FINAL TECHNICAL REPORT

1. COVER PAGE DATA ELEMENTS

a. Federal Agency and Organization Element to Which Report is Submitted

Department of Energy, Office of Science, Neutron Scattering Program

b. Federal Grant or Other Identifying Number Assigned by Agency: DE-SC0008681

c. Project Title:

Application of *in situ* Neutron Diffraction to Understand the Mechanism of Phase Transitions During Electrochemical Cycling of High Capacity Mg/Si Nanostructured Electrodes

d. PD/PI Name, Title and Contact Information (e-mail address and phone number)

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e. Name of Submitting Official, Title, and Contact Information (e-mail address and phone): NA

f. Submission Date: 2/9/2018

g. DUNS Number: 009095365

h. Recipient Organization (Name and Address):

University of Utah
Salt Lake City, UT 84121

i. Project/Grant Period (Start Date, End Date): 8/15/2012 through 8/31/2017

j. Reporting Period End Date: 8/31/2017

k. Report Term or Frequency (annual, semi-annual, quarterly, final, other): Final Report

l. Signature of Submitting Official (electronic signatures (i.e., Adobe Acrobat) are acceptable)

Dr. Ravi Chandran (PI)
Department of Metallurgical Engineering, The University of Utah, Salt Lake City, UT 84112.

2. ACCOMPLISHMENTS: Mandatory

a. What are the major goals and objectives of this project?

The major goals and objectives of the project are described below under two themes, as these were the tow broad topics under which the research was performed.

A. In Situ Neutron Diffraction

The primary objective of this work is to design an in situ electrochemical cell for neutron diffraction experiments that can use low volume electrodes, which can be fabricated in laboratory. The requirement is that the cell should accommodate planar electrode configurations (anode/separator/cathode arrangement) that are commonly manufactured. This would allow rapid experimentation with different electrode compositions, as often as necessary. It also should allow the use of about 100 μm thick battery electrodes in small volumes (with active material area of about 12 mm x 5 mm), made using standard laboratory procedure. The electrodes are normally fragile (mixture of C, or $LiCoO_2$ or $LiMn_2O_4$ mixed with binder and conductive carbon) and slurry-coated on Cu or Al current collectors. It is also important that the cell creates sufficient diffracted intensities for Rietveld refinement—this means that incoherent scattering from the container or windows requires to be minimized. For this purpose, design using (100) Si wafers, cut to the window size, needs to be pursued. Finally, the cell should be easy to assemble and seal hermetically to prevent electrolyte oxidation and permit the use of various electrolyte arrangements, that is, either soaked separator or flooded chamber.

The second part of this research theme is to use the in situ cell for the study of lithiation of Si under neutron diffraction. The process of amorphization of Si or crystallization into some other phase have been well studied earlier in literature using XRD, NMR, and/or TEM techniques. However, the earlier studies did not focus on the changes that occur in the atomic Si-Si bonding scale in the process of shape change caused by volume expansion. The lithiation process of Si can be best studied in real time by use of neutron diffraction, owing to higher depth of penetration of neutrons and their ability to detect Li atoms despite low Z. This research focused on the study of changes that occur in microporous Si (100) electrodes using an in-situ neutron diffraction technique. In particular, the objective is to use the in situ cell designed, as above, for these experiments and determine the changes that occur in Si upon lithiation or delithiation.

B. Neutron Tomographic Imaging

The objective of the first part of the research was to determine if Li removal and deposition from Mg-Li alloy electrodes can be imaged three-dimensionally using the neutron tomographic technique. In this part of the research, Li/Mg alloy anodes, with different states of charge/discharge (Li insertion/removal), were examined via *ex situ* neutron imaging to understand the evolution of Li concentration profiles and the phase transitions during Li insertion/removal within Li/Mg electrodes. The key objective is to get the Li concentration profile as a function of depth or the state of charge/discharge. By comparing these profiles with theoretical models for solid-state diffusion, the Li diffusivity through the electrodes and the extent of phase transition/boundary movement can be obtained. Such understanding of Li diffusion, phase transitions and interface Li deposition in Mg/Li electrodes can provide insights on electrode chemistry and design to achieve high energy-storage capacity Li-Mg cells.

The objective of the second part of the research is whether Li distribution within the electrodes of a Li button cell can be successfully mapped using neutron imaging. In small Li-ion button cells, vanadium pentoxide (V_2O_5) is commonly used as the cathode material. The advantages of V_2O_5 include the low cost of synthesis and the high Li-storage capacity (147 mAh g^{-1}) compared with other cathode materials such as $LiCoO_2$ (137-140 mAh g^{-1}). Specifically, the relatively large electrode thickness (~1 mm) of V_2O_5 makes it advantageous for detailed spatial investigations using neutron imaging. In most batteries, it is well known that the high C-rates during charge/discharge cycles will rapidly diminish the capacity. Hence, the investigation of how Li is distributed spatially in a bulk cathode, such as V2O5, by neutron imaging, and how such distribution leads to capacity loss, under high rates of cycling, will be very valuable.

b. What was accomplished under these goals?

A. In Situ Neutron Diffraction

In-situ cell for tracking phase transitions in small volume electrode materials was successfully developed in this research, as planned. It was shown that the phase transitions could be studied in a better way using this cell. The data quality is in such a way that when data of 1 hr were binned, Rietveld refinement could be successfully performed. The presence of two phases while charging $LiMn_2O_4$ could be observed, which was not possible by prior *ex-situ* and *in-situ* neutron works. This indicates that cell was able to give data of better resolution than prior *in-situ* works. The data quality can be further increased by use of deuterated electrolyte and multiple electrode layers. The use of amorphous Si sheet can also be tried. All the structural transitions in graphite, $LiCoO_2$, $LiMn_2O_4$ reported in literature could be observed which validates the novel cell design.

This part of research also led to the discovery of a new Si electrode architecture, having columnar micro-pores, which provides a very high mass specific Li-storage capacity (~1212 mAh/g), and, the highest total Li-storage capacity (~1.21 mAh/cm^2) relative to other Si electrodes. These capacities were found to be sustainable for over 200 cycles. It was found that columnar micro-porous Si architecture could store a greater amount of charge (~250%) than solid-Si, due to the increased surface area provided by the columnar pores. Further, the most exciting finding of this study is that the pore walls of the columnar microporous architecture do not appear to crumble even after a large number of cell cycles, mitigating the Si cracking issues. Electron microscopy revealed that the superior performance is due to the accommodation of volume changes, caused by lithiation, within the pores. The present findings reveal a new pathway for architecturing Si electrodes for much larger and highly reversible total charge-storage capacities for on-chip Li-ion cells.

As planned, the Si electrode was employed in the in situ cell neutron diffraction experiments at SNS, Oak Ridge National Laboratory. We could successfully observe the crystallographic changes occurring in the Si lattice during lithiation from pores just 12 μm in depth. The neuron diffraction observations, coupled with TEM studies at the University of Utah, established that the Si lattice becomes mosaic during the process of lithiation. This is a very novel finding.

B. Neutron Tomographic Imaging

Li-Mg alloy electrodes with two different compositions (Mg-70 wt.% Li and Mg-50 wt.% Li) were successfully prepared in the laboratory. Delithiation process was successfully controlled to achieve electrodes with different depths of Li depletion for neutron imaging. Using neutron tomography, Li spatial distributions in the bulk Li-Mg alloy electrodes with various depths of delithiation, were determined. The variations in Li concentration profiles along the direction of

delithiation were successfully determined from the neutron imaging data. This technique can be a very powerful tool to non-invasively study bulk distribution of the elements that are highly interactive with neutrons, such as Li in Li-ion batteries and H in fuel cells. Further, a comprehensive analytical diffusion model for the delithiation of Li-Mg alloy, including the β→α phase transition, has been developed. It considers exactly the β-phase and porous α-phase structure before and after phase transition using appropriate initial and boundary conditions as well as the flux-controlled boundary movement. The simulated Li concentration profiles are consistent with the concentration profiles determined from imaging data. The agreement is good within the region where edge-enhancement effects are not present. The modeling approach is exact and is applicable for modeling delithiation of any Li-containing electrode.

The research also successfully demonstrated that Li concentration profiles within the electrodes of small coin cells could be successfully measured using neutron computed tomography. Sufficient imaging contrast between lithiated/delithiated states of vanadium oxide electrodes was demonstrated. Li spatial distribution was found to be non-uniform within the bulk vanadium oxide cathodes, and the non-uniformity is higher in the electrode where lithiation occurred relatively faster during the discharge (lithiation). However, during charge (delithiation) no pronounced difference in non-uniformity of Li spatial distribution was observed between the two rates. In addition, the differences in the capacity during charge and the terminal potential after full discharge, between the two different C-rates were found to correlate qualitatively the neutron attenuation map and the distribution of Li within vanadium oxide.

c. What opportunities for training and professional development has the project provided?

Two PhD level graduate students were employed during the course of this research. The research project enabled successful completion and graduation of the two students. The names and the thesis titles of these students, and their current employment, are given below.

1. Name: Dr. B. Vadlamani
PhD Thesis Title: In Situ Neutron Diffraction Studies on Li-ion Battery Electrodes
Graduation Date: 12/31/2017
Present Employment: Intel Corporate Research & Development, Salem, OR

The above student was trained in microfabrication and characterization of of Si such that he developed an in-depth knowledge of Si and its etching behavior. This has helped him in getting hired at Intel.

2. Name: Dr. Y. Zhang
PhD Thesis Title: Neutron Tomographic Imaging of Li ion batteries
Graduation Date: 5/31/2017
Present Employment: Spallation Neutron Source, Oak Ridge National Laboratory, TN

The above student developed and mastered techniques of neutron imaging, and digital methods of analysis of neutron tomographic data. Based on these skills, he has been hired by Oak Ridge National Laboratory to continue to work there as research scientist.

d. How have the results been disseminated to communities of interest?

The results of research were disseminated by two ways:

1. Conference Presentations:

A list of conference presentation are presented in section 3 of this report.

2. Other Presentation:

The presentations were made to fellow scientists in program review meetings and in visits to Oak Ridge National Laboratory.

e. What do you plan to do during the next reporting period to accomplish the goals and objectives?

Not Applicable. This is final report.

3. PRODUCTS:

a. Publications, conference papers, and presentations

i. Journal publications.

1. Y. Zhang, K. S. Ravi Chandran, H. Z. Bilheux, "Imaging of the Li spatial distribution within V_2O_5 cathode in a coin cell by neutron computed tomography," Journal of Power Sources, Vol. 376, 2018, pp. 125-130
2. Y. Zhang, K. S. Ravi Chandran, M. Jagannathan, H. Z. Bilheux, and J. C. Bilheux, "The Nature of Electrochemical Delithiation of Li-Mg Alloy Electrodes: Neutron Imaging and Modeling of Delithiation Phenomenon," Journal of The Electrochemical Society, Vol. 164, 2017, pp. A28-A38.
3. B. Vadlamani, K. An, M. Jagannathan, K.S.R. Chandran, "An In-Situ Electrochemical Cell for Neutron Diffraction Studies of Phase Transitions in Small Volume Electrodes of Li-Ion Batteries," Journal of The Electrochemical Society, Vol. 161, 2014, pp. A1731-A1741
4. M. Jagannathan, K. S. Ravi Chandran, "Analytical modeling and simulation of electrochemical charge/discharge behavior of Si thin film negative electrodes in Li-ion cells," Journal of Power Sources, Vol. 247, 2014, pp. 667-675
5. M. Jagannathan, K. S. Ravi Chandran, "Electrochemical Charge/Discharge Behavior and Phase Transitions during Cell Cycling of Li (Mg) Alloy Anodes for High Capacity Li Ion Batteries," Journal of The Electrochemical Society, Vol. 160, 2013, pp. A1922-A1926
6. B. Vadlamani, M. Jagannathan and K. S. Ravi Chandran, "Energy Storage Capacity and Electrochemical Cyclability of Si Porous/Columnar Structures as Anodes for Li-ion Batteries," ACS Energy Materials, Accepted for Publication, Jan. 2018.

ii. Books or other non-periodical, one-time publications. None.

iii. Other publications, conference papers and presentations.

1. B. Vadlamani, K. An, K.S. Ravi Chandran, "In Situ Neutron Diffraction Investigation of Lithiation Phenomenon and Formation of Mosaic Structure in Columnar Si (100) Electrodes for Li-Ion Batteries," Symposium CM04: In Situ and Operando Characterization of Materials

and Devices by X-Ray and Neutron, 2018 Materials Research Society Spring Meeting, Phoenix, April 4, 2018.

2. Y. Zhang, K. S. Ravi Chandran, H. Z Bilheux, M. Jagannathan. “Investigation of Li Spatial Distribution inside Bulk Li-Mg Alloy Electrode after Delithiation Using Neutron Imaging, Symposium on Energy Storage VI: Materials, Systems and Applications, MS&T 2016 Conference, Oct 23, 2016
3. B. Vadlamani, K. An, M. Jagannathan, K.S. Ravi Chandran, “In situ Electrochemical Cell for Neutron Diffraction Studies of Phase Transitions in Small Volume Electrodes of Li-Ion Batteries,” Symposium EE4: Electrode Materials and Electrolytes for Lithium and Sodium Ion Batteries, 2016 Materials Research Society Spring Meeting, Phoenix, March 27-31, 2016.
4. M. Jagannathan and K. S. Ravi Chandran, “Analytical Modeling and Simulation of Electrochemical Charge/Discharge Behavior of Li-ion Cells with Si Thin Film Negative Electrodes" 2nd World Congress on Integrated Computational Materials Engineering (ICME), Salt Lake City, July 7-11, 2013.
5. M. Jagannathan, K. S. Ravi Chandran, and Joshua E. Ramos, "Energy Storage Capacity and Cyclability of Si Anodes with Nanoscale Columnar Structure for Li-ion Batteries", Symposium F: Materials for Vehicular and Grid Energy Storage, 2013 Materials Research Society Spring Meeting, San Francisco, April 1-5, 2013.
6. M. Jagannathan and K. S. Ravi Chandran, "Computational Modeling of Electrochemical Charge/Discharge Behavior of a-Si Thin Film Anodes in Li-ion Cells", Symposium G: Electrochemical Interfaces for Energy Storage and Conversion- Fundamental Insights from Experiments and Computations, 2013 Materials Research Society Spring Meeting, San Francisco, April 1-5, 2013.

b. Website(s) or other Internet site(s)

None

c. Technologies or techniques

A successful design of in situ electro-chemical cell for the ND beam experiments was achieved and several cells were manufactured for experiments. Several validation experiments were successfully run with this cell. This cell uses small volume electrodes for neutron diffraction experiments.

This in situ cell is shared with researchers at the Oak Ridge National Laboratory, for those interested in using the cell for in situ electrochemical experiments at Spallation Neutron Source.

d. Inventions, patent applications, and/or licenses

None

e. Other products

None

4. PARTICIPANTS & OTHER COLLABORATING ORGANIZATIONS: Optional

a. What individuals have worked on the project?

A. Principal Investigator:

Name: Dr. Ravi Chandran
Total Number of Months: 3.0
Project Role: Principal Investigator
Researcher Identifier: NA
Contribution to Project: Provided project direction and management and scientific guidance
State, U.S. territory, and/or country of residence: UT, U.S.A.
Collaborated with individual in foreign country: No
Country(ies) of foreign collaborator: NA
Travelled to foreign country: No

B. Graduate Students:

Name: B. Vadlamani
Total Number of Months: 41
Project Role: Graduate Research Assistant
Researcher Identifier: NA
Contribution to Project: Built the in situ cell, travelled to ORNL and performed experiments
State, U.S. territory, and/or country of residence: UT, U.S.A.
Collaborated with individual in foreign country: No
Country(ies) of foreign collaborator: NA
Travelled to foreign country: No

Name: Y. Zhang
Total Number of Months: 36
Project Role: Graduate Research Assistant
Researcher Identifier: NA
Contribution to Project: Created electrodes/cells and travelled to ORNL to perform imaging
State, U.S. territory, and/or country of residence: UT, U.S.A.
Collaborated with individual in foreign country: No
Country(ies) of foreign collaborator: NA
Travelled to foreign country: No

b. Has there been a change in the active other support of the PD/PI(s) or senior/key personnel since the last reporting period?

Nothing to Report.

c. What other organizations have been involved as partners?

Nothing to Report.

d. Have other collaborators or contacts been involved?

Two collaborators from Oak Ridge National Laboratory were involved in research during the course of this project.

Name: Dr. Ke An
Total Number of Months: ~1.5
Project Role: Collaborator at SNS, Oak Ridge National Laboratory
Researcher Identifier: NA
Contribution to Project: Provided assistance for Vulcan Experiments
State, U.S. territory, and/or country of residence: TN, U.S.A.
Collaborated with individual in foreign country: No
Country(ies) of foreign collaborator: NA
Travelled to foreign country: No

Name: Dr. H. Bilheux
Total Number of Months: ~1.5
Project Role: Collaborator at SNS, Oak Ridge National Laboratory
Researcher Identifier: NA
Contribution to Project: Provided assistance for Imaging Experiments in CG-1D beamline
State, U.S. territory, and/or country of residence: TN, U.S.A.
Collaborated with individual in foreign country: No
Country(ies) of foreign collaborator: NA
Travelled to foreign country: No

5. IMPACT: Optional

a. What was the impact on the development of the principal discipline(s) of the project?

The present study demonstrated that the tools of physics can be used to understand scientific phenomena involved in energy storage batteries. Batteries are ever increasing commodities and there is constant need to find better and higher capacity batteries. The scientific understanding provided by this research helped to discover new materials for building better batteries and new diagnostic ways to study the performance of batteries.

b. What was the impact on other disciplines?

Nothing to Report

c. What was the impact on the development of human resources?

The project contributed significantly in human resource development, that is training of two scientists (starting as graduate students and completing successfully their PhD theses) in the filed of materials science. More details are in section 2.

d. What was the impact on teaching and educational experiences?

Nothing to Report

e. What was the impact on physical, institutional, and information resources that form infrastructure?

Nothing to Report

f. What was the impact on technology transfer?

The project has resulted in a method to make microcolumar Si that could serve as a potential electrode for Li-ion batteries. An invention disclosure will soon be filed with respect to the technology of making columnar Si electrodes, as developed in this research. This will potentially lead to the filing of a US patent.

g. What was the impact on society beyond science and technology?

Nothing to Report

h. What percentage of the award's budget was spent in foreign country(ies)?

None. 100% was spent in USA.

6. CHANGES/PROBLEMS: Optional

No changes from the original project objectives and plan. So nothing to report here.

7. SPECIAL REPORTING REQUIREMENTS: Mandatory

No special reporting requirements were specified in the award terms and conditions.

8. BUDGETARY INFORMATION: Mandatory

This is provided separately by Office of Sponsored Projects, through form SF-425

9. PROJECT OUTCOMES: Optional

(i) Design, construction of demonstration of an electrochemical cell for neutron studies

Lithium based energy storage material is the primary focus of energy storage research now, and will be in future, because the performance of today's Li-ion batteries is far below the target for adaptation in transportation, wind and grid-scale energy storage applications. A major challenge in Li-ion battery materials science, however, is the lack of knowledge about how Li is stored in the electrodes during charging or discharging and how the electrode can be structured to maximize the energy storage capacity. Neutron diffraction, especially *in operando* studies, can make a great impact in this field, by helping to reveal the nature of *bulk* phase transitions that occur, the phases that form, and their correspondence to specific cell voltages or trends during charging or discharging. There are distinct advantages of neutron diffraction, especially for the *in operando* studies of lithiation/delithiation phenomena of battery electrodes. Although lithiation of battery electrodes can be studied using other tools such as X-ray diffraction (XRD) or electric impedance spectroscopy (EIS), these techniques are limited in various ways. Conventional XRD has a limited depth of penetration, revealing only details close to the surface. Practical electrodes that are of interest are ~100 μm in thickness, so the entire volume of which cannot be examined by conventional XRD. In-operando experiments, where ND diffraction patterns can be obtained while the battery is electrochemically cycled, can provide a wealth of information that can be gathered in a single experiment. However, this requires a reliable electrochemical cell that can be placed in the neutron diffractometer. In completed research, neutron diffraction of small volume electrodes were investigated using an *in situ* cell.

One major outcome is the successful construction of an electrochemical cell (Figure 1) for neutron diffraction investigations of Li-ion battery electrodes. This cell allows very small volumes of electrodes for experiments, hence is superior to many cells that have been constructed before. The phase transitions could be studied in a better way using this cell.

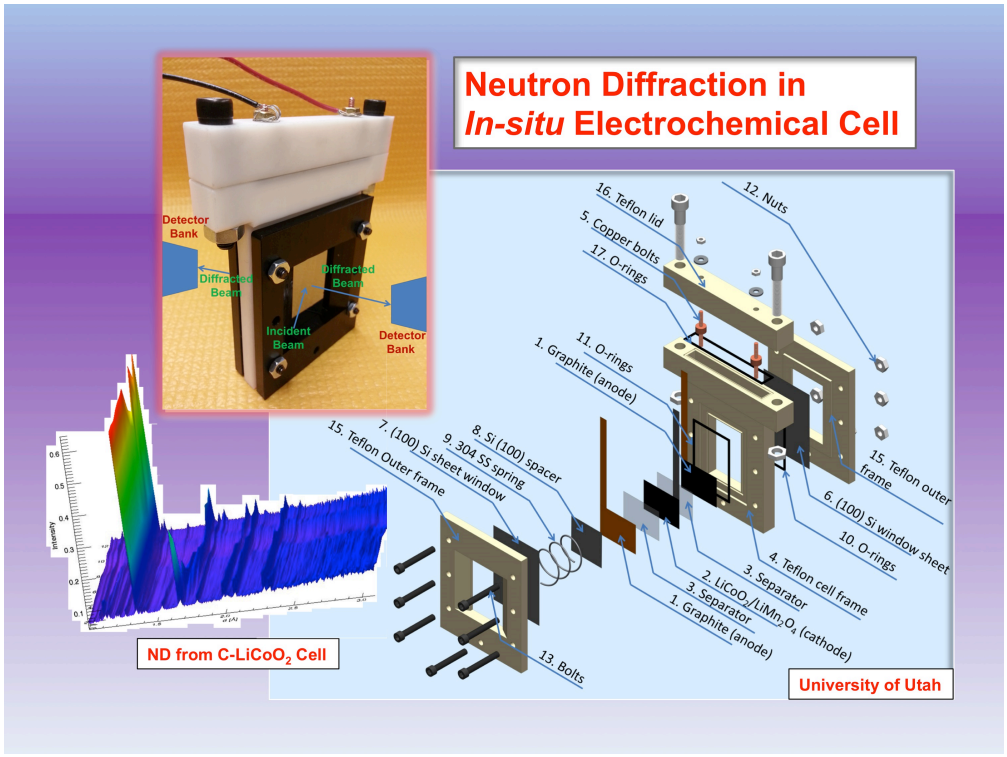

Figure 1. Exploded view of in situ electrochemical cell design and construction.

(ii) Discovery and the making of microcolumnar Si electrodes

In this research, it was discovered that small variations in micro-columnar/porous architecture of Si greatly alters the electrode performance in terms of capacity and reversibility. By architecture we mean Si column thickness, depth and contiguity and other subtle morphological parameters. Figure 2 shows (top and side views) some structures that were created in the experiments.

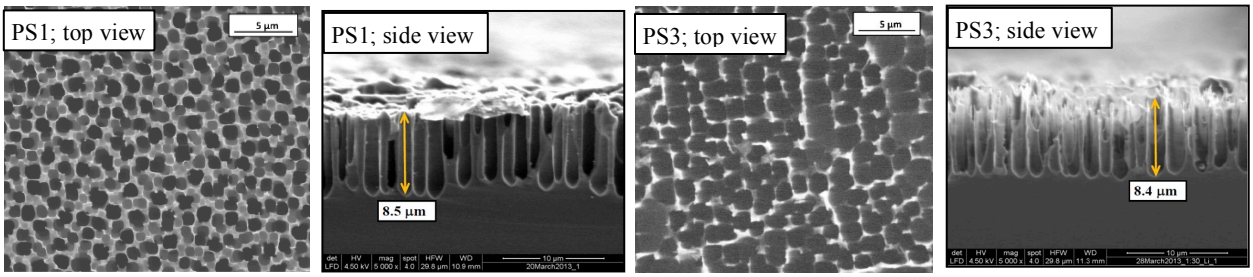

Figure 2. Si micro-column/pore morphologies that can produced by the technique developed

The Si electrodes were created by electrochemical etching of (100) Si wafers in an electrolyte at varied potential/current conditions. These Si electrodes are novel and there are several interesting aspects or attributes of the Si micro-column architecture that are interrelated. They all will affect

the Si electrode lithiation performance. A thinner Si column/wall increases the extent of Li insertion/removal (and facilitates higher C-rates) in a Li-ion battery. The porous structure increase the ionic transport. Both factors have been found to contribute to high Li storage capacity.

The structures also lead to a large variation of surface to volume ratio of Si columns in different column architectures, which is desirable for finding an optimum electrode structure. The pore shape and its connectivity was found to help accommodate the volume changes during Li insertion. The research has created a rich set of variants of Si morphology, which are of great interest in finding good electrodes for high capacity Li-ion batteries.

(iii) 3D imaging of Li coin cells

An understanding of Lithium (Li) spatial distribution within the electrodes of a Li-ion cell, during charge and discharge cycles, is essential to optimize the electrode parameters for increased performance of Li-ion batteries.

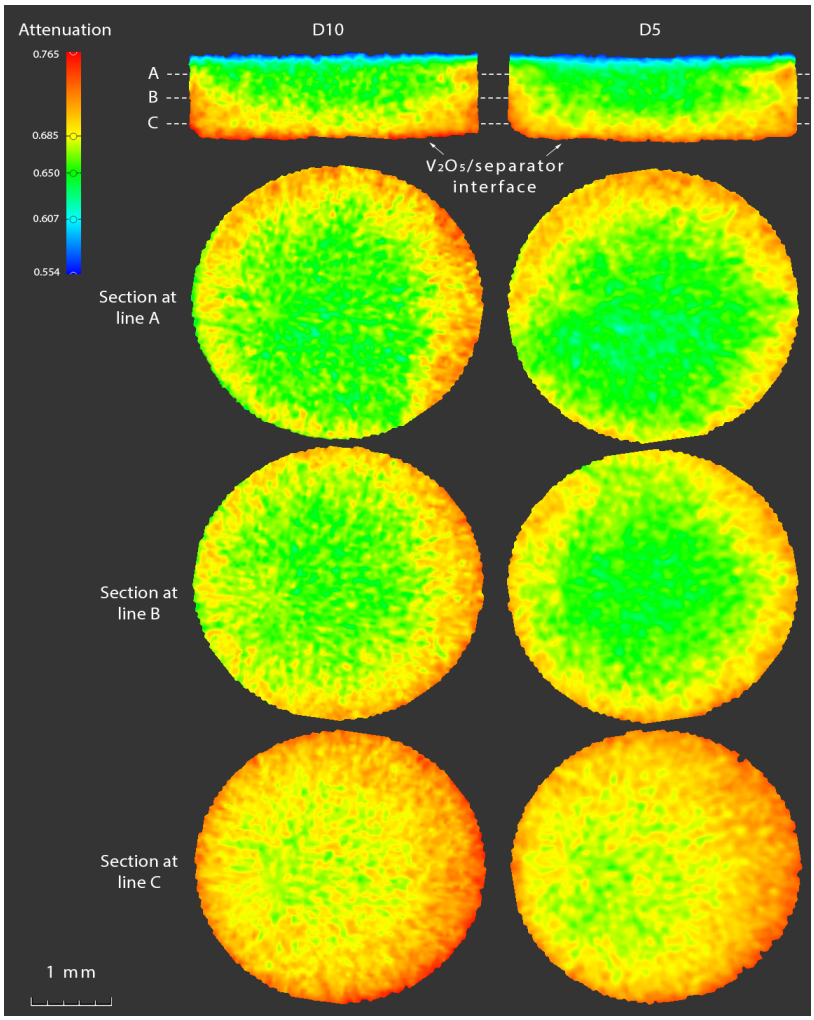

Figure 3. Neutron tomographic imaging of Li button cells

The research also demonstrated that the spatial distribution of Li within vanadium pentoxide electrodes of a small coin cell could be imaged by neutron computed tomography. The neutron

attenuation data was successfully used to construct the three-dimensional Li spatial images. Specifically, it was shown that there is sufficient neutron imaging contrast between lithiated and delithiated regions of vanadium pentoxide electrode making it possible to map Li distributions even in small electrodes with thicknesses < 1 mm. The images reveal that the Li spatial distribution is inhomogeneous and a relatively higher C-rate leads to more non-uniform Li distribution after Li insertion. The non-uniform distribution suggested the limitation of Li diffusion within the electrode during the lithiation process under the relatively high cycling rates.

APPENDIX

DEMOGRAPHIC INFORMATION FOR SIGNIFICANT CONTRIBUTORS

1. Name: Ravi Chandran
Gender: Male
Ethnicity: Not-Hispanic or not-Latino
Race (select one or more): Asian
Disability Status: Not Disabled

2. Name: B. Vadlamani
Gender: Male
Ethnicity: Not-Hispanic or not-Latino
Race (select one or more): Asian
Disability Status: Not Disabled

3. Name: Y. Zhang
Gender: Male
Ethnicity: Not-Hispanic or not-Latino
Race (select one or more): Asian
Disability Status: Not Disabled