

Application Note: An Ultra-High Precision Coulometry Study of Solid-State Batteries

Connor P. Aiken¹, Yadong Huang, and Andrew van Bommel

NOVONIX Battery Technology Solutions, 177 Bluewater Road, Bedford, Nova Scotia, B4B 4H4, Canada

Ultra-high precision coulometry (UHPC) and associated battery cell testing techniques requiring precision and accuracy beyond the capabilities of conventional testers are typically used to quickly assess lifetime capability and cell performance. The need for ultra-high precision and accuracy is often mistakenly thought of as only necessary when studying cells with very, very long lifetimes, and therefore only applicable to conventional Li-ion cells containing liquid electrolyte and graphite anodes. The value of applying UHPC testing to cells with a solid-state electrolyte is demonstrated. This includes a characterization of cell performance, investigation of degradation mechanisms, and providing insight into assembly quality and outlier behaviour.

Lithium-ion batteries (LIBs) have become the cornerstone of modern energy storage systems, enabling the widespread adoption of portable electronics, electric vehicles (EVs), and renewable energy integration. Despite their success, conventional LIBs face critical challenges, including safety concerns, limited energy density, and the environmental impact of liquid electrolytes. To overcome these limitations, the development of solid-state lithium-ion batteries (SSLBs) has garnered significant attention due to their potential to offer enhanced safety, higher energy density, and improved thermal stability [1–3].

One of the most promising avenues for advancing SSLB technology lies in the incorporation of solid-state electrolytes (SSEs). SSEs eliminate the flammability risks associated with liquid organic electrolytes, offering a pathway to safer batteries [4,5]. Furthermore, their ability to suppress lithium dendrite growth can enhance the cycling stability of lithium-metal batteries [6,7]. Among the various types of SSEs, ceramic-based electrolytes, such as garnet-type (Li₇La₃Zr₂O₁₂) and sulfide-based (Li₁₀GeP₂S₁₂) materials, have emerged as leading candidates due to their high ionic conductivities and chemical stability [8–10]. However, challenges such as poor interfacial compatibility and mechanical rigidity remain significant barriers to widespread adoption [11,12].

Solid-state electrolytes and advanced anodes, such as lithium metal and alloying materials, presents a compelling synergy for nextgeneration SSLBs. The rigid nature of SSEs has the potential to mechanically constrain anode morphology or expansion while maintaining a stable electrochemical interface, thereby mitigating degradation mechanisms [13,14]. However, typical implementations have several hurdles to overcome, including the formation of high-resistance solid-electrolyte interphases (SEIs) and interfacial delamination [15].

Recent advances in material engineering and processing techniques have begun to address these issues. For instance, coating strategies such as atomic layer deposition (ALD) and the use of artificial interlayers have shown promise in stabilizing the anode/SSE interface [16,17]. Furthermore, the development of flexible and ductile SSEs has facilitated better mechanical properties, conformity and accommodation of anode volume change [18,19]. These advancements indicate the potential of advanced anodes with next-generation solid-state electrolytes to achieve high-performance SSLBs with long cycle life and superior energy density [20,21].

As battery technologies advance, the need to apply improved test methods increases to continue development. This is due to both degradation mechanisms becoming more complex and convoluted, while improvements tend to deliver smaller relative performance improvements as time goes on. Ultra-high precision coulometry (UHPC) and associated ultra-high precision charging and discharging techniques, that are capable of high-resolution study of many battery technologies, can identify subtle underlying differences and direct future development.

This paper explores the application of UHPC testing to cells with lithium as the working ion and featuring solid-state electrolytes. It demonstrates the understanding that can be gleaned from brief but effective testing with ultra-high precision testing equipment and the value UHPC testing provides to both established and emerging battery technologies. This places UHPC as an integral and necessary piece of test equipment to the ongoing efforts to develop commercially viable SSLBs and other next-generation lithium and beyond lithium battery chemistries.

Experimental

Cells.—Demonstration scale pouch cells, of nominal capacity 7 mAh, were produced with a layered transition metal oxide cathode, an undisclosed anode and an undisclosed solid-state electrolyte. Cells were prepared for testing using a typical formation procedure. Formation and testing were completed with cells mechanically constrained under plate-and-spring cell fixtures to ensure adequate pressure was maintained on the electrode stack for optimal performance.

Test Hardware and Protocol.—Testing was conducted using a 2A NOVONIX UHPC System. Fixtured cells were connected to NOVONIX pouch cell holders, inserted into a NOVONIX 16-position thermal chamber and finally connected to the UHPC system. All testing was completed at a temperature of $25^{\circ}C \pm 0.2^{\circ}C$.

Cells were divided into three test groups and testing was divided into two rounds. The three test groups were specified by three sets of cycling voltage limits: (a) 2.0-4.2 V, (b) 2.0-4.1 V, and (c) 2.5-4.2 V. The two rounds of testing were specified by the cycling current or rate, where the cells were cycled in the first round at a rate of C/10, and in the second round at a rate of C/5. In both rounds, charging was conducted in a CCCV sense, where the cell voltage was held constant when the charge voltage limit was reached until the current diminished to a value of C/20. 10 cycles were completed in the first round and 25 cycles were completed in the second round to yield approximately the same test duration per round.

Results and Discussion

Round 1.—Figure 1 shows a summary of conventional cycling metrics for the first round of testing. Specifically, Figures 1a and 1c show the discharge capacity and the fractional discharge capacity (often referred to as state of health) plotted against the cycle number, respectively. Both cells that charge to 4.2 V deliver approximately 6% more capacity than those that charge to 4.1 V. This is due to the

¹E-mail: <u>connor.aiken@novonixgroup.com</u>



Figure 1. Summary of conventional cycling metrics measured during C/10 cycling at 25 °C. (a) Discharge capacity, (b) fractional discharge capacity, (c) ΔV (the difference between the average charge and discharge voltage) and (d) fractional ΔV growth are all plotted versus cycle number. Cells were divided into three test groups based on discharge and charge voltage limits, as indicated in the legend.

sloped nature of the cathode voltage-capacity relationship, allowing more capacity to be stored as the charge voltage is increased. The difference of lower voltage limits of 2.0 V and 2.5 V did not yield a noticeable difference in capacity, likely due to both the cathode and anode being nearly fully discharged by 2.5 V, and very little capacity remains between 2.0 V and 2.5 V.

Figure 1c shows that cells that discharge to 2.0 V have lower rates of fractional capacity fade, or better capacity retention, indicating less lithium inventory loss, perhaps due to a more stable anode-electrolyte interface that consumes less charge per cycle to maintain an adequate passivation layer. When a linear rate of capacity fade is assumed, both cells that discharge to 2.0 V project to yield a cycle life of approximately 1000 cycles, which is an impressive achievement, on par or exceeding conventional Li-ion cells that have liquid electrolytes and are designed for extremely high energy or power density, not lifetime.

Figures 1b and 1d show the quantity ΔV (or Delta V) and fractional ΔV growth versus cycle number, respectively. ΔV is computed by taking the difference between the average charge voltage and the average discharge voltage. It represents a measure of the average polarization of the cell during cycling and is typically reported as a proxy for the cell impedance. Larger values of ΔV tend to indicate higher cell impedance. ΔV was higher for the cells discharged to 2.0 V for all cycles tested in round 1. This suggests that there may be a small amount of capacity that is accessed at very low voltage and is accompanied by reduced kinetics.

Figure 2 shows the coulombic efficiency (CE) versus cycle number. The CE is the ratio of capacity discharged from the cell to the capacity charged into the cell. It is a metric that quantifies the fraction of processes happening in the cell that are associated with reversible charge storage. Any deviation of the CE from 1 (specifically < 1) represents the presence of side reactions that may cause excessive charge capacity or diminished discharge capacity.

The CE for cell groups that discharge to 2.0 V is notably higher (with the exclusion of outliers) than the cell that discharges to only 2.5 V. This correlates well with the capacity retention reported in Figure 1c, because CE has contributions related to the capacity retention, but detailed discussion of this follows in the subsequent paragraphs.



Figure 2. Coulombic efficiency, measured during C/10 cycling at 25 °C, versus cycle number. Cells were divided into three test groups based on discharge and charge voltage limits, as indicated in the legend.

Contrary to common misconception, the CE alone is not inherently predictive of how the capacity of a cell will unfold under continuous cycling in a laboratory setting, or continuous usage in a certain application. It also does not indicate the origin of the underlying mechanisms leading to inefficiencies. The processes that cause the CE to be less than 1 can be categorized as those causing capacity to be irreversibly consumed at the anode, resulting in higher capacity fade, and those causing capacity to be generated at the cathode, resulting in higher charge endpoint capacity slippage. These two quantities represent undesirable side reactions that are not associated with reversible charge storage, and as such are thought of as inefficiencies in the cell. When the CE is 1, the capacity fade and the charge endpoint capacity slippage are normally 0.



Figure 3. (a) Discharge capacity fade and (b) charge endpoint capacity slippage, measured during C/10 cycling at 25 °C, versus cycle number. A discussion of the meaning of these metrics can be found in the accompanying text. Cells were divided into three test groups based on discharge and charge voltage limits, as indicated in the legend.

Figure 3a and 3b show the discharge capacity fade and the charge endpoint capacity slippage versus cycle number. The discharge capacity fade can be computed from the difference in discharge capacity between consecutive cycles. In this sense, it can be thought of as the amount of capacity lost per cycle. Figure 3a shows that cells that discharge to 2.5 V, rather than 2.0 V, have higher capacity fade. This corresponds to the low CE results for the same group that are shown in Figure 2, because as discussed, capacity fade measures inefficiencies that consume charge at the anode, which contribute to CE being less than 1. Similarly, the results in Figure 3a are higher resolution representation of the results in Figure 1a and 1c. A linear projection of cycle-life can be made using the steady-state capacity fade values obtained after 10 cycles as the slope. For the two cells discharged to 2.0 V, this projection would correspond to approximately 1000 cycles, which agrees with what was previously discussed, based on the results Figure 1. Close inspection of the data would possibly suggest that the 2.0-4.1 V group has slightly lower capacity fade, and although the difference to the 2.0-4.2 V group is minimal, it is measurable and clear using a UHPC. A suggested approach to determine if this subtle difference is true would be to increase the aggressiveness of the test to see if this difference would broaden. This could be through increased cycling rate, or increased temperature. Additional cycles or duplicate cells could also improve a statistical approach to confirming this difference.

The charge endpoint capacity slippage is computed by taking the difference in capacity at the end of the charge step for consecutive cycles, when capacity is tracked cumulatively from the beginning of test. It quantifies excess charge capacity due to mechanisms occurring at the cathode such as electrolyte oxidation or transition metal dissolution. These processes are independent to steady-state capacity fade processes and as such, their effects are not readily observed in conventional cycling data until the onset of sudden failure. High charge endpoint capacity slippage is typically an indicator that sudden and unexpected failure modes will occur after some period of seemingly innocuous or benign cycling. Figure 3b shows that the charge endpoint capacity slippage for all cells is essentially the same.



Figure 4. Summary of conventional cycling metrics measured during C/5 cycling at 25 °C. (a) Discharge capacity, (b) fractional discharge capacity, (c) ΔV (the difference between the average charge and discharge voltage) and (d) fractional ΔV growth are all plotted versus cycle number. Cells were divided into three test groups based on discharge and charge voltage limits, as indicated in the legend.

This indicates that the difference between charge voltage limits of 4.1 V and 4.2 V does not cause increased reactivity between the solidstate electrolyte and the cathode or induce other problems with the cathode. The value of the charge endpoint capacity slippage after 10 cycles is at least a factor of 2 higher than the discharge capacity fade, indicating higher rates of parasitic reactions occurring at the cathode.

Round one of testing revealed that lower discharge voltage limits are accompanied by improved CE as a result of lower capacity fade. The lower capacity fade translates to improved cycle-life, which, when projected linearly, can be predicted as approximately 1000 cycles. This is under the specified test conditions of 25 °C and C/10 rate. All cells showed identical charge endpoint capacity slippage, indicating excellent electrochemical stability of the solid-state electrolyte against the cathode. Overall, the cells yield competitive cycling results, and degradation is capacity fade dominant, and therefore improved performance is likely best directed into improving anode and/or anode-electrolyte stability.



Figure 5. Coulombic efficiency, measured during C/5 cycling at 25 °C, versus cycle number. Cells were divided into three test conditions based on discharge and charge voltage limits, as indicated in the legend. Data is plotted on (a) an expanded scale to show all cells, and (b) on a zoomed scale to resolve fine differences that are close to CE = 1.

Round 2.—The execution of the second round of testing was carried out in the same manner as round 1, therefore results are communicated in the same order and formatting. Cells that completed round 1, where cycling was completed at C/10, were used in the same test groups for round 2, where cycling was completed at C/5. To simplify the discussion, certain results in Round 2 that are unchanged from Round 1 will not be mentioned.

Figure 4 shows a summary of conventional cycling metrics for the first round of testing. Specifically, Figures 4a and 4c show the discharge capacity and the fractional discharge capacity (often referred to as state of health) plotted against the cycle number, respectively. It was previously mentioned in the discussion of Figure 3a, that the 2.0-4.1 V group had slightly lower capacity fade that the 2.0-4.2 V group but that this difference was difficult to resolve without taking a statistical approach or changing an experimental parameter to broaden the difference. Figure 4c shows that when cells are cycled at C/5, cell cycled between 2.0-4.1 V show better fractional capacity retention than the cells in the 2.0-4.2 V group, where they had capacity retention that was seemingly the same when cells were cycled at C/10. This better capacity retention for the 2.0-4.1 V group in turn would correspond to lower capacity fade, as was identified in the discussion of Figure 4a. Like in Round 1, the 2.5-4.2 V group has the worst capacity retention, again indicating some benefit to a lower discharge voltage limit.

Figure 4d shows that when the cycling rate is increased to C/5, cycling between 2.0-4.2 V causes the highest rate of fractional ΔV growth. This contrasts with Round 1, where all groups showed the same fractional ΔV growth (see Figure 1d). The combined results of the 2.0-4.2 V condition showing worse capacity retention and increased fractional ΔV growth relative to the 2.0-4.1 V condition, where no differences existed in Round 1, indicates possible instability that occurs at higher voltage and is exposed by high rate. This would likely be slight impedance growth that in turn causes reduced apparent capacity. To be clear, increased impedance (or internal resistance) does not cause true capacity loss, where lithium inventory is consumed and cannot be cycled. It simply causes the cell capacity to be less accessible within a fixed voltage window due to reduced kinetic performance.

Figure 5 shows the CE vs cycle number, where Figure 5a shows an expanded scale, while Figure 5b shows the same data with a scale zoomed in to the region much closer to 1. The cell cycling between 2.0-4.1 V shows significantly lower CE, around 0.995, than the other cells, which are around 0.9995. This low CE, accompanied by a loss of smoothness in the CE data indicate this cell cycling with 2.0-4.1 V limits may be suffering from assembly issues. It is unclear without further investigation if the assembly quality is exposed by higher rate cycling or simply manifests after a few cycles and were therefore not exposed during Round 1 testing. It is common that UHPC metrics such as low CE, specifically underscored by high charge endpoint capacity slippage, can quickly indicate quality control issues. This cell is likely just an outlier, and increased sample size is necessary to determine a distribution that can assess true build quality. As previously mentioned, high charge endpoint capacity slippage (and associated lower CE) is not always correlated with rates of steadystate capacity loss measured during continuous cycling.

Figure 5b shows that the cell cycling with 2.0-4.2 V voltage limits has higher CE than the cell cycling between 2.5-4.2 V. This is connected to lower capacity fade that was implied in the discussion of capacity retention shown in Figure 4. Worse capacity retention for the cell cycling between 2.5-4.2 V corresponds to higher capacity fade and in turn, lower CE.

Figures 6a and 6b show the discharge capacity fade and the charge endpoint capacity slippage versus cycle number. The cell that is cycling between 2.0-4.1 V, having previously been mentioned to have possibly assembly quality issues is off scale in Figure 6b and therefore not shown. Again, this is an example of high charge endpoint capacity slippage being a quality control indicator. This is most easily seen in the data in Figure 6a for the two cells in the 2.0-4.1 V. The average values for capacity fade shown in Figure 6a are generally the same value as those seen in Figure 3a. This implies that capacity fade is mostly occurring at the same rate each cycle, regardless of the time each cycle takes. Materials that undergo large structural and morphological changes each cycle tend to have a strong cycle-based contribution to capacity fade due to the cyclic nature of the expansion. Examples of this include metallic and alloying anodes. It is quite possible that in this case, where the capacity fade seems almost entirely cycle-dependent, that there is little to no lithiumconsuming reactivity between the solid electrolyte and the anode, and that capacity fade is just due to mechanical degradation of the anode.



Figure 6. (a) Discharge capacity fade and (b) charge endpoint capacity slippage, measured during C/5 cycling at 25 °C, versus cycle number. A discussion of the meaning of these metrics can be found in the accompanying text. Cells were divided into three test groups based on discharge and charge voltage limits, as indicated in the legend.

Figure 6b shows the charge endpoint capacity slippage versus cycle number for the second round of testing. The results for cells cycling between both 2.0-4.2 V and 2.5-4.2 V are nearly identical, which is expected due to the fact that the cells contain the same cathode, charge to the same upper voltage limit and charge endpoint capacity slippage is typically associated with parasitic reactions happening at the cathode.

The cell cycling between 2.0-4.1 V, as previously stated, had excessively low CE due to high charge endpoint capacity slippage that is off scale in Figure 6b, and in this sense is very useful as a rapid screening tool for manufacturing and assembly quality control. Charge endpoint capacity slippage is connected to a number of underlying mechanisms. Examples such as soft shorts and anodically unstable contamination can easily be connected to manufacturing issues. In the case of the former, a soft short will contribute to extra capacity, not associated with energy storage, flowing during the charge step. With the latter, oxidation reactions of contaminants can donate electrons to cathode and be counted as excess capacity during the charge step. If said contaminants exhibit shuttling behaviour, this excess capacity will be measured continuously, each cycle during charging. Of the metrics commonly reported during coulometry experiments, charge endpoint capacity slippage is the most demanding on charger precision and accuracy, to the extent that it is impossible to measure with low quality instruments. This highlights the value of NOVONIX UHPC and high precision and accuracy coulometry as part of any battery quality control program

Generally, the results of Round 2 reaffirm what was previously discussed in Round 1. The primary failure mode appears to be related to the longevity of the anode active material. A variety of approaches, namely UHPC metrics like CE and capacity fade, along with careful examination of volage curves support this. It can again be echoed that improvements to the anode seem like a logical next step for improving the cycle-life of these cells. Comparing the results from this round with the prior, it appears that the degradation in these cells is primarily cycle-based. This may direct development towards controlling morphology, volume expansion and physical resilience, or similar approaches.

Conclusion

NOVONIX has demonstrated the application of ultra-high precision and accuracy testing to batteries containing solid-state electrolytes. This represents a system typically thought of as next-generation, but the results reported here suggest that the technology is closer to commercialization than may be implied by the latest academic research or mainstream media publications. Cycle-life approaching 1000 cycles is projected and operation at room-temperature with rates of up to C/5 is demonstrated.

UHPC testing, specifically using a NOVONIX UHPC system, is shown to not only rapidly provide valuable information about cell performance and degradation characteristics, thereby guiding development, but also can be used as a tool for assessing build quality with only a small amount of data.

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