

## The use of analytical techniques to study battery chemistry

by Ernst Ferg, Department of Chemistry, Nelson Mandela University; and Nico Rust, uYilo, e-Mobility Technology Innovation Programme, Nelson Mandela University

**The increase in the sophistication of modern instrumentation and their ability to characterise a range of substances at almost the atomic level from gases, liquids and solids both qualitatively and quantitatively has led to the understanding of materials used in batteries at the fundamental level. The ability to characterise the materials that are used in the batteries, often in-situ, has contributed to the rapid improvement and performance of batteries in application in terms of its power ability per weight and its useful life in terms of capacity cycling and its recycling ability. There are also a range of electrochemical techniques available that try and close the gap between the chemical interpretations at the materials level to its actual electrochemical behaviour.**

Yet there are still gaps between the fundamental understanding of the chemical and electrochemical behavior of a battery system at the laboratory scale and its reproducibility within full scale manufacturing to its application as a final product for a range of uses. The capabilities of a particular cell can be reasonably well simulated and understood at the laboratory scale, where the challenges are often in the scaling up of the particular chemistry to large battery systems in series and parallel configurations.

In addition, the battery packs ability to work effectively within an application are often controlled by external factors such as charging and discharging limits and temperatures that have a profound effect of the performance and long-term durability in application. Where pre-mature failure is often ascribed to the poor performance of the battery with little consideration of the correct configuration of its working environment, which in some cases can have dire consequences in terms of causing explosions and fires.

Hence, understanding some of the basic and fundamental chemical processes involved in a battery and some useful interpretation of a material's analysis, the processes of manufacturing can be optimised and the way the battery is configured in application can be optimised for its longevity in application. The presentation aims at highlighting some of the modern techniques used in battery material analysis and some of the interpretation of results reported in typical scientific journal articles. The scaling up process to economic feasible industrial manufacturing plays an important role in the battery's performance in application and the limitations thereof. Some misinterpretation of certain battery terminologies that are typically encountered in application will also be looked at.

With the emerging of new technologies both in portable electronics and the transport sector, there is an accompanying emergence of energy storage devices to provide reliable energy and power. Even though energy storage devices such as batteries are but only one component of system, its ability to deliver the right energy has revolutionised the communications and transport industry and is playing a major role in the decentralisation of the electrical grid storage that is combined with renewable energy.

The understanding of the workings of the battery relies heavily on the traditional analytical and physical chemistry where a range of techniques would give insight into the material behavior within typical applications. These include the determination of the elemental composition of materials such as Inductive Coupled Plasma (ICP), Atomic Adsorption Spectroscopy (AAS) and X-ray fluorescence (XRF) to material phase composition using primarily X-ray powder diffraction (PXRD).

The qualification and quantification ability of the phase composition of the materials used in batteries has developed extensively with the availability of relatively large databases to identify the phases present as well as reasonably good quantification techniques that are widely used in a range of material related industries [1, 2]. Accurate quantification of the phases in powders should always be accompanied by good analytical practices that include the "spiking" with known pure phase or the accurate preparation of a set of standards with known amounts of the phases of interest. These procedures can often be challenging, when no pure chemical phases are available or when new materials are being developed with unknown crystal structures.

The speed and accuracy of the phase composition analysis of powders makes use of high speed computing and the development of user-friendly software that can do full pattern Rietveld refinement of the diffraction pattern [1, 2]. For example, in the quantification of the phases of pre-cursors used in the manufacturing of lead-acid battery plates (Fig. 1).

The analysis is done by using the crystallographic structural information of litharge (tetragonal or  $\alpha$ -PbO), massicot (orthorhombic or  $\beta$ -PbO) and Lead (Pb) and the instrumental parameters of the equipment. Reasonably good results are achieved, but care needs to be taken where there are crystallographic and material anomalies that are reflected in the diffraction pattern and should be taken into consideration when interpreting the results. These would relate to the type of material under investigation, in this case Pb, which is a strong absorber of X-rays.

The Pb in the sample, also referred to as free Pb is usually significantly higher in concentration when determined by wet chemical methods. This can be largely ascribed to the fact that the surface of the Pb particles are covered by its oxide. Hence, the diffracted X-rays would interact with the underlying actual Pb phase significantly lower and reflect this by a lower value in its quantification results. Also, the comparison between the actual and calculated diffraction pattern that is determined by the least squares Rietveld refinement (between  $27^\circ$  and  $37^\circ$  in Fig. 2), would show some differences which is shown by the difference line (grey) at the bottom of the pattern.

These differences are often due to the material and its crystalline characteristics that is contained within the structure of the phase. These could range from preferred orientation, lattice stress-strain and disorders that influence the crystalline phase and deviate from the pattern of an ideal crystallographic structure. The observed diffraction pattern is an average contribution of all the crystallographic and phase characteristics of the material studied and is influenced by the material's manufacturing conditions.

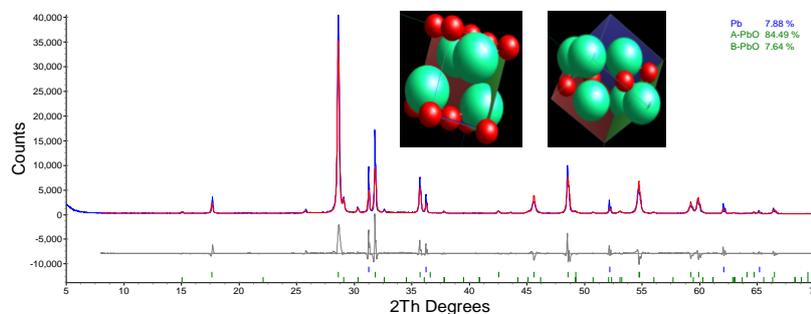


Fig 1. PXRD pattern of a pre-cursor Barton Pot lead oxide showing the quantification of lead and lead oxide phases using Topas® V5 full pattern Rietveld refinement. The two types of lead oxides phases typically found in the material is the Alpha (A) and Beta (B) phases respectively.

Other benefits of using the Rietveld refinement approach in material phase analysis is the ability to determine relative phase composition of material that contain amorphous material or partial crystal structural information. The technique is known as partial or no known crystal structure (PONKCS) and a diffraction pattern of corundum containing 50% amorphous silica is shown in Fig. 2 [3, 4].

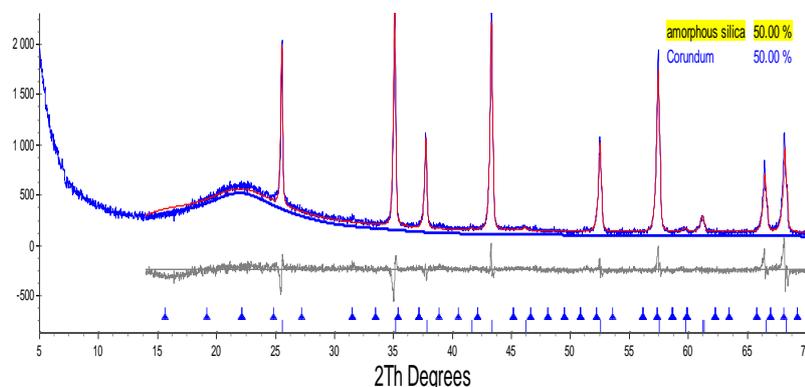
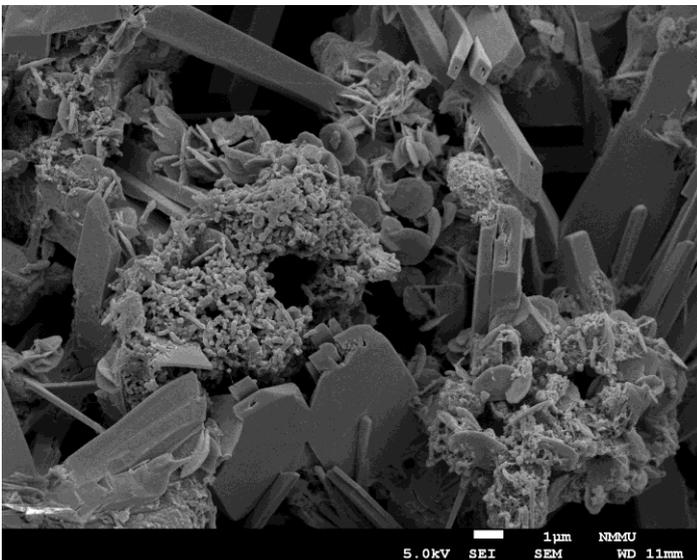


Fig 2. PXRD pattern of a 1:1 mixture of amorphous silica with crystalline corundum showing the amorphous halo. Quantification was done using PONKCS method [ref].

In developing materials for batteries, the focus would be on the respective cathode and anode material. Other properties of interest would be the particle size and surface area of the active material. These analyses would primarily be done by Laser particle size diffraction and BET surface area determination by nitrogen adsorption. In many cases, the analysis would not only be of interest of the final electro-active material, but also the pre-cursors that led up the final product. For some battery related materials, such as in the lead-acid battery, additional properties such as the porosity of the active material would be of interest.

In the past porosity determination was done using Mercury (Hg) porosimetry, however, with increasing health concerns regarding the use of Hg, even in analytical laboratories, these complications have prompted the need for the development of alternative, more environmentally friendly methods that can give the same information [6].

At the fundamental level, Scanning Electron Microscope (SEM) as well as Transmission Electron Microscope (TEM) analysis would look at the particular electrode active material features. For example, the dispersion of nano-carbon additives within the lead matrix of a negative plate used in Pb-acid batteries is shown in Fig. 3. However, these types of analytical equipment are expensive and usually located at universities or research institutions and require specialist operators.



*Fig. 3: Example of negative active material containing nano-carbon additives from a Pb-acid battery that was subjected to long term deep capacity testing. The image shows large rectangular shaped  $PbSO_4$  crystals amongst the plate like Pb crystals with the some clglomeration of carbon fibrous material.*

Within the field of electrochemistry, the levels of elemental contaminants or material purity becomes an important parameter when the process of scaling up the manufacturing of a large number of cells or batteries that are consistent in their performance. Besides the high levels of purity that is required for the electrode active cathode and anode materials, this is also required for the periphery components such as separators, current collectors, electrolyte and the battery housing.

Even small traces of impurities in the plastic battery case used in the manufacturing of the lead-acid battery such as chromium (Cr) can easily leach in to the battery during service and can contribute to excessive water loss. Challenges often occur during the scaling up of materials processing where the careful control of particle size, particle coating and surface area becomes difficult. Especially if some of these materials are made by using a batch process, where certain parameters such as heating and airflow become difficult to control uniformly across the bulk material that can range up to a few tons of material at a time.

For example, in the manufacturing of lithium-ion batteries, care needs to be taken in the use of organic based electrolytes where the contamination with water in the assembled cell can lead to unnecessary formation of corrosive acids such as HF gas during active use [5]. The challenge is often that when small amounts of a certain additive or coating had shown to be beneficial during research at the laboratory scale, but during the scaling up of such processes in manufacturing it does not always show the same level of benefit to a battery.

Besides the electrode material characteristics, the final battery or cell has to be understood within the context of its electrochemical performance.

Here, basic redox chemistry is required that describes and shows at the laboratory scale an understating of the basic electrochemical process. Some of the more common techniques used fall within the field of potentiometry. These include cyclic voltammetry (CV), Tafel plots and Electrochemical Impedance Spectroscopy (EIS). The analyses at the laboratory scale are usually done on small test cells such as CR2032 coin cells or custom-made 3-electrode cells that can incorporate a reference electrode.

True electrochemical performance should however be made on a full-sized cell or battery, which in the field lead-acid batteries is often done on a 12V starter lighting and ignition battery (SLI) or a cylindrical 18 650 cell when working with lithium ion battery material. These are usually linked to capacity performance analysis where there are various types of terminologies and units depending on the type of battery chemistry used. In general electrochemistry, the unit of capacity is in coulombs (C or Ampere.seconds).

Within the field of batteries, capacity is usually expressed in Ampere.hours (Ah). Of interest to battery developers, the material utilisation is usually determined in mAh/g or Ah/kg of active electrode material. Which can again be different to actual battery capacity or energy density in terms of Ah/kg of final battery's mass in an application. Sometimes of interest is the Ah/L of the battery in terms of its occupied volume. The capacity of the battery or cell is usually expressed at their respective  $C_n$  rate.

This can be written as  $C_1$ ,  $C_5$  or  $C_{10}$  which reflects the capacity over a specified discharge time "n". The discharge current (in Amps) is calculated by  $1/n \times C$ . Hence, 1C would be the current that is required to discharge the battery in 1 hour. The performance of a battery is also reported in terms of Energy Density (Wh/kg) which relates the achievable capacity of the battery at its nominal or average discharge voltage.

A more challenging parameter in the field of battery electrochemistry is the determination and reporting of the batteries state of charge (SoC), its depth of discharge (DoD) and its state of health (SoH). This relates to the amount of capacity that can be obtained from the battery within certain voltage limits. These limits are usually determined by the type of battery chemistry and in some cases the rate of discharge and temperature. Battery capacities are usually reported under ambient conditions with certain characteristics such as the cold cranking ability (CCA), performed at  $-18^\circ$  or  $-30^\circ\text{C}$  and very high discharge rates for very short periods of time.

The DoD is usually related to a percentage of the battery's complete capacity at a specified lower voltage limit. Hence, a 100Ah battery was discharged to only 50% DoD implies that the discharge was discontinued when the battery achieved 50Ah and is still within the lower voltage limits specified by the supplier. The recharge of the cell or battery is usually limited with certain upper voltages and current rates and is dependent on the type of chemistry and cell construction. For many years, the OEM would have their own battery experts which dictated to the battery manufacturer the relevant needs and requirements of the required product. This has allowed both the advancement of technology and the establishing of testing criteria for applications such as the recent Start/Stop use in vehicles in order to reduce the vehicles carbon emissions.

As a cell or battery is subjected to a variety of charging and discharging modes at various temperatures, it would be of interest to investigate the behavior of the material located at the anode and cathode as it undergoes the electrochemical changes. In an ideal system, the chemical changes at the anode and cathode should be perfectly reversible. Deviations of the electroactive material, the current collectors, the separators and electrolyte from the repeatable electrochemical process between charging and discharging mechanisms generally leads to the end of life of the battery and is of primary interest to researchers.

Factors such as active material volume change and subsequent loss in material integrity, corrosion of current collectors, degradation of electrolyte and the formation of passivation layers is typically studied. In addition, the factors that limit the rate at which ions can move through the active material or electrolyte is also of interest. Some of the electrochemical processes can be investigated by the use of a non-destructive technique such as electrochemical impedance spectroscopy (EIS), where the challenges are often around the interpretation of the resulting spectra in terms of the fitting of a suitable equivalent circuit model to the experimental data. In particular, EIS as a technique is able to

measure the ion diffusion kinetics of electroactive materials, where particle size, surface area and conductive coatings play an important role. Hence, when scaling up the manufacturing of electrode material, from a laboratory to large scale, the influence on the consistency of distribution and overall surface area of the material becomes important and such measurements that are done in the research laboratory should not be ignored.

Particle size distribution is also a parameter that can vary significantly when the material is not always homogenous and which can influence the hardness of relevant phases of material present and have an influence on how the material behaves in processing. Sometimes the relationship between surface area to particle size is not always straight forward, where particle pores and particle shape factors plays a role. Other particle sizing techniques such as SEM or TEM where visual measurements are taken from images is often not always a good representation as it only considers into consideration small part of the bulk material.

The conundrum is often around the relationship between life cycle ability of a battery in application to the number of capacity cycles the battery could perform under controlled conditions during testing. At a certain DoD and temperature, a battery supplier would report or specify the number of capacity cycles that can be achieved. The end of life or the number of capacity cycles are usually reported when the battery achieved 80% SoH. The SoH, which is the remaining capacity compared to the nominal capacity, is usually reported as a percentage.

The challenge is usually in relating the achievable number of cycles of a single or group of cells to a calendar year of a battery. Applications and usage of the battery can vary in terms of its DoD, the charging rate ability and whether the charging cycle could achieve the full state of charge or only partial. Temperature at which the battery was exposed to during both charge and discharge processes plays an important role. Once the group of cells are assembled into a battery pack, many new and additional factors start playing a role, which are sometimes outside of the actual battery chemistry and relates more to the engineering battery management system (BMS). The larger the battery (can range from 12 V to 400 V) the more complex the BMS.

The challenges are often around finding a relationship between a laboratory simulated test and the battery life during its intended application its expected calendar life upon storage. It is not always possible to simulate exact calendar life cycles where some applications have batteries that last up to 10 years or longer. Hence, accelerated type testing is done by changing the temperature, rates and cycle conditions. No “one size fits all” battery system exists, and therefore careful understanding of the applications is required and what the levels of tolerances in battery manufacturing should be for the particular battery exposed working conditions of the cells in a pack must be taken into account when developing such battery packs. In addition, consideration of the batteries’ exposure to abuse conditions that are outside of the supplier’s specification is not always apparent.

If cells or battery packs are exposed to physical or electrical abuse that it is not intended for, accidents can happen which can result in thermal runaways and cause fires or personal injury. Electrochemical abuse can take place by short-circuiting as well as over-charging or discharging the cell or battery. Temperatures of the cells in a battery are often not operating at the same temperature due to impedance differences, which has a significant influence on the performance and expected life in application. The use of modern BMS systems can easily monitor and manage temperature effects within a battery pack. Another example would be effect of cell balancing within a battery.

This is particular important in the use of Li-ion cells. Manufactured cells generally differs when applied at the micro and macro levels. Literature and suppliers usually report the performance of one cell and rarely give average performances from a group of cells or battery with certain confidence intervals and standard deviations. Nominal capacities of cells are usually reported in terms of the minimum expected capacity. Slight differences in effective capacity (Ah) can exist between cells within a large battery. These differences become important when the battery is discharged at different rates within specified voltage limits.

### **Examples and discussion**

As an example, the following study showed the performance of a 12V battery that was capacity cycled between set voltage limits. The battery consisted of four new 32 650 Li-ion cells (LFP) in series with a nominal capacity of 5 Ah. EIS analysis of each cell was done, showing their differences (Fig. 4) followed by discharges at different rates and a 1C charge rate (Fig. 5). The battery would discharge to a lower voltage limit of 10 V and be recharged to 14,5 V. The slight differences in the lower voltages limits of the individual cells during discharge is shown in Fig. 6

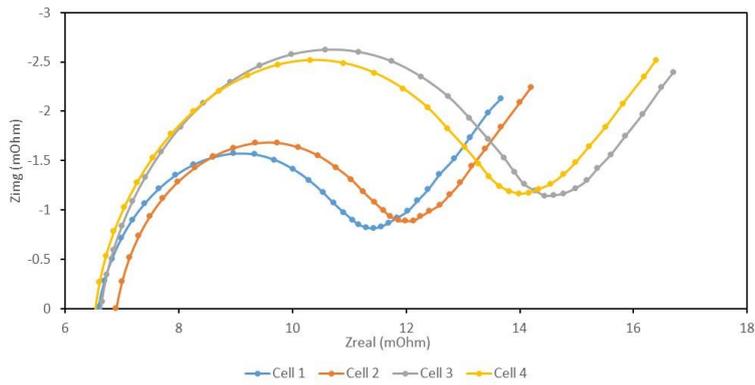


Fig 4: EIS spectra of 4 new LFP cells used in the assembling of a 12V battery showing differences in their impedance characteristics.

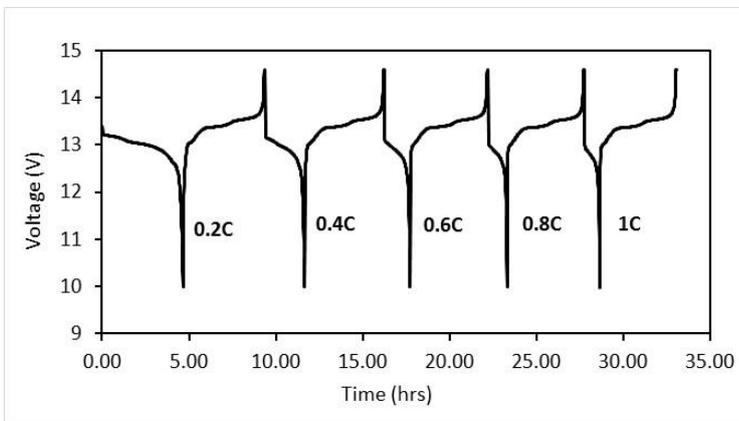


Fig 5: Capacity discharge and charge of the 12V LFP battery at different rates

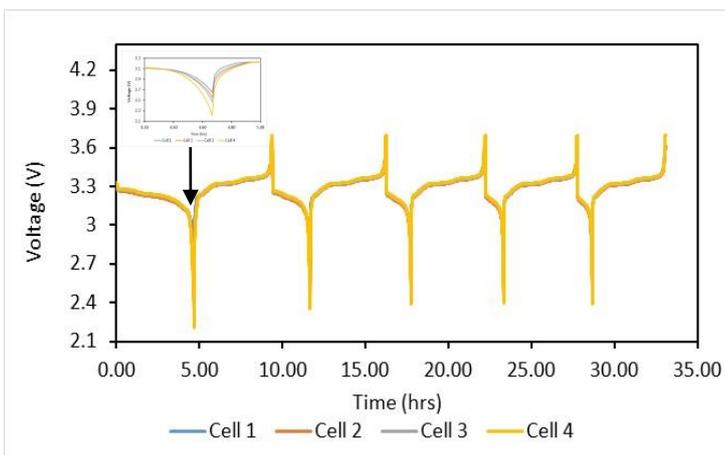


Fig 6: Individual cell voltages of the cells assembled in series showing the differences in end of discharge voltages between the cells

The battery was then connected to simple commercially available protection circuit board BMS (Fig. 7) that limited the discharge and charge voltage of each cell with in the battery. The circuit would stop the test once one of the cells had reached either the lower or upper voltage limits. Hence, the battery’s capacity would be limited by the cell that reaches

the lower voltage limit first. Upon capacity cycling, this would be shown by a slight capacity loss due to the limit of the recharging of the battery to its full capacity (Fig. 8), where a 2,4% loss in capacity was already observed after 65 cycles.

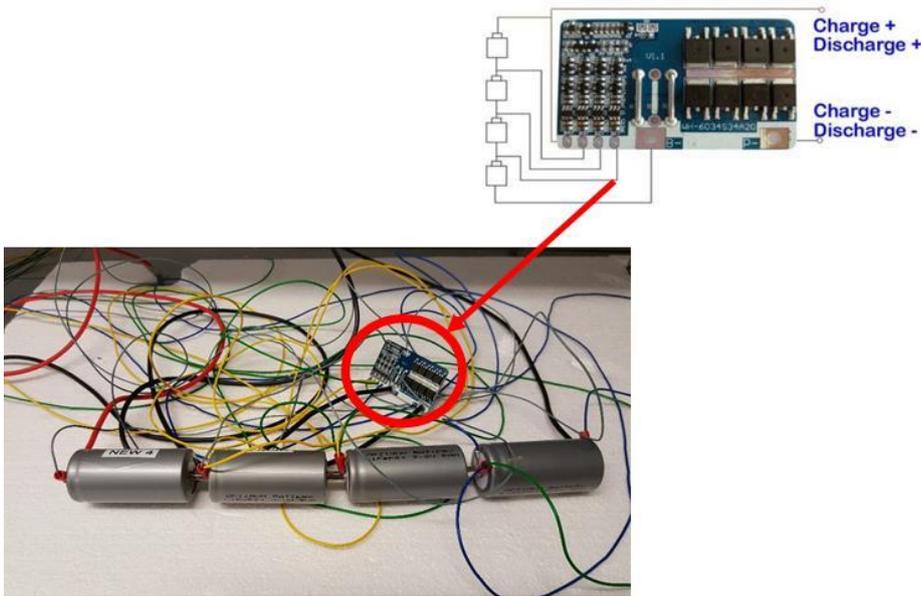


Fig 7: Assembling of the 4 LFP battery with a PCB BMS. Each cell's voltage was monitored during the capacity cycle test

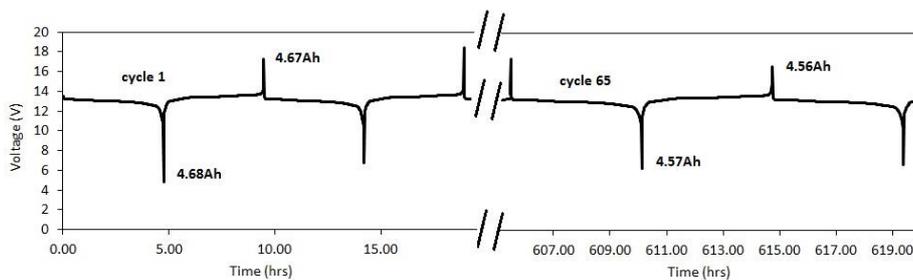


Fig 8: 1C Capacity cycle sequence over 65 cycles showing the slight loss in capacity of the battery connected to the CPB BMS

The effect of over discharging and overcharging a Li-ion cell was shown by subjecting an 18 650 cell to a life cycle sequence outside the supplier's specified voltage limits. The cell was capacity cycled at the 1C rate until failure (Fig 9) and the cell's surface temperature was monitored during the test (Fig. 10). An X-ray CT scanned image (Fig. 11) was obtained of the internal construction of the cell before and after failure. The Li-ion cell was a 2,5 Ah LNMCM with 4,2 V and 2,5 V, charge and discharge limits, respectively. The over charge and discharge were set at 4,7 V and 2 V respectively. The results showed how quickly the cell lost its capacity, which corresponded to the large increase in temperature. The internal damage caused the capacity test can be seen by the deformation of the electrodes which relates to the large increase in temperature that was measured on the surface of the cell. According to literature, the internal temperature at the core of the cell can vary by as much as 20°C when compared to the surface of the cell [7, 8].

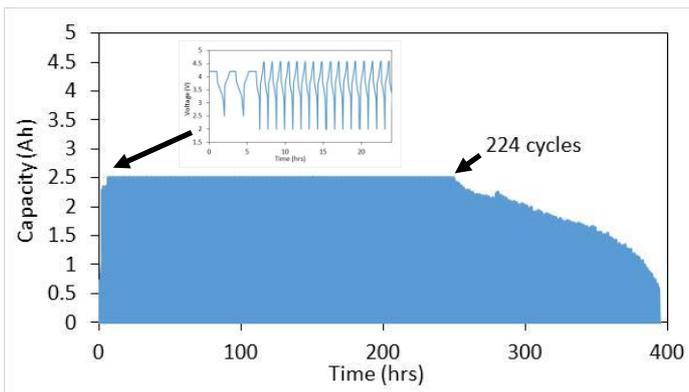


Fig 9: 18 650 cell was capacity cycled at the 1C rate outside the specified voltage limit until failure. The insert shows the first few cycles of the test

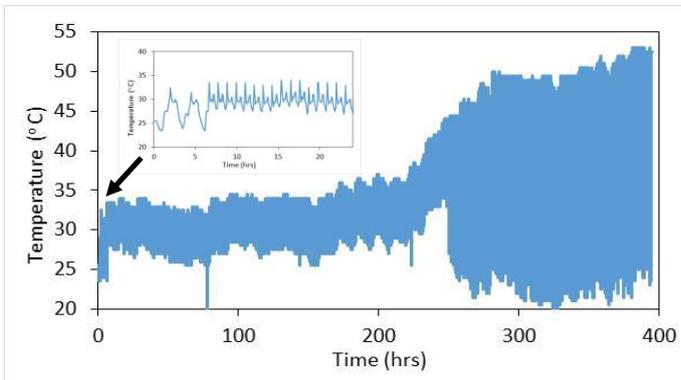


Fig. 10: The temperature change on the surface of the 18650 cell. The sudden increase in the temperature fluctuation corresponds to the loss in performance of the cell's capacity and ambient conditions.

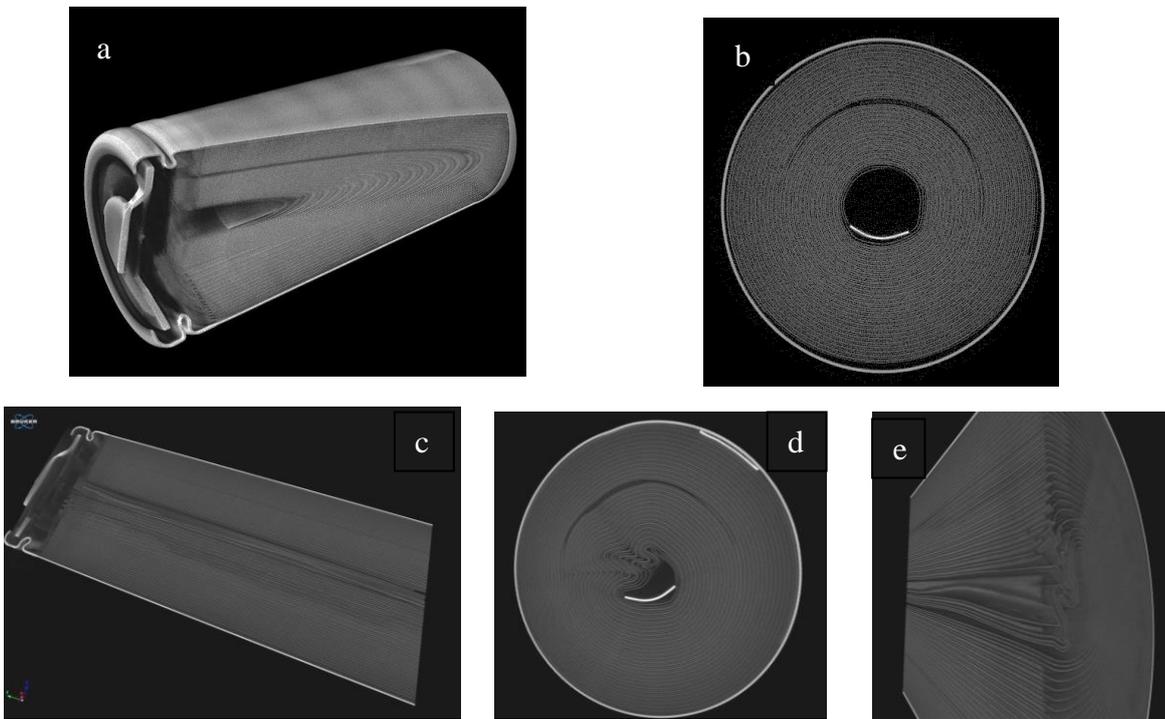


Fig. 11: X-ray CT scans of an 18650 Li-ion cell. (a) Vertical slice through a new cell; (b) Cross-section of a new cell showing “jelly roll” of electrodes and center current collector; (c) Vertical slice through aged cell; (d) Cross-section of aged cell showing internal damage; (e) Zoomed vertical section showing that delamination of active material and damage throughout the cell

### Conclusion

The field of battery chemistry and engineering covers a wide field of disciplines, where a range of analytical techniques are required to make sure that the cell or battery is compliant and consumer safety ensured. Each technique often requires further understanding of the material's properties to ensure careful interpretation of the result in application to the electrochemistry of a battery. In addition, good engineering practices are required to ensure the right configuration

of cells are combined to build the right battery for its intended “fit for use”. The influence of the external factors during application on the cycle life and chemistry needs to be taken into consideration, in order to enhance the performance of the battery over its intended lifespan.

## References

1. IC Madsen, NVY Scarlett, LMD Cranswick and T Lwin: “Outcomes of the International Union of Crystallography Commission on powder diffraction round robin on quantitative phase analysis: samples 1a to 1h”, *J App Cryst* 34(4); (2001) 409–426.
2. F. Guirado and S. Galf: “Quantitative Rietveld analysis of CAC clinker phases using synchrotron radiation”, *Cement and Concrete Research*, 36; (2006) 2021–2032.
3. EE Ferg and B Simpson: “Using PXRD and PONKCS to determine the kinetics of crystallisation of highly concentrated  $\text{NH}_4\text{NO}_3$  emulsions”, *J. Chem. Crystallogr* 43; (2013) 197-206.
4. NVY Scarlett and IC Madsen: “Quantification of phases with partial or no known crystal structures”, *Powder Diffraction* 21(04); (2006) 278–284.
5. U Heider, R Oesten and M Jungnitz: “Challenge in manufacturing electrolyte solutions for lithium and lithium ion batteries quality control and minimising contamination level”, *J Power Sources*. 81; (1999) 119-122.
6. EE Ferg, P Loyson and N Rust: “Porosity measurements of electrodes used in lead-acid batteries”, *J. Power Sources* 141(2); (2005) 316-325.
7. MR Palacín and A de Guibert: “Why do batteries fail?”, *Science* 351(6273); (2016) 1253292.
8. T Waldmann, S Gorse, T Samtleben, V Knoblauch and M Wohlfahrt-Mehrens: “A mechanical aging mechanism in Lithium-Ion Batteries”, *Electrochem. Soc* 161(10); (2014) A1742-A1747.

Contact Ernst Ferg, Nelson Mandela University, Tel (041) 504-3160, [ernst.ferg@mandela.ac.za](mailto:ernst.ferg@mandela.ac.za)