# Transmission microscope analysis of battery materials at the nanoscale

Frédéric Voisard,

Mining and Materials Engineering

McGill University, Montreal

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# Abstract

Quebec's electrical power production is mostly composed of Hydro-electric dams. This renewable resource is used the people and industries of the province for lighting, heating and cooling. However, transportation of people and goods still relies on fossil fuels as energy source. In order to achieve one, the provincial's government's goal of electrification of transports, better electrical power storage solutions must be made available. The current generation of lithium batteries is allowing care to autonomously travel similar distance as would their gasoline-powered counterparts. The charging time of such vehicles, however, is still much longer then the time required to fill a gas tank. Furthermore, many batteries technologies release hydrogen under high load, and can fall into thermal runaways. Such thermal runaways, or when batteries become to hot, leak charge internally and heat further, can lead to catastrophic explosions. Therefore, batteries able to carry more charge, with safer chemistries are required. Two candidate materials are of particular interest to be used in the next generation of batteries. Lithium-metal orthosilicates,  $Li_2MSiO_4$ , where the metal, M, is iron, manganese, or a mixture of both materials, could be used in the current battery geometry, coupled to a carbon anode. These orthosilicates have twice the lithium carrying capabilities of materials such a lithium-cobalt oxide or lithium iron phosphates. Furthermore, the de-litihiation chemistry of orthosilicates does not release hydrogen, therefore eliminating the risk of explosion. The second material of interest is lithium metal, for use in the lithium-air battery. This system has one of the highest theoretical power density of any battery system.

In order to implement these chemical systems in real batteries, their micro- and nanoscale properties need to be well understood. The transmission electron microscope (TEM), is one of the only tools that can study the morphology and chemistry of materials at scales ranging from sub-nanometers to microns. TEMs rely on a high energy electron beam to probe samples. Both Li<sub>2</sub>FeSiO<sub>4</sub> and metallic lithium are sensitive to such high energy beam, and are readily damaged. This work is centered around minimising the beam-induced specimen damage when possible, or minimising the effect on damage on experimental results when some damage in unavoidable. Golden ratio acquisition is a tomographic acquisition scheme which reduces the effect changes in a sample, such as carbon contamination or beam damage. SR-EELS is used as a low-dose method of gathering localised chemical information.

# Résumé

La production d'énergie électrique du Québec provient principalement d'hydro-électricité. Cette ressource renouvelable est utilisée dans la province pour subvenir aux besoins de la population et de l'industrie en matière d'éclairage, de chauffage et de climatisation. Par contre, le transport des gens et des marchandises se fait toujours à l'aide d'énergies fossiles. Il est alors nécessaire, de manière à atteindre les cibles gouvernementales en matière d'électrification des transports, que de meilleures solutions de stockage d'énergie électrique deviennent disponibles. La génération actuelle de batteries au lithium permet aux voitures électriques de parcourir, de façon autonome, des distances similaires à celles atteintes par des voitures carburant à la gazoline, sur un plein d'essence. Le temps de charge des batteries de ces voitures, quant à lui, est bien plus long que le temps que requis pour faire un plein d'essence. De plus, plusieurs types de batteries actuelles, lorsque soumises à de trop importantes charges, peuvent relâcher de l'hydrogène et initier un emballement thermique. Ces emballements thermiques sont caractérisés par des réactions internes irréversibles et inarrêtables prenant place dans les batteries. Dans des cas extrêmes, des explosions peuvent survenir. Il est donc important que des batteries ayant de plus hautes capacités, basées sur des réactions chimiques sécuritaires, soient développées. Deux systèmes chimiques sont d'un attrait particulier. L'orthosilicate de métal lithié Li<sub>2</sub>MSiO<sub>4</sub>, où le métal, M, est du fer ou du manganèse, ou encore un mélange des deux, couplé à une anode en graphite. De par la formule chimique des orthosilicates lithiés, ces matériaux ont une capacité de charge théorique faisant le double de celles de matériaux actuellement en service, tel que l'oxyde de cobalt et le phosphate de fer. De plus, la décomposition des orthosilicates ne rejette pas d'hydrogène, éliminant ainsi les risques d'explosions. Le deuxième système d'intérêt est la batterie lithium-air, où du lithium métallique est oxydé par l'atmosphère. Ce dernier système a la plus haute densité énergétique théorique de tous les systèmes connus à base de lithium.

Avant que de mettre ces systèmes chimiques en service dans des batteries, leurs propriétés physiques doivent être caractérisées, à des échelles micro- et nanoscopiques. Le microscope à électron en transmission (MET) est un des seuls outils de caractérisation qui peut étudier la morphologie et la chimie de matériaux à des échelles sub-nanométriques. Les MET fonctionnent grâce à un faisceau d'électrons à haute énergie qui bombardent un échantillon. L'orthosilicate de métal lithié et le lithium métallique sont deux matériaux sensibles au faisceau d'électrons et s'endommagent facilement lors d'observations dans un MET. Ce travail est centré autour du but de minimiser l'endommagement des matériaux lors d'observation MET. L'acquisition tomographique suivant le ratio d'or est un stratagème d'acquisition qui réduit les artéfacts de reconstruction dûs à des modifications de l'échantillon au cours de l'acquisition de données. Le SR-EELS, quant à lui, est une méthode d'acquisition d'information chimique qui a la capacité de réduire la dose d'électrons à laquelle un échantillon est soumis. Ces deux méthodes permettent l'analyse MET de matériaux fragiles, qui, autrement, ne pourrait pas être étudier avec le même niveau de profondeur.

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# Chapter 1:

# Current State of the techniques for the Observation of Lithium in Lithium-Bearing Materials Using Transmission Electron Microscopy

# 1 Lithium in Lithium-Bearing Battery Materials

Lithium-ion batteries are currently the most used type of rechargeable batteries, and that in all sorts of sectors, from electronics (phones, laptops, tablets, etc.) to transport (airplane controls, electric vehicles). The most commonly used lithium-ion battery chemistry for small electronics is lithium-cobalt oxide. This type of cathode is known for its thermal runaway tendency and also for its tendency to release oxygen when failing. The Boeing 787 Dreamliner grounding is an example of the consequences of such battery failure. Examples of exploding batteries in portable electronics are also common on websites such as youtube.com. The danger inherent to such explosions mandates research into safer chemistry alternatives. Lithiated iron silicates, Li<sub>2</sub>FeSiO<sub>4</sub>, and lithiated manganese silicates, Li<sub>2</sub>MnSiO<sub>4</sub>, have been proposed by chemists as safer alternatives for battery cathodes. Furthermore, these silicatebased cathodes have theoretical storage capacity and charge rate which exceed that of currently used chemical compounds. Lithium-air batteries are also attracting attention, as they have the greatest theoretical energy density(Zaghib et al., 2013). In order to assess the efficiency of these materials, several of their attributes must be understood. Amongst these attributes, their nanomorphology and the variations in composition at the nanoscale are of special interest. In order to investigate these physical and chemical nanoscale attributes, the use of a transmission electron microscope (TEM) is required, in conjunction with an electron energy loss spectrometer (EELS).

### 1.1 The TEM and its optical components

### 1.1.1 Limits of visible light microscopy

Visible light microscopes (VLMs) are composed of an illumination system, a condenser lens, a specimen stage, magnifying optics and finally an imaging system (an eye or a camera or both). Due to

the wave-particle nature of light, the ability of visible light microscope to resolve small features is dependent on the wavelength of the light used. The visible part of the electromagnetic spectrum consists of light of wavelength from 390 to 700 nm(Freeman et al., 2003). The Rayleigh criterion is commonly used to describe the theoretical resolution limit for two point sources and a circular aperture due to diffraction

$$\theta = 1.22 \frac{\lambda}{D} \tag{1}$$

where  $\theta$  is the angular resolution, D is the diameter of a lens aperture and  $\lambda$  is the wavelength of light. In the case of microscopy, this relationship can be converted to

$$R = \frac{1.22\lambda}{NA_{Condenser} + NA_{Objective}} \text{ with } NA = \eta \sin\theta$$
(2)

where R is the resolution in units of distance and  $\eta$  is the refraction index of the medium between the lens and sample. The numerical aperture values of the condenser and objective apertures, NA, can be approximated to 0.95 for lenses in air. In the case immersion, the numerical aperture can be as high as 1.52. In the best of cases, using the shortest wavelength of visible light, 400nm, corresponding to violet, the best resolution achievable is of 203nm. Super-resolution visible light microscopy can break the diffraction limit. However, these techniques require labeling of biological structures with phosphors or fluorophores and, as such, are not applicable to the study of battery cathodes at the nanoscale.

In order to use the electromagnetic spectrum to probe nanometer-sized features of materials, one would need photons of sub-nanometer wavelengths. Photons of such wavelengths are known as X-rays. Although commonly used for imaging of internal structures in radiography, the fact is that X-rays have the capacity to penetrate matter, as they have very low interaction with electrical and magnetic fields. This lack of interaction makes the control and focus of X-rays challenging(Als-Nielsen and McMorrow, 2011). This difficulty in controlling X-rays (albeit, in non-synchrotron facilities) makes X-rays unsuitable for nanoscale microscopy. Systems such as the Zeiss X-ray microscopes have feature resolution limits of the order of 0.7 μm.

### 1.1.2 The Electron as Probe

Since photons are not suited for nanoscale imaging, the next most available sub-atomic particle is the electron. Owing to their small but non-negligible mass, electrons have significantly shorter wavelength then X-Rays for similar energies(Williams, 2008). Louis de Broglie found that a particle wavelength,  $\lambda$ , is equal to the inverse of the particle momentum, p, multiplied by Plank constant, h.

$$\lambda = \frac{h}{p} \tag{3}$$

The free electron momentum is equal to the electron mass,  $m_0$ , times its velocity, v. The electron kinetic energy, eV, is proportional to the square of the electron velocity and the mass of the electron.

$$eV = \frac{m_0 v^2}{2} \tag{4}$$

Therefore, the wavelength of an electron is related to its energy by

$$\lambda = \frac{h}{(2m_0 eV)^{1/2}}\tag{5}$$

At high energy, such as used in TEM operation, relativistic effects must be taken into consideration. The above equation must therefore be corrected to

$$\lambda = \frac{h}{\left[2m_0 eV\left(1 + \frac{eV}{2m_0 c^2}\right)\right]^{1/2}}$$
(6)

Table 1 shows how the accelerating voltage applied to an electron influences the wavelength, relativistic wavelength, mass and velocity of the electron(Williams, 2008).

Table 1: Relativistic and non-relativistic wavelengths of electron where the electron mass is described in term of  $m_0$ , the rest mass of the electron(Williams, 2008).

| Accelerating voltage (kV) | Non-relativistic<br>wavelength (nm) | Relativistic<br>wavelength (nm) | Mass $(\times m_0)$ | Velocity<br>(× 10 <sup>8</sup> m/s) |
|---------------------------|-------------------------------------|---------------------------------|---------------------|-------------------------------------|
| 100                       | 0.00386                             | 0.00370                         | 1.196               | 1.644                               |
| 120                       | 0.00352                             | 0.00335                         | 1.235               | 1.759                               |
| 200                       | 0.00273                             | 0.00251                         | 1.391               | 2.086                               |
| 300                       | 0.00223                             | 0.00197                         | 1.587               | 2.330                               |
| 400                       | 0.00193                             | 0.00164                         | 1.783               | 2.484                               |
| 1000                      | 0.00122                             | 0.00087                         | 2.957               | 2.823                               |

Furthermore, electrons are susceptible to both electrical and magnetic fields. Ernst Ruska was amongst the first to discover how to use magnetic lens to magnify and focus an electron beam, in 1931(Ruska, 1987).

### 1.1.3 Elements of a transmission electron microscope

The optics of a transmission electron microscope (TEM) have originally been inspired by visible microscopes. Thus several components have names and functions that are similar in electron and visible light microscopy (VLM)(Williams, 2008).

#### 1.1.3.1 The Gun

The illumination source of an electron microscope is the electron source. The first source design was the thermionic tungsten filament, followed by hexaboride (LaB<sub>6</sub>) cathodes. These two types of thermionic sources operate essentially in the same fashion. Thermionic emission guns produce electron beam with a significant achromaticity. That is, although the mean energy of the electrons in the beam will be at the desired level, individual electrons energy will follow a normal distribution, with a standard deviation of up to a few eV.

In order to minimise chromatic aberrations and optimize EELS analysis, field-emission guns where developed. Two flavors of these guns exist: the Schottky and the cold field emission (cold-FEG). The main difference between a Schottky and a cold-FEG is that the cathode tip of a Schottky gun is flat and heat is used in conjunction with strong electrical field to overcome the work function required to extract electrons. In cold-FEGs cathodes, tips are made to be extremely sharp. An electric field is used to induce tunneling of electrons from the extremely sharp tip, without external heat input. The liberated electrons are then accelerated by a series of charged annular plates. Because cold-FEG tips are not heated, the electron beam from such tips has a smaller energy distribution than the beam from a Schottky source. The energy distribution of the electron beam is referred to as chromaticity. An incoherent source produces an chromatic beam, which is prone to chromatic aberrations (loss of image resolution), and also broadens the zero-loss peak (loss of energy resolution in EELS).

### 1.2 The Lenses

One familiar with visible light optics knows that lenses can fall in two general categories: convergent and divergent lenses. Furthermore, the successive placement of lenses of different strengths, or diopter, yields an effective lens strength which follows equation (7).

$$\frac{1}{f} = \frac{1}{f_1} + \frac{1}{f_2} + \dots + \frac{1}{f_n}$$
(7)

7

where f is the focal length of the assembly and  $f_1$  to  $f_n$  are the focal lengths of the component lenses. A convergent lens will project an image on an image plane of an object on an object plane according to the thin lens formula equation (8).

$$\frac{1}{d_o} + \frac{1}{d_i} = \frac{1}{f} \tag{8}$$

where  $d_0$  and  $d_i$  are the respective distance between the lens and the objective and image planes, while f is the focal length of the lens, as can be seen in Figure 1.

The lenses used to interact with electron beams are actually magnetic fields generated by a complex winding inside a metal casing, which shapes the magnetic field to the desired specifications. This casing is called the pole-piece. The casing further shapes the magnetic field. Magnetic lenses used in TEMs are always convergent. In order to magnify an object with convergent lenses, the image plane needs to be located past a crossover, the back focal plane.



Figure 1: Ray diagram of a convergent lens, identifying the object plane, the image plane and the back-focal plane. The relationship between these planes is described in equation (8)

#### 1.2.1.1 The Condenser Lenses

The condenser system of modern TEMs is composed of multiple lenses. The purpose of the lenses is to demagnify the beam and to form either a parallel probe, as used in conventional TEM, or a convergent probe, as used in scanning transmission electron microscopy (STEM) and in convergent beam diffraction. Most S/TEM systems rely on 3 condenser lens to handle the large variation in convergence angle between parallel and convergent beams. The third lens can have a proprietary name and some manufacturers set this lens apart from the other two condenser lens.

### 1.2.1.2 The Objective Lens

The objective lens, which, in a TEM, is always a lens pair, is the central lens of the microscope, as this lens controls the defocus of the beam. It is also at the level of the objective lens that spherical and chromatic aberrations are the most detrimental to the resolution of thin samples. Furthermore, any stigmatism in the objective lens is directly observable on the projected image. Several factors influence how well an objective lens will resolve small features, but the distance between the two pole-pieces is the most sensitive factor.

Since a smaller pole-piece gap helps achieve higher resolution, the smallest gap is desired. However, since the sample, the sample holder and, often, the objective aperture must fit within this gap, some free play is necessary. In addition, in systems designed for high sample tilt, the pole-piece gap must be further increased. Many systems have different pole-piece choices as options at the moment of purchase. However, once commissioned, changing a pole-piece is not usually practical, if at all possible. A machine that will be used for tomography will require a large gap. A machine that will be used for high resolution imaging will require having a small pole-piece gap. Therefore, it is critical that the intended applications of a microscope have been properly assessed prior to the selection of a microscope lens.

### 1.2.1.3 The Intermediate and Projector Lenses

Two sets of lens are located below the sample, the intermediate and the projector lenses. These lenses are often referred to as the "lower column" or the "imaging lenses". These names refer to the position of the lenses or their function, respectively. The intermediate lens is responsible for setting up the nature of the image, that is, whether an image or a diffraction pattern (DP) that will be sent to the projector lens. By changing the strength of the intermediate lens, one can set either the objective image plane or the back focal plane to be coincidental with the intermediate object plane. When the image plane of the objective lens is the object plane of the intermediate lens, an image is sent to the viewing screen. Alternatively, when the objective back focal plane is the object plane of the intermediate lens, a diffraction pattern is sent to the viewing screen. In all modern TEMs, this process is effortless for the user and simply requires the pressing of the dedicated diffraction button.

The projector lens is the final lens of a conventional S/TEM. This lens is responsible for the magnification of the image formed at the intermediate lens in imaging mode and for the "camera length" value in diffraction mode. In TEM, both magnification and camera length values are related to the physical size of the image/DP on the viewing screen. These values must be properly calibrated by the manufacturer service team. In STEM machines, the projector lens is used to adjust the collection angle of lower detectors, while magnification is due to the scanning pattern used.

When recording images, the use of a scale bar is the accepted method of conveying the scale. To illustrate that such graphic information is pertinent, one can think of an image projected on a presentation screen. If the image is acquired at some level of magnification, the projected image will be further magnified by several orders of magnitude. The scale bar, however, scales with the image and is therefore always correct.

### 1.2.2 The Camera

The first TEMs used film cameras to acquire images. However, TEM image capture technology has followed the development of the semi-conductor industry. Most systems are based on a coupled scintillator/CCD arrangement. From there, manufacturers have developed increasingly sensitive CCDs and faster read-out electronics. CCD cameras have two factors limiting their frame rate. The first is the decay rate of light emission from the camera scintillator. This decay can leave a temporary ghost image on subsequent images. Ghost spot can also appear when a condensed beam is projected on the scintillator, which can easily happen when changing magnification. The second limitation is the read-out rate of the camera; a faster read-out typically increases noise in the image.

In order to overcome the problem of scintillator-based detection, direct-detection electron cameras have been recently introduced on the market. These systems forgo the electron-photon conversion and instead use direct-detection devices (DDD). DDDs are ideal for low-dose and in-situ work because of the high sensitivity and low noise of the detector. DDD cameras are a new development and are available at a substantial premium. This prohibitively high price is the main drawback of these new cameras.

### 1.2.3 Spectrometers

Although the images acquired with electron microscopes are usually presented in grayscales, not all the electrons that reach the imaging device have the same energy. Electrons leave the gun with a very small energy spread. However, once the electron reaches the sample, the electrons from the beam will interact with the sample in several different ways, which are described below in section 3. These interactions will remove energy from the beam electrons. This change in energy is measurable by using an electron energy loss spectrometer.

Some of the more prominent features of the EELS spectrum are the ionization edges. The energy removed from the electron beam is transferred to the sample, which re-emits the energy in several fashions. One path to de-excitation is the emission of electro-magnetic radiation, or photons of characteristic energy. These photons can be in the energy of a few eV's (hard ultraviolet (UV)) to several thousands of eV's (X-Rays). High energy electro-magnetic spectra are collected using X-ray energy dispersive spectroscopy (EDS).

For light elements, roughly one ionization event in 10000 will generate a characteristic X-ray. This low signal yield is offset by the fact that a beam current of a few nanoamperes represents several million electrons hitting the sample every second. Furthermore, X-ray collection efficiency can be improved by using large detectors close to the sample, or even using multiple detectors. The system detector angular coverage is given in steradians (sr). A full coverage would equate to  $4\pi$ , or approximately 12.56. In practice, an angular coverage of under one steradian is commonly found on TEMs.

### 1.2.4 Scan Coils and STEM Imaging Detectors

In conventional transmission electron microscopy, a parallel electron beam is used to generate an image of the whole field of view (FOV) at once. However, because the whole sample is illuminated, the chemical information gathered by EDS and EELS is the convolution of the parts of the illuminated region of the sample. In order to obtain local information, a convergent probe must be used. This probe is then scanned across the region of interest in a raster pattern. This scan is performed with a set of dedicated scan coils. Since thin samples and a high energy electron probe are used, most of the electron can pass through the samples. The term scanning transmission electron microscopy (STEM) is used to describe this kind of machine. Three types of imaging detectors are commonly seen on STEM microscopes. These are the bright field, dark field and secondary electron detectors. The bright and dark field detectors are located below the sample while the secondary electron detector is located just above the sample.

As the name implies, secondary electrons (SE) do not originate from the gun, but are rather generated within the sample. Secondary electrons have low energy, of at most 50 eV, but tend to have lower energies, in the three to five eV range. Because of their low energy, only the electrons generated near the surface of the sample will escape, and the information given by SE is mostly topographical. However, since detectable secondary electrons are generated by electrons from the beam penetrating the sample and by back scattered electrons (BSE) leaving the sample, contrast mechanisms, usually associated with BSE images in an SEM, can also yield contrast in SE images. SE images have good imaging capabilities for all atomic elements. For example, it is possible to image gold particles and a carbon support structure with both components in the dynamic range of the picture.

The electrons that reach the bright field (BF) detector are the electrons from the beam that are not, or only slightly, scattered. The resulting image has a white background where the beam is not scattered. A second detector may surround the BF detector. This is the annular dark field detector or ADF. The contrast given by the ADF is mostly due to diffraction and channeling of the electron beam as it passes through the sample. In cases where the internal collection angle of an annular detector is greater than 50 mRad, this detector is said to be a high angle annular detector (HAADF). In the HAADF range, atomic scattering events are the dominating scattering mechanism. Since atomic scattering is dependent on the Z-number of atoms, the contrast from HAADF detectors is mostly due to composition and thickness(Liu and Cowley, 1991; Williams, 2008). High resolution image of crystalline compounds taken by HAADF STEM along preferred crystallographic axes can yield images with atomic columns differentiable by composition(Abe et al., 2002; Yamazaki et al., 2002).



Figure 2: High Resolution TEM (HRTEM) (A) and High Angle Annular Dark Field (HAADF) (B and C) images as well as simulations (D and E) of a layered structure within a Mg-1 at% Zn-2 at% Y alloy. The HAAFD image, (b), contrary to the HRTEM image, (a), shows a significant variation in signal related to the local atomic number of the sample. This behavior matched simulated images (d and e) (Abe et al., 2002).

# 2 Contamination in the TEM

# 2.1 Hydro-Carbon Contamination

Beam-induced carbon contamination in electron microscopes consists of the deposition of a layer of carbon on the surface of a sample illuminated by the electron beam. The proposed explanation for this deposition mechanism is that adsorbed hydrocarbons present on the surfaces of samples inserted in the vacuum of the TEM evaporate in the said vacuum. These volatile hydrocarbons may then be trapped in the electron beam, cracked into free radicals and propelled onto the specimen surface, where the carbon forms a highly stable amorphous layer(Reimer and Wächter, 1978). This layer can be quite detrimental to the quality of the acquired data, especially for thin samples and for chemical mapping(Cheng et al., 2006). Carbon contamination is best avoided by frequent plasma cleaning of the holders and, if possible, of the sample. Ozone cleaning is also a good option to remove potentially volatile hydrocarbon residues from a sample.



Figure 3: Typical hydrocarbon contamination ring on a substrate after exposure in the TEM. Notice how the contamination is most important on the edges of where the beam was condensed (Reimer and Wächter, 1978).

If contamination cannot be avoided at the source, observation conditions can be optimized to avoid the evaporation or the deposition of carbon. By maintaining a specimen temperature at -100°C or colder, hydrocarbons cannot evaporate and therefore cannot contribute to contamination(Williams, 2008). Cryo electron microscopy, however, does lead to the possibility of ice buildup on the sample. On the other extreme, by using a hot stage, heated to several hundreds of degrees Celsius, carbon cannot redeposit, also alleviating the contamination problem. Woking at high temperature can also prove to be detrimental, since some materials may react adversely to the heat(Williams, 2008). Due to all these factors, finding the optimal operating condition can prove to be difficult.

### 2.2 Ice Buildup

Since cooling a sample can reduce the reaction kinetics and radiolysis damages, it may seem more sensible to work at low temperatures (Cryo-TEM). In such cases, the quality of the vacuum in the specimen chamber becomes of central importance. Even more so, the partial pressure of water is critical, since if given the chance, ice will form and build up on a cryo-sample. Much like carbon contamination, ice buildup is detrimental to chemical mapping and elemental analysis, especially if the sample in question is expected to contain oxygen or hydrogen.

# 3 Electron Energy Loss Spectroscopy

As electrons interact with a sample by inelastic collisions, they deposit energy in the sample and this energy is described as lost energy of the electron. Several mechanisms lead to electron energy loss, namely: phonon excitation, plasmon excitation, secondary electron emission, auger electron emission, X-ray ionization and bremsstrahlung radiation. Since plural scattering events make the interpretation of the EELS signal difficult, sample thickness control is imperative in order to obtain a comprehensible signal and is explained below.

### 3.1 Thickness Criterion: $t/\lambda$

In order to assess the proper sample thickness for EELS analysis, one must calculate the inelastic mean free path ( $\lambda$ ) of the said material. This can be done by using analytical models, such as the one proposed by Malis et al(Malis et al., 1988).

$$\lambda \approx 106 \frac{106 F E_o}{E_0 \ln(2\beta E_0/E_m)} \tag{9}$$

where  $\lambda$  is given in nm,  $E_0$  is the incident beam energy in eV,  $E_m$  is a mean energy loss value in eV, F is a relativistic factor and  $\beta$  is the collection angle of the spectrometer.

$$F = \frac{1 + (E_0/1022)}{\left(1 + (E_0/511)\right)^2} \tag{10}$$

and E<sub>m</sub> gives the material dependence on Z by

$$E_m = E_1 Z^m \tag{11}$$

where  $E_1$  and m are constants of value  $E_1$ =7.6 and m=0.36. For compounds, the model can be used with an effective atomic number  $Z_{eff}$  of the form

$$Z_{eff} \approx \frac{\sum_{i} f_{i} \sigma_{i} Z_{i}}{\sum_{i} f_{i} \sigma_{i}} \approx \frac{\sum_{i} f_{i} Z_{i}^{l+r}}{\sum_{i} f_{i} Z_{i}^{r}}$$
(12)

This method gives a mean free path value which falls within a 20% variation of experimental data (Malis et al., 1988). It is also possible to access experimentally-acquired mean free path data from material databases, such as the "NIST Electron Inelastic-Mean-Free-Path Database" (US Department of Commerce, n.d.). Once the mean-free path is assessed, the optimal thickness for EELS analysis is usually considered to be 60-110% of the mean free path (Attarian Shandiz et al., 2015; Egerton, 2011). Having a sample thicker than the mean free path will lead to plural scattering, which, in turn, leads to a convolution of the EELS signal and an increase in the background of the spectrum. This relationship is given as the unitless relationship  $t/\lambda$ . Figure 4 shows how the signal to noise ratio of an edge is dependent on the  $t/\lambda$  of a material (Attarian Shandiz et al., 2015).



Figure 4: Simulation of the signal to noise ratio of electron energy loss of the L<sub>3</sub> orbital shell of various compounds and incident beam energies. Notice that the signal to noise ratio is highly dependent on the  $t/\lambda$  value of the sample(Attarian Shandiz et al., 2015).

It is also possible to measure t/ $\lambda$  directly in energy filtered TEM (EFTEM) in the form of t/ $\lambda$  maps. This direct method is especially useful on electro-jet polished samples since these samples typically have a wedged-shaped cross-section. Because of this wedge shape, the optimal observation region can easily be identified. A t/ $\lambda$  map consists of taking a zero-loss EFTEM image (10 eV window centered at zero eV) followed by an unfiltered image. The logarithm of the quotient of the intensity of unfiltered (I<sub>T</sub>) image with respect to the zero-loss (I<sub>ZL</sub>) peak will yield a thickness (t) map normalized to the inelastic mean free path of the sample,  $\lambda$  (Brydson, 2001), as seen in equation (13).

$$t_{\lambda} = \ln \left( \frac{I_{T}}{I_{ZL}} \right) \tag{13}$$

 $t/\lambda$  maps are a powerful tool for EELS analysis, as they can help in the selection of the most appropriate region of a sample to be analyzed. In order to obtain a high count rate, sufficiently thick samples are required, but electrons traveling through thicker samples have higher chances of undergoing multiple inelastic scattering events (Egerton, 2011; Malis et al., 1988).

### 3.2 Energy Filtered TEM (EFTEM)

Energy filtered transmission electron microscopy relies on the use of a magnetic prism. This prism, as seen in Figure 5, is used to intentionally induce a controlled severe chromatic aberration to the transmitted electron beam. The chromatic aberration is severe enough that the exact location of the cross-over point will now be different for each electron energy. By knowing the position of these crossovers, a slit is used to select a range of electron energy. The selected electrons are then re-focused on an imaging device. The resulting image is called an energy-filtered image. The highest energy window resolution of an EFTEM image is typically of 4 eV, in the low-loss regime, however, windows of 10 eV and above are commonly used in order to increase the acquisition signal. Since the EELS spectrum intensity decays exponentially with energy, the signal of EFTEM images also decreases exponentially. Because of this decrease in intensity the energy resolution is often decreased by using a larger slit and the binning of the image is increased, in order to acquire images in a reasonable time and minimize the possibility of sample drift.



Figure 5: Diagram of a 90° filter, where the energy slit is located at Q. The sample, not drawn, is located well above the entrance slit. The diagram shows a side-view (above) as well as a section view (below left) which follows the optical axis as it is bent in the detector. The two views show how the magnetic field induces a y-shift to electrons of different energy. No shift is observed along the z axis (Reimer, 1995).

EFTEM imaging, as described in the above section, is one of the simplest methods to acquire a  $t/\lambda$  map. Similarly, one can use energy filtered images to compute elemental maps. For elemental analysis, two methods can be used: the jump ratio method and the three-window method, the latter being the most robust. This method consists of taking three consecutive EFTEM images of the same area of a specimen. Two of these are taken just before the elemental edge of interest, and the third just after, as can be visualised in Figure 6.



Figure 6: Energy loss spectrum, showing how three EFTEM images can be used to gather chemical maps. The two pre-edge images, referred to as pre-edge energy windows W1 and W2, are used to calculate the expected exponential decay background profile. The post-edge intensity can then be compared to the expected background value. This operation is performed for every corresponding pixel of the three images to generate a map of the intensity of the edge (Reimer, 1995).

The two pre-edge frames are used to generate a background model for each pixel. This background is extrapolated to the predicted energy of the post-edge window. A positive difference between the post-edge window and the background is indicative of the presence of the element of interest. In the case of Figure 6, the three-window method, as applied, would produce a map of oxygen in the specimen.

As mentioned earlier, a second method also exists, the jump ratio. This method consists of only one pre- and one post-edge images and is less robust then the three-window method. However, in circumstances where the background cannot be properly assessed by the three-edge method, such as when the edge of interest is in the low-loss region or if a neighboring edge falls within the pre-edge windows, the jump-ratio method can provide a good qualitative map.

### 3.3 Electron Energy Loss Spectroscopy (EELS)

The electron energy loss signal is the result of inelastic scattering of the electron beam in the sample. The probability of scattering can be represented by a scattering cross-section. Event cross-

sections are given in units of area and are proportional to the scattering cross section of a particle compared to that of a solid object. Therefore, a larger scattering cross-section represents a larger chance of a scattering event occurring. Scattering cross-sections due to different types of interactions can be summed. Figure 7 shows the plasmon excitation cross-section and the total inelastic crosssection of various pure elements. Plasmon excitation is shown to be the most important mode of energy loss for some elements. However, since plasmon excitation takes place in the valance and conduction band of materials, the bonding state of elements can severely influence the plasmon scattering cross-sections.



Figure 7: Total-inelastic cross section ( $\sigma_i$ ) and plasmon cross section( $\sigma_p$ ) for 200-keV electrons (Egerton, 2011)

However, since the units of cross sections are not quite relatable, the mean free path,  $\lambda$  (not to be confused with the wavelength), is often used to decide on the likelihood of a scattering even occurring within a given sample.

$$\lambda = \frac{1}{\sigma_{total}} \tag{14}$$

The mean free path is the inverse of the scattering cross-section, and represents the average travel distance within a material before an energy loss event occurs.

### 3.3.1 Bulk Plasmon Excitation

Although plasmon resonance can be observed in most solids, the most intuitive description of the phenomenon comes from the "electron sea" of metals. In the simplest approximation, plasmon resonance is explained by a standing wave of charge density within this sea (Callister and Rethwisch, 2011; Egerton, 2011). Bulk plasmon waves are standing waves bound by the electric field of a sample. As such, the energy that plasmon excitation removes from the TEM beam is a harmonic of the plasmon wave energy. This harmonic can readily be seen in thick samples, as a successive series of peaks in the low loss regime.

### 3.3.2 Ionisation Edges

One of the better known characterisation techniques available in the TEM is X-ray energy dispersive spectroscopy, or EDS. EDS relies on the ionization and relaxation of electrons for the emission of X-rays. The emission of X-rays is a statistical process. Only a small fraction of ionization events leads to the generation of X-rays. However, each ionization event requires an energy source. In the TEM, the ionisation energy source is the electron beam. Therefore, each ionization event is recorded in the electron energy loss spectrum. The intensity and position of an ionization edge can be extracted from the generalized oscillator strength (GOS)(Egerton, 2011).

### 3.3.3 Near Edge Structures

Due to the high energy resolution of EELS spectrometers, the fine structures of the shape of ionization edges is detectable. The shape of EELS edges has two main components to its structure. The first is the actual EELS edge, where the ionization of electrons is caused by the incident beam. The second is the background, composed of electrons which did not lose energy and electrons who lost energy by non-characteristic processes, such a bremsstrahlung. However, the incident beam is never exactly monochromatic. This can be seen in the "zero-loss peak", which is generally a very narrow Gaussian distribution. Furthermore, plasmon excitation can also affect the zero-loss peak, especially in samples with  $t/\lambda$  of 1 and more. The resulting low-loss feature can be seen as a convolution kernel, applied to the entire spectrum.

### 3.4 EELS Analysis

An ionisation edge on the EELS spectrum is an indication of the presence of the associated element within the sample. STEM-EELS, or using a scanning probe to collect a series of spectra, is a good method to perform localised analysis. A qualitative map can be generated by exacting the strength of an edge at each position. In cases where samples consist of well-defined regions, a qualitative map may provide enough information to the user. If quantitative chemical composition analysis is required, the signal must be deconvoluted. In order to perform deconvolution, the zero-loss peak must be available. The Fourier-log method is often used for this deconvolution and is described in greater length by Egerton's book(Egerton, 2011). Implementations of the Fourier-log technique is available in many EELS packages.

### 3.5 EELS analysis of lithium metals and lithium compounds

Lithium is the first metal of the periodic table. Similarly to all alkali metals, lithium is highly reactive. To this day, there is dearth of EELS investigation on lithium. The first EELS spectrum of lithium metal, Figure 8, was collected by Lru and Williams in 1996(Lru and Williams, 1986), using an analytical TEM, a vacuum transfer holder and a Gatan 607 spectrometer. Within a chamber vacuum of 10<sup>-6</sup> torr, lithium crystal growth and oxidation was observed. William and Lru commented on the high reactivity of lithium and the difficulty to obtain the EELS spectrum of lithium metal.



Pure-Li energy-loss spectrum (a) and spectra of progressively oxidized Li ((b)-(f)).

Figure 8: EELS Spectra of lithium metal and various oxidation states of lithium, from (Lru and Williams, 1986) showing that the spectra evolve along with the oxidation state of the metal. Although the edge always begins at 55eV, the sharpness and position of the ionization peaks are variable.

The data collected by William and Lru show that the near edge structure of the k-edge of lithium can give an insight on the oxidation state of the material. Aside from the proposed lithium-air batteries, lithium ions batteries do not contain metallic lithium, but rather lithium ions bound to other elements. One of the better knowns systems is the lithium cobalt batteries. However, current research in the field of lithium batteries is targeting iron and manganese phosphates and silicates as potential lithium-bearing cathodes. Iron and manganese have their M-edges close to the K-edge of lithium, at 54 and 49 eV, respectively. This proximity in energy makes the analysis of lithium challenging, as F. Wang et Al noticed while studying the lithiation of FeF<sub>2</sub> cathodes (Feng Wang et al., 2012).

### 3.6 Relevance of EELS Analysis of Lithium and Lithium Minerals

Due to the high demand of efficient and safe batteries, new cathode materials much be developed. In order to study these materials, techniques able to measure the chemical composition of material at the nanoscale are required. Using a TEM in combination with EELS is currently one of the only possible analysis techniques capable of nanometer range resolution and which is sensitive to lithium.

Electron beam induced sample damage is a significant hurdle for the analysis of lithiated metal silicates. It is therefore important to minimise the electron dose applied to a sample.

# 4 Tomography in the TEM

Computerized axial tomography (CAT) is a technique that was first implemented for medical imaging. The technique requires a series of projection images of an object to be taken and the information contained in these images is then used to virtually reconstruct the original object. Since Xray images are projection images, they were the first imaging method used in tomography systems. However, in principle, any imaging system for which the signal is an increasing function of the sample composition and thickness could be used. Because of this, computer assisted tomography has been conducted with various other imaging systems, such as neutron radiography and transmission electron microscopy.

### 4.1 Radon Transform and its Inverse

The radon transform is the name of the mathematical transform which links a tomography subject to its projection. Figure 9 shows an example of such transform, where the projection of an object is the acquired signal. The inverse radon transform is at the core of tomographic reconstructions. However, since most tomography systems gather a discrete radon transform, several algorithms are used in order to solve reconstructions.



Figure 9: A) reconstructed chest X-ray CT scan, B) Radon transform, or sinogram, of the CT slice ("Two-Dimensional Fourier-Based Reconstruction Methods," 2008). The information contained in the sinogram is the basis of the reconstruction. In this case, the relationship between a projection angle and the sinogram is shown with the gray arrows and the dashed line.

### 4.1.1 Back Projection and Weighted Back-Projection (WBP)

Back-projection algorithms are the simplest form of reconstruction. These algorithms overlay smears of the projection radially out of a central axis, while preserving the angular relationship of the projections with respect to each other. Since simple back projection oversamples the center of the reconstruction volume, a weighting scheme is often used in order to account for the central oversampling. WBP is often considered the most robust reconstruction algorithm, although it is susceptible to create reconstruction artefacts, especially in space tilt series.



Figure 10: Example of artefacts due to insufficient sampling of the Fourier space, given by simulations of different acquisition parameters in a 200keV HAADF STEM(Voisard et al., 2014).

### 4.1.2 Simultaneous Iterative Reconstruction Technique (SIRT)

Simultaneous Iterative Reconstruction Technique (SIRT) is an algorithm which takes an initial reconstruction, usually performed by WBP, compares the volume projections to the initial tilt series, and tries to adjust reconstruction parameters. This type of reconstruction algorithm can achieve good detail resolution with less artefacts then a WBP reconstruction, especially if the tilt series is sparely sampled. However, iterative algorithms, as the name suggests, take several iterations to achieve the desired results. Therefore, reconstruction is significantly longer using this type of algorithm.

### 4.1.3 ART/DART

Algebraic reconstruction technique (ART) is a technique which relies on solving a system of linear equations which represent the system. Each pixel of a tilt series expresses a change in intensity due to interactions with a given set of voxel on the reconstruction. Unfortunately, the number of variable (voxels) usually far outnumbers the number of equations and, thus, an infinite number of solutions exists. Most solutions to these systems are riddled with salt and pepper noise. Averaging multiple solutions smooths out the noise while maintaining global features and, since the sum of solutions of a linear system of equations is also a solution of the said system, using the average of reconstructions is a mathematically valid method (Gordon et al., 1970).

Although more computationally expensive than other techniques, ART has the advantage of easily allowing the introduction of prior knowledge to reconstructions. Discrete algebraic reconstruction technique (DART) is an example of such algorithm. In DART, the reconstruction is only allowed to yield a certain number of values. This number of values, which correspond to different zones within a material, must be previously known for the reconstruction to properly converge. However, in cases with high contrast values and required specimen knowledge, DART can prove more accurate than back projection algorithms (Batenburg and Sijbers, 2007).

### 4.1.4 Compressed Sensing (CS) algorithms

As mentioned in the previous section, the algebraic reconstruction problem has more unknowns than equations and, as such, the problem has an infinite number of solutions. Compressed sensing is a signal processing method which postulates that signal may be re-parametrised in a fashion which reduces the number of variables of the system. Several different approaches exist.

Although all these reconstruction techniques exist and can yield significant gains in resolution, weighted back projection is the simplest technique to use, as it does not rely on used input to fine-tune various parameters. As such WBP is a good technique to test the value of acquisition schemes.

### 4.2 Bright Field Tomography

The needs of biologists for the understanding of the tridimensional structures within organisms have led to the development of electron beam tomography. Due to the quasi-amorphous nature of biological samples, conventional TEM imaging techniques yield a simple contrast, which can be directly used for reconstructions (Frank, 2006; Mastronarde, 2005; Williams, 2008). However, due to diffraction and channeling effects in crystalline materials, BF tomography is not readily applicable to such materials.

### 4.2.1 Axial Tomography

Axial tomography is the technique used for most large structures. A single structure is identified, and a tilt series is acquired around this structure. Most tilt series are initiated at a tilt of zero, and the tilt increased in one direction at regular intervals, where pictures are acquired. After the maximum tilt is reached, the tilt is reset to zero and the sample is tilted in the opposite direction in the same intervals. Where available, dual axis tomography is performed. Dual axis tomography consists of acquiring images along two different axes. The purpose of double axis tomography is to reduce the missing wedge artifact down to a missing pyramid.

### 4.2.2 Single-particle

Single particle tomography relies on the fact that many small biological systems are composed of identical molecular machines. If these machines can be isolated and suspended on a grid, several hundred molecules can be imaged at once. If the suspension process can deposit the particles randomly on the substrate, all the possible orientations can then be simultaneously sampled(Radermacher et al., 1987; van Heel et al., 2000).

Once a suitable dataset is acquired, one must then separate each particle and then classify each image according to its orientation. Once the orientation of the particles known, the projection images can be used as input for reconstruction(van Heel et al., 2000).

Single particle tomography allows for low-dose tomographic acquisition, since only one image per particle is required. However, single particle tomography can only be used in cases where a large amount of identical structures can be isolated and laid out on a specimen grid with a certain level of disorder(Radermacher et al., 1987), such as biological molecular structures. Most material science samples are not sufficiently identical for this technique to be applicable.

### 4.3 Energy Filtered Tomography (EFTEM-TOMO)

EFTEM-TOMO is a tomographic acquisition technique which uses three-window EFTEM elemental maps for three-dimensional chemical mapping. Although EFTEM tomography can provide good three-dimensional chemical mapping, the acquisition of the data provides greater challenges then conventional tomographic techniques. In EFTEM, each tilt requires three frames per element of interest. Furthermore, EFTEM frames require more integration time than conventional imaging. EFTEM tomography is therefore an inherently high-dose technique. Furthermore, consistent EFTEM elemental mapping is difficult to achieve when the specimen thickness is changing, which is the case when acquiring a tilt series of a flat sample. In order to mitigate this effect, needle shaped-samples, made by focused ion beam (FIB) milling can be used in conjunction with full-rotation holders. Using this specimen shape and holder combination can also eliminate the wedge artefact, as the whole Fourier space is sampled(Weyland and Midgley, 2003).

### 4.4 High Angle Annular Dark Field Tomography

Due to dynamical effects of the electron beam in crystalline materials, bright field imaging has intensity variations which are not compatible with reconstruction algorithms. In order to achieve a good

tomography of crystalline material in the TEM, a scanning probe coupled to a high angle annular dark field (HAADF) detector is used. Acquiring tomographic information from a scanning probe has advantages over conventional TEM. The image from a scanning probe does not rotate with changes in objective defocus, as can be the case in conventional TEM. This lack of rotation simplifies the image alignment procedure of STEM axial tilt series, since the stack can be aligned with simple translations of individual frames.

Although the acquisition route is slightly different for HAADF and conventional TEM tomography, the reconstruction methods are generally the same. Freeware, such as the IMOD package and TOMOJ can be directly used to reconstruct HAADF tomography(Kremer et al., 1996; Messaoudi et al., 2007).

### 4.5 Application of tomography for nanoparticle analysis and lithium

TEM tomography is the only way to directly measure the morphology of nanoparticles and aggregates. Furthermore, tomography is the only technique which can measure closed pores or structures situated within the particles. As such, TEM tomography is more and more used. Successful examples of tomography of metal-based particles performed in TEM are given by several research groups(Batenburg et al., 2009; Cha et al., 2006; Muller and Ercius, 2009; Weyland, 2002). However, published results on STEM tomography of beam sensitive materials, such as lithiated metal silicate battery materials is lacking.

# Chapter 2: Golden Ratio Acquisition Scheme in HAADF Tomography

This article is intended for submission to the Journal "Ultramicroscopy" with authors Frédéric Voisard, Hendrix Demers, Raynald Gauvin.

The base idea, methodology and TEM acquisition were developed and performed by Voisard. Simulation were designed and performed by Voisard, using automation scripts written by Demers. Demers and Gauvin offered supervision of the work. Voisard wrote 90% of the paper. Demers and Gauvin contributed to writing and editing.

# 1 Abstract

Scanning Transmission Electron Microscope (STEM) Height Angle Annular Dark Field (HAADF) tomography is a well-established technique used to study the three-dimensional nanostructure of crystalline materials. However, some materials, as lithiated nano-particles, undergo damage and deformation during acquisition due to interactions with the electron beam. The possibility of sample damage must be therefore taken into account while acquiring tomograms of beam sensitive materials. The golden-ratio tomographic acquisition scheme is a non-sequential acquisition scheme originally developed for the in-situ observation of particle swelling in neutron tomography. Golden Ratio tomography has the ability of reducing the severity of sample motion/deformation artefacts but has not yet been applied in TEM. This paper demonstrates the applicability of the Golden-Angle acquisition scheme by simulation and experiments. First the validity of Monte-Carlo simulation for the simulation of artefact is explored using a well-known TEM tomography artefact, the missing wedge. This artefact of TEM tomographic reconstructions is characterized by the elongation of reconstructed features in the direction of the beam and is known to be caused by the limited angular coverage in most TEMs. Second, Monte Carlo simulations are performed applying the Golden-Ratio acquisition scheme and introducing synthetic displacement/deformation on the sample. The results are compared with reconstructed tomograms results using sequential acquisition. Improvements in terms of faithfulness of morphology of the nanoparticles are found. Finally, a tilt series using Golden-Ratio acquisitions on lithiated

nanoparticles mounted on a rotating sample holder acquired in S-TEM HAADF tomography are successfully reconstructed despite the displacement of the sample with respect to the holder. Additionally, this work shows how validated simulations can support electron microscopy developments and, in particular, acquisition schemes.

Keywords: HAADF, Tomography, Golden Ratio, Beam Damage.

# 2 Introduction

Morphology at the nanoscale is fundamental information towards the understanding of materials. Three-dimensional imaging techniques are continuously improving, pushing the limits of material characterization. One such development is the use of transmission electron microscopy (TEM) tomography with tilting or rotating sample holders. TEM tomography is the only way to directly measure the morphology of nanoparticles and aggregates. Furthermore, tomography can document closed pores or structures situated within the particles. As such, TEM tomography is more used in the materials community. Due to the quasi-amorphous nature of biological samples, conventional TEM bright field (BF) imaging techniques yield a simple contrast, which can be directly used for reconstructions (Frank, 2006; Mastronarde, 2005; Williams, 2008). However, due to diffraction and channeling effects in crystalline materials, BF-tomography is not applicable to such materials. Nevertheless, successful examples of tomography of metal-based particles performed in HAADF-STEM operation mode are given by several research groups (Batenburg et al., 2009; Cha et al., 2006; Muller and Ercius, 2009; Weyland, 2002). However, published results on STEM tomography of beam sensitive materials that undergo displacement or deformation, such as lithium-bearing battery materials, is lacking.

High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) tomography is a technique used to assess the three-dimensional structure of crystalline materials (Bals et al., 2006; Midgley and Weyland, 2003). The technique consists of tilting a sample and acquiring a projection image of the sample at regular intervals. Most reconstruction algorithms assume that image contrast is only due to the localized scattering cross-section and the thickness of the sample. Diffraction contrast and dynamical effects can lead to significant levels of noise in a reconstruction. HAADF-STEM imaging is used for crystalline materials because it produces images which are mostly free of diffraction contrast (Bals et al., 2006; Midgley and Weyland, 2003). However, some materials, such as lithiated nano-particles, readily undergo damage, displacement and deformation during acquisition due to interactions with the electron beam. The possibility of sample damage must therefore be taken into account while acquiring tomograms of beam sensitive materials. The Golden-ratio tomographic acquisition scheme is a non-sequential acquisition scheme originally developed for the in-situ observation of particle swelling in neutron tomography (Kaestner et al., 2011; Kohler, 2004). Golden ratio tomography has the ability of reducing the severity of sample motion/deformation artefacts but has not yet been applied in TEM. This paper demonstrates the applicability of the golden-ratio acquisition scheme by simulation and experimentally.

This paper is structured as follows. After the presentation of the methodology used, the validity of Monte-Carlo trajectory simulation software, CASINO 3 SEM/S-TEM (Demers et al., 2011)specially developed for complex tridimensional simulation scenarios, to STEM tomography and reconstruction artefacts, is explored using a well-known TEM tomography artefact, the missing wedge. This artefact of TEM tomographic reconstructions is characterized by the elongation of features in the direction of the beam and is understood to be caused by the limited angular coverage in TEMs which use tilting sample holders. This approach is used to explore the effects of Fourier space coverage coupled to sample damage during high annular dark field tomography in 200 to 300 keV scanning transmission electron microscopes. Second, once the application of the software for tomography is validated, simulations are performed applying the golden-ratio acquisition scheme and including synthetic deformation on the sample. The reconstruction results from golden ratio and sequential acquisitions are compared. Finally, a golden-ratio acquisitions on lithiated nanoparticles mounted on a rotating sample holder are actually performed in S-TEM HAADF tomography and reconstructed, despite the occurrence of displacement/deformation. The paper ends with a discussion of the applicability of golden ratio in TEM tomography and needs for further work.

### 3 Methods

This section presents the procedure used for the sample parameter used in the simulation software, as well as the transmission electron microscope and the reconstruction algorithm used for the work presented in this paper.

### *3.1* Simulation of tomography

Given the scarcity of high-performing TEM equipped for tomography, simulations are more and more used to optimize the scanning parameters prior to experimental work. CASINO is a Monte-Carlo method simulation software used to generate the trajectories of electrons as they interact with matter.

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CASINO applies the ELSEPA model of total and partial cross sections to individually traveling electrons. By simulating a large number of these trajectories thought virtual samples, an image is built. The images generated by CASINO are then used as tilt series in reconstruction software. The reconstruction software used in this work is TomoJ (Messaoudi et al., 2007), a plug in for the image analysis software ImageJ(https://imagej.nih.gov/ij/index.html).

Simulations are here carried out using CASINO 3 SEM/S-TEM (Demers et al., 2011), an electron trajectory simulation software developed for complex tridimensional simulation scenarios. Using a Monte Carlo scheme, backscattered, secondary, transmitted electron signals and absorbed energy can be modeled by this software. Scan points and shot noise are some of the software features allowing the simulation and the study of realistic experimental conditions. The ability of creating complex sample geometries allows the user to simulate the effect of morphological changed in samples during tomographic acquisition on the reconstructed volumes.

The synthetic sample is generated as follows. A set of 200 titanium dioxide spheres is generated using a randomized direction vector and with diameters ranging between seven and nine nanometers. The direction vectors are generated using python's random number generator, constrained between zero and one. Three numbers are generated and given to the x, y, and z components of the vector. The particle diameter relies on the same random number generator, multiplied by 2 and added to 7, to yield the desired particle radius range. All spheres are spawned at the origin, and moved along their respective direction vector until no contact is sensed between individual spheres. Intersection is calculated by Pythagoras's theorem applied to vectors in space as follows

$$R_1 + R_2 < \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2}$$
(1)

The sum of the radii,  $R_1$  and  $R_2$  of the spheres must be smaller the square root of the sum of the square of the difference of the partial vectors, x, w, and z describing the location of the center of each sphere.

Sample growth is simulated by increasing each individual sphere diameter by 1% and allowing the system to expand enough so that no two spheres are in contact. Once the no contact condition is achieved for all the particles in the system, their coordinates are saved. This step is iterated 10 times, giving 10 different time points.

Once the synthetic sample fixed in place, the software CASINO is used. Images are simulated using a 100 by 100 pixels grid. In each pixel, 10000 electrons trajectories are simulated at a 200 keV

energy with shot noise. This number of electrons is representative of a Hitachi HF-3300 E-TEM operating in high resolution STEM mode with a dwell time of 13 milliseconds/pixel, as measured with a faraday cup.

Two modes of acquisition are simulated. Conventional tomography and golden ratio tomography are simulated by covering the full rotational space in 91 frames. In conventional tomography this translates in a ±90° rotation with a 2° tilt interval. For the golden ratio tomography, the rotation angles are given in section 4.

### 3.2 Experimental HAADF-STEM tomography

Two microscopes are used to acquire tomographic tilt series. Both microscopes are transmission electron microscopes equipped with scanning modes. A FEI Technai TF20, comprising a 200 keV field emission gun, a tomography holder and HAADF detectors, is used for conventional tilt series. The FEI's objective lens pole-piece and sample holder combination allows for sample rotations up to ±80°. A Hitachi HF 3300 E-TEM/STEM 300 keV cold-field emission gun, with a Hitachi 3D holder, capable of full rotation, is used to perform golden ratio tomography experiments

Samples for validation are powder of titanium dioxide (Yasin et al., 2016), sonicated in isopropanol and deposited on a grid with a pipette. Samples for golden ratio are lithiated iron ortho silicates deposited on the edge of the 3d-holder micro pillar by a single bristle brush. The micro pillar used for golden ratio acquisition has been prepared by focussed ion beam milling to decrease the size of the pillar from 20  $\mu$ m to 100nm, in a Hitachi NB-5000 duel beam FIB/SEM.

Cold-field electron microscopes, although capable of very high resolution, can prove difficult to use for tomography, since the gun usually undergoes a significant reduction in beam intensity over the course of a tilt series. This translate in the necessity for a normalization of the brightness and contrast of the HAADF images. The normalisation preformed consists of using the minimum value (black) and the maximum value (white) for each frame. The brightness and contrast of each frame is then rescaled in order to make the dark and light regions match. This normalisation does not affect the linearity of the signal, as the gamma value of the detector as well as the gamma of each specific image is set to unity.

### 3.3 Reconstruction

In order to show the effects of sample swelling during the data acquisition on the reconstructed images, a simple weighted back-projection reconstruction is used for the simulated data. The software used is TomoJ, a plug-in for imageJ (Messaoudi et al., 2007). A weighted back-projection (WBP)

algorithm, with a weighting radius roughly equivalent to the radius of the cluster, is used for the reconstructions. WBP is used since the reconstruction relies solely on the acquired data (Batenburg and Sijbers, 2007; Messaoudi et al., 2007). Furthermore, since WBP is the first step to many reconstruction strategies, it is a crucial step in the process (Andersen and Kak, 1984; Gordon et al., 1970). Therefore, reducing artefacts at the source can lead to increased post-reconstruction resolution.

# 4 Validation

It is good practice to validate the capacity of a code to capture accurately the phenomenon of interest. We thus used the software to simulate a TEM tomographic acquisition of a deforming sample and compare the thus-obtained reconstruction with experimental results.

### 4.1 Missing wedge as artefact to recreate with simulation

Two major artefacts are investigated in this work, the missing wedge, described in this section, and the comma artifact, found in the section 4. As the name implies, the missing wedge artefact is due to a lack of information. Due to geometric constraints in the TEM, it is impossible to acquire a full tilt series of a sample mounted on a standard grid.



Figure 1: Geometrical diagram of the rotational limitation of standard TEM grids and holder, the high tilt overlap of the grid and sample projection is hatched in red, image not to scale.

Figure shows how the increasing tilt leads to the overlap of the projection of the grid onto the projection of the sample. In the best-case scenario, the grid is the absolute limiting factor of the tilt range. However, depending on the microscope, the holder-pole piece combination may be the limiting factor. This limitation is especially the case of high resolution TEM, where the pole-piece gap is made a small as possible in order to increase resolution, since the sample must rotate within this gap.

This missing information will lead to a wedge artefact on a reconstructed image. When looking at a slice taken perpendicularly to the tilt axis, the reconstructed image will show an elongation.

### 4.2 Simulation of missing wedge and comparison with actual TEM

The tomography of the synthetic sample of 200 titanium spheres described above is simulated with CASINO over the range of  $\pm$  60°, at 2° interval, so 61 projections covering 120°. The results are shown in Figure 12. Due to the under sampling of the Fourier space, the reconstruction, Figure 12a clearly shows a general elongation of the spheres, in addition to streaking. This elongation is distinctive of the wedge artefact.



Figure 2: Slices (a and c) of reconstructed tomography showing missing wedge artifact and Fourier transform (b and d) of simulation (A and B) and experimental tomography (C and D).

Also, a cluster of nanoparticles of titanium dioxide (anatase) is imaged using a TEM and tilting from -72° to 66°, over a range of 138° and reconstructed. Figure 2 C shows a slice taken from this experimental tomography. Since the particle are synthesized by hydro-thermal processes, they are expected to have regular features. The area surrounding the particle is vacuum, and therefore should not contribute to any signal. Again, typical signs of missing wedge artefacts can be seen. Most of the particles are distorted along the beam axis and streaking is present.

The fast Fourier transform (FFT), which represents the real part of the Fourier series representation of the image, are computed using ImageJ and shown in Figure 2 B and Figure 2 D. Both figures show a pair of dark triangular region. This is the distinct Fourier space representation of the missing wedge clearly found on both figures.

In conclusion, this exercise shows the capacity of the image simulation software to generate tilt series, which, when reconstructed, show the same artefacts than experimental tilt series. Given the clarity of the missing wedge artifact found in the simulation reconstruction, which actually reproduce the ones seen in a similar-shaped reconstruction of a real sample, we conclude that the software is valid for TEM projections simulations.

### 5 Golden ratio acquisition

The golden ratio method is first presented and then applied on synthetic and real TEM full tomography acquisition. Golden ratio tomography was first implemented in neutron radiography, to avoid comma artefact due to changes in the samples during tomographic acquisitions, as well as to gain a temporal dimension to the tomographic reconstructions (Kaestner et al., 2011).

### 5.1 Presentation of the theory of golden ratio acquisition

Golden ratio acquisition (Kaestner et al., 2011; Kohler, 2004) is achieved by titling a sample by the golden angle  $\alpha$ , which is described as the angular analogue of the golden ratio,  $\phi$ . These quantities are defined in equations (2 and (3.

$$\varphi = \left(\frac{1+\sqrt{5}}{2}\right) \tag{2}$$

$$\alpha = 360 * \left(1 - \frac{1}{\varphi}\right) = 137.507764 \dots \approx 137.5^{\circ}$$
 (3)

Since the golden angle is irrational, the modulo of integer multiple of  $\alpha$  over 360° is irrational and therefore never repeats itself (Kohler, 2004).

### $(n\alpha)mod360 \notin \mathbb{Q}$

Furthermore, each successive new increment always falls in the most sparsely sampled region of the circle (Kohler, 2004). For data acquired in ideal situations, where a sample is perfectly immobile with respect to the rotation axis of the tomography system and morphological stable, sequential and golden ratio acquisition schemes carry equivalent information, assuming the same number of projections is taken and that the same rotational space is covered. However, if the sample undergoes some transformation during the acquisition process, the golden ratio acquisition scheme can reduce the displacement/deformation effect.



Figure 3: Plot of apparent particle size vs projection angle of a particle growing at a regular rate. The sequential acquisition scheme induces a bias in the sampling, where the larger tilts correspond to larger particles. Here, 45 projections are shown, instead of the 90 used in the simulation, for the sake of not over-saturating the plot. In the golden ratio scheme, the increase in thickness is evenly distributed through all the angular range. Note that the golden ratio projections have been numbered according to their acquisition order of acquisition for clarity.

### 5.2 Comma as the artefact of swelling samples

In a conventional sequential tomographic tilt series, physical processes affecting the sample are cumulated through the tilt series. Carbon contamination and specimen icing are examples of such cumulative process. In a tilt series, the sample mass and size effectively increases throughout the series. This cumulative effect is visible in reconstruction as a comma shaped artefact, where the body of the comma is indicative of the early stage of the tilt series, the tail of the comma come from the physical changes of the sample. This type of artefact has been documented in neutron tomography, where

water uptake of the sample dramatically changes the sample size and neutron scattering cross section of the sample (Kaestner et al., 2011).



Figure 4: Typical "comma" shaped artefact due to sample swelling during sequential tomography acquisition, obtained by simulation.

As an illustrationFigure 4 shows a slice from a CASINO simulation of a sequential tomographic dataset imaging an aggregate of 200 spherical particles which undergo a step-wise swelling of 1%, ten times, for a total particle radius increase of 10% over a sample rotation of 180°, in 2° increments. The cross section is taken perpendicularly to the rotational axis. Each particle on the reconstruction has a circular body, but a tail can be seen growing. This comma-shape give the name to the artefact (Kaestner et al., 2011). Inset shows a close-up of the main image. The comma artefact is more prominent on the particles furthest from the rotation axis.

### 5.3 Simulation of acquisition of deforming sample with golden ratio

Carbon contamination, as an example of cause of deformation, can build up during a TEM tomography tilt series. Individual particles gather an increasingly thick carbon coating. Two simulations are performed on the same synthetic aggregate of 200 particles used above. Carbon contamination is simulated by increasing linearly the diameter of the particles from the initial size of 10 arbitrary units to a size of 10.45 arbitrary units at each successive scan. The sequential acquisition consists in 90 projections with a tilt of 2°. The golden ratio scheme acquisition consists also in 90 projections with tilt angles similar to those shown in Figure 3. Two slices across the aggregate are chosen from the both acquisition schema and shown in Figure 5.

Figure 5 a) and c), showing the slices from the sequentially acquired dataset, illustrates the effect of the size sampling bias between the low and high angle tilts. This mismatch of measured sizes clearly gives rise to the comma artefact (Kaestner et al., 2011).

Figure 5 b) and d), showing slices from the same example, where golden ratio acquisition is used instead of sequential tilting, the size sampling is not related to the tilt angle. Therefore, the size mismatch is not localized on the rotational space, but rather spreads uniformly. The comma artefact is no longer apparent, while the general shape of the sample is preserved. The non-sequential nature of golden ratio is immune to comma artefact. Although the sample motion induces blur in the reconstruction of golden ratio acquired dataset, the general shape of particle is better preserved then in sequential acquisition schemes.



Figure 5: Simulation of the effects of sequential (a and c) vs golden-ratio (b and c) acquisition of swelling nanoparticle aggregates. Frames a and c show example of comma-shaped streaks, called comma artefacts.

Golden ratio tilting schemes does not prevent specimen contamination and damage, however, the effect of such events is minimized during reconstruction. That is, since the rotational space is continuously sampled during the acquisition, the reconstruction will maintain the general features of the sample. The transient process that induce the comma artefact in conventional tilt series are still present in golden ratio acquisition. However, since the Fourier space is decoupled from the time in golden ratio acquisition, the effect of the size increase is spread evenly around the specimen features. This allows for the general shape of the sample to be conserved.

Furthermore, in the event of severe specimen damage or contamination, partial data acquired using the golden ratio can be reconstructed. This reconstruction will be inherently noisy but, since the full rotational space is sampled quickly, the wedge artefact will not be significant. This salvaging capability is a further significant benefit of golden ratio acquisition over conventional tomography, as sample damage or even sample loss is a real possibility in experiments which can take hours to accomplish.

### 5.4 Actual TEM acquisition with golden ratio

A golden-ratio acquisitions of lithiated iron orthosilicate nanoparticles mounted on a rotating sample holder are performed in S-TEM HAADF tomography on a Hitachi HF-3300. and reconstructed, despite the occurrence of displacement. The material used for this experiment is Li<sub>2</sub>FeSiO<sub>4</sub>. This lithium bearing mineral is produced by hydrothermal processing and subsequent vacuum annealing at 900 °C. The processing requires that a mixture of SiO<sub>2</sub>(silica), CH<sub>3</sub>COOLi·2H<sub>2</sub>O (lithium acetate), Fe(NO<sub>3</sub>)<sub>3</sub> (iron(III) nitrate) in H<sub>2</sub>O, mixed with ethylene glycol and ethylenediamine, is inserted in an autoclave, heated to 180°C and allowed to react for 12 hours(Lu et al., 2015). This processing yields nanoparticles in the 10-20nm range, which grow to several hundred nm after the annealing process. This material has been found to be beam sensitive. Therefore, some damage/displacement is expected to occur over the course of the tomographic acquisition.

In order to achieve full rotational coverage in the TEM, a special holder is required. Figure 6 shows the rotation mechanism of a Hitachi 3D-Holder. A motor housed in the stem of the holder engages a set of gears. Both of the gears are made to receive small pins, on which focused ion beam (FIB) milling can be performed to reduce the tip size or to weld needle samples. In this case, FIB milling was used to create a square sectioned 100nm sided pillar onto which powder samples are deposited. The golden ratio is an irrational number 137.507764 ...  $\approx 137.5^{\circ}$ . However, the holder rotates only in

discrete integer increments. Selecting between 137 and 138, 137 is a prime and therefore no angle will repeat until the 360<sup>rst</sup> frame while using 138-degree interval would result in redundant information after the 60<sup>th</sup> frame. That is

$$(137 * n) mod \ 360 \ \neq 0 \ if \ \{n \in \mathbb{N} | 0 < n < 360\}$$
(5)

While in the case of 138°

$$(138 * n) mod 360 = 0 if n \in \{60, 120, 160, 240, 300\}$$
(6)

Therefore, a larger part of the rotational space is sampled using a 137° rotation angle than a 138°.



Figure 6: Tip of a full rotation TEM sample holder. An external controller and motor are linked to the gear set, which allow mounting a sample for rotation in either the alpha (co-axial with the holder) of beta (perpendicular to both the column and holder) axis. Mounting on the beta position allows for the sample to be prepared in focus ion beam milling system.

A golden ratio tilt series of the aggregate is acquired using 51 frames, with a 137° rotation angle. At this point, the sample detached itself from the holder and the tilt series could not be continued. Furthermore, the sample seems to have undergone a slight tilt with respect to the rotation axis at some point near the middle of the tilt series acquisition. The nature of golden ratio acquisition allows for significant results to be extracted from experiments which would have been considered failures using conventional rotation schemes. Reconstruction is performed using TomoJ's SIRT algorithm (Messaoudi et al., 2007) Despite the low number of projection, i.e. 51, the reconstruction is nevertheless successful as shown in a 3D reconstruction volume rendering in 7a and the rotation axis orthogonal slice in 7b. 7b shows how the missing wedge artifact is not existent despite the shifting of the sample during the acquisition, which is the cause of the light rings around the aggregate. In a typical sequential

acquisition scheme, the lacking frames (here only 51 out of 180 frames) and the sample motion usually leads to wedge and comma artefacts would make the reconstruction impossible to use.



Figure 7: a) 3D rendering of a  $Li_2FeSiO_4$  nanoparticle aggregate. The scale is indicated on the volume bounding box, in nanometers. b) slice of the rendering taken perpendicular to the rotation axis.

# 6 Conclusion

The simulation and experimental work performed for this paper supports that the use of golden ratio tomography, as proposed by Kohler, is applicable to STEM-HAADF tomography.(Kohler, 2004)

Beam-sensitive materials undergo damage and deformation during acquisition due to interactions with the electron beam, carbon deposition and/or other mechanisms. The Golden-Ratio tomographic acquisition scheme being a non-sequential acquisition scheme provides a viable and promising avenue for imaging such materials. The ability of reducing the severity of sample motion/deformation artefacts offered by golden ratio is applied for the first time in TEM in this paper. The applicability of the Golden-Angle acquisition scheme by simulation and experimentally. Monte Carlo simulations, show that a significant reduction in comma artefacts can be achieved using this acquisition scheme. Experimental work corroborates the feasibility of golden ration acquisition in the STEM despite the displacement of the sample. Improvements in terms of faithfulness of morphology of the nanoparticles are found.

In a field where access to high level equipment for students is competitive and where beamtime use should be optimized, this work shows how validated simulations can support electron microscopy developments and, in particular, acquisition schemes, leading to better preparation for acquisition. In terms of further development, a better understanding of the capacity of the golden ratio acquisition to deal with displacement/deformation should be sought by providing expected maximum displacement of deformation that can be acceptable. The implementation of golden ratio acquisition for neutron tomography has lead to the capability of decomposing the tilt series in sub-time frames. This allowed the timewise recording of the transient processes within the sample. Replicating this property of golden-ratio acquisition in the TEM could allow for tomographic in-situ work to be performed.

# Interface

As seen in the previous chapter, TEM tomography is an excellent method to document and study the morphology of materials at the nanoscale. Furthermore, golden ratio acquisition allows the minimization of the effect of specimen damage on tomographic reconstruction. In particular, regions with significant differences in composition and density can yield different shades of gray on the reconstruction. And prior knowledge of the sample constituents can be used for associative phase analysis. However, HAADF-tomography is limited in the chemical information the technique can provide. In order to measure a material chemical composition with certainty, a different approach must be taken. Energy dispersive X-Ray spectroscopy (EDS or EDX) is a well known technique used for chemical analysis of materials in the TEM and SEM. However, the protective window used in most detectors, composed of a few nanometers of silicon nitride or beryllium, is enough to absorb the X-Ray signal emitted from light elements such as lithium. Alternatively, electron energy loss spectroscopy (EELS) is a TEM technique which measures the energy of an electron beam after interactions with a sample. The next chapter will present the technique as applied to metallic lithium.

# Chapter 3: Spatially-Resolved Electron Energy Loss Spectroscopy of Lithium Sheets

This article is aimed for submission to the Journal of Power Sources with authors Frédéric Voisard<sup>1</sup>, René Veillette<sup>2</sup>, Michel Trudeau<sup>2</sup>, Karim Zaghib<sup>2</sup>, Raynald Gauvin<sup>1</sup>. The work was conceived and planned by the 5 authors equally, material preparation by Veillette, methods development by Trudeau and Voisard, images and spectra acquired by Voisard, data analysis performed by Voisard, paper was written by Voisard 70% and all remaining authors equally.

<sup>1</sup>McGill University, Department of Mining and Materials Engineering, Montréal, Quebec, Canada <sup>2</sup>Hydro-Quebec Research Institute (IREQ), Varennes, Quebec, Canada

### Abstract

Lithium metal sheet is a core material for the lithium-air battery. During the production of lithium metal sheets, used in the fabrication of the batteries, a mixture of lithium carbonate and lithium oxide can form on the sheet surface. The thickness and chemical profile of these passivation layers play a strong role in the electrochemical properties of the lithium sheets and must therefore be understood. Electron Energy-Loss Spectroscopy (EELS) is a powerful chemical analysis tool in the transmission electron microscope (TEM). EELS can be used to quantify the composition of a sample by detecting ionization edges, as well as the chemical bonding states, of the elemental components, by analysis of the fine near-edge structures. By scanning the condensed electron probe across a specimen, with a scanning transmission electron microscope (STEM), a chemical map can be obtained. STEM-EELS, however, results in high electron dose administered to a specimen, which can damage beam-sensitive materials such as lithium. In this paper, Spatially Resolved EELS (SR-EELS), a low dose method that relies on conserving the information contained in the non-dispersive direction of the energy-filtered beam, is applied and maps successfully the elemental distribution and chemical state of a lithium laminate, as a function distance from the lithium sheet surface.

Keywords: Lithium, EELS, TEM, spatially resolved electron energy loss

# Highlights

- Chemical analysis of laminate structure of lithium laminates
- Line scan equivalent information is attained at low dose
- Acquisition of plasmon and elemental edge information
- SR-EELS allows for chemical analysis of lithium

# 1 Introduction

The current demand for more efficient and environmentally friendly cars has driven the demand for electric vehicles. One of the main hurdles for market breakthrough of such vehicles is their power plant (Bini et al., 2015; Girishkumar et al., 2010). The best battery technologies on the market today are heavy and bulky. The weight and bulk of the batteries limit how much energy can be stored in a given space. This storage capacity limits the drivable range of the vehicle. Lithium-air battery chemistries have been proposed to bridge the gap in energy density between lithium ion batteries and internal combustion engines. Several chemical mechanisms have been proposed to describe the oxidation of lithium and the resulting electric potential. However more detailed information on the actual oxidation states of lithium metal is needed and it is the purpose of this work is to capture and document these lithium oxidation states.

Lithium is the first metal on the periodic table of the elements. As such, lithium is a very simple atom. The surface of lithium is reactive and a layer of lithium oxide and lithium carbonate is expected to be present on the surface of the lithium metal sheet (Mallinson et al., 2013). The ionization of a lithium core electron happens at low energy, between 54 and 67 eV, depending on the chemical state of the atoms (Wang et al., 2011; F Wang et al., 2012). The electromagnetic radiation emitted by most elements falls in the X-ray energy range making X-ray Energy Dispersive Spectroscopy (XEDS or EDS) an effective technique for elemental analysis. However, the electromagnetic radiation emitted by lithium is closer to far UV light then to X-ray radiation. This low energy range is difficult to measure using EDS, since the bulk of the radiation is absorbed by the protective window of most detectors. Some window-less EDS systems equipped with dedicated low-energy counting electronics are able to detect the lithium ionization peak. These systems are unfortunately not very common, while being limited in energy resolution and their ability of resolving near-edge structures. Furthermore, the statistical nature of the emission of X-rays in the low energy range translates in the need for high specimen dose, therefore the exposure of sensitive materials to beam damage.

Electron Energy Loss Spectroscopy (EELS) is a technique which measures the energy distribution of an electron beam after sample interaction. Since the ionization events which lead to the generation of X-rays find their energy in the probing electron beam, the post-specimen beam will have electrons displaying an energy loss equivalent to the ionization energy of the atomic shells. The working principle of EELS spectrometers is thus very different to that of EDS. The energy resolution of an EELS spectrum is higher, being a fraction of a eV. However, the EELS spectrum intensity decays exponentially with energy and EELS information above 2 keV is usually insignificant. However, in the case of the lithium-oxygencarbon system which results from the presence of carbonate and oxide, the highest energy peak is that of oxygen, at 523 eV. Therefore, EELS is the ideal transmission electron microscopy (TEM)-based spectrometry technique to probe lithium metal and asses the chemical species present on the surface of the metal (Brydson, 2001; Egerton, 2011).

In general, lithium metal and compounds are known to be electron-beam sensitive (Rossell et al., 2009; Wang et al., 2011). While traditional STEM-EELS transfers a high electron dose to the specimen, as several scan points are required to generate an image, energy-filtered TEM (EFTEM) can also produce elemental maps, but not for lithium as its edge is in the tail of the plasmon, i.e. the oscillation of the free electron gas in the metal, peak and the typical power-law background fitting algorithm does not yield good results.

In case of EELS analysis where edges are located in the plasmon peak tail, a first-order logpolynomial background fitting has been found more accurate (Brydson, 2001; Egerton, 2011). Furthermore, conventional EELS does not conserve the spatial resolution of the microscope. Localized EELS analysis can be performed by working at high magnification and using a condensed electron beam, since the EELS signal is limited to the part of the electron beam which passes through the EELS detector aperture. Instead of performing this kind of localised analysis, STEM mode is used as simple way to control the area of the sample used for analysis. With the control given by STEM operation, local EELS analysis can be performed. The major drawback of STEM-EELS is the high electron dose imposed on the specimen (Brydson, 2001; Egerton, 2011; Rossell et al., 2009).

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In summary, EELS is a powerful chemical analysis tool in STEM that can be used to quantify the composition of a sample by detecting ionization edges as well as to identify the chemical bonding state by analysis of the fine near-edge structures. EELS, however, results in high electron dose administered to a specimen, which can damage beam-sensitive materials such as lithium. In this paper, Spatially Resolved EELS (SR-EELS), a low dose method that relies on conserving the information contained in the non-dispersive direction of the energy-filtered beam, is applied to a lithium lamella extracted from a lithium sheet using focused ion beam milling, with the aim of mapping the distribution and chemical state of lithium, as a function depth in the material sheet.

This paper is structured as follows: presentation of the methodology used, description of material preparation and a description of EELS. SR-EELS spectral images are acquired and the results presented. The paper ends with a discussion of the applicability of SR-EELS to the study of lithium metal and needs for further work.

# 2 Experimental methodology

### 2.1 Sample Preparation

The sample is extracted from a sheet of lithium metal. As lithium is reactive, a layer of lithium oxide and lithium carbonate is expected to form on the surface of the sheet. The thickness of this layer, as was as it's composition is of interest, since the layer can play a significant role in the properties of batteries made with the material. The lamella to be investigated with SR-EELS is extracted by focus ion beam as follows.

A carbon layer is deposited on the surface of the sample in order to minimize gallium implantation in the specimen. The gallium beam is then used to dig two trenches in the lithium, in order to leave a thin area untouched by the gallium beam to a depth of approximately  $4\mu$ m. The gallium beam is then used to cut around the lamella. Before the lamella is fully detached from the bulk, a micro manipulator is inserted near a corner of the lamella. The micro-manipulator is then welded to the lithium lamella. The lamella is then fully detached from the bulk. A lift-out grid in inserted and the lamella is welded to a post, in flag configuration. Once solidly welded, the lamella is thinned by iterative passes of the gallium beam, until a target thickness of 100nm is achieved. As a result, the 100nm-thin lamella has a surface of  $6\mu$ m by  $4\mu$ m, where the dimension corresponding to the depth perpendicular to the laminate surface is  $4\mu$ m. The modified surface layer is expected to be in the rage of 5 to 15 nm. The superfluous surface of the lamella allows for better structural rigidity and heat transfer in the sample. The lift-out grid is then inserted in a Hitachi vacuum cryo transfer holder. The holder is closed, retracted from the FIB and inserted in the Hitachi HF-3300 TEM. The sample is then cooled to -100°C to minimize beam damage on the sample. A liquid nitrogen cooled cold trap is used to minimize ice accumulation on the sample.

STEM-EELS mapping was attempted on the material. The resulting spectral images carries a significant amount of compositional information. Figure A to C shows the elemental maps extracted from the spectral images. Figure D is a false color combination of the tree maps. A strong concentration of oxygen seems to be present near the original surface of the sample.



Figure 1: STEM-EELS maps of the lamella near the surface. The region rich in carbon is what remains of the protective carbon layer added during the FIB milling steps. The spectral images where acquired at a beam energy of 300 keV.

However, by taking a look at the before and after secondary electron STEM images of the region where the map was taken, evidence of beam damage can be seen. The rectangular features seen in Figure 2 B are a strong indication that the sample was damaged during the STEM-EELS map process.



Figure 2: Secondary electron image showing before (A) and after (B) of the sample undergoing STEM EELS maps. The rectangular marks in B are traces of beam-induced damage to the material.

### 2.2 Microscope

The TEM investigation is performed on a Hitachi HF-3300 TEM outfitted with a Gatan Quantum ER energy filter. The microscope is operated at 300 keV. In order to minimize sample damage, a vacuum transport cryo-holder is used to transport the specimen from the dual beam FIB/SEM to the TEM. Once under TEM vacuum, the sample is cooled to -100°C. Care is taken to minimize the electron dose on the sample before SR-EELS analysis.



Figure 3: HF-3300 300 keV E-TEM equipped with a GIF Quantum ER spectrometer and dedicated EELS slit.

### 2.3 SR-EELS

In conventional EELS acquisition, the energy loss information is spatially limited to the area of the electron beam collimation. That is, the part of the image which enters the magnetic prism is the part of the specimen for which a signal will be collected. A simple method to gain spatial resolution is to use a convergent scanning probe and gather a spectrum at each scan point. This method is called STEM-EELS and the information gathered is a spectral image. However, STEM imaging imparts a high electron dose on samples, since all the probe current is localized in the smallest possible area.

In order to reduce the dose on the sample, SR-EELS is used. A slit aperture, oriented perpendicular to the energy-dispersive direction of the energy filter is used to collimate the post-sample beam. The filter is tuned in such a fashion as to maintain an imaging focus along the non-dispersive direction, as shown in Figure 4. The resulting two-dimensional image has different units along the x and y axis. The Y axis is in units of length (nm), while the X axis in units of energy (eV) (Kimoto et al., 1997, 1999).



Figure 4: Simplified Diagram of the SR-EELS geometry, showing how the X-axis is dispersed in energy while the y-axis preserves the spatial resolution. After the specimen interaction, the electron beam is collimated by a thin slit, located above the spectrometer. The spectrometer then disperses the beam in energy. The resulting spectra are collected on a CCD camera. The resulting image, such as shown in Figure 5, can be seen as a line-scan of an interface, where the y dimension is spatial, the x is energy dispersed and the intensity of the pixels are related to the number of electron counts at a position y and energy x.

A limit of SR-EELS is the polychromatic nature of the electron beam analyzed. Since electron energy loss signal is collected, the electron beam will necessarily be polychromatic (Egerton, 2011). The effective strength of magnetic lens on an electron beam is a function of both the lens current and the electron beam energy. Because the beam is polychromatic, it is impossible to focus all the electrons at once. A point on the sample therefore becomes a disk on the image. The radius of this disk for a particular energy loss,  $r_{chr}$ , is related to the initial beam energy,  $E_0$ , the electron energy loss,  $\Delta E$ , the collection angle of the lens,  $\beta$ , and a chromatic-aberration coefficient of the lens,  $C_c$  by equation 2 (Williams, 2008).

$$r_{chr} = C_c \frac{\Delta E}{E_o} \beta \tag{1}$$

In order to minimize the effect of chromatic aberration, the energy dimension is sampled in increments of 100 eV, with a dispersion of 0.05 eV per channel. Furthermore, beam energy is used to

control the observed dispersive energy range. Because the beam energy is modulated, an accurate high voltage centering is critical in order to maintain a proper spatial focus.

$$E_0 + E_{shift} - \Delta E = E_{obs} \tag{2}$$

That is, by modulating the beam energy, with a stable voltage center, the post-specimen electron energy is maintained with the spectrometer's optimal operating condition.

A dedicated slit is used to limit the electrons entering the filter. This slit, perpendicular to the dispersive direction, allows for observation of a small area, as well as in a more even illumination in the non-dispersive direction. Figure 5 shows how the SR-EELS signal is projected on the CCD. A three dimensional plot can be used to visualise the three axes and their respective units, which are electron energy loss, length, and intensity. In Figure 5 B and C, one can notice a significant change in the near-edge peaks



Figure 5: SR-EELS data of a lithium laminate structure, shown as the raw image (top), and as a 3dimentional surface (bottom). The surface plots emphasize that each row of data corresponds to a spectrum, and that the intensity of the pixel is related to the number of counts.

### 2.4 Data Collection Program

Elements of interest in this study are lithium, carbon and oxygen, which have core ionization edges at 55, 283 and 532 eV of electron energy loss, respectively. The spectra are collected with dispersions of 0.05 eV per channels, in order to prevent chromatic aberrations to affect the nondispersive dimension of the spectra. The spectra of the lithium edge are collected first, in order to obtain an spectra of the pristine sample. The beam is blanked for 20 seconds before the collection of the oxygen spectra, so that the scintillator can de-saturate. Beam blanking is not required prior to the collection of the carbon edge spectra, as the intensity of the EELS spectrum at the carbon edge is much brighter than at the oxygen edge.

Three regions of interest (ROI) are used for the analysis of the data. The same ROIs are used in all three spectral images. Figure 6 shows the three spectral images as well as the ROIs used for the extraction of the spectra analyzed further.



Figure 6: SR-EELS data of the lithium, carbon and oxygen energy loss edges. The corresponding region of interest (ROI) of each image represents the same region on the sample. The data is collected with a spectrometer dispersion of 0.05 eV per channel.

### 2.5 Analysis of results

Once the desired spectral images are acquired, the EELS spectra of region of interest are

extracted.



Figure 7: Spectra extracted from the data in Figure 6, a) lithium, b) carbon and c) oxygen energy loss edge. Since the different ROIs are expected to be constituted of different materials, the different spectra should have variation in their features. The energy loss edge of lithium is a good example of such variation, as the edge gains a 3<sup>rd</sup> peak, in region three, while only two peaks are present in region one and two.

### 2.6 Background-subtracted Spectra

In order to better visualise the spectra, the background must be fitted and subtracted. In the case of carbon and oxygen, a power-law function is fitted over a 15 eV window prior to the respective edge of each spectrum. In the case of lithium, the edge is located in the tail of the plasmon peak and, as such, a first order log-polynomial is a better fit to the background. A 10 eV window is used, due to the proximity of the lower energy feature present on the spectra near 30 eV.



Figure 8: EELS spectra shown in Figure 7 with background subtraction, on an arbitrary scale, a) lithium, b) carbon and c) oxygen energy loss edge. Appling background subtraction allows the comparison of signal intensities. The use to background substation also allows users to visualize faint features, such as the onset of the non metallic lithium edges (region 2 and 3 in the lithium plot).

### 2.6.1 Lithium Edge

The lithium K-edge structure is known to differ greatly depending on the oxidation stage of lithium. Metallic lithium shows three peaks superimposed on the edge, with an abrupt onset of the first peak coinciding with the edge. This first peak is not present the energy loss spectrum of oxidised lithium. Because the first peak of lithium metal is not present in region 2 of Figure 8 a), it can be stated that nonmetallic lithium is present near the surface of the lithium sheet.

### 2.6.2 Carbon Edge

The structure of the carbon EELS edge is dependent on the bounding state and, in the case of pure carbon, on the structure of carbon. The EELS spectra of amorphous carbon, graphite, graphene and diamond all show variations in the fine structures of the edge. In the case of this sample, a carbon edge is observable at all positions, in the form of a peak at 285 eV. However, this peak is minimal in region 3, indicating significantly lower carbon content in the bulk lithium. Furthermore, a second peak in region 1 of Figure 8 b) at 280 eV, is indicative of a different bonding state of carbon in the second region in comparison with its state in the first and third regions. The presence of lithium carbonate on the original surface of the lithium sheet could explain this difference near the surface.

### 2.6.3 Oxygen Edge

The oxygen edge in this system is characterized by two sharp peaks followed by the broad edge. This broad edge is less defined in the third region. The presence of oxygen over the entire sample can be explained by ice accumulation on the sample or by redisposition of lithium oxide on the sample during the FIB milling process.

# 3 Discussion

Once the SR-EELS spectra of interest are acquired, spectrum processing is used to further refine features. Background subtraction and non-linear least square (NLLS) fitting are standard analysis procedures, implemented in Gatan's Digital Micrograph image analysis software (Egerton, 2011). While background subtraction allows the comparison of intensity and shape of core loss edges, NLLS can be used to measure changes in energy, intensity and broadness of fine features.

### 3.1 Non-Linear Least Square Fitting (NLLS)

Non-linear least square fitting is an analysis technique which relies on the fitting of a Gaussian curve to a feature. The extracted parameters are the shift of the center of the peak in eV, the amplitude of the Gaussian in counts, the full width half max (FWHM) of the peak and the reduced chi-squared fit of the Gaussian to the peak. Since in most cases a Gaussian is not an appropriate fit for features of EELS spectrum, the measured reduced chi-squared is usually found to have values much larger than one. However, the values for the shift of the center of the Gaussian usually accurately corresponds to a shift

in the central value of a peak of interest.



Figure 9: SR-EELS image of the lithium edge of the sample, showing the region used for NLLS fitting of the plasmon peak. Plot of the NLLS fitting is shown in Figure 10.

For the plasmon resonance peaks, changes in the energy of a peak are linked to changes in the nature of the sample.



Figure 10: Plot of the parameters extracted form the non-linear least squared fitting of a Gaussian over the Plasmon peak of the lithium laminate.

The plot of the peak center, amplitude and width, in Figure 10 shows three defined regions. A feature of interest in plasmon peak analysis is the position of the center of the plasmon peak. Bulk plasmon excitation is a material property, and is therefore dependent on the material's composition. The

amplitude trend can be used to track the edges of the EELS aperture, near 27 and 74 nm, between which the signal is interpretable. By analysing the three signals, three plasmon zones can be defined. So, what are the chemical changes with depth?

### 4 Conclusion

The purpose of this work was to investigate the use of EELS for the analysis of lithium metal sheets, a core material for lithium-air battery. STEM-EELS is found to be too aggressive for lithium metal sheet analysis. Therefore SR-EELS, a low dose method that relies on conserving the information contained in the non-dispersive direction of the energy-filtered beam, was successfully applied to the material. The present work shows how SR-EELS can be used to gather localize chemical information, at low specimen dose. Low dose work allows for the analysis of extremely beam sensitive materials, such as metallic lithium.

During the production of lithium metal sheets, used in the fabrication of the batteries, a mixture of lithium carbonate and lithium oxide can form on the sheet surface. SR-EELS documents the thickness and chemical profile of the passivation layer, which play a strong role in the electrochemical properties of the lithium sheets. Given the extraction geometry retained here for the sample, SR-EELS is maps successfully the elemental distribution and chemical state as a function of the distance from the lithium sheet surface.

Spatially Resolved Electron Energy-Loss Spectroscopy (SR-EELS) is shown to be a powerful chemical analysis tool in the transmission electron microscope (TEM). SR-EELS can be used to quantify the composition of a sample by detecting ionization edges, as well as the chemical bonding states, of the elemental components, by analysis of the fine near-edge structures, without damaging of beam sensitive materials such as lithium. Further work includes the simulation of the fine structures of the energy loss of lithium, carbon and oxygen for compounds known to be present in the surface layer of lithium sheet metal, such as lithium oxide and lithium carbonate.

# **Final Remarks**

The purpose of this work was to apply TEM analysis techniques to materials with potential for use in the future generations of batteries. These materials are highly electron beam sensitive. In order to obtain meaningful results, it is therefore necessary to use technique which minimize specimen exposure to the electron beam, or minimize the effects of such exposure on the final results.

Morphological information is gathered using electron beam tomography with golden ratio acquisition. This acquisition scheme, invented for tomography of transient process, had been effectively used in neutron beam tomography to minimize comma artefacts. Due to geometrical constraints in the TEM, a micro-pillar holder is required in order to use this acquisition scheme. Golden ratio acquisition was successfully conducted on a lithiated iron orthosilicate sample, and this regardless of the problems that occurred during the acquisition process. The sample shifted and finally was lost before the end of the planned run. Further investigations of this acquisition scheme is needed in order to add temporal information to the reconstruction, as was done in neutron tomography

Using the TEM to gather chemical information of lithium materials is a challenging problem. Other techniques, such as XPS, have been able to obtain compositional information about lithium, but the spatial resolution of these systems cannot resolve the thin surface layer of the material. STEM-EELS, which has good sensitivity and spatial resolution, has been found to impart significant beam damage on the sample. Therefore, SR-EELS has been found to be the best compromise of low dose and high resolution. Using this technique, it has been possible to distinguish the different layers of the lithium sheet. That is, the bulk metallic lithium, the transformed surface layer and the carbon protective layer deposited for sample preparation. Furthermore, the fine-structure of the various elemental edges are preserved, allowing further chemical analysis to be preformed. In order to properly analysis the chemical information carried by these fine structures, ab-inito simulation of the EELS spectrum of the material is needed.

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