APPLIED MATERIALS®

Modular Process Equipment for Low Cost Manufacturing of High Capacity Prismatic Li-Ion Cell Alloy Anodes

2012 DOE Vehicle Technologies Program Annual Merit Review

Project ID#: ES128

Principal Investigator: Sergey D. Lopatin

Project Manager: Ajey M. Joshi

Energy & Environmental Solutions

Alternative Energy Products

May 14-18, 2012

Overview

Timeline

Project Start	Oct. 1, 2011
Project End	Sep. 30, 2014
Percent Complete	~15%

Barriers Addressed

- ***Cost of manufacturing***
- ***Cycling lifetime of high capacity materials***
- ***Prismatic cell format***

Budget

Total Project Funding

DOE Share: 51% ($4.90M)

Applied Materials: 49% ($4.63M)

FY11 Funding Received: $20K

FY12 Funding Expected*: $2.0M

***DOE Share**

Partners

- **J. Nanda, Oak Ridge National Laboratory**
- **G. Liu, Lawrence Berkeley National Laboratory**
- **M. Yakovleva, FMC**
- **V. Vu, A123 Systems**
- **K. Adjemian, Nissan-TCNA**

Summary of the Project Objectives

Low Cost Manufacturing of High Capacity Prismatic Li-Ion Cell Alloy Anodes

- **A. PROJECT OBJECTIVES**

The objective of this project is to research, develop, and demonstrate novel high capacity Li-ion battery cell anodes that are capable of achieving an energy density of at least 500 Watthours per liter (Wh/l) and a power density of at least 500 Watts per liter (W/l) while maintaining comparable performance standards in terms of cycle life (300-1000 cycles at 80% depth of discharge), calendar life (5-10 years), and durable cell construction and design capable of being affordably mass produced.

- **B. PROJECT SCOPE**

The project includes research, development, test, and demonstration of an advanced High Volume Manufacturing (HVM) prototype module for fabricating high capacity Li-ion anodes in a continuous roll-to-roll configuration at low cost. The HVM prototype module will manufacture a new class of Li battery anodes with a high capacity based on an innovative micro-cell porous 3D Cu – Li alloy structure. The project will focus on demonstrating the innovative high rate deposition technique suitable for the micro-cell porous 3D Cu – Li alloy architecture.

Project Objectives: Modular Process Equipment

Phase 1: Develop and verify the process models and line design for Micro-cell 3D Cu - Li alloy architecture of controlled thickness. Developing a 3D roll-to-roll manufacturing methodology for building 3D structured current collector. Optimizing the process and materials required for a high loading anode.

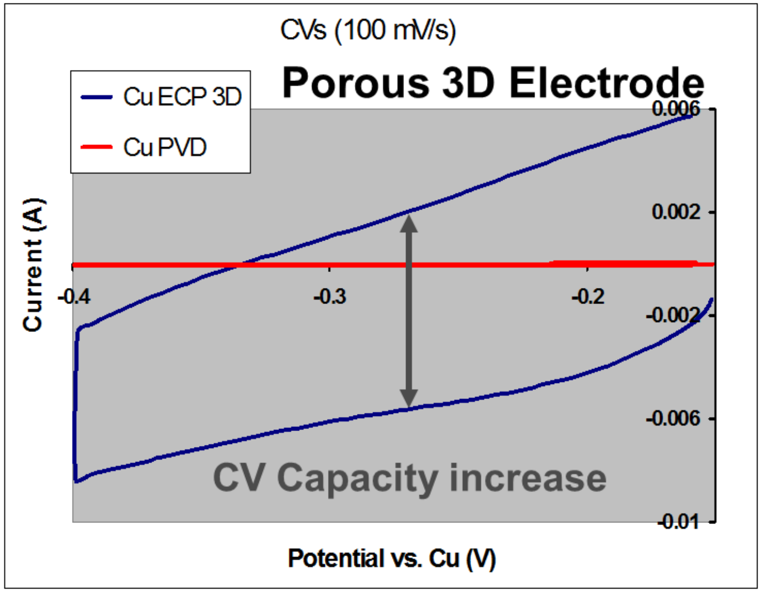
Phase 2: Develop the manufacturing equipment prototypes necessary to demonstrate the scalability of the HVM line by incorporating water based process, copper foil electrodeposition, and accelerated drying.

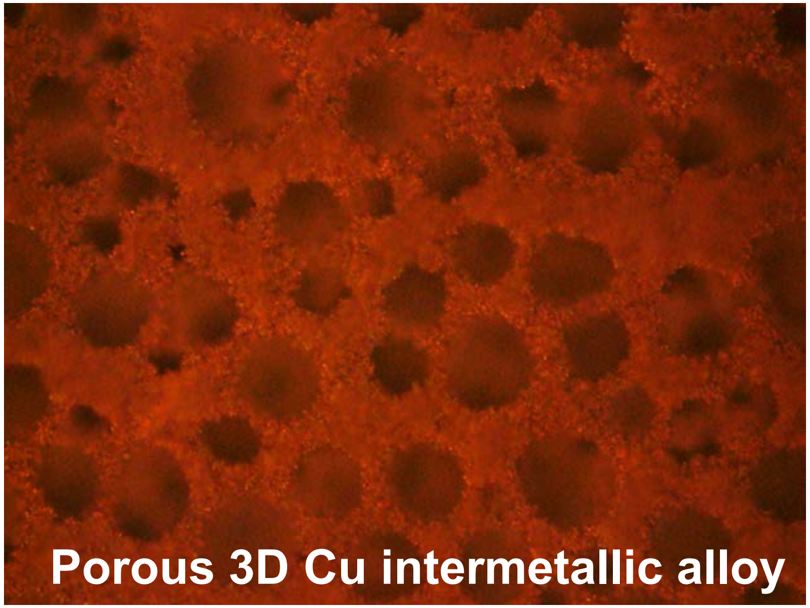
Phase 3: Optimize the throughput though the use of previously developed anode-active electroplating, material sprays processing method while incorporating scaled and optimized separator coating method into the modular in-line system.

Phase 4: Demonstrate the integrated equipment capabilities of the electrode structure to include the integrated protection separator. The improved electrodes will be assembled into prismatic battery cells and will be tested to demonstrate the feasibility of producing Li-ion battery Anodes.

3D Electrode Concept

- Nano-structured architecture
- Porous Cu plating with dynamic H_2 template





Advantages of Expanded Area Electrode

- Increased capacity as measured by Cyclic Voltametry (CV)
- Fast charge using high conductivity nanomaterial
- Large energy and power densities

3D Cu Anode Development Roadmap

Capacity, mAh/g

1000

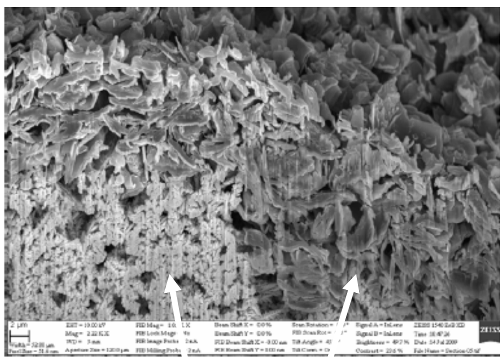
750

500

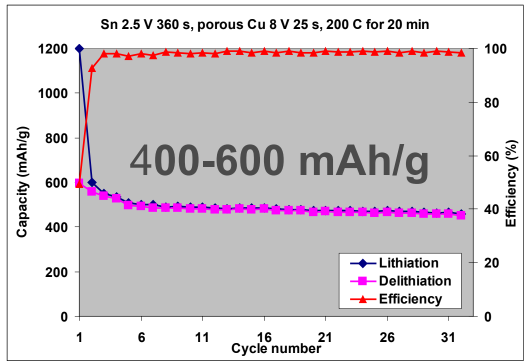
250

Goal: to Develop Next Generation 3D Anode

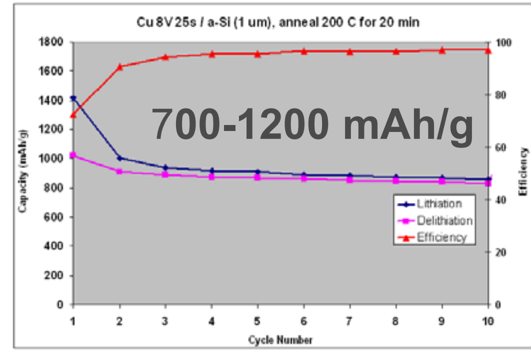
- Capacity
- Current loading
- Cycling lifetime



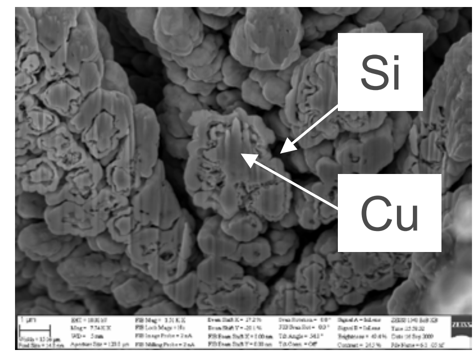
3D Cu + Graphite



3D CuSnFe



3D CuSnFe + Si



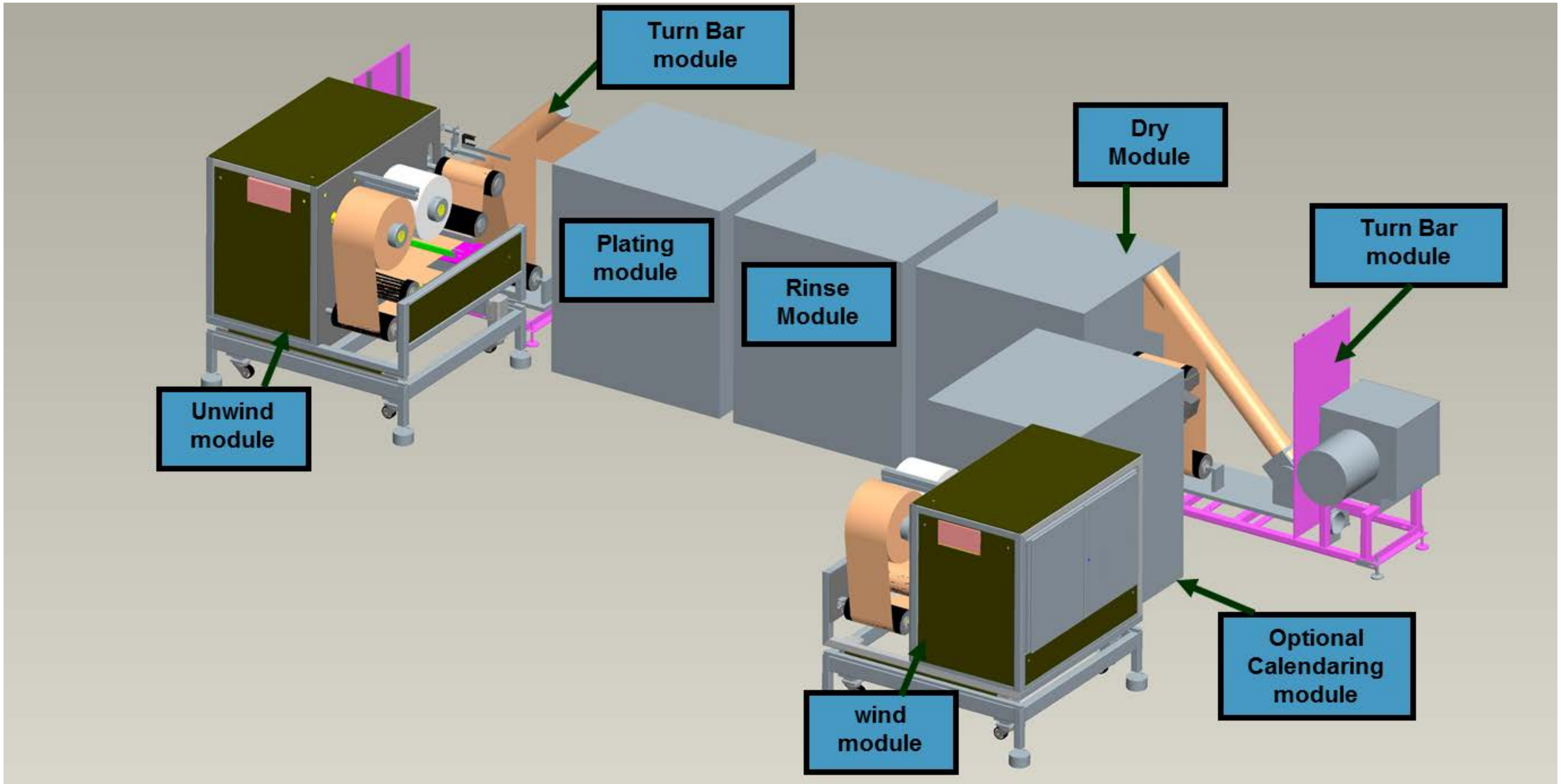
3D electrode concept

← Current Technology

Reduced Anode Cost ($/m²) and ($/Wh) at Higher Performance

Collaboration: A123(cell development), FMC (pre-lithiation), LBNL(conductive binder) Nissan-TCNA (testing), ORNL (characterization)

Schematic Design of the Modular Equipment for 3D-structure Formation on Cu Foil



Plan & Milestones

Task 1.0: Project Management and Planning: achieve the project objectives, covering the entire Project Period.

- Task 1: Program Management.
- Task 1.1: Periodic update on progress, milestones, Go/No-Go decisions, program variances, if any and plans.
- Milestone M1.1 - Deliver PMP with 60 days of program launch – **Complete.**
- Milestone M1.2 - Quarterly project update reports – **PQ1 Complete** (Continuing task)**.**

Task 2.0: Baseline Characterization: performance and cost of the baseline anode technology.

- Task 2: Develop Initial Process Module and Line Design, Simulation and Modeling.
- 2.1: Concept design of initial modular equipment to allow multiple electrodeposition and spray processes and thus alloy anode coating – **In progress, update in this report.**
- 2.2: Cell modeling with alloy anodes – **In progress, update in this report.**

Task 3.0: Technology Design: define the system overall anode and anode manufacturing line design.

- Task 3: Develop 3D Current Collector.
- 3.1: Demonstrate prototype method anode coating module with in-line electrodeposition for thin Cu foil formation with 3D Cu current collector - **In progress, update in this report.**
- 3.2: Develop water soluble process for Graphite coating and demonstrate high rate performance - **In progress, update in this report.**

Task 4.0: Technology Development: design, develop, optimize and improve anode and anode manufacturing line design characteristics; use prototype, mock-ups, production, or specifically fabricated technology to obtain or validate engineering data on the performance of the system.

- Task 4: Develop High Capacity Alloy Anode.
- 4.1: Develop high capacity, high current loading, Si /CuSnFe alloy anode electrode with 3D current collector architecture - **In progress, update in this report.**

Technical Summary

Baseline Characterization:

- A cell level design model has been developed for two chemistry combinations,
  - baseline cell having $Li_{1-x}(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ (NMC333) positive electrode with 3D-Cu Graphite negative electrode, and
  - interim cell having NMC positive electrode with 3D-CuSn negative electrode.

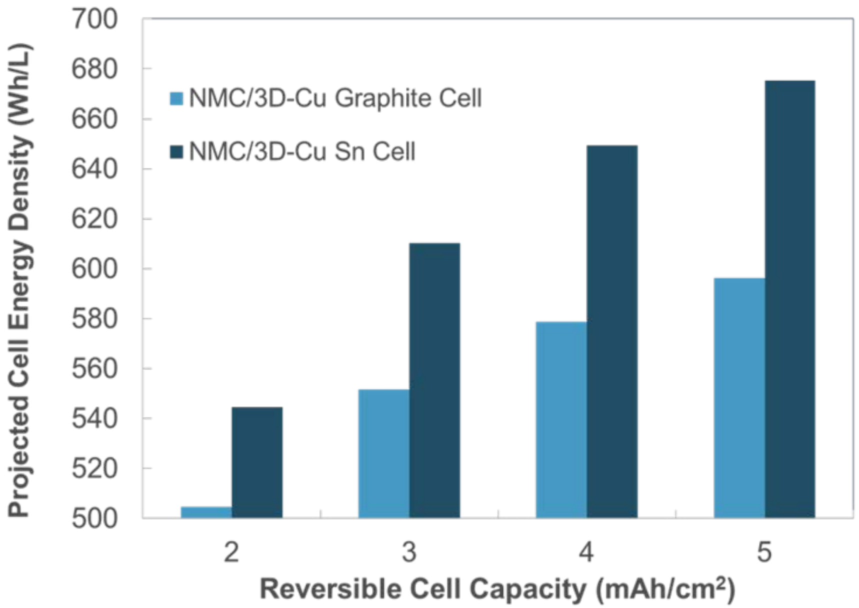
Technology Design:

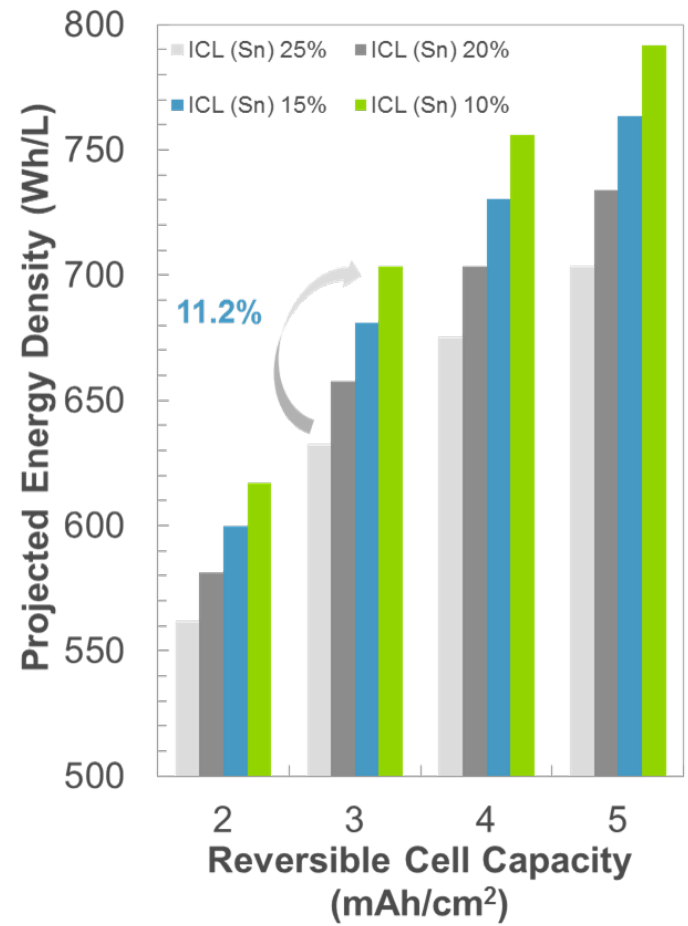
- Experimental development focused on concept design of initial electrodeposition module which allows for 3D-porous structure formation in a single prototype tool for both 3D-Cu collector and 3D-CuSn alloy anode coating.
  - Baseline processes have been developed for (a) 3D-Cu current collector and (b) for Graphite coating using a water soluble process.
  - Scanning Electron Microscopy (SEM) analysis of 3D-Cu Graphite structures shows pore fill and crack-free coating. Preliminary testing rate performance in half-cell assembly vs Li demonstrated capacity retention advantages at 1C, 2C, and 3C.

Technology Development:

- For the high capacity, we have started CuSnFe electrodeposition process development and obtained nano-structure alloy for high loading NMC / CuSnFe cell testing.

Modeling Results: Cell Level Design for Baseline and Interim Cells



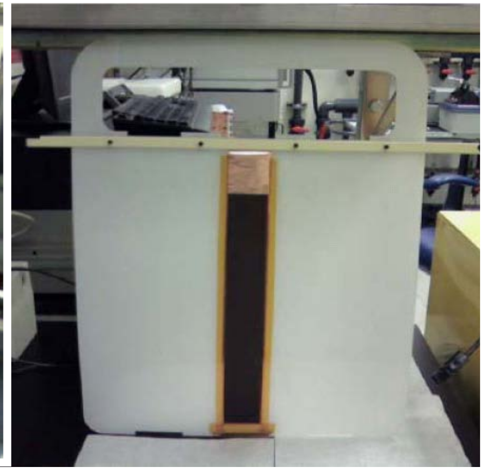


Project Target >500 Wh/L

Energy Density of up to 750 Wh/L is achievable by reducing Irreversible Capacity Loss (ICL)

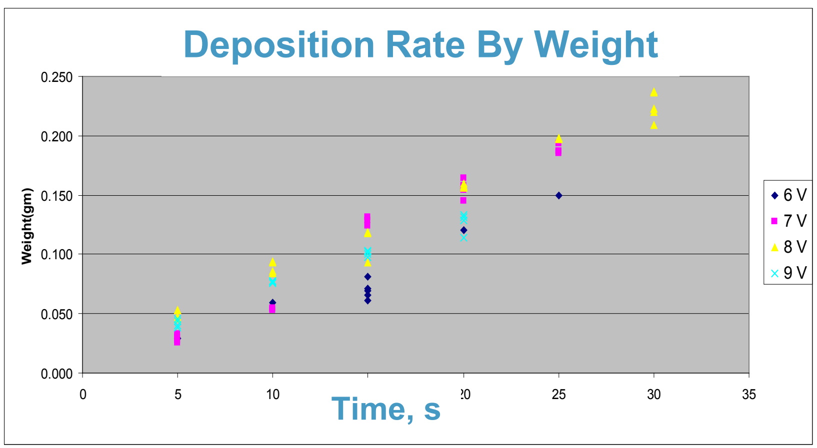
Plating 3D Cu on Large Surface Area

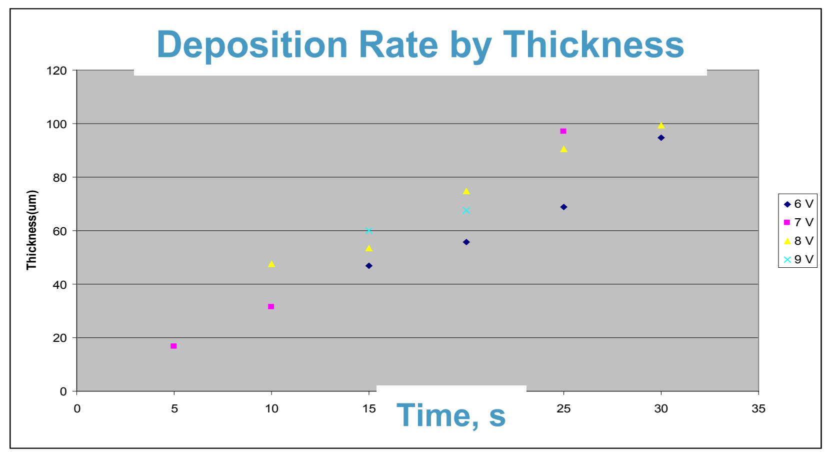
Lab prototype tool



Foil Area 6cm x 30cm

Foil Area 15cm x 20cm





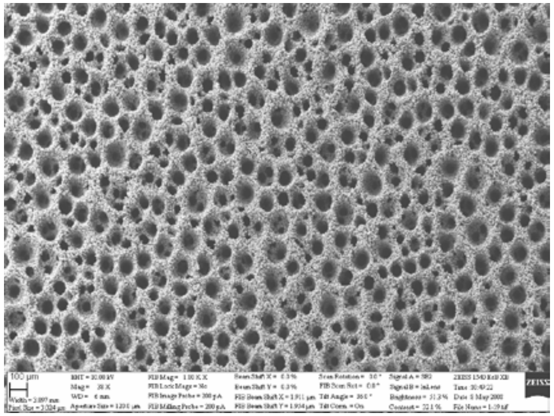
Deposition Rate Controllable by Both Weight and Thickness

Deposition Rate of 3 μm/s is Many Times Faster than Conventional Approach

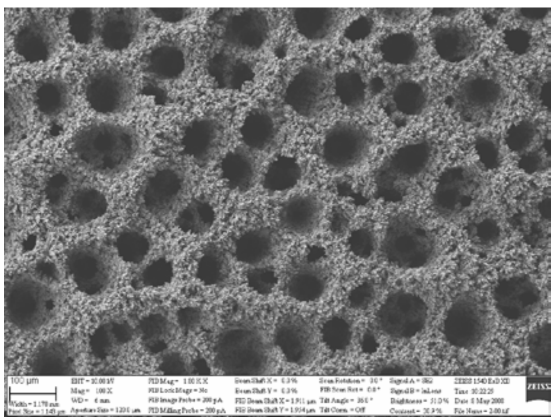
3D Cu Plated on Cu Foil: Structural Analysis

Top View

100 µm

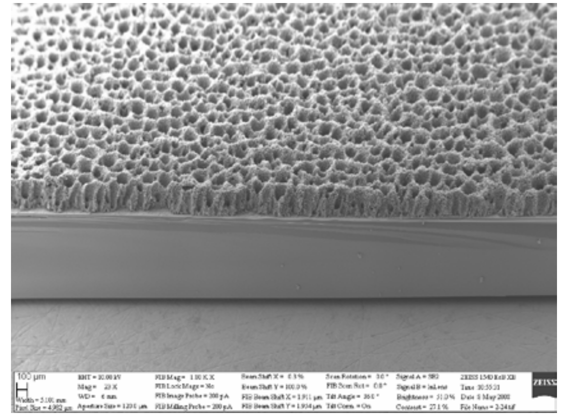


100 µm



Cross-Sectional View

100 µm



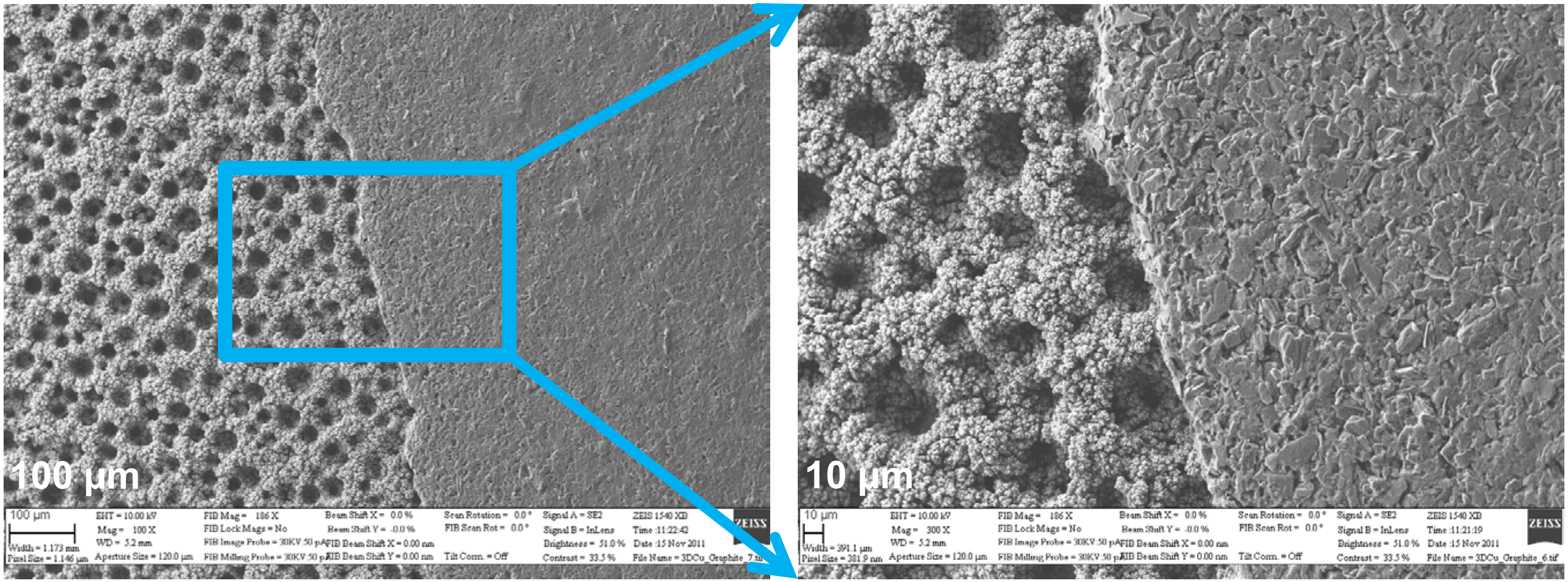
20 µm

3D Cu Porous Structure Showing Micro, Meso and Nano Porosity

Water Based Process for Graphite Coating on 3D Cu

SEM lower magnification — SEM higher magnification

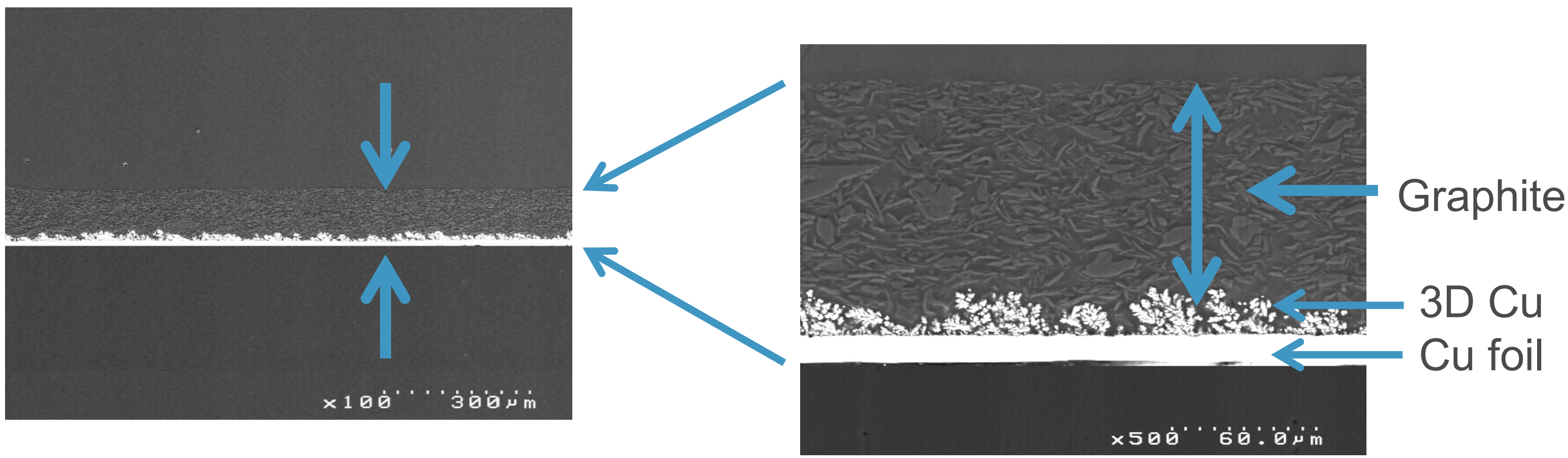
3D Cu — Graphite — 3D Cu — Graphite

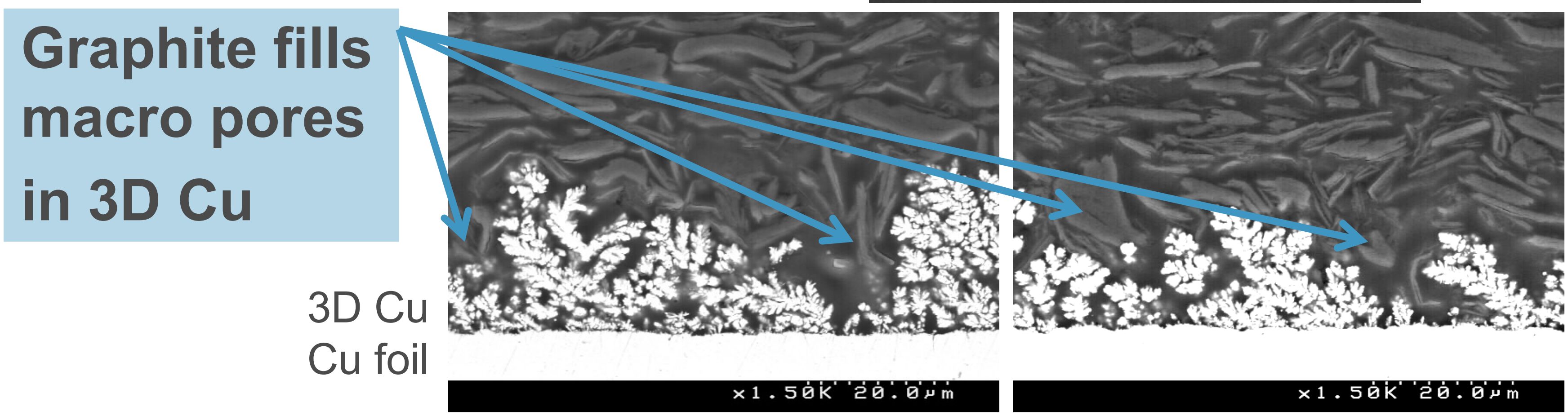


Thick Graphite Coating with Good Adhesion and No Cracking

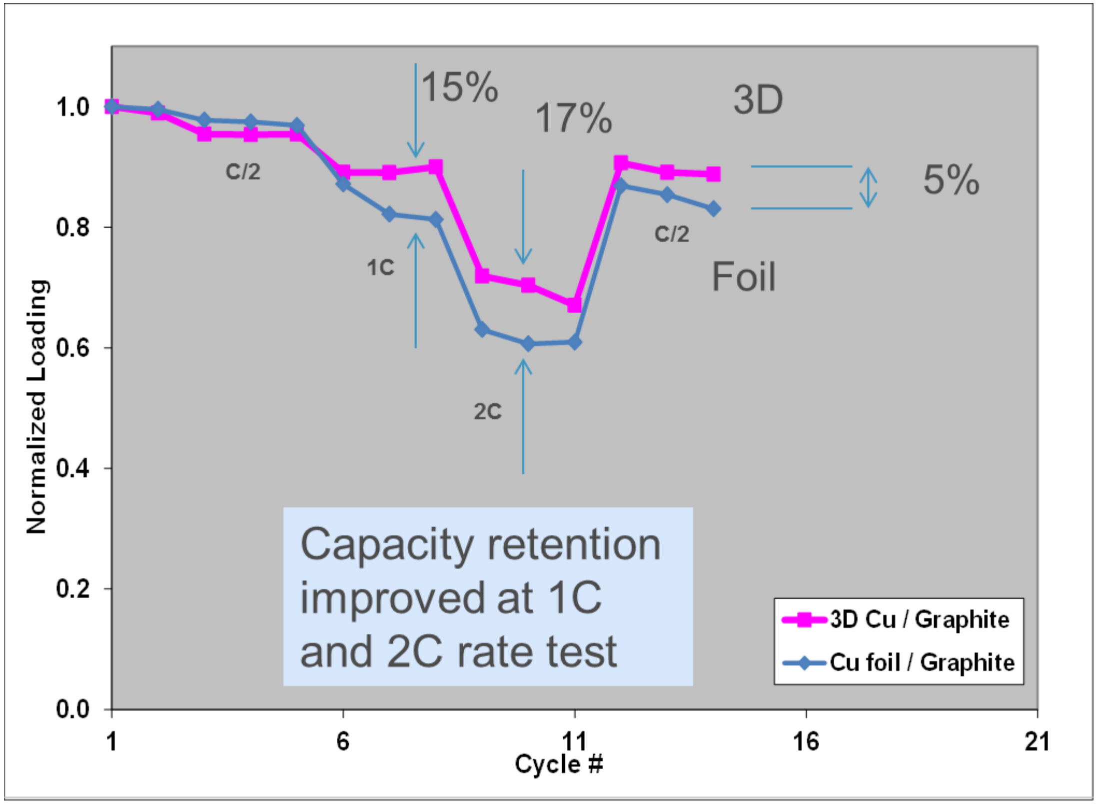
150 µm Graphite Fill of 3D Cu Pores without Cracking (SEM cross sections)

- 150 µm thick graphite





Capacity Retention Comparison for 3.3 mAh/cm^2 Cells 3D Cu/Graphite *vs.* Cu Foil /Graphite



Up to 17% Capacity Retention Improvement at 2C (Baseline Cell)

Collaborators

	Partners for Evaluation and Technology Validation
1. Federal Laboratory	Lawrence Berkeley National Laboratory / Dr. G. Liu - Matching anode-cathode for cell balancing, conductive binder and electrolyte additive evaluation
2. Federal Laboratory	Oak Ridge National Laboratory / Dr. J. Nanda - Materials characterization and degradation analysis using advanced spectroscopic techniques (micro-Raman mapping, X-ray characterization, etc.)
3. Industry	FMC Lithium Division / Dr. M. Yakovleva - Stabilized Lithium metal powders and coating on anode structures for pre-lithiation
4. Industry	A123 / Dr. V. Vu - Evaluation of Applied Materials electrodes using testing equipment for half coin cell, full coin cell, and full scale 63450 prismatic cell.
5. Industry	Nissan Technical Center N. America / Dr. K. Adjemian - Cell performance measurements and final cell validation to USABC requirements.

Planned Work for 2012

Task 2: Cell Design Optimization

- Develop a cell level design model capable of predicting cell level energy density (Wh/L) & specific energy (Wh/kg).
- Compare specific energy and energy density between 3D-Graphite electrode vs. conventional graphite electrode, with NMC as positive electrode.
- Compare specific energy and energy density between 3D-CuSn electrode vs. conventional graphite electrode, with NMC as positive electrode.
- Effect of design parameters (reversible capacity, first cycle capacity loss, loading) on cell level metrics.
- Develop cell level design model for CuSn/Si electrode and update with ongoing experimental data.

Task 3: Baseline Cell Optimization

- Demonstrate baseline cell process with 3D Cu/Graphite
- Optimize 3 mAh/cm^2 cell assembly and formation for 100 cycles & test it
- Complete capacity retention comparative analysis at 2C and 3C
- Develop thick graphite without cracking for > 3.5 mAh/cm^2 cell
- Complete capacity retention analysis with increased thickness at 2C and 3C

Task 4: Interim Cell Development

- Optimize high loading CuSnFe alloy electrode

Project Summary

- The project is in its early phase
- Applied Materials designed modules for fabricating high capacity anodes
  - Developed approach includes
    - Depositing 3D electrodes with micro-cell porous structure
    - Water based processing
- Alloy Anode Development showed advantages of selected materials
  - 3D Electrode structures
    - Modeling Energy Density Requirements
    - 3D Electrode Roadmap
    - 3D Cu / Graphite with better Rate Performance at 2C and 3C
    - 3D Cu(SnFe) with Increased Current Loading
    - 3D Cu(SnFe) / Si Nanometer Grain Size Material
- 2012 work includes High Loading Cell Testing
  - 3.0 - 4.5 mAh/cm^2
    - Cycling Improvements in collaboration with partners
    - Cost Reduction, Manufacturing Economics

Acknowledgment

"This material is based upon work supported by the Department of Energy under Award Number DE-EE0005455."

DISCLAIMER:

- "This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof."

INDEMNIFICATION:

- "By submitting a presentation file to Alliance Technical Services, Inc. for use at the U.S. Department of Energy's Hydrogen and Fuel Cells Program and Vehicle Technologies Program Annual Merit Review Meeting, and to be provided as hand-out materials, and posting on the DOE's website, the presentation authors and the organizations they represent agree to defend, indemnify and hold harmless Alliance Technical Services, Inc., its officers, employees, consultants and subcontractors; the National Renewable Energy Laboratory; the Alliance for Sustainable Energy, LLC, Managing and Operating Contractor of the U.S. Department of Energy's National Renewable Energy Laboratory; and the U.S. Department of Energy from and against any and all claims, losses, liabilities or expenses which may arise, in whole or in part, from the improper use, misuse, unauthorized use or disclosure, or misrepresentation of any intellectual property claimed by others. Such intellectual property includes copyrighted material, including documents, logos, photos, scripts, software, and videos or animations of any type; trademarks; service marks; and proprietary, or confidential information."

Turning innovations
into industries.™