4D Study of Silicon Anode Volumetric Changes in a Coin Cell Battery using X-ray Microscopy
Battery capacity is a key area of development that influences our everyday lives. To date, most work has focused on the electrochemical side. However, as the chemistry and geometry of batteries change, there is more and more emphasis on understanding microstructural changes. In this work, VARTA Microbattery examines how the ZEISS Xradia Versa can be used to evaluate volumetric changes in a silicon anode coin cell, a material which can provide tremendous capacity improvements but also presents new volumetric challenges versus today’s graphite anodes.

Introduction
Lithium Ion batteries provide energy for every day mobile life. Today’s communication, mobile self-monitoring, and entertainment choices would not be possible without the extensive development of lithium ion batteries over the last 20 years. Additionally, areas such as internet of things (IoT), smart cities, and large-scale energy storage are key drivers pushing capacity developments for batteries. Without continued—and potentially accelerated—capacity improvements, these megatrends could be delayed in reaching their full potential.

The history of commercially available lithium ion batteries started in the 1990s with Sony’s development of the Lithium Cobalt Oxide (LCO) cell. Over the last 25 years, cell capacity and energy density has increased stepwise by the implementation of new materials, better production processes, and higher efficiency in volume usage. Today, spirally wound 18650 batteries can easily reach energy densities of 700 Wh/l and more.

Paths towards increased cell capacity
To increase capacity in batteries today, two routes are possible: geometrical changes for more efficient volume use or chemical advances in the active materials. These are outlined in Figure 1 which, shows some of the key metrics involved with either approach, not least of which are performance and safety. Regarding chemical changes for the active material, silicon as an active material for the anode is under strong consideration. The advantage of silicon would be a large increase in specific capacity. In theory, silicon can provide up to 10X improvement over graphite. However, a major drawback with silicon is a substantial increase in volumetric change during charging and discharging, resulting in expected improvements of only ~1.5X to 3X over graphite—still substantial gains over today’s technology. In literature (e.g. Journal of Power Sources 196 (2011) 13–24), different possibilities have been discussed to solve the volumetric problem as changes during cycling need to be considered during the cell design. One possible route might be nano-structuring of active material which can enable much better coping of stress than bulk materials. A second route would be the use of composite materials, where dramatic volume changes of silicon can be buffered by a matrix material ensuring material grain integrity. In either case, understanding the microstructural evolution during charge and discharge will be key to optimizing a solution.

Approval Scenario

- Mechanical stability
- Permeability
- Safety
- Yield loss
- Self discharge
- Performance
- Processability

Volume usage
- Cell housing
- Dead space

Capacity enhancement

Materials
- Anode
- Cathode

- Safety
- Self discharge
- Performance
- Processability

Figure 1 Pathways for increased battery capacity
Increasing the energy density through greater volume efficiency is typically done by reducing dead space or reducing non-active electrochemical materials, e.g. optimization of separator thickness, current collector foil thickness, or thickness of housing material. All these changes require advances in fabrication process technology and are ultimately still limited by the chemistry for maximum charge capacity.

**Volume changes of active materials**
Numerous factors contribute to volumetric changes within a battery. Lithium intercalation, electrolyte wetting, and SEI growth all affect swelling of the active material. In current graphite based structures, this can result in an overall swelling of 12-15% under normal operation. Although silicon has great potential for increased charge capacity, the swelling can be in orders of magnitude more than graphite resulting in a very challenging environment for the engineering of the overall battery structure.

**Materials and methods**
The aim of this investigation was to observe the swelling effects of new anode materials, namely silicon. The underlying question was: how might cell design be affected by volume changes? To gain initial insight into this question, an investigation was carried out on VARTA CoinPower® CP1254, modified to have silicon as the active material in the anode. This rechargeable lithium ion coin cell has a diameter of 12 mm and a height of 5.4 mm. An example of this type of coin cell battery, along with larger form factor versions, is shown in Figure 2. In the current generation A3 (graphite anodes) capacity of cell is 60 mAh. VARTA’s first generation of Si based CP1254 A3 batteries are expected to have capacities of 75-80 mAh, allowing for ~20% longer run times between charges, a substantial improvement.

**High resolution tomography with XRM**
To observe volumetric change of the battery structure in a single coin cell, 3D tomographic data was collected using a ZEISS Xradia Versa. As shown in Figure 3, Versa utilizes microscope objectives, in a unique detector design, which decouples geometric magnification with resolution. This allows much greater flexibility than traditional CT, enabling such capabilities as Scout-and-Zoom and Resolution at a Distance (RaaD). Please see the ZEISS website for additional literature on these concepts and others XRM related topics.

The coin cell was imaged at different charge states: a) fresh activated cell, directly after electrolyte dosing, before formation; b) after first charge up to 4.2 V voltage level; and c) after first discharge down to 3.0 V voltage level. Utilizing Scout-and-Zoom on ZEISS Xradia Versa, an overview tomography was collected and then used to identify and navigate to a specific region of interest (ROI) for higher resolution imaging. For this study, the same ROI was imaged at each charge state of the coin cell. The overview scan was collected at ~5 μm voxel resolution over the entire sample using the flat panel extension (FPX) while the ROI scan was collected at ~2.5 μm voxel resolution utilizing RaaD and one of the microscope objectives. Figure 4 shows a volumetric rendering of the ROI scan (yellow) within the full overview scan (blue). Figure 5 provides a view from a single 2D virtual cross section of a high resolution scan. The exceptional contrast and resolution of Versa allows clear visualization of the different elements in the “jelly roll” structure.
Using Volume Graphics VGStudio MAX 3.0, displacement differences were calculated between the different charge states. VGStudio is especially suited to this type of analysis with its proven measurement capability as well as its capacity to handle large data sets. In this analysis, at times up to four data sets (20+GB) were loaded at the same time. As demonstrated in Figure 4, the ROI was positioned and indexed to the overview scan. After registering the position of the “0 V” (uncharged), “4.2 V” (initial full charge), and “3.0 V” (first discharge) high resolution ROI scan data, the displacement of copper foil between each state was calculated and visually represented. The copper foil was specifically chosen due to its high contrast which enabled easier tracking of displacement changes for each charge state.

**Results and discussion**

Figure 6 shows results of analysis between the uncharged state (“0 V”) to fully charged state (“4.2 V”). False color representations clearly show that displacement of the copper foil is a function of position in the jelly roll. The further away from center, the larger the displacement. Knowing that the center of jelly roll is a mechanical stable winding core, it seems to be quite obvious that swelling will lead to an increase in the jelly roll diameter and subsequent stress on the external housing.

Repeating the calculation from the fully charged state (4.2 V) to the discharged state (3.0 V), the false color representation reveals a more interesting behavior, shown in Figure 7. The outer layers do not seem to move at all, whereas the inner layers start to move away from the center. The expected contraction of layers, movement of outer layers back towards the center of jelly roll, does not occur. Instead the inner layers have continued to displace, presumably after some outer layer relaxation during the discharge.
Figure 7: Displacement mapping from initial charge to initial discharge. At this point, radial displacement occurs more prominently in the inner layers with displacements \(\sim \frac{1}{5}\) those of the initial displacements (\(\sim 20\ \mu\text{m}\)).

When examining the thickness of the anode coating layer by layer, another oddity was observed. In CoinPower® cells, a double side coated anode is used, as can be seen in detail picture Figure 8. During original production these layers are nominally the same thickness. The Inner electrode area is facing the center of the battery and the outer electrode area is facing the housing material. Interestingly, these layers do not stay equivalently thick depending on the charge or discharge state. It seems that during the first charge, the outer electrode increases in thickness, while the inner electrode does not change much. During the first discharge the outer electrode thickness decreases, but the inner electrode area will harvest some of the freed area and will expand. The first explanation for this observation might be the different forces on the particles in the coating—the inner coating is under compression, whereas the outer coating is under tension. What this ultimately means in long term performance and capacity needs to be further investigated.

Figure 8: Analysis of anode coatings show that thickness depends on which side of the foil, inner or outer, is being measured. As fabricated, these layers are nominally the same thickness.
Summary and future outlook
This study has shown the effectiveness of high resolution x-ray microscopy (XRM) to obtain meaningful and insightful volumetric information for the evaluation of new materials in Li-ion batteries. By utilizing the unique RaAD and Scout-and-Zoom capabilities of Xradia Versa, VARTA researchers were able to quantify displacement during initial charging and discharge cycles for a coin cell battery which had silicon as the primary anode material. The details learned have led VARTA to new insights, and new questions, all helping to advance battery development. This type of study opens the door for VARTA and other battery manufacturers to a better understanding of the complete battery system, not only the electrochemistry, but also the microstructural and volumetric changes.

Future work could include similar displacement studies throughout the battery life cycle, or effects of nano-structuring or composites on displacement. Non-destructive investigations of this type could also be expanded to other types of battery geometries, including pouch cell and larger jelly roll batteries such as 18650 cells. Regardless of the direction, the amount of new knowledge gained by such studies could catapult battery development to the next level, thereby advancing a number of socio-economic megatrends.

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