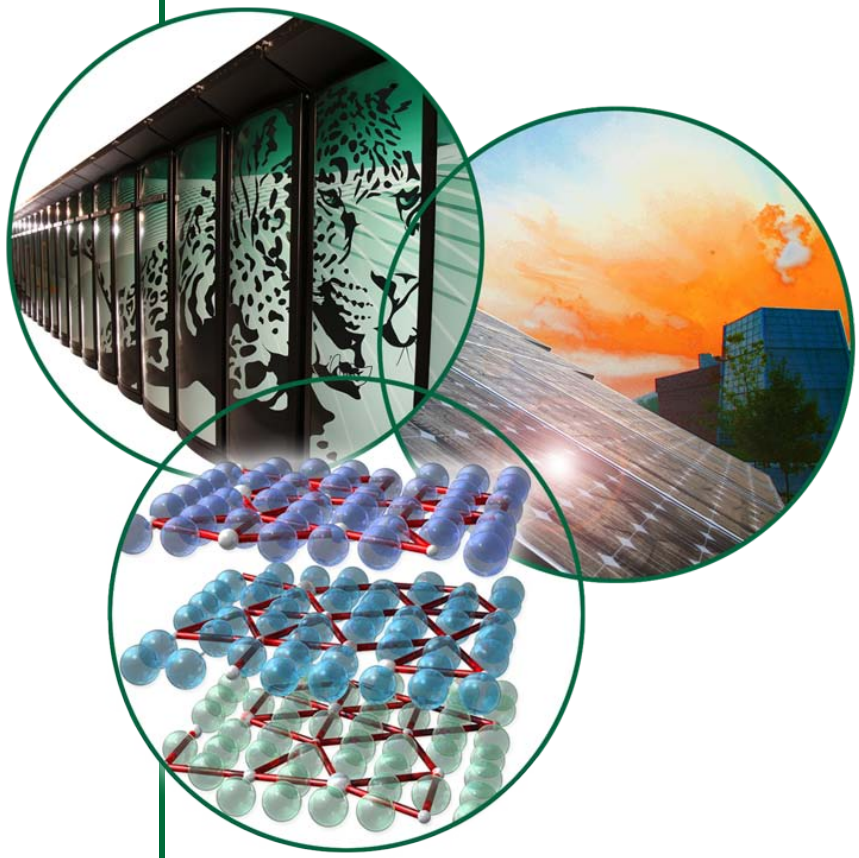
U.S. DEPARTMENT OF ENERGY
JUNE 7-11, 2010
Washington, D.C.
Annual Merit Review & Peer Evaluation Meeting
2010 U.S. Department of Energy Hydrogen Program and Vehicle Technologies Program

Project ID #ES093

Coupled Kinetic, Thermal, and Mechanical Modeling of FIB Micro-machined Electrodes



Claus Daniel

Oak Ridge National Laboratory

June 8, 2010

This presentation does not contain any proprietary, confidential, or otherwise restricted information

U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

MichiganEngineering

Overview

Timeline

- Start: Aug. 2009
- End: Sept. 2012
- 25% Complete

Budget

- Total Project Funding: $1.8M
- Funding for FY09: $600K
- Funding for FY10: $600K

Barriers

- Poor cycle life

Goals

- Cycle life: 5000 cycles
- Calendar life: 15 years

Partners

- University of Michigan, Ann Arbor

Objectives

Coupled Kinetic, Thermal, and Mechanical Modeling of FIB Micro-Machined Electrodes

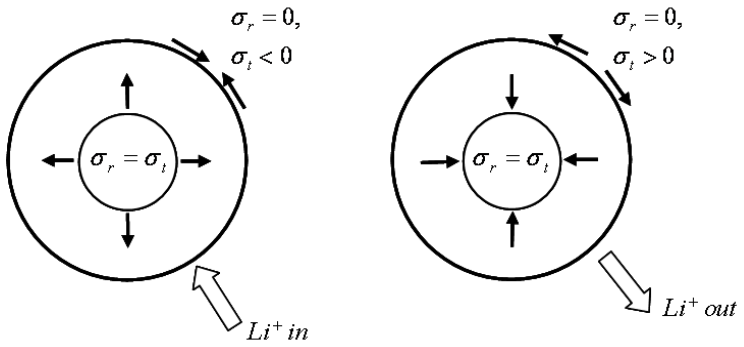
- **Fundamental understanding of deformation processes and stress generation during Li intercalation (deintercalation) from active cathode material via experimental work on Focused Ion Beam (FIB) micro-machined samples.**
- **Development and validation of coupled kinetic, thermal and mechanical model based on the experimental results.**
- **Micro-electrodes allow the understanding of those phenomena on the particle level**

Milestones FY2010/11

Month/Year	Milestone or Go/No-Go Decision
Oct 09 	Preparation of thin film samples and subsequent FIB milling Preliminary FE modeling of micro-machined samples
Apr 10 	Optimizing samples for AFM studies Successful charge/discharge of micro-electrodes
Sept 10 	Successful *in situ* AFM scan of FIB micro-machined samples.
Sept 11 	Full combination of morphology change and intercalation kinetics
Sept 12 	Full understanding and verified modeling of stress-strain relationship and intercalation kinetics

Approach
Understanding mechanical response to lithiation and lithiation kinetics

- **Understanding lithiation mechanism and probability of damage in brittle materials**



- **The material constants are determined from the series of load-to-rupture experiments and may be size dependent.**

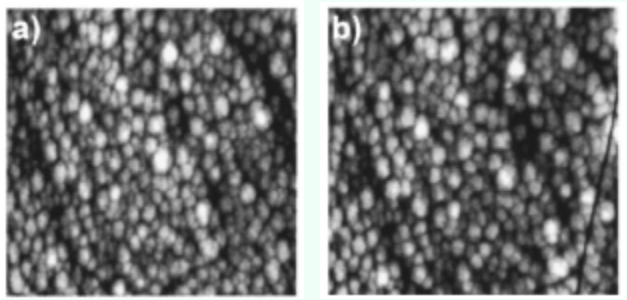
J. Lemaitre, R. Desmorat, Engineering damage mechanics, Ductile, creep, fatigue and brittle failure, Springer, Berlin, 2005

Micro- and nano-pillars allow for small scale behavior studies on exclusive features

Need for experimental approach based on study of isolated micro- and nano-samples of pre-defined geometry.

Work on thin film scale

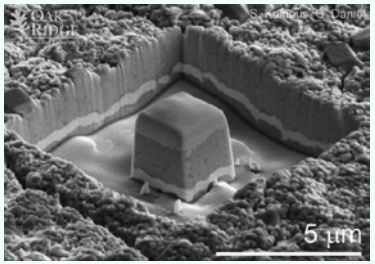
- **AFM scans allow for observation of surface changes.**
- **Experimental data can hardly be used for simulations.**

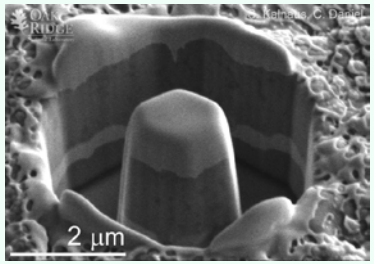


L.Y. Beaulieu et al, Rev. Sci. Instruments, 72(8) 2001, pp: 3313-19

Work on micro-specimen scale

- **FIB micro-machined samples can be considered as representative volume elements of cathode material.**
- **Known pre-defined geometry.**



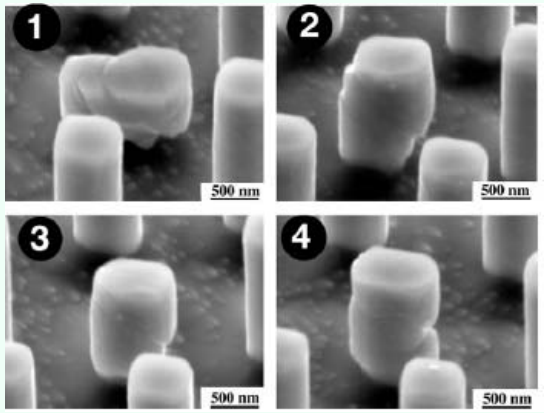


- **Known boundary conditions.**
- **Experimental data can be used in simulations**

As example micro- and nano-pillars allow the understanding of mechanical behavior and deformation for the development of materials

Pre-Straining Effect

- Effect of pre-strain application on subsequent mechanical behavior.

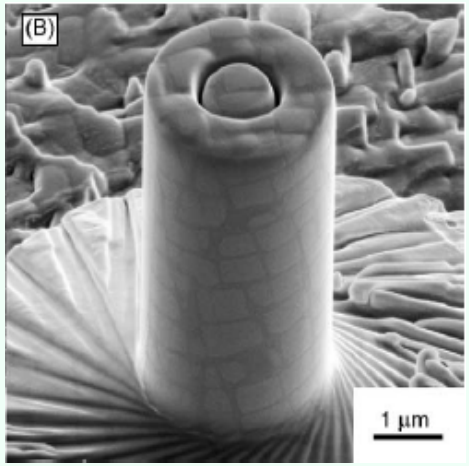


H. Bei et al, Acta Mater. 56 2008, pp: 4762-70.

- Approach can be applied to investigation of pre-straining on subsequent electrochemical behavior (overload effect in mechanical fatigue is known to retard crack growth).

Microplasticity

- Cylindrical specimens milled using FIB are used in studies of scale-dependant plastic behavior.

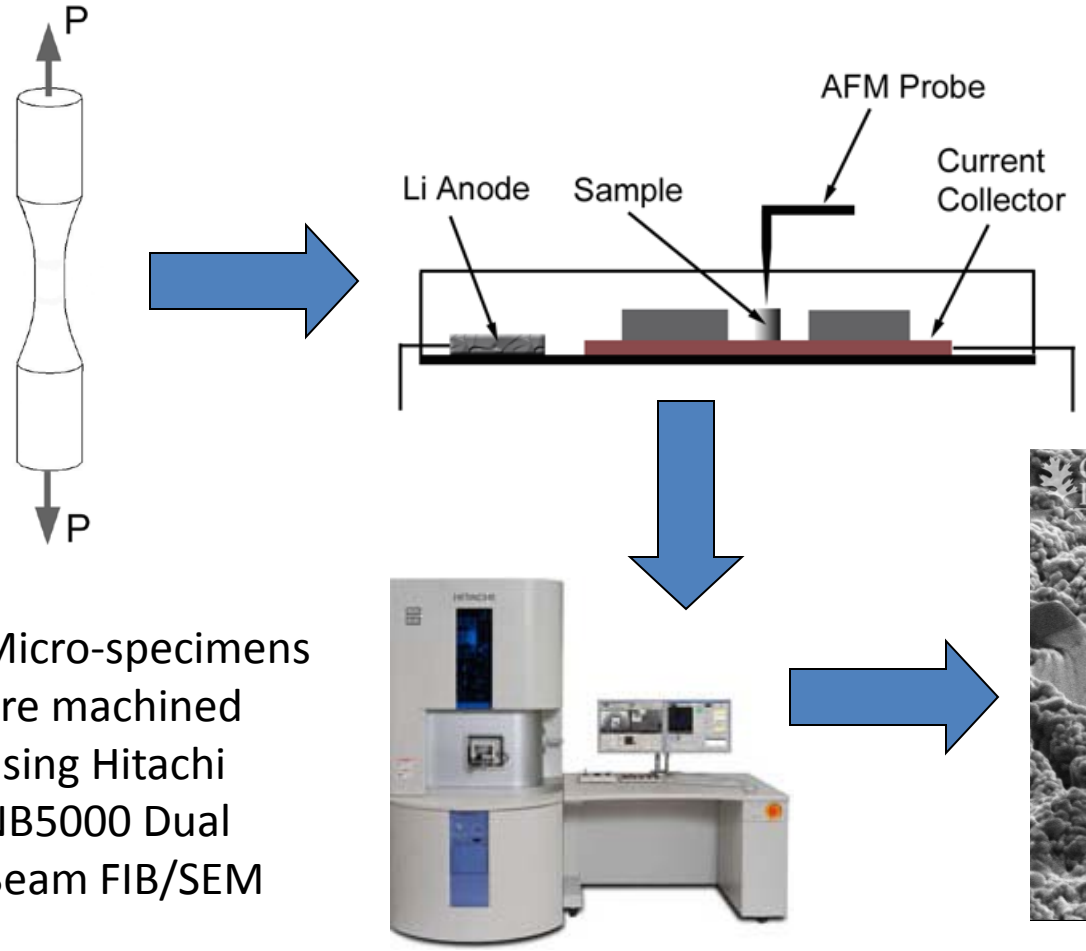


M.D. Uchic, D.M. Dimiduk, Mat. Sci. Engng, A400-401 2005, pp: 268-78.

These examples are for structural materials.

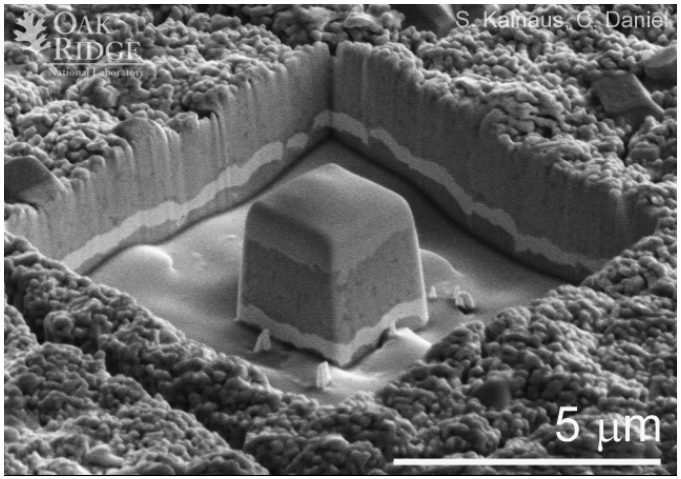
Experimental setup for in-situ studies on cycling micro-electrodes

Analogy between mechanical and electrochemical experiments are determined in order to investigate and describe constitutive behavior of the material.



Work on small scale model specimens of pre-defined configuration

Micro-specimens are machined using Hitachi NB5000 Dual Beam FIB/SEM



Approach

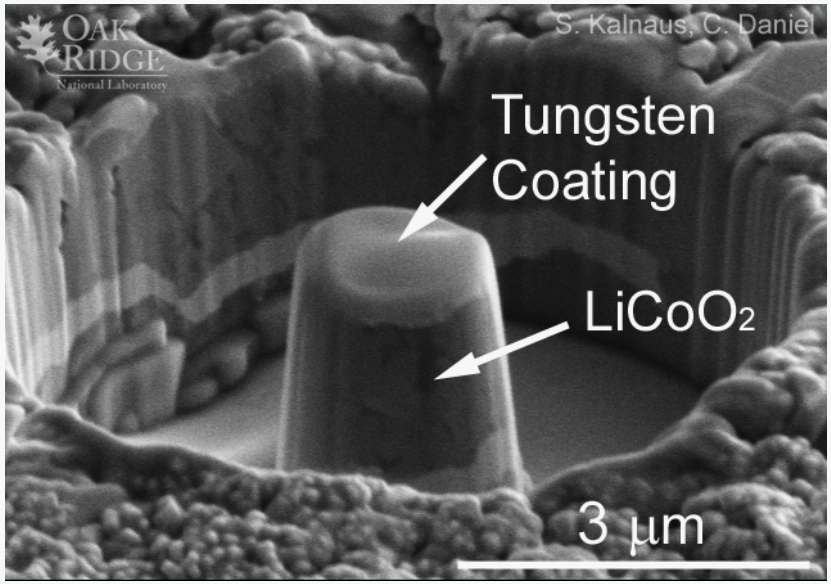
- Cathode samples are prepared as thin films by RF Magnetron Sputtering and annealed to achieve crystallinity.
- Samples of pre-defined geometry are micro-machined from the thin film layer.
- Specially designed fluid cell allows for in situ AFM characterization of morphology change of the sample during electrochemical cycling thus connecting mechanical parameter (strain) with electrochemical parameter (state of charge).
- Experimental results are used for further development of the thermal analogy model to a full scale model for prediction of stress-strain state in active electrode material.

Technical accomplishments

Active electrode material is conditioned and micro-machined

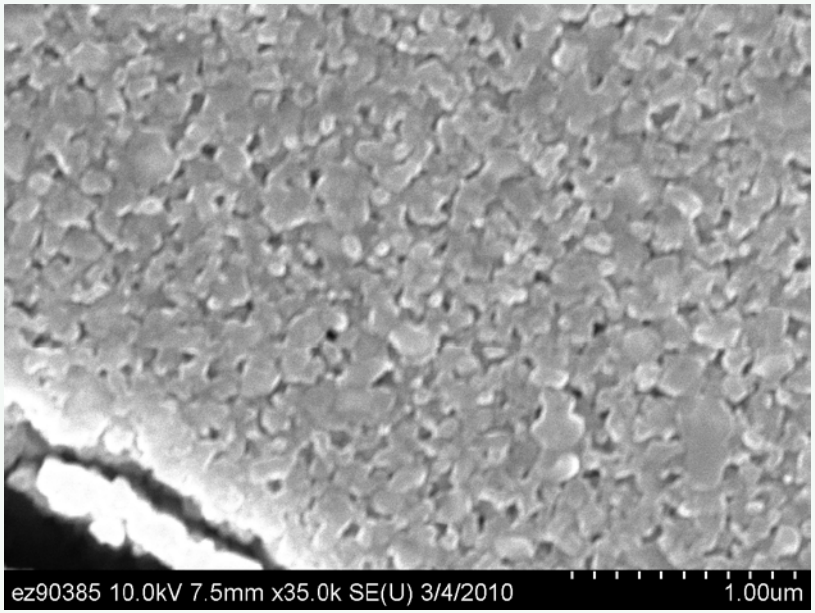
Sample Preparation

- Thin films of $LiCoO_2$ deposited on Al_2O_3 substrates.



Annealing Conditions

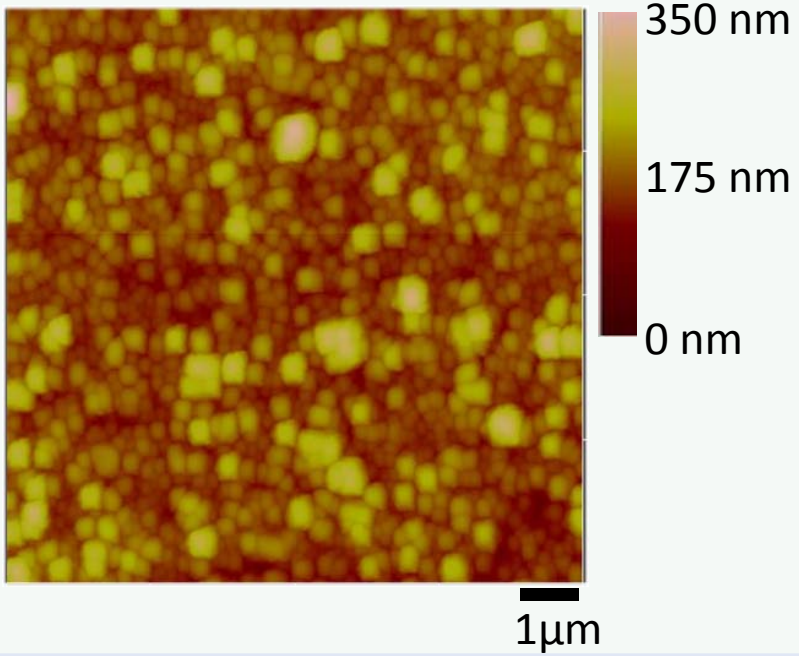
- Annealing at 700^0C produces fine nano-scale crystallinity in the samples.



Sample surface has to be optimized to be applicable for atomic force microscopy

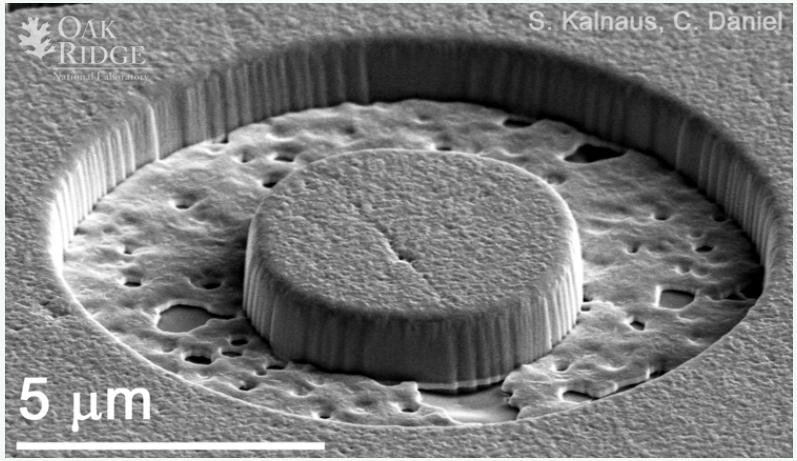
AFM

- Surface scan of the electrode in contact mode.



Surface Improvement

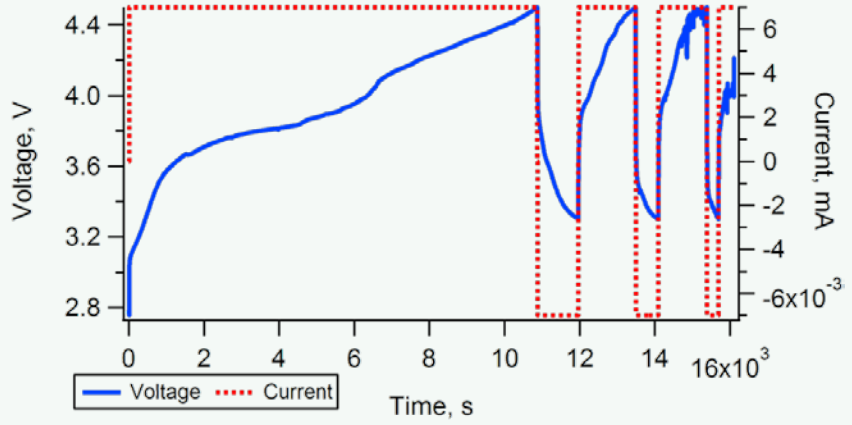
- Polishing of substrates to surface roughness of 500 Angstrom eliminates the need for Tungsten deposition.



Prepared micro-electrodes have been cycled in in-situ AFM and stress-strain simulations are under way

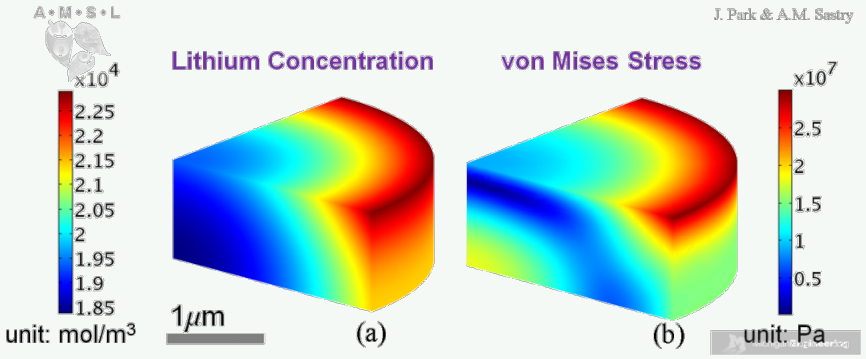
Electrochemical Cycling

- Constant Current Cycling of thin film samples.



FEM Computations

- FE modeling of sample geometry under constant current boundary conditions.



Collaborations

Partners

- University of Michigan, Ann Arbor: Dr. Ann Marie Sastry
  - In situ AFM cycling experiments and modeling of stress-strain relationship

Future Work

- Improvements in thin film adhesion to substrates will be made through continuing experimentation with sputtering and annealing techniques.
- Investigation of $LiMn_2O_4$ and Si based electrodes.
- Experimentation with samples of different geometries produced by FIB micro-machining.
- Determination of electrochemical cycling conditions which produce the least possible gradients in stress-strain state within a sample.

Summary

- The project targets the fundamental understanding of stress-strain state development in active electrode material of Li ion battery during charge/discharge process.
- Unique experimental approach allows for in situ characterization of morphology change in the sample.
- The samples of known pre-defined geometry serve for experimental determination of fundamental constitutive behavior.
- The model developed is capable of predicting the stress-strain state inside the material.

Acknowledgements

- Contributors
  - ORNL: Sergiy Kalnaus, Nancy Dudney
  - UMich: Jonghyun Park, Sangwoo Han, Yoon Koo Lee, Greg Less

This research at Oak Ridge National Laboratory, managed by UT Battelle, LLC, for the U.S. Department of Energy under contract DE-AC05-00OR22725, was sponsored by the Vehicle Technologies Program for the Office of Energy Efficiency and Renewable Energy. Parts of this research were performed at the High Temperature Materials Laboratory, a National User Facility sponsored by the same office and at the Shared Research Equipment Collaborative Research Center sponsored by the Office of Science, Basic Energy Sciences Program.