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# **Precision Measurements of the Coulombic Efficiency of Lithium-Ion Batteries and of Electrode Materials for Lithium-Ion Batteries**

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Undesired reactions in Li-ion batteries, which lead to capacity loss, can consume or produce charge at either the positive or negative electrode. For example, the formation and repair of the solid electrolyte interphase consumes Li<sup>+</sup> and e<sup>-</sup> at the negative electrode. High purity electrolytes, elimination of water, various electrolyte additives, electrode coatings, and special electrode materials are known to improve cycle life and therefore must impact coulombic efficiency. Careful measurements of coulombic efficiency are needed to quantify the impact of trace impurities, additives, coatings, etc., in only a few charge–discharge cycles and in a relatively short time. The effects of cycle-induced and time-related capacity loss could be probed by using experiments carried out at different C-rates. In order to make an impact on Li-ion cells for automotive and energy storage applications, where thousands of charge–discharge cycles are required, coulombic efficiency measurements and give examples of its use on commercial Li-ion cells and Li half-cells. High precision coulombic efficiency measurements and give examples of its use on commercial Li-ion cells and Li half-cells. High precision coulombic efficiency measurements can detect problems occurring in half-cells that do not lead to capacity loss, but would in full cells, and can measure the impact of electrolyte additives and electrode coatings.

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Li-ion batteries for computer, camera, and phone applications can be marketed effectively if their cycle life exceeds a few hundred cycles because the devices have a limited lifetime due to technology obsolescence. New applications for Li-ion cells, such as in electrified vehicles [hybrid electric vehicle, plug-in hybrid electric vehicle (PHEV), extended-range electric vehicle (EREV), and all-electric electric vehicle (EV)], and for energy storage from wind and solar sources have more demanding cycle-life requirements. In automotive and energy storage applications where the device lifetime is 10–30 years, a desirable cycle life (assuming 1–2 cycles per day for PHEV, EREV, and EV) would be at least 3000 and preferably more than 10,000 cycles. In fact, if batteries outlived the vehicles in which they were placed, the batteries could be transferred to another vehicle if vehicles were designed to accommodate the transfer.

Testing cycle life as long as 3000 and 10,000 cycles under conditions that simulate actual use is extremely problematic because the testing takes an extremely long time. One of the most impressive papers on aging mechanisms in Li-ion cells<sup>1</sup> follows cells in cycling and in storage for up to 3 years. To quantitatively measure the benefits imparted to the lifetime of cells by changes to electrode materials, by electrode additives, and by electrode material coatings, under actual testing conditions, extremely long times are required if simply charge–discharge cycling methods are used.

Undesired reactions in Li-ion batteries, which lead to capacity loss, can consume or produce charge at either the positive or negative electrode. For example, the formation and repair of the solid electrolyte interphase (SEI) consumes Li<sup>+</sup> and e<sup>-</sup> at the negative electrode.<sup>1,2</sup> Electrolyte oxidation at the positive electrode produces an excess charge compared to that which would occur in its absence.<sup>2</sup> High purity electrolytes, scavenging of water,<sup>3</sup> various electrolyte additives,<sup>4-10</sup> electrode coatings,<sup>11-16</sup> and special electrode materials<sup>17</sup> are known to improve cycle life and therefore must impact coulombic efficiency (CE). Ohzuku et al.<sup>18</sup> recognized the importance of the CE in a

Ohzuku et al.<sup>10</sup> recognized the importance of the CE in a thoughtful paper on factors affecting capacity retention of lithiumion cells. In that paper, it was stated that matched CEs for the positive and negative electrodes, even if different from 1.000, could still lead to excellent cycle life for full Li-ion cells. However, the Li-ion cells used in the experiments were flooded, with significant amounts

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of excess electrolyte, so electrolyte consumption could occur without capacity loss. In a practical Li-ion cell with a limited amount of electrolyte, electrolyte consumption (by oxidation at the positive electrode, for example) leads to eventual and catastrophic capacity loss.

Many authors who study electrode materials for Li-ion cells report their CE during the first 100-200 cycles. For example, Wang et studied TiO<sub>2</sub> hollow spheres as anode materials for Li-ion cells al. and reported that "the coulombic efficiency is approximately 98% after 40 cycles, indicating excellent cycling stability and reversibility." Of course, full Li-ion cells incorporating such a negative electrode would have a short cycle life. Yi et al.<sup>20</sup> reported the CE of half-cells using LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> and LiMn<sub>1.4</sub>Cr<sub>0.2</sub>Ni<sub>0.4</sub>O<sub>4</sub>, showing improved CE for the latter. However, the latter also had increased capacity fade, suggesting that the relationship between CE and cycle life of half-cells is not necessarily simple. Li et al.<sup>21</sup> reported CE measurements on Si/graphite/carbon composite electrodes and show an improvement in CE from about 97.5 to about 99% when mixed LiBOB and LiPF<sub>6</sub> salts were used instead of LiPF<sub>6</sub> or LiBOB salts individually. Liu et al.<sup>22</sup> reported the CE of various Si-based negative electrode materials, which showed values between 95 and 98%. Obrovac and Krause<sup>23</sup> reported the CE of crystalline Si electrodes made with an unspecified binder to be 99.8% after about 50-90 cycles (Fig. 16 in Ref. 23). In Ref. 19-22, the CE measurements show a significant amount of noise and scatter, about  $\pm 0.5\%$ , when CE is plotted vs cycle number. More care in the measurements may have been taken in Ref. 23 because the scatter in the CE measurements is only about  $\pm 0.1\%$ . However, based on scatter in literature CE data, it is our contention that none of the measurements of CE presented in the literature are accurate or precise enough to be able to distinguish the impact that additives could play in increasing cycle life from 1000 to 2000 (or more) charge-discharge cycles. Such CE measurements would have to be precise on the scale of at least  $\pm 0.01\%$ .

#### Requirements for Precise CE Measurements and Capabilities of Commercial Charge–Discharge Equipment

As shown later in this paper, precision measurements of CE are possible and can lead to greater understanding of the degradation processes taking place at the electrodes of Li-ion cells. It is important to consider the experimental factors that must be controlled to measure the CE precisely during a constant current charge and discharge between fixed voltage limits. There are four factors that need to be considered, as indicated in Table I: (*i*) accuracy of the set

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Table I. Factors that affect the ability to precisely and accurately measure CE. For the purpose of these estimates, dQ/dV has been assumed to be the full cell capacity in 1 V and dV/dT has been assumed to be 100  $\mu$ V/K.  $\Delta Q$  is the percentage error in the cell capacity,  $\Delta I$  is the percentage accuracy in the current,  $\Delta V$  is the precision of the voltage measurement,  $\Delta t$  is the interval between voltage measurements, and  $\Delta T$  is the precision of the temperature control.

Parameter	Associated error	Desired error in $Q$ (%)	For C/10 rate measurements	For C-rate measurement
$\Delta I$	$\Delta Q = \Delta I t$	< 0.01	$\Delta I < 0.01\%$	$\Delta I < 0.01\%$
$\Delta V$	$\Delta Q = dQ/dV \Delta V$	< 0.01	$\Delta V < 0.0001 \text{ V}$	$\Delta V < 0.0001 \ \mathrm{V}$
$\Delta t$	$\Delta Q = I \Delta t$	< 0.01	$\Delta t < 3.6 \text{ s}$	$\Delta t < 0.36$ s
$\Delta T$	$\Delta Q = dV/dT \ dQ/dV \ \Delta T$	< 0.01	$\Delta T < 1  { m K}$	$\Delta T < 1  { m K}$

currents, (*ii*) precision of the voltage measurements, (*iii*) time between voltage measurements, and (*iv*) precision of the controlled cell temperature. If the goal is to be able to measure the charge delivered by the cell to an accuracy of  $\pm 0.01\%$ , then it is necessary



**Figure 1.** Schematic diagram showing the data points collected in the vicinity of the discharge limit potential. The values  $\Delta t$  and  $\Delta V$  are the time between potential measurements and the precision of the voltage measurement, respectively.

to control the accuracy of the current  $\Delta I$ , the precision of the voltage measurements  $\Delta V$ , the time between voltage readings  $\Delta t$ , and the precision of the controlled cell temperature  $\Delta T$  to the levels given in Table I. For the purpose of the estimates in Table I, dQ/dV has been assumed to be the full cell capacity in 1 V and dV/dT has been assumed to be 100  $\mu$ V/K.<sup>24</sup>

Figure 1 shows an expanded view of some hypothetical data collected during the discharge of a cell near its lower cutoff potential. Each data point is collected a time  $\Delta t$  apart. The vertical error bars in Fig. 1 represent the precision to which the voltage is measured  $\Delta V$ . Figure 1 demonstrates that the maximum error in measuring the charge due to the data collection interval  $\Delta t$  is  $\Delta Q = I\Delta t$ . Figure 1 demonstrates that the maximum error in measuring the charge due to the voltage precision  $\Delta V$  is  $\Delta Q = dQ/dV \Delta V$ .

Table II compares specifications of battery charge–discharge equipment, which was gathered from the manufacturer websites and by phone and e-mail contact. Table II suggests that none of the commercially available instruments are capable of measuring CE to  $\pm 0.01\%$ . The Maccor 4000 series has some of the strictest specifications available but still does not meet the current accuracy requirements. In addition, if a 5 V Maccor system were obtained, the voltage accuracy would be 5 V  $\times 0.02\% = 1$  mV. Table I suggests that an order of magnitude better voltage measurements are required for measuring CE to 0.01%. It is important to realize that time is required to measure voltages accurately, and the Maccor system has been designed for many purposes, including pulse discharge, which require voltage measurements in short time intervals, making it impossible to simultancously measure voltage to higher accuracy. The other commercial systems are less capable of precision CE measure

Table II. Specifications of commercial charge-discharge equipment obtained from manufacturer websites and through phone and e-mail exchange. A 16 bit resolution corresponds to 1 part in 65,536 or 1 part in  $10^{4.8}$ . Even though a 16 bit device is used, the accuracy and stability may not be as good as 16 bits.

Manufacturer	Current resolution	Voltage resolution	Current accuracy	Voltage accuracy	Time between measurements
Maccor 4000 series	16 bit	16 bit	0.02–0.05% of full scale	0.02% of full scale	0.01 s
Arbin BT2000	16 bit	16 bit	0.02-0.05% of full scale	0.05% of full scale	0.1 s
Bitrode MCV	100 nA	100 μV	0.1% of full scale	0.1% of full scale	0.1 s
Neware BTS-5V1mA	16 bit	16 bit	0.05% of full scale	0.05% of full scale	5 s
Lisun PCBT-100- 32D	0.1%	0.1%	<0.5%	<0.1%	1 s
Land CT2001	0.1%	0.1%	N/A	N/A	N/A
Xeno WBCS 5000	16 bit	16 bit	N/A	N/A	0.05 s
Biologic VMP	0.0003%	16 bit	0.05%	0.1%	0.02 s
Dalhousie HPC	1 in. 19,999 (0.005%)	10 μV	0.05% (over 1 year)	0.0025% of full scale	<1 s (by software interpolation)



Figure 2. (Color online) Photograph of the HPC at Dalhousie University. Major components are labeled.

ments than the Maccor. The best CE measurement with the least scatter we could find in the literature (we did not do an exhaustive search) was measured using a Maccor system.<sup>23</sup>

#### Design of the Dalhousie HPC

The factors described in Table I were considered in our design of a prototype high precision charger (HPC) system. We decided to use dedicated commercially available precision current sources from Keithley Instruments for each charger channel. The state-of-the-art precision current supply from Keithley is the model 6220 programmable current source, which sells for about \$4000. The previous generation precision current supply was the Keithley model 220, which is no longer for sale from Keithley, but has exactly the same specifications as the Keithley 6220. Given the global economic downturn, there are numerous Keithley 220s available on eBay and available from used equipment resellers. We were able to purchase 44 used Keithley 220s for an average price of about \$1000. These units communicate on an IEEE interface and have current accuracy listed as  $\pm 0.05\%$  over a 1 year period.

The received Keithley 220 current supplies were all calibrated according to the procedures in the model 220 instruction manual. Most interesting is the fact that the equality between positive and negative current magnitudes is set by a single adjustment, which holds over all current ranges. We ensured that the positive and negative currents matched to within 1 part in  $10^5$  during the calibration process. The published specifications of the instrument, used to generate the values for the Dalhousie HPC in Table II, do not indicate this fact, which is actually the most important feature for a device designed to measure CE. However, we do not yet know how stable this adjustment is; further operation/testing will identify this. Furthermore, the Keithley 220 has a current range for every decade of current, and the accuracy is  $\pm 0.05\%$  of full scale for each range. Most commercial chargers do not have a current range for every decade.

High precision Keithley Instruments scanning voltmeters, either model 2750 or 2000, were selected to monitor the voltage of the cells during charge and discharge. Each voltmeter was designed to scan sequentially over 10 cells, each controlled by a model 220. Our 40-channel system therefore has 40 model 220 current sources and four precision voltmeters. Figure 2 shows a photograph of the assembled HPC system. These voltmeters measure 2 V < V < 5 V to a precision of 10  $\mu$ V and 0.2 V < V < 1.99 V to a precision of 1  $\mu$ V. This satisfies the requirements for the precision of voltage measurements given in Table I.

Software to control the scanning voltmeters and the current sources was written in LabView. Testing showed that the scanning rate at the highest voltage precision could be set so that each cell was sampled once per 5 s. This rate is not fast enough to meet the goals set forth in Table I. Therefore, postprocessing software was used to interpolate linearly between the last data point before the voltage limit and the final data point collected after the voltage limit (two rightmost points in Fig. 1) to determine the exact time when the cell potential crossed the voltage limit. We estimate the accuracy of the time determination by this method to be better than 1 s, sufficient for C/10 testing, as shown in Table I.

Cells are placed into one of five home-built thermostats at either 30.0 (two thermostats), 40.0, 50.0, or  $60.0^{\circ}$ C. The temperature in the thermostats is maintained to a precision of  $\pm 0.1^{\circ}$ C by Omega CNi3233 or Omega 4201A-PC2 controllers. This precision meets the specifications given in Table I.

A "patch panel" shown in Fig. 2 was constructed so that any current source could be connected to any cell holder position in any thermostat. All wiring to the cells was done using the "four-wire" method, with two wires carrying the current and two other wires used to monitor the potential of the tested cell at its terminals.

#### Experimental

Commercial full Li-ion cells were used for some preliminary baseline testing of the HPC. Fifty LiCoO<sub>2</sub>/graphite 18,650 size cells (nominal 2400 mAh) were obtained from a reputable manufacturer. Cylindrical Sony Nexelion-type Li-ion cells were obtained by disassembling a Sony NP-FH70 battery pack obtained from the Sony store. These Nexelion cells incorporate a Sn-based negative electrode material and incorporate a fluoroethylene carbonate (FEC) additive in the electrolyte. The commercial cells were charged and discharged at C/24 rates between 4.2 and 3.0 V (LiCoO<sub>2</sub>/graphite) or between 4.1 and 2.5 V (Nexelion-type) at a temperature of  $30.0 \pm 0.1^{\circ}$ C.

2325 coin-type Li/electrode material half-cells were used to demonstrate the capabilities of the HPC. Electrodes of standard materials, such as graphite,  $Li_{4/3}Ti_{5/3}O_4$ ,  $Sn_{30}Co_{30}C_{40}$ , and  $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ , were used. Graphite-type mesocarbon microbeads (Osaka Gas, heated to about 2650°C) were obtained from E-One Moli (Energy Canada) Limited.  $Li_{4/3}Ti_{5/3}O_4$  was obtained from NEI Corporation (Piscataway, NJ).  $Sn_{30}Co_{30}C_{40}$  samples were alloyed mechanically using a vertical-axis attritor mill (Union Process 01-HD attritor), as described in Ref. 25. A  $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$  (NMC) sample was obtained from a commercial supplier.

The graphite electrode slurry was prepared by mixing 86% active mass, 7% Super S carbon black (MMM Carbon, Belgium), and 7% poly(vinylidene difluoride) (PVDF) in an *n*-methyl pyrrolidone (NMP) solvent. The slurry was spread on a Cu foil with a notch bar and dried at 105°C for at least 3 h. The  $Li_{4/3}Ti_{5/3}O_4$  electrode slurry was prepared by a similar method. The slurry was spread on Al foil with a notch bar and was dried under the same conditions as the graphite electrodes. The  $Sn_{30}Co_{30}C_{40}$  electrode slurry was prepared by mixing a weight to weight ratio of 80% attried powder, 12% Super S carbon black (MMM Carbon, Belgium), and 8% proprietary binder. The slurry was spread on Cu foil with a notch bar and dried at 90°C for 4 h. The NMC electrode slurry was made from 86% NMC, 7% Super S carbon black, and 7% PVDF binder using an NMP solvent. The slurry was spread on Al foil with a notch bar spreader and then dried at 105°C for at least 3 h.

The electrolyte used in most of the cells in this work was 1 M LiPF<sub>6</sub> in ethylene carbonate/diethyl carbonate (1:2 v/v, Novolyte Corp.) solution. In some of the Li/Sn<sub>30</sub>Co<sub>30</sub>C<sub>40</sub> cells, 10 wt % fluoroethylene carbonate (Fujian ChuangXin, China) was added. 2325 coin-type cells with two Celgard 2300 separators and a lithium foil

common counter and reference electrode were assembled in an argon-filled glove box using the electrodes described above. Except where indicated as a special case, before moving the active electrodes to the glove box, the electrodes were redried at 90°C for at least 4 h and then "instantly" transferred to the glove box antechamber while hot. All coin-type cells were charged and discharged between fixed voltage limits at C/10 rates at a temperature of  $30.0 \pm 0.1$ °C.

#### **Conventions Used for Measurements of CE**

In this paper, regardless of cell type, the word "discharge" is used to describe the direction of current flow that would take place if a cell were short-circuited. Thus, for a Li/graphite half-cell, discharge corresponds to lithiation of graphite and for a Li/NMC halfcell, discharge also corresponds to lithiation of NMC. However, discharge of a graphite/LiCoO<sub>2</sub> cell corresponds to delithiation of the graphite electrode and lithiation of the LiCoO<sub>2</sub> electrode.

CEs for half-cells are measured as the ratio of the capacity of the charge  $Q_c$  immediately following the previous discharge  $Q_d$ . Thus, for half-cells, CE =  $Q_c/Q_d$ . Given this definition, we expect that CE < 1.000 for Li/graphite, Li/Sn<sub>30</sub>Co<sub>30</sub>C<sub>40</sub>, and Li/Li<sub>4/3</sub>Ti<sub>5/3</sub>O<sub>4</sub> half-cells where consumption of Li by continual SEI rebuilding during discharge is expected. For Li/LiCoO<sub>2</sub> and Li/NMC half-cells, we expect that CE > 1.000 because electrolyte oxidation at high potential or transition-metal dissolution should cause  $Q_c > Q_d$ .

CEs for full Li-ion cells are reported here as the ratio of the next discharge to the present charge. Given that the meaning of charge and discharge is reversed for the negative electrode in the full cell compared to the half-cell, this definition gives the capacity of the delithiation of the negative electrode divided by the capacity of its lithiation and is therefore equivalent to the half-cell definition as far as the negative electrode is concerned.

#### **Results and Discussion**

Figure 3 shows the result of CE measurements on 30  $\text{LiCoO}_2/\text{graphite 18,650}$  size cells. All cells were charged and discharged at 30°C using currents corresponding to C/24. Data for some cells at cycle 2 were lost due to power failure caused by a hurricane. The top panel of Fig. 3 shows individual data points for each cell to demonstrate the small scatter of the equipment and of the cells. The lower panel of Fig. 3 compares the CE of one particular cell selected for further study to the average of the data collected for the 30 cells. The error bars shown for the data points representing the average of the 30 cells are the standard deviation for the 30 points about the average. Figure 3 demonstrates that the cell selected for further analysis and for comparison to other cells is representative.

Figure 4 shows the capacity and CE of commercial  $LiCoO_2/$ graphite and commercial Nexelion cells plotted vs cycle number. The capacity is plotted on two different scales so that both the capacity stability and the capacity fade can be observed. We do not know how the cells may have been conditioned by the manufacturer before shipping and before our experiments. The vertical scale of the CE graphs runs from 99.5 to 100%, which is rather uncommon because the scatter produced by most chargers would be as large as the scale limits. The error bars on the CE data represent the maximum error that the 5 s measurement interval (out of 24 h) could give.

The LiCoO<sub>2</sub>/graphite cell was cycled for 9 cycles and reached a CE of about 99.9%. Then the charger was stopped for a few days for a software modification. When it was restarted, the LiCoO<sub>2</sub>/graphite cell returned to 99.90% CE after a few cycles. By contrast, the Nexelion cell shows a lower CE of about 99.75%, which is presumably caused by the difficulty in maintaining a perfect SEI layer on large-volume-change materials such as the Sn-based negative electrode used in this cell. The capacity loss rates for the two cells are about 0.052% per cycle for the LiCoO<sub>2</sub>/graphite cell and 0.20% per cycle for the Nexelion cell is close to the departure of



**Figure 3.** Top panel: CE vs cycle number for 30  $\text{LiCoO}_2/\text{graphite } 18,650$  size cells. All cells were charged and discharged at a C/24 rate at 30°C. The potential limits were 4.2–3.0 V for all cells. Bottom panel: Average CE of the 30 cells (error bars are standard deviation) compared to one cell selected for further charge–discharge cycling and further comparison (Fig. 4 and 6) to other cells.

the CE from 1.0000. This correlation is to be expected in the case where Li loss at the negative electrode through a thickening/ rebuilding SEI is the source of the coulombic inefficiency as is most likely in the Nexelion cell.

Figure 5 shows the cell potential plotted vs the capacity of the Nexelion cell in the left panel and the capacity of the cell at the voltage limits plotted vs cycle number in the right panel. Figure 5 shows that the capacity measured at the bottom of the discharge steadily increases. This is most likely due to the combined factors of lithium lost in SEI formation/rebuilding and the possible inability to extract all lithium from the Sn-based negative electrode when the cell reaches 2.5 V. The hollow data points at the bottom of the right panel of Fig. 5 give the maximum value that the discharge end-point capacity could have if the CE were actually exactly 100.00%, and the departure of the end-point capacity from zero was caused by an error in the charger system, where we have used the maximum that the error could be (0.05%) and have accumulated that error every cycle. From this estimate, it is clear that the increase in the discharge end-point capacity is a real effect.

The charge end-point capacity does increase with cycle number, but at a much slower rate than the discharge end-point capacity. The potential (vs Li) vs capacity of the negative electrode changes slowly at the top of the charge because it is dominated by the potential plateaus in the graphite component of the Nexelion electrode at that point. Therefore, the potential (vs Li) vs capacity profile of the positive electrode controls the charge end-point capacity position. Provided electrolyte decomposition and transition-metal dissolution rates are low, the charge end-point capacity position should be well-fixed with the cycle number, as observed.

Experiments made on half-cells can be used to help understand the behavior of the Li-ion cells in Fig. 4 and 5. Although we do not have access to the actual electrode materials and electrolytes used in the full Li-ion cells, we constructed Li/graphite and Li/Sn<sub>30</sub>Co<sub>30</sub>C<sub>40</sub> coin cells as approximations to the negative electrode materials used



**Figure 4.** Capacity vs cycle number and CE vs cycle number for a  $LiCoO_2/graphite 18,650$  cell and a Sony Nexelion-type cylindrical cell. Both cells were charged and discharged at a C/24 rate at 30°C. The potential limits were 4.2–3.0 V for the  $LiCoO_2/graphite$  cell and 4.1–2.5 V for the Nexelion-type cell. [The error bars in capacity are smaller than the data points. The error bars on the CE data represent the maximum error that the 5 s measurement interval (out of 24 h) could give.]

in the full cells. Figure 6 shows the CEs of the corresponding halfcells plotted on the same axes as the full cells. The Li/graphite cell reaches a CE of 99.9%, just like the LiCoO<sub>2</sub>/graphite cell, and the Li/Sn<sub>30</sub>Co<sub>30</sub>C<sub>40</sub> cell reaches a CE of about 99.75% just like the Nexelion-type cell. The Li/Sn<sub>30</sub>Co<sub>30</sub>C<sub>40</sub> cell contained 10% FEC electrolyte additive. Without FEC, a lower CE is obtained, as will be discussed later below.

It may be claimed that the agreement in Fig. 6 is fortuitous for many reasons. The electrode materials and electrolytes were not the same in the full cells and the "corresponding" half-cells. The charge–discharge rates, C/24 for the full cells and C/10 for the half-cells, were different. Many researchers have noted that capacity loss



**Figure 5.** (Color online) Left panel: Potential vs capacity for the measured cycles of the Nexelion cell. The inset shows the details at the bottom of the discharge curve. Right panel: The charge ( $\blacktriangle$ ) and discharge ( $\odot$ ) end-point capacities plotted vs cycle number. An estimate of the maximum possible error due to the charger system is also given ( $\bigcirc$ ).



**Figure 6.** CE vs cycle number for (left panel) LiCoO<sub>2</sub>/graphite 18,650 cell compared to Li/graphite cell and (right panel) Nexelion-type cylindrical cell compared to a Li/Sn<sub>30</sub>Co<sub>30</sub>C<sub>40</sub> cell. The Li/Sn<sub>30</sub>Co<sub>30</sub>C<sub>40</sub> cell contains 10% FEC in the electrolyte. The error bars on the CE data represent the maximum error that the 5 s measurement interval (out of 24 or 10 h) could give.

occurs in Li-ion cells during stand<sup>1,26</sup> as well as during cycling. Therefore, the capacity loss rate (per cycle) should increase as the time per cycle increases,<sup>26</sup> provided one works at rates low enough that impedance growth is not dominant. Nevertheless, it is clear that high precision CE measurements could be used to make correlations between full and half-cells. This can be used to learn about the impact of electrode additives, electrode drying, potential limits, etc., on a single electrode as we discuss below.

Figure 7 shows the specific capacity and CE vs cycle number for Li/graphite, Li/Li<sub>4/3</sub>Ti<sub>5/3</sub>O<sub>4</sub>, and Li/Sn<sub>30</sub>Co<sub>30</sub>C<sub>40</sub> cells. The Li/Sn<sub>30</sub>Co<sub>30</sub>C<sub>40</sub> cell did not contain FEC in its electrolyte in this case. All cells show good capacity retention over the first 25 cycles. However, there are clear differences in the CE, which would cause differences in the capacity retention in full Li-ion cells. The Sn<sub>30</sub>Co<sub>30</sub>C<sub>40</sub> electrode particles undergo a 160% reversible volume change during each cycle,<sup>27</sup> which could damage the SEI. By contrast, the graphite electrode only has a 10% volume change over the



**Figure 7.** Specific capacity vs cycle number and CE vs cycle number for  $\text{Li}/\text{Li}_{4/3}\text{Ti}_{5/3}O_4$ , Li/graphite, and  $\text{Li}/\text{Sn}_{30}\text{Co}_{30}\text{C}_{40}$  cells. All cells were charged and discharged at C/10 at a temperature of 30°C. The electrolyte used in all cells was 1 M LiPF<sub>6</sub> ethylene carbonate:diethyl carbonate (EC:DEC) (1:2 v/v). [The error bars in specific capacity are smaller than the data points. The error bars on the CE data represent the maximum error that the 5 s measurement interval (out of 10 h) could give.]



**Figure 8.** Specific capacity vs cycle number and CE vs cycle number for Li/graphite cells with different electrode drying procedures. All cells were charged and discharged at C/10 at a temperature of 30°C. The electrolyte used in all cells was 1 M LiPF<sub>6</sub>/EC:DEC (1:2 v/v). [The error bars in specific capacity are smaller than the data points. The error bars on the CE data represent the maximum error that the 5 s measurement interval (out of 10 h) could give.]

same potential region so the SEI should be more stable. The lithium titanate electrode operates at about 1.5 V vs Li/Li<sup>+</sup> and also undergoes no volume change at all, so one might expect less loss of lithium to SEI formation. Typical lithium-ion battery electrolytes are not thermodynamically stable in contact with  $Li_{7/3}Ti_{5/3}O_4$ SO some SEI formation on the surface of lithium titanate is expected and a CE of exactly 1.0000 should not be expected. Figure 7 shows that the CE increases from  $Sn_{30}Co_{30}C_{40}$  (99.65% at cycle 25) to graphite (99.90% at cycle 25) and then to lithium titanate (99.93% at cycle 25). In all materials, the CE increases gradually during the first 25 cycles and appears to have reached an asymptotic value near cycle 25. A comparison between the results for the  $Li/Sn_{30}Co_{30}C_{40}$ cells in Fig. 6 (electrolyte has FEC) and 7 (no FEC) clearly shows the impact of the electrolyte additive, FEC, on the CE of largevolume-change materials.

The electrolytes used in these studies are Li-ion battery grade electrolytes which have never been exposed to air since their receipt



Figure 9 shows specific capacity and CE vs cycle number for Li/NMC cells charged and discharged at 15 mA/g between fixed potential limits at 30°C. Cells cycled to upper limits of 4.4 V and below show virtually no capacity loss with cycle number. The cell cycled to 4.6 V shows a clear, significant capacity loss with cycle number. The CE results show that all the cells, even those charged only to 3.8 V, have CE > 1.00. (The data for the cell charged to 3.8 V are particularly noisy for reasons we do not yet understand). Cells charged to 3.8 and 4.0 V have CEs of about 100.2% after 50 cycles, while cells charged to 4.2, 4.4, and 4.6 V have CEs of 100.4, 100.8, and 101% after 40 cycles. As expected, the CE increases with increasing charging potential, perhaps due to electrolyte oxidation and transition-metal dissolution. It should be noted that this particular batch of NMC from this particular supplier shows this behavior. Further studies on other NMC samples are in progress.

According to the literature, electrolyte additives and coatings of various types can improve the cycle life of NMC and related materials to 4.5 and 4.6 V at temperatures even as high as  $55^{\circ}$ C.<sup>7,11-14</sup> However, the work in the literature does not quantify the relative possible advantages of one coating method or one electrolyte addi-



Figure 9. Specific capacity vs cycle number and CE vs cycle number for Li/NMC cells charged to different upper cutoff potentials as indicated. All cells were charged and discharged at C/10 at a temperature of 30°C. The electrolyte used in all cells was 1 M LiPF<sub>6</sub>/EC:DEC (1:2 v/v). [The error bars in specific capacity are smaller than the data points. The error bars on the CE data represent the maximum error that the 5 s measurement interval (out of the full time of a discharge) could give.]

tive compared to another. High precision measurements of the CE would allow this quantification to be made in 20 cycles or so, based on the results in Fig. 9.

#### Conclusions

The few experimental results reported here show the promise of CE measurements made using an HPC. Some expected trends were confirmed: (i) A LiCoO<sub>2</sub>/graphite cell had a higher CE (99.90%) than a Nexelion-type (Sn-based anode) cell (99.75%); (ii) Li/Li<sub>4/3</sub>Ti<sub>5/3</sub>O<sub>4</sub>, Li/graphite, and Li/Sn<sub>30</sub>Co<sub>30</sub>C<sub>40</sub> cells had CEs of 99.93, 99.90, and 99.65% at cycle 25, respectively; (iii) the CE of  $Li/Sn_{30}Co_{30}C_{40}$  cells improved from 99.65 to 99.75% upon the addition of 10% FEC to the electrolyte; (iv) removal of water from Li/graphite cells by electrode drying improved the CE from about 99.87 to 99.90% after 25 cycles; and (v) Li/NMC cells showed CE > 1.000 and a CE which increased as the upper cutoff potential was increased. This work also identified some unexpected results: (i) Li/Li<sub>4/3</sub>Ti<sub>5/3</sub>O<sub>4</sub>, Li/graphite, and Li/Sn<sub>30</sub>Co<sub>30</sub>C<sub>40</sub> cells require about 25 cycles for their CEs to stabilize asymptotically and (ii) the impact of upper cutoff potential on the CE of the NMC sample studied was extremely dramatic.

It is believed that careful measurements of CE can be used to quantify, using half-cell experiments, the impact of electrolyte additives, electrode coatings, impurities, electrode materials, temperature, electrolyte salts, etc., on the cycle life of full Li-ion cells. This could represent good news for university-based and other researchers who do not have access to facilities for the construction of production quality Li-ion cells, but who still want to do meaningful research focused on developing solutions for automotive and energy storage batteries.

There can be no doubt that high precision measurements of CE can play an important role in the worldwide effort to produce Li-ion batteries with the cycle life that is required for automotive and energy storage applications. We have designed and built a system for this purpose. However, it is believed that it would be useful to increase the accuracy of the CE measurements by another order of magnitude compared to our system. This presents challenges for the makers of precision current sources and voltmeters capable of sampling rapidly at high precision. Hopefully some equipment manufacturers will take up those challenges so that the needed equipment can be made available in a timely manner for the research at hand.

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