

Screening Graphite Materials for Lifetime Based on UHPC Measurements of Parasitic Current in Half Cells

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Introduction

Conventional Ultra-High Precision Coulometry (UHPC) testing involves constant-current cycling between an upper and lower voltage limit, while metrics like the coulombic efficiency (CE) gradually approach a steady-state value. This is often performed on full cells and requires long test times, particularly with cells that are tested at beginning of life. Changes in cell chemistry or processing are typically ranked by which results in superior UHPC metrics, such as higher CE. Figure 1a shows the CE measured as a function of cycle number for two cells constructed with the same cathode and a different negative electrode. After 25 cycles of testing at a rate of C/20, it is clear that the cell type containing "Anode #1" has a higher CE and therefore should yield a longer service life in the field. Obtaining this result, while very useful, requires 800 to 1000 h of testing, which identifies the need for complementary test methods with higher throughput.

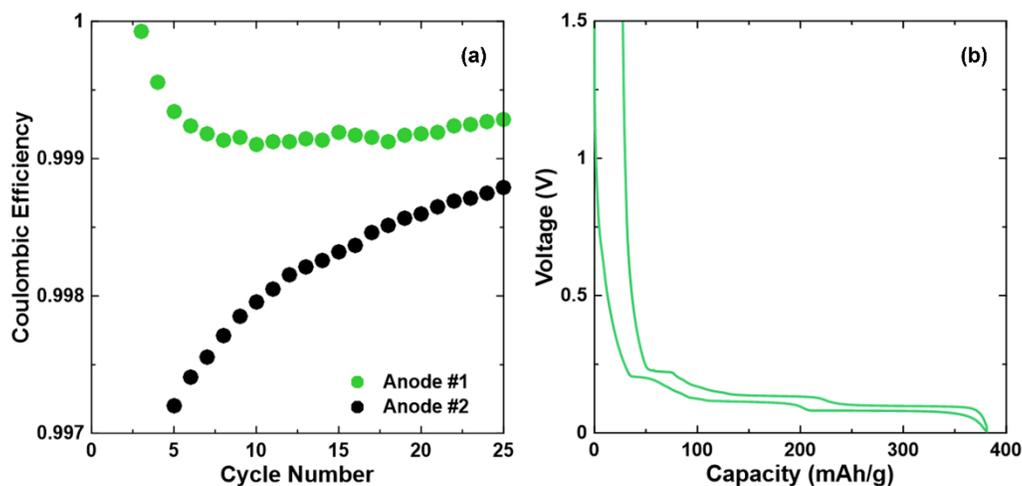


Figure 1. (a) Coulombic efficiency versus cycle number for full cells containing identical cathodes and different anodes. (b) Voltage versus specific capacity for an anode half cell.

Electrochemical screening of active materials, in its simplest form, is typically achieved by measuring the first cycle lithiation and delithiation capacity in half-cells and calculating a corresponding

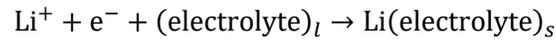
first cycle coulombic efficiency (FCE). Figure 1b shows the voltage-capacity curve of a graphite anode, measured versus a lithium foil counter electrode in a half coin cell. The information obtained in this type of testing can be useful for cell design, computing initial energy density and requires approximately 20 h. It does not, however, offer information that can help in making lifetime predictions for when the active material is used in full cells. Metrics like CE measured in half cells are usually obscured by the near-infinite lithium inventory of lithium foil that is accessible each lithiation. Typically, lifetime predictions are made and confirmed based on data collected in full cells. This is accompanied by the time and expense of a full cell build, along with lengthy full cell testing times.

Many of the best active materials for Li-ion cells (e.g., single-crystal $\text{Li}[\text{Ni}_{1-x-y}\text{Mn}_x\text{Co}_y]\text{O}_2$, synthetic graphite) show degradation that is largely time-dependent rather than cycle-dependent. The act of cycling a cell containing these materials allows for the calculation of per cycle metrics but does not add to the degradation. For such materials, in addition to time, the degradation is both temperature and voltage-dependent. By implementing constant-voltage holds at full state of charge, the cathode remains at high potential and the anode remains at low potential, where they are respectively most reactive towards the electrolyte.

The method presented here is designed to allow a quantitative ranking among different materials to be made from tests on coin half cells, that can be translated to form a qualitative lifetime prediction in full cells. This facilitates high throughput, laboratory scale testing that can respond quickly to material developments without requiring the assembly of full cells, which often requires access to pilot scale facilities.

Theory

Electrolyte reduction can occur at a charged negative electrode can, consuming active lithium, according to many reactions. A generic reaction that describes the irreversible reduction of lithium to form solid products, such as the solid electrolyte interphase (SEI), is given by the equation below.



The formation of a robust SEI offers passivation at the negative electrode surface that ideally prevents further Li-consuming reactions altogether. As the negative electrode intercalates increasing amounts of Li (as $x \rightarrow 1$ in Li_xC_6), the potential decreases towards 0 V and the above reaction becomes thermodynamically more favorable, thus increasing the passivation demands.

Conventionally, graphite half cells are often lithiated until the voltage reaches 5 mV, which is selected as a compromise between fully lithiating the graphite while avoiding lithium plating, which occurs at 0 V. If the cell voltage is held at 5 mV, the current can be described as

$$I(t) = I_{eq}(t) + I_{mat}(t) + I_p$$

where I_{eq} is the current required to reach an equilibrium, fully lithiated phase due to the kinetic limitations of the cell and of the graphite used; I_{mat} is the current associated with the time dependent maturation of the SEI; and I_p is the parasitic current associated with electrolyte reactions due to imperfect passivation of the SEI. This mathematical treatment ignores the contributions of shuttling or similar mechanisms that may lead to situations conventionally described as self-discharge or leakage current. These mechanisms may be captured withing I_p . Both I_{eq} and I_{mat} should tend to zero given sufficient time as the active material reaches equilibrium and the SEI reaches maximum maturity. Therefore, in the limit of long times holding at 5 mV, the current measured simplifies to

$$\lim_{t \rightarrow \infty} I(t) = I_p$$

The passivation current, I_p , should depend on the temperature of the experiment, the electrolyte formulation, and properties of the graphite (e.g., surface area, particle shape, synthetic versus natural graphite, etc.). I_p can also be interpreted as an upper limit on the time rate of capacity fade due to lithium consumption at the negative electrode. This hypothesized upper limit assumes that a graphite electrode is more strongly reducing at higher fractional lithiation. In the testing presented here, the graphite is fully lithiated over the entire experiment, whereas in conventional testing, the graphite continuously cycles between fully lithiated and delithiated. The time spent in the delithiated or partially lithiated states should be less reactive and hence contribute to lower rates of parasitic lithium consumption. The connection to capacity fade can be easily understood via unit analysis, where the unit of current, in this case mA, can be written as mAh/h which may be thought of as capacity loss per unit time.

If the same temperature and electrolyte formulation are used throughout a series of experiments, measuring I_p , or more specifically the parasitic current per unit active mass, I_p/m_A , for many graphite half cells with different active materials should then allow for a ranking of those active materials. That ranking, by parasitic current, can then be correlated to capacity fade when each graphite is used in a full cell and aid material selection and design choices.

Methods

For this work, 2032-sized coin graphite half cells were assembled from hand coated electrodes. Slurries were prepared with graphite, carbon black, sodium carboxymethyl cellulose (CMC) and styrene butadiene rubber (SBR) combined in either 94.5/1.3/1.4/2.8 or 95.6/1.0/1.1/2.3 mixtures, by weight. Slurries were mixed in a Mazerustar KK 250S planetary mixer. Slurries were coated onto 10 μm Cu foil using an adjustable height doctor blade, with drying applied by heating the coating bed to 60 °C. Coating weight varied from sample to sample but were generally $>10 \text{ mg/cm}^2$. Electrodes were compressed to approximately 1.5 g/cm^3 and dried for 8 h at 130 °C under vacuum to remove residual moisture.

Circular coin cell electrodes were made from each electrode sheet with a 13.00 mm diameter using a Nogami punch and transferred to an Ar-filled glovebox. Coin cells were assembled with two (2) pieces of Celgard 2500 separator, a 15 mm diameter piece of lithium foil mounted on a stainless steel spacer and held under axial compression with a stainless steel wave spring. Cells were filled with approximately 100 μL of electrolyte consisting of 1.2M LiPF_6 in a 25:5:70 (weight ratio) mixture of ethylene carbonate, ethyl methyl carbonate and dimethyl carbonate, with vinylene carbonate added at 2% of the total electrolyte weight (Reference + 2% VC). Cells were crimped using an automated electric press. Triplicate cells were made for each active material tested.

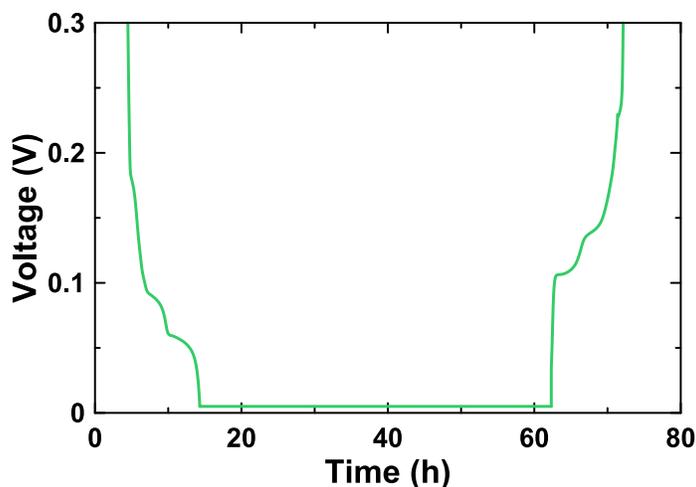


Figure 2. Voltage profile versus time for test protocol detailed in this section and used throughout.

Assembled cells were placed in cell holders, which were then installed in a NOVONIX thermal chamber, set to 45 °C. Cells were connected to either a NOVONIX 2A UHPC system or a Maccor Series 4000 charger. After a period of 4 h to achieve thermal equilibrium, cells were discharged at a rate of C/10 to 5 mV at which point the voltage was held constant for 48 h. Finally, the cells were charged to 1.5 V. Figure 2 shows a representative voltage profile as a function of time for this protocol. Figure 3 shows the required programming in NOVONIX UHPC Protocol software to execute this test.

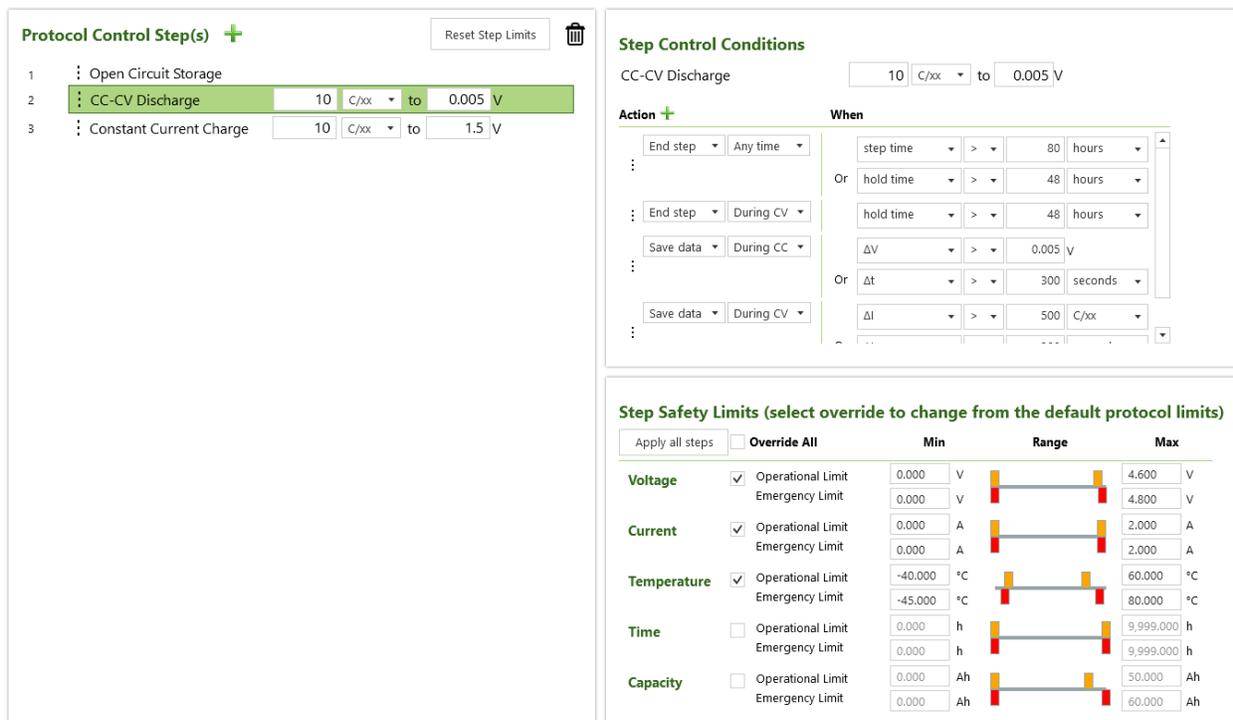


Figure 3. Test protocol as programmed in NOVONIX UHPC Protocol (v2.5.1). Step Control Conditions shown detail the discharge to 5 mV and following 48 h hold at constant voltage.

Readers well-versed in traditional electrochemistry may recognize that this testing protocol is simply the application of chronoamperometry methods to Li-ion coin cells. For some unknown reason, battery science and traditional electrochemists have opted to use different and even conflicting jargon (e.g., “CV” meaning either constant-voltage or cyclic voltammogram). Chronoamperometry has even previously been applied to the study of Li-ion coin cells, a notable example of which can be found under the reference: Nupur Nikkan Sinha *et al* 2011 *J. Electrochem. Soc.* **158** A1400 (doi: 10.1149/2.080112jes).

To facilitate a comparison in full cells, nominally 1 Ah stacked pouch cells were constructed using the pilot production facilities at NOVONIX. A cathode slurry, with a 94/4/2 mixture by weight of a $\text{Li}[\text{Ni}_{1-x-y}\text{Mn}_x\text{Co}_y]\text{O}_2$ (NMC) active material, Super P carbon black and polyvinylidene fluoride binder, was coated onto an aluminum current collector. This cathode coating was used with all negative electrodes. Various negative electrode slurries, with a 94.5/1.3/1.4/2.8 mixture by weight of graphite, carbon black, CMC and SBR. Slurries were prepared in 2 L or 5 L double planetary mixers and coated using a roll-to-roll slot-die coater, which included drying at 60 °C via heating elements positioned above and below the coating. Individual electrodes assemblies were punched and assembled into a multi-layer, stacked pouch cells. Cells were dried under vacuum at 100 °C for 16 h before filling with an electrolyte of Reference + 2% VC. Cells were vacuum sealed and underwent a typical formation procedure before being degassed. Long-testing was completed on a Neware battery test system, at a temperature of 40 °C with a protocol consisting of C/3 cycling between voltage limits of 2.8 V and 4.2 V.

Results and Discussion

Both panels of Figure 4 shows raw current data collected during the constant voltage hold at 5 mV, plotted versus the time spent at constant voltage. The current values are negative as the lithiation of graphite is achieved through discharge of coin cells, where current is assigned a negative value. Current values that are closer to zero have lower absolute magnitude and are placed higher in Figure 4. The current profiles for all cells generally show a decay behaviour. To place the values in context, at the beginning of the constant voltage step, the current is approximately -35 mA/g (C/10), so a value of -0.1 mA/g (C/3500) represents a 350-fold reduction. Accounting for the active mass in the cells, -0.1 mA/g corresponds to approximately -1.5 μ A. This is approximately 0.67% of the lowest current range for a NOVONIX 2A UHPC System and 1% of a Maccor Series 4000 charger.

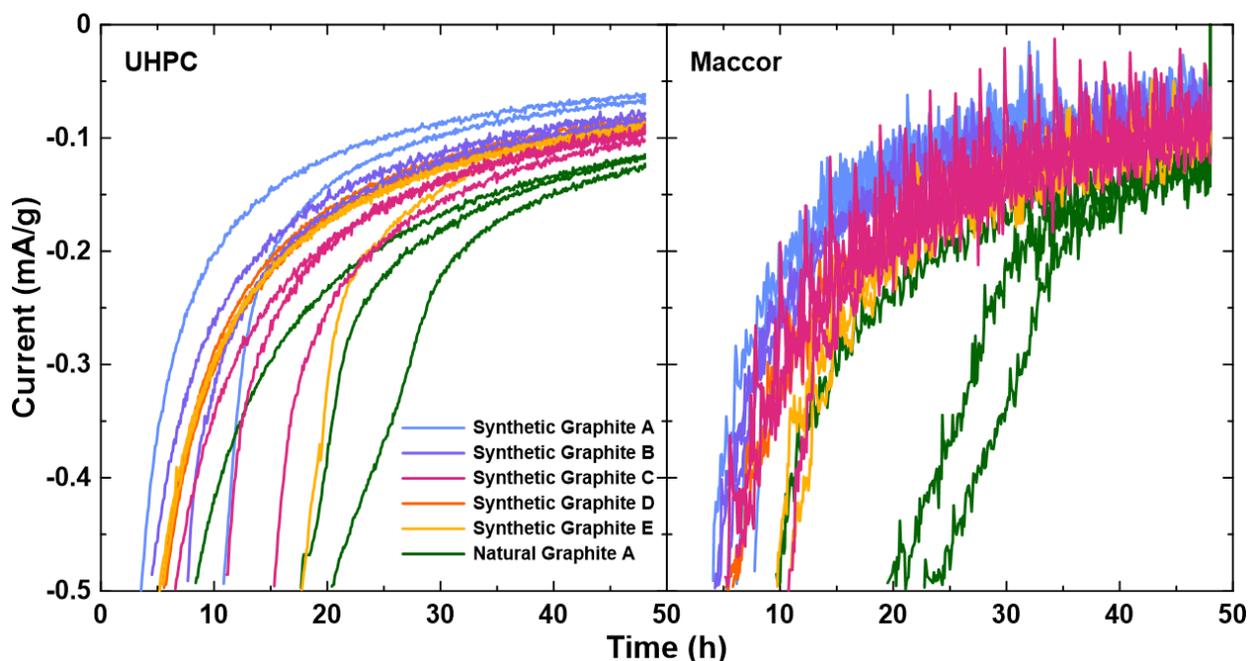


Figure 4. Specific current versus time, or chronoamperogram, for anode half cells during a 48 h constant voltage hold at 5 mV. Cells contained different active materials as indicated by the legend and were tested on a NOVONIX UHPC or a Maccor Series 4000 charger.

After 48 h, the current values have not reached a truly constant or quiescent value, but the profiles are well separated to the extent that comparisons and ranking can be made. This is akin to how 20 cycles of UHPC cycling on cells at beginning of life is often sufficient to rank cells based on CE, even if the CE has not reached a constant value. Longer time under test could yield current values that become increasingly constant, however pursuit of this is likely not time or channel efficient for most users. It should be noted that 48 h of constant voltage time was deemed enough to form a comparison in this case but is not an optimized time.

The decay behavior of the current profiles is consistent with the notion of the lithium-graphite phase getting closer to equilibrium and SEI maturation increasing as time increases. This corresponds to I_{eq} and I_{mat} approaching zero. As mentioned in the Methods section, multiple cells were built and tested for each active material. These duplicates are plotted in Figure 4 with traces in identical colours. As time increases, the current profiles converge along nearly identical trajectories. This occurs even when

the current profiles initially, at early time followed a much different trajectory. This is likely due to the fact that coin cells are manually assembled, and their kinetics can be highly sensitive to electrode misalignment. Any difference in kinetics between otherwise identical cells will result in different current decay behavior, particularly early during the constant voltage period, when currents are relatively large. It is reassuring that with sufficient time, small assembly differences don't influence the end result.

Comparing Figure 4a to Figure 4b illustrates the difference in data collected on a NOVONIX UHPC compared to a Maccor Series 4000. There is far more noise in the measurements performed on a Maccor Series 4000, to the extent that it is challenging to distinguish the current profiles from different materials. When measurements on identically made cells are performed on a NOVONIX UHPC, there is far less noise and different materials can be distinguished clearly enough that a ranking can be constructed simply through visual inspection of the raw data, in Figure 4a.

Processing the raw data enables an estimate of uncertainty and better comparison of active materials. It was assumed that during the final 4 h of the constant voltage period, contributions to the current from processes like lithium phase equilibration, SEI maturation and any kinetic artefacts introduced by poor assembly were negligible. A polynomial of the form

$$I(t) = I_0 + I_1t + I_2t^2 + \dots$$

was fit to the data. If the current is assumed to be slowly varying, neglecting the terms past a linear fit should not significantly affect the quality of the fits and the resulting comparison. A linear regression was therefore applied to the final 4 h of current data for each data series in Figure 4. The fit parameters were used to compute the value of the current at $t = 47$ h, along with uncertainty according to

$$I(t) = I_0 + I_1t$$

$$\delta I = \sqrt{(\delta I_0)^2 + (\delta I_1 t)^2}$$

where δI_0 and δI_1 are uncertainties associated with linear regression parameters. The current was calculated at 47 h rather than 48 h, to select a point that is reasonably within the domain of the regression data, not at the end. The values for each cell were then averaged over any duplicate cells along with uncertainty propagated to determine the uncertainty on the final, average current.

$$\bar{I} = \frac{1}{n} \sum_{i=1}^n I_i$$

$$\delta \bar{I} = \frac{1}{n} \sqrt{\sum_{i=1}^n (\delta I_i)^2}$$

Figure 5 shows the average current plotted versus each active material type. After 48 h of equilibration at 5 mV, data collected on a NOVONIX UHPC show that synthetic graphite (SG) A has the parasitic current with the lowest magnitude (or nearest to zero) of all materials tested. This suggests it should yield the lowest rates of lithium inventory loss in full cells, assuming there is no influence of crosstalk reactions that are introduced when a cathode is paired with the anodes in question. Additionally,

synthetic graphites all show parasitic current closer to zero than the one natural graphite (NG) tested. This agrees with common observation that SG tends to deliver superior lifetime.

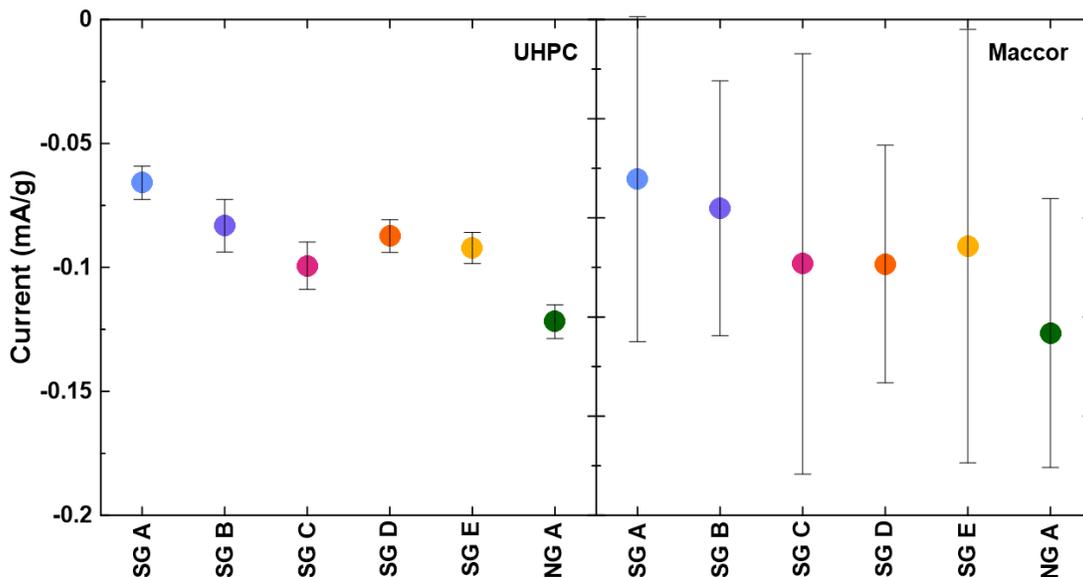


Figure 5. Average specific current near the end of a 48h constant voltage hold at 5 mV versus active material types for anode half cells. Raw data can be found in Figure 4. Cells were tested on a NOVONIX UHPC or a Maccor Series 4000 charger.

Data collected with a Maccor Series 4000 charger show nearly identical trends as data collected with a NOVONIX UHPC, however there is significant overlap of error bars. This implies that a Maccor charger has sufficient accuracy to perform this measurement with comparable accuracy to a NOVONIX UHPC but lacks the precision and low noise to deliver statistical certainty without requiring very large sample sizes and high consumption of instrument channel-time.

Figure 6 shows fractional capacity as a function of cycle number during long-term testing of full cells with a common NMC cathode, and some of the different anodes for which data is shown in Figures 4 and 5. Figure 6 shows that SGs A, B and possibly C show superior capacity retention compared to SG D and NG A. The ordering of graphites in Figure 6, from best to worst capacity retention, loosely follows the ordering in Figure 5, from parasitic currents closest to furthest from zero. The correlation is not perfect, as SG C is significantly better than SG D, according to the results in Figure 6, but within uncertainty, the two materials are not very different according to the results in Figure 5. It should be noted that the parasitic current results in Figure 5 captures the rate of lithium inventory loss at the graphite electrode in a half cell. The long-term cycling results shown in Figure 6 capture contributions of lithium inventory loss, reactions at and crosstalk with the positive electrode, and/or impedance growth.

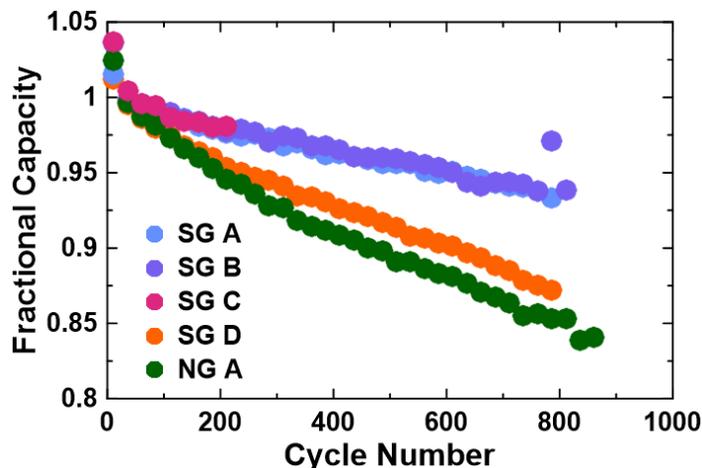


Figure 6. Fractional capacity versus cycle number for stacked pouch cells consisting of a common NMC cathode and different graphite anodes. Cycling was performed on a Neware battery test system, at a temperature of 40 °C, at a rate of C/3 between voltage limits of 2.5 V and 4.3 V.

The method described in this document is not designed to replace testing in full cells. It is intended as a useful and rapid means of electrochemically screening materials by a single parameter that does contribute partially, but not exclusively, to full cell performance. Typical certificates of analysis or datasheets provided by material vendors specify electrochemical properties such as reversible capacity, measured at a particular rate and temperature. It is easy to imagine that with widespread adoption, parasitic current, measured at a particular temperature after a certain period of time at constant voltage could become a mainstay on future datasheets.

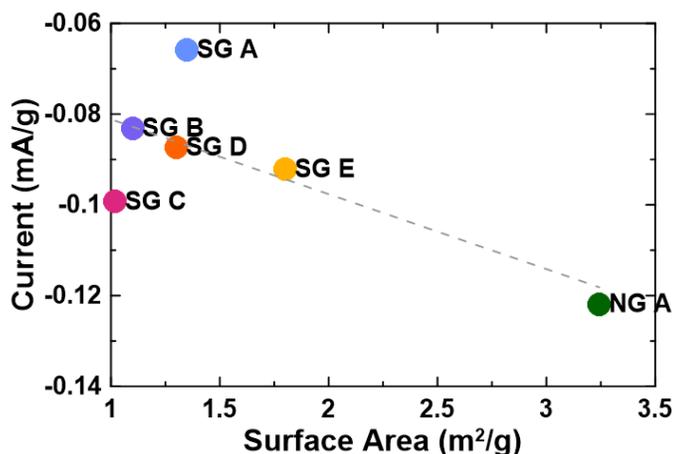


Figure 7. Average specific current near the end of a 48h constant voltage hold at 5 mV versus specific surface area for different graphite active materials. Raw current data can be found in Figure 4. A trendline is drawn to guide the eye to the general relationship, although it is not intended to imply a necessarily linear correlation between parasitic current and surface area.

Finally, Figure 7 shows how the parasitic current reported in Figure 5 compares to the surface area, as determined by Brunauer, Emmet and Teller analysis. Lithium consumption and parasitic reactions that occur at negative electrodes often occur in amounts that are proportional to the specific surface area of the negative electrode. This is because it is the surface of the active material particles that is in contact with the electrolyte and requires passivation to prevent endless consumption of lithium. Figure 7 shows

that the majority of the graphites tested have a current-surface area relationship that falls very close to a linear trendline. Of SG B, D, E and NG A, as the surface area increases, the magnitude of parasitic current increases linearly. SG A and C are outliers from the group in that SG A has a lower parasitic current magnitude than would be expected based on its surface area, while SG C has a higher parasitic current magnitude than its surface area would suggest. These outlier results may possibly be explained by differences in particle morphology, surface coating or electrode microstructure.

Conclusions

Measuring the parasitic current of graphite electrodes in half cells, held at constant voltage when fully lithiated can yield a metric for classifying and ranking materials using a metric with connection to lifetime of full Li-ion cells. This metric should be viewed as a quantification of electrochemical performance that is complementary to other electrochemical and physical specifications. Efficient measurement of this metric requires instrumentation with high precision and accuracy but can be done at the lab scale in a few days. This allows for high throughput and rapid process development for material synthesis without requiring pilot scale, full cell-making facilities.

This publication may periodically be updated as more materials are tested, and existing cells accumulate more cycles. The technique presented herein is not unique to graphite active materials alone. It would be quite interesting to consider different active materials, such as silicon, or even cathode materials at various upper cutoff voltages. This technique could conceivably be leveraged to screen different electrolyte formulations for use with a single active material.

It should be noted that the information obtained from the parasitic current measured at constant voltage does not capture impedance effects, nor crosstalk between electrodes in a full cell. Both of these may have large ramifications in cycling experiments in full cells, at higher rates. To gain a full picture of these behaviors requires a host of complementary techniques and test vehicles.

Idea

This whole method can also be applied in QC in full cells or process optimization in manufacturing to look for unwanted mechanisms, deviations intra and inter cell batch, etc.

As an example, different batches of the same material may not be identical and give identical performance. Screening every batch of received material via the method proposed here is relatively low time investment and can indicate lifetime differences prior to the time and resource investment of a full cell build. This is an important QC step in terms of delivering reliable cells construction, along with validating quality and consistency in materials purchased from a third party.