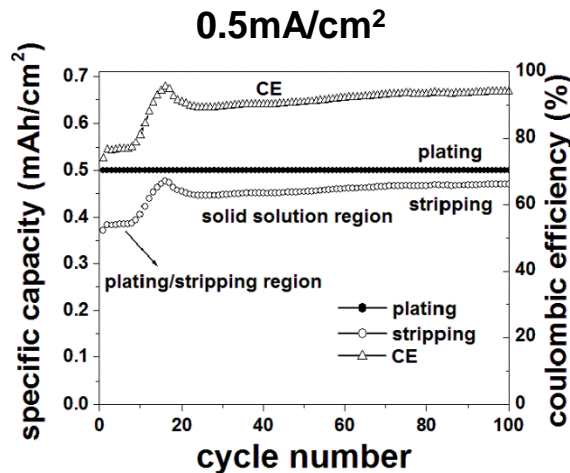
Technical Accomplishments and Progress

Structurally Isomorphous Alloy (SIA)

- Formation of solid solution with Li metal
- Host alloy for Li metal (No significant volume change)
- Exhibit excellent lattice registry and adhesion energy

Electrolyte: 1.8M LiTFSI + 0.1M LiNO₃ in DOL:DME (1:1 v/v)

Electrode : 12 mm diameter 0.1 mm thick foil

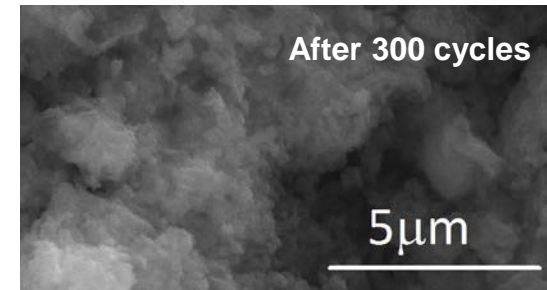


Low coulombic efficiency for first 10 cycles

- Excellent cycle life
- Excellent adhesion of Li metal with SIA alloy
- No cellular or dendritic structure

Need to improve the coulombic efficiency of SIA alloy

- Need to improve the Li ion diffusivity to promote faster reaction kinetics and dealloying reaction



Cell or Dendrite free morphology

Any proposed future work is subject to change based on funding levels

Technical Accomplishments and Progress

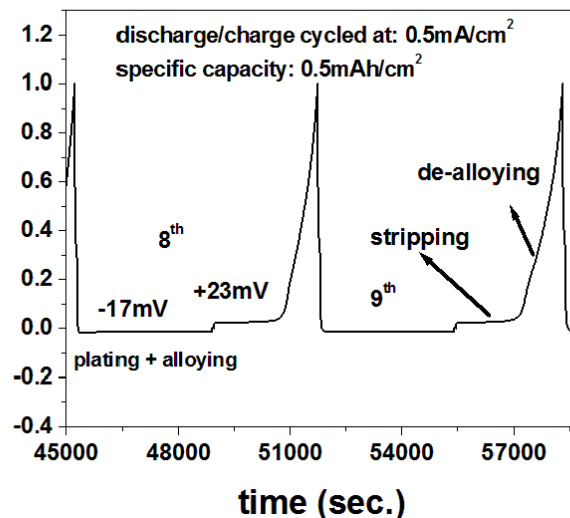
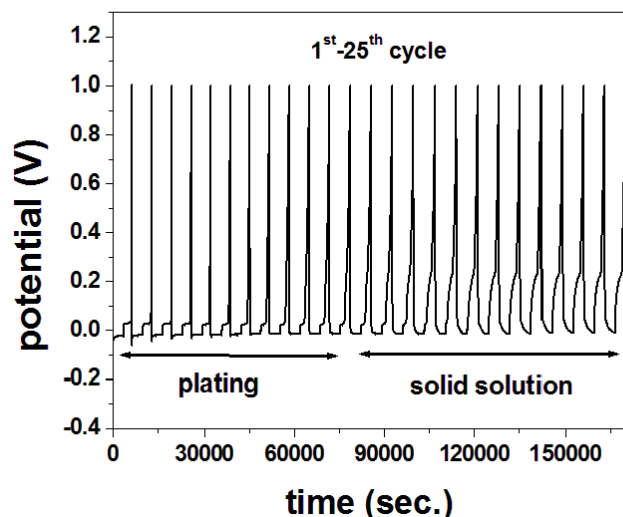
Structurally Isomorphous Alloy

Nucleation, alloying and dealloying behavior

Electrolyte: 1.8M LiTFSI + 0.1M LiNO₃ in DOL:DME (1:1 v/v)

Electrode : 12 mm diameter 0.1 mm thick foil

1-25th cycle; 0.5mAh/cm²



8th and 9th cycle

Alloying and dealloying occurs after 10th cycle

Low Li ion diffusivity with SIA alloy

- Results low coulombic efficiency
- SIA alloy also reactive with electrolyte

Zero nucleation underpotential

Growth potential : -17mV

- Need to improve the Li ion diffusivity and dealloying kinetics

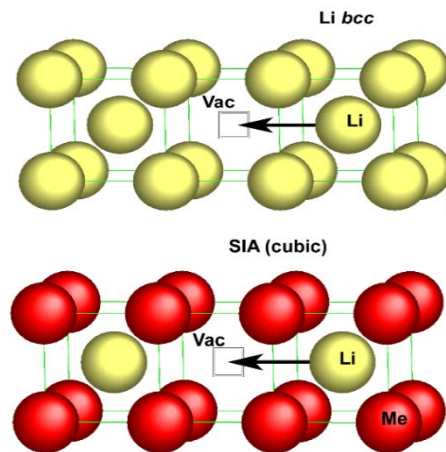
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Technical Accomplishments and Progress

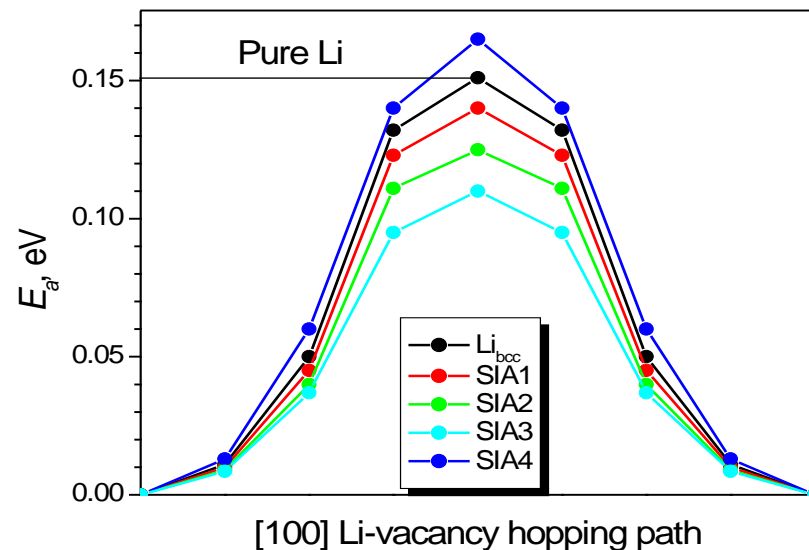
Li-mobility in SIA: an *Ab-initio* study

- ❑ Theoretical study to determine Li mobility in Li-based SIA conducted for several alloying elements using DFT approaches
- ❑ Alloying elements have been identified for improving the Li-ion conductivity and introduce lattice stability during electrochemical cycling

Crystal lattice of modeled SIA



Activation barriers for vacancy hopping



- **Future work: Synthesize doped SIA alloys to improve the reaction kinetics**
- **Coating of 20-40 μm Li metal on SIA alloy for testing in the Li-S battery system**

Any proposed future work is subject to change based on funding levels

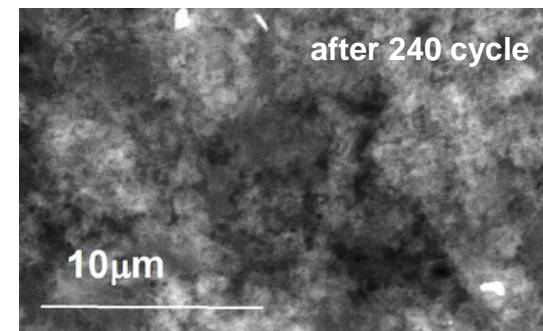
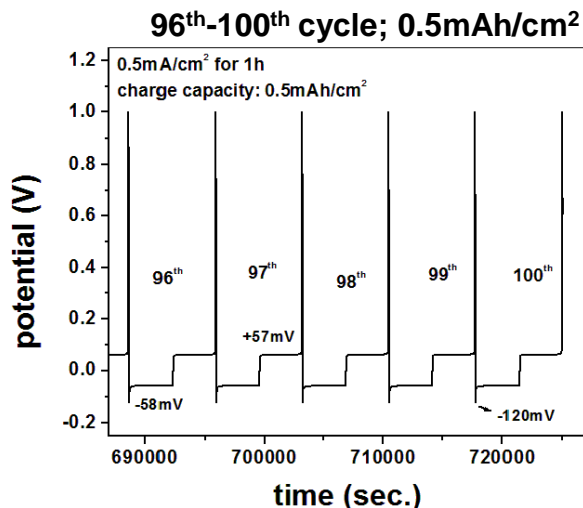
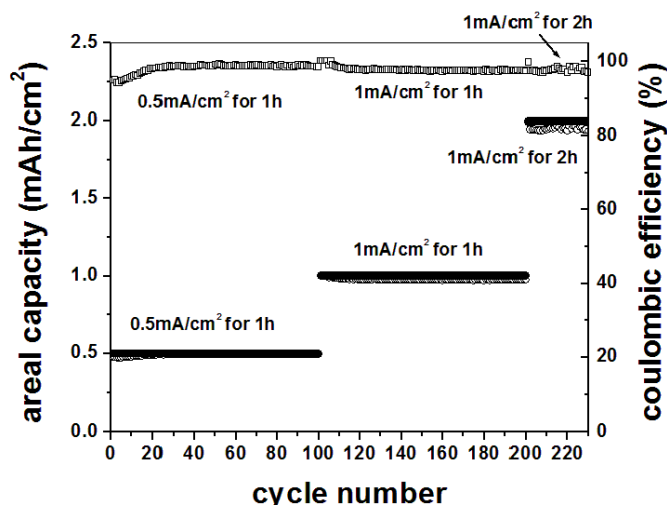
Technical Accomplishments and Progress

Interfacial Engineering (IE) of traditional Cu substrate

Porous coating of high adhesion energy non Li ion reacting (inert) IE materials on copper foil

Electrode : 100 μm thick coating (90wt% IE:10wt% PVDF) on copper foil (12mm diameter electrode)

Electrolyte: 1.8M LiTFSI + 0.1M LiNO₃ in DOL:DME (1:1 v/v)



Cell or dendrite free morphology after 240 cycle

- Significant improvement in cycle life in comparison to bare Cu
- No significant change in growth potential
- No intermetallics or solid solution formation observed
- Higher growth potential (-58mV) with respect to pure Cu current collector (~24mV) due to decrease in electronic conductivity (increase in charge transfer resistance)

- Future work: Improve electronic conductivity of IE layers
- Coating of 20-40 μm Li metal on the substrate for testing in the Li-S battery system

Responses to Previous Year Reviewer's Comments

The project was reviewed last year. However, no comments were received.

Collaboration and Coordination with Other Institutions

- **Dr. D. Krishnan Achary (University of Pittsburgh):** Solid-state nuclear magnetic resonance (MAS-NMR) characterization to study the failure mechanisms
- **Malvern Panalytical:** Materials and phase evolution characterization using in-situ XRD
- **Kurt J. Lesker Co. (KJL):** Thin film deposition and vacuum techniques
- **Complete Solutions:** Potential licensing partner
- **Nanomaterials for Energy Conversion Storage Technology (NECST) Laboratory– Energy Innovation Center, Pittsburgh:** Development of modified coin cell testing and carbon nanoarchitectures, development of pouch cell testing

Remaining Challenges and Barriers

➤ Challenges

- Improve the low coulombic efficiency (≤ 99.0) of SIA alloys by enhancing the diffusivity of Li ion with incorporation of suitable dopants in SIA alloys
- Minimize/eliminate the side reaction of SIA alloy with electrolyte by interface engineering to minimize the 1st cycle irreversible loss
- Enable manufacturing using 20-40 μm Li metal coating on the multicomponent alloy (MCA) substrate, SIA alloy substrate and non Li-ion reacting (inert) coated substrate for testing in full cell Li-S battery system

➤ Barriers

- Enable infrastructure to streamline scale up related variability of multicomponent alloys (MCA), SIA alloys and coated electrodes
- Achieving reproducible performance due to change in morphology and microstructure during rolling of the developed substrate to enable fabrication of foils of desired thickness

Proposed Future Work

Milestones	Type	Description
Effect of high current density (2mA/cm²-4mA/cm²) on the cyclability of multicomponent alloys (MCA), SIA alloys and coated electrodes	Technical	High capacity ~4mAh/cm ² , current density: 1-4 mA/cm ² ≥300 cycles, growth overpotential ≤0.01% per cycle, CE: ~99.95%
Development of 20μm thick Li metal coated substrates	Technical	High capacity ~4mAh/cm ² , current density: 1-4 mA/cm ² ≥300 cycles
Full cell studies of Li metal coated developed substrates with Sulfur cathode	Technical	High capacity ~4mAh/cm ² , ≥300 cycles, CE: ~99.95%
Determine and analyze the cost of the electrodes, electrolytes, separators, binders, and related processes	Technical	Cost target: \$75/kWh from current \$200/kWh or 75% reduction in cost to the end-user
Pouch-type Li-S full cell assembly with optimum thickness of S electrode and Li metal coated developed anodes	Technical	Target: (≥350Wh/Kg, ≥750Wh/l and 10 mAh full cell configuration)

Summary

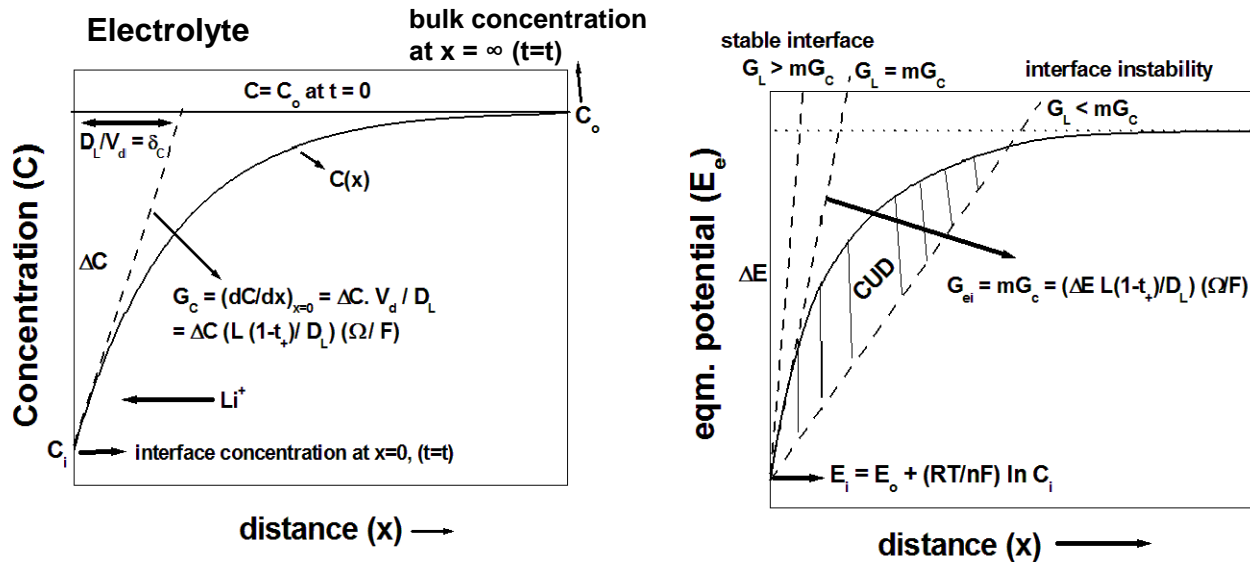
- Detailed study of mass and charge transfer kinetics as well as perturbation and dendrite kinetic conducted to understand the fundamental mechanisms of dendrite formation, and determine the operating conditions (e.g. current density), current collector properties (e.g. Gibbs Thomson parameter) and electrolyte properties (e.g. diffusivity constant) for controlling the Li metal/electrolyte planar interface stability
- Develop high Gibbs Thomson parameter and adhesion energy of multicomponent alloys (MCA), structurally isomorphous alloys (SIA) and non Li ion reactive (inert) IE materials as a promising current collector for Li metal batteries
- Zero nucleation underpotential of multicomponent alloys (MCA) demonstrate dendrite-free structures indicating promise of these novel materials as lithium metal battery (LMB) anodes
- Use of structurally isomorphous alloys (SIA) allows for zero nucleation underpotential and inhibits non-planar growth at the interface (favoring dendrite-free structures) reflected in the improved cycling stability
- Surface modification of traditional Cu electrode has been implemented using IE materials to alter the nucleation and growth phenomena, thus inhibiting the development of cellular and dendritic growth of Li metal

Technical Backup Slides

Technical Accomplishments and Progress

Basic understanding on how battery cycling conditions, electrolyte properties and the current collector properties influence the microstructure

Mass and Charge transfer Kinetics: **Effect of Potential gradient and Concentration gradient**



$G_L > m G_c$ interface stability; $G_L < m G_c$ interface instability

D_L : Li ion diffusivity constant (cm²/sec)
 L : current density (A/cm²)
 ΔE : $RT/F (\ln C_o/C_i)$ (V)
 t_+ : transference number
 F : faraday constant (96500 Coulomb/mole)
 Ω : molar volume of Li metal (cm³/mole)
 G_c : concentration gradient at the interface
 $m G_c$: potential gradient at the interface
 G_L : potential gradient at electrolyte
CUD: compositional underpotential deposition

Morphological stability \rightarrow

$$\frac{G_L}{L} > \Delta E \left(\frac{(1 - t_+)}{D_L} \right) \left(\frac{\Omega}{F} \right)$$

Any proposed future work is subject to change based on funding levels

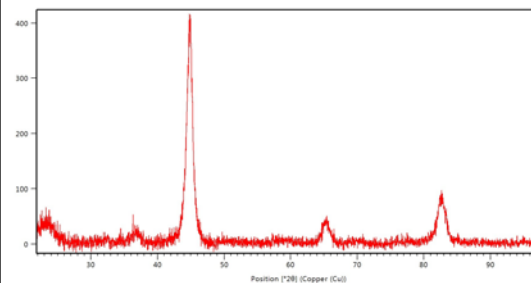
Technical Accomplishments and Progress

Multicomponent alloy (MCA) of bcc structure

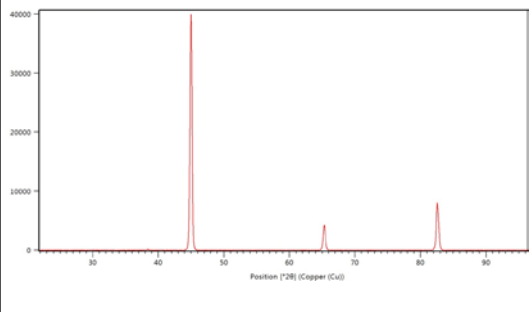
Electrolyte: 1.8M LiTFSI + 0.1M LiNO₃ in DOL:DME (1:1 v/v)

Electrode: 100 μm thick coating (90wt% MCA: 10wt% PVDF) on copper foil (12mm diameter electrode)

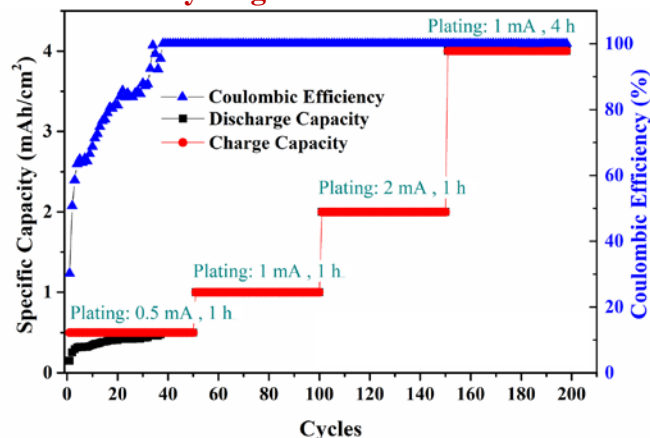
XRD Pattern of MCA



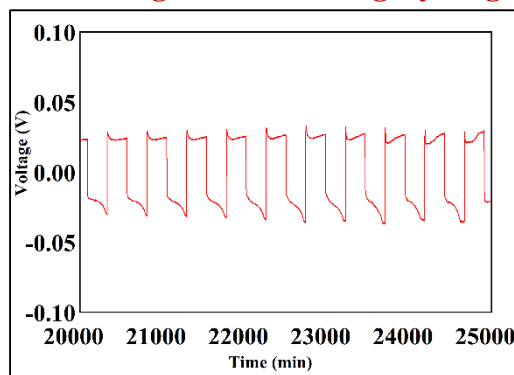
XRD Pattern of BCC structure



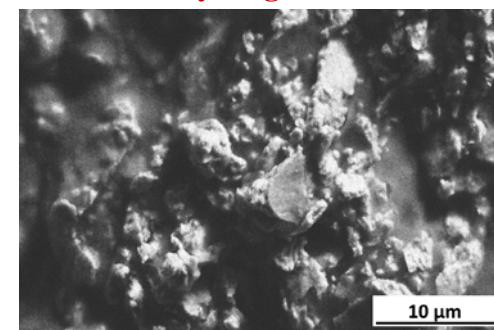
Cycling Performance



Stable Voltage Profile During Cycling

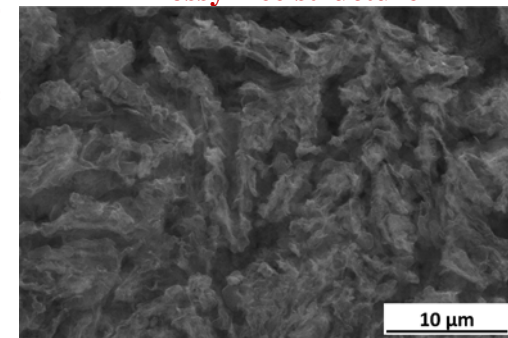


Pre-Cycling SEM



Post-Cycling SEM, after 200 Cycles

▪ Mossy free structure



SEM Characterization

- MCA modify Li plating phenomenon favoring uniform homogeneous nucleation and growth regime due to similar crystallographic morphology as Lithium
- Stable cycling observed up to 200 cycles with stable voltage profile and absence of dendritic lithium

Any proposed future work is subject to change based on funding levels

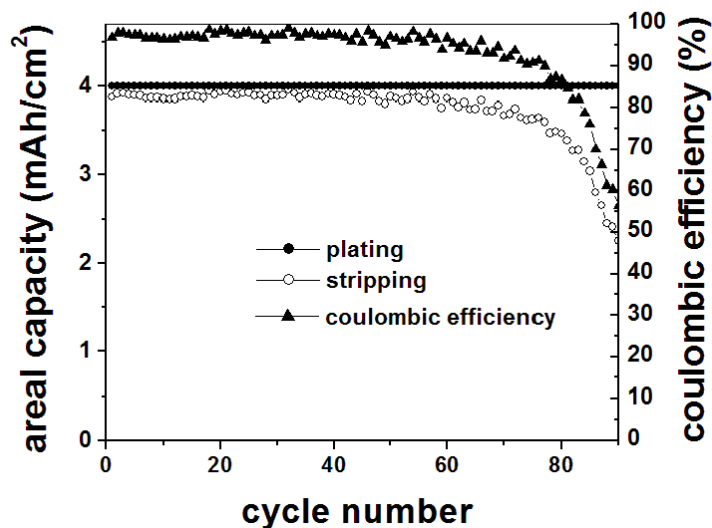
Technical Accomplishments and Progress

Multicomponent alloy (MCA) with poor lattice registry and positive adhesion energy

Electrolyte: 1.8M LiTFSI + 0.1M LiNO₃ in DOL:DME (1:1 v/v)

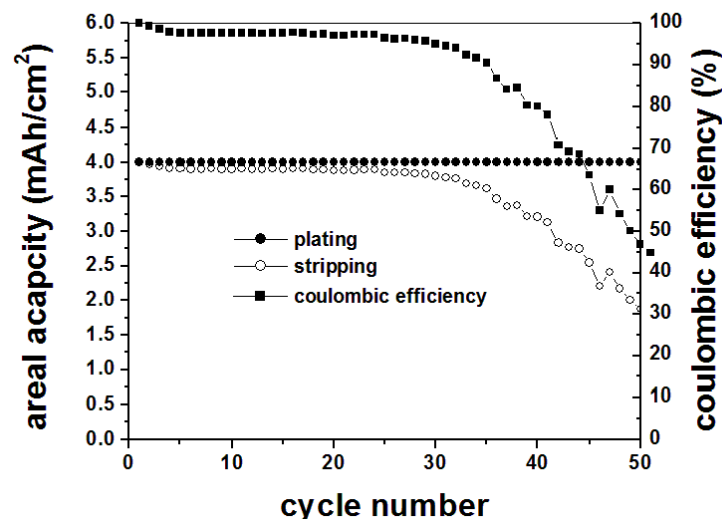
Multicomponent alloy

Electrode : 13mm diameter 1 mm thick pellet; 95wt% MCA:5wt% PVDF)



Base metal

Electrode : 12mm diameter 0.1 mm foil



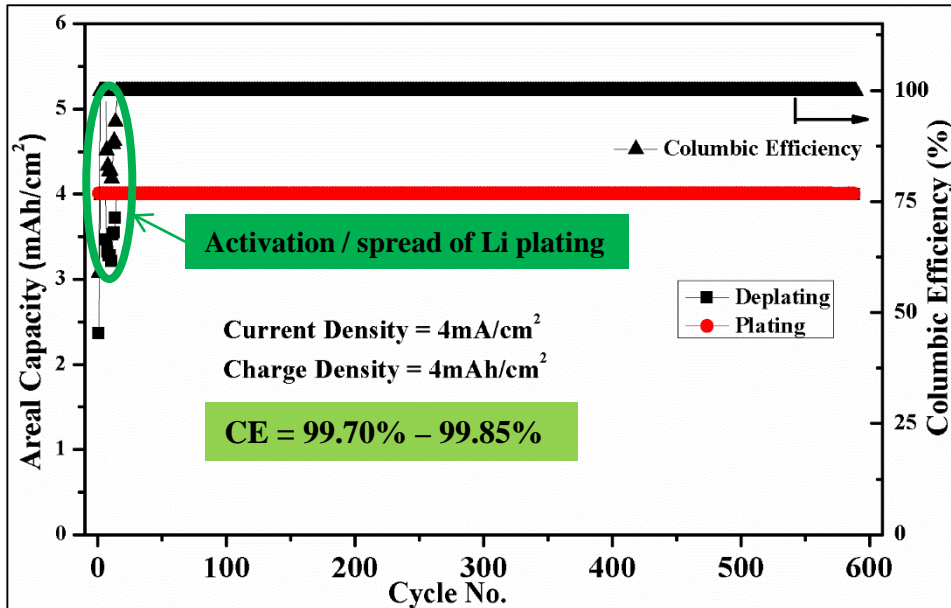
Need for proper alloy design to achieve negative adhesion energy and perfect lattice registry

Any proposed future work is subject to change based on funding levels

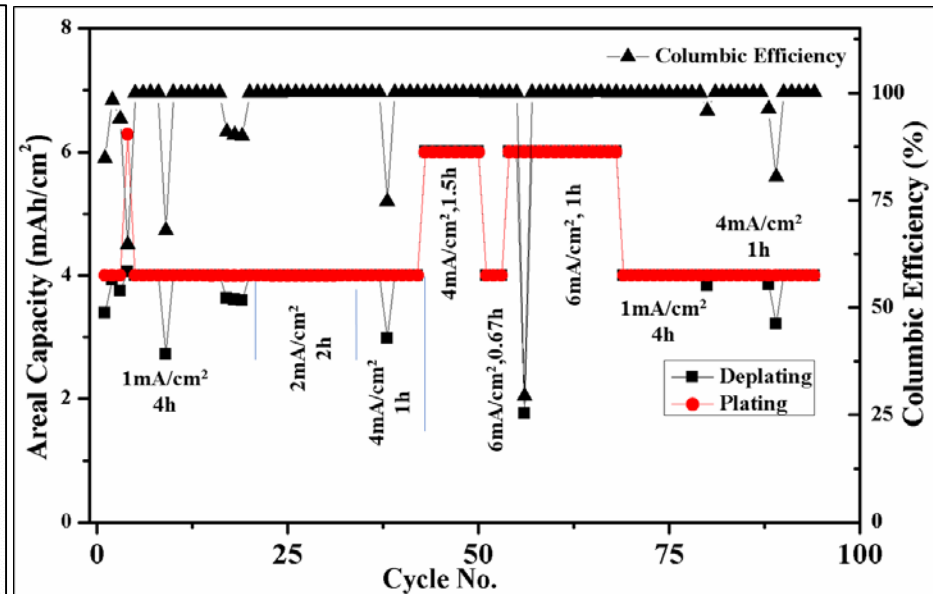
Technical Accomplishments and Progress

High adhesion energy Carbon nano-architectures engineered on Cu foil

Long Term Testing



Rate and Charge capability



➤ Counter/Reference – Lithium foil , [Insulated Coincell](#)

➤ Electrolyte = 1M LiPF₆ EC:DEC:FEC

➤ Active Material loading = 2 – 3 mg/cm²

Formation cycle = 3 cycles @ 25mA/g, 0.01V – 1.2V

Specific Capacity ~ 1500-2500mAh/g

- Carbon based architecture shows a high columbic efficiency of ~99.70 – 99.85% for 600 cycles
- The rate capability study shows stable plating efficiency for areal current rates ranging from 1mA/cm² to 6mA/cm² giving a charge density varying from 4mAh/cm² to 6mAh/cm²
- The gravimetric specific capacity of the carbon based systems for plating is ~2000-2500mAh/g based on the areal charge density of plating

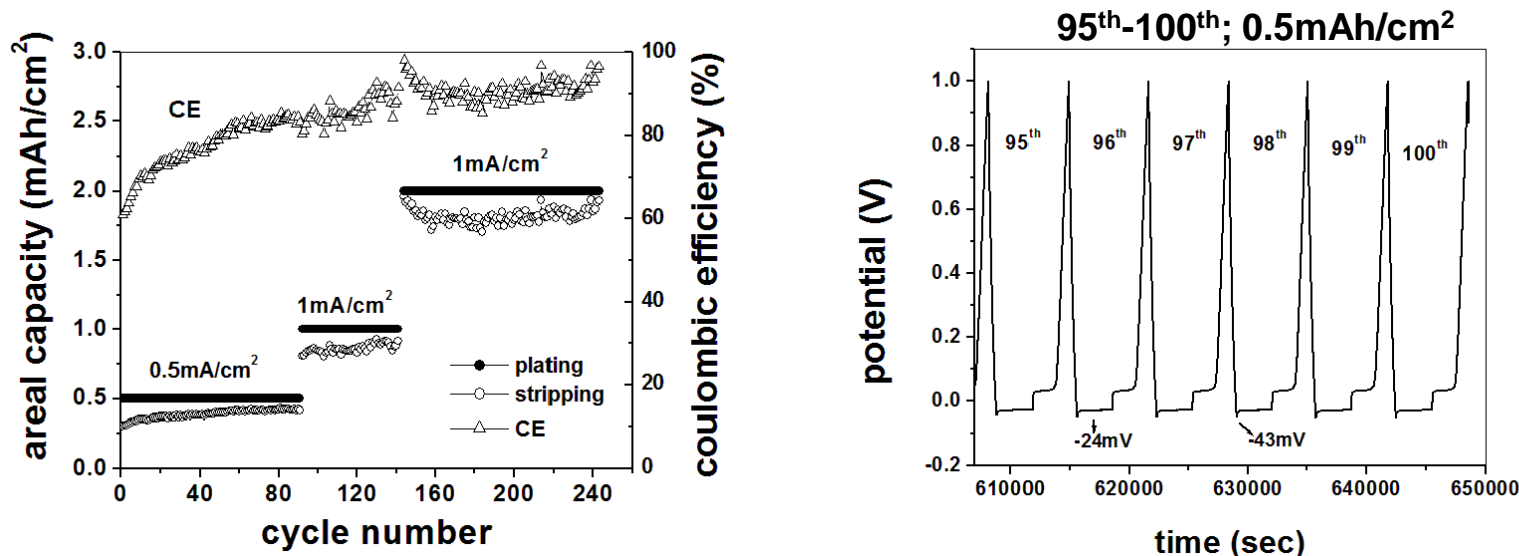
Any proposed future work is subject to change based on funding levels

Technical Accomplishments and Progress

Low adhesion energy non Li ion reacting (inert) IE materials coated on copper foil

Electrode : 100 μm thick IE materials coating (90wt% IE:10wt% PVDF) on copper foil (12mm diameter electrode)

Electrolyte: 1.8M LiTFSI + 0.1M LiNO₃ in DOL:DME (1:1 v/v)



- Significant improvement in cycle life in comparison to bare Cu
- Low coulombic efficiency (~60-97%) due to reduced electronic conductivity (increase in charge transfer resistance)
- No intermetallics or solid solution formation
- Low growth potential (-24mV) and nucleation potential (-43mV) in comparison to bare Cu (nucleation potential ~120mV)

Future work

- ✓ Improve electronic conductivity of IE layers
- ✓ Decrease the coating thickness to ~nm level

Any proposed future work is subject to change based on funding levels