3-D Nano-Structured Carbon/Tin Composite Anodes

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TASK 5.1
Diagnostics - Electrode Surface Layers

I. Microwave Plasma-Assisted Chemical Vapor Deposition (MPACVD) of 3-D Nano-Structured Carbon/Tin Composite Anodes

Purpose of Work: Design and manufacture nano-composite C/Sn composite electrodes with improved power and energy density, and extended cycleability

Barriers Addressed: Low energy (related to cost), poor Li-ion battery cycle lifetime

Approach: Use MPACVD to produce 3-D nano-structured C/Sn thin film electrodes

Accomplishments: 3-D nano-structured thin-film C/Sn electrodes exhibit superior electrochemical performance

II. Interfacial Studies of Li-ion Electrodes

Purpose of Work: Establish direct correlations between Li-ion electrodes surface chemistry, morphology, interfacial phenomena and electrochemical performance

Barriers Addressed: Low power, poor Li-ion battery cycle/calendar lifetime

Approach: *In situ* Raman and FTIR microscopy, *ex situ* SPM, SEM, HRTEM, and standard electrochemical methods were used to detect and characterize detrimental surface phenomena in high voltage cathodes and intermetallic anodes

Accomplishments: Evaluation of carbon additives in high-voltage (>4.3 V) cathodes; single particle Raman imaging; preliminary evaluation of surface processes on Sn

Collaborations: V. Battaglia, M. Doeff, T. Richardson, V. Srinivasan, S. Whittingham K. Zaghib,

Responses to 2006 BATT Program Merit Review

2006 Reviewers' Recommendations:

1. Should continue, creative
2. Always compare benefit of MPACVD to industry SOA
3. Industrial coater investment should be addressed
4. An increased emphasis on collaborations with other PIs and battery industry partners

FY2007 Research Directions:

- Collaborations on fundamental problems of material science as well as engineering issues of composite electrodes manufacturing
- Further optimization of the structure, morphology ad topology of composite electrodes produced by vacuum deposition techniques
- Innovative diagnostic methodologies to determine basic thermodynamic and kinetic parameters of Li-ion materials and electrodes

C/Sn Anodes for Li-ion Batteries

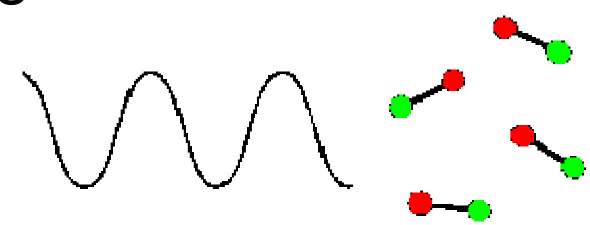
- Purpose of Work:
  - Intermetallic Li-ion anodes offer high capacity, improved safety and low cost
- Barrier
  - Sn exhibits large volumetric expansion during alloying with lithium, which leads to particle decrepitation
  - Loss of mechanical and electronic integrity of the active material leads to severe degradation of anode upon cycling
- Approach
  - Fine dispersion of active material within 3-D architecture constitutes an effective strategy to prevent degradation
  - Carbon-Me nano-composites combine the cyclability of graphite and high charge capacity of Li-Me alloy.

Microwave Plasma-Assisted Chemical Vapor Deposition of Nanomaterials

- MPCVD offers a fast, inexpensive, and convenient method of material synthesis at relatively low temperatures
- Carbon-metal composites can be produced from organo-metallic precursors without stabilizers or reducing agents
- Large-scale thin-film vacuum deposition process in a reel-to-reel configuration has become the industry standard

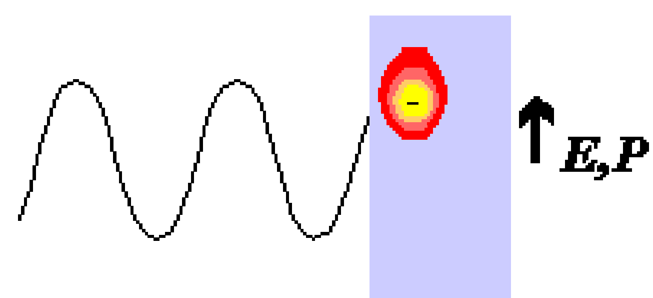
Three principal microwave heating mechanisms

I. Dipolar polarization - molecules with permanent or inducible dipoles follow oscillating electric field

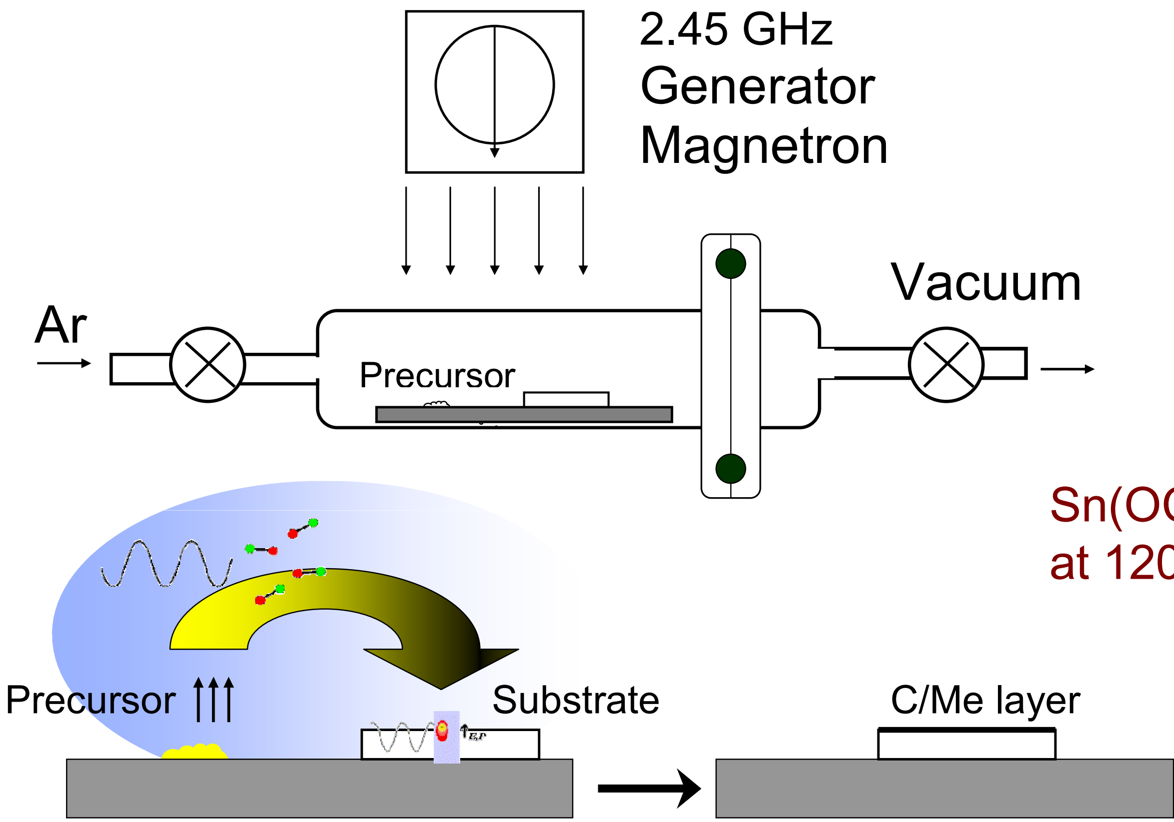


II. Conduction mechanism - charge carriers move in the electric field, inducing currents

III. Interfacial polarization - conducting inclusions in non-conducting material



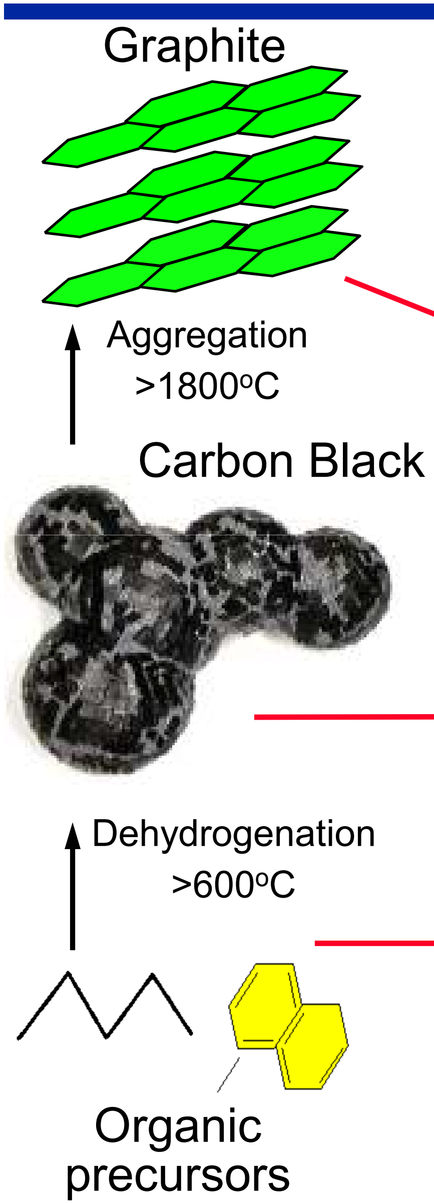
MPCVD of C/Sn Thin-Films Experimental Methodology



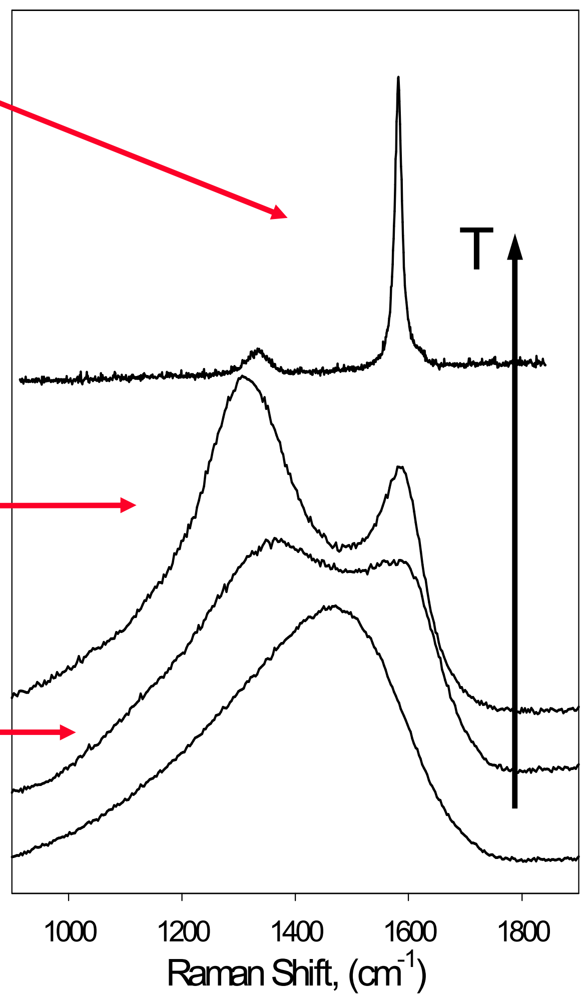
$Sn(OC(CH_3)_3)_4$ is pyrolized for 10 s at 1200 W in microwave Ar-plasma

- We developed a fast, one-step MPCVD method for co-synthesis of nano-structured C/Sn thin-film electrodes for Li-ion applications
- Thin C/Sn composite thin-films show ~2.5:1 of C/Sn wt.% ratio
- The thickness and composition of the film were reproducible and independent of the type of substrate.

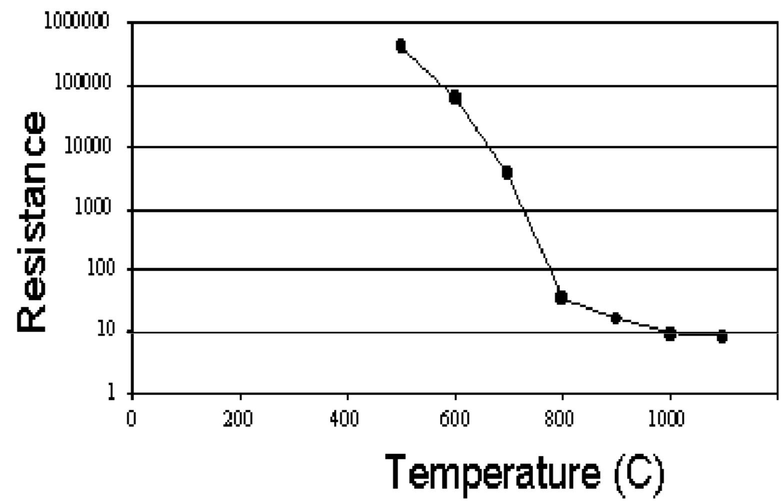
The Structure and Conductivity of Pyrolyzed Carbons



Raman Spectra of Pyrolitic Carbons



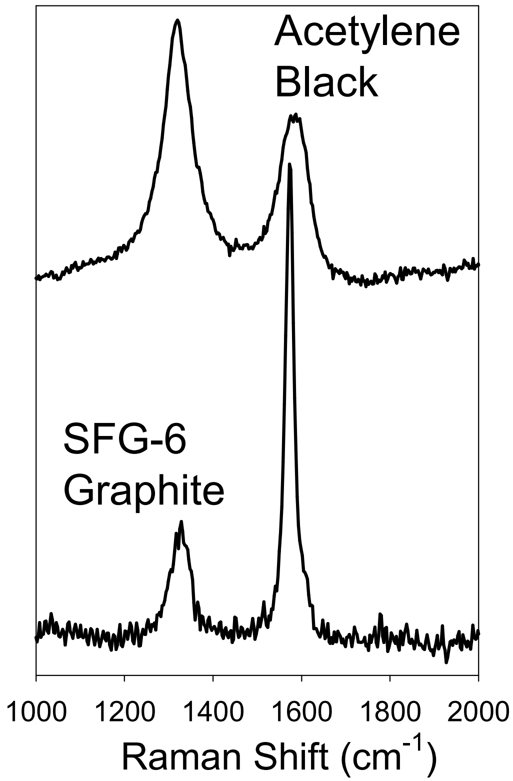
Electronic Resistance of Pyrolitic Carbons



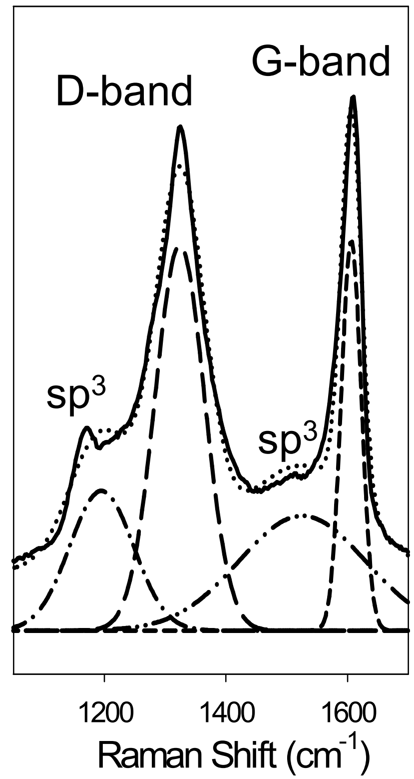
- The structure and electronic conductivity of carbon change dramatically at 600-800°C.
- Conductive graphite-like carbons can not be obtained by simple pyrolysis at T<1800°C

Raman Spectroscopy of C/Sn Thin-Films

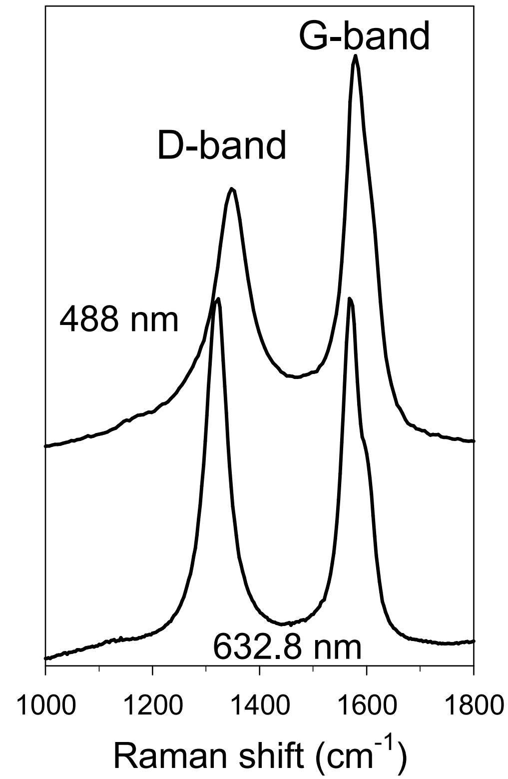
Raman Spectra of Carbons



Deconvoluted Raman Spectrum of Carbon

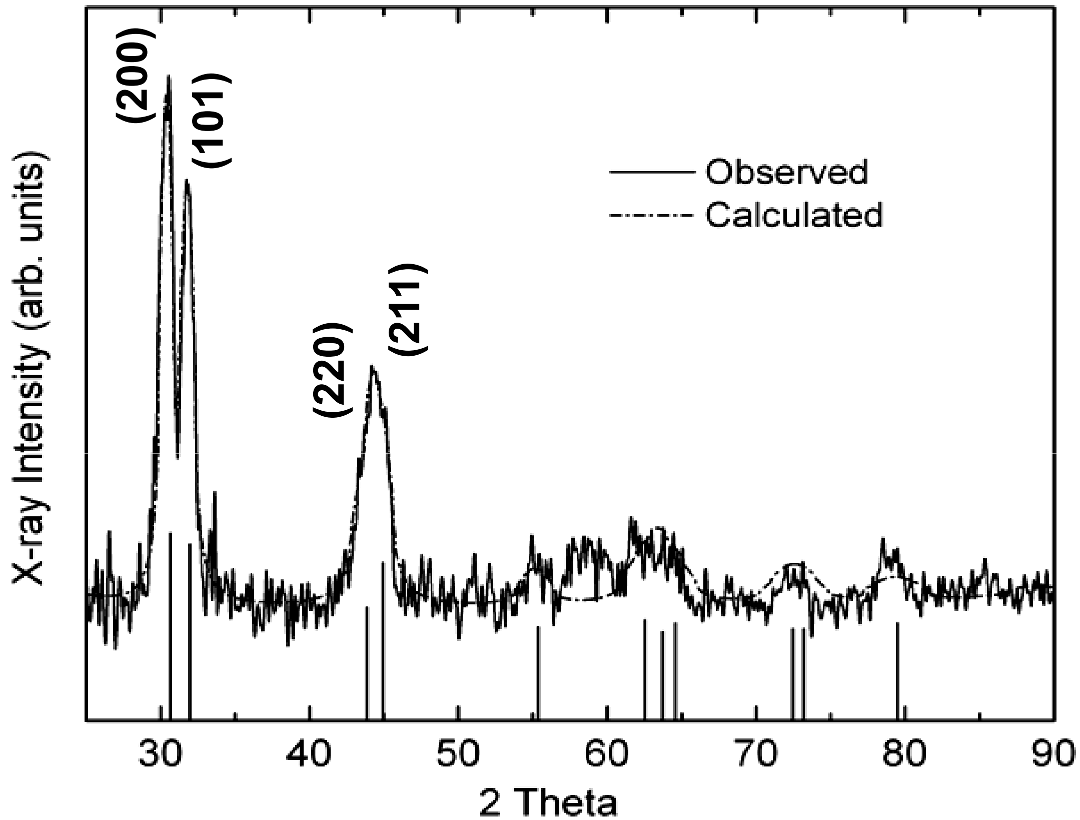


Raman Spectrum of C/Sn Thin-Film



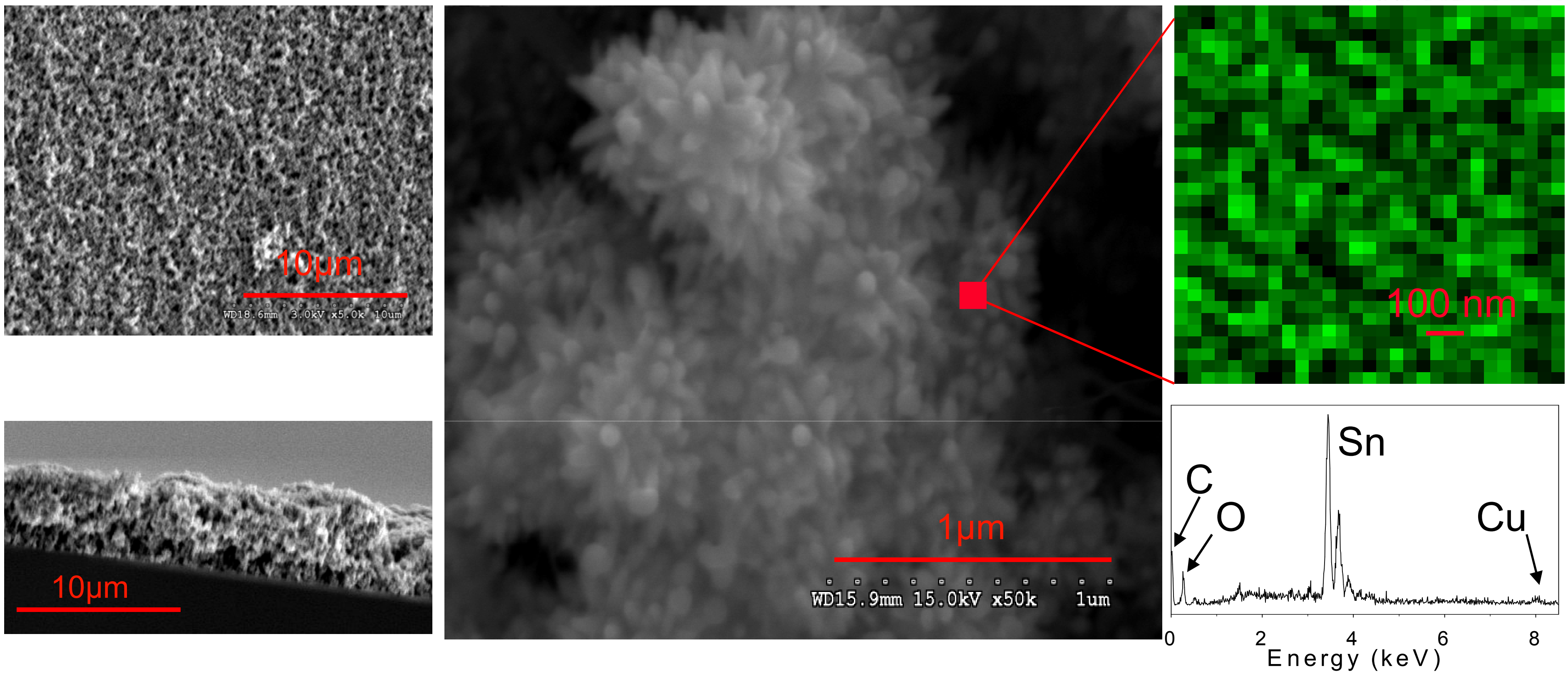
- Strong G and D Raman bands suggest the presence of sp^2-coordinated nano-crystalline graphitic carbon
- Graphitic carbon matrix is expected to display better electronic conductivity and lower Q_{irr} than standard carbon black additive

XRD Analysis of C/Sn Thin-Films



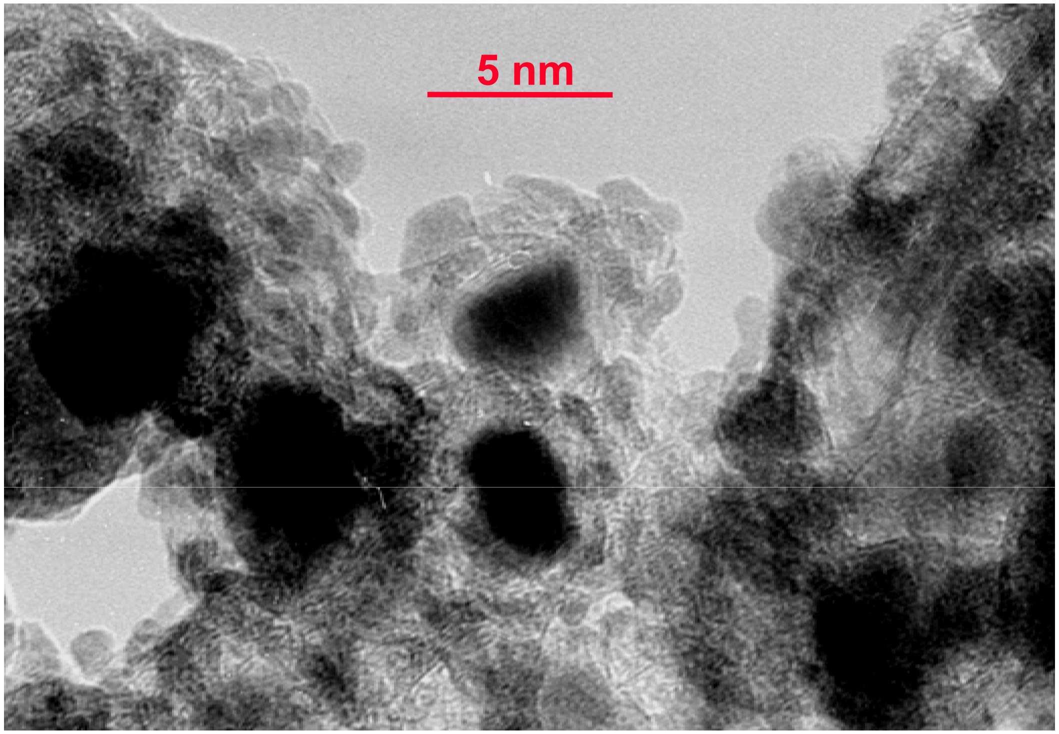
- XRD pattern of the 5 µm think C/Sn film displays broad peaks characteristic for Sn ($I4_1/amd$) tetragonal structure (a_0 = 5.86 Å, c_0 = 3.19 Å)
- Average Sn crystallite size calculated using the Scherrer formula ~15 nm

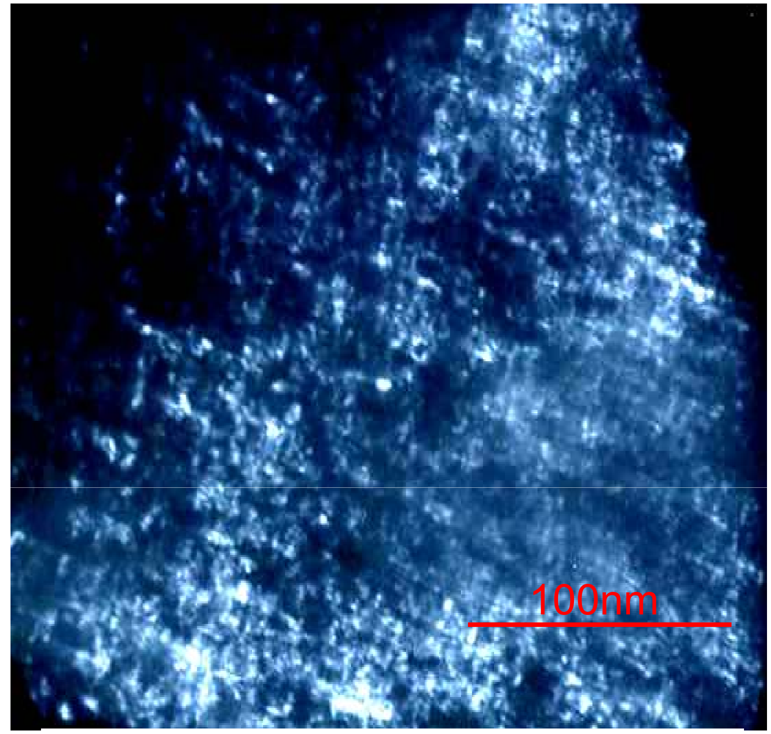
SEM/EDX of C/Sn Thin Films

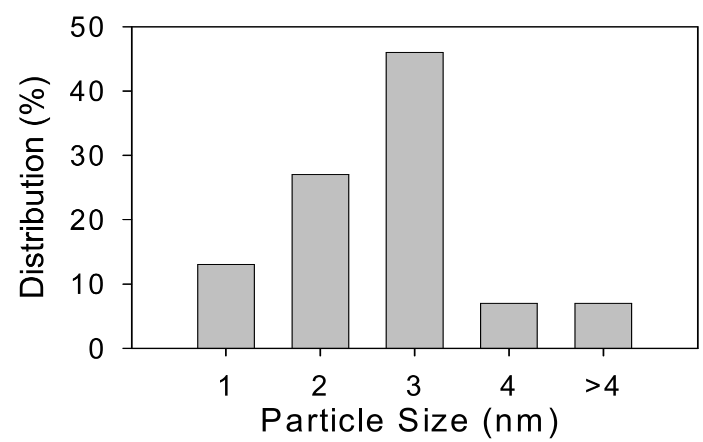


- Porous 5-7 µm thick C/Sn films were grown directly on Cu-foil
- The film consists of ~300-600 nm, agglomerates, which are fused together into a micro- and nano-porous “lava rock”-like structure
- The EDX spectrum shows strong signals characteristics for Sn, C and Cu
- Small contribution from oxygen suggests the presence of SnO impurities

HRTEM of C/Sn Composites



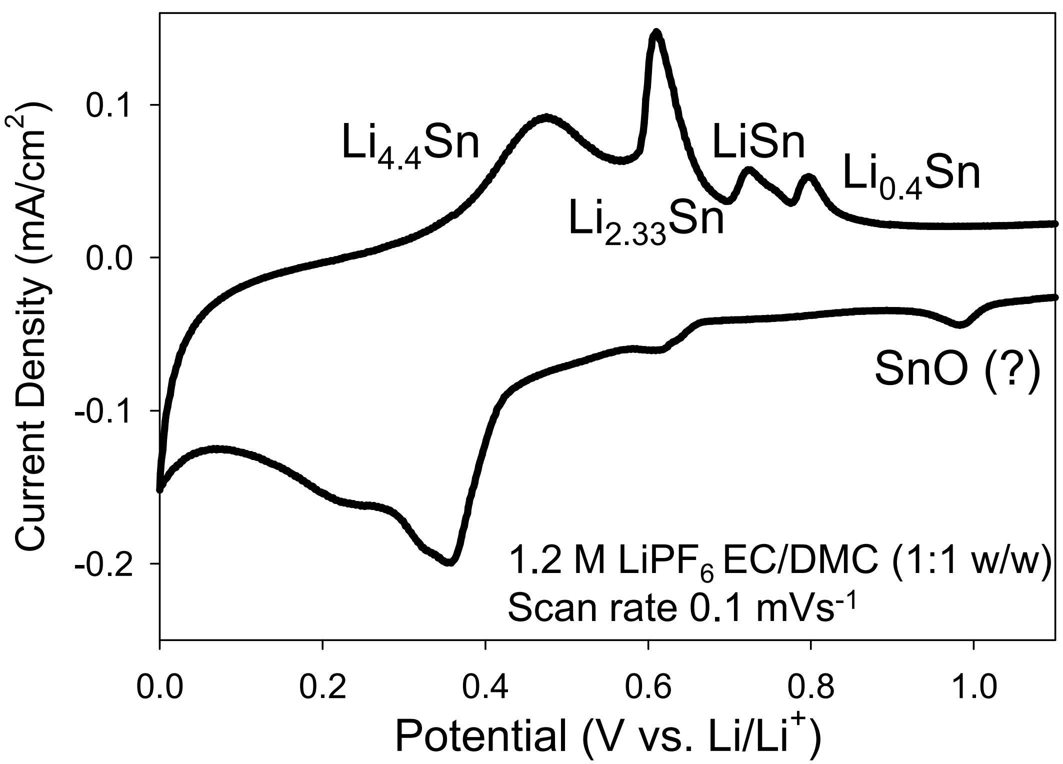




- HRTEM images reveal 1-5 nm Sn particles
- TEM bright-field images show a uniform dispersion of Sn in the carbon matrix
- Carbon matrix displays 10–15 nm graphene domains and regions typical of carbon blacks

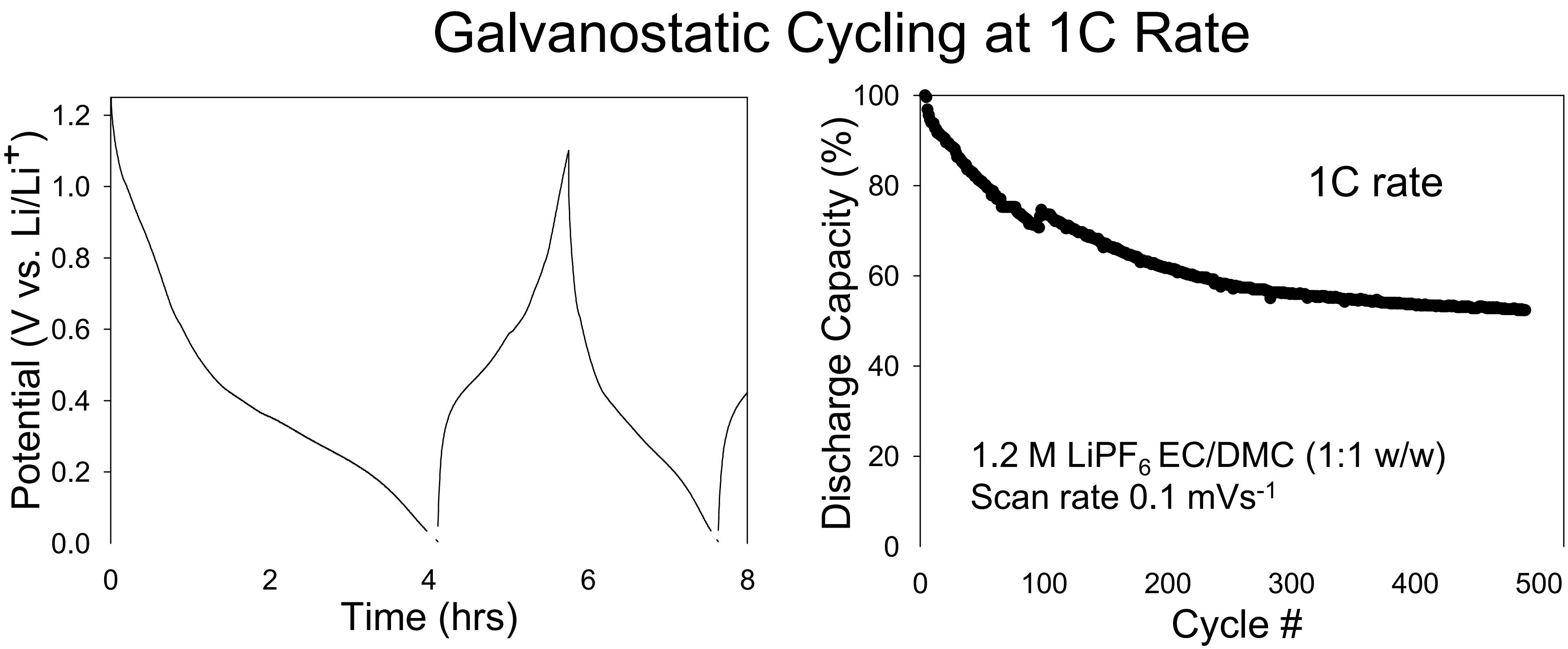
Electrochemical Behavior of C/Sn Thin-Film Electrode

Cyclic Voltammogram -1st scan



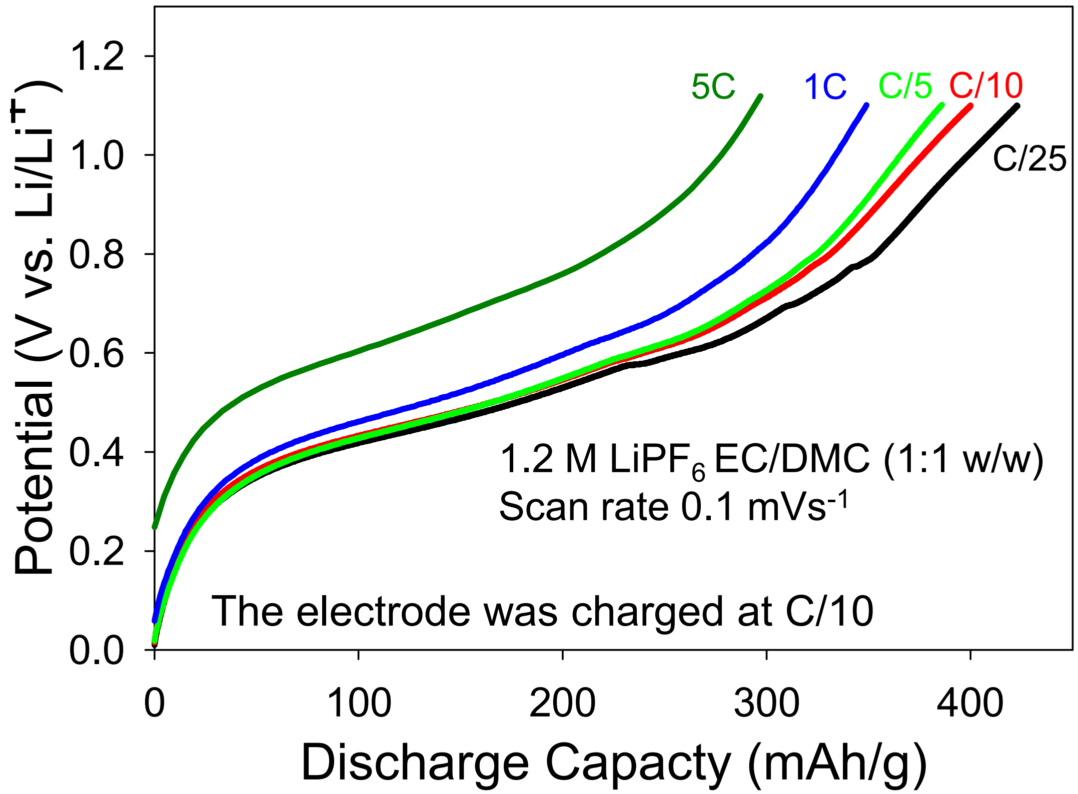
- The reversible capacity of ca. 440 $mAhg^{-1}$ originates exclusively from Sn
- The irreversible capacity (~400 $mAhg^{-1}$) is mainly associated with the SEI layer formation on the carbon matrix
- The cathodic peak at 0.98 V is attributed to SnO impurities

Galvanostatic Cycling of C/Sn Thin-Film Electrodes



- The C/Sn thin-film electrodes exhibits very good cycling performance (~40% capacity fade after 500 cycles at 1C rate)
- The electronic integrity of the C/Sn electrode is retained during cycling
- The decrease of the reversible capacity is likely associated with large Sn particles weakly bounded to the carbon matrix

Rate Capability of C/Sn Thin-Film Electrodes



- The C/Sn thin-film anode shows significantly improved rate capability
- Fine dispersion of Sn particles within the carbon matrix, high porosity and network-like 3D architecture contribute to faster response of the electrode

Conclusions

- We demonstrated a novel synthesis technique for the production of nano-composite anodes for Li-ion batteries
- C/Sn binderless thin-films can be manufactured in a fast, inexpensive, single-step process on any type of substrate
- Thin-film C/Sn anodes display significantly improved electrochemical behavior
- Nano-structured C/Sn anodes ameliorate the dimensional changes and retain good electronic contact between the active material and the current collector
- The significant improvement in cycleability is attributed to the high porosity and fine dispersion of Sn in 3-D carbon matrix

Summary

- Fundamental research for improved batteries
  - ➢ Nanomaterials for new generation Li-ion batteries
  - ➢ Diagnostic studies of detrimental processes in Li-ion cells
  - ➢ Interfacial processes – fundamental studies of processes at the electrode surface
- Approach
  - ➢ Use MPACVD to produce 3-D nano-structured C/Me thin film electrodes
  - ➢ Innovative use *of in situ* and *ex situ* spectroscopic, microscopic, X-ray, and related techniques to charcaterize Li-ion electrodes
- Accomplishments
  - ➢ New synthesis routes for better materials and new electrode designs
  - ➢ Demonstrated important electrochemical behavior of carbon additives in high voltage cathodes

Future Work

- Study mass and charge transfer mechanisms through the electrolyte/HOPG interface and lithium diffusion in graphite
  - Design, construct and apply and electrochemical cell of the Devanathan-Stachurski type to study kinetics of Li intercalation and diffusion
  - Study possible correlations between formation and physico-chemical properties of the SEI layer
- Apply *in situ* and *ex situ* instrumental methods to detect and characterize surface processes in Li-ion electrodes
  - Cooperate with the BATT Interfacial Studies Group to investigate the structure and morphology of carbons and the corresponding SEI layer
  - *In situ* studies of surface processes at model electrodes (collaboration with S. Whittingham)
- Develop plasma deposition techniques to synthesize nano-composite C/Sn-Me and C-Si thin-film anodes
  - Evaluate vacuum deposition techniques to produce new electrodes architectures and compositions

Publications and Patents

1. Marca M. Doeff, James D. Wilcox, Rong Yu, Albert Aumentado, Marek Marcinek and Robert Kostecki, “Impact of Carbon Structure and Morphology on the Electrochemical Performance of $LiFePO_4$/C Composites”, *J. Solid State Electrochem.*, accepted
2. M. Marcinek, L. J. Hardwick, T. J. Richardson, X. Song and R. Kostecki, “Microwave Plasma Chemical Vapor Deposition of Nano-Structured Sn/C Composite Thin-Film Anodes for Li-ion Batteries”, J. Power Sources, 173, 965 (2007)
3. Marek Marcinek , Xiangyun Song, and Robert Kostecki, “Microwave Plasma Chemical Vapor Deposition of Nano-Composite C/Pt Thin-Films”, *Electrochem. Commun.,* 9, 1739 (2007)
4. Marie Kerlau, Marek Marcinek, Venkat Srinivasan, Robert M. Kostecki, "Studies of Local Degradation Phenomena in Composite Cathodes for Lithium-Ion Batteries”, *Electrochimica Acta*, 52, 5422 (2007)
5. James D. Wilcox, Marca M. Doeff, Marek Marcinek, Robert Kostecki, “Factors Influencing the Quality of Carbon Coatings on $LiFePO_4$”, *J. Electrochem. Soc.* 154, A389-A395, (2007)
6. Marie Kerlau, Marek Marcinek, Robert Kostecki, “Diagnostic Evaluation of Detrimental Phenomena in ^{13}C-labeled Composite Cathodes for Li-ion Batteries”, *J. Power Sources*, accepted, 174, 1046 (2007)

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1. Robert Kostecki, Marek Marcinek, “Graphitized Carbon Coatings for Composite Electrodes”, US Patent Application, IB-2176PCT

Acknowledgements

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