

Acoustic Emission and X-Ray Diffraction Techniques for the In Situ Study
of Electrochemical Energy Storage Materials

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Abstract

Current demands on lithium ion battery (LIB) technology include high capacity retention over a life time of many charge and discharge cycles. Maximizing battery longevity is still a major challenge partly due to electrode degradation as a function of repeated cycling. The intercalation of lithium ions into an active material causes the development of stress and strain in active electrode materials which can result in fracture and shifting that can in turn lead to capacity fade and eventual cell failure. The processes leading to active material degradation in cycling LIBs has been studied using a combination of acoustic emission (AE) and in situ X-ray diffraction (XRD) techniques. Safe, low cost custom electrochemical cells were designed and developed for use in battery AE and XRD experiments. These tools were used to monitor the time of material fracture through AE and link these events to lattice strain and phase composition as determined by XRD. Both anode and cathode materials were studied with an emphasis on graphite, silicon, and $\text{Li}(\text{Mn}_{1.5}\text{Ni}_{0.5})\text{O}_4$, and tin. A thermal analogy model for lithiation/delithiation induced fracture of spherical particles capable of predicting when AE should be detected in a cell containing a composite silicon electrode. The results of this work were used to develop an understanding of when and how active materials are degrading as well as to suggest methods of improving their performance and operational longevity.

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Abbreviations

AE	Acoustic Emission
a-Si	Amorphous Silicon
c-Si	Crystalline Silicon
CCCV	Constant Current-Constant Voltage
ΔT	Thermocouple
EC	Ethylene Carbonate
EMC	Ethyl Methyl Carbonate
EMI	Electromagnetic Interference
FFT	Fast Fourier Transformation
LIB	Lithium Ion Battery
LiPF ₆	Lithium Hexafluorophosphate
NDE	Non-destructive Evaluation
Ni-MH	Nickel-Metal Hydride
NMP	N-Methyl-2-pyrrolidone
OM	Optical Microscopy
PC	Propylene Carbonate
PVDF	poly(vinylidene fluoride)
SEI	Surface Electrolyte Interphase
SEM	Scanning Electron Microscopy
TEC	Thermo-electric cooling stage
XRD	X-ray Diffraction

Variables

β	Full with – half maximum
c	Lithium concentration
d	Inter-planar distance
D	Damage parameter
D_{Li}	Diffusion coefficient
e	Dilatational strain
E	Modulus of elasticity
$\tilde{E}^+$	Modulus of elasticity in tension
$\tilde{E}^-$	Modulus of elasticity in compression
F	Faraday constant
K	Shape factor
h	Material constant related to partial closure of micro defects
i_s	Surface current density
J	Flux
λ	X-ray radiation frequency
m	Weibull modulus
P_{f1}	Probability of fracture
r	Radial coordinate
R	Gas constant
R_0	Radius of the particle
t	Time
τ	Estimated crystallite size
T	Temperature
θ	Incident angle of X-rays with the sample surface
α	Coefficient of thermal expansion
δ_{ij}	Kronecker delta
ε_{ij}	Components of strain tensor

ε_r	Radial component of strain
ε_t	Tangential component of strain
n	Order of X-ray reflection
$\vec{\eta}_k$	k^{th} eigenvector of stress tensor
ν	Poisson ratio
σ_{eq}	Equivalent stress
σ_H	Hydrostatic stress
$\langle \sigma \rangle_{ij}^+$	Components of stress tensor
σ_k	k^{th} eigenvalue of stress tensor
σ_r	Radial component of stress
σ_t	Tangential component of stress
σ_{VM}	Von Mises stress
σ_w	Weibull stress
$\langle \sigma \rangle_{ij}^+$	Positive part of stress tensor
$\langle \sigma \rangle_{ij}^-$	Negative part of stress tensor
χ	Triaxiality parameter
Ω	Partial molar volume
$tr(\sigma)$	Trace of tensor σ
$\langle \rangle$	Macauley bracket

Chapter 1: Introduction and Motivation

1.1 Rechargeable Batteries

The capture, storage, and distribution of energy are among the most pressing challenges currently facing modern society. Climate control, communications, logistics, and national defense all rely heavily on the availability of a safe, reliable, and continuous supply of clean power. Furthermore, environmental concerns are becoming more and more imposing as we begin to see the deterioration of the ozone layer and the onset of global warming conditions. With an every growing world population and limited oil supplies, the development of efficient portable energy supplies is also a matter of national security since it may help reduce the countries reliance on foreign oil by allowing the distribution of energy that is centrally generated by means of natural gas and nuclear or harvested from solar, hydro-electric, or wind power stations. Technologies that can provide an ever growing, energy hungry population with clean power must be developed in order to preserve the planet while maintaining the quality of life to which billions have grown accustomed.

The storage and portability of energy is a major issue in improving the energy chain. Renewable energy sources such as solar and wind are clean but fluctuate too much to make them a viable direct power source. An electrochemical energy storage (EES) device is needed to store energy when it is available and then allow for its controlled release when a demand is present. In a similar manner, EES devices are needed to buffer power grids due to periodic fluctuation in demand. Mobile electronic devices including cell phones and laptop computers require a light weight and high capacity EED device to make them portable and able to operate for long intervals away from a power outlet. Electrical vehicles (EV) and hybrid electrical vehicles (HEV) aimed at reducing harmful emissions and reducing the nation's dependence on oil, much of which is imported at high cost from countries with which America has strained relations, will also require a high energy density (the amount of energy stored per unit weight, often expressed in mAh/g or Ah/kg) plus a fast charge rate and high power output. On top of all of these demands, modern EES devices must be safe, long lasting, and cost effective.

The use of portable EES devices has become wide spread over the past couple decades and has been the focus of extensive research efforts [1]. In the case of lithium ion

batteries (LIB), one of several promising types of EES devices first commercialized by Sony in 1991, annual worldwide production numbers in the billions with applications including cell phones, laptop computers, power tools, and next generation EVs and HEVs [2]. As the third lightest element at 6.941 g/mol and also the most strongly reducing with a standard potential of -3.04V , lithium can provide much higher energy densities than lead acid, nickel-cadmium, or nickel-metal hydride (Ni-MH) batteries [3] allowing for lighter and more compact portable EES devices. In addition, lithium is abundant in the earth's crust and has a low toxicity making it an excellent choice for mass produced consumer devices. The relatively high operating voltage and broad window of operating temperature [4], owing to the use of organic electrolytes, makes LIB well suited for many specialized applications.

Current demands on EES technology include high capacity retention over a life time of many charge and discharge cycles. Maximizing battery longevity is still a major challenge partly due to electrode degradation as a function of repeated cycling [2]. In the case of LIBs, the lithiation and delithiation of active materials, accomplished through an intercalation, alloying, or conversion reaction, is a non-equilibrium process and sets up concentration gradients in the material that cause the development of stress and strain gradients both inside the active material and in the surrounding composite matrix. The presence of the lithium atoms causes host atoms of the active material to be stretched from their original lattice positions. In some cases this can lead to phase change or amorphization of the active material which can cause degradation of its electrochemical properties. Furthermore, if the yield strength of the active material is exceeded particles may fracture. If this occurs, new surface area will be exposed where side reactions with the electrolyte can take place. In addition, fractured active material may lose contact with the current collector prohibiting it from taking part in further cycling processes. These effects can reduce the capacity of a cell and, over the course of many cycles, ultimately lead to cell failure. Similar degradation processes are present in other types of EES devices.

Several materials characterization techniques including X-ray diffraction (XRD) [5, 6, 9-11], scanning electron microscopy (SEM) [8, 12], transmission electron

microscopy (TEM) [13, 14], nuclear magnetic resonance [15], atomic force microscopy [7, 16-18], Raman infrared spectroscopy [18-21], and optical microscopy [22] can provide a glimpse of the inner workings of EES devices. Each of these tools can provide important information but also has its own set of limitations. As battery technology continues to improve new tools will be needed in order to develop a deeper understanding of these devices.

1.2 Project Motivation

The production of advanced EES devices with increased specific capacities and prolonged operational lifetimes is largely dependent upon the establishment of a comprehensive understanding of in situ (meaning under the actual operating conditions of the cell) active materials behavior and degradation. By identifying how and when various material changes are occurring, researchers can more efficiently direct their efforts towards the development of advanced material chemistries, modifications, and manufacturing processes. Although several powerful techniques are available to characterize various aspects of EES device performance, very little work on the physical degradation of active materials caused by cycling induced stress has been performed and few characterization methods are suitable for studying this phenomenon.

Acoustic emission (AE) is a diagnostic technique often used for non-destructive evaluation (NDE) applications wherein high frequency sounds emanating from a sample are recorded by a piezoelectric transducer mounted on the samples surface. The recorded signals, known as hits, result from source events such as cracking, bubbling, or phase transitions in the sample. With recent improvements in computer technology and the ability to store and manipulate large volumes of data, AE has become a powerful tool for in situ monitoring of a material or structures internal processes [23]. However, few attempts to apply AE to EES devices have been published.

Ideally, the information about when a crack event occurs in a battery that could be provided by AE would be coupled with information about the state of stress and phase composition within the active material. XRD is the standard method for measuring lattice parameters and indentifying phases in a laboratory setting, however, the task of looking

inside an operational cell to track changes to materials as they are cycled presents special challenges. Although a synchrotron source may be able to perform such in situ studies on an unmodified EES device, a special cell design is required that allows X-ray penetration to the active material when using a standard laboratory diffractometer. However, because beam time on synchrotron sources is very limited and expensive, the ability to conduct in situ XRD studies in a laboratory setting has a value that far exceeds its limitations. By designing an in situ XRD cell such that it permits simultaneous AE sensing, it may be possible to make direct correlations between AE and XRD data.

1.3 Scope of Work

A novel in situ AE-XRD cell was developed and tested to see if any direct correlation between AE hits and active material internal stress/strain was identified. This cell is capable of being used with both cathode and anode materials and of providing data similar to that obtained from a synchrotron beam while using only a laboratory diffractometer. This cell offers a cheap, safe, and easy to use method of performing lab based in situ XRD measurements on cycling electrochemical systems which will allow for its future wide spread application and a means of providing preliminary data for the intelligent design of more costly and time limited synchrotron beam experiments.

Using AE, recorded emissions have been correlated with cycling parameters including voltage, capacity, cycle stage (charge or discharge), and cycle number. The source of different emission types was identified using SEM, cycling data, AE test parameter variation, and available literature. Data mining of the extracted waveform parameters was conducted to identify trends and statistical averages. These findings served as a baseline for the application of these novel combined in situ techniques.

Ultimately the work presented here aimed to develop in situ characterization methods capable of guiding the development of improved electrode materials and cell assemblies as well as providing a powerful NDE tool for the study of a wide range of current and future EES devices. In this work, in situ AE and XRD techniques were applied to LIB devices built with different active materials in order to identify and characterize the degradation behavior of each. LIBs were selected as the subject EES

device because of their widespread implementation and promise in many cutting edge technologies such as EVs and HEVs.

The data collected has been used to develop a depictive model of how active material particles fracture and degrade due to cycling. In addition, the newly developed in situ XRD technique has been applied to the study of phase change behavior evolution due to cell cycling and to investigate the internal processes of new styles of lithium ion batteries including those with thin film electrodes. This work will set the ground work for the use of these in situ AE and XRD techniques in the study of other types EES devices.

A range of active materials were explored using the techniques developed in this work both to show the robustness of these characterization tools and to provide insight to the specific degradation behavior of several materials currently of interest to the EES research community. The LIB materials studied in various parts of this work were selected based on special features of each. Initially, graphite anodes were used because of their omnipresence in current commercial LIB devices. Any information gleaned from the study of this material has a direct and immediate impact on the state of LIB technology. Silicon was studied because it is known to undergo extensive fracturing during cycling which made it an ideal material for the development of AE techniques. Additionally, if progress can be made in reducing this degradation in silicon it could be an excellent anode material due to its availability, safety, and extremely large specific capacity. For the application of in situ AE and XRD techniques to cathode materials, $\text{Li}(\text{Mn}_{1.5}\text{Ni}_{0.5})\text{O}_4$ was used because of its possible high power applications and the presence of several interesting phase changes that occur during its charge and discharge. Finally, tin was explored in the form of thin film electrodes because of the many phase changes that lithiated tin undergoes as well as the ease of preparation of high quality tin thin films. This made tin an ideal candidate for the development of in situ XRD techniques for thin film electrode applications.

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Chapter 2: Background Review

2.1 Lithium Ion Battery Operation

When set to work inside a LIB, lithium moves between two electrodes through an electrolyte soaked porous separator as show in Fig. 1. Note that all tables and figures are located in the appendix. In discharge, lithium ions migrate through the electrolyte from the anode to the cathode as a current travels through an external load from the cathode to the anode (electrons moving from the anode to cathode). Conversely, during charge the lithium ions migrate from the cathode to the anode as the external current flows from the anode to the cathode (electrons moving from cathode to anode). Composite electrodes (aka paste electrodes) are made of small particles of an active material mixed with a polymeric binder and a conductive additive that is laminated onto a current collector. Thin film electrodes may also be made by sputtering or evaporating the desired active material onto a current collector. Although the principle of operation is fairly simple, the reality inside a LIB is far more complex and processes that limit the systems efficiency and degrade its performance can occur.

During cycling, lithium ions enter the active materials by one of several processes including intercalation, alloying, or conversion. Intercalation is the process by which a small atom or molecule is reversible inserted between two or more other atomic structures [1] such as planes of carbon in graphite. Intercalation of lithium occurs in many of the most common active materials for LIBs including graphite, LiCoO_2 , LiFePO_4 , and LiMnO_4 . In principal intercalation is a completely reversible process that does not alter the crystalline structure of the host material. However, in practice side reaction and electronic isolation of regions in the host material limit and degrade the efficiency of this process.

Alloying is another method of lithium storage observed for some active materials such as silicon, tin, and germanium [1]. Here, lithium enters the crystalline material extensive reordering of the host lattice may be observed which is not always highly recoverable. Conversion type electrodes undergo a reaction as shown below which creates transition metal nano-domains and some lithium compound where $X = \text{H, N, O, F, P, or S}$ [2].



Regardless of the process by which lithium enters and exits a host material, some similar effects are routinely observed. The first of these is the formation of a film composed largely of LiF, Li₂CO₃, and alkylcarbonates known the surface electrolyte interphase (SEI) [3]. The SEI is formed due to the decomposition of electrolyte at the solid/liquid interface. The initial formation of this layer is generally responsible for much of the irreversible capacity loss observed during the first cycle of a cell. In this case a considerable fraction of the lithium that accounted for the observed discharge capacity is consumed by SEI formation and is no longer available for participation in useful energy storage reactions. The SEI layer formed is very important to LIB performance because all lithium ions must cross this layer before they can enter the active material.

The next commonly observed effect of lithium penetration into an active material is extensive volume dilation [4]. As lithium enters or exits a material a concentration gradient is developed. Since the material's volume is directly related to the concentration of lithium present, strain occurs within a particle of active material. This can lead to loosening of the binder material and particle fracture [5-7] which can cause a loss of contact with the current collector. Freshly exposed surface area may also lead to more SEI formation and a depletion of active lithium inside a cell.

2.2 Cycling Induced Stress and Damage

As previously stated, the lithiation/delithiation of an active material causes the development of stress and strains that can lead to fracture and degradation of the active material. Take for example a spherical particle of active material. As lithium enters at the outer surface, the concentration of lithium in the active material near the particle surface reaches levels significantly higher than that in the not yet lithiated core of the particle. As lithium is added to a material a volume expansion is generally observed. As a result the material near the particle surface is trying to expand as its lithium content is increased, but this expansion is resisted by the delithiated material near the core. This causes a

push/pull situation to develop along the particles radius where the surface material is in compression and the core material is in tension. Similarly, when a fully lithiated particle is delithiated a state of tension occurs on the particle surface relative to the core and surface fracture may occur.

How the stress field inside a particle develops is dependent on many factors including particle shape, size, lithium diffusivity, anisotropy, electronic conductivity, and cycling conditions. Furthermore, whether a given particle will fracture under a certain stress condition depends on additional material properties including ductility, grain structure, volume dilation, and the presence of any stress concentrators such as voids, inclusions, or micro-cracks. Obviously this problem becomes very complicated when applied to a real system. Several groups have attempted to model the stress state of a particle of active material using different approaches.

The Christensen-Newman model was developed in 2006 and describes the stress state as a function of radius in a homogeneous and isothermal spherical particle [8]. This work included effects of diffusion coefficient, charge rate, and particle size. Parameters representative of carbonaceous materials generally used in LIB applications were used. Results showed that maximum tangential stresses in the particle occurred in the center of the particle near the start of lithiation and at the particle surface at the beginning of delithiation. A significant finding of this work is that pressure driven diffusion of lithium plays an important role in what stresses are experienced in the material. Additionally, stresses in the particle increase as the Poisson's ratio of the active material is increased.

Later that same year the Christensen-Newman model was extended to be applicable to systems with a two phase moving boundary [9]. When a certain lithium concentration is reached a material can shift from one atomic arrangement to another. It is not uncommon for these phases to have quite dissimilar lattice parameters or even completely different space groups which can cause a stress at the phase boundary. $\text{Li}_x\text{Mn}_2\text{O}_4$ is known to undergo a Jahn-Teller distortion to go from a cubic to tetragonal spinel phase at low potentials. Modeling of this material shows that the moving phase boundary should indeed increase the stress maximum in the material and could be a likely cause of fracturing.

After the papers out of the Sastry group modeled the stress in a particle by analogy with a thermal stress model [10, 11], the results agreed with previous work showing that increased particle size and cycling rate increased the maximum stress observed. This work also showed that the maximum stress could be significantly affected by aspect ratio with a peak in stress levels occurring at about 1.5 and diminishing thereafter.

In 2009, Verbrugge and Cheng published a model based on strain-energy density in cyclically deformed electrode particles [4]. This approach allows for the fatigue induced degradation of the material where the cumulative strain-energy density in a region is used to determine the likelihood of failure. Strain-energy density calculations offer the advantage of accounting for surface tension and surface modulus. A major finding of this work was that the maximum tensile and shear stresses occur just after the switch from lithium insertion to extraction and are found at the particle surface. This transient stress, which diminishes as the system approaches a steady state, indicates that fracture should occur at the particle surface.

2.3 Acoustic Emission

A rarely exploited technique capable of providing a unique perspective in LIB research is acoustic emission (AE). In AE a piezoelectric sensor is used to record mechanical vibrations emanating from a sample as in Fig. 2. When yielding or fracturing of a material occurs, strain energy is released from a localized point into its surroundings. A transient elastic stress wave propagates away from its source and can be detected by a sensor coupled to the sample [12]. This process is analogous to an audible sound wave propagating through the air and causing a displacement of a microphone's diaphragm. Also, just as the voices of a man and a woman can generally be discerned from a recording so can certain properties about the event that generated a given acoustic emission hit.

AE studies fall into one of two categories: parameter-based or signal-based. In parameter-based studies each hit is recorded as a set of variables that describe the signal but no waveform is stored. In contrast, a signal-based study records the waveform of each hit from which many parameters can be extracted. Due to the large amount of computer

speed and memory needed to record all of the waveforms in a study, signal-based techniques have only become available in recent years. The signal-based approach offers the advantage of extensive post processing options and a graphical view of each waveform.

Each recorded waveform can be described using parameters such as duration, amplitude, counts, and frequency as depicted in Fig. 3. Careful assessment of the sample can help identify the specific source of different AE event types. When accomplished, AE can provide a convenient method of in situ monitoring capable of assessing both when and what events are occurring [13]. By using an array of several sensors affixed to a sample at known locations, the location where an AE hit was emitted may be triangulated based on the time that the hit reaches each sensor.

2.4 X-ray Diffraction

XRD has the ability to provide detailed structural information about atomically ordered materials [14]. Just as light can be diffracted by a plane of slits, X-rays can be diffracted by planes of atoms because the wavelength of the radiation is on the same order or magnitude as atomic spacing. The underlying physics of the diffraction process is shown in Fig. 4. From this diagram of the fundamental equation of XRD, Bragg's Law shown in Eqn. 1 can be derived where θ is the incident angle of the X-rays with the sample surface, λ is the X-ray frequency, d is the inter-planar distance, and n is the order of the reflection.

$$2d \sin(\Theta) = n\lambda$$

Eqn. 1: Bragg's Law.

From Bragg's Law it is obvious that the diffraction angle is inversely related to the plan spacing. This means that for a crystal with a small planar spacing, such as a metal, peaks can be expected at higher angles than for materials with larger spacing of their atomic planes such as ceramics and polymers. By rotating a single crystal in 3D the

spacing and special relationship between all of the atomic planes can be determined and a detailed crystal structure may be constructed.

In powder diffraction, a collection of many crystalline particles are used as a sample and diffraction peaks from all of the planes present (barring the presence of extensive preferred orientation) may be observed along a single arch. The position of these peaks is a measure of spacing between atomic planes, peak widths give information about crystallite size, and peak intensities can be used to determine atomic ordering on a given lattice and used to track the relative amount of phases present.

In practice, powder XRD is generally performed in reflection mode as shown in Fig. 5. Here the collimated X-ray beam emanates from an X-ray tube (normally having a Cu, Ag, or Mo target) and shines on the power sample. Any crystal planes correctly oriented with the incident beam will generate a constructive beam on the diffraction pattern. Since the crystals are randomly oriented (assuming no preferred orientation) then all orientations of each lattice plan are represented and a full diffraction pattern can be obtained by scanning the X-ray source/detector goniometer about a fixed axis. The term “powder” can be loosely interpreted to include many sample types from true crystalline powders to solid materials such as steel that are very polycrystalline.

Although powder diffraction is a powerful tool for identifying samples and determining the phase composition and atomic arrangements more rigorous applications can be used to study lattice strain and crystallite size. The stress-strain state of a deformed material can be determined by measuring plane spacing's, more commonly known as d-spacing. By knowing the d-spacing of an unstrained sample of the material and comparing this with spacing measured after some treatment the lattice strain may be measured. If the treatment is performed while XRD is performed this is considered an in situ experiment and the lattice strain, or some other parameter of interest, may be directly tracked as a function of the applied stimulus which could be an applied load or heat as an example. If the strain is occurring only in the elastic regime and the elastic modulus of the material is known the applied stress may be calculated.

Crystallite size plays an important role in determining the bulk properties of materials so its determination is often of practical interest. In cases where a phase

transformation occurs in a material it may also be important to determine how the new phases are growing and how their crystallite size changes in response to an applied stimulus. In other cases, the properties of nanoparticles or nanocrystalline aggregates are under study and crystallite size determination is extremely important in understanding the behavior of such materials.

As crystallite size becomes small, less than about 0.1 μm , the destructive interference caused by the lattice is no longer complete and waves near a constructive Bragg angle are no longer completely canceled out [14]. This actually occurs for any crystal that is not infinitely large but at dimensions above about 0.1 μm this effect becomes negligible small. The end effect is that diffraction peaks from samples with small crystallite size are broadened. Peak broadening can be used to estimate the crystallite size using the Scherrer equation shown below.

$$\tau = \frac{K\lambda}{\beta \cos \theta}$$

Eqn. 2: Scherrer equation

Here the crystallite size is given by τ , λ is the wavelength of the incident radiation, θ is the Bragg angle of the peak being used in the calculation, K is a shape factor related to the morphology of the crystallites of interest, and β is the width of the diffraction peak measured at half the peaks maximum intensity (aka full width-half maximum). In practice, the peak broadening due to instrument optics must be accounted for before crystallite size can be accurately calculated [14]. This is accomplished by taking an XRD scan of a very stable material standard with large crystallite size and very stable peak width such as Si, SiO₂, or LaB₆. As long as the same optics and scan parameters are used for the sample, the standard effect of instrument broadening may be accounted for.

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Chapter 3: Acoustic Emission from MCMB Electrodes in Cycling Lithium Ion Cells

3.1 Disclosure

This chapter is based on the manuscript submitted to the Journal of the Electrochemical Society (J. Electrochem. Soc., (In Review)). The full list of authors includes Kevin Rhodes, Nancy Dudney, Edgar Lara-Curzio, and Claus Daniel. The role of Kevin Rhodes was to design and perform all experiments, process and analyze all data, and prepare the manuscript for submission.

3.2 Abstract

Acoustic emissions (AE) from lithium ion cells with lithium foil anode and composite mesocarbon microbead cathode were studied under galvanostatic cycling. Likely sources of AE include solid electrolyte interphase (SEI) fracture, gas formation, particle shifting, and electromagnetic interference (EMI). Gas events were detected with greatest frequency and intensity during the first cycle. Fracture emissions were observed at a steady rate after about 40 cycles. Particle shifting emissions occurred primarily after about 40 cycles, possibly indicating a loosening of the binder matrix. Potential diagnostic and materials development applications of the presented AE techniques are discussed.

3.3 Introduction

Current demands on lithium ion battery technology include high capacity retention over a life time of many charge and discharge cycles. Maximizing battery longevity is still a major challenge partly due to electrode degradation as a function of repeated cycling. The intercalation and deintercalation of lithium ions from an active material causes the development of stress and strain both internally and in the surrounding composite matrix. If the yield strength of the material is exceeded fracture may occur immediately, but even at lower stress levels defects such as dislocations or interstitial atoms may pile up and eventually cause crack initiation and growth. Over time particles of active material may fracture and shift, losing electronic contact with the current collector, which leads to capacity fade and a decrease in a cell's operational life time. Models exist that can predict the stress and strain state in particles of active material caused by a flux of lithium [1-4].

Several techniques including X-ray diffraction (XRD) [5-7], environmental scanning electron microscopy (ESEM) [8], transmission electron microscopy (TEM) [9, 10], nuclear magnetic resonance (NMR) [11], atomic force microscopy (AFM) [12-14], Raman spectroscopy [14-16], and optical microscopy [17] can provide insight into the inner workings of lithium ion cells. Another less exploited technique capable of providing a unique perspective is acoustic emission (AE). In AE a piezoelectric sensor is coupled to and used to record mechanical vibrations emanating from a sample. This provides a convenient method of in situ monitoring capable of assessing both when and what types of events are occurring. Several groups have successfully applied AE to the study of electrode materials in various systems [18-23]. Ultimately the current work aims to develop AE methods capable of guiding the development of improved electrode materials and cell assemblies as well as providing a powerful non-destructive evaluation (NDE) tool for performance diagnostics and early failure detection of in-service cells.

Mesocarbon microbeads (MCMB) are a graphitic material commonly used in commercial lithium ion cells. Reasonable cost, high specific capacity (372 mAh/g), good cycling stability, and low environmental impact make it one of the best choices for an active anode material currently available [24, 25]. The results of an AE study of MCMB composite electrodes in lithium ion cells are reported here. Multiple event types were recorded and categorized using waveform and Fast Fourier Transform (FFT) data. Events in each category share a common source type likely attributed to solid electrolyte interphase (SEI) fracture, gas bubble formation, particle shifting, or electromagnetic interference (EMI). Evidence to support these event source assignments was compiled from SEM, complimentary AE tests, and a survey of previous published work. Scatter plots of emission parameters were explored as a method for high throughput emission grouping and computational filtering. A time resolved distribution of events is presented, and its relationship with cell capacity fade, is discussed.

3.4 Materials and Characterization

Loose MCMB particles and MCMB composite electrodes were provided by Hydro-Québec. Composite electrodes were 93.1%wt MCMB with polyvinylidene

fluoride (PVDF) binder and vapor grown carbon fibers as the conductive additive. Films stood 25 μ m on a 15 μ m thick Cu current collector. An active material density of 2.0 mg/cm² and theoretical capacity of 0.74 mAh/cm² were calculated.

Cells were constructed as shown in Fig. 6. Two Grade 304 stainless steel plates were used to sandwich a stack of 0.7mm thick Li foil as anode, Celgard 2325 separator, and a ½” circular disk (1.27 cm²) of MCMB composite electrode as cathode. Each disk had a theoretical capacity of 0.94 mAh. A 1.2M solution of LiPF₆ in ethylene carbonate and ethyl methyl carbonate (Ferro Purolyte) with a weight ratio of 3:7 was used as the electrolyte. A Teflon gasket was used along with silicon grease to give the cell a hermetic seal. Cell components were held in contact by nylon screws along with the correct selection of gasket thickness. All assembly was performed inside a glove box filled with argon with ≤ 1 ppm O₂.

Cell cycling was performed using a Maccor battery tester. Freshly assembled cells had an open cell potential between 2.3-2.4V. The cell was cycled between 10mV and 1.5V with the first conditioning cycle performed at a rate of C/5 (0.19 mA) and all subsequent cycling at a rate of 1C (0.94 mA). A total of 182 cycles were performed before bringing the cell to 2V for 24 hours to fully remove Li from the MCMB. The cell was then disassembled inside the glove box and the composite electrode rinsed with propylene carbonate and dried under vacuum before performing SEM.

All AE measurements were performed using a 4 channel DiSP system loaded with WinAE from Physical Acoustics. Physical Acoustics S9220 sensors with 1220A preamplifiers with 10 kHz – 3 MHz band pass filter were used. A thin film of silicone grease was used as couplant between the cathode plate and AE sensor which was held in place by a tight rubber band. A threshold of 24dB and sample rate of 1MHz was used.

Post processing, including manual event classification, channel filtering, and event parameter calculation, was performed using AEPPost software. The feature parameters extracted with AEPPost were exported to JMP statistical software for scatter plot analysis and data mining.

Laser diffraction particle size analysis (LDPSA) was performed on a Horiba LA-700 both before after sonication for three minutes. SEM was performed using a Hitachi

S3400. XRD was done on a Panalytic X'Pert Pro and peak fitting was done using X'Pert High Score software. Prior to all post-cycling analysis, cells were charged to 2V and held there for 24 hours to ensure full deintercalation of Li from the MCMB electrode. Cells were then disassembled and the composite electrodes were rinsed with propylene carbonate before drying overnight under vacuum.

3.5 Results and Discussion

LDPSA of loose MCMB particles indicated an average particle diameter of 12.96 μ m and 10.36 μ m before and after sonication for 3 minutes respectively. The particle size distribution is shown in Fig. 7. Little difference was observed between the two distributions suggesting the absence of agglomeration. SEM revealed spherical particles with a mild degree of surface roughness. The composite electrode showed a tightly packed and homogeneous film as in Fig. 8a. XRD of loose MCMB revealed that the only phase present was 2H graphite with d_{002} of 3.378Å.

From the AE data, four classes of events were identified; three of these are shown in Fig. 9 as the waveform (red) and the FFT (green). Type 1 emissions are characterized by large frequency content between about 1MHz and 2.5MHz. The average peak frequency for this type is 486.8 kHz and the average frequency centroid is 1227.4 kHz. 95% of these emissions had an amplitude of 27.0-27.4dB with a maximum observation of 42.0dB. The duration of this type of emission is variable with an average of 10.8 μ s with standard deviation of 23.9 μ s and observed range 0.3-267.1 μ s. These emissions may result from crack initiation or propagation in the SEI layer that develops on and around individual MCMB particles [18, 20, 23].

Type 2 emissions have a much more consistent waveform and frequency peak at 238 kHz on average. Other authors have associated similar emissions with gas formation [18, 21, 22, 26]. Because CO₂ is a byproduct of SEI formation, the formation of CO₂ bubbles is a likely source of this emission type [21]. These emissions show an average duration of 24.0 μ s and 95% had an amplitude between 26.0-32.5dB, however during the first discharge cycle some Type 2 events were observed with duration and amplitude as

high as 203.2 μ s and 72.9dB, respectively. The average frequency centroid for this type of emission was 649.4 kHz.

Type 3 is characteristically very similar to the Type 2 emission, but with a less defined waveform and frequency peak average of 357.6 kHz. 95% of these emissions had amplitude of 25.3-26.2dB, and an average duration and frequency centroid of 5.4 μ s and 357.6 kHz, respectively. The source of this event type is unclear but may result from shifting of the MCMB particles past one another as they expand and contract, or tearing of the composite film.

The final class of events corresponds to unwanted EMI and relay switching noise from the battery tester. Several variations of EMI were observed. These events are readily identified by their rigidly consistent waveforms and, in case of relay switching, very regular emission amplitude. Since these events did not emanate from the composite electrode the details pertaining to this emission type has been omitted.

Events were manually sorted and the following parameters were used to perform a scatter plot analysis: duration, amplitude, counts, counts to peak, energy, rise time, rise angle, decay angle, zero crossings, zero crossing frequency, FFT amplitude, and frequency centroid. The value of an event's duration, amplitude, and frequency centroid parameters proved particularly important in discriminating between different event types. Amplitude was very useful in filtering EMI events that showed very regular emission amplitudes. Duration and frequency centroid proved to be statistically different between Type 1, 2, and 3 emissions based on Student's t-tests with 95% confidence. Fig. 10 shows a scatter plot matrix of these three parameters. Clear clustering of events by type occurs and may be useful in the development of an automated event classification scheme.

Fig. 11 shows the cumulative number of Type 1 events as a function of cycles. These emissions are observed in both the charge and discharge steps. The cumulative plot is largely featureless, much like the results reported by Ohzuku et al [19]. There is a slight increase in emission rate at around 40 cycles, which loosely coincides with the onset of capacity fading. Cracking of the SEI layer exposes new surfaces on which additional SEI can form.

Fig. 12 shows the cumulative number of Type 2 and Type 3 events as a function of cycles. Both types are observed in both the charge and discharge step. Type 2 events were emitted at the highest rate on the first cycle, likely due to the initial SEI formation and consequent CO₂ bubble formation [22]. The highest amplitude Type 2 events occurred during the first few cycles. These gas formation events were mostly detected during initial cycling, while SEI layer cracking continued. The rate of occurrence of Type 3 events increased significantly after about 40 cycles and quickly outnumbered the Type 2 events.

SEM of the cycled electrode showed the presence of a fractured SEI layer, as in Fig. 8b and 8c. The formation of these cracks is the most likely source of Type 1 events. SEM of the electrodes in cross-section showed a 28% increase in thickness, from 25 to 32µm, as a result of cycling. This may indicate a loosening of the composite film as cycling proceeds, which may allow for an increased amount of particle shifting and hence the observed increase in Type 3 emissions as cycling proceeds.

For comparison with Type 2 events, the acoustic emissions from a can of carbonated beverage as it bubbled due to carbonation were recorded. Fig. 13 shows the waveform and FFT of the cola bubbling emissions. This event closely resembles the waveform of Type 2 events and also has a sharp FFT peak. With an average peak frequency of 180 kHz, the bubbles from the carbonated beverage are lower than the 238 kHz peak recorded from Type 2 events. This difference may be due to the large differences in the two emitting systems, but others have reported peak frequencies for the formation of bubbles in this range [18, 21, 26].

3.6 Conclusion

The use of AE to identify and monitor various processes inside of a cycling lithium ion cell has been demonstrated. Events likely corresponding to SEI cracking, gas formation, and particle shifting were detected and grouped. This demonstrates the ability of AE to provide not only information of when events occur during cycling within the system, but also about their nature. Knowing the source of emissions and how to identify their characteristics from MCMB composite electrodes may allow for their identification

in more complex commercial cells where additional sources of AE may exist. The inherent in-situ nature of AE may allow for its combination with other characterization techniques, such as XRD, SEM, AFM, and Raman IR to provide insights not possible with any of the techniques alone. Projects are currently underway to explore the usefulness of such composite techniques, as well as to record and characterize the AE emitted from several other cathode and anode materials.

3.7 Acknowledgments

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Chapter 4: Acoustic Emission from Silicon Electrodes in Cycling Lithium Ion Cells

4.1 Disclosure

This chapter is based on the manuscript published in the Journal of the Electrochemical Society (J. Electrochem. Soc., 157 (2010) A1354). The full list of authors includes Kevin Rhodes, Nancy Dudney, Edgar Lara-Curzio, and Claus Daniel. The role of Kevin Rhodes was to design and perform all experiments, process and analyze all data, and prepare the manuscript for submission.

4.2 Abstract

Silicon is a promising anode material for lithium ion battery application due to its high specific capacity, low cost, and abundance. However, when silicon is lithiated at room temperature it can undergo a volume expansion in excess of 280% which leads to extensive fracturing. This is thought to be a primary cause of the rapid decay in cell capacity routinely observed. Acoustic emission (AE) was employed to monitor activity in composite silicon electrodes while cycling in lithium ion half-cells using a constant current-constant voltage procedure. The major source of AE was identified as the brittle fracture of silicon particles resulting from the alloying reaction that gives rise to Li_xSi phases. The largest number of emissions occurred on the first lithiation corresponding to surface fracture of the silicon particles, followed by distinct emission bursts on subsequent charge and discharge steps. Furthermore, a difference in the average parameters describing emission during charge and discharge steps was observed. Potential diagnostic and materials development applications of the presented AE techniques are discussed.

4.3 Introduction

The use of lithium ion batteries (LIB) has become wide spread over the past couple decades and has been the focus of extensive research efforts [1]. Annual worldwide production of LIB cells numbers in the billions with applications including cell phones, laptop computers, powers tools, and hybrid electrical vehicles [2]. As the third lightest element, lithium can provide much higher energy densities than lead acid, nickel-cadmium, or nickel-metal-hydride (Ni-MH) batteries [3] allowing for lighter and

more compact portable power supplies. In addition, lithium is abundant in the earth's crust and has a low toxicity making it an excellent choice for mass produced consumer devices. The relatively high operating voltage and broad window of operating temperature [4] owing to the use of organic electrolytes makes LIB well suited for many specialized applications including transportation and remote energy storage.

In spite of all its promise, several materials and engineering challenges still remain to be overcome with LIB. Current demands on LIB technology include high capacity retention over a life time of many charge and discharge cycles. Maximizing battery longevity is still a major challenge partly due to electrode degradation as a function of repeated cycling [2]. As a LIB is cycled lithium ions move in and out of active electrode materials through intercalation or alloying processes as depicted in Fig. 1. This flux of lithium ions is a non-equilibrium process and sets up concentration gradients in the material that cause the development of stress and strain both inside the active material and in the surrounding composite matrix. Some groups have modeled this process in order to predict the stress and strain state in particles of active material caused by a flux of lithium [5-9]. If the strength of the active material is exceeded particles may fracture and shift, losing electronic contact with the current collector, which leads to capacity fade and a decrease in a cell's operational life time.

Silicon is an attractive anode material for use in lithium batteries due to its wide availability, low environmental impact, and exceedingly large specific capacity attainable at room temperature (3579mAh/g at $\text{Li}_{15}\text{Si}_4$) [10, 11]. Unfortunately, silicon undergoes a volume expansion of 280% at full lithiation [12] and suffers from severe capacity fade which has limited its successful application in commercial cells. This is believed to arise in large part from the pulverization of the silicon particles that occurs as cycling proceeds [13-17]. Several approaches including the use of narrow cycle voltage windows, nano-scale silicon particles, thin film silicon, and different binder materials have been explored with limited success [16, 18]. It is apparent that a more thorough understanding of how the material is degrading is necessary to help identify processing and cycling techniques that may be capable of improving overall performance and reduce capacity fading.

Several materials characterization techniques including X-ray diffraction (XRD) [10, 11, 19-21], scanning electron microscopy (SEM) [15, 22], transmission electron microscopy [23, 24], nuclear magnetic resonance [25], atomic force microscopy (AFM) [13, 26-28], Raman infrared spectroscopy (Raman IR) [28-31], and optical microscopy (OM) [32] can provide a glimpse of the inner workings of lithium ion cells. Each of these tools can provide important information but also has its limitations. As battery technology continues to improve new tools will be needed in order to develop a deeper understanding of these devices. Another less exploited technique capable of providing a unique perspective is acoustic emission (AE).

In AE a piezoelectric sensor is used to record mechanical vibrations emanating from a sample as in Fig. 2. When yielding or fracturing of a material occurs, strain energy is released from a localized point into its surroundings. A transient elastic stress wave propagates away from its source and can be detected by a sensor coupled to the sample. Each recorded waveform can be described using parameters such as duration, amplitude, counts, and frequency as depicted in Fig. 3. Careful assessment of the sample can help identify the specific source of different AE event types. When this is accomplished, AE can provide a convenient method of in situ monitoring capable of assessing both when and what events are occurring. This technique has received only limited application to the study of energy storage electrode materials in various systems including LIB [33-36], Ni-MH [37-39], and hydrogen-palladium [40]. Those papers dealing specifically with AE from LIB demonstrated a correlation between cell cycling and AE activity including what was reported to be particle fracture and bubble formation events in LiMnO_2 composite electrodes. However, these works did not include rigorous waveform analysis which has only become possible in recent years due to improvements in computers and AE equipment.

Ultimately the current work aims to develop AE methods capable of guiding the development of improved electrode materials and cell assemblies as well as providing a powerful non-destructive evaluation (NDE) tool for performance diagnostics and early failure detection of in-service cells. The results of an AE study of coin cells containing a silicon composite electrode cycling in a lithium half cell configuration (versus lithium

foil) are reported here. Testing under both galvanostatic and potentiostatic conditions were performed. The source of different emission types were identified using SEM, cycling data, AE test parameter variation, and available literature. From this understanding the relation of silicon particle degradation with electrochemical cycling was assessed.

4.4 Materials and Characterization

-100+325 mesh crystalline silicon particles (99.999%) were obtained from Alfa Aesar and used as received. A Partica LA-950V2 by Horiba was used to perform laser scattering particle size distribution analysis in ethanol with PS-220 as a dispersant. This measured a bell shaped distribution with mean particle size of 132.85 μ m, standard deviation of 56.59 μ m, and chi square value of 0.001443. The crystalline of the particles was confirmed by XRD conducted on a Scintag XGEN-4000. A scan rate of 0.10°/min from 27°-97° was employed.

Composite electrodes were prepared by spreading slurry of silicon particles, polyvinylidene fluoride (PVDF), and Super-S carbon (8:1:1 by weight) in N-methylpyrrolidone (NMP) over a 0.1mm thick copper foil. To make the slurry, first PVDF was dissolved in NMP by stirring for one hour. Next Super-S carbon was slowly stirred into the solution. This mixture was then sonicated for 15 minutes followed by stirring for 15 minutes. Finally the silicon particles were added and the mixture was stirred for another 30 minutes. The slurry was pipetted onto a clean copper foil and spread to a uniform film using a doctor blade set to blade height of 250 μ m. NMP was allowed to evaporate overnight in a hood before drying in a vacuum oven at 90°C for 2 hours. While heating, the electrode was compressed using an aluminum ingot to reduce electrode porosity and prevent delamination. Electrodes were next moved to an argon filled glove box held at ≤ 1 ppm O₂ where they were cut into 1/2" disks, weighed, and stored until use. Each disk held approximately 3mg of silicon corresponding to about 10mAh.

Stainless steel 2032 hardware was used to assemble coin cells containing a lithium foil disk (0.7mm thick), Celgard 2325 separator, and a composite silicon

electrode disk. A 1.2M solution of LiPF_6 in ethylene carbonate (EC) and ethyl methyl carbonate (EMC) mixed 3:7 by weight served as electrolyte. A stainless steel wave spring and compression disk was used in the cell on the lithium side to keep the components in good contact.

Assembled cells were removed from the glove box and cycled on a Maccor battery tester. Open cell potentials for fresh cells were about 3.2V. Constant current-constant voltage (CCCV) tests were performed. CCCV tests applied a constant current until a voltage threshold was reached. The voltage was then held constant until the current had dropped to $1/5^{\text{th}}$ its initial value at which point the next charge or discharge step was commenced. Generally, cycling was limited between 50mV and 1.3V but some cells were cycled between 170mV and 1.3V for comparison. All experiments were conducted on multiple cells to ensure reproducibility of results.

Cycle rates are commonly expressed as a C-rate which indicated the theoretical number of hours needed to completely charge or discharge a cell. A rate of C corresponds to a complete charge or discharge in one hour. A rate of C/20 would indicate a theoretically complete charge or discharge in 20 hours. This was the rate employed for cells in this study and since the theoretical capacity of silicon at room temperature is 3579mAh/g this corresponds to a rate of about 180mA/g.

A Physical Acoustics DiSP-4 system with 1220A preamps and S9220 sensors was used for monitoring AE activity. Sensors were attached to the composite silicon electrode side of the coin cell. Silicon grease was used as a couplant to improve signal transmission and rubber bands kept the sensor securely in place. The entire assembly was placed onto of a dense foam pad to increase isolation.

A preamp gain of 60dB, band pass filter of 100kHz-2MHz, and sample rate of 10MHz were used. Activity was registered as a hit on the system when the signal exceeded at threshold of 22dB. In order to clearly identify events resulting from electromagnetic interference (EMI) AE from a sensor placed near but not in contact with a cycling cell was also recorded. A front end filter to exclude hits with less than 3 counts was applied which eliminated almost all unwanted EMI and low amplitude events that could not be clearly discerned from the noise floor. This is a method commonly

employed with AE especially when using a very high sensitivity as employed here [41]. Any remaining noise events were removed by inspection of waveforms and fast Fourier transform (FFT). AE parameters were extracted using AEPPost and then exported to JMP statistical software for analysis.

Prior to all post-cycling analysis, cells were charged to 2V and held there for 48 hours to ensure full delithiation of the silicon. This allowed the electrodes to be handled outside of the glove box without undergoing extensive surface reactions of lithium with the air. Cells were disassembled in the glove box and the silicon composite electrodes were rinsed with propylene carbonate before drying overnight under vacuum. SEM was performed using a Hitachi S3400.

4.5 Results and Discussion

AE resulting from particle fracture in CCCV experiments had a waveform and FFT as shown in Fig. 14. Although each emission of this type was slightly unique, all shared a similar envelope and frequency content. The duration, amplitude, and frequency content of these hits were in good agreement with those recorded from fracture of comparably sized electrode particles in Ni-MH systems [37-39]. When experiments were conducted with no front end filter to remove EMI a plot of hit amplitude versus duration as in Fig. 15 was obtained. Two types of EMI were identified characterized as either a pulse type with high amplitude and short duration or continuous type with low amplitude and long duration. Emission from silicon fracture fell in an intermediate region which was easily distinguishable. During periods when a high emission rate was observed, two silicon fracture events would occasionally overlap and be recorded within the same hit. This was observed in the low amplitude range and made the hit appear to have an increased duration. Such emissions were omitted from AE parameter average calculations.

Fresh and cycled silicon particles are shown in Fig. 16. SEM of fresh particles showed multifaceted silicon particles with no penetrating fractures. At the end of the first lithiation step the appearance of many cracks on the surface of the particles was observed. After the first delithiation the particles appeared similar but with the cracks less

open, a result of a reduction in particle swelling due to less lithium content. After 5 cycles many smaller cracks emanating from the large fissures had appeared and small silicon particles resulting from the pulverization of the original structures were noted. Similar damage for each case was observed in all regions of the electrode. In general, cracks were spaced about 15-20 μm apart which may indicate a threshold particle size at which fracture may be avoided. Examination of the fracture surfaces showed no evidence of striations but rather a smoothly cleaved surface indicating brittle fracture as expected.

The cumulative hits per mg of silicon and cycling voltage of a sample are also plotted at the bottom of Fig. 16. The greatest number of events occurred during the first discharge stage. Subsequent charge and discharge stages showed a much sharper emission peak with much less events. With each cycle the number of events recorded during both charge and discharge stages decreased.

By modeling each particle as a sphere with diameter of 133 μm and density of 2.329g/cm³ an estimate of the number of particles on each electrode and subsequently the number of hits observed per particle was made. The number of events per particle was 11.1 for the first lithiation and about 1.7 for the first delithiation. The following cycle steps gave between 1.2 and 0.4 events per particle with this number decreasing with each step. This is consistent with the SEM images from Fig. 16 since many fractures were observed after only the first lithiation with a less pronounced but continuous increase in damage occurring thereafter.

Capacity fading in silicon cells has been shown to be significantly reduced by setting the lower voltage limit to 170mV [12]. However, this approach reduces the capacity that can be stored using silicon electrodes. Cells cycled between 170mV and 1.3V emitted no observable AE signals. Examination of the silicon composite electrodes from these cells showed no particle fracture.

A histogram of hit amplitudes is given in Fig. 17 and shows a maximum population of hits at 31dB. The bell shape of this plot indicates brittle fracture as expected for the fracture of silicon where as a distribution with a maximum at the lowest amplitude would indicate fracture in a tough material [42]. This supports the notion that these emission are in fact emanating from the fracture of silicon particles.

Voltage and capacity plots versus time with hit density contours are shown in Fig. 18. The highest hit density occurred on the first lithiation at 50mV and between about 150-500mAh/g. This stage shows a single density peak with very few emissions towards the end of the lithiation. During this period crystalline silicon becomes amorphous as lithium alloys the particles. The first delithiation shows a hit density peak at about 400mV and 400-500mAh/g. A lesser density peak is also observed at 1.3V where current is allowed to fall off. Subsequent lithiation stages all show two density peaks, one at around 200mV and 100mAh/g and the other below 100mV and above 1000mAh/g. Subsequent delithiation stages are similar to the first except that the first density peak is seen at about 300-320mV and 100-150mAh/g. The fact that the largest emission rates occur at voltage plateaus provides strong evidence of their correlation with alloying and phase change processes within the silicon particles.

When stress in a particle exceeds the tensile strength of silicon, reported as 3790MPa for a single crystal [43], fracture occurs in the particle and an AE signal may be recorded. Modeling indicates that tensile stress should occur at the center of a spherical particle during the initial lithiation with a state of compression existing at the surface [5]. In this case fracture should be occurring inside the particle and the surface cracks seen after the first discharge in Fig. 16 should not exist. Similar result with AE from cracking occurring during the penetration of the active material was observed in some Ni-MH battery anode materials [37-38]. This discrepancy may be due in part to the non-spherical nature of the silicon particles used here. Another contributing factor may also be the increased electrical conductivity of Li_xSi over unalloyed silicon which has not been rigorously addressed in the available models. This may contribute to a pile up of lithium at the interface where silicon is transformed from crystalline to amorphous and result in tensile stresses at the surface that give rise to the observed fractures.

Because the majority of emissions are observed at low capacities it is likely that they are resulting from transient stress in the particles. This type of behavior was predicted in the model by Verbrugge and Cheng [9], whose results indicate that a maximum tensile stress should occur at or near the surface of the particle just after the beginning of lithiation and delithiation. This could explain why the highest density of AE

is recorded near the beginning of charge and discharge steps. However, this model does not address the case when a particle completely void of lithium is alloyed for the first time so it cannot explain the surface damage seen in Fig. 16 after the first discharge of the silicon/lithium coin cell.

Fig. 19 shows the correlation of number of emission with cell capacity as well as the average values shown with 99% confidence intervals for emission duration, amplitude, energy (defined as the measured area under the rectified signal envelope [44]), rise time, and frequency as a function of cycling stage. The largest capacity loss of 1040mAh/g occurred between the first lithiation and delithiation stages and was accompanied by the largest number of emissions from the first lithiation of 3877 hits/g. In general the capacity continued to decrease with each stage as did the number of emissions. This strongly indicates that the number of emissions and hence the amount of particle fracture and pulverization is related to capacity loss.

Duration, amplitude, and energy are intimately related parameters in acoustic emission so their correlation in Fig. 19 is expected. In all cases these parameters were significantly higher during silicon lithiation. Furthermore, the first lithiation showed higher values than all following stages. Emission energy can be related to the size of a crack formed and this would indicate that the largest cracks are being formed as lithium penetrates the silicon for the first time [44]. Rise time shows a similar trend but tends to decrease more with each cycle. Due to its apparent correlation with cycle number, this parameter may prove useful in diagnostic applications where AE is used to determine the cycle history and remaining life of a cell.

From the bottom graph of Fig. 19 it is clear that the frequency content of the emissions remains fairly consistent with each stage. Rise, decay, and average frequencies remain steady at about 145, 175, and 385 kHz respectively. The increased variability of the average frequency as opposed to the other two is expected since it takes into account the variability in both of the others.

A moving average of the AE energy was calculated and plotted along with cell voltage as a function of time as shown in Fig. 20. The moving average was calculated by averaging groups of 75 hits. Just as in the energy versus cycle stage plot in Fig. 19, the

energy of hits during lithiation of silicon is significantly higher than for events during delithiation. During the first lithiation step two peaks in the moving average energy are observed. The first peak occurs near the beginning of lithiation when the cell reaches 50 mV. The second peak occurs at the end of lithiation when the silicon is nearly fully lithiated. In all lithiation steps that follow only the peak near the end of lithiation is observed. The trend for moving average during silicon delithiation steps are less obvious but tend to peak as the cell approaches 1.3V and nears full delithiation.

The peaks in moving average energy differ from the location of hit density peaks shown in Fig. 18. The highest energy hits tend to occur near the end of silicon lithiation or delithiation where as the largest number of hits was recorded near the beginning of these stages. This may indicate that many small cracks are formed at the beginning of a silicon lithiation or delithiation stage and that as the stage nears its end a smaller population of larger cracks are formed.

4.6 Conclusion

The use of AE to identify and monitor processes inside of a cycling lithium ion cell containing a composite silicon working electrode has been demonstrated. AE corresponding to silicon particle fracture were detected and analyzed. This demonstrates the ability of AE to provide not only information of when events occur during cycling within the system, but also about their nature. Knowing the source of emissions and how to identify their characteristics from silicon composite electrodes may allow for their identification in more complex commercial cells where additional sources of AE may exist.

AE also provided information useful for comparison with available numerical models of particle lithiation. Development of transient maxima and minima in fractional occupancy of lithium could result in tensile stresses capable of causing fracture near a particles surface as predicted by Verbrugge and Cheng [9]. Support for this is provided by the peak in AE density near the start of a lithiation or delithiation step. Further work with different cycle rates and particle sizes will explore this and any differences in the recorded AE signals.

Finally, the inherent in situ nature of AE may allow for its combination with other characterization techniques, such as OM, XRD, SEM, AFM, and Raman IR to provide insights not possible with any of the techniques alone. Work is currently underway to explore the usefulness of such composite techniques, record and characterize the AE emitted from several other cathode and anode materials, and develop methods for applying AE as a diagnostic tool for non-destructive cell evaluation.

4.7 Acknowledgments

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Chapter 5: Modeling Intercalation Induced Fracture of Silicon Particles for Lithium Ion Batteries

5.1 Disclosure

This chapter is based on the manuscript submitted to the Journal of Power Sources (S. Kalnaus, K.J. Rhodes, C. Daniel, “A study of lithium ion intercalation induced fracture of silicon particles used as anode material in Li-ion battery”, *J. Power Sources* (Accepted), DOI: 10.1016/j.powsour.2011.05.049). The full list of authors includes Sergiy Kalnaus, Kevin Rhodes, and Claus Daniel. The role of Kevin Rhodes was to design and perform all lab experiments, process and analyze all acoustic emission data, and collaborate on the interpretation of model results and manuscript preparation.

5.2 Abstract

The fracture of Si particles due to internal stresses formed during the intercalation of lithium ions was described by means of a thermal analogy model and brittle fracture damage parameter. The stresses were calculated following the diffusion equation and equations of elasticity with an appropriate volumetric expansion term. The results were compared with the acoustic emission data from the experiments on electrochemical cycling of Li ion half-cells with silicon electrodes. A good correlation between experiment and prediction was observed.

5.3 Introduction

Electrification of automotive drivetrains or powertrains is one of the primary research directions for the reduction of petroleum dependence. Lithium ion based electrochemical energy storage technology is the primary candidate for plug-in hybrid electric vehicles (PHEV) and fully electric vehicles (EV), and an ongoing collaborative research between companies and research institutions provides evidence for a high potential of application of Li-ion batteries in vehicle development. Despite attractive features and wide range of applications in smaller scale devices such as consumer electronics, the service life of Li-ion battery systems is still limited due to the processes of degradation of electrode material with repeated charging and discharging, and mechanisms of such degradation have not been sufficiently investigated and understood.

The working principle of Li ion battery is based on repeated transport of lithium ions through electrolyte and insertion/extraction from the electrode host structure (intercalation compound). It has been well documented that cycles of charge and discharge lead to capacity fade in a battery over its lifetime. Such capacity fade is suggested to be partially attributed to mechanical cracking of the active material particles induced by repeated lithium intercalation/deintercalation. While the fracture of particles has been observed and documented, investigation of processes leading to crack formation and development of models capable of predicting initiation of cracking is still under way. It should be mentioned that historically the area of battery research was driven predominantly by electrochemical expertise and materials development. This resulted in an enormous gap in research on mechanical behavior of electrode materials. At the present stage it is evident that the mechanical engineering side of the problem needs to be explored. Determination of the stress state of a particle during charge/discharge will lead to understanding the origin of fracture and will provide a solution in order to improve the battery service life.

It is well known that electrochemical cycling leads to capacity fade in lithium ion batteries, which creates significant limitations as far as lifetime and reliability of a product is concerned [1,2]. In addition to processes associated with chemical reactions, a major source of capacity fade is the failure of electrode particles due to the stresses developed during lithium intercalation/deintercalation. Higher lithium insertion rates generally result in higher rate of fracture due to significant lattice strain [3]. There is a multitude of experimental evidence supporting the notion of active electrode particle failure due to intercalation stresses [4-7]. The process of cyclic expansion and contraction of active electrode material can be viewed from the standpoint of fatigue and damage mechanics. However, to the present day, the term “mechanical fatigue” has rarely been applied to the processes involved in electrochemical cycling.

Involvement of mechanical stresses in battery degradation has been realized only recently and the modeling efforts have started utilizing a combination of diffusion laws with continuum mechanics [8-13]. Most known is the thermal analogy approach developed by Yang [8] for calculation of chemical stresses, which has been adopted in

subsequent investigations [9-11]. The idea of description of volumetric expansion due to diffusion based on equations of thermal expansion is rather appealing due to simplicity of elastic equations and this approach is used in the current work. Computations based on such approach can give a good approximation of stress distribution, provided an appropriate diffusion law is available.

The electrochemical cycling of the electrochemical cell imposes cycles of expansion and contraction similar to repeated cycles of thermal straining. Following the analogy, the notion of thermal fatigue could be applied to failure of electrode material. The phenomenon of thermal fatigue has been investigated over a long period of time [14-16] and the presence of temperature induced plastic deformation in ductile materials has been reported [14]. In such cases the relation between accumulation of damage and plastic strain energy results in the fatigue criterion for life prediction [17-19]. The majority of Li-ion battery electrode materials (Si, LiMn_2O_4 , LiCoO_2 , representing the typical anode and cathode compounds) are however brittle in nature and the accumulation of damage in this case is best described by the change in elastic properties due to formation of microcracks. When the microcracks reach the critical size (typically very small compared to critical cracks in ductile materials) complete failure occurs. In this regard the damage can be related to the fraction of Young's modulus available for further elastic deformation and the value of modulus equal to zero would represent complete fracture. Development of the relationship between the stress state and damage parameter cannot be based on Von Mises stress, as in case of ductile materials, and should include a different formulation of equivalent stress [20, 21].

The present work represents investigation of fracture in Si particles used as an active material for anodes in a Li-ion battery. Without venturing into details of electrochemical aspects of battery operation, the problem is treated from the stress analysis point of view. The results are compared with the acoustic emission data from Si electrode cycling and a good correlation was found between the peak of emissions and the predicted time when the damage parameter reaches its maximum.

5.4 Evaluation of Intercalation Induced Stress

The overall problem of ionic diffusion in solid particles is very complex from both electrochemical and mechanical points of view and therefore necessary approximations are made to reflect particular aspects of the overall process. By considering binary diffusion coefficients and thermodynamic driving force for diffusion, Newman and Christensen [12, 13] developed a continuum model for computation of internal stresses in a spherical particle of cathode material. Another approach is based on a rather natural analogy between volumetric thermal expansion and three-dimensional diffusion [8-11]. The following section provides brief description of the thermal analogy model in terms of mathematical formulation within continuum mechanics framework. The particle is approximated as a homogenous isotropic sphere for simplicity. The process of Li-ion solid state diffusion is considered as a process analogous to the thermal expansion of a homogeneous sphere submerged into liquid media which has higher temperature than the sphere. The elastic thermal analysis of an isotropic media is governed by Hooke's law with additional thermal expansion term [22].

$$\varepsilon_{ij} = \frac{1}{E} \left[(1 + \nu) \sigma_{ij} - \nu \sigma_{kk} \delta_{ij} \right] + \alpha \Delta T \delta_{ij}$$

Eqn. 3: Hook's Law with additional thermal expansion term

A dummy index summation convention is used in Eqn. 3 with δ_{ij} being the Kronecker delta, ε_{ij} , and σ_{ij} representing strain and stress tensor components respectively, ν is the Poisson ratio, α is the coefficient of thermal expansion, and ΔT represents temperature change at the material point. Analogous to Eqn. 3 the bulk diffusion in isotropic media can be represented by the following stress-strain relationship [8]:

$$\varepsilon_{ij} = \frac{1}{E} \left[(1 + \nu) \sigma_{ij} - \nu \sigma_{kk} \delta_{ij} \right] + \frac{\Delta c \Omega}{3} \delta_{ij}$$

Eqn. 4: Thermal expansion analog for bulk diffusion

where Ω is the partial molar volume and c is the concentration of diffusing species at the material point. Since Ω is a volumetric quantity it can be determined analogously to volumetric coefficient of thermal expansion as:

$$e = \Omega \Delta c$$

Eqn. 5: Volumetric strain due to bulk diffusion

where $e = \varepsilon_{kk}$ is the volumetric strain.

The case of the spherical geometry of a particle produces only two components of the stress tensor in spherical coordinates: radial component (σ_r) and tangential component (σ_t). The equilibrium condition for the stress tensor in case of a spherical particle reduces to:

$$\frac{d\sigma_r}{dr} + \frac{2}{r}(\sigma_r - \sigma_t) = 0$$

Eqn. 6: Equilibrium condition for spherical particle

The stresses are functions of elastic strains following the Hooke's law:

$$\begin{cases} \sigma_r = \frac{E}{(1 + \nu)(1 - 2\nu)} \left[(1 - \nu)\varepsilon_r + 2\nu\varepsilon_t - (1 + \nu)\frac{\Omega c}{3} \right] \\ \sigma_t = \frac{E}{(1 + \nu)(1 - 2\nu)} \left[\nu\varepsilon_r + \varepsilon_t - (1 + \nu)\frac{\Omega c}{3} \right] \end{cases}$$

Eqn. 7: Diffusion induced stress in a spherical particle

where the components of strain are determined from the radial displacement as:

$$\varepsilon_r = \frac{dU}{dr} \quad \varepsilon_t = U / r$$

Eqn. 8: Relation between strain and radial displacement

Substitution of Eqn. 8 in expressions for stress (Eqn. 7) and then to equilibrium equation (Eqn. 6) leads to the ordinary differential equation for displacement as a function of radial coordinate r :

$$\frac{d^2U}{dr^2} + \frac{2}{r} \frac{dU}{dr} - \frac{2U}{r^2} = \frac{1+\nu}{1-\nu} \frac{\Omega}{3} \frac{dc}{dr}$$

Eqn. 9: Differential relation between radial coordinate and displacement

Provided the instantaneous concentration of diffusing species is known, solution of Eqn. 9 with back substitution in Eqn. 8 and Eqn. 7 gives the stress state within the particle. The diffusion equation is introduced as an extension of the Fick's law with the component corresponding to diffusion driven by the hydrostatic stress σ_H [8, 9]:

$$\frac{\partial c}{\partial t} = D_{Li} \nabla^2 c - \frac{D_{Li} \Omega}{RT} (\nabla c \nabla \sigma_H + c \nabla^2 \sigma_H)$$

Eqn. 10: Stress state within spherical particle

where D_{Li} is the diffusion coefficient, R is the gas constant, T is the absolute temperature, and $\sigma_H = \sigma_{kk}/3$ is hydrostatic stress. When dependence on radial coordinate r only is considered, as in the case of isotropic spherical particle with uniform distribution of solute at the surface, the diffusion equation becomes:

$$\frac{\partial c}{\partial t} = D_{Li} \left[\frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} - \frac{\Omega}{RT} \frac{\partial c}{\partial r} \frac{\partial \sigma_H}{\partial r} - \frac{\Omega c}{RT} \left(\frac{\partial^2 \sigma_H}{\partial r^2} + \frac{2}{r} \frac{\partial \sigma_H}{\partial r} \right) \right]$$

Eqn. 11: Stress state within isotropic spherical particle

Eqn. 7-9 together with the diffusion equation (Eqn. 11) describe the problem of ionic diffusion in a homogenous spherical particle. In fact, Eqn. 9, being an ordinary differential equation, can be solved analytically which results in the following expressions for stress components:

$$\begin{cases} \sigma_r = \frac{2\Omega E}{3(1-\nu)} \left[\frac{1}{R_0^3} \int_0^{R_0} cr^2 dr - \frac{1}{r^3} \int_0^r cr^2 dr \right] \\ \sigma_t = \frac{\Omega E}{3(1-\nu)} \left[\frac{2}{R_0^3} \int_0^{R_0} cr^2 dr + \frac{1}{r^3} \int_0^r cr^2 dr - c \right] \end{cases}$$

Eqn. 12: Expression for radial and tangential stress in a spherical particle

where R_0 is the radius of the particle. After substituting $\sigma_H = \frac{\sigma_r + 2\sigma_t}{3}$ with stress components expressed in Eqn. 11 and Eqn. 12 the differential equation for concentration evolution becomes:

$$\begin{aligned} \frac{\partial c}{\partial t} &= D_{Li} \left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} + \theta \left(\frac{\partial c}{\partial r} \right)^2 + \theta c \left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} \right) \right), \\ \theta &= \frac{2\Omega^2 E}{9RT(1-\nu)} = \text{const.} \end{aligned}$$

Eqn. 13: Differential expression of concentration evolution

Eqn. 13 represents a boundary-initial value problem and can be solved numerically on the one-dimensional space grid. It should be mentioned, that the statement of the problem in form of Eqn. 12 and Eqn. 13 is performed based on the assumption of instantaneous mechanical response, i.e. the stress-strain state depends on time only implicitly via concentration function $c(r, t)$. At each particular time step during electrochemical cycling process, the Eqn. 13 is solved first and the stresses are obtained as a function of radial coordinate by integration of Eqn. 12. The values of concentration of Li ions from the previous time step serve as initial conditions for the numerical procedure at the next time step. The boundary condition imposed at the surface of the particle is controlled by the current density as [9]:

$$J = -D_{Li} \left(\nabla c - \frac{\Omega c}{RT} \nabla \sigma_H \right) \Big|_{r=R_0} = i_s / F$$

Eqn. 14: Current density at a particle surface

where F is the Faraday constant, J is the species flux and i_s is the current density at the surface of the particle. Considering solution for stresses (Eqn. 12) this boundary condition becomes

$$J = -D_{Li} (1 + \theta c) \frac{\partial c}{\partial r} \Big|_{r=R_0} = i_s / F$$

Eqn. 15: First boundary condition. Surface current density.

The second boundary condition reflects the symmetry of concentration distribution with respect to the center of the particle and is represented by the equation:

$$\left. \frac{\partial c}{\partial r} \right|_{r=0} = 0$$

Eqn. 16: Second boundary condition. Symmetry of concentration distribution.

5.5 Damage and Brittle Fracture

Eqn. 13 with the boundary conditions stated in Eqn. 15 and Eqn. 16 describes the evolution of concentration of Li ions in a solid homogenous spherical particle with time, following the cyclic charge/discharge curve. Such a curve is typically given as a current (voltage) versus time diagram of an electrochemical cell. By solving Eqn. 13 the concentration as a function of a radial coordinate is found at a particular time and the stresses are obtained by integration of expressions in Eqn. 12. Thus the stress distribution is obtained.

The above procedure is based on the analogy of chemical diffusion stresses to the thermal stresses in continuum mechanics. In the case of ductile materials, the thermal cyclic loading is known to contribute to the fatigue damage accumulation governed by cyclic plasticity [14-16]. Many of the typical active electrode materials in lithium chemistries are brittle in nature, such as LiCoO_2 , LiMn_2O_4 , Si, etc. Therefore the damage parameter cannot be based on accumulated plastic strain energy as in the case of ductile engineering materials [19-21]. Electrode material deforms volumetrically with cyclic insertion and removal of Li ions from its crystallographic structure. Such cycles of lithiation/delithiation produce corresponding compressive and tensile stresses within a particle, as schematically illustrated in Fig. 21.

The representation of strength of brittle materials (e.g. ceramic) is not deterministic in nature and follows the Weibull distribution [23, 24]. The assessment of tensile strength is based on the results of load-to-rupture tests performed on large set of specimens with application of corresponding statistical analysis [25]. The likelihood of fracture is governed by the distribution of flaws in the specimen and is based on the weakest link approach. The distribution of flaws is assumed to be stable and no slow

crack growth is occurring during the loading [25]. In this case the probability of fracture of a specimen subject to tensile stress σ is represented as [24]:

$$P_{f1} = 1 - e^{-\left(\frac{\sigma}{\sigma_w}\right)^m}$$

Eqn. 17: Weibull distribution of fracture probability

where σ_w and m are the Weibull stress and the Weibull modulus correspondingly determined from the series of load-to-rupture experiments.

The process of material deformation as a result of ionic diffusion is a time-dependent process which changes material itself and thus the assumption that the initial population of internal flaws does not change with time is no longer valid. Formulation for damage accumulation as the material is subject to rising stresses due to species concentration gradients is done adopting a quasi-brittle approach [24, 26, 27]. In case of uniaxial loading, the damage D is described as the ratio of the failed area of the sample to the original area. If the specimen is represented as an assembly of N identical fibers out of which n have failed at a given time increment, then the damage is n/N and represented by Eqn. 17. The effective tensile stress resulting from the re-distribution of load due to reduction in load-bearing area is then $\tilde{\sigma} = \sigma/(1 - D)$. The effective compressive stress is $\tilde{\sigma} = \sigma/(1 - hD)$ and the constant h reflects the partial recovery of elasticity in compression due to closure of micro-cracks. The effective Young's modulus in tension and compression is represented as:

$$\begin{cases} \tilde{E}^+ = E(1 - D) \\ \tilde{E}^- = E(1 - hD) \end{cases}$$

Eqn. 18: Effective Young's modulus in tension and compression

where the constant h is therefore $h = (E - \tilde{E}^-)/(E - \tilde{E}^+)$. For most materials, the ratio h has a value close to 0.2 [24] and this value is adopted in the present investigation. The above reasoning can be extended to the case of multiaxial stress state in which case the effective stress tensor is introduced. The positive and negative parts of a stress tensor are constructed from its positive (negative) eigenvalues σ_k and corresponding eigenvectors η^k as follows:

$$\begin{aligned}\langle \sigma \rangle_{ij}^+ &= \sum_{k=1}^3 \langle \sigma_k \rangle \eta_i^k \eta_j^k \\ \langle \sigma \rangle_{ij}^- &= \sigma_{ij} - \langle \sigma \rangle_{ij}^+\end{aligned}$$

Eqn. 19: Construction of stress tensor from eigenvectors

where $\langle \rangle$ represents Macauley brackets such that $\langle x \rangle = \begin{cases} x, & \text{if } x \geq 0 \\ 0, & \text{if } x < 0 \end{cases}$.

The above definition results in the following expression for the effective stress tensor in multiaxial stress state:

$$\tilde{\sigma}_{ij} = \frac{\langle \sigma \rangle_{ij}^+}{1-D} + \frac{\langle \sigma \rangle_{ij}^-}{1-hD} + \frac{\nu}{1-2\nu} \left(\frac{\delta_{kl} \langle \sigma \rangle_{kl}^+ - \langle \sigma_{kk} \rangle}{1-D} + \frac{\delta_{kl} \langle \sigma \rangle_{kl}^- + \langle -\sigma_{kk} \rangle}{1-hD} \right) \delta_{ij}$$

Eqn. 20: Effective multiaxial stress state.

As for the damage parameter under multiaxial stress, the quantity σ in Eqn. 17 should be substituted with a corresponding equivalent stress parameter representing the current stress state. Thus the damage parameter becomes represented by:

$$D = 1 - e^{-\left(\frac{\sigma_{eq}}{\sigma_w}\right)^m}$$

Eqn. 21: Damage parameter from effective stress state

We choose the equivalent stress definition in form that depends on the hydrostatic stress [24]:

$$\begin{aligned}\sigma_{eq} &= \sigma_{VM} \sqrt{\chi} \\ \chi &= \frac{2}{3}(1+\nu) + 3(1-2\nu) \left(\frac{\sigma_H}{\sigma_{VM}} \right)^2\end{aligned}$$

Eqn. 22: Hydrostatic stress

where σ_{VM} is the Von Mises stress and χ is the triaxiality parameter. With inclusion of elasticity change due to damage the equivalent stress is expressed by:

$$\sigma_{eq} = \sqrt{(1+\nu) \langle \sigma \rangle_{ij}^+ \langle \sigma \rangle_{ij}^+ - \nu \langle tr \sigma \rangle^2 + \frac{1-D}{1-hD} \left[(1+\nu) \langle \sigma \rangle_{ij}^- \langle \sigma \rangle_{ij}^- - \nu \langle -tr \sigma \rangle^2 \right]}$$

Eqn. 23: Elasticity change responsive equivalent stress state

It can be seen that the damage evolution and stress state are interrelated by the Eqn. 21 and Eqn. 23 via the equivalent stress parameter. The overall solution procedure can be described as follows. The electrochemical “loading curve” is represented by the variation of current with time. At the initial moment the initial concentration of Li inside the particle is known and the stresses can be obtained from Eqn. 12. The initial damage is taken to be zero and then corrected by the Eqn. 21 using the equivalent stress from Eqn. 23. The solution is continued following the same steps for each point along the current

versus time curve. Following the assumption of isotropic material, the damage is isotropic as well and represented by one scalar variable.

5.6 Comparison with Experimental Data

In the present section the computational results of the damage accumulation are compared to the results of acoustic emission (AE) experiments on anodes with Si active material. A series of experiments were conducted on lithium half cells with Li counter electrode under different charge/discharge conditions. The silicon particles (-100/+325 mesh from Alfa Aesar) were mixed with 10%wt PVDF binder and 10%wt Carbon Black as conductive additive, and spread over 12 mm copper circular disks. The surface density of Si was 2.5 mg/cm^2 . Silicon particles in as received condition are shown on the SEM picture in Fig. 22. The average size of the particles was $100 \text{ }\mu\text{m}$.

The half cell employed in the experiments consisted of two stainless steel plates and insulating PTFE gasket in which the Si composite anode, separator and Li foil were placed. A 1M solution of LiPF_6 in ethylene carbonate and ethyl methyl carbonate (Ferro Purolyte) was used as electrolyte. The half cells were cycled using Maccor battery tester. The AE data was collected using a 4 channel system from Physical Acoustics. The experiments were conducted under constant current – constant voltage (CCCV) conditions with corresponding cut-off values. CCCV process consists of periods of time when the cell is held at constant current until the voltage reaches desired cut-off value and then the cell is held at constant voltage until the current drops to the designed value. The details of CCCV procedure can be found in [28, 29]. The representative cyclic curve is shown in Fig. 23. Total of eleven cells with Si anodes were cycled with current amplitudes ranging from 0.29 to 2.3 mA.

In order to eliminate noise, acoustic emissions representing particle cracking were filtered based on 21 dB threshold. The electromagnetic interference (EMI) events were registered by an additional AE sensor placed near the cell and these events were filtered out. The acoustic emission parameters (i.e. duration, amplitude and frequency) were compared to those available in the literature [30-32] and a good agreement was observed.

The details of signal collection and post-processing can be found in corresponding references [29-32].

Determination of several material constants is required in order to use the equations specified above. The partial molar volume was determined based on the analogy with volumetric coefficient of thermal expansion. The volumetric strain (e_T) due to the temperature change ΔT is expressed as $e_T = \alpha_v \Delta T$, where α_v is the volumetric coefficient of thermal expansion. Analogously, for volumetric expansion due to intercalation of lithium, $e_C = \Omega \Delta C$, where ΔC is the change in lithium concentration.

Based on 300% volume increase in Li_xSi when x changes from 0 to 4.4 [28] the value of Ω is $7.69 \cdot 10^{-6} \text{ m}^3/\text{mol}$. In the current work the diffusion coefficient is assumed to be constant and independent of state of charge (stress state). The parameters of Weibull distribution for strength of Si were adopted from the literature [23]. The apparent value of the diffusion coefficient and other material constants is shown in Table 1 together with corresponding references reporting these values.

The solution of the diffusion equation (Eqn. 13) is controlled by the surface current density boundary condition (Eqn. 15). At each point in time, the current density at the particle surface was obtained by dividing the total current by the average number of Si particles in the electrode and by the average surface area of a particle. Thus each point from the current cycling curve (Fig. 23) can be converted to an average surface current density of a particle. Each time interval from the cycling electrical data was split into sub-intervals for time integration of Eqn. 13. The numerical solution of initial-boundary value problem was performed by backward time centered space (BTCS) method. The overall arrangement of the solution steps is shown in Table 2, where indexes k and l indicate time step and node numbers respectively. The primary interests were the evolution of maximum damage within a particle with time, distribution of stress and distribution of damage inside the particle. Influence of cycling conditions on damage development was investigated. The results are compared with experimental AE data records of cracking events.

As an example, the acoustic emission data for a representative specimen (sample ID 48) is shown in Fig. 24 together with the cyclic current as a function of time. The markers represent the amplitude of the acoustic events (hits) distributed within the duration of experiment. It can be seen that most of the cracking associated with the AE hits occurs during the first discharge, i.e. at the beginning of the first cycle. This situation appears to be typical for all of the specimens investigated. The subsequent emissions registered at the beginning of the corresponding charge (positive current) and discharge (negative current) portions of the cyclic curve can be attributed to the formation of new cracks within the grains fractured during the first cycle. The influence of the newly created cracks on the electrochemical and mechanical properties of the particle is beyond the scope of current investigation.

At the present stage it appears to be essential to verify that the approach described above can predict the fracture of particle in agreement with the acoustic emission data during the first cycle. That is the “safe-life” approach is taken and only the accumulation of damage in the initially not fractured particle is considered. Under this condition, the first maximum of emission rate should coincide with the maximum of the damage parameter.

The damage evolution with time is shown together with the rate of emissions in Fig. 25 for the specimen ID 48. Only the first discharge portion of the cycle is shown. Since the silicon electrode is cycled against lithium, the former becomes a cathode in the half-cell and the intercalation of Li ions occurs during discharge. The dash-dotted line in Fig. 25 represents the rate of the emissions collected during the experiment and the solid line represents the calculated damage based on the current evolution in time. Emission rate was calculated by differentiating the number of events versus time data. The data is most successfully fitted with the Hill equation:

$$F(x) = b + \frac{m - b}{1 + \left(\frac{I_h}{x} \right)^r}$$

Eqn. 24: Hill equation

where b, m, I_h , and r are fitting parameters. The point where the rate of acoustic emission events reaches its maximum is considered to be the point where most of the particles within electrode experience fracture.

With the use of the damage parameter, the time when $D = 1$ represents the time to failure of a particle. It can be seen from Fig. 25 that the maximum of damage parameter (value of 1.0) correlates well with the maximum of emissions rate.

The correlation between experimental data and predicted fracture based on $D = 1.0$ criterion is shown in Fig. 26. The markers represent data for individual specimens. The solid line indicates perfect correlation and dashed lines show the boundary within the factor-of-two dispersion from the perfect correlation. It can be seen that the experimental data is in good agreement with computed values of time to failure based on the brittle damage parameter.

Out of eleven specimens under investigation, ten were cycled between 1.3 V and 50 mV under different cut-off currents. One specimen was tested with higher cut-off voltage, and cycled between 1.3 V and 170 mV. The particles in this electrode did not fracture and no acoustic emission was detected during cycling. This specimen is indicated by an arrow in Fig. 26 implying that the electrode particles did not fail. An arbitrary time of $80 \cdot 10^4$ seconds was chosen to represent the infinite time to fracture. Higher cut-off voltage resulted in only partial lithiation of Si which reduced the internal stresses within particles thus reducing the damage. The maximum damage in this specimen reached the value of 0.15 only, therefore predicting the experimentally observed non-failure.

In Fig. 25 the maximum value of damage within the particle is shown for each corresponding moment of time. The distribution of damage within the particle is of particular interest since the location of its maximum would represent the point where the fatal crack originates. The damage as a function of the radial coordinate and time ($D(r,t)$) is plotted in Fig. 27. The three-dimensional representation in Fig. 27 depicts the evolution of damage profiles with time as the lithiation proceeds following the initial discharge curve in Fig. 23. The particle size was chosen as 40 μm and thus the radial coordinate

changes from zero (center of the particle) to 20 μm (surface of the particle). Since the damage at the initial stages of discharge lithiation is close to zero, the portion of the damage surface corresponding to onset of lithiation is not plotted. The intersection of the surface with the Damage-Radial Coordinate planes represents the two dimensional plots of the function $D(r)$ corresponding to different points in time. The intersection of the surface with Damage-Time plane where damage attains its maximum represents time evolution $D_{\text{max}}(t)$ similar to that shown in Fig. 25. The computation continued until the value of $D(r,t)$ reached its maximum and thus the damage profile at the last point in time represents the spatial distribution of damage at the moment of fracture. It can be seen that within the entire time span, the maximum damage occurs at the center of the particle which is where the peak of damage is situated when the cracking initiates. Thus the particle is expected to fracture in the center when the lithium is inserted.

The results reported above are based on the experimental data suggesting that the peak of acoustic emissions occurs during the first discharge; that is most of the particles fracture during the initial insertion of Li. The calculations show rapid increase of the damage and the points of $D=1$ coincide well with the peaks of acoustic emission (Fig. 26). The predictions are based on the average radius of the particle ($50\mu\text{m}$) used in the experiments. At this point it seems only logical to investigate the effect of particle size on damage evolution with time. Once again the loading conditions applied to specimen 48 were used as the input values. The damage-time curves for the particles of three different sizes are shown in Fig. 28. The time period shown in Fig. 28 corresponds to the initial discharge part of the loading curve (Fig. 23). Two trends can be clearly seen from Fig. 28. The value of maximum damage decreases with decrease in particle radius and the time to the peak of the damage also decreases as the particle size is reduced. The former observation is rather intuitive as the larger particle would produce greater stress fields which would lead to fracture. The location of the damage maxima closer to the onset of discharge follows from the fact that the shorter time is needed for lithiation of a smaller particle.

The continued investigation of the size effect is shown in Fig.29, where the maximum damage and the time until this maximum damage is reached is plotted against the particle radius ranging from $1\mu m$ to $50\mu m$. The vertical dashed line represents boundary between two particle sizes identified by the mesh numbers and will be explained in the Discussion section of the paper. It can be seen that as the particle size decreases so does the damage, reaching the limit close to zero for infinitely small particle. The damage then increases rapidly within the range of particle radii between 10 and 20 μm and asymptotically reaches the plateau with the value of 1.0. Finally, it can be seen that for particles smaller than 10 μm in radius the value of damage is rather negligible suggesting that the particles of this range of sizes will not fracture upon the initial discharge. It should be mentioned that the scale of 10 μm is far greater than nanoscale typically considered to be “stress safe” on a single particle level [2, 38].

5.7 Discussion

The present investigation represents the analysis of diffusion induced fracture of Si particles during lithium insertion and extraction based on a working principle of a Li-ion battery. The problem is treated from the continuum mechanics point of view. The probabilistic formalism of deformation analysis of brittle materials resulted in damage parameter reflecting the probability of fracture with $D \rightarrow 1$ representing the prediction of complete failure. Within this notion the stress state is in turn affected by the change in the elastic modulus due to damage following Eqn. 21. Distinction between tension and compression is made through consideration of microcracks closure when the stress state is compressive.

Examination of AE data from electrodes tested (Fig. 24) reveals the maximum density of emission events during the first discharge of the cyclic curve. In a half-cell, an anode formally serves as a cathode as it is cycled against lithium metal and thus discharge portion of a cycle represents insertion of Li ions into Si particles. While the highest density of emissions occurs during the first discharge, Fig. 24 shows spikes of emissions during subsequent cycling. The AE events occur during both the discharge,

when the stress state on the surface is compressive as well as during charging, when the particle surface stress state is tensile. At the present moment it is rather difficult to make a definite statement as for the cause of subsequent bursts of emissions. It could be suggested that the initial burst of emissions is due to cracking while later on in subsequent cycles the fretting of the existing fracture surfaces and small increments of crack growth can be attributed. Since the examination of electrode material is done *ex situ* it is impossible to determine the exact sequence of events leading to final fracture of a particle into pieces. The continuation of the current research will be done by *in situ* optical microscopy using a specially designed Li half cell. Such *in situ* observations will give valuable information regarding development of cracking with electrochemical cycling.

An example of cycled particle is shown on SEM image in Fig. 30. Multiple cracks separating the particle into smaller blocks can be observed, however the location of crack initiation cannot be deduced from this picture. It is quite possible that the cracking during the initial discharge started from the center of the particle where the prediction places the maximum of the damage parameter (Fig. 27) separating the particle into several blocks. Subsequent charge would introduce the surface cracks in those blocks producing the burst of emissions corresponding to the charging part of the cycle. Then during the next discharge the internal cracks would appear again and so on, until the block reaches a critically small size to develop enough stress for fracture. The geometry of the internal crack produced during the first discharge depends on the distribution of initial internal defects in the particle and is impossible to predict within the generalized homogeneous spherical body approach. In other words it is impossible to quantify the amount of blocks produced by initial fracture of a particle.

Investigation of the particle size effect on the evolution of damage produces the result which reveals the existence of particle size range, for which the value of maximum damage is less than 1 (Fig. 29). Additional examination of Fig. 29 yields observation that as the particle radius comes close than 10 μm the damage becomes negligibly small. The particle size in the vicinity of 10 μm in radius thus can be considered as fracture safe under the current cycling conditions. It should be mentioned that the above size range is

still much larger than expected in the electrochemical community where the shift towards nano-sized electrode particles is considered to be the solution for extension of battery life. In order to validate the size effect shown in Fig. 29, one of the electrodes was prepared with Si particles of - 325 mesh, that is less than 44 μm in radius. The electrode was cycled between 1.3 V and 50 mV with 0.53 mA current amplitude. The results are shown in Fig. 31 and compared to the AE results from the electrode with -100/+325 mesh particles (average radius 50 μm) cycled under the same conditions. According to ASTM-E11 standard, the mesh numbers are used in description of sizes of particulate materials and denote the sieve openings through which particles are passed. The sign in front of the number corresponds to whether particles go through the sieve or are trapped. In our case, the designation -325 mesh indicates that particles smaller than 44 μm will pass through the sieve, and designation -100/+325 means that particles will pass through 150 μm openings (-100) but will be stopped by 44 μm sieve (+325). The line corresponding to particle diameter of 44 μm and thus demarcating the two meshes is placed in Fig. 29 in order to distinguish the corresponding values of damage. It can be seen in Fig. 29 that the part of the maximum damage curve corresponding to the particles smaller than 44 μm is distinguished by the abrupt drop in values of damage parameter, while for the particles larger than 44 μm the damage approaches the asymptotic maximum value of unity. Confirming the predictions from Fig. 29, Fig. 31 shows that the number of hits registered in the small-particle electrode is magnitudes less than in the case of 50 μm particles. The experimental work, which targets investigation of size effect on fracture time, is under way and should further reveal the dependence of damage on particle size as well as demonstrate the existence of critical size following the computational results presented in current manuscript.

5.8 Conclusion

The problem of Si particles fracture upon insertion of lithium in a Li-ion half-cell was treated within the continuum mechanics approach with brittle damage parameter. The results predict fracture upon the immediate first discharge and are in agreement with experimental acoustic emissions data obtained from charge/discharge cycling of a half

cell with Si as anode active material. Consideration of particle size effect on developed chemical stresses suggests a critical size of a particle which would not fracture upon initial lithiation. Such critical size appears to be within micrometer scale.

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Chapter 6: Novel Cell Design for Combined In Situ Acoustic Emission and X-ray
Diffraction Study During Electrochemical Cycling of Batteries

6.1 Disclosure

This chapter is based on the manuscript submitted to Review of Scientific Instruments (K. Rhodes, M. Kirkham, R. Meisner, C.M. Parish, N. Dudney, C. Daniel, “Novel Cell Design for Combined In Situ Acoustic Emission and X-ray Diffraction Study During Electrochemical Cycling of Batteries”, *J. Sci. Instruments*, 82, 075107 (2011)). The full list of authors includes Kevin Rhodes, Melanie Kirkham, Roberta Meisner, Chad Parish, Nancy Dudney, and Claus Daniel. The role of Kevin Rhodes was to design and develop the novel in situ XRD cell, perform in situ AE and XRD experiments, process and analyze all data, and preparation of the manuscript.

6.2 Abstract

An *in situ* acoustic emission (AE) and X-ray diffraction (XRD) cell for use in the study of battery electrode materials has been designed and tested. This cell uses commercially available coin cell hardware retrofitted with a metalized polyethylene terephthalate (PET) disk, which acts as both an X-ray window and a current collector. In this manner, the use of beryllium and its associated cost and hazards is avoided. An AE sensor may be affixed to the cell face opposite the PET window in order to monitor degradation effects, such as particle fracture, during cell cycling. Silicon particles, which were previously studied by the AE technique, were tested in this cell as a model material. The performance of these cells compared well with unmodified coin cells, while providing information about structural changes in the active material as the cell is repeatedly charged and discharged.

6.3 Introduction

Building batteries with higher rate capabilities, lower capacity fade, improved durability, and increased safety, is one of the greatest challenges facing battery researchers today [1]. The successful implementation of an electrical vehicle fleet aimed at reducing emissions and our nation’s dependence on foreign oil hinges on the performance and cost of batteries. Reliable energy storage devices are also vital to the portable electronics industry as well as remote sensing and power grid buffering.

Currently, commercial secondary batteries are based on nickel metal hydride (NiMH) or lithium ion battery (LIB) technologies. In a NiMH cell, hydrogen is stored in the anode during charging by a reaction with a mixture of rare earth metals. At the same time the Ni(OH)_2 in the cathode is oxidized to NiO(OH) . In effect, hydrogen is shuttled from cathode to anode through an electrolyte as electrons are passed through an external circuit. Discharge of a NiMH cell occurs through the reversal of the same reactions.

As a LIB is cycled lithium ions move in and out of active electrode materials through intercalation or alloying processes. During charging lithium is moved from the cathode to anode and is accompanied by a flow of electrons through an external circuit. The reverse of this process is the case for cell discharge.

The flux of hydrogen or lithium ions is a non-equilibrium process and sets up concentration gradients in the active materials. This causes the development of stresses and strains inside the material. If the strength of the active material is exceeded, particles may fracture, which can result in a loss of electronic contact with the current collector or side reactions at the newly exposed surfaces, which may lead to capacity fade and a decrease in a cell's operational life time.

In order to develop improved material formulations and charge/discharge programs, a better understanding of the relation between material strain, fracture, and cell performance is necessary. Currently no single characterization method can provide a full picture of how these properties interact in a functioning cell, thus there is an obvious need for new methods to fill this void.

X-ray diffraction (XRD) is a powerful tool for probing structural information in atomically ordered materials [2]. This can be used to determine strain and phase composition within a material of interest, but cannot directly give information about macroscopic processes such as fracturing. Acoustic emission (AE) is a technique capable of determining when fractures occur by sensing elastic vibrations at a sample surface that emanate from an internal event. By combining these two approaches, and comparing the results with the electrochemical diagnostics of a cycling LIB, new insight into how active materials are evolving and degrading can be achieved.

A novel *in situ* cell design for the simultaneous AE and XRD data acquisition has been developed. This design allows for *in situ* AE-XRD on an ordinary laboratory XRD unit without the use of any beryllium components, which makes it widely accessible, inexpensive, and safe to use. A detailed overview of related work, cell design, and basic testing using LIB chemistry is presented here.

6.4 Background of AE and In Situ XRD of Lithium Ion Batteries

In situ XRD of LIBs has been successfully used to study the crystallographic changes that these materials undergo during cycling. Phase changes, reaction mechanisms, and material stability can all be monitored through XRD, and by conducting these experiments *in situ*, a more accurate insight regarding actual electrochemical processes can be developed than with more conventional *ex situ* methods. Several *in situ* XRD cell designs have been applied previously to the study of LIBs. The first of these was XRD operated in reflection mode and was reported by Dahn et al. in 1982 [3]. This design used a stainless steel or brass cell top, which had a 0.25mm thick beryllium window that was sealed in place using silicon vacuum grease. The cell bottom was made of nickel plated brass and was temperature regulated by fluid channels and a thermistor.

In 1992 Gustafsson, et al. showed that prismatic battery cells in a polymer pouch could be used for *in situ* XRD experiments [4]. A commercial cell from Innocell Co. inside a sealed pouch was cycled while performing XRD in transmission mode. The pouch was made of an aluminum foil laminated on the outer face with polyester and on the inner face with polyethylene.

Richard, et al [5] reported an *in situ* XRD cell design, operated in reflection mode, whereby Rayovac 2325 coin cell hardware was modified with a 1.75cm diameter hole in the cell can to allow X-ray penetration through a 0.25mm beryllium window. Pressure sensitive adhesive was applied to seal the window to the modified can. Since beryllium dissolves in a liquid electrolyte when raised above 3V, contact between the cathode and window was prevented by using plastic electrode technology where the composite cathode and anode were laminated onto the separator. This sandwich was saturated with

electrolyte and an aluminum spacer disk was used to prevent direct contact between the saturated cathode and beryllium window.

In an attempt to overcome preferred orientation issues faced by previous designs, Bergström, et al. developed a transmission mode, *in situ* cell capable of oscillating perpendicular to the incident radiation beam [6]. Here, a transparent poly(methyl methacrylate) window was used and the entire cell assembly could rotate 180° using an electric motor.

In 2001, Balasubramanian, et al. [7] published research using a novel *in situ* XRD cell designed for use in transmission mode with synchrotron radiation. The cell consisted of two aluminum plates each drilled with screw holes and X-ray windows. Adjacent to each plate was a 250µm Mylar sheet, which served as both window and insulator. Between the Mylar sheets, a cathode, separator, and anode were placed along with a rubber gasket. Current was run to each electrode using thin copper and aluminum strips.

Roberts and Stewart published a paper in 2004 detailing their *in situ* XRD cell [8]. This design consisted of two machined steel plates that encased the battery electrodes and a spring to keep all of the internal components in contact. A beryllium window was attached to the X-ray window face of the cell using a conductive epoxy. Results from an *in situ* experiment on a graphite electrode were presented. Diffraction peaks from lithium, beryllium, beryllium oxide, copper, and graphite were observed. The shift of the graphite peak to higher angles was detected by taking sequential XRD scans during cell discharge.

AE has also found some use in the field of LIB development. The first series of papers dealing with AE during battery operation came from the Ohzuku group at Osaka City University in Osaka, Japan in 1997. In their first publication in this area [9], the group cycled both compressed pellet and paste electrodes while recording AE. The electrodes were cycled versus lithium foil in a simple cell consisting of one steel and one aluminum plate separated by a Teflon gasket and held together by screws. An AE sensor was mounted to the aluminum side, which served as the cathode current collector. Two papers from this group using the same testing procedure on different materials followed [10, 11].

Several years later, the Ohzuku group published a final paper using AE where the technique was compared with dilatometry to study anomalous expansion in graphite electrodes [12]. Volume expansion was measured on cycling cells using a home-built dilatometer and these results were compared with AE recorded from cells similar to those used in their previous work.

Two recent papers on AE from LIB electrode materials have been published. The first study focused on AE recorded from composite silicon electrodes cycled in standard coin cell hardware [13]. This work took advantages of the recent improvements to AE testing systems to investigate when AE events occurred during cycling and the nature of each event. Waveforms for each event were recorded and used to distinguish between events arising from silicon particle fracture and those from background noise such as electromagnetic interference (EMI). Characteristic parameters such as amplitude, duration, frequency, and energy were extracted from the waveforms and correlated with the state of charge in the cell. AE was found to correlate with voltage plateaus and the amount of AE detected diminished with each cycle. Scanning electron microscopy (SEM) confirmed the presence of large fractures in the cycled silicon particles. The results of this work were modeled using the diffusion equation and equations of elasticity [14]. Good agreement between the predicted and experimental results was observed.

The second publication summarized results from using AE to monitor particle fracture in a conversion-type electrode material for LIBs [15]. In particular, the compound NiSb_2 was cycled in a Swagelok cell versus lithium foil while monitoring AE over a period of three cycles. The cumulative AE energy was monitored and compared with cell potential. Sudden jumps in cumulative AE energy were observed at voltage plateaus corresponding to SEI formation and active material conversion. Pulverization of the NiSb_2 particles was confirmed by SEM of electrodes prior to cycling as well as after the first discharge.

6.5 Design and Operation of the Integrated In Situ AE-XRD Cell

A novel in situ AE-XRD cell was developed for this experiment. Polyethylene terephthalate (PET, commercially known as Mylar) disks with a diameter of 19mm and a

thickness of 125 μ m were sputtered with copper to create a beryllium-free X-ray window. PET was selected for its low gas permeability, appropriate rigidity, and small X-ray absorption. One side of the disk was completely sputtered with a 300nm copper foil and the other was only sputtered on its outer edge with a copper foil 600nm thick, as shown in Fig. 32. This approach reduced X-ray absorption by requiring penetration through only one copper layer. Prior to sputtering, the disks were polished with hexane to remove any surface scratches and then rinsed with isopropanol to remove any residue. Copper sputtering was performed at 40W and 16 mTorr in 20 sccm of argon, and patterning was accomplished using aluminum masks.

Stainless steel 2032 coin cell hardware (20mm diameter, 3.2mm height) obtained from Pred Materials (part #CR2032) was modified to include a 0.7cm diameter hole in the center of the can piece. After punching, any burs were sanded off and the part was then sonicated in a solution of Branson MC-3 (10% by volume) in deionized water for 30 minutes before rinsing with deionized water, then hexane, and finally in isopropanol to remove any grease or surface contaminants. A thin film of degassed Loctite 1C epoxy-patch adhesive was applied to the inner face of the punched can around the hole. A metalized PET window was placed into the can and pressed into the epoxy to create a hermetic seal. This assembly was placed in an oven at 100°C for 2 hours to fully cure the epoxy. After removing from the oven, the weight of the assembly was recorded and conductivity between the can and the metalized window was tested using a multimeter.

Next, a slurry containing 80 wt.% -100+325 mesh silicon (Alfa Aesar, 99%), 10 wt.% poly(vinylidene fluoride) (Sigma Aldrich, M_w 534,000), and 10 wt.% Super S carbon (M.M.M. Carbon) suspended in N-methylpyrrolidone (NMP) (Sigma Aldrich, 99.5%), was applied to the window. The NMP was allowed to evaporate in a hood for 12 hours, leaving behind a composite silicon electrode on the window surface. The component was then placed in a 100°C vacuum oven at -100kPa for 1 hour to remove any residual moisture before being transferred to an argon filled glove box.

Prior to assembly, the laminated window assembly was again weighed to precisely determine the amount of silicon applied. Each cell contained roughly 15mg of active material, corresponding to a theoretical capacity of 54mAh when using a

theoretical specific capacity of 3579mAh/g for silicon. Cells were assembled using a Celgard 2325 separator, a disk of lithium foil (Alfa Aesar, 0.75mm thick, 99.9%), and 1.2M LiPF₆ in ethylene carbonate and ethyl methyl carbonate (3:7 wt) (Ferro), as show in Fig. 33.

A Physical Acoustics Micro-II digital AE system running AEwin for PCI2 version E4.00 with 2/4/6 preamps and S9220 sensors was used for monitoring AE activity. Sensors were placed on the cap side of the coin cell using silicon grease as a couplant to facilitate signal transmission across the sensor/cell interface. The AE sensor and cell, placed in a plastic coin cell holder, were mounted in putty attached to a flat plastic tray, as shown in Fig. 34. This served to keep the cell and sensor in good contact as well as to keep the cell stationary throughout the experiment. AE system parameters, signal filtering, and data processing were performed as previously described [13]. Briefly, the preamp gain was set to +60dB with no analog filter. A digital band pass filter was applied to the incoming waveforms between 100kHz and 2MHz along with a sample rate of 8MHz. Threshold, peak detection time, hit definition time, hit lock-out time, and maximum hit duration were set to 22dB, 50 μ s, 80 μ s, 100 μ s, and 1ms, respectively. These values were determined to be appropriate based on previous work and preliminary testing.

Cycling was performed using a Biologic SP-200 controlled by EC-Lab v10.02. Constant current-constant voltage tests were conducted at approximately 0.18mA/mg (exact value depended upon the measured weight of silicon in the cell), which corresponded to a 20 hour charge or discharge step when assuming a theoretical specific capacity of 3579mAh/g for silicon. This rate may be given by the notation C/20, where C denotes the full theoretical capacity of the cell and the denominator indicates the time needed to charge/discharge this capacity based on the current into the cell. For example, at a rate of C it would take one hour, at C/50 it would take 50 hours, and at 2C it would take ½ hour to complete a single charge or discharge step. Upper and lower potential limits were set at 1.5V and 10mV, respectively. Once the potential limit was reached the current was allowed to drop off to C/100 while holding a constant potential before proceeding to the next cycling step.

XRD was performed on a PANalytical X'Pert Pro MPD system. A 2kW Cu target was used along with an automatic divergence slit and beam width of 5mm. Scans were taken between 35°-60° every 15 minutes as the cell was cycled. Vertical displacement of the cell was accounted for by using the copper peaks as an internal standard. Rietveld refinement was performed using PANalytical High-Score Plus v.3.0.1 to find peak positions and calculate lattice dimensions. Lattice strain was then calculated from these measurements using an unstrained lattice parameter of 5.430Å measured from the pristine material.

6.6 Supplementary Materials Characterization

SEM analysis of as received silicon particles was performed using a Hitachi S3400. An accelerating voltage of 30kV was used. The working distance for imaging was set to 12.1mm. In order to SEM cycled electrodes, the cells were first charged to 2.0V and held there for 48 hours to ensure full delithiation of the silicon. Cells were then disassembled in an argon filled glove box, rinsed with propylene carbonate, and allowed to dry under vacuum. Samples were sealed in air tight containers for transport to the SEM where they were quickly transferred to the vacuum chamber for imaging.

A Hitachi NB5000 combined focused ion beam (FIB)-SEM tool was used for *in situ* milling, electron backscatter diffraction (EBSD), and scanning transmission electron microscopy (STEM) analysis. A single silicon particle was milled with 40 keV Ga⁺ ions at glancing incidence and then polished with 2 keV Ga⁺ 5-10° off-glancing incidence. The polished face was then rotated and tilted in the FIB-SEM instrument for EBSD measurements using 20keV electrons.

For higher resolution analysis, the FIB-SEM instrument and *in situ* micromanipulator system was used to lift out a small (~5×5×2µm) section from the polished surface, which was then thinned to electron transparency (~5×5× less than 0.2µm) using the Ga⁺ beam. This thinned section was then imaged at 30 keV in the FIB-SEM instrument using the SEM beam and a bright-field solid-state STEM detector, giving a STEM-in-SEM image.

6.7 Results

The starting silicon particles had an irregular, faceted shape, as shown by the SEM images in Fig. 35. As previously reported, the particles had a mean particle size of $132.85\mu\text{m}$ with a standard deviation of $56.59\mu\text{m}$ measured by laser scattering particle size distribution analysis and were determined to be crystalline Si by XRD [13]. The presence of inclusions and voids within the particle has been shown to have a significant impact on the stresses that develop during lithiation/delithiation [16], thus the internal structure of the Si particles was further explored using FIB, SEM/STEM, and EBSD, the results of which are also shown in Fig. 35. The particle cross-section (Fig. 35(b)) clearly shows many large voids, as indicated by arrows. The STEM image in Fig. 35(c) shows that the particles are polycrystalline with oblong crystal shapes that are $\sim 500\text{nm}$ in length. The STEM image (Fig. 35(c)) also revealed the possible presence of smaller voids between some of the Si grains. EBSD imaging confirmed the STEM observations and revealed a random crystal texture. Because of the small grain size of the silicon, EBSD shows areas of high and low image quality: when the SEM beam is incident on more than one grain, the EBSD pattern is non-indexable and image quality is low.

The cumulative number of fracture AE events recorded per mg of active material in the cell is plotted along with voltage versus time in Fig. 36. This AE comes from the fracturing of Si particles as they are lithiated/delithiated. The bulk of these events occur at the beginning of a charge or discharge step as previously reported [13]. Cell performance was consistent with that of coin cells having the same composition but with no window modifications. The periods of highest AE rate occurred near the beginning of charge and discharge stages in voltage plateau regions. This parallels the AE behavior previously described for similar cells in unmodified coin cell hardware [13]. The only departure from previous results is the decreased overall number of hits recorded. The AE-XRD cell gives fewer emissions because, unlike in previous work, the AE sensor must be placed on the cap side of the cell (lithium foil side) in order to accommodate the X-ray window. The increased distance allows only the AE from higher intensity events to reach the sensor. This decrease in cumulative hits provides further indirect evidence in support of previous conclusions that the AE source is the silicon composite electrode.

SEM images of the silicon particles after 5 cycles are shown in Fig. 37. A combination of deep fissures and shallow surface cracks can be observed on all particles as previously reported [13]. The larger fractures spanned the entire diameter of particles in some cases and penetrated deep into the particle. Surface cracks tended to be shorter, generally around 20 μm long and a similar depth into the particle. This degradation behavior is in agreement with the previously observed when this material was cycled in unmodified coin cells.

A series of hit waveforms recorded during electrochemical cycling of the silicon along with each hit's respective Fast Fourier Transform (FFT) is shown in Fig. 38. The wave characteristics of these hits are in excellent agreement with previous observations from AE experiments on this material performed without XRD [13]. From top to bottom the hits have decreasing amplitude. This allows the frequency peaks from this type of hit to be easily discriminated from background frequencies by looking at what FFT peaks diminish in magnitude with decreasing hit amplitude. The primary frequency component of these particle fracture hits lies primarily between 280-340 kHz.

Diffraction patterns for a cell at various stages of cycling are shown in Fig. 39. Crystalline silicon is known to become amorphous upon lithiation [17-19]. The change in peak area (broadening) after the first discharge stage indicates that extensive amorphization of the silicon occurred. Upon recharging the cell by delithiation of the silicon, the crystallinity was not recovered and the transformed region remained amorphous upon repeated cycling. Near full lithiation, amorphous silicon can order into a Li_5Si_4 phase. A very weak peak appears after the first discharge which likely corresponds with the (332) peak of $\text{Li}_{15}\text{Si}_4$.

As lithium alloys/dealloys with silicon, the individual silicon particles swell and contract, which may cause the metalized PET window to simultaneously flex. Vertical displacement of the sample surface was determined from the (111) copper peak position. Fig. 40 shows a strong correlation between cell voltage and sample surface displacement. Error bars indicate the standard error in each measurement. Following an initial settling period, which may be related to reorientation of the silicon particles in the composite electrode allowing them to lay flatter against the current collector, the surface repeatedly

falls during charging steps (silicon delithiation) and rises during discharge steps (silicon lithiation). This behavior directly correlates with the expected volume fluctuation in the silicon particles. At full lithiation silicon has been shown to reach a volume expansion of over 280% [19], which corresponds to a linear expansion of 140%. In particles with a diameter near 130 μm , such as those used here, this corresponds to a linear expansion of about 52 μm . From Fig. 40 the sample surface displacement change between charged and discharged states is seen to be close to 50 μm , putting it in excellent agreement with the predicted displacement if volume fluctuations in the silicon particles are indeed the source of AE events.

The amorphization of the initially crystalline silicon particles was monitored by tracking the (022) and (311) silicon peak areas during cycling. For each measurement, the silicon peak areas were normalized to the (111) copper peak area. The relative percent crystallinity of the silicon particles was calculated using Eqn. 25, where A_{Si} is the area of a crystalline silicon peak, A_{Cu} is the area of the (111) copper peak, and A_{Si_o} and A_{Cu_o} are the areas of the same peaks as measured from the sample prior to cycling for silicon and copper respectively.

$$\%Crystallinity = \left(\frac{A_{Si}}{A_{Cu}} \right) \bigg/ \left(\frac{A_{Si_o}}{A_{Cu_o}} \right) * 100\%$$

Eqn. 25: Relative percent crystallinity

Fig. 41 shows the relative crystallinity of the silicon from each scan as determined from the (220) silicon peak (the same results, which are not shown here, were obtained using the (311) silicon peak). During the first discharge step, the silicon is lithiated and a nearly 65% drop in crystallinity is observed. After this initial discharge step, only a slight decrease in crystallinity can be detected upon further cycling. The remaining crystalline portion of the silicon is most likely at the core of the particles [19]; however, the highly

polycrystalline nature of the particles could have an effect on how lithium diffuses into the particles and further work is necessary to verify.

Lattice parameters for the crystalline portion of the silicon were calculated from each can. These values were then converted to engineering strain through the use of Eqn. 26, where L is the lattice parameter measured from a given scan and L_o is the lattice parameter measured for the silicon prior to any cycling.

$$\varepsilon = \frac{(L - L_o)}{L_o}$$

Eqn. 26: Engineering strain

The estimated standard deviation (as reported by HighScore Plus) for each lattice parameter measurement was converted to the standard deviation for its respective strain value by using the propagation of error properties shown in Eqn. 27 and Eqn. 28 [20].

$$u(A - B) = \sqrt{u(A)^2 + u(B)^2}$$

Eqn. 27: Difference law for propagation of errors

$$u\left(\frac{A}{B}\right) = \left(\frac{A}{B}\right) \sqrt{\left(\frac{u(A)}{A}\right)^2 + \left(\frac{u(B)}{B}\right)^2}$$

Eqn. 28: Division law for propagation of errors

When these two properties are combined with the definition of engineering strain given in Eqn. 26, the standard error of strain can be expressed as in Eqn. 29. Here, $u(L)$ is the uncertainty in the lattice parameter for a give scan and $u(L_o)$ is the uncertainty in the lattice parameter measured for the silicon prior to any cycling.

$$u(\varepsilon) = \varepsilon \sqrt{\frac{u(L)^2 + u(L_o)^2}{(L - L_o)^2} + \frac{u(L_o)^2}{L_o}}$$

Eqn. 29: Error propagated to strain from lattice parameter measurements

A plot of silicon lattice strain as a function of time is shown in Fig. 42, where the error bars indicate the propagated standard error in each measurement. A simple correlation between strain and charge/discharge steps is not observed until the second charge is applied. Following this step, the crystalline silicon is in tension during charge and compression during discharge. The highest tension and fastest rate of amorphization both occur during the first 5 hours of discharge. Furthermore, this overlaps with the largest population of AE indicating a strong correlation between silicon amorphization and the fracturing processes.

6.8 Conclusion

A new *in situ* AE-XRD setup has been successfully designed and tested. The cell can provide an operating environment similar to those of real coin cells while monitoring structural changes and fracture events in the active material. Additionally, all of this can be done using no beryllium, in a laboratory diffractometer rather than a synchrotron X-ray beam. In this way the cell is safer, cheaper, and can be charged to higher cell potentials than system designs containing beryllium. By using laboratory XRD systems, long-term *in situ* cycling experiments, spanning days or weeks, may be performed, which would be largely unobtainable using synchrotron sources due to high beam-time demand. Since different metals can be applied to the XRD window, this same cell can be used to study both anode and cathode materials. Recently, the cell has been used to study cathode materials with potentials up to 4.9V [21]. By acquiring a series of scans during the charge and discharge cycling of *in situ* AE-XRD cells, the change in lattice strain in the active materials may be monitored and correlated with particle damage detected by simultaneously acquired AE signals. This technique is currently being used to gain new insight into the degradation of several anode and cathode materials for LIBs.

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Chapter 7: Evolution of Phase Transformation Behavior in $\text{Li}(\text{Mn}_{1.5}\text{Ni}_{0.5})\text{O}_4$ Cathodes
Studied By In Situ XRD

7.1 Disclosure

This chapter is based on the manuscript submitted to the Journal of the Electrochemical Society (K. Rhodes, R. Meisner, Y. Kim, N. Dudney, C. Daniel, “Evolution of Phase Transformation Behavior in $\text{Li}(\text{Mn}_{1.5}\text{Ni}_{0.5})\text{O}_4$ Cathodes Studied By In Situ XRD”, *J. Electrochem. Soc.*, 158 (2011) 1-8). The full list of authors includes Kevin Rhodes, Melanie Kirkham, Roberta Meisner, Chad Parish, Nancy Dudney, and Claus Daniel. The role of Kevin Rhodes was to design and develop the novel in situ XRD cell, perform in situ AE and XRD experiments, process and analyze all data, and preparation of the manuscript.

7.2 Abstract

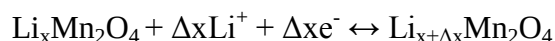
In situ X-ray diffraction of $\text{Li}(\text{Mn}_{1.5}\text{Ni}_{0.5})\text{O}_4$ was performed using a novel electrochemical cell based on coin cell hardware. The pristine material had a cubic spinel structure with a Ni^{2+} oxidation state. As the cell was charged through its 4.75V plateau, a transition between spinels with Ni^{2+} , Ni^{3+} , and Ni^{4+} oxidation was observed. As the oxidation of the nickel increased, the lattice parameter of the corresponding spinel diminished. During discharge, the spinel reversed its phase changes until only the Ni^{2+} spinel was observed. As the discharge potential reached a plateau at 2.75V a tetragonal spinel phase was formed, which upon subsequent cell charging was completely converted back to a cubic spinel phase. Lattice parameter changes of each phase were calculated and showed a characteristic strain release during phase changes. After 15 full cycles the transition between cubic spinels was no longer complete and the formation of the tetragonal spinel phase was no longer detected. This suggests a gradual change from an ordered to disordered MNO structure and lithium trapping in the active material. These cycle-induced changes to phase transition behavior can be related to capacity fade and overall cell performance.

7.3 Introduction

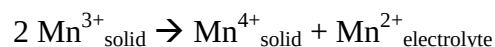
A global demand for portable, high power energy storage systems has made the development of improved lithium ion batteries (LIBs) an important research priority [1].

Consumer electronics, electrical vehicles, power grid regulation, and remote sensing applications all stand to benefit from LIBs with higher power, greater capacity, and longer life. To achieve this goal the structural behavior of the active electrode materials must be well understood at multiple levels from lattice, to particle, to composite. How the structure changes as the material is reversibly intercalated or alloyed with lithium as well as how the structure evolves over the course of many lithiation/delithiation cycles are important considerations in the design, development, and selection of active materials.

Among current cathode materials for lithium ion batteries those based on the LiMn_2O_4 spinel structure are advantageous in their non-toxicity, low cost, and ease of preparation [2-7]. The spinel structure of this material offers a 3D diffusion pathway for lithium intercalation/deintercalation. Lithiation occurs reversibly as per the following reaction:



However, use of this material faces several challenges including somewhat limited rate capabilities [8], dissolution of Mn^{2+} ions into the electrolyte [9,10], and a strong Jahn-Teller distortion at low potentials [10-12]. At low potentials the $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox couple produces Mn^{3+} ions which may participate in the following disproportion reaction at the interface between the particle and the electrolyte:



At high degrees of lithiation, LiMn_2O_4 will undergo a Jahn-Teller distortion that forces it from a cubic to tetragonal spinel structure as $\text{Li}_2\text{Mn}_2\text{O}_4$ is formed [10-12]. Any regions of material in this tetragonal phase, most likely formed at the particle surface [11] near the end of a deep discharge, are no longer dimensionally compatible with neighboring cubic spinel material [12]. This can cause significant intra-particle defect formation which may ultimately lead to fracture. Fracturing has been detected in many LIB electrodes [13-22] and can cause a loss of cell capacity as damaged particles lose

contact with their current collector or undergo non-reversible reactions at freshly exposed fracture surface area.

$\text{Li}(\text{Mn}_{1.5}\text{Ni}_{0.5})\text{O}_4$ (denoted MNO) is an important member of transition metal substituted LiMn_2O_4 series with the general formula $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ where M is Co, Mg, Cr, Ni, Fe, Al, Ti, or Zn [23,24]. MNO offers a high operating voltage of 4.7V and improved capacity retention and rate capability at the cost of having a slightly reduced capacity compared with LiMn_2O_4 [25,26], making it a promising cathode material for high power LIB applications. In its stoichiometric composition the cations exist as Mn^{+4} and Ni^{+2} . Nickel doping limits Mn^{2+} dissolution by keeping the cation as Mn^{+4} [27]. Structural studies have shown the appearance of 3 distinct cubic spinel phases at around 4.75V which correspond to the Ni^{+2} , Ni^{+3} , and Ni^{+4} [28]. At this potential, Li-ion inserts/extracts from tetrahedral positions in the MNO. At 4.1V there is an oxidation/reduction reaction between Mn^{+3} and Mn^{+4} may occur. At 2.75V Li-ions insert/extract from octahedral lattice positions and corresponds to the formation of a tetragonal spinel phase.

MNO is has been prepared and studied as both an ordered and a disordered structure [28-30]. In the ordered structure, a $P4_332$ space group is observed where 4a and 12b lattice positions are occupied by Ni and Mn ions respectively. In contrast the disordered MNO structure has an $Fd3m$ space group where cations are distributed on 16d sites. On both charge and discharge, only the ordered structure shows a voltage plateau at 4.0V.

X-ray diffraction (XRD) is a powerful tool for monitoring changes in lattice parameters, phase composition, and atomic ordering making it an ideal method of characterizing the atomic structure of electrode materials. In the field of LIB research, ex situ XRD studies can provide information about how materials respond to lithiation/delithiation, but samples can only be tested after cells have been disassembled and the electrodes have been rinsed with solvents and dried to remove any residual electrolyte salts. In situ XRD is a preferable method since this approach gives direct information about what is happening to materials inside of a cycling cell without any

convolution from post cycling sample preparation. In past decades several in situ XRD cell designs for the study of battery materials have been developed [31-37].

Some previous work concerning the phase change behavior in MNO as it is lithiated/delithiated has been previously conducted using both ex situ [24] and in situ [28] XRD techniques. The first of these papers [24] cycled cells between 3.60 and 4.95V one time. Results showed the expected decrease in lattice parameter during the first charge step and an increase in lattice parameter during the first discharge. Some indication of phase transformation between Ni oxidation states could also be detected in the diffraction patterns.

The ex situ findings were soon expanded upon by means of in situ XRD on both ordered and disordered MNO spinels cycled between 3.5 and 5.0V [28] for two cycles. In the ordered MNO material, three distinct spinel phases were detected relating to each of the Ni^{+2} , Ni^{+3} , and Ni^{+4} oxidation states. These phases transitioned into one another by way of two distinct two-phase regions and were nearly completely reversible for the first two charge/discharge cycles. In contrast, the disordered MNO material showed a smooth peak shift to higher angles with no clear two phase region until nearing the end of charging. This behavior was also nearly completely reversible over the two charge/discharge cycles studied.

Our group has focused on the in situ study of lithium intercalation compounds with an emphasis on structure/property changes due to electrochemical cycling by means of acoustic emission (AE) [21], computer modeling [38], and in situ XRD [39]. A novel in situ XRD cell suitable for studying electrode materials on a laboratory diffractometer without the cost and hazards associated with beryllium X-ray windows has been designed and tested on silicon anode materials [39]. By not using beryllium as has been done by some researchers in the past, the cell can be cycled to potentials about 4.2V where beryllium would normally corrode [33]. This cell was used to monitor changes to the crystal structure of MNO as it was cycled over a wide potential range. In situ XRD was performed on the initial two cycles as well as after 15 cycles to determine how the structure and phases transition steps were evolving with repeated cycling. This will serve

as the baseline for future work aimed at using this technique to develop new material modifications and cycling protocols.

7.4 Materials and Methods

To prepare the in situ cells, a 10mm hole was punched in the can component of 2032 stainless steel coin cell hardware. A 19mm diameter disk of 50 μ m thick Kapton tape (Bertech, KPT2-1) was punched and affixed inside the can over the hole. The internal face of this component was sputtered with a 300nm thick film of aluminum. Sputtering of aluminum was performed at 30W, 25 mTorr, and 20 sccm of argon. The sputtered can assembly was weighed and stored in a desiccator until use.

A slurry containing 85% weight MNO (Alfa Aesar, 99%), 5% weight poly(vinylidene fluoride) (Sigma Aldrich, M_w 534,000), and 10% weight Super S carbon black (M.M.M. Carbon) suspended in N-methylpyrrolidone (NMP) (Sigma Aldrich, 99.5%) was prepared and applied by pipette to the metalized Kapton window. NMP was evaporated by heating at 60°C for 10 minutes in a vacuum oven at -100kPa. The resulting composite electrode films were 350-400 μ m thick. The components were then dried at 100°C for 2 hours to remove any moisture before transferring to an argon filled glove box. Here the final weight of the component was measured to determine the weight of active material present. Cells were assembled as shown in Fig. 43 using Celgard 2325 separator, lithium foil (Alfa Aesar, 0.75mm, 99.9%), and an electrolyte of 1.2M LiPF₆ in ethylene carbonate and ethyl methyl carbonate (3:7 wt) (Ferro).

Cycling of the cell during in situ XRD was performed using a Biologic SP-200 controlled by EC-Lab v10.02. Constant current-constant voltage tests were conducted at C/5 rate (corresponding to a specific current of about 30mA/g of active material when assuming a specific capacity of 147mAh/g). Upper and lower potential limits were set at 4.9V and 2V respectively. During the constant voltage step the current was allowed to fall to C/25 before proceeding. The open circuit voltage of a fresh cell was about 2.8V. For cycling outside of the X-ray diffractometer, a Maccor Series 4000 battery cycler was used. In parallel work, unmodified coin cells containing electrodes cast from the same

MNO slurry described above were cycled at identical rates. These showed cycling behavior and capacity fade very similar to that recorded from in situ cells.

XRD was performed on a PANalytical X'Pert Pro MPD system with 2kW copper target and automatic divergence slit. Scans from 35° - 70° 2θ were collected every 20 minutes during cycling. Any vertical displacement of the cell was corrected for using the aluminum peaks as an internal standard. Processing and Rietveld refinement of each diffraction pattern was performed using PANalytical High-Score Plus v.3.0.1. Volume fractions of each phase were calculated directly from peak area measurements and, as with the reported lattice parameters, represent an average value through the depth of X-ray penetration into the composite electrode film.

7.5 Results and Discussion

Freshly assembled in situ XRD cells containing an MNO cathode versus lithium foil showed an initial open circuit potential of about 2.8V. The diffraction patterns of an as-received MNO powder and an uncycled MNO in situ cell are shown in Fig. 44. Both patterns show peaks from the cubic spinel cathode material with a lattice parameter of $8.1709\text{\AA}$. The in situ cell also shows Kapton and aluminum peaks (the latter served as an internal standard). The estimated error in the fit of each lattice parameter, as reported by High-Score Plus, gave a 3σ interval of less than $\pm 0.0021\text{\AA}$ for all refinements. Relative peak intensities were in good agreement with the calculated diffraction pattern for MNO throughout the experiments indicating very little preferred orientation effect.

An isoplot of the diffraction scans from the first two cycles is shown in Fig. 45. As the cell is charged, and lithium is removed from the MNO, three discrete cubic spinel phases are sequentially formed. This can be clearly seen in the (400), (511), (440), and (531) peaks. These phase changes indicate the oxidation of Ni^{+2} to Ni^{+3} to Ni^{+4} . All three phases coexist until the MNO is nearly fully delithiated. At that point strong Ni^{+4} spinel peaks with very weak Ni^{+2} spinel peaks are observed. As the cell is subsequently discharged and lithium intercalates the MNO the same phase transformations occur in reversed order until only the Ni^{+2} spinel phase is present.

As discharge continues a new tetragonal spinel structure is formed but it should be noted that the Ni^{+2} cubic spinel phase is not completely eliminated, resulting in a phase transformation which is not complete. As this cell is then recharged and lithium is removed from the MNO, the tetragonal phase is completely transformed back to the cubic spinel structure.

The lattice parameters for every phase present in each diffraction scan were determined by fitting and plotted against time along with cell voltage and capacity in Fig. 46. The values and trends in the fitted lattice parameters were in good agreement with those previously reported [28]. The reversible transition between cubic spinel phases occurs at a voltage plateau near 4.75V. The lattice parameter of each phase becomes smaller as the oxidation of Ni increases. The initial Ni^{+2} spinel had a lattice parameter of 8.1709Å which begins to drop as the 4.75V plateau is reached and after about 27mAh/g of lithium has been removed. This lattice parameter reaches a minimum at 8.139Å after 82mAh/g charging and it is at this point that the Ni^{+3} spinel phase began to form with a lattice parameter of 8.085Å. After this point the Ni^{+2} spinel began to increase its lattice parameter up to about 8.152Å. This rebounding behavior in the Ni^{+2} spinel indicates a significant release of compressive stress on this phase as the Ni^{+3} spinel is formed. After 125mAh/g of charging the Ni^{+4} spinel phase appeared with a lattice parameter of about 8.003Å.

At a capacity of 131mAh/g, 89.5% of the theoretical charge capacity, the first charge was completed and the Ni^{+3} spinel phase disappeared, leaving only the Ni^{+2} and Ni^{+4} spinels. As the following charge step proceeded at about 4.65V the described transitions proceeded in the reverse order and at 134mAh/g of discharge the material had fully returned to the Ni^{+2} spinel phases with a lattice parameter slightly lower than the starting material at 8.167Å.

A second voltage plateau was observed at about 2.75V after 134mAh/g of discharge. Here the lattice parameter of the Ni^{+2} cubic spinel held steady. At 156mAh/g the formation of a tetragonal spinel phase was detected. The *a* and *c* lattice parameters were 5.732Å and 8.685Å, respectively, and did not change significantly from these

values. Shortly after the appearance of tetragonal spinel phase the voltage fell to the lower limit of 2V. The first discharge ended with at 210mAh/g, which is 54mAh/g past the capacity where the tetragonal phase was first observed.

The second charge step proceeded to 47mAh/g at which point diffraction peaks from the tetragonal spinel phase disappeared. The remainder of the second cycle proceeded as the first with full reversal of all phase transitions and similar lattice parameters as seen in Fig. 46.

Fig. 47 shows the phase composition in the cell as it was cycled. During the first charge there is a smooth transition from between the three cubic spinel phases with nearly complete transformation being achieved. As mentioned previously, near full delithiation the Ni^{+3} spinel completely disappears leaving only the Ni^{+2} and Ni^{+4} spinels. As the volume fraction of Ni^{+3} spinel drops below about 20% there is an observed increase in the volume fraction of the Ni^{+2} spinel. As discharge ensues this behavior is reversed. As discharge precedes the tetragonal spinel phase forms from the Ni^{+2} spinel until it reaches a maximum volume fraction of 57.3%. The complete reversal of this transition is observed as the second charge step begins and the second cycle repeated the phase composition behavior of the first.

The cell was cycled outside of the diffractometer up to the 14th discharge step when it was returned to the beam for further data collection. The capacity of each charge and discharge step is shown in Fig. 48. The first charge had a much lower capacity than all other steps because the open cell potential of the fresh cell was about 2.8V so no capacity from the 2.75V plateau was occurred. Steady capacity drop was observed all the way up to the 16th cycle.

An isoplot of the diffraction scans taken between the 14th and 16th discharge is shown in Fig. 49. Most notably, at low potentials there is no longer any indication of tetragonal spinel formation. Also, the cubic spinels no longer transform completely from one phase to another during charge and discharge at high potentials. Instead, all three phases are observed simultaneously. At the onset of discharge the MNO is again lithiated and the Ni^{+3} and Ni^{+4} phases revert fully to the Ni^{+2} spinel.

The lattice parameters for the cubic spinel phases between the 14th and 16th discharge are shown in Fig. 50. The detailed behavior of the lattice parameters is different here than was observed in the first two cycles. The Ni⁺² spinel appears to swing between 8.173Å when at high lithiation to 8.155Å at low lithiation when the other two cubic spinel phases are present. The Ni⁺³ spinel shows a decreasing lattice parameter as it is formed which levels off to 8.091Å as the Ni⁺⁴ spinel appears. The Ni⁺⁴ spinel behave similarly to how it did during the first two cycles with a lattice parameter of 8.017Å. As the cell is discharged the Ni⁺³ spinel reverses the dimensional change it underwent during charging and shows an increasing lattice parameter as soon as the Ni⁺⁴ spinel phase disappears.

A dramatic difference in the phase composition behavior of the MNO material between the 14th and 16th discharges can be seen in Fig. 51. As previously noted, no tetragonal spinel phase is formed at low potentials as was the case in the first two cycles. As the cell is discharged a smooth transition from one cubic spinel phase to another is observed but the Ni⁺³ spinel never fully disappears. Again there is an observed increase in the volume fraction of the Ni⁺² spinel phase near the end of lithiation that appears to be formed from the Ni⁺³ spinel.

From Fig. 51 it is seen the phase composition behavior of the Ni⁺³ is not the same in charge and discharge. As the cell is discharged this phase reaches a maximum volume fraction of about 33%. However during charging the phase reaches a maximum volume fraction of over 40%. The observed phase transformation behavior was very similar for the 15th and 16th cycles.

7.6 Conclusion

In situ XRD of MNO cathode material was performed using a novel electrochemical cell based on coin cell hardware. This technique has been shown to provide diffraction patterns and cell performance without the use of beryllium windows and without the need for a synchrotron radiation source. Diffraction patterns showed the presence of three distinct cubic spinel phases corresponding to Ni⁺², Ni⁺³, and Ni⁺⁴ oxidation states. At low potential the formation of a tetragonal spinel phase was detected which upon delithiation was completely converted back to a cubic spinel phase upon

delithiation. Lattice parameter changes of each phase were refined and showed a characteristic strain release during phase changes. After repeated cycling the transition between the cubic phases was no longer complete and the formation of the tetragonal spinel phase was no longer detected.

The observed breakdown of structural transition behavior observed for MNO is likely caused by a combination of effects including lithium trapping and disordering of the NMO cation arrangement. As the materials is cycled, regions of the active material may become electronically isolated due to particle pulverization or side reactions, effectively prohibiting that region from further cycling. AE studies on MNO are currently in progress to determine to what extent particle fracture and pulverization is occurring in the material.

A gradual shift from an ordered to disordered structure may also be responsible for the variation in phase change behavior as cycling progresses. Although the material initially showed very distinct two-phase regions, as has been previously reported for an ordered MNO material [28], repeated cycling caused these transitions to become much less pronounced as observed for the disordered structure. The shift from an ordered to disordered structure is also supported by the gradual loss of the 4.0V voltage plateau with progressive cycling. The current in situ XRD technique did not allow for observation of the low angle diffraction peaks related to cation ordering due to the prominent X-ray scattering from the Kapton window in this region. Work is currently underway to gain a better understanding of this phenomenon.

Both of these effects could contribute to the observed capacity fade by isolating parts of the MNO material or by limiting the degree of lithiation that can be achieved in active regions. Another major factor in the loss of capacity is the drastic reduction in the 2.75V plateau as cycling progresses, which corresponds to the disappearance of the tetragonal spinel phase at higher cycle numbers. Although progress has been made to the performance of MNO materials in the 3.5-5.0V range, significant capacity loss is still a major issue at low potentials. If cycling in this low potential region can be stabilized, the available capacity of the MNO could be nearly doubled as compared to cycling only in the high voltage region.

Methods to improve the material performance and reduce capacity loss such as particle surface coatings have been successfully demonstrated in similar materials [40-43]. These coatings are known to modulate how and to what extent the surface electrolyte interface forms and also have a significant effect on how lithium enters and exits the particle. If the mode by which lithiation/delithiation occurs is augmented it could have a definite effect on how the concentration gradient, moving phase boundary, stress/strain field propagate within the particle. These changes could then reasonably effect how particles fracture and how lithium becomes irreversible trapped. In Situ XRD work on MNO is currently underway to study the effect of novel surface coatings on the lattice structure and how it changes with repeated cycling.

7.7 Acknowledgments

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Chapter 8: In Situ XRD Thin Film Tin Electrodes for Lithium Ion Batteries

8.1 Disclosure

This chapter is based on the manuscript recently submitted to the Journal of the Electrochemical Society. The full list of authors includes Kevin Rhodes, Melanie Kirkham, Roberta Meisner, Nancy Dudney, and Claus Daniel. The role of Kevin Rhodes was fabrication and assembly of all batteries for testing, planning and execution of in situ XRD cycling studies, processing and analysis of all data, and preparation of the manuscript.

8.2 Abstract

Thin film electrodes for lithium ion batteries (LIB) poses several attractive advantages over traditional composite electrodes including size and shape constraints, operating temperature range, and volumetric energy density. Tin is an attractive candidate for LIB anode applications due to its exceptional specific capacity, cascading voltage profile, safety, wide availability, and low cost. Tin thin film electrodes were sputtered onto the current collector of a recently developed in situ X-ray diffraction (XRD) and were monitored continuously by XRD while cycling. A phase transformation from white tin, to Li_2Sn_5 , to $\beta\text{-LiSn}$, to $\text{Li}_{22}\text{Sn}_5$ was observed during lithiation with the same phases detected in reverse order during delithiation. Preferred orientation and crystallite size information for these phases was extracted from the XRD data in order to develop a clearer picture of how lithium enters and exits thin film tin electrodes.

8.3 Introduction

Lithium ion battery (LIB) technology has become omnipresent in the daily lives of most people. From cellular phones and laptop computers to electrical vehicles and power grid buffers, LIB's offer a level of reliable portable power only available within recent decades [1]. However, along with its success comes an endless demand for improvement and the development of LIB's that are lighter, last longer, and store more charge. Additionally, these batteries need to be as flexible as possible, both figuratively and literally, in order to meet the strict geometric and functional constraints of modern devices.

Thin-film LIB's offer several attractive advantages over traditional composite electrodes including size and shape constraints, operating temperature range, and volumetric energy density [2]. Through a sequence of sputtering steps a thin-film battery can be directly applied to a substrate without the need for any binder material. One can easily envision the use of this technique to integrate batteries directly into the paneling and structural components of cars, buildings, and other devices. Additionally, the unique properties and design flexibility of these devices makes them an excellent candidate for micro-battery applications in things such as sensors and implantable devices.

Thin-film electrodes also offer a unique opportunity to study crystallographic changes that occur inside of an active material as it reversibly lithiated and delithiated. By applying in situ X-ray diffraction (XRD) the atomic structure of thin films may be monitored throughout the charge-discharge cycle, revealing information such as lattice strain and phase composition [3]. Such information is crucial to understanding the degradation of active materials and the design of materials, processes, and cycling parameters that can maximize cell performance and longevity [4, 5]. Because thin-film electrodes contain no binder or conductive additive they offer a much denser layer of active material for X-rays to scatter from and should be able to provide improved peak intensities over their composite electrode counterpart.

As with other group IV elements, tin is of interest as a LIB anode materials due to its high theoretical specific capacity (993mAh/g for $\text{Li}_{22}\text{Sn}_5$), non-toxicity, and low cost [6-9]. Although tin offers a specific capacity more than 2.5 times higher than the commercial standard, graphite, it is known to suffer from large irreversible capacity losses during the first few cycles and poor capacity retention thereafter. This can be partially attributed to the large volume expansion of tin as it is alloyed with lithium which causes stresses and fracturing in the material. Issues with the formation of an unstable surface-electrolyte interphase have also been noted and are also likely to play an important role in the poor capacity retention when cycled in an organic liquid electrolyte. Further development of tin as an anode material for LIB's requires a clearer picture of the lithium alloying/de-alloying process.

In situ XRD cells adapted from a recently reported design [10, 11] were used to study the atomic structure of thin film tin electrodes produced by sputtering. XRD scans were continuously collected over the entire first cycle. To the authors best knowledge this represents the first report of in situ XRD from tin anodes and the first thin film application of this in situ XRD cell design.

8.4 Materials and Methods

In situ XRD cells were prepared as previously described [10, 11] with some modifications. The in situ XRD cell is shown in Fig. 52 at various stages of fabrication. Briefly, a hole with 6.35mm diameter was punched in the can component of 2032 stainless steel coin cell hardware (Hohsen, CR2032). Holes were punched from the inside of the can so that any resulting burr would be facing out of the cell. The outer faces of the punched cans were then ground smooth before rinsing with de-ionized water and isopropanol. A 19mm disk of 50 μ m thick Kapton tape (Berstech, KPT2) was applied to the inside face of the punched can to form a window. Three small tabs cut from 25 μ m thick copper foil (Puratronic, 99.999%) were inserted just under the edge of the Kapton disk and extended up over the can wall. The can components were loaded in the sputtering chamber which was then pumped down to 7.3mTorr. A 600nm titanium foil was sputtered onto the internal face of the Kapton window at 55W and 15 mTorr at 20 sccm argon. This gave a deposition rate of 3.8Å/s as measured by a quartz crystal microbalance (QCMB). The copper tabs were cut off at the height of the can wall and then folded over onto the titanium layer, thus ensuring contact between the current collector and the cell can.

Tin thin film electrodes were applied directly to the titanium current collector of the in situ cells. Holes with a 7.14mm diameter were punched into coin cell caps. These were then placed upside down into the in situ cell cans to serve as a sputtering mask. A copper sheet with 12.7mm diameter holes punched in it was used to keep the masks in place during sputtering and to mask the outside of the component. To deposit the tin film, the sputtering system was first pumped down to 0.84mTorr to ensure the removal of any oxygen that could lead to the formation of SnO₂. A 5 μ m thick disk of tin was sputtered at

25W and 15 mTorr at 20 sccm argon for a deposition rate of $21.2\text{\AA}/\text{s}$ as measured by QCM. From the prescribed geometry and taking the density of tin as $7.365\text{g}/\text{cm}^3$ each tin disk should have a weight of 1.47mg which was consistent with measured values.

Masks were removed and completed units were dried in a vacuum for 2 hours at 100°C and -100kPa before being transferred to an argon filled glove box. Coin cells were then assembled as normal using a 2325 Celgard separator, Li foil (Alfa Aesar, 0.75mm, 99.9%), and an electrolyte of 1.2M LiPF_6 in ethylene carbonate and ethyl methylcarbonate mixed 3:7 by weight (Ferro). The various stages of cell fabrication including the modified coin cell can, tin thin film, and a fully assembled cell are shown in Fig. 52.

Cell cycling consisted of a constant current-constant voltage protocol performed using a Biologic SP-200 controlled by EC-Lab v10.12. Cells were cycled at a C/16 rate (about $6.24\text{E-}5\text{mA}/\text{g}$ and $0.230\text{mA}/\text{cm}^2$) between 1.5V and 5mV. During the constant voltage step the current was allowed to fall to C/80 before proceeding.

As the cell cycled a PANalytical X'Pert Pro MPD system was used to collect XRD data. A copper target at 2kW was used along a 5mm mask and automatic divergence slit. Scans were collected between 28° - 48° 2θ every hour as cycling proceeded. Processing and Rietveld refinement of diffraction data was performed using PANalytical High-Score Plus v.3.0.3. Crystallite size was estimated by first accounting for instrument induced peak broadening using diffraction scans of a silicon crystal standard. This scan was fitted in High-Score Plus and then used to determine crystallite size for each phase detected by in situ XRD scans.

8.5 Results and Discussion

Freshly assembled in situ XRD cells showed an initial open circuit potential of about 2.75V. A diffraction pattern of the tin thin film taken prior to cell assembly showed a tetragonal phase with space group I41/amd known as white tin, which was also evident from the unreflective films white color as seen in Fig. 52. No other tin phases were detected. Rietveld refinement indicated initial lattice parameters of $a = 5.8382(2)\text{\AA}$ and $c = 3.1803(2)\text{\AA}$. The vertical positioning of the tin thin film in the assembled cell was

adjusted by matching the diffraction angle of the peaks with those observed from the tin film before assemble when it was aligned at zero vertical displacement. XRD scans from tin thin films both before and just after cell assembly (prior to cycling) are shown in Fig. 53. In both cases a strong degree of preferred orientation was present. Tin peaks from the (220) and (200) planes were stronger and the (101) and (211) peaks were weaker than expected for a randomly oriented sample. This indicates a preferred orientation in the as sputtered film that has the (100) vector perpendicular to the film surface.

XRD scans are shown as an isoplot in Fig. 54. A decrease in tin peak intensity was observed immediately upon the onset of lithiation. As the tin peaks continued to diminish in intensity, peaks indicating the presence of a Li_2Sn_5 phase began to appear. The Li_2Sn_5 phase was first detected at a degree of lithiation of $x = 0.2$ (as in Li_xSn) and peaks increased in intensity until $x = 1.0$. After that point Li_2Sn_5 peak intensities decreased along with those from the pure tin and at $x = 1.3$ both phases were no longer detected.

Just prior to the intensity maximum for Li_2Sn_5 peaks the appearance of a $\beta\text{-LiSn}$ phase was observed at $x = 0.8$. These peaks experienced an intensity maximum at $x = 1.4$ and diminished thereafter before completely disappearing by $x = 2.5$. Just as the $\beta\text{-LiSn}$ became undetected, the (660) peak of a $\text{Li}_{22}\text{Sn}_5$ phase appeared and grew in intensity until $x = 3.3$. During the remainder of the discharge stage this peak maintained its intensity and no other phases were detected. Unlike other peaks that had been observed, the $\text{Li}_{22}\text{Sn}_5$ (660) peak experienced a shift to higher diffraction angles in the range from initial detection at $x = 2.5$ to $x = 3.5$. After this the peak remained stationary until near the end of discharge at $x=4.5$ when a second shift to lower angle was noted. No further phase composition or peak angle changes were seen for the remainder of discharge which ended at about $x = 4.7$.

The phase change behavior seen during discharge was observed in reverse order during charging with some variations. Just after the onset of charging no change was observed until $x = 4.1$ at which point the $\text{Li}_{22}\text{Sn}_5$ (660) peak shifted to a higher angle coincident with the angle measured in the range of $x = 3.5$ to $x = 4.5$ during discharge. No further change was noted until $x = 2.9$ when the $\text{Li}_{22}\text{Sn}_5$ peak again began shifting to

higher diffraction angles and β -LiSn peaks became detectable. A maximum in β -LiSn peak intensity was seen at $x = 1.9$ after which peak intensities decreased, and upon reaching $x = 1.5$ peaks from both $\text{Li}_{22}\text{Sn}_5$ and β -LiSn phases were no longer detected.

The formation of the Li_2Sn_5 during cell charging was first detected at $x = 2.1$, just prior to the maximum in β -LiSn peak intensity. Li_2Sn_5 peaks showed a maximum intensity at $x = 1.3$ and then faded away until completely disappearing by $x = 1.0$. Peaks from a white tin phase were first observed at $x = 1.5$ and grew until the end of charging. The tin diffraction pattern observed after the first cycle did not show the preferred orientation seen in the original as sputtered thin film.

The areas of a representative peak from each phase are plotted along with cell voltage as a function of time in Fig. 55. Here the transition between the pure tin, Li_2Sn_5 , β -LiSn, and $\text{Li}_{22}\text{Sn}_5$ phases is seen to be sequential with a strong correlation to the observed voltage plateaus. As lithiation of the white tin commences there is a rapid reduction in the tin peak area which continues until it is no longer detected. The 0.56V discharge plateau is clearly related to the transition between Li_2Sn_5 and β -LiSn phases. Similarly, the discharge plateau at 0.38V is obviously the result of the β -LiSn and $\text{Li}_{22}\text{Sn}_5$ two phase region. Following the end of the 0.38V plateau there is very little change in the peak area of the $\text{Li}_{22}\text{Sn}_5$ phase indicating little change in its overall volume fraction. As charging ensues, a voltage plateau at 0.59V is seen during the transition from $\text{Li}_{22}\text{Sn}_5$ to Li_2Sn_5 . The final transition occurs from Li_2Sn_5 to white tin at a potential of 0.80V. During this period, the intensity of the white tin peak increases very rapidly.

The lattice parameters fitted to each XRD scan for each phase detected are shown plotted all together in Fig. 56. Here the drastic mismatch in lattice parameters between the different phases is evident. The Li_2Sn_5 , β -LiSn, and $\text{Li}_{22}\text{Sn}_5$ phases that form as the white tin is lithiated have volume dilations of about 19%, 50%, and 280% respectively [7]. This mismatch is likely to be a source of great stress and strain in the tin film which could cause cracking and subsequent capacity loss and performance degradation.

When each lattice parameter is plotted separately, as in Fig. 57, the effect of lithiation and phases changes on lattice parameters can be more clearly seen. These strains most likely result from a moving phase boundary in the film. During lithiation no

significant change to the tin lattice parameters are observed even as the Li_2Sn_5 and β - LiSn phases became detectable. As the peak area for the Li_2Sn_5 starts to diminish the lattice parameters begin to shift. The value of a drops by about $0.03\text{\AA}$ while the c value increases by about $0.01\text{\AA}$. From its first detection the lattice parameters of the β - LiSn phase begin to change by a much larger degree than any of the other phases. As the a value drops by only about $0.03\text{\AA}$, the b increases by about $0.12\text{\AA}$ and the c parameter drops by about $0.35\text{\AA}$. This relatively large strain is likely due to the formation of the $\text{Li}_{22}\text{Sn}_5$ phase and the large lattice parameter mismatch between these two phases. The $\text{Li}_{22}\text{Sn}_5$ phase first increases its lattice parameter by about $0.02\text{\AA}$ and then dropping by $0.05\text{\AA}$

As delithiation begins, first a drop of about $0.04\text{\AA}$ is observed in the $\text{Li}_{22}\text{Sn}_5$ phase followed shortly by an increase of about $0.08\text{\AA}$. As the peak area from this phase begins to rapidly decrease and the Li_2Sn_5 phase begins to reappear, the $\text{Li}_{22}\text{Sn}_5$ lattice parameter is seen to rapidly decrease by about $0.09\text{\AA}$. At the same time the $\text{Li}_{22}\text{Sn}_5$ phase increases its a parameter by about $0.03\text{\AA}$, then after all of the $\text{Li}_{22}\text{Sn}_5$ is gone and white tin is reformed, the parameter drops back down by about $0.03\text{\AA}$. During detection of the Li_2Sn_5 phase the c parameter decreases by about $0.03\text{\AA}$ as the $\text{Li}_{22}\text{Sn}_5$ phase disappears. After this the c parameter remains steady. The newly formed white tin phase shows an unchanging lattice during its formation.

Fig. 58 shows the crystallite size of each phase versus time. The white tin phase is seen to have an initial crystallite size of about $850\text{\AA}$. As the Li_2Sn_5 phase becomes detectable, the crystallite size increases from about $440\text{\AA}$ to its peak value of about $640\text{\AA}$ at its maximum. After this the grain size rapidly decreases as the phase is further lithiated and transformed into β - LiSn . Crystallites of this new phase are first detected with a size of about $185\text{\AA}$ and show only a small growth to $215\text{\AA}$ before rapidly decreasing they are transformed to the $\text{Li}_{22}\text{Sn}_5$ phase. $\text{Li}_{22}\text{Sn}_5$ is first detected with a crystallite size of about $110\text{\AA}$ before increasing to a maximum average size of about $290\text{\AA}$. At this point, which corresponds to a small shoulder in the voltage plot, the value drops to about $200\text{\AA}$ and continues to gradually increase from there to a maximum of about $265\text{\AA}$ at the end of discharge. This behavior may be caused by an increase nucleation rate at observed

potential where a second population of $\text{Li}_{22}\text{Sn}_5$ crystallites are formed, effectively reducing the average value and causing it to gradually increase as they grow throughout the remainder of the lithiation.

As delithiation ensues, the $\text{Li}_{22}\text{Sn}_5$ crystallite size initially drops slightly and then remains fairly constant until the 0.6V plateau is reached. At this point the crystallite size increases which may indicate the preferential disappearance of the smallest grains or their assimilation into some of the large crystallites present. At the midpoint of this voltage plateau the crystallite size begins to rapidly decrease back to a minimum of 110Å before the phase is no longer detected. At this point the Li_2Sn_5 is formed and rapidly increase from a crystallite size of only about 80Å to a maximum of about 785Å. These relatively large crystallites of Li_2Sn_5 are then rapidly converted to white tin which show a crystallites that grow until the end of delithiation.

The observed lattice parameters and crystallite size behavior appear to indicate the presence of a moving phase boundary within the thin film. Lattice mismatch between two adjacent phases causes compression in the phase with larger volume dilation relative to the initial white tin phases and a tension in the phase with the smaller volume dilation. In the case of thin film geometry, lithium can only enter the active material from the film surface adjacent to the separator. As a result lithiation should result in compressive stresses at this face and tensile stresses in the film on the current collector side. This could result in delamination effects at the thin film/current collector interface. In the case of delithiation, the stresses should be reversed and tension should occur at the film surface adjacent to the separator. At this point fracture of the thin film in a manner analogous to the cracking of drying mud is more likely.

8.6 Conclusion

In situ XRD of thin film electrode has been demonstrated using a recently developed in situ cell. With this method the phase transformation behavior of sputtered tin thin films was monitored throughout an entire lithiation/delithiation cycle performed at room temperature. The presence of four phases including white tin, Li_2Sn_5 , $\beta\text{-LiSn}$, and $\text{Li}_{22}\text{Sn}_5$ were clearly identified. Fitting of diffraction patterns showed tension and

compression effects for each phase that were caused by the formation of subsequent phases with dissimilar lattice parameters. Crystallite sizes showed a strong correlation with both overall phase's composition and cell potential. Further work including in situ TEM and acoustic emission [11-13] studies may be used to gain further insight into how the phase boundary is moving through the thin film and what damage the film may incur as this proceeds.

8.7 Acknowledgments

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8.8 References

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Chapter 9: Final Conclusions and Recommendations

9.1 Summary of Important Conclusions

EES devices are an extremely important part of everyday life and reliance on them to provide clean, safe, and portable energy will only grow in future years. As market trends continue to drive the development of more powerful portable devices the demand for better EES devices will continue to drive research and development in this field. However, it is the implementation of large scale EES devices for applications such as HEV and EV that will present the most challenging performance requirements. In the case of a cell phone or laptop battery, drastic capacity loss over a device life time of 2-3 years is a major inconvenience. If the same capacity loss is experienced in a large and expensive battery pack in a car designed to last 10 years this same effect can make the entire vehicle design impractical and unviable commercially. As research on EES materials continue to advance it is reasonable to expect more attention will be focused on the mechanical degradation active materials and how this can be prevented.

The work presented here has served both to develop new techniques for studying mechanical degradation processes in EES materials as well as to provide specific insights into the cycling induced degradation behavior of several important to LIB active materials. Through the use of AE, a largely undeveloped tool in the field of EES research, and in situ XRD several interesting results have been obtained from MCMB, silicon, MNO, and tin electrode materials.

In the case of MCMB, the current standard for LIB anode materials in commercial cells multiple types of AE events were detected. These were related to events such as gas bubble formation and SEI cracking. For in service cells one can envision using this technique to detect cell damage that may allow oxygen into the cell and cause the formation of thick surface layers on the carbon. By using multiple sensors it may be possible to detect the location of particular damaged cells.

Silicon is well known to experience extensive fracturing caused by its huge volume dilation upon lithiation. Such expansion is expected to cause considerable stresses to develop in the active material which can lead to cracking and pulverization in a brittle material such as silicon. AE was used to identify fracturing events as -100+325 mesh silicon particles were repeatedly cycled and provided strong evidence that small

and medium sized cracks are formed at the beginning of charge or discharge stages while a much smaller population of large fractures appeared near the end of these stages. Computer modeling used to predict when fracturing should occur in silicon particles matched well with experimental results for particles of different average diameters and indicated that at diameters less than about 20 μm fracturing could largely be avoided.

By combining AE with in situ XRD performed using a specially designed cell a correlation between lattice strain and fracturing in these silicon particles was accomplished. At points of peak AE activity, inflection points in the lattice strain were observed that brought the strain closer to zero. This may be attributed to release of stress in the material as fractures are formed. The complex strain behavior observed in the silicon studied here is likely due to small grain size and high grain boundary density in the material as detected by EBSD and TEM.

The application of the in situ XRD cell presented here to cathode materials was realized by simply changing the current collector material from copper to aluminum and improved peak intensities were obtained by switching from a Mylar to a Kapton window material. This design was applied to the study of MNO and detailed lattice parameter and phase composition information was collected. A comparison of cycling behavior of the material during the first two cycles with the behavior after 15 cycles showed a degradation of phase transition behavior which could be a major cause for the observed capacity fade. This may be due to a loss of smooth phase boundary movement in the material due to regions of active material becoming inactive or lithium trapping.

The applicability of in situ XRD to the study of thin film electrode materials was demonstrated using sputtered tin films. During these experiments Ti was used as the current collector metal and was shown to have excellent X-ray transmission and battery cycling properties that make it the current best choice of use with the in situ XRD cell. Room temperature in situ XRD experiments clearly showed the reversible formation and disappearance of white tin, Li_2Sn_5 , $\beta\text{-LiSn}$, and $\text{Li}_{22}\text{Sn}_5$ phases with enough resolution to monitor crystallite size change for each phase through use of the Scherrer equation. These phase transformations showed clear correlations with the measured cell potential and the fitted lattice parameters gave indication of large mismatch between the Li_2Sn_5 and

$\text{Li}_{22}\text{Sn}_5$ as well as the $\beta\text{-LiSn}$ and $\text{Li}_{22}\text{Sn}_5$ which could be a major cause of damage to the tin film.

Overall, AE has proven to be a unique and interesting tool in the quest to understand exactly what is happening inside of EES devices. Although not applicable to all materials, in cases where events such as fracture or bubble formation that is capable of producing detectable sonic signatures, AE can provide information about when and to what extent these events occur which cannot be obtained by any other means. Because of the challenges associated with identifying source events and relating them to recorded hits as well as its applicability to only certain materials, AE is unlikely to see as much use in EES research as tools such as SEM and XRD. However, because it is inherently in situ and can be easily combined with other characterization techniques it is likely that it will gain increased use among researchers in the near future.

In situ XRD is a very powerful tool for studying EES materials either when combined with AE sensing or performed by its self. Using the in situ XRD cell design developed in this work, detailed crystallographic data may be obtained on a standard laboratory diffractometer that can absolve the need of synchrotron studies for basic studies and even provide certain advantages such as the ability to perform studies extending many cycles. In cases where very high resolution diffraction data is required, laboratory studies using this in situ cell can provide excellent support data for beam time proposals as well as guide the development of synchrotron experiments so that the limited beam time is used to its maximum potential. Additionally, the use of a safe and inexpensive metalized polymer window rather than one made of beryllium allows this cell design to be used in many more research labs without the concerns and problems associated with beryllium. It is expected that this design as well as future designs which may stem from it will play an important role in making true in situ XRD studies of EES materials more accessible and widely used.

9.2 Future Work

In addition to the compelling results it has delivered, this work has also paved the way for many exciting future experiments. The true value of the techniques developed here will be fully realized as this future work comes to fruition. As this pertains to EES research at Oak Ridge National Laboratory, several research projects are planned or are currently underway.

AE work on MNO and tin thin films is currently underway and some preliminary results have been obtained. Fig. 59 shows a histogram of the number of hits recorded per cycle as broken down into charge and discharge stages. Almost all events were detected during the delithiation of the MNO material and had properties generally observed for fracture type events. During delithiation the particle surface is expected to be under tension and is the most likely site of crack formation. A very interesting feature of this data is the delayed onset of AE detection which may be the result of fatigue type behavior where dislocation pile up during the first few cycles finally results in crack formation which has a maximum occurrence at about 10-12 cycles. When a histogram showing number of hits versus cell potential is plotted, as in Fig. 60, it is clear that the events are highly correlated with the Jahn-Teller distortion and Ni oxidation processes experienced at about 3.2V and 4.7V respectively. Work on this material is underway to better understand these results and how they can be used to improve performance and reduce capacity fade.

In situ XRD work on MNO is also currently underway to assess the effects of particle surface coatings of materials such as LiPON. The in situ XRD studies of MNO presented here serve as a base line for these studies. The goal is to determine if thin coatings of LiPON and other materials can help to preserve the phase transition behavior seen during the first few cycles thereby reducing capacity fade. Other LIB active materials currently being studied using in situ AE-XRD techniques include germanium (a group IV element being studied both as particles and thin films), CuF_2 (a high potential conversion type active material), and $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ (a promising layered cathode material with the LiCoO_2 structure).

A particularly interesting project is the design and implementation of a heating/cooling stage for performing in situ AE-XRD experiments. This stage, depicted in Fig. 61 uses a thermo-electric cooling stage (TEC) affixed to the in situ cell on one face and a heat sink on the other to regulate the cell temperature for the duration of experiments. A thermocouple (ΔT) affixed to the in situ cell is used to monitor the cell temperature. This device is intended to allow for the study of EES materials in range from -20°C to 80°C .

Appendix A: Figures

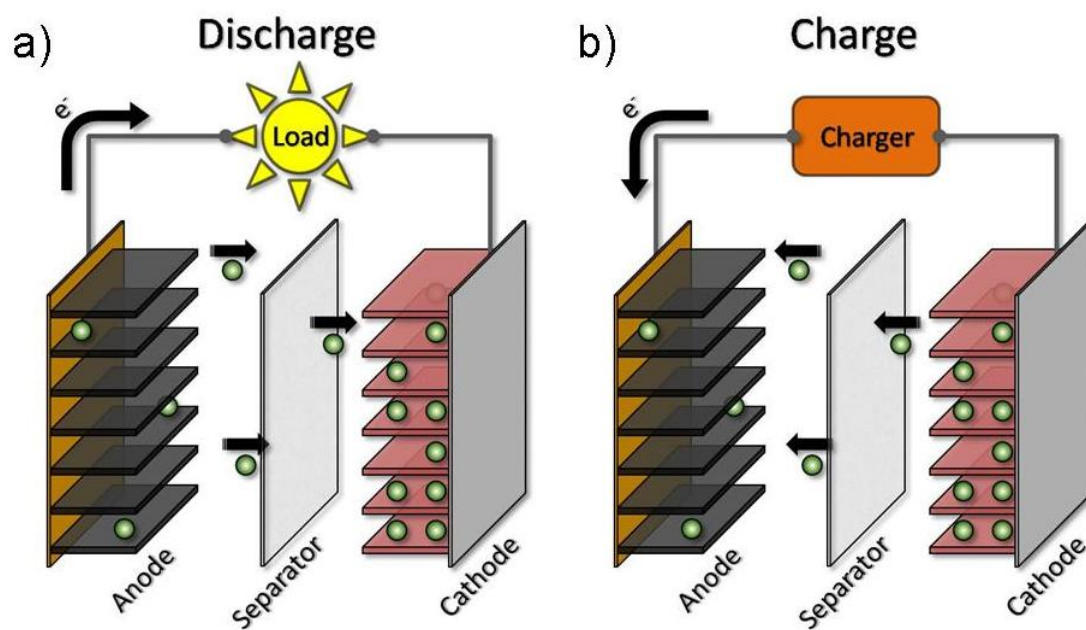


Fig. 1: Principle of lithium ion battery operation.

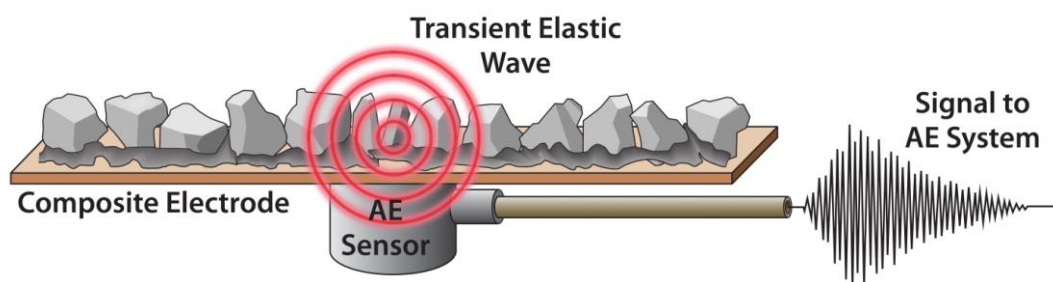


Fig. 2: Schematic depiction of AE generation, propagation, and transduction.

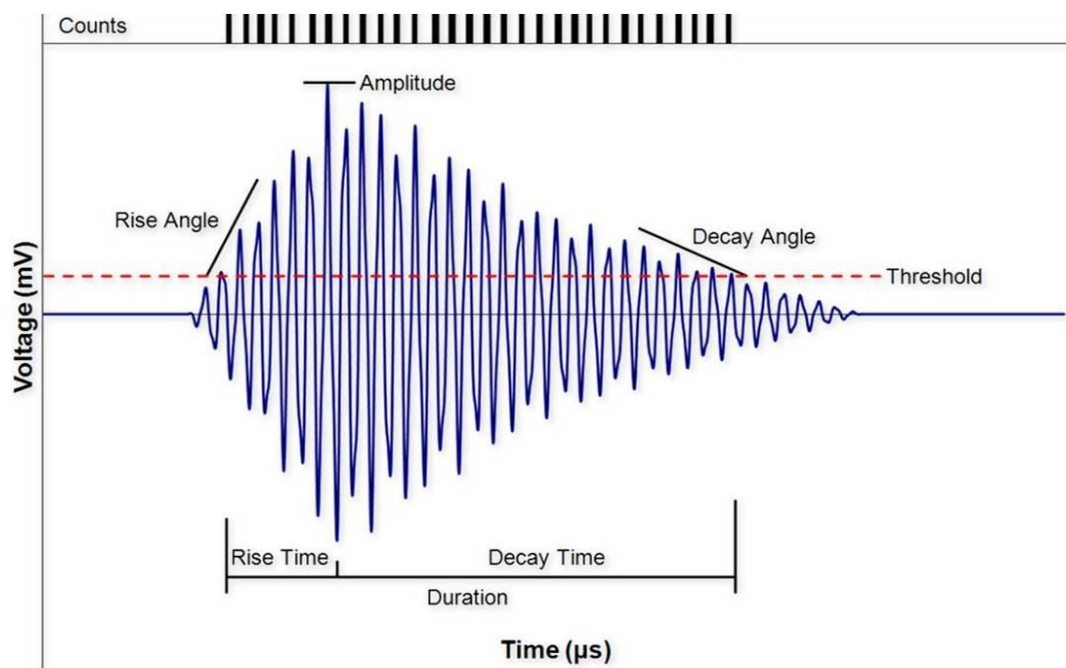


Fig. 3: Parameters for characterizing AE hits.

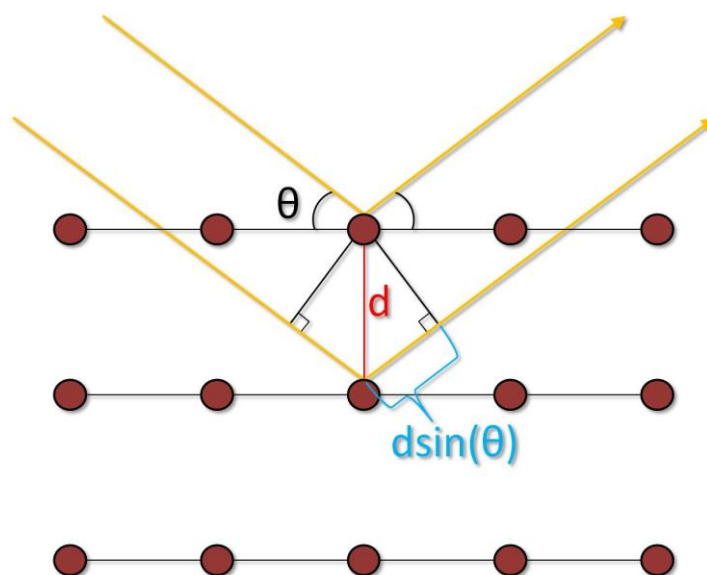


Fig. 4: Physics of XRD from atomic planes

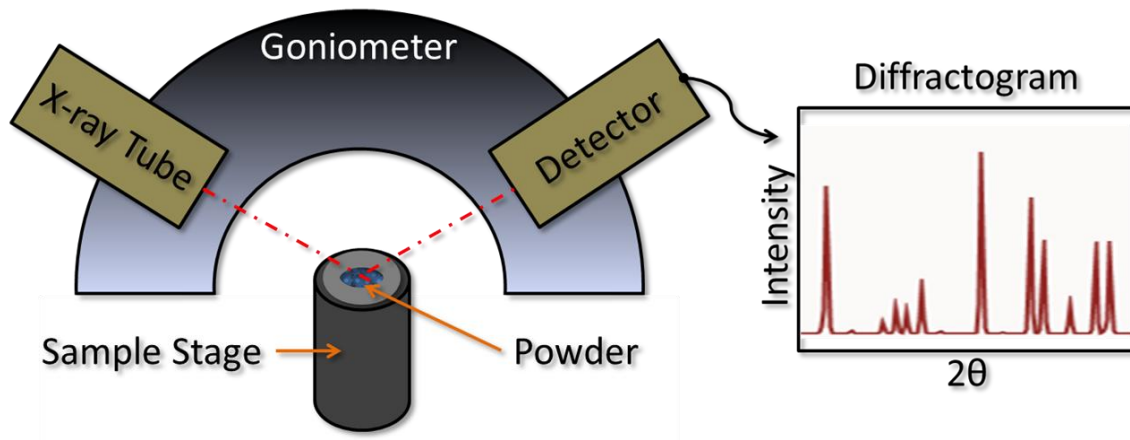


Fig. 5: Schematic depiction of powder diffraction.

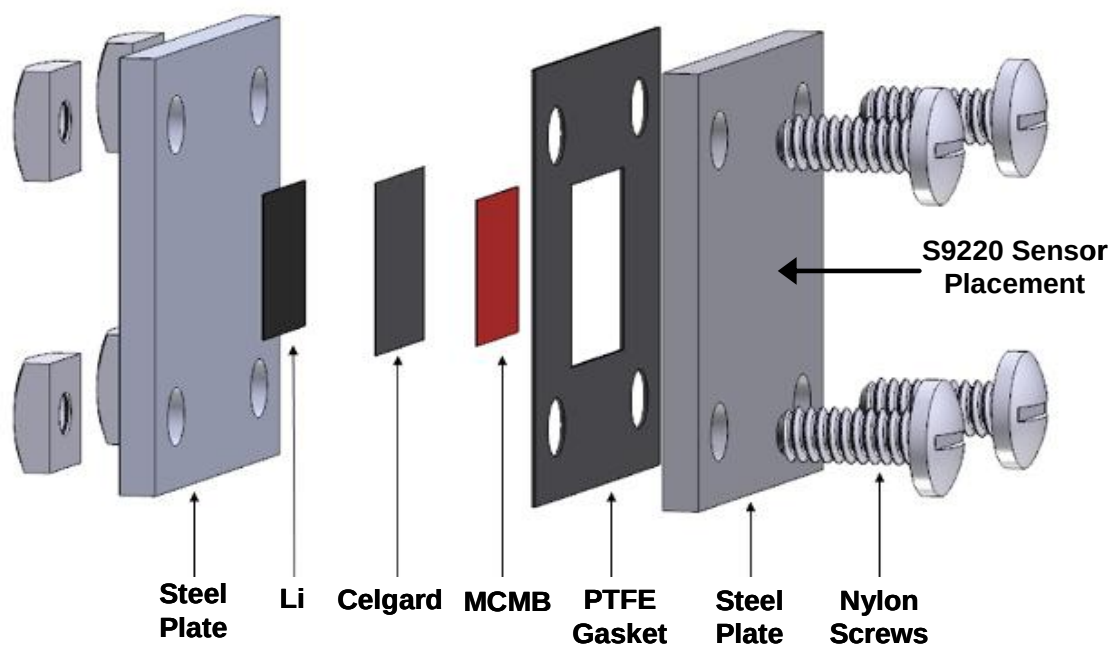


Fig. 6: Exploded view of the cell used for monitoring AE during cycling.

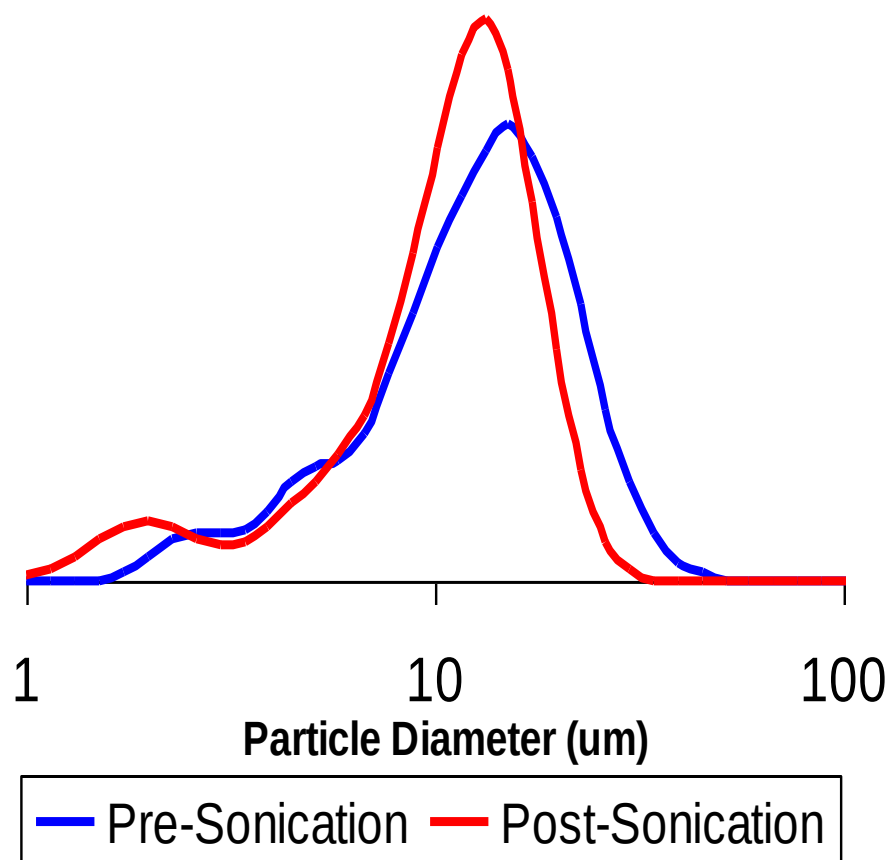


Fig. 7: LDPSA of MCMB particles before and after sonication.

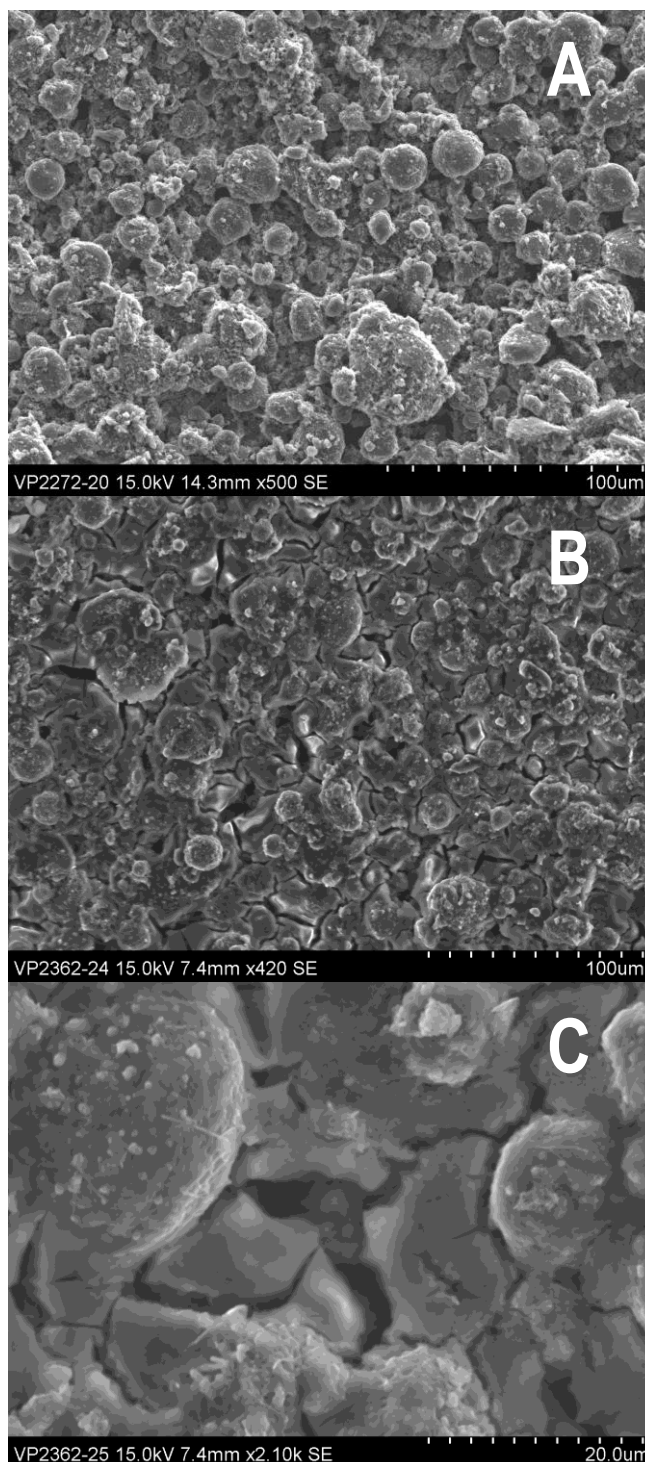


Fig. 8: SEM of cycled a fresh MCMB electrode (A) and the electrode after cycling at showing fractured SEI layer (B, C).

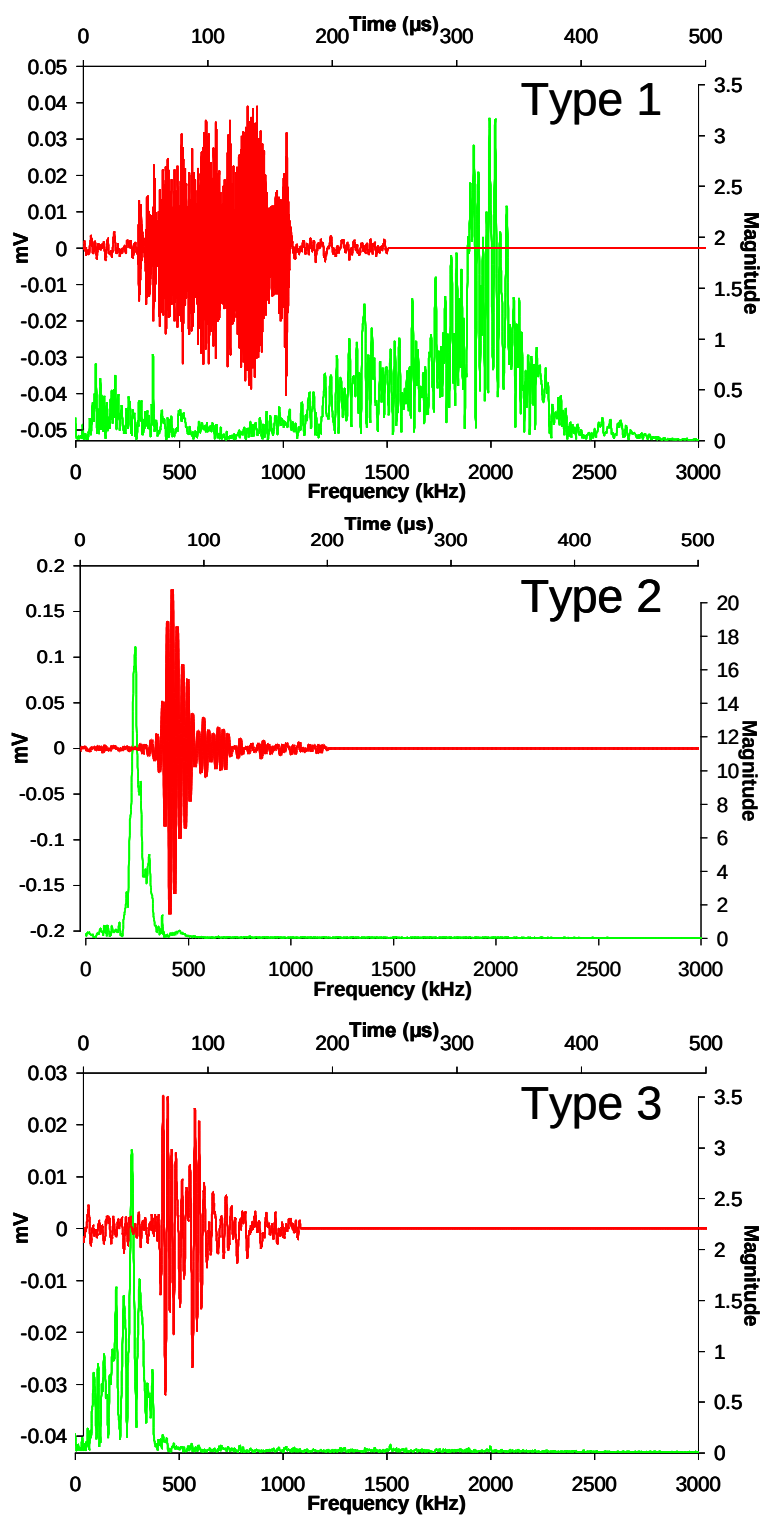


Fig. 9: Waveform types identified from AE of cycling MCMB cells.

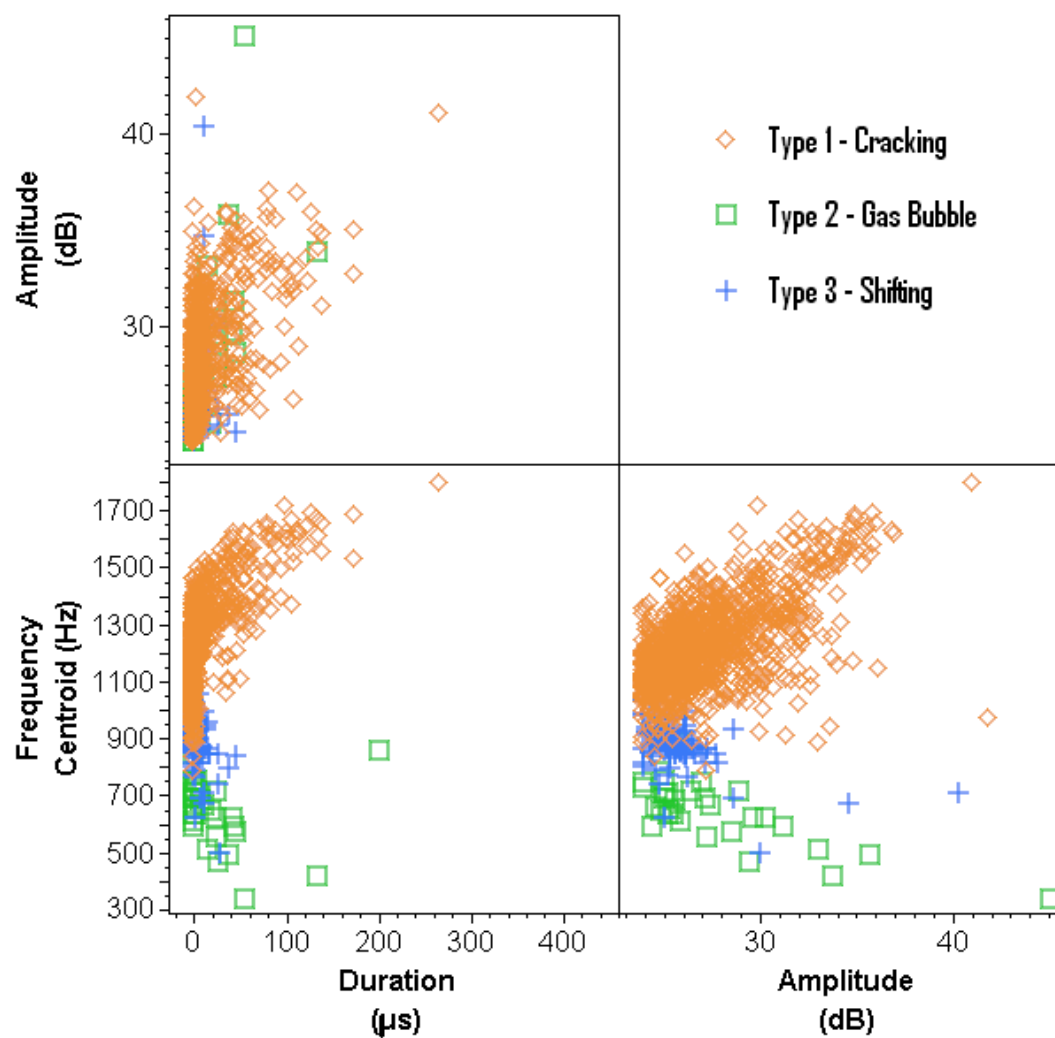


Fig. 10: Scatter plot of Duration, Amplitude, and Frequency Centroid showing grouping of emissions useful for identifying event types.

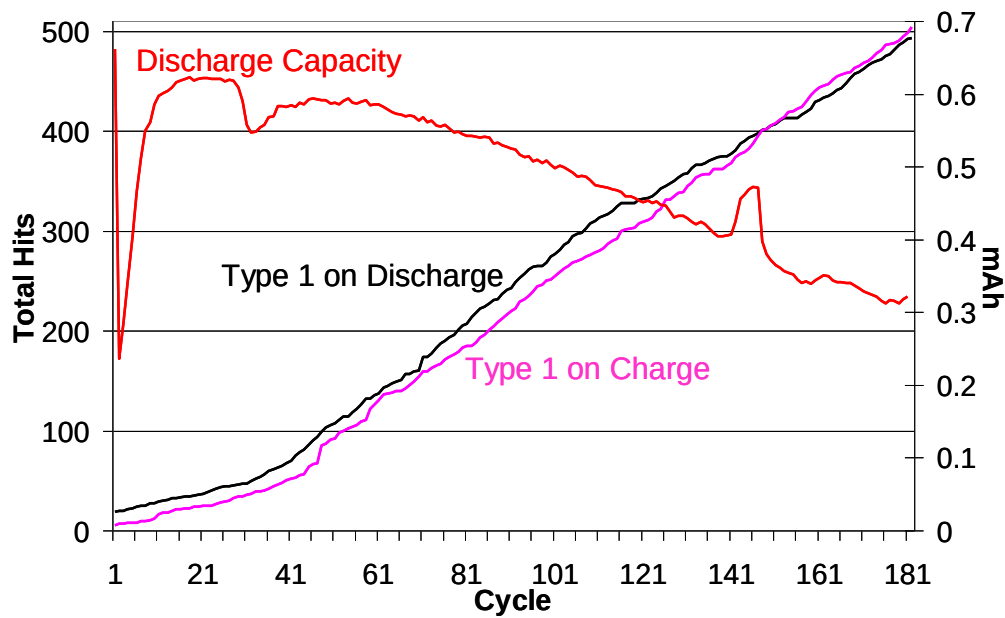


Fig. 11: Cumulate Type 1 event versus time and discharge capacity.

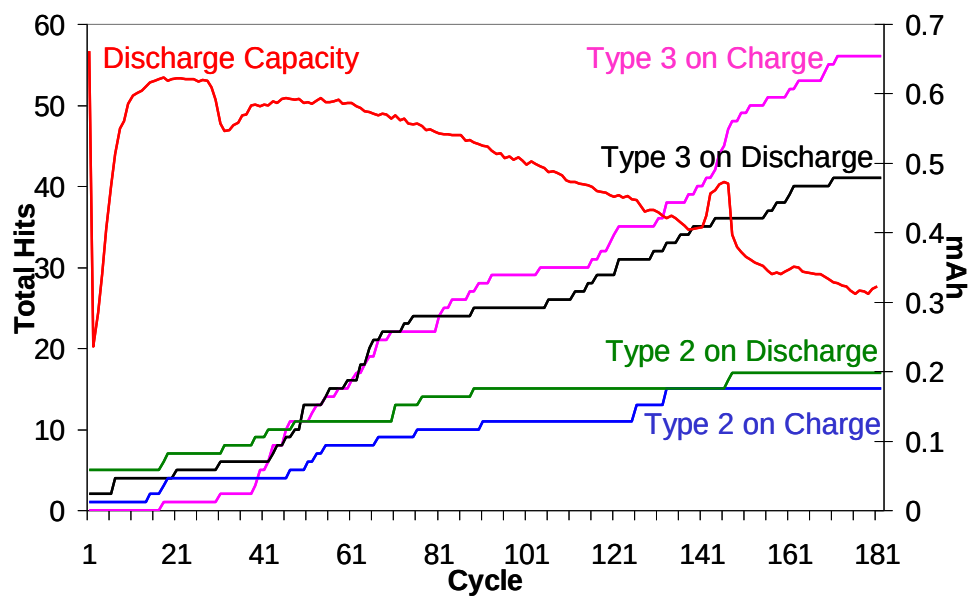


Fig. 12: Discharge capacity with cumulative Type 2 and Type 3 events versus time and discharge capacity.

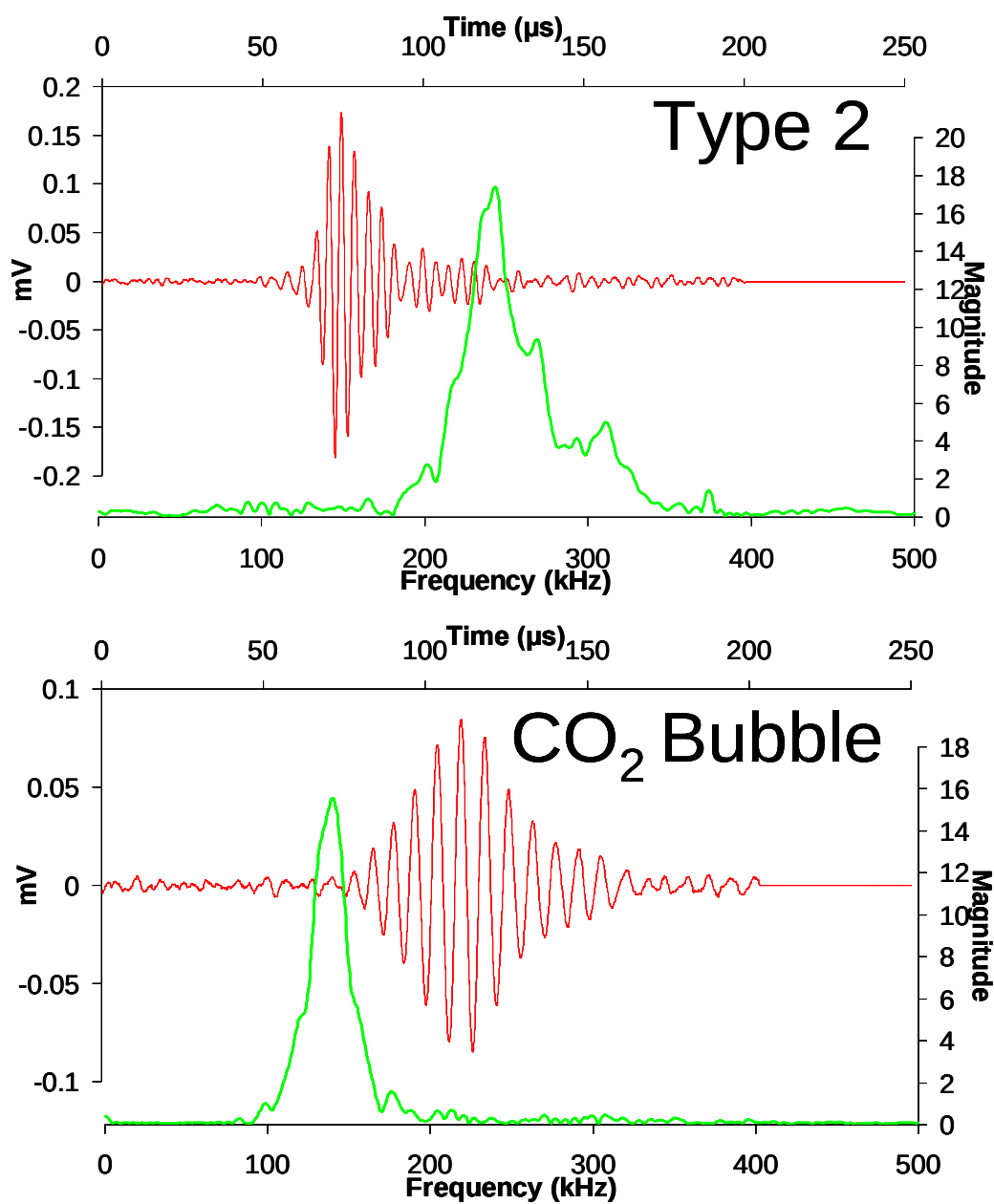


Fig. 13: Comparison of waveform and FFT observed for Type 2 emissions and those bubbling of carbonated beverage.

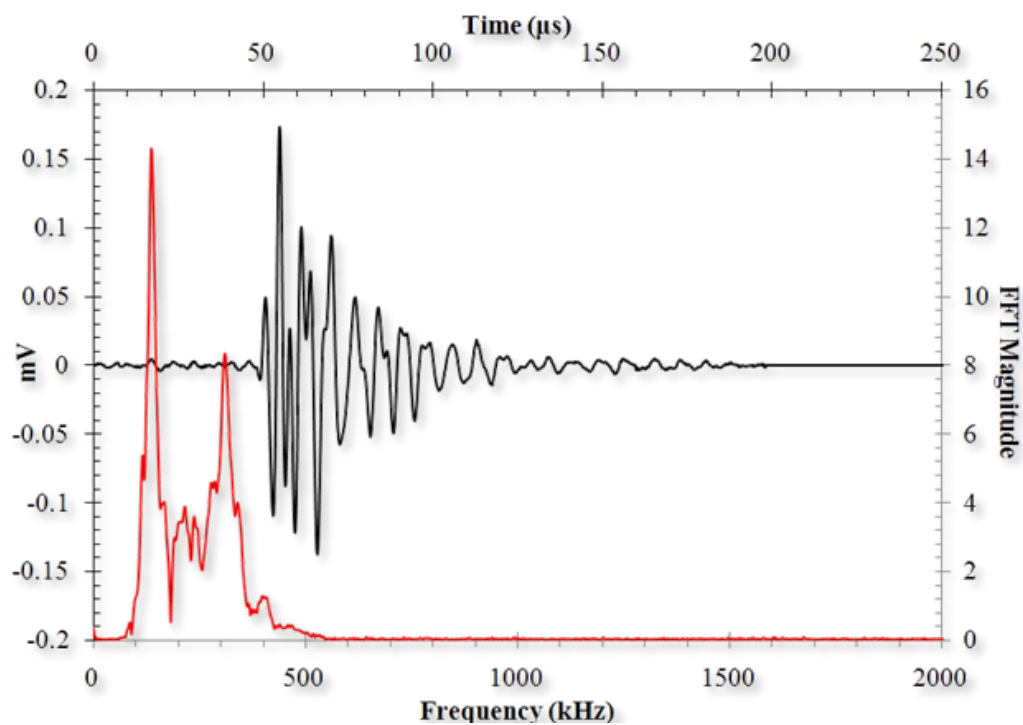


Fig. 14: Representative waveform (black) and FFT (red) from -100+325 mesh silicon electrodes cycled in lithium ion coin cells.

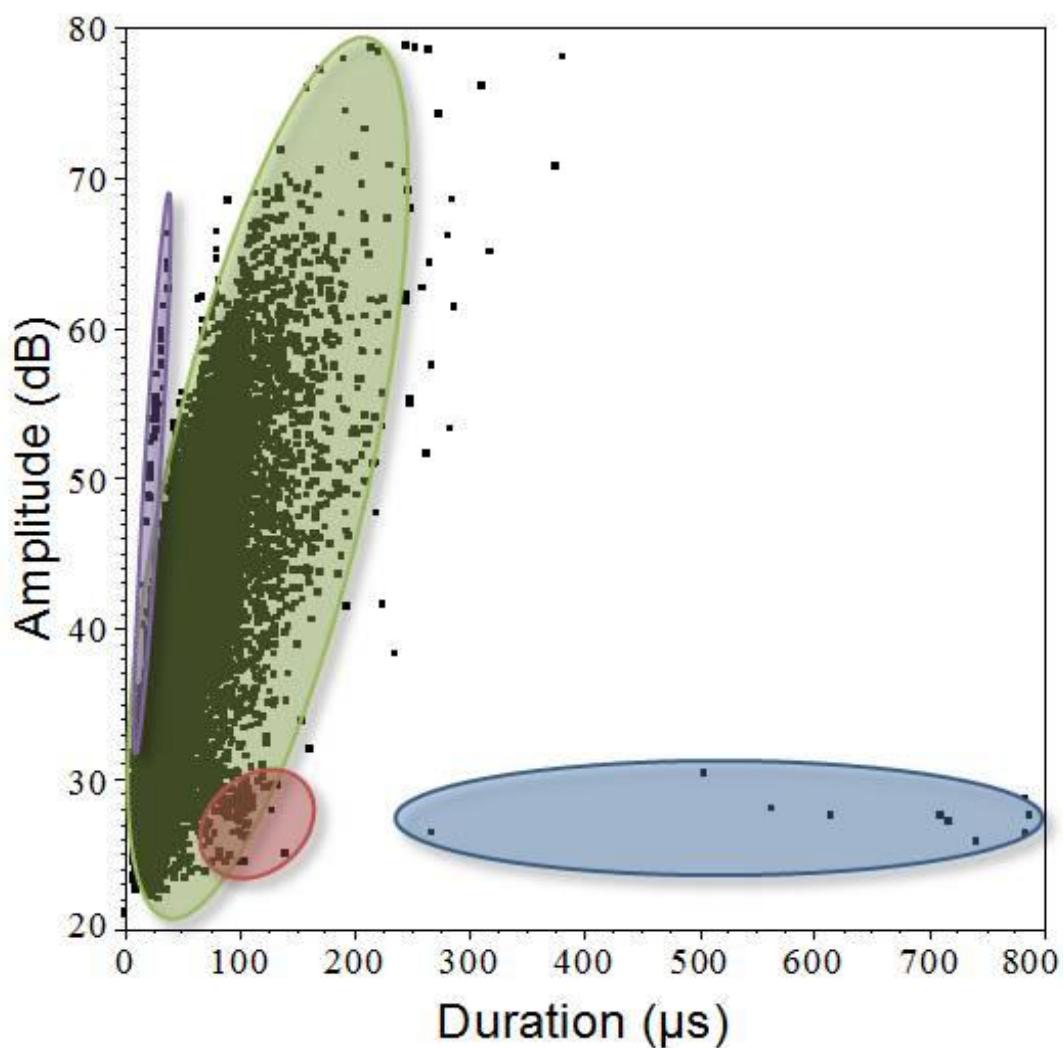


Fig. 15: Amplitude versus duration plot of unfiltered AE hits. Most hits resulting from silicon fracture fall in the green region with some of this type having two signals recorded on the same hit in the red region. Pulse EMI falls in the purple region while continuous EMI falls in the blue region

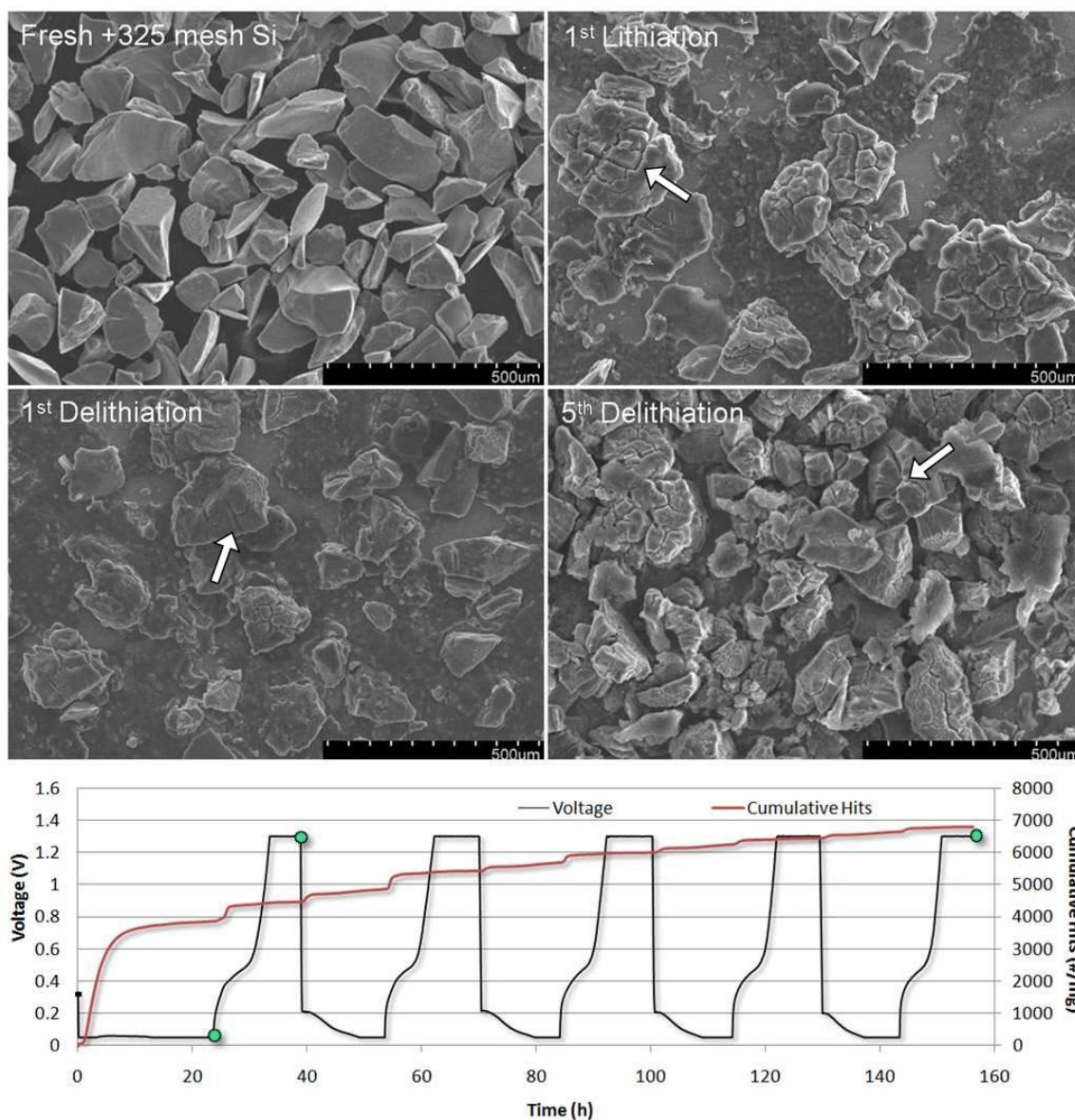


Fig. 16: SEM -100+325 mesh silicon particles at various stages of cycling (top).

Fractures on the particle surface were observed after the first lithiation with increase damage at increase cycling and examples of these are indicated with arrows. Cumulative hits (red) and voltage (black) versus time are shown with markers for where in cycling electrodes were examined by SEM (bottom).

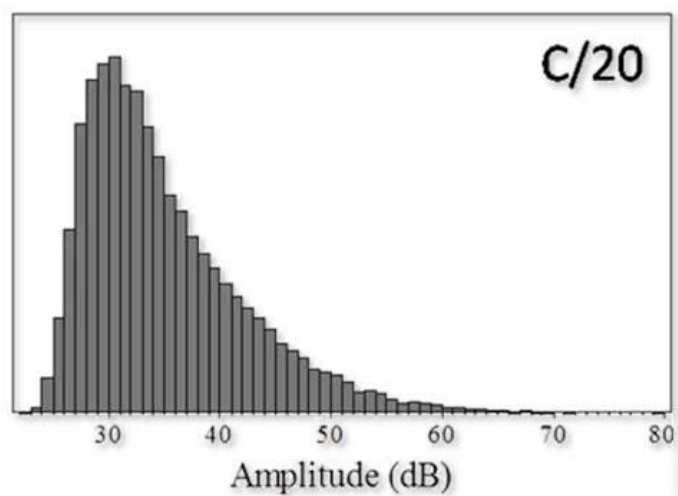


Fig. 17: Histograms of hit amplitudes showing a peak at 31dB.. The bell shape indicates a brittle fracture type which is expected for silicon.

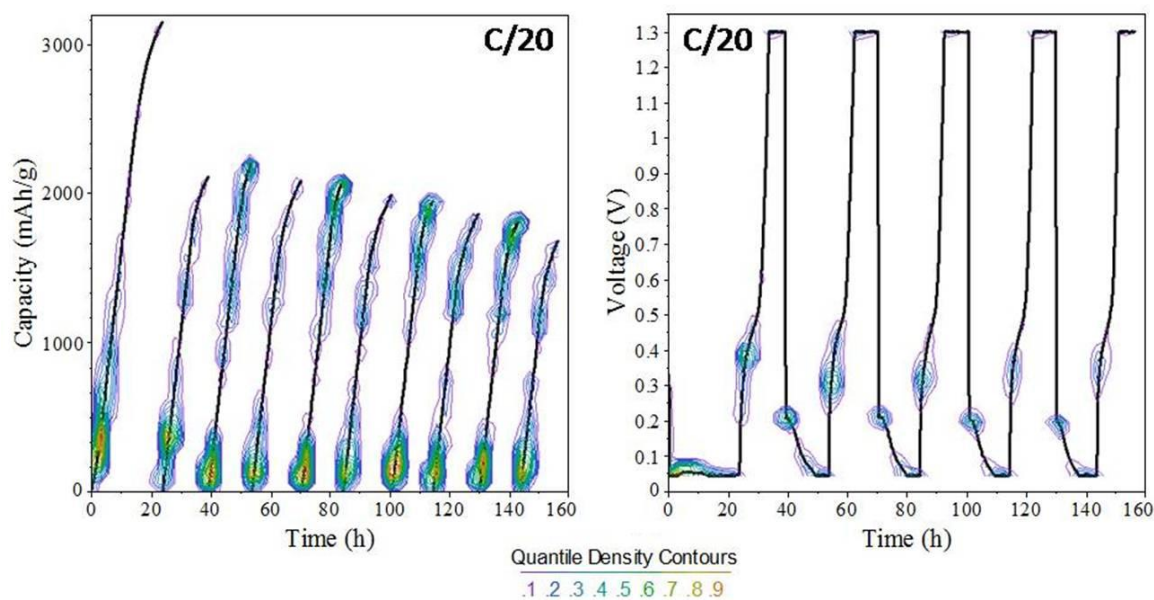


Fig. 18: Plot of cell capacity (left) and voltage (right) versus time with density contours to indicate the regions of high AE activity.

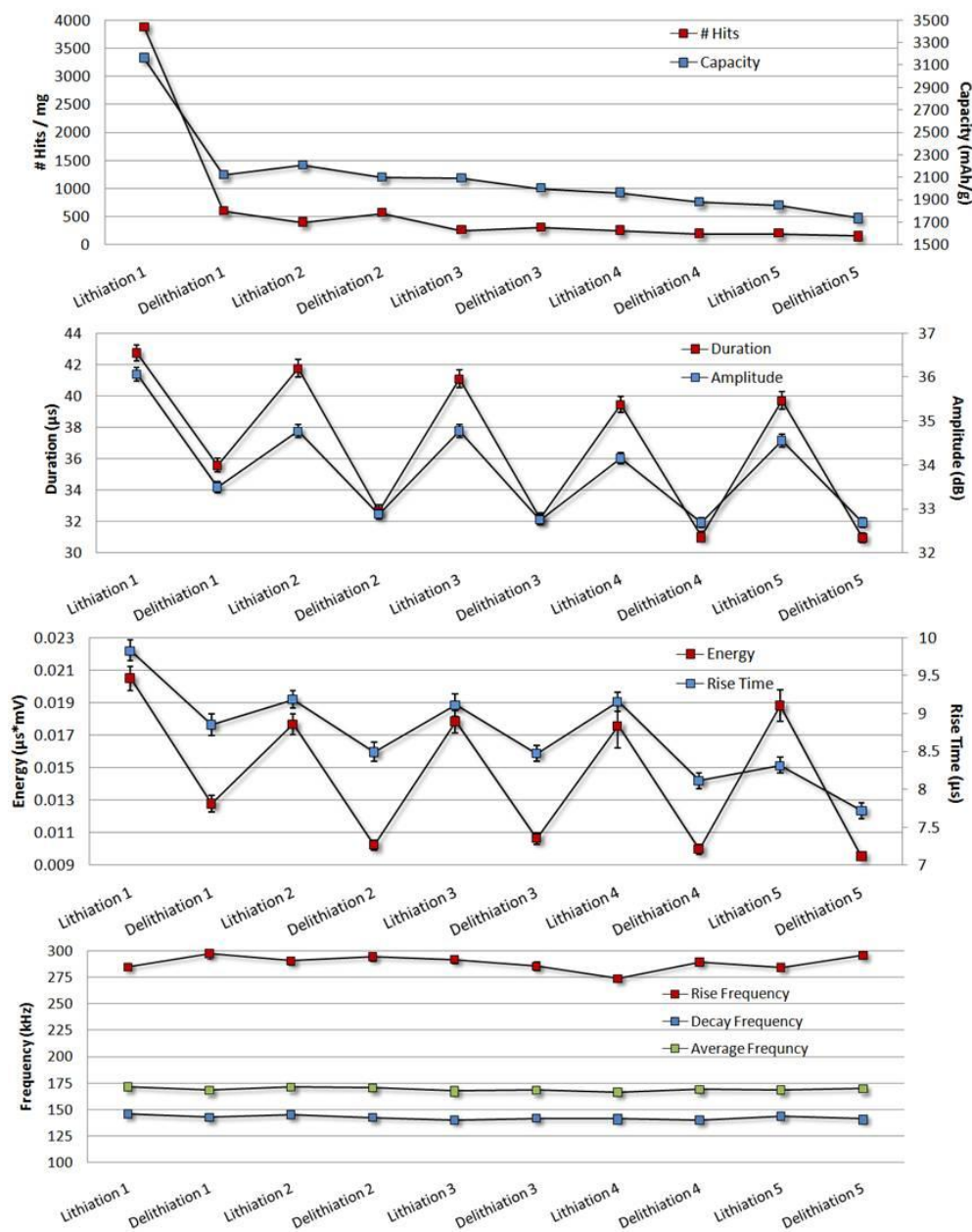


Fig. 19: Electrochemical and AE parameters as a function of cycle stage. From top to bottom: cell capacity and number of recorded emissions, mean emission duration and mean amplitude, mean emission energy and mean rise time, and mean emission frequencies.

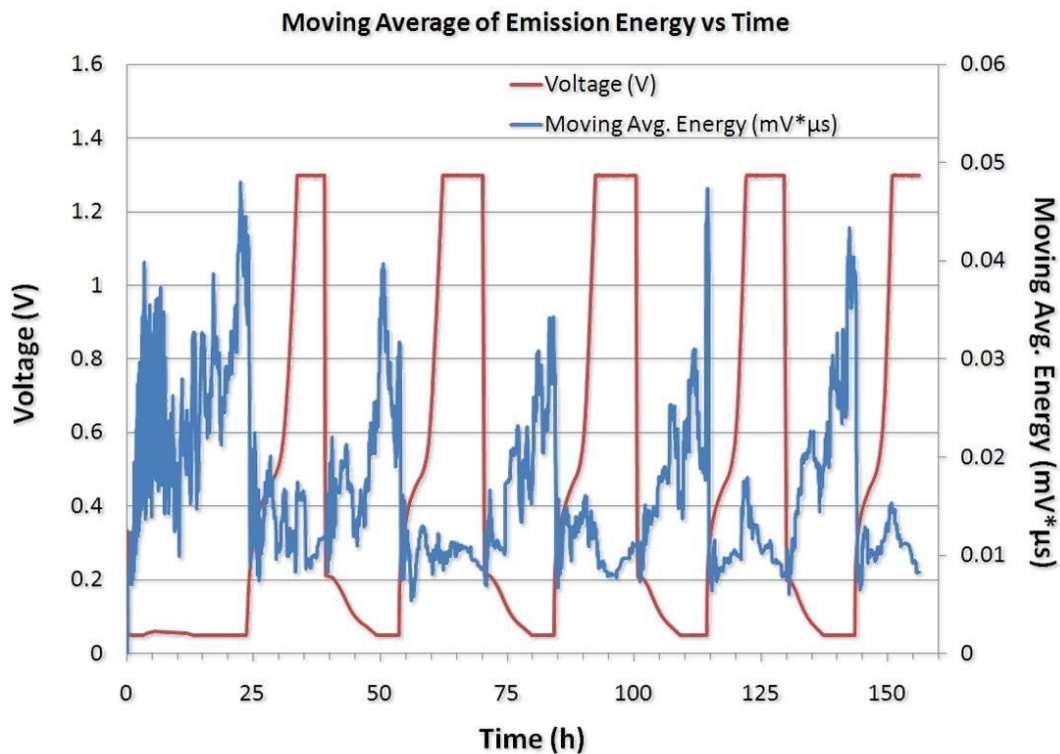


Fig. 20: Moving average of AE energy and cell voltage plotted as a function of time. A distinct increase in AE energy from beginning to end of silicon lithiation is observed.

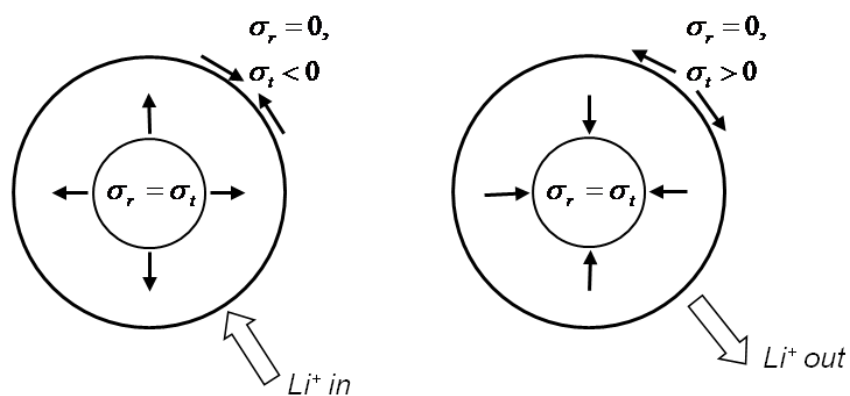


Fig. 21: Schematic depiction of lithium intercalation/deintercalation induced stresses in a spherical particle.

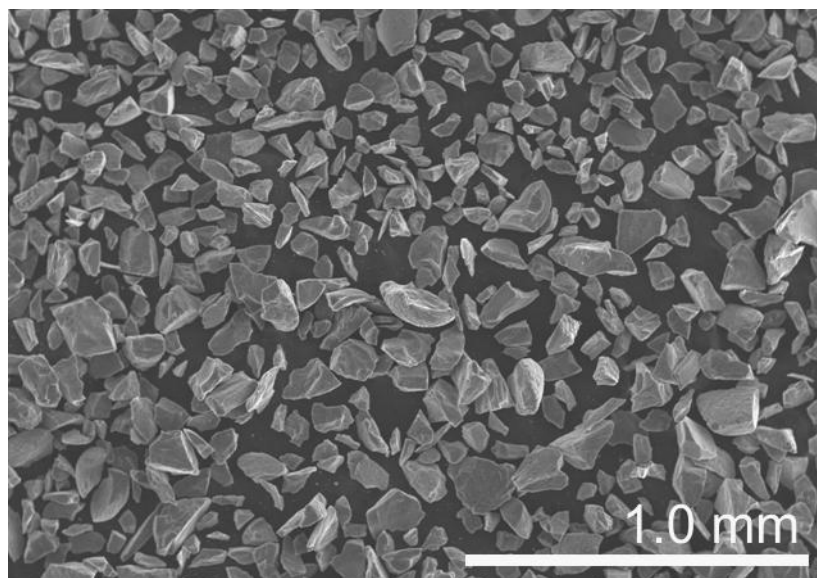


Fig. 22: Fresh Si particles used in acoustic emission experiments

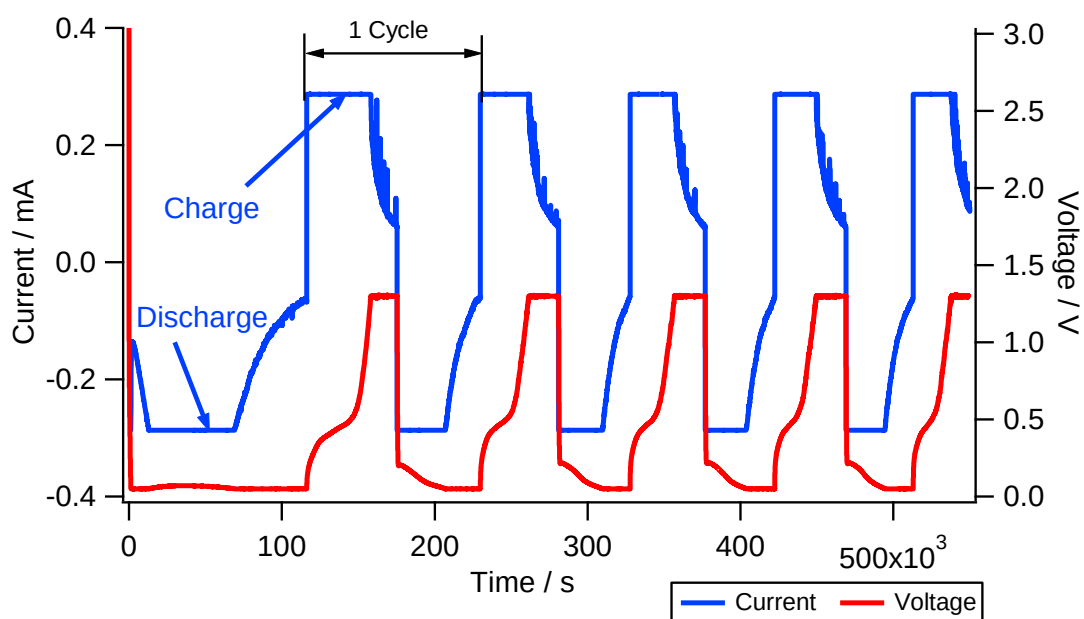


Fig. 23: Example of constant current-constant voltage cycling curve used in acoustic emission experiments

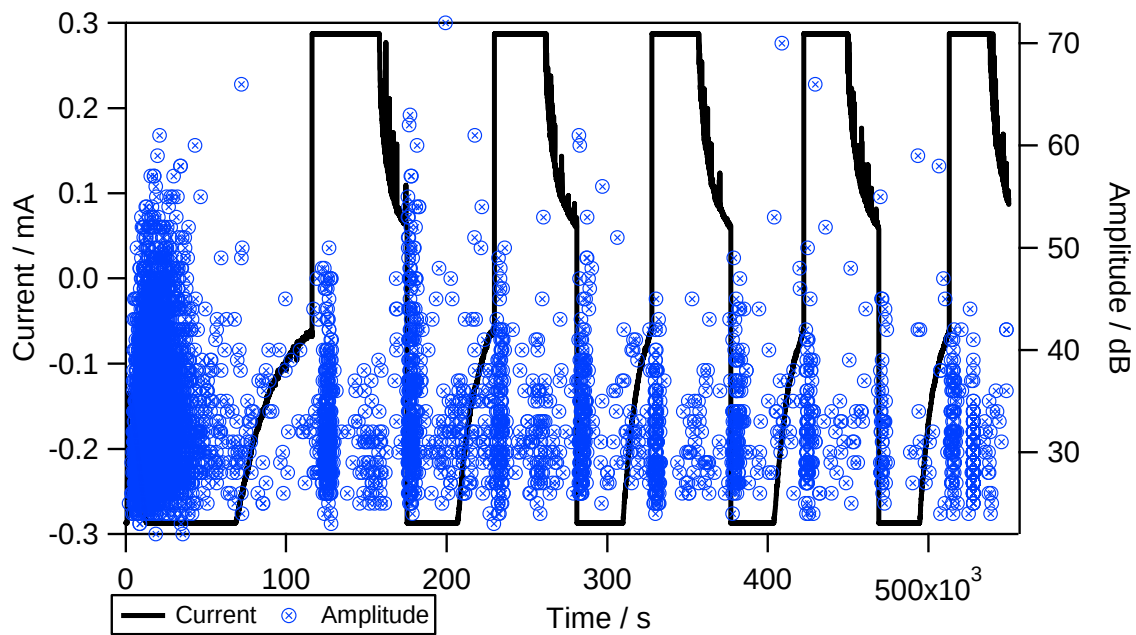


Fig. 24: AE data for electrochemical cycling of Si anode: specimen ID 48

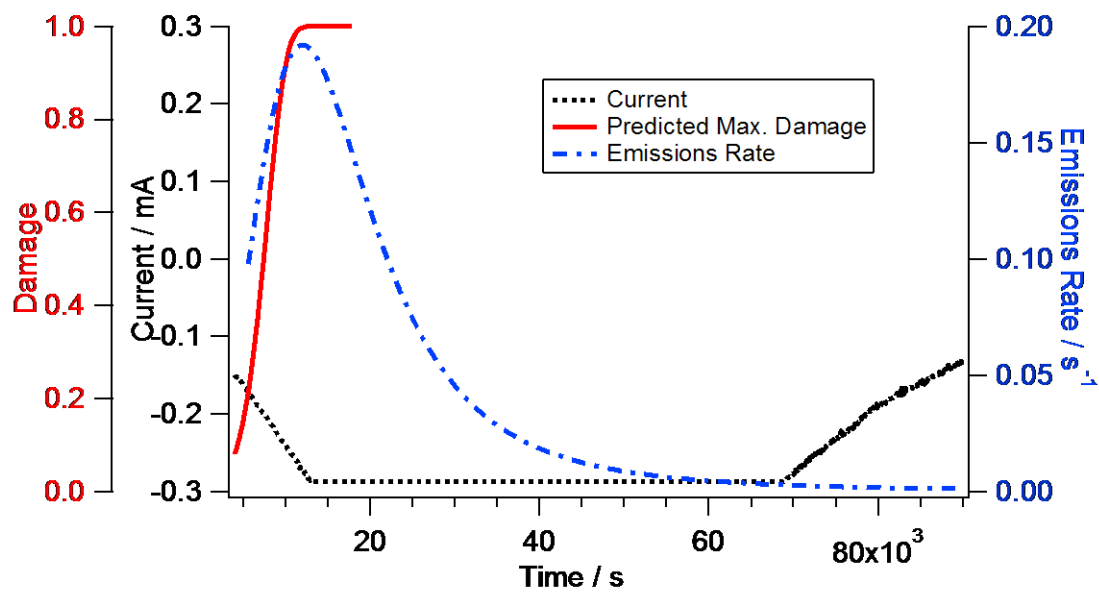


Fig. 25: Correlation between emissions rate from experiment and computed evolution of maximum damage

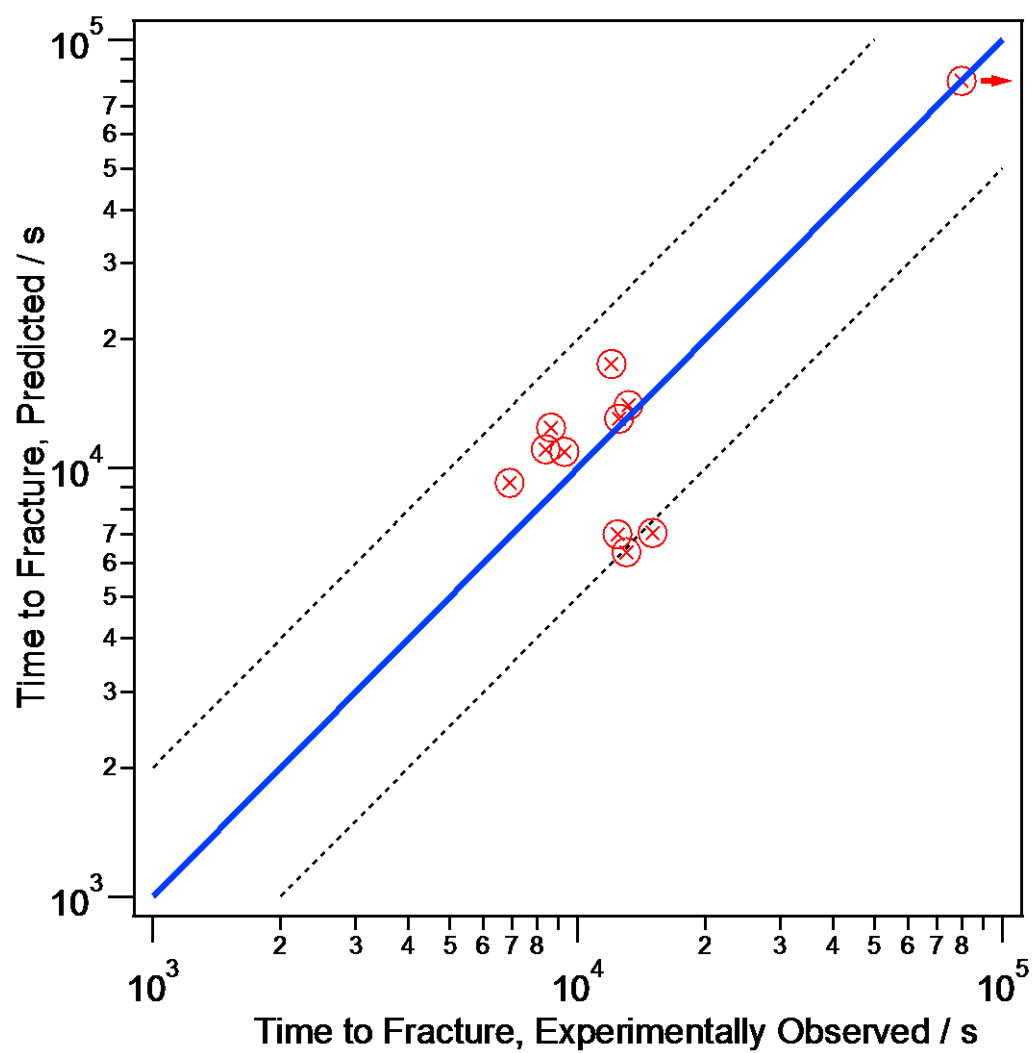


Fig. 26: Correlation between observed and predicted fracture times

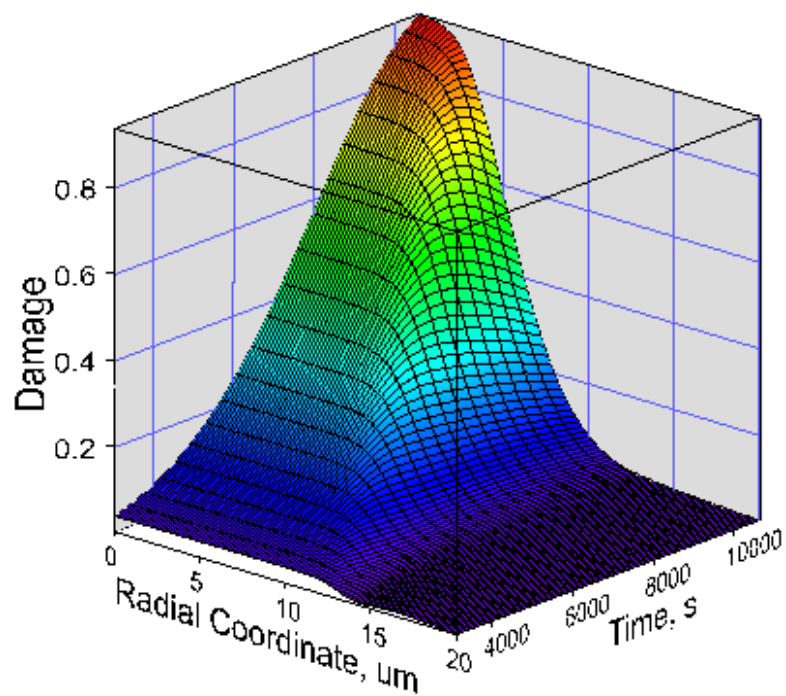


Fig. 27: Computed damage evolution as a function of time and radial coordinate of a spherical particle

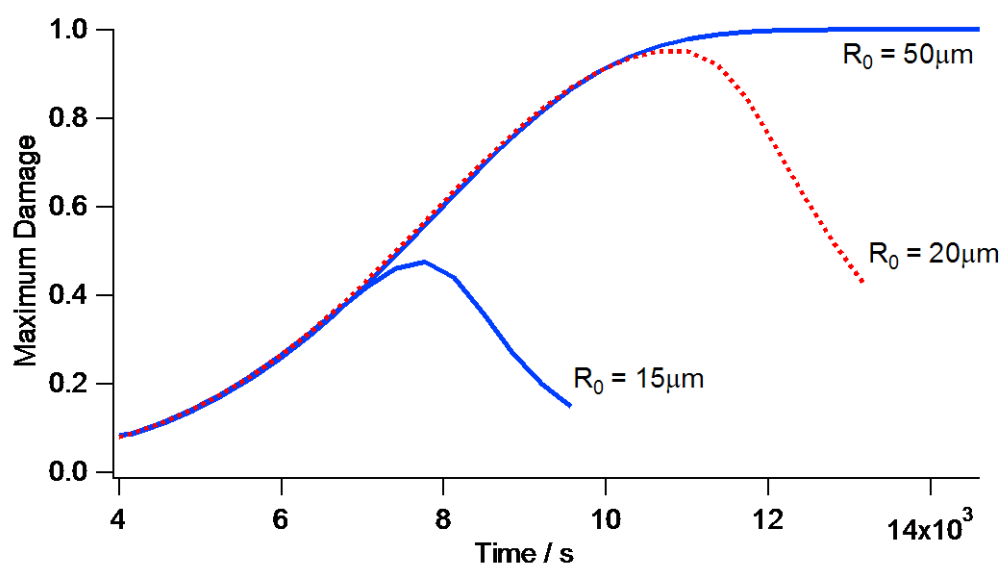


Fig. 28: Distribution of maximum damage for three different radii of Si particle

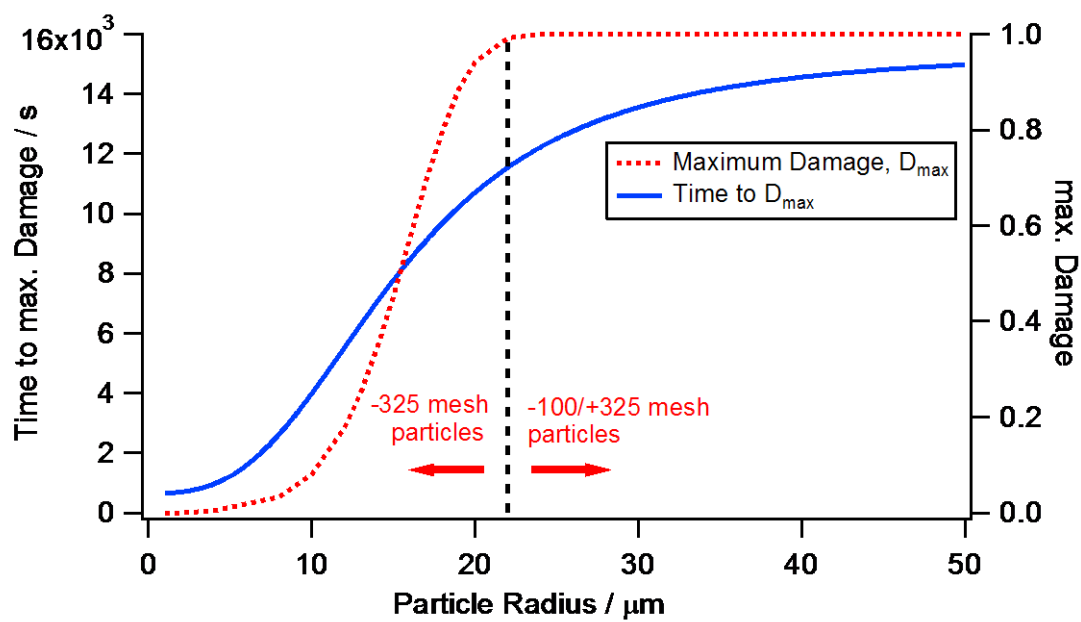


Fig. 29: Damage parameter as a function of particle size

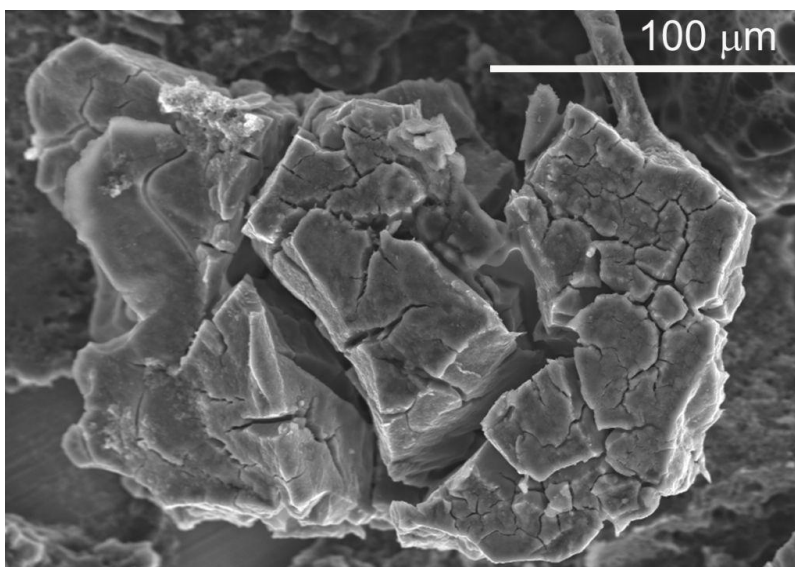


Fig. 30: SEM of a cycled Si particle

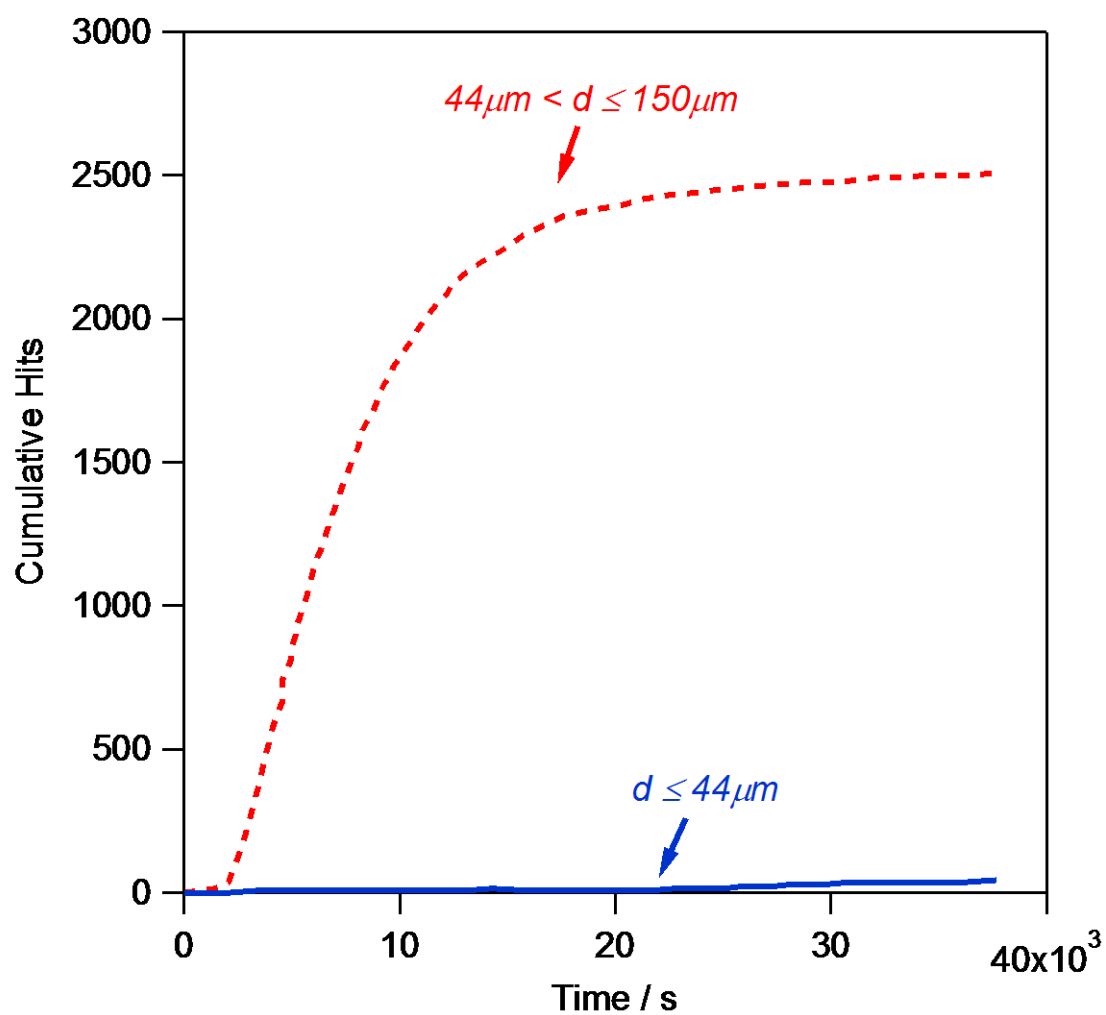


Fig. 31: Comparison between AE cumulative events from two different particle size distributions

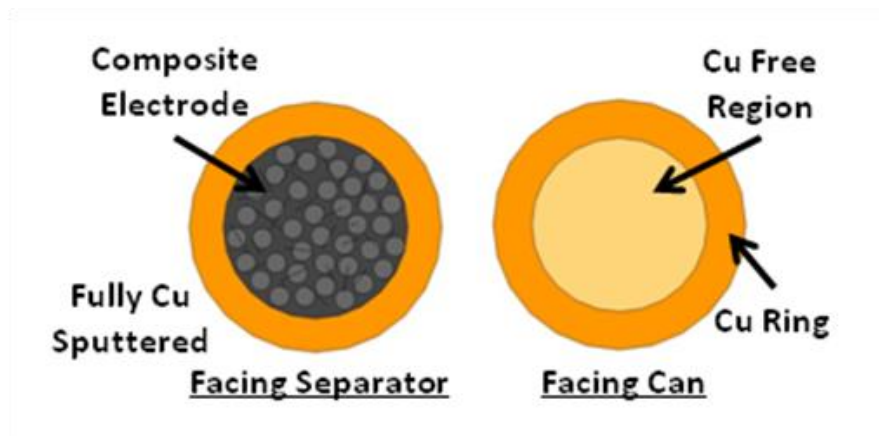


Fig. 32: PET disks were sputtered with copper or aluminum to produce a conductive X-ray window. The disk face intended for composite electrode application was metalized over its entire surface, while the opposite face was only metalized in a ring along its outer edge.

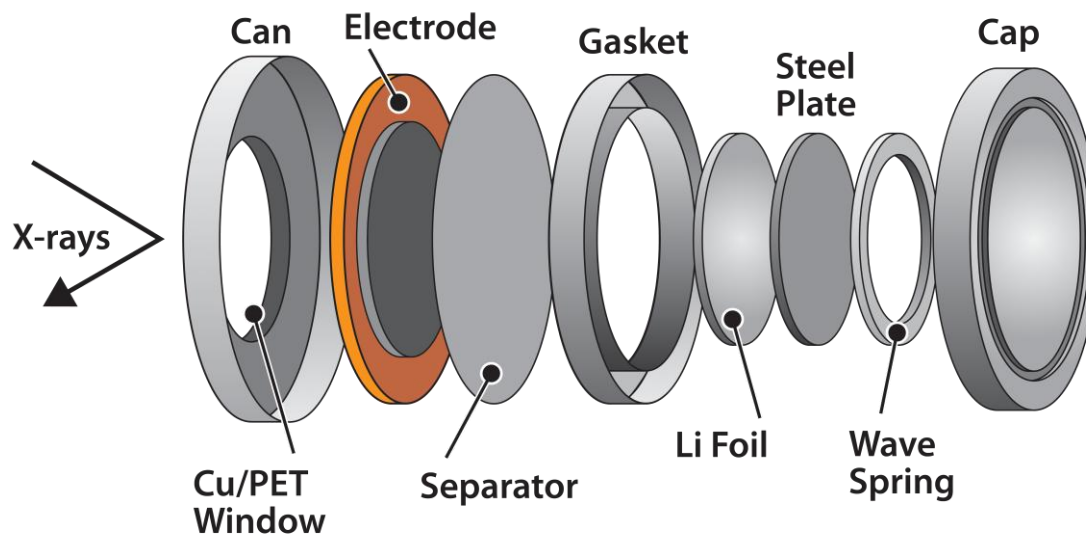


Fig. 33: Schematic diagram of the in situ AE-XRD cell assembly

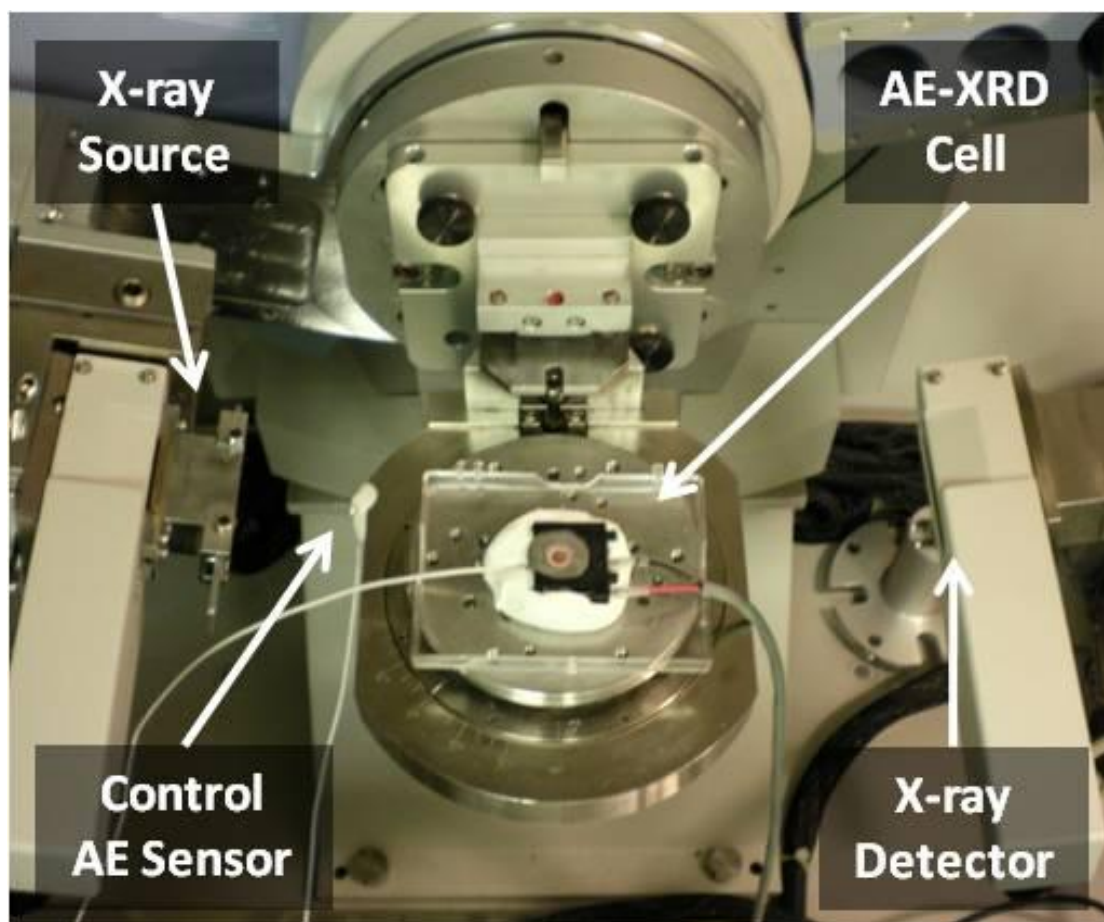


Fig. 34: Setup used for in situ AE-XRD experiments.

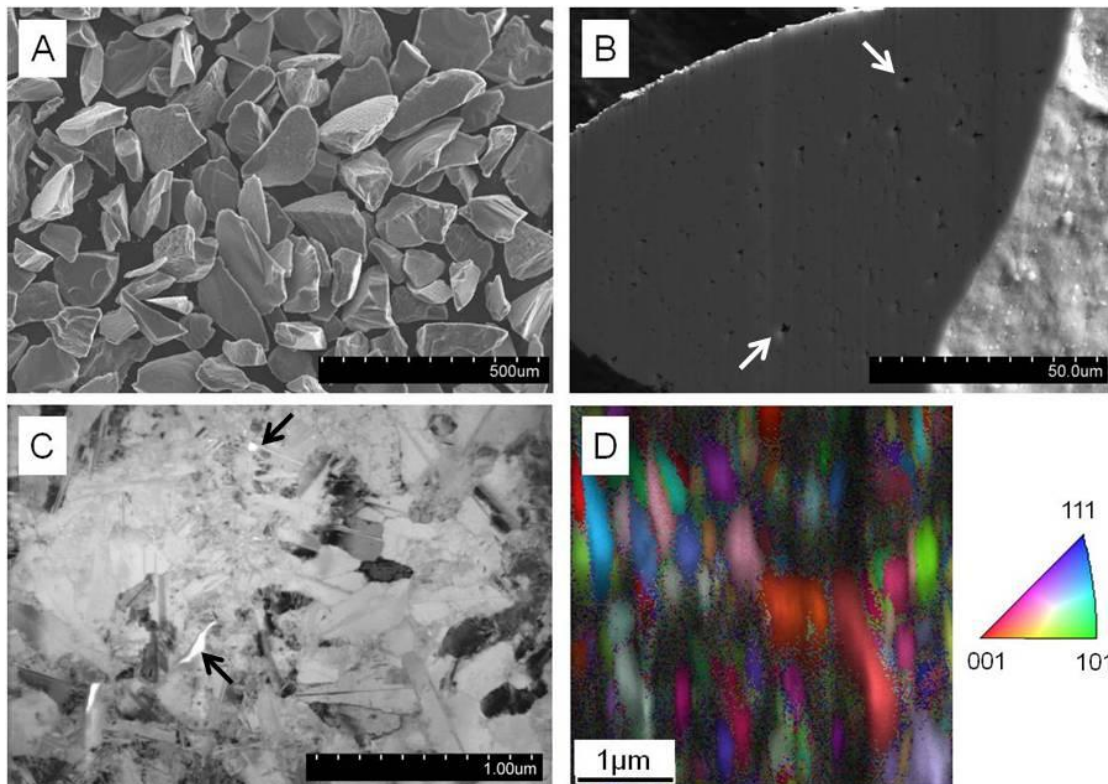


Fig. 35: Characterization of pristine silicon particles was performed by SEM (a). Particles were cut, polished, and imaged using a FIB-SEM to observe the internal structure of individual particles, including voids (b). FIB was used to cut a thin section of material from a single particle to perform STEM (c). Silicon crystallite size, shape, and orientation were determined by EBSD from a FIB polished surface (d). Arrows in (b) and (c) indicate voids in the particle.

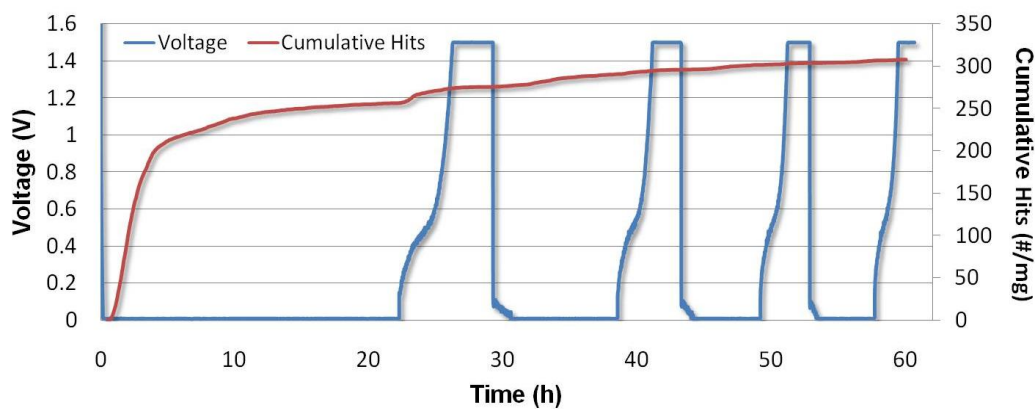


Fig. 36: Cycling voltage and cumulative particle fracture type AE events recorded during the cycling of an in situ AE-XRD cell containing silicon as the active material.

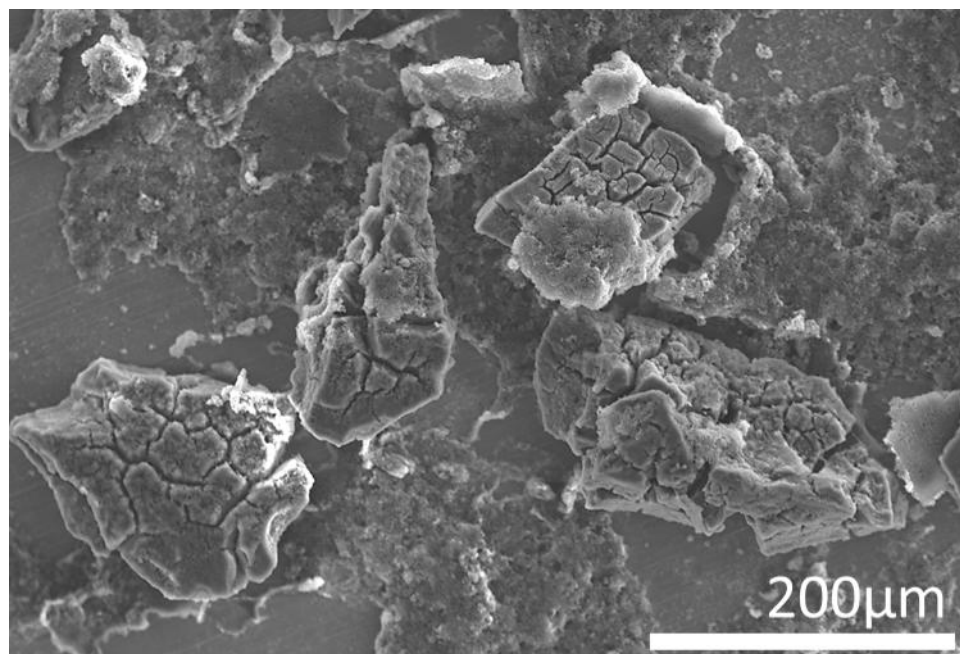


Fig. 37: SEM image of Si particles after 5 complete charge/discharge cycles. Deep fissures and shallow surface cracks can be clearly seen.

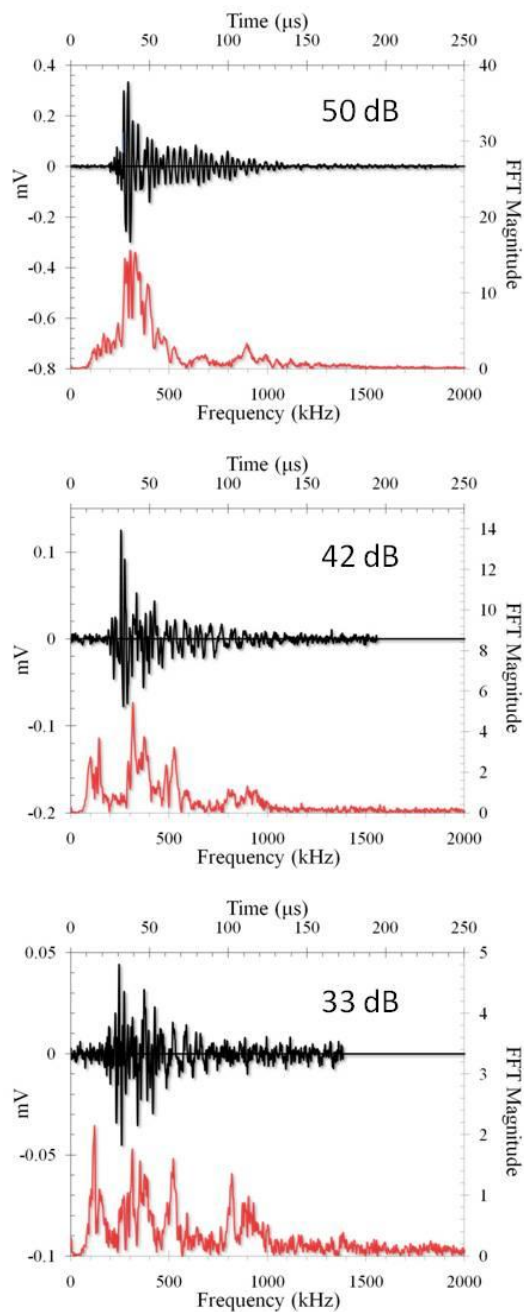


Fig. 38: Hit waveforms recorded during cycling of the in situ AE-XRD cell containing a silicon composite electrode. This waveform is characteristic of particle fracture and hits of various amplitudes are shown with their associated FFT to illustrate the frequency peaks related to the fracture event rather than background signal.

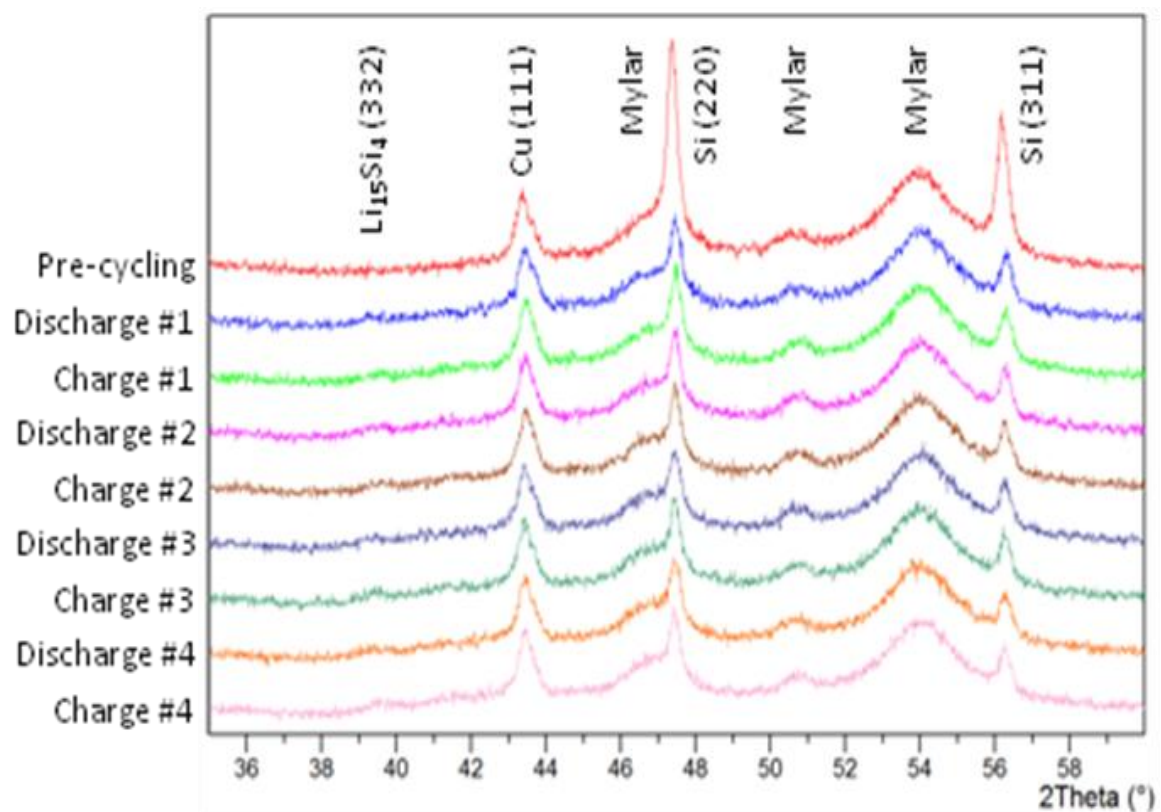


Fig. 39: Fig. 38: XRD scans taken from an in situ AE-XRD cell, where the active material was initially crystalline silicon. Extensive silicon amorphization was observed during the first lithiation (charging) of the silicon. The possible formation of a small amount of the $\text{Li}_{15}\text{Si}_4$ phase following the first lithiation was also detected.

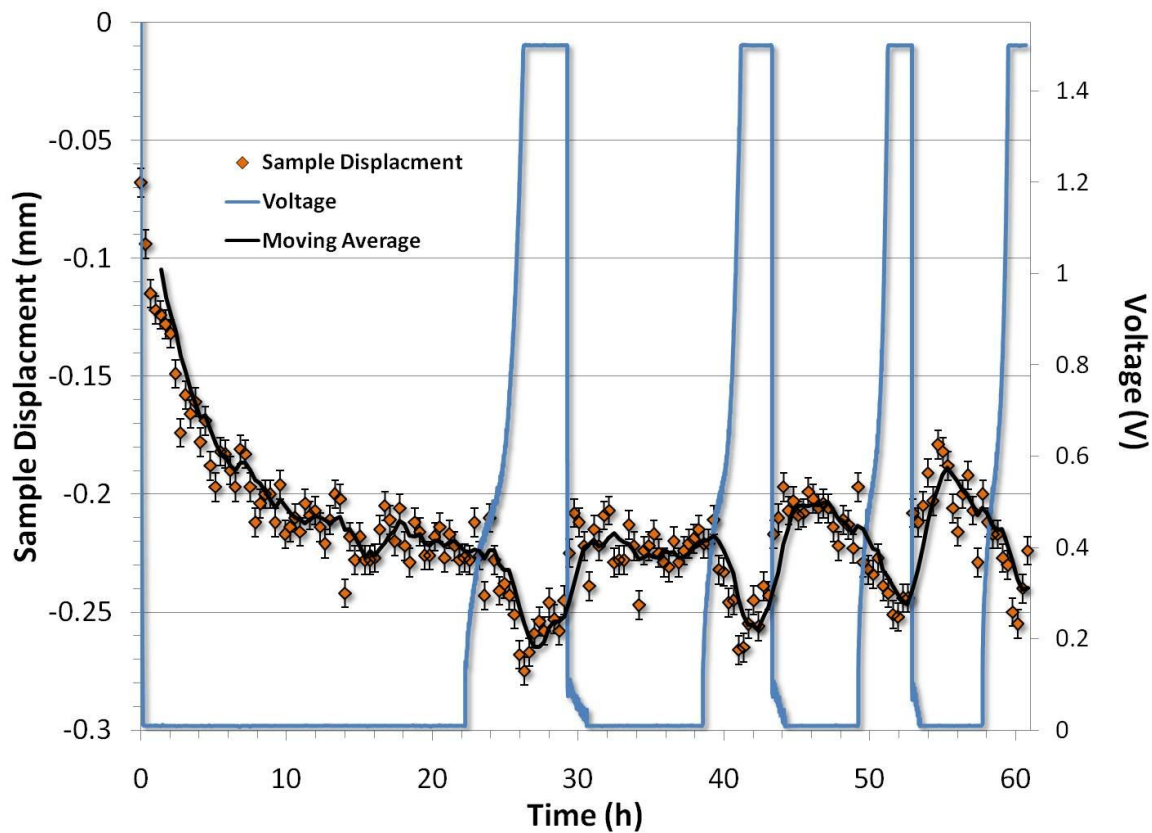


Fig. 40: Vertical displacement of the sample surface during cycling as determined from the (111) copper peak. Following an initial settling period during the first discharge, the surface displacement directly correlates with the volume fluctuation in the silicon electrode. As the silicon is delithiated during discharging, the sample surface falls and as the silicon is lithiated during charge, the surface rises. Error bars indicate the standard error in each measurement.

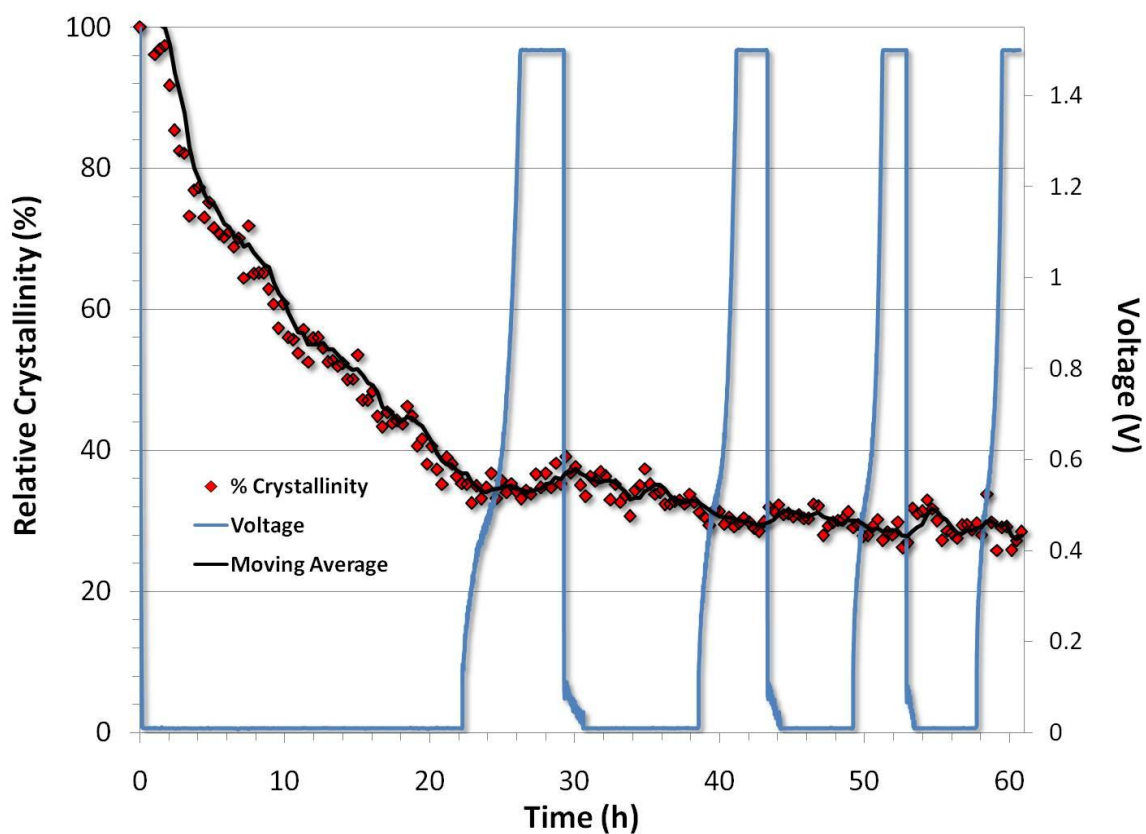


Fig. 41: Relative percent crystallinity of the Si particles during cycling as determined from the silicon (022) peak area. Nearly identical results (not shown) were obtained by tracking the silicon (311) peak.

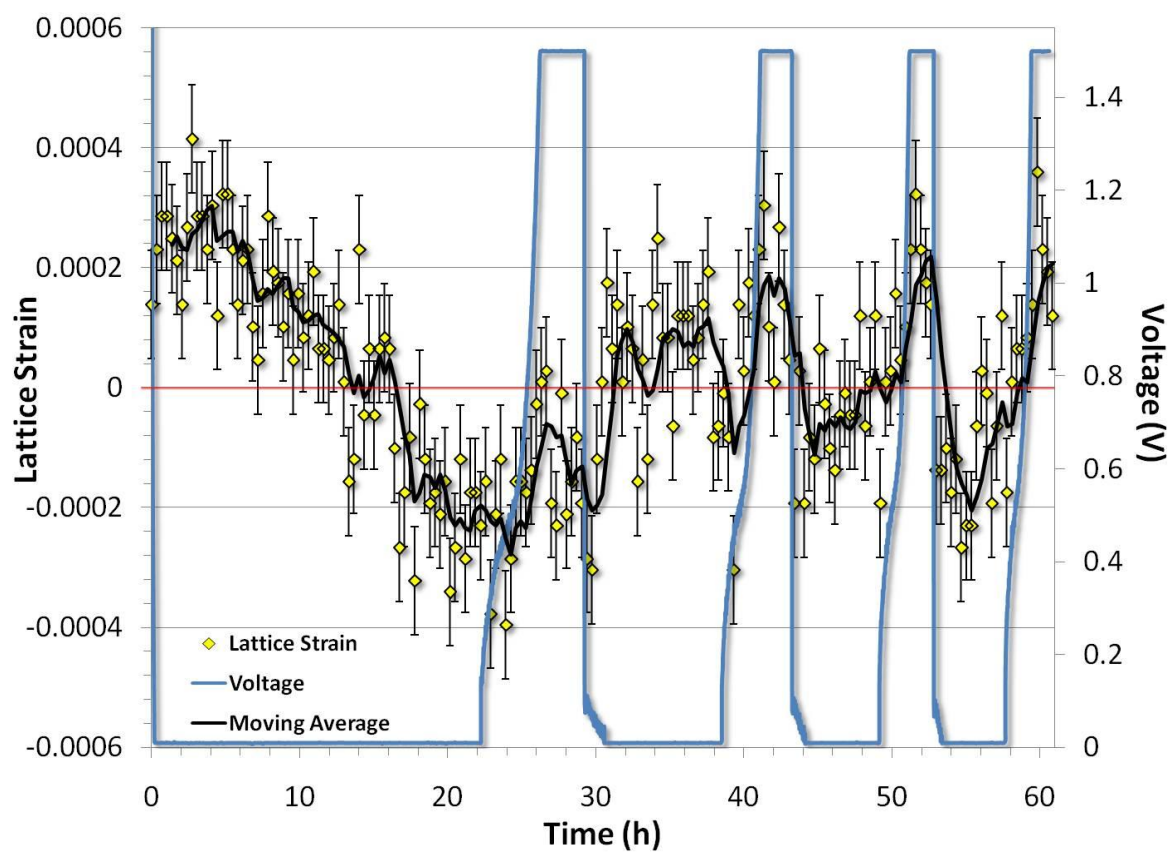


Fig. 42: Lattice strain of the crystalline region of Si particles during cycling, as determined by Rietveld refinement of each pattern. Error bars indicate the standard error in each strain measurement.

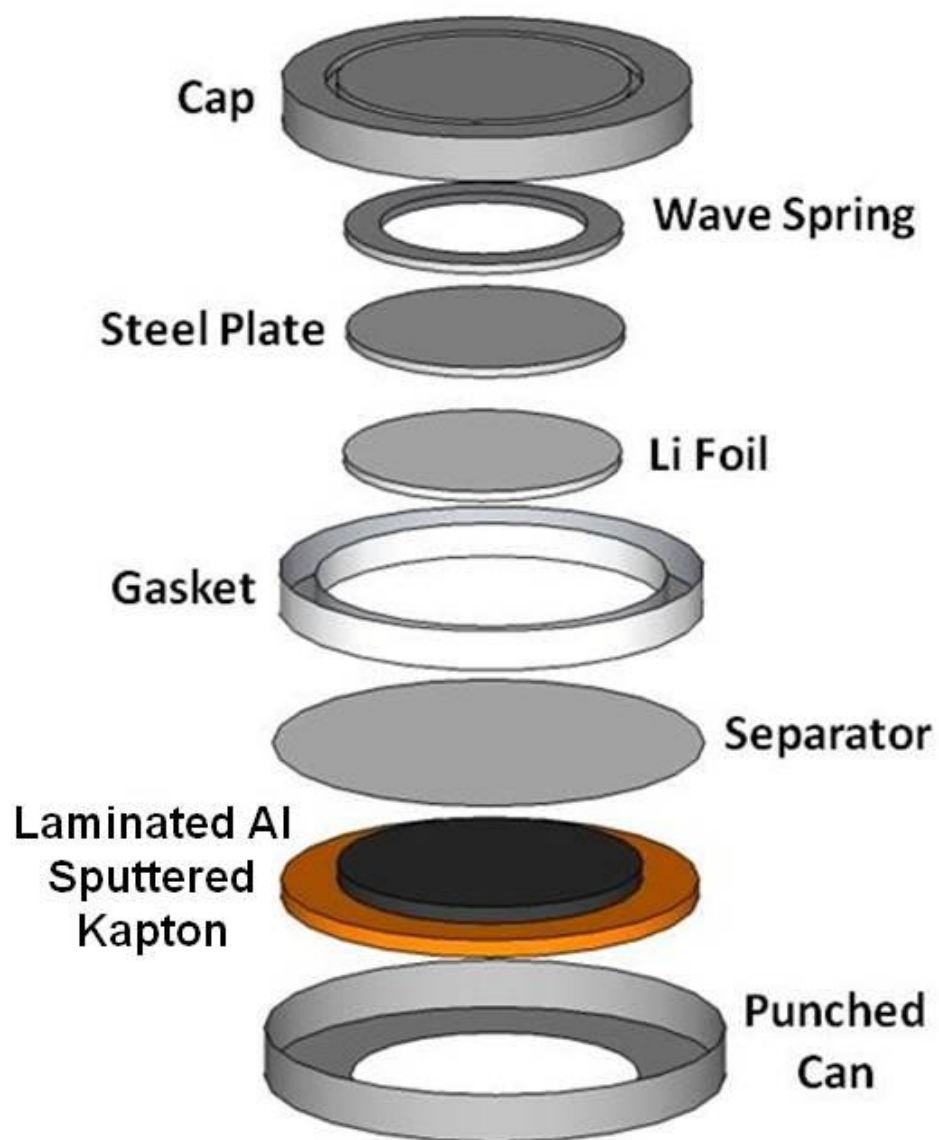


Fig. 43: Exploded view of in situ XRD cell assembly. A disk of 50 μ m thick disk of Kapton tape sputtered with a 300nm layer of aluminum serves as both a current collector for the MNO composite electrode and a window for X-ray penetration.

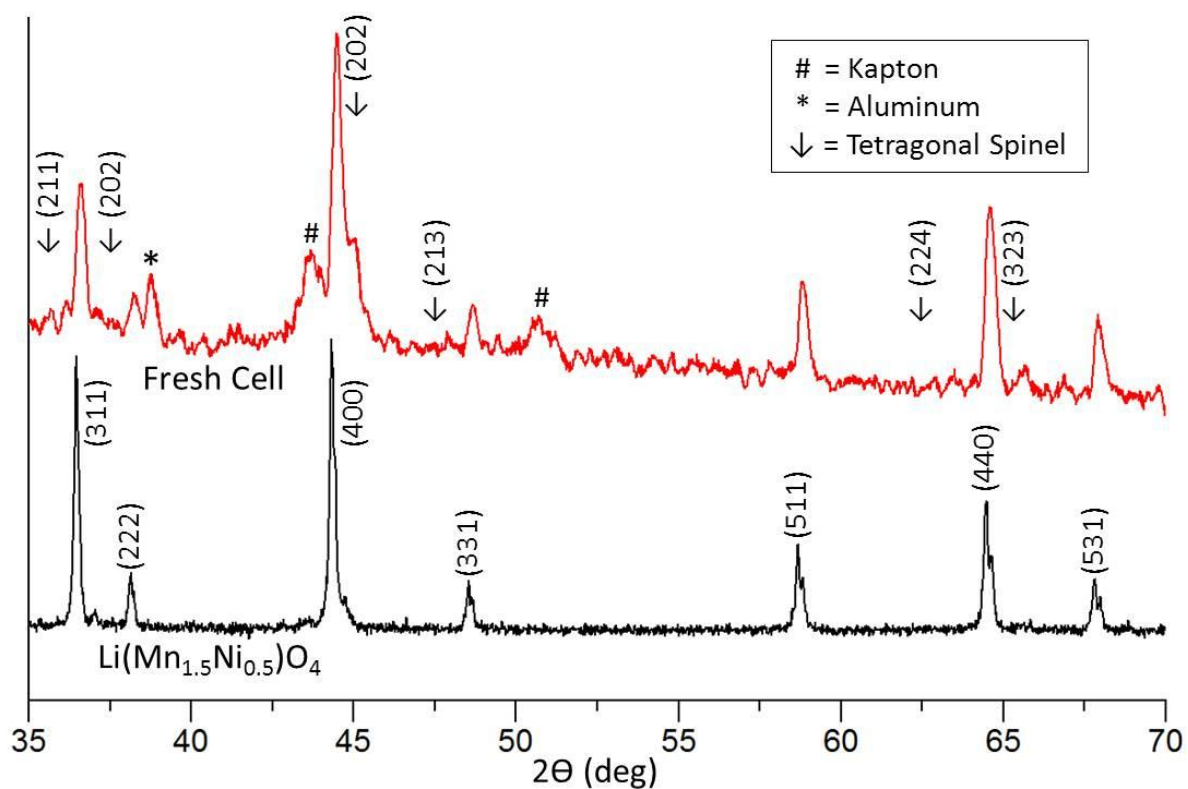


Fig. 44: XRD pattern of fresh MNO powder (bottom) and the pattern observed through the aluminized Kapton window of a freshly assembled MNO vs. Li foil in situ XRD cell. Diffraction peaks from the MNO are labeled on the bottom scan and peaks resulting from the aluminum and Kapton components are labeled on the top. The locations where peaks from the tetragonal spinel phase appear at high degrees of lithiation are also shown on the top scan.

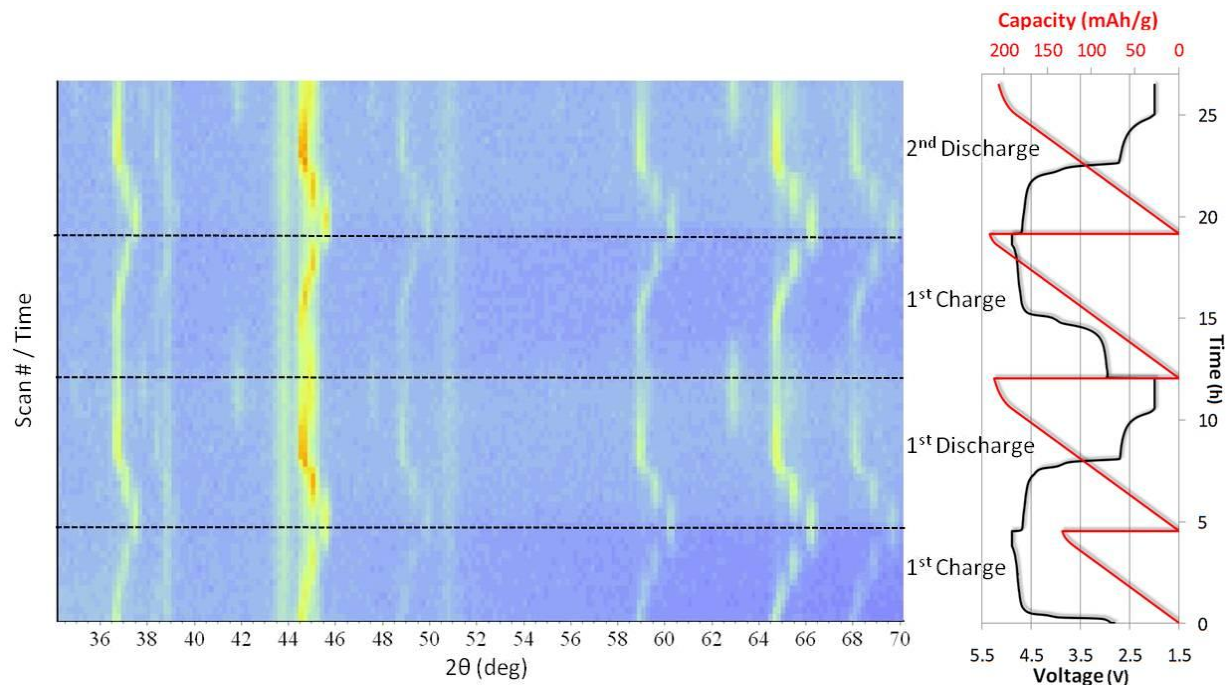


Fig. 45: Isoline view of XRD patterns recorded throughout the first and second cycles.

Three distinct cubic spinel phases are observed during charging steps (delithiation) that are completely reversible upon delithiation. At low potentials of the discharge steps (lithiation) the appearance of a tetragonal spinel phase is observed which completely disappears upon delithiation.

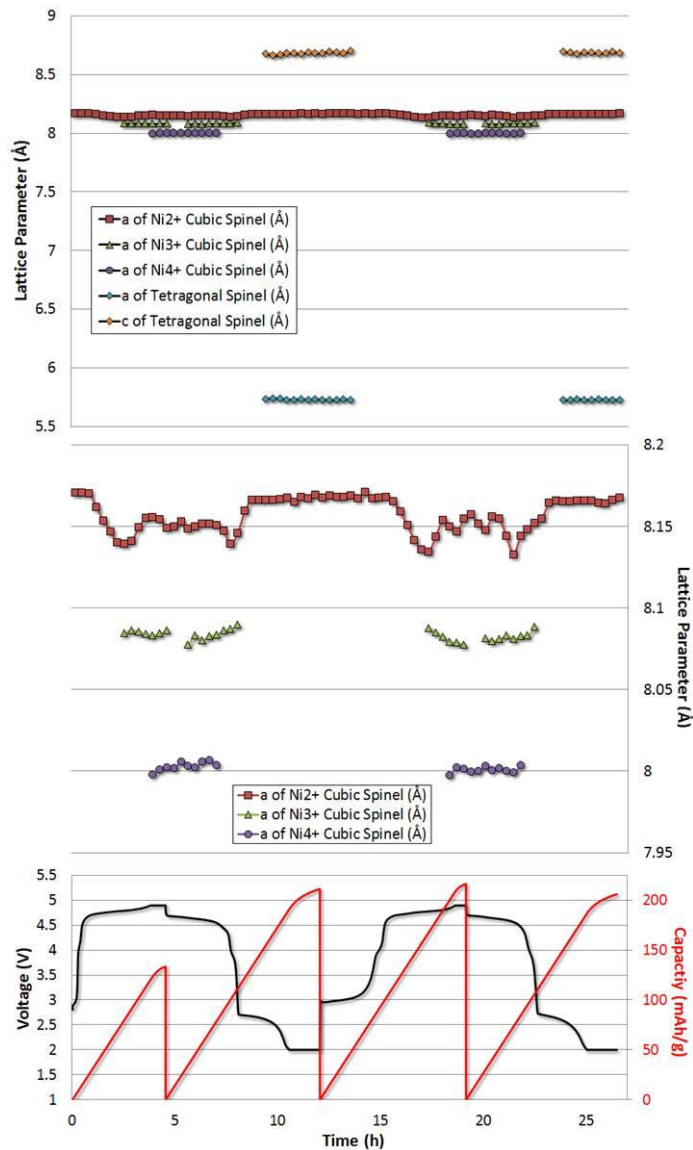


Fig. 46: Lattice parameters measured during the first two cycles were refined from the XRD data. The transition between the four spinel phases is shown plotted against time on top with the cell potential and capacity shown on bottom. An expanded view of the lattice parameters measured for the cubic spinel phases is also shown in the middle. The estimated standard error in lattice parameter values were between $0.0005\text{\AA}$ and $0.0007\text{\AA}$ for all fits.

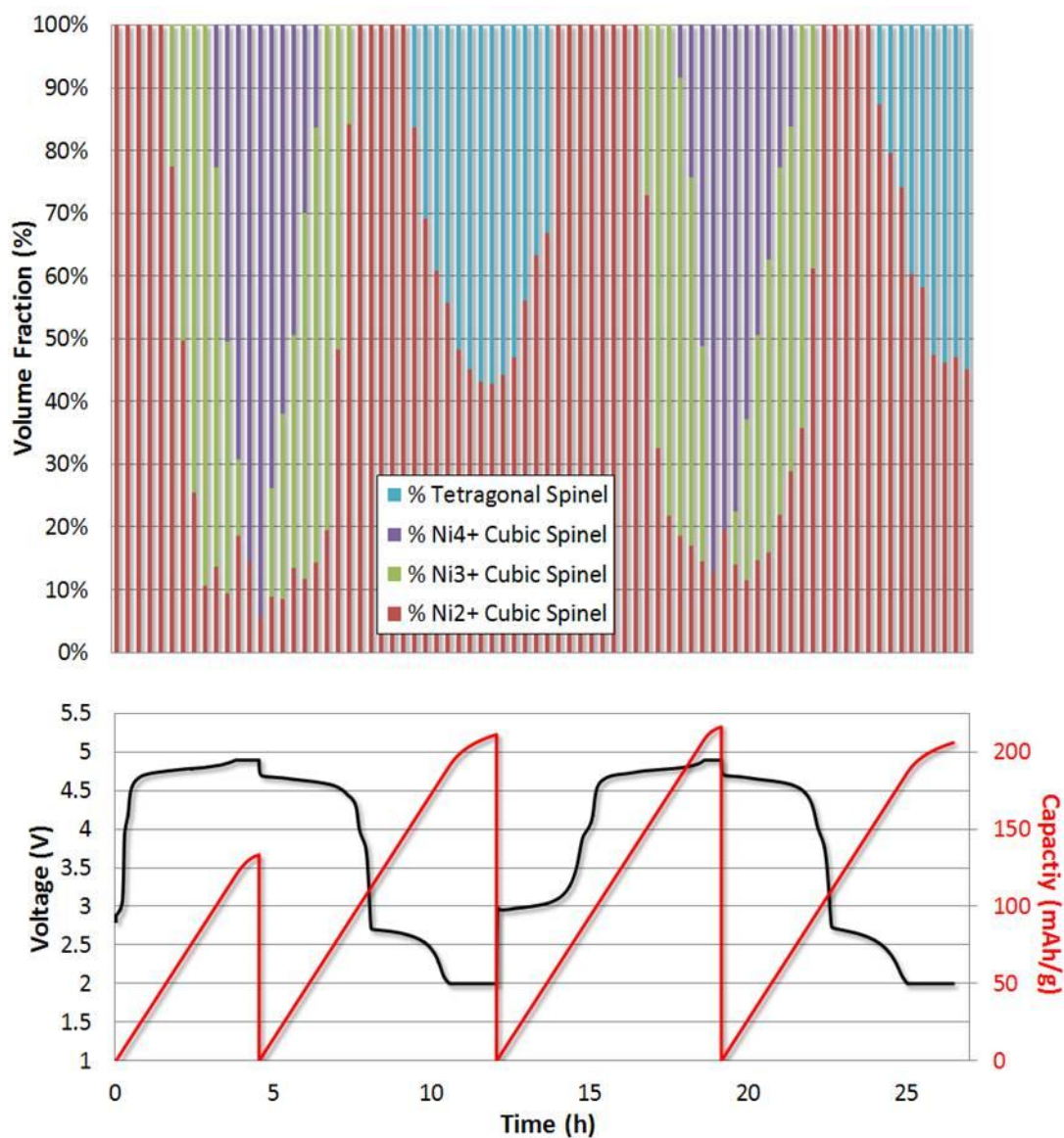


Fig. 47: The volume fraction of each spinel phase present during the first two cycles determined by Rietveld refinements of the XRD data. The percent composition of each phase is shown plotted with cell voltage and capacity below.

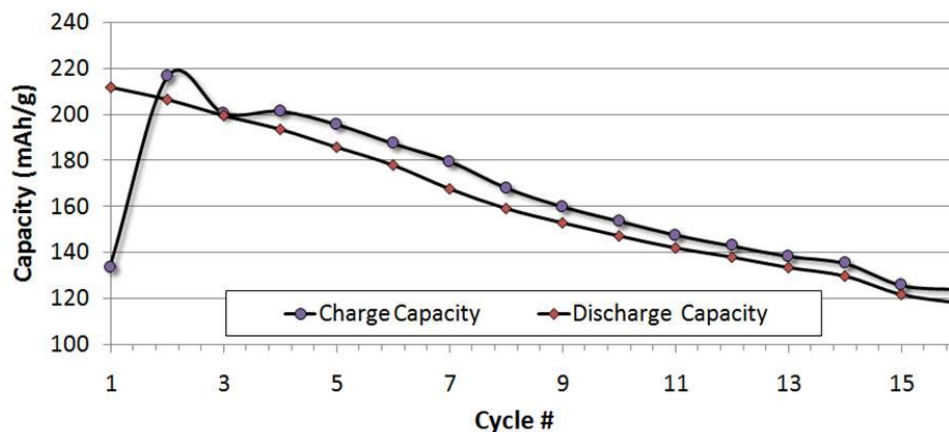


Fig. 48: Charge and discharge capacities of MNO in situ XRD cell.

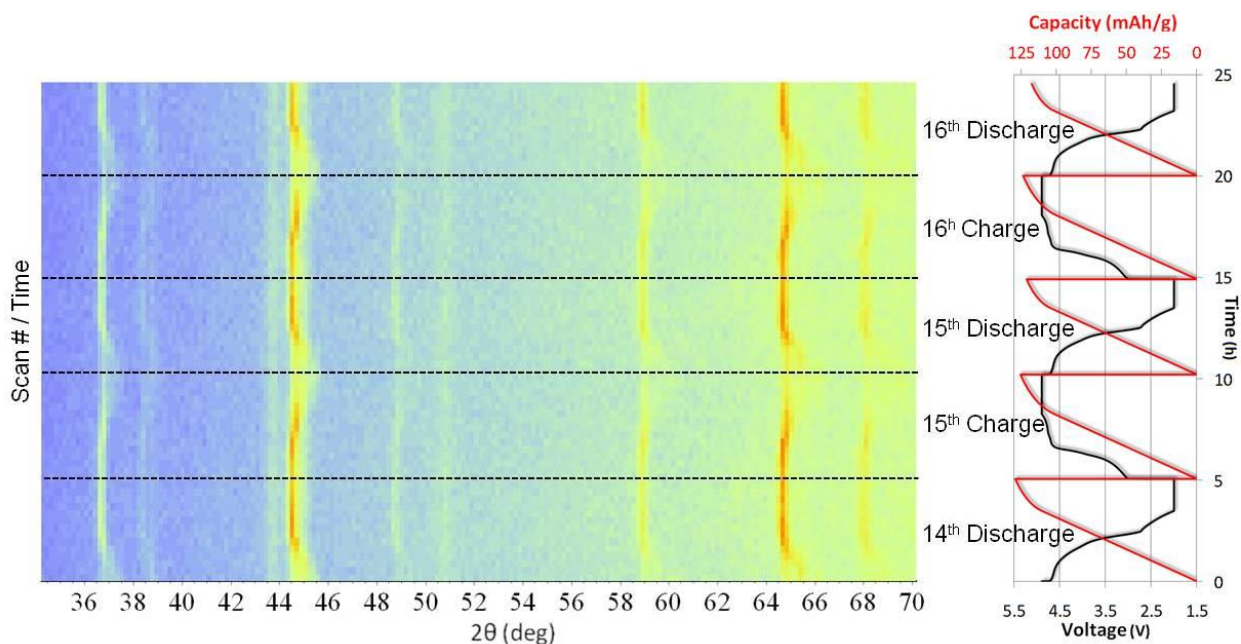


Fig. 49: Isoline view of diffraction patterns recorded between the 14th and 16th discharge.

The three cubic spinel phases no longer undergo a complete phase change during charging steps (delithiation) and all coexist at full delithiation. At low potentials of the discharge steps (lithiation) the tetragonal spinel phase is no longer observed.

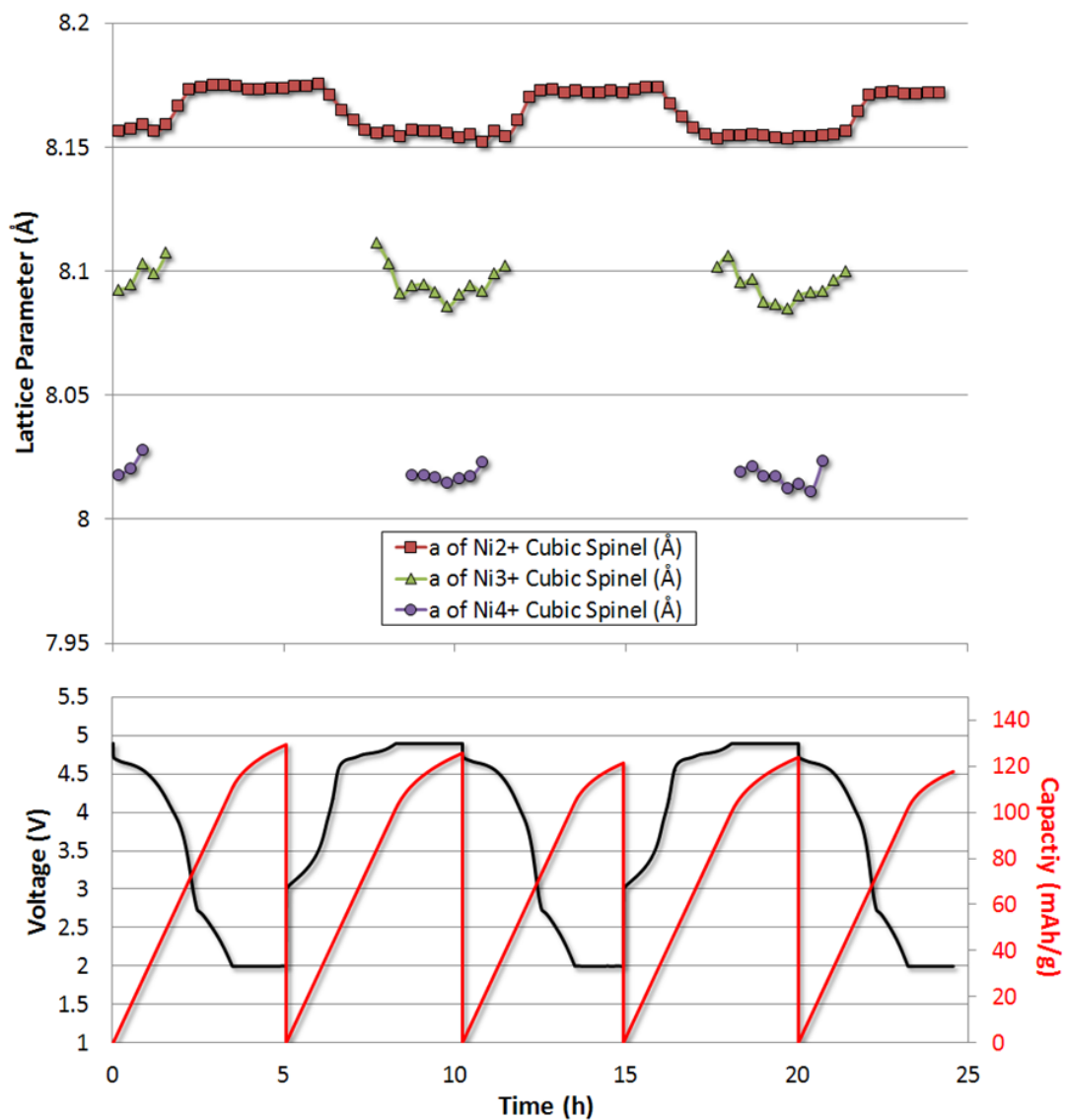


Fig. 50: Lattice parameters measured between the 14th and 16th discharges were refined from XRD data. The transition between the three cubic spinel phases is shown plotted against time on top with the cell potential and capacity shown on bottom. The estimated 3σ error interval for lattice parameter values was less than $\pm 0.0021\text{\AA}$ for all fits.

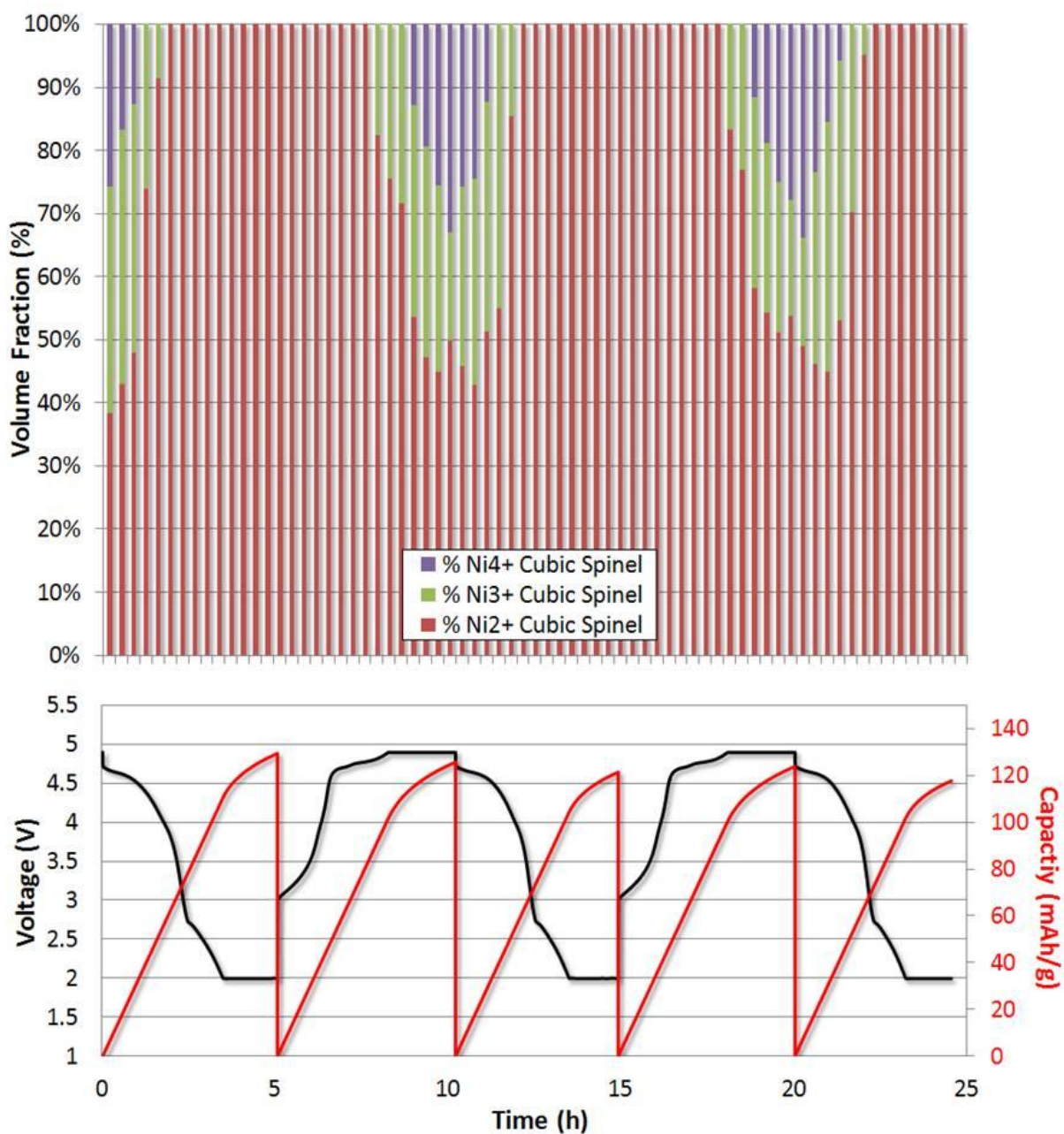


Fig. 51: The volume fraction of each spinel phase present between the 14th and 16th discharges was determined by Rietveld refinement of the XRD data. The volume percent composition of each phase is shown plotted with cell voltage and capacity below.

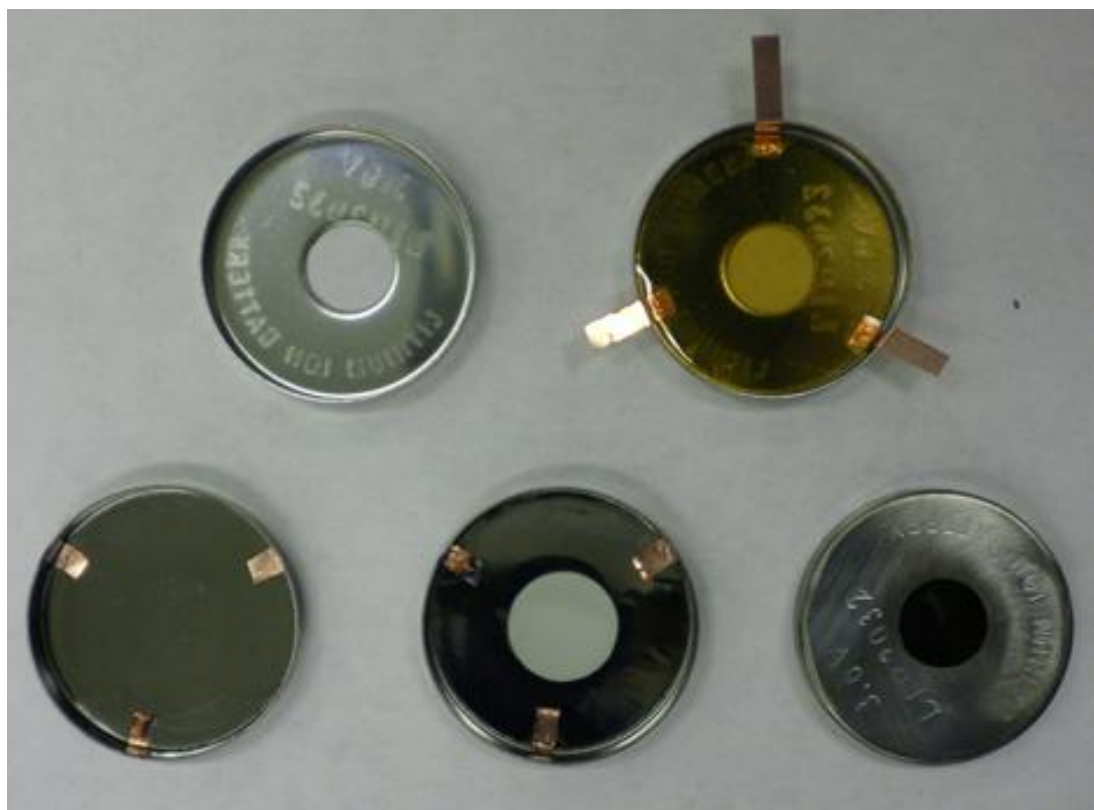


Fig. 52: In situ XRD cells with tin thin film electrodes shown at various stages of fabrication. In the top right is a coin cell can after being punched and de-burred. Top left shows the components after application of the Kapton disk and copper tabs. The bottom left show the component after sputtering with titanium and the bottom middle shows the piece after applying the tin electrodes. The window side of fully assembled cell is shown in the bottom right.

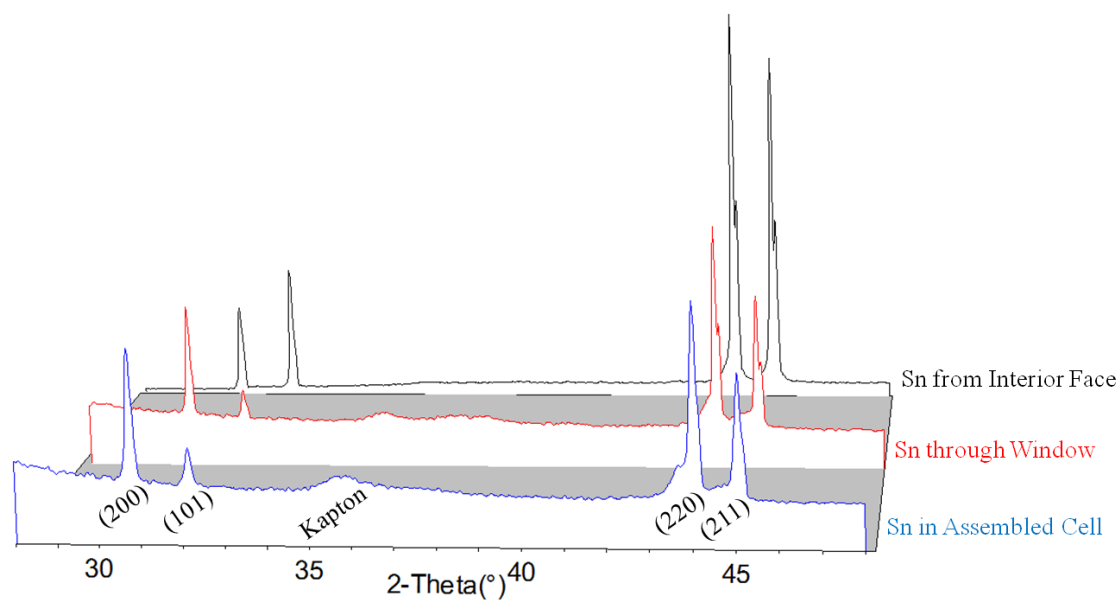


Fig. 53: XRD scans of tin thin film taken in direct reflection, after passing through the metalized Kapton window, and from a fully assembled cell.

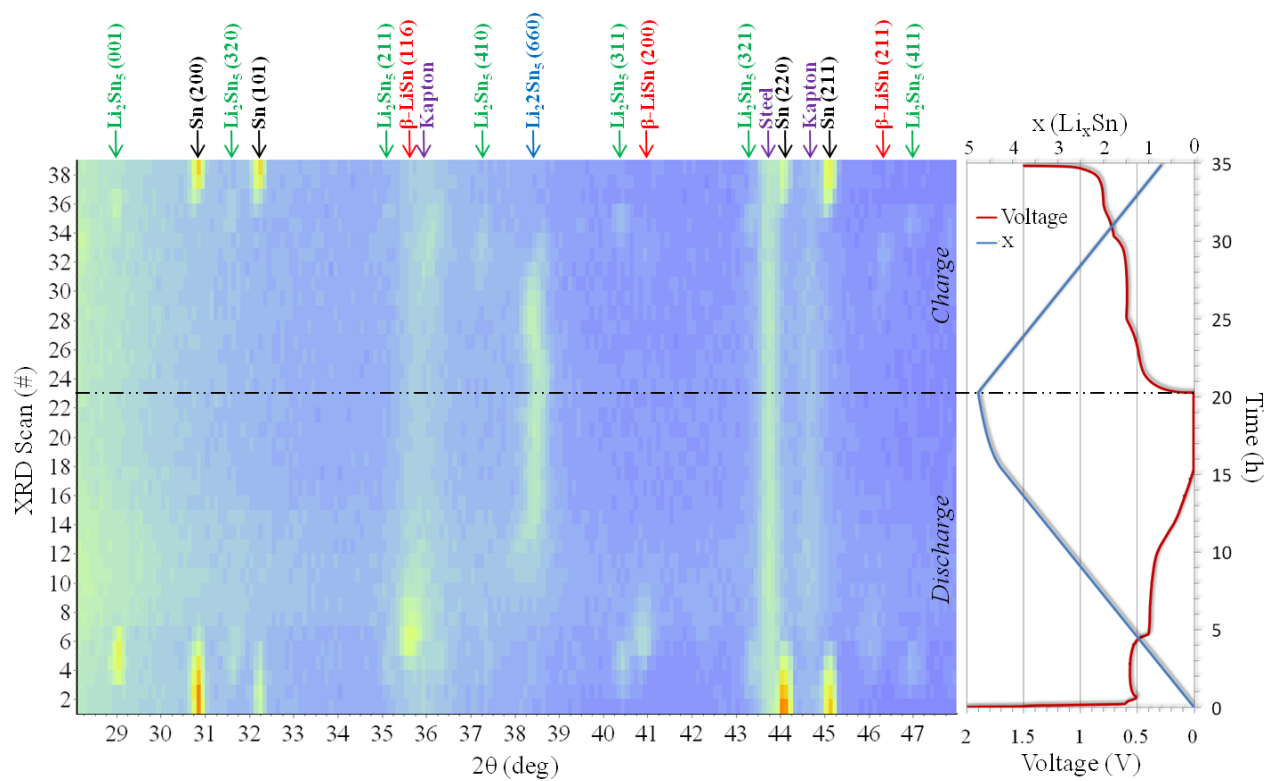


Fig. 54: An isoplot of XRD scans taken during the first discharge/charge cycle of a cell containing a tin thin film electrode. The identity of each peak is shown along the top and cell potential and degree of lithiation data is plotted to the right.

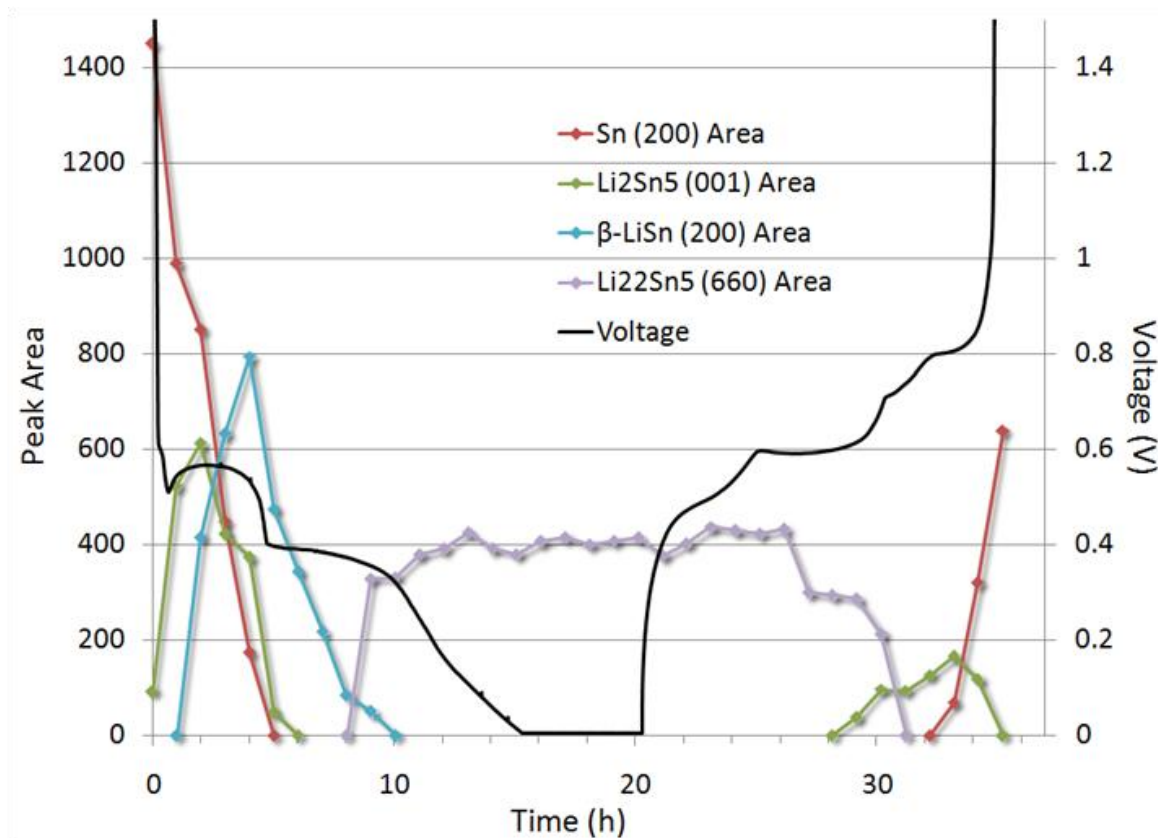


Fig. 55: Peak areas for selected planes from each tin phase are shown plotted along with voltage and degree of lithiation. The peaks used for Sn, Li₂Sn₅, β-LiSn, and Li₂₂Sn₅ were (200), (001), (200), and (660) respectively.

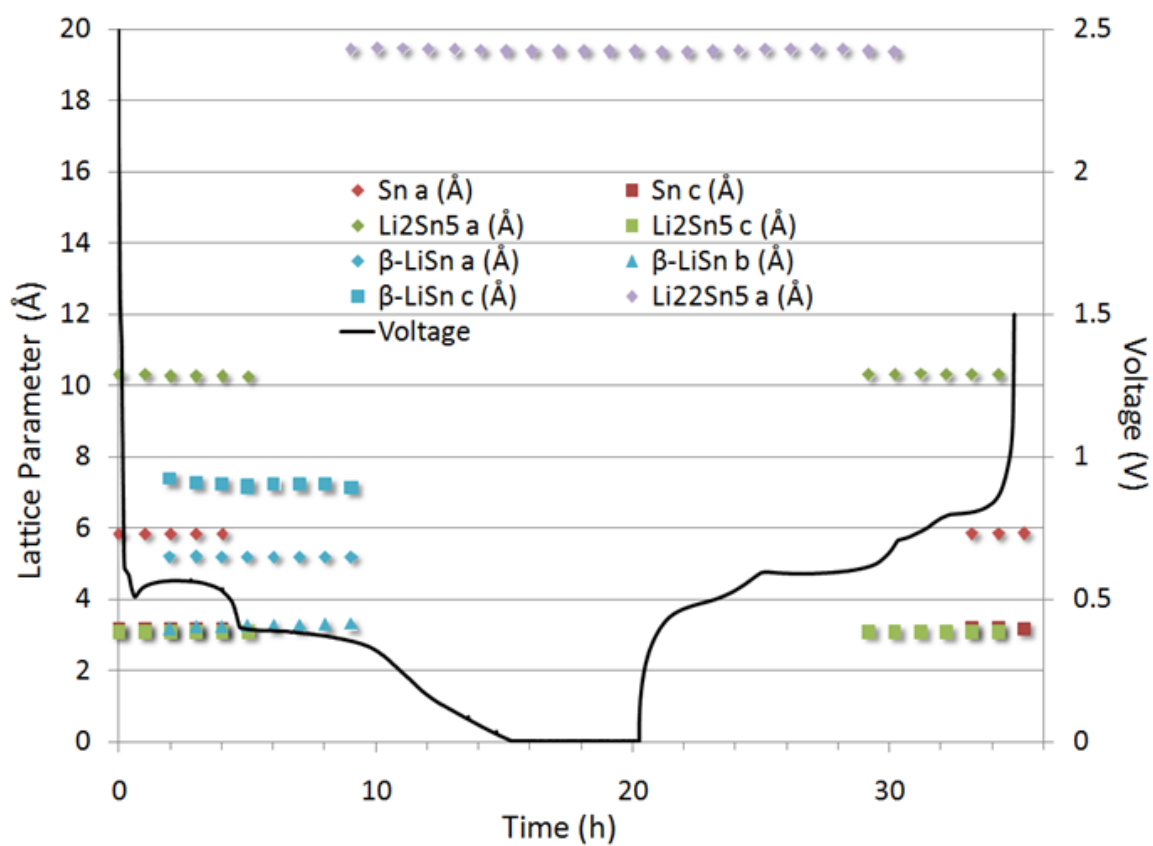


Fig. 56: Fitted lattice parameters from the various Li-Sn phases observed during cell cycling as a function of time.

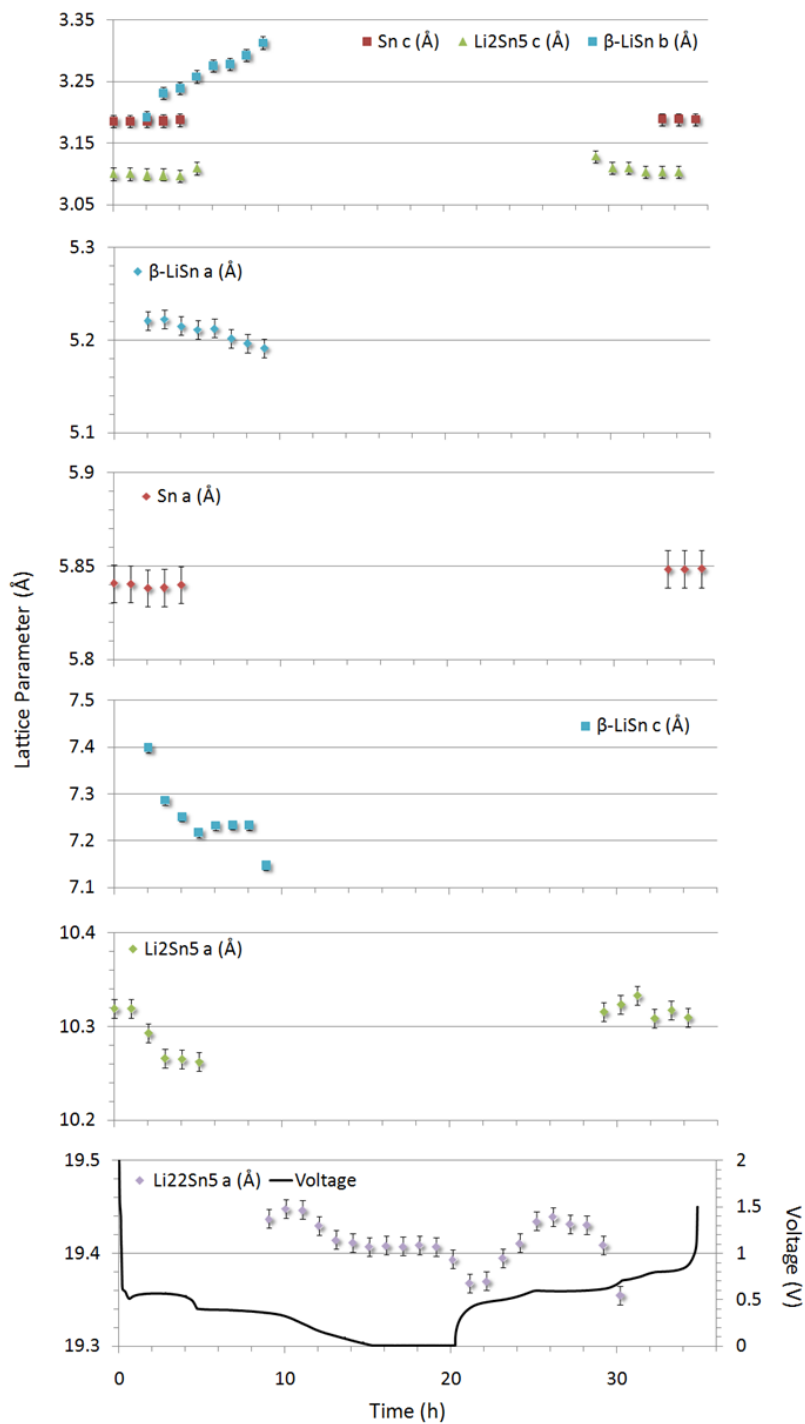


Fig. 57: Zoomed in view of lattice parameters showing their response to phase transformations.

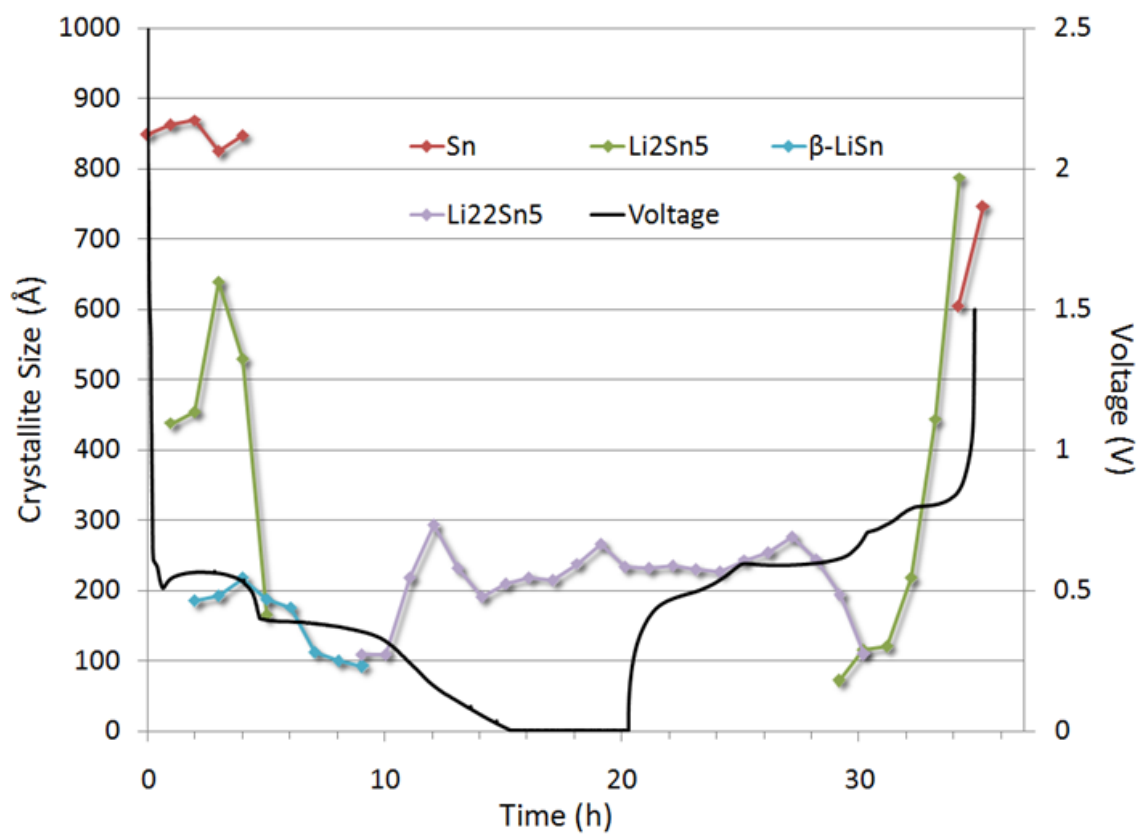


Fig. 58: Estimated crystallite size for the phases present on each scan.

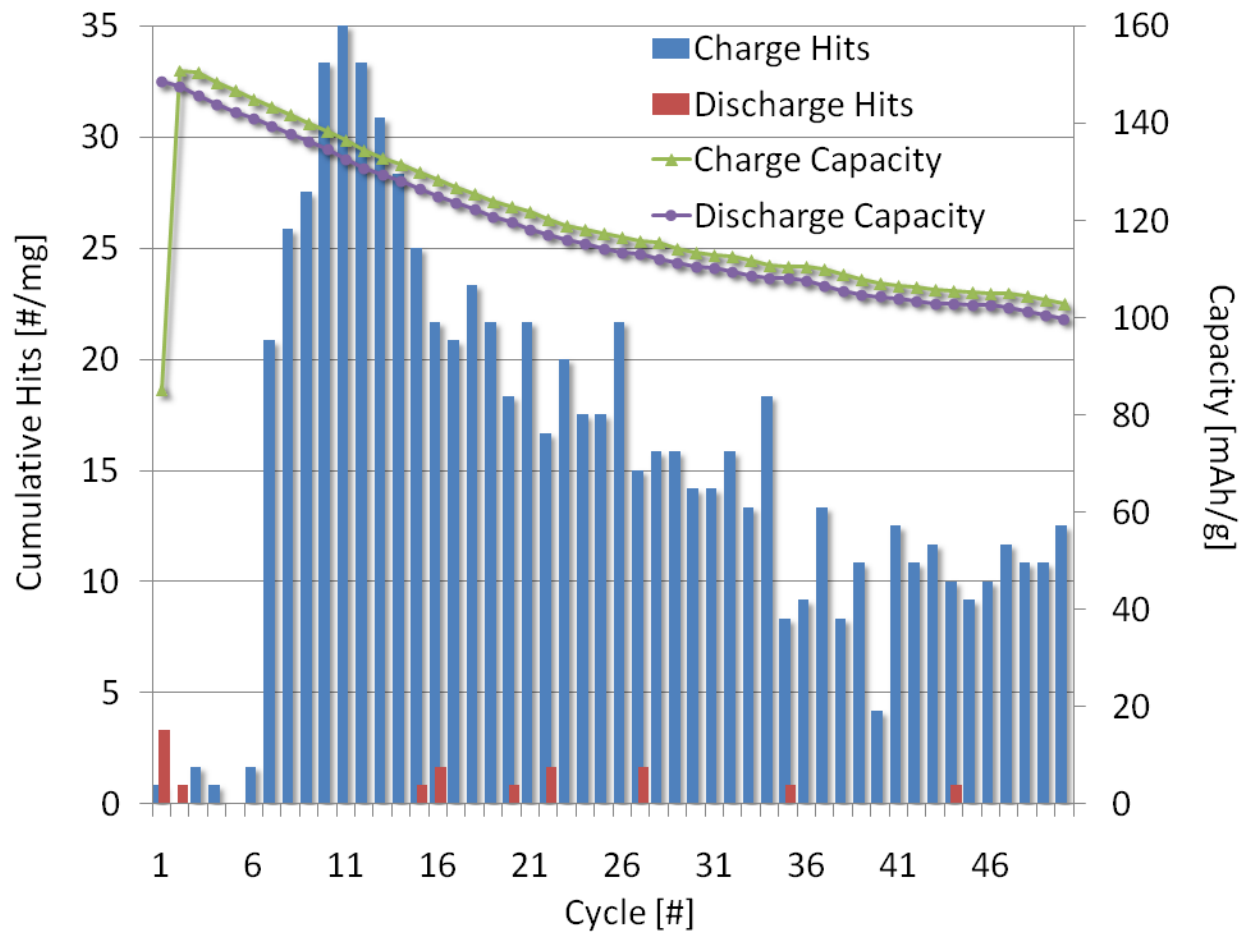


Figure 59: Histogram of AE from MNO partitioned by cycle and charge/discharge stage.

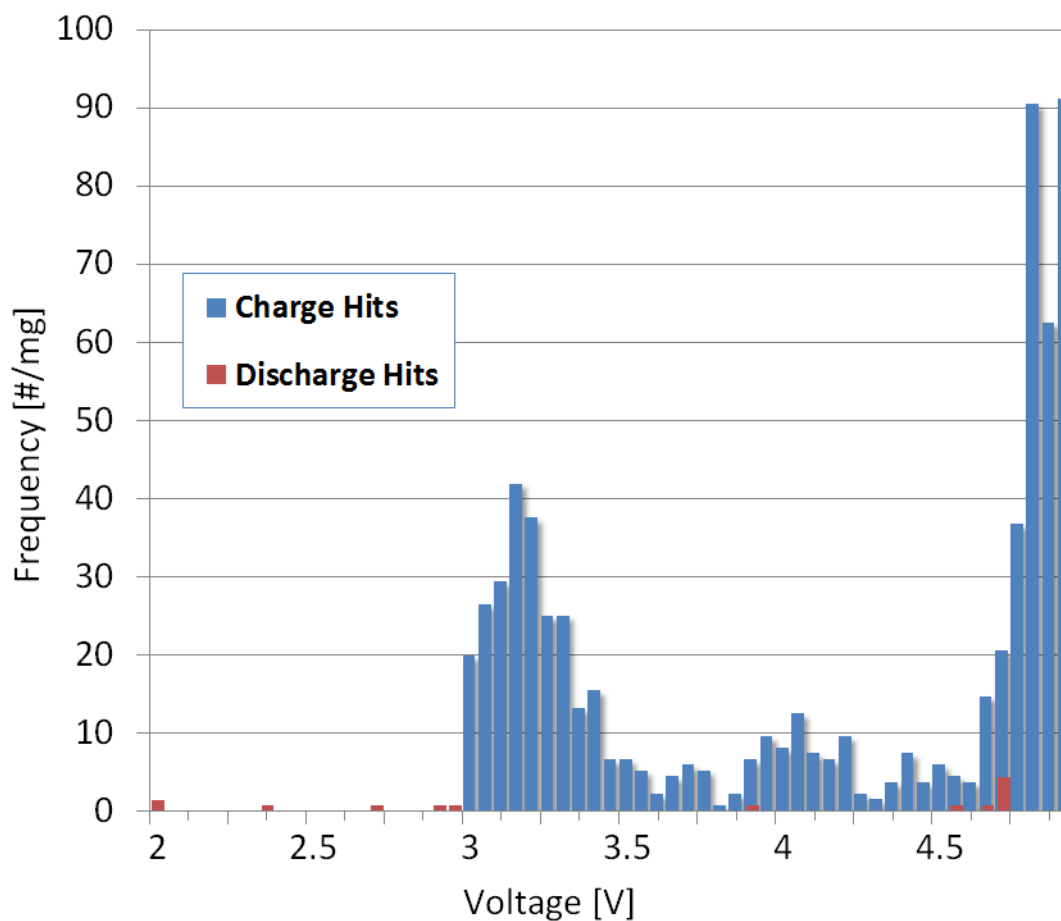


Figure 60: Histogram of AE from MNO partitioned by cell voltage and charge/discharge stage.

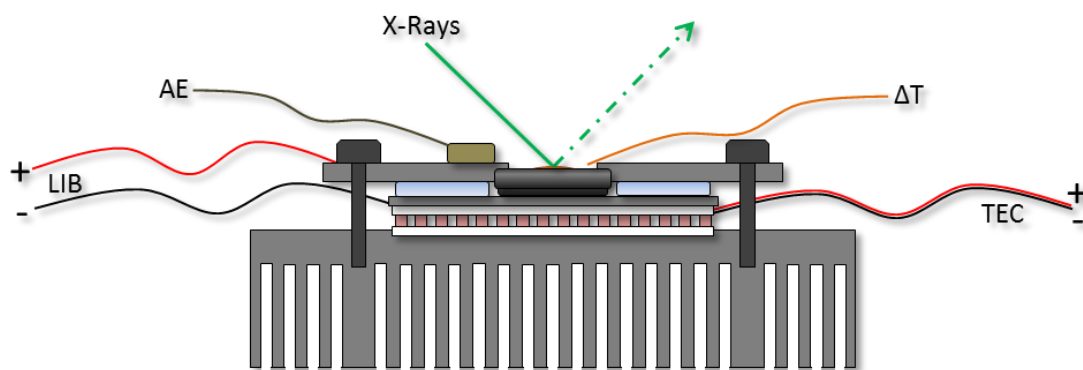


Figure 61: Diagram of proposed heating/cooling stage for advanced in situ AE-XRD studies.

Appendix B: Tables

$D_{Li}(\text{m}^2/\text{s})$	$\Omega (\text{m}^3/\text{mol})$	$E (\text{GPa})$	ν	$\sigma_w (\text{GPa})$	m	$\rho (\text{kg}/\text{m}^3)$
$5.1 \cdot 10^{-16}$	$7.69 \cdot 10^{-6}$	190	0.218	6.1	3.6	$2.33 \cdot 10^3$
[34-37]	[28]	[23, 33]	[33]	[23]	[23]	[33]

Table 1: Material properties used for modeling fracture of silicon particles

1. <i>Input cyclic curve I_k, t_k</i>
2. <i>$t = 0, D_0 = 0, c_{0l} = 0$</i>
3. <i>For each t_k:</i>
3.1 <i>Obtain $i_s^{(k)}$ for BC Eqn. 14</i>
3.2 <i>Solve FDE form of Eqn. 12 for nodal c_{kl} (Thomas algorithm is used for tridiagonal matrix).</i>
3.3 <i>$\underline{\sigma}^{(k,l)}$ - Eqn. 11</i>
3.4 <i>$\sigma_{eq}^{(k,l)}$ - Eqn. 23</i>
3.5 <i>$D_{k,l}$ - Eqn. 19</i>
3.6 <i>Search for $\max D_k$</i>
3.7 <i>$t = t_k + \Delta t$ and go to 3.1</i>

Table 2: Solution steps for determination of damage parameter

Appendix C: Matlab Code for Correlating Cycling Parameters with AE Hits

```

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Title:  Data Cross Plot and Interpolation
% Author: Kevin J. Rhodes
% Data:   March 2, 2010
% Purpose: This script takes two time driven data files and makes a data matrix
% of parameters versus one another. In this way files recorded from
% different instruments with different time scales can be plotted against
% each other. Specifically this will plot cycle data versus some acoustic
% emission parameter. As is this requires two column matrix: CycleData and
% HitData. CycleData = [CycleTime Voltage Capacity Stage] and HitData =
% [HitTime]. HitTime is the time of each hit in the AE file.
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Clear home screen.
home

% Setup loop to step through cycle data points and load in relevant parameters.
index=1;
for ii=2:length(CycleData)
    TimeLow=CycleData(ii-1,1);
    VoltageLow=CycleData(ii-1,2);
    CapacityLow=CycleData(ii-1,3);
    TimeHigh=CycleData(ii,1);
    VoltageHigh=CycleData(ii,2);
    CapacityHigh=CycleData(ii,3);
    Stage=CycleData(ii-1,4);

```

```

% Setup loop to step through each hit to see if it falls between a cycle
% data point. If it does then the cycle parameters for the hit time are
% interpolated from the cycle data.
for jj=1:length(HitData)
    if (HitData(jj)>=TimeLow) && (HitData(jj)<TimeHigh)
        HitVoltage=(HitData(jj)-TimeLow)/(TimeHigh-TimeLow)*(VoltageHigh-
VoltageLow)+ VoltageLow;
        HitCapacity=(HitData(jj)-TimeLow)/(TimeHigh-TimeLow)*(CapacityHigh-
CapacityLow)+ CapacityLow;
        HitOutput(index,1) = HitData(jj); %Hit time.
        HitOutput(index,2) = HitVoltage; %Hit voltage.
        HitOutput(index,3) = HitCapacity; %Hit capacity.
        HitOutput(index,4) = Stage; %Hit stage.
        index = index+1;
    end
end
end
end

```

Appendix D: Matlab Code for Thinning Oversampled Data Sets

```

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Data Thinning Script
% Kevin Rhodes
% July 27, 2010 - Updated January 27, 2011
%
% This script takes a data file and reduces its size based on the change in
% value for data on each line. In particular the change in voltage and current
% are used to determine if a line should be included in the output matrix
% or not. Input and output data are in the same column format. Thinned data
% may then be used in Excel and other programs without going over the data
% plotting and processing limit.
%
% InpData = [RawTime(s) Time(s) Time(h) Voltage(V) Current(mA) Capacity(mAh/g)
%      Cycle(R) Cycle(Mod) Stage(0=Charg/1=Discharge)]
%
% OutData = [RawTime(s) Time(s) Time(h) Voltage(V) Current(mA) Capacity(mAh/g)
%      Cycle(R) Cycle(Mod) Stage(0=Charg/1=Discharge)]
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Clear command window
home

% Define target steps. 300 seconds, 0.02V, and 0.05mAh are good starting values.
StepT = 300; % Time (s)
StepV = 0.02; % Voltage (V)
StepI = 0.05; % Current (mAh)

% Set first line of output same as first line of input.

```

```

OutData(1,:)=InpData(1,:);

% Setup counters for what row operations will work on.
OutLine = 2;
LastRowKept=1;

% Test for step conditions and move approved lines to output matrix.
for ii = 2:length(InpData)
    if abs(InpData(ii,2)-InpData(LastRowKept,2))>=StepT || abs(InpData(ii,4)-
InpData(LastRowKept,4))>=StepV || abs(InpData(ii,5)-
InpData(LastRowKept,5))>=StepI
        OutData(OutLine,:)=InpData(ii,:);
        LastRowKept = ii;
        OutLine = OutLine+1;
    end
end
end

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Vita

Kevin James Rhodes was born in 1982 in El Paso, TX. He earned his bachelor's degree in Biomedical Engineering with dual minors in Chemistry and Materials Science & Engineering in 2006 as well as his master's degree in Polymer Engineering in 2008, both from the University of Tennessee, Knoxville. While pursuing a PhD in Materials Science and Engineering, Kevin was an active student member of the Electrochemical Society, Materials Research Society, and American Crystallographic Association. During this time he also taught classes in chemistry and materials science at Pellissippi State Community College and the University of Tennessee. He performed his doctoral research focused on materials degradation in lithium ion batteries at Oak Ridge National Laboratory under the guidance of Dr. Claus Daniel. In 2011 he prepared a dissertation on this work and submitted it as the final criteria for graduation. Upon completion of this doctoral degree, Kevin accepted a research engineer position in the energy storage division of Ford Motor Company.

List of Publications

1. K. Rhodes, R. Meisner, M. Kirkham, N. Dudney, C. Daniel, "In Situ XRD of Thin Film Tin Electrodes for Lithium Ion Batteries", *J. Electrochem. Soc.*, (In Preparation)
2. K. Rhodes, R. Meisner, Y. Kim, N. Dudney, C. Daniel, "Evolution of Phase Transformation Behavior in $\text{Li}(\text{Mn}_{1.5}\text{Ni}_{0.5})\text{O}_4$ Cathodes Studied By In Situ XRD", *J. Electrochem. Soc.*, 158 (2011) 1-8
3. K. Rhodes, M. Kirkham, R. Meisner, C.M. Parish, N. Dudney, C. Daniel, "Novel Cell Design for Combined In Situ Acoustic Emission and X-ray Diffraction Study During Electrochemical Cycling of Batteries", *Rev. Sci. Instruments*, 82, 075107 (2011)
4. S. Kalnaus, K.J. Rhodes, C. Daniel, "A study of lithium ion intercalation induced fracture of silicon particles used as anode material in Li-ion battery", *J. Power Sources* (Accepted), DOI: 10.1016/j.powsour.2011.05.049
5. K. Rhodes, N. Dudney, E. Lara-Curzio, C. Daniel, "Understanding the Degradation of Silicon Electrodes for Lithium Ion Batteries Using Acoustic Emission", *J. Electrochem. Soc.*, 157 (2010) 12, A1354-A1360
6. K. Rhodes, N. Dudney, E. Lara-Curzio, C. Daniel, "Acoustic Emission from MCMB Electrodes in Cycling Lithium Ion Cells", *J. Electrochem. Soc.*, (In Review)
7. B.L. Fletcher, J. Fern, K. Rhodes, T.E. McKnight, J.D. Fowlkes, S.T. Retterer, D.J. Keffer, M.L. Simpson, M.J. Doktycz, "Effects of Ultramicroelectrode Dimensions on the Electropolymerization of Polypyrrole", *J. Appl. Phys.*, 105 (2009) 124312
8. J.B. Berry, R. Schwass, J. Teigen, R. Fiskum, K. Rhodes, "Advanced Absorption Chiller Converts Turbine Exhaust to Air Conditioning", *Proceedings of the International Sorption Heat Pump Conference*, Denver, CO, ISHPC-095-2005 (2005)
9. K. Rhodes, "The Orbits of Titan and Iapetus", *RVCC Nota Bene*, (2003) [<http://www.raritanval.edu/notabene>]

List of Oral Presentations

1. "In Situ XRD of $\text{Li}(\text{Mn}_{1.5}\text{Ni}_{0.5})\text{O}_4$ Cathodes for Lithium Ion Batteries During Formation and Operation Cycles", K. Rhodes, M. Kirkham, Y. Kim, N. Dudney, C. Daniel, 2011 ACA Meeting – New Orleans, LA, May 28 – June 2, 2011
2. "In Situ Acoustic Emission and XRD Characterization for the Development of Cathode Materials", K. Rhodes, M. Kirkham, R. Meisner, C. Daniel, 219th ECS – Montreal, QA, May 1-6, 2011
3. "In Situ Acoustic Emission and XRD from Cycling Lithium Ion Batteries", K. Rhodes, C. Daniel, E. Lara-Curzio, N. Dudney, 2010 MRS Fall Meeting - Boston, MA, Nov. 29 – Dec. 3, 2010
4. "Combined In Situ Acoustic Emission and XRD Analysis of Lithium Ion Battery Materials", K. Rhodes, C. Daniel, E. Lara-Curzio, N. Dudney, 218th ECS Meeting - Las Vegas, NV, Oct. 10-15, 2010
5. "Degradation Mechanisms in Batteries", C. Daniel, K. Rhodes, S. Kalnaus, National Academy of Engineering, Frontiers of Engineering Symposium, Armonk, NY, Sept. 23-25, 2010
6. "Probing mechanical degradation in energy storage applications", C. Daniel, K. Rhodes, S. Kalnaus, International Workshop on SPM for Energy Applications, Oak Ridge, TN, Sept. 15-17, 2010
7. "Acoustic Emission from Silicon Electrodes in Cycling Lithium Ion Cells", K. Rhodes, C. Daniel, E. Lara-Curzio, N. Dudney, 217th ECS Meeting - Vancouver, BC, April 22-25, 2010
8. "Application of Acoustic Emission for Characterization of Lithium Ion Batteries", K. Rhodes, C. Daniel, E. Lara-Curzio, N. Dudney, TMS '10 - Seattle, WA, Feb. 14-18, 2010
9. "Development of a Combined In-Situ AE-XRD Technique for Advanced Characterization of Lithium Ion Batteries", K. Rhodes, C. Daniel, E. Lara-Curzio, N. Dudney, UT Materials Science and Engineering Graduate Seminar - Knoxville, TN, Nov. 10, 2009
10. "Analysis of Cycling Induced Fatigue in Electrode Materials for Lithium Ion Batteries", K. Rhodes, C. Daniel, E. Lara-Curzio, N. Dudney, MS&T '09 – Pittsburgh, PA, Oct. 25-29, 2009

11. "Characterization of Acoustic Emission Events from Li Ion Half Cells", K. Rhodes, C. Daniel, E. Lara-Curzio, N. Dudney, 215th ECS – San Francisco, CA, May 25-29, 2009

List of Poster Presentations

1. "In Situ XRD Characterization of Thin Film Electrodes for Lithium Ion Batteries", K. Rhodes, M. Kirkham, R. Meisner, A. Payzant, N. Dudney, C. Daniel, 220th ECS Meeting - Boston, MA, Oct. 9-14, 2011
2. "Novel Acoustic Emission and XRD Cell In Situ Cell for Characterization of Lithium Ion Batteries" K. Rhodes, M. Kirkham, R. Meisner, A. Payzant, N. Dudney, C. Daniel, Denver X-Ray Conference – Colorado Springs, CO, Aug. 1-5, 2011
3. "Combining Acoustic Emission and XRD for In Situ Characterization of Lithium Ion Batteries", K. Rhodes, M. Kirkham, R. Meisner, A. Payzant, C. Daniel, SPM for Energy Application Workshop - Oak Ridge, TN, Sept. 15-17, 2010
4. "In-situ Acoustic Emission Spectroscopy Combined with Stress Analysis", K. Rhodes, S. Kalnaus, C. Daniel, N. Dudney, E. Lara-Curzio, Beyond Lithium Ion: Computational Perspectives, Chicago, IL, May 31-June 1, 2010
5. "Degradation and Fatigue of Active Electrode Materials for Lithium Ion Batteries", K. Rhodes, C. Daniel, E. Lara-Curzio, N. Dudney, TMS '10 - Seattle, WA, Feb. 14-18, 2010
6. "Monitoring Electrode Degradation in Lithium Ion Batteries by Acoustic Emission", K. Rhodes, C. Daniel, N. Dudney, E. Lara-Curzio, ASM Materials for Megawatts Symposium – Oak Ridge, TN, Apr. 22, 2009
7. "Advanced Applications of Polypyrrole in the Development of Fluid Pumps and Gates for MEMS Devices", K. Rhodes, B.L. Fletcher, T.E. McKnight, S.T. Retterer, M.J. Doktycz, M.L. Simpson, ASM/SPE Student Poster Session – Knoxville, TN, Nov. 16, 2006

Honors and Awards

1. American Crystallographic Association Margaret C. Etter Student Lecture Award
2011 – Powder Diffraction Scientific Interest Group
2. 2010 Los Alamo National Laboratory Neutron School in Structural Materials
Alumni
3. American Society of Materials “Materials for Megawatts Symposium” – 2nd
Place Poster