Design of Positive Electrodes for Li-Ion Full Cells with Silicon

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Wound pouch cells with a Li(Ni0.6Mn0.2Co0.2)O2 (NMC622) positive electrode and graphite/Si alloy negative electrode are shown to have significantly better performance than equivalent cells with a LiCoO2 (LCO) positive electrode. Silicon containing NMC622 full cells have better performance with a 4.35 V upper cutoff voltage (UCV) than with a 4.25 V UCV. The addition of small amounts (≤8 wt%) of high surface area NMC622 to LCO-based positive electrodes in single layer pouch cells with graphite/Si alloy negative electrodes improves cycling performance and coulombic efficiency. Adding fluoroethylene carbonate (FEC) further improves the performance of cells showing the benefits of NMC622 and FEC can be combined. High precision calorimetry and cycling, Archimedes volume measurements, and cross-section scanning electron microscopy support the hypothesis of interplay between the parasitic reactions at the positive and negative electrodes. The NMC622 positive electrode is proposed to stabilize the Si alloy in the negative electrode via a CO2 release mechanism, though further confirmation of the mechanism is needed.

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Experimental

Wound pouch cell construction.—Machine wound pouch cells were used in this work. They were obtained from LiFUN Technology (Xinma Industry Zone, Hunan Province, China) as sealed dry cells. Two families of cells were tested. Table I lists the attributes and formulations of the electrodes and cells. There are small variations in negative electrode formulations, though we expect the negative electrodes to have similar behaviors. The Si alloy used has a reversible capacity of 1180 mAh/g, a density of 3.5 g/cm3, a surface area of 6.9 m2/g and a median particle size of 5.2 μm. The LF129 and LF872 cells differ primarily in the type of active material used in the positive electrode. The LF129 and LF872 had LiCoO2 (LCO) and Li(Ni0.6Mn0.2Co0.2)O2 (NMC622) positive electrode materials respectively. Cells were first opened in a dry room and dried at 70 °C under vacuum overnight. The cells were then filled with 0.9 g of electrolyte in a dry room with an operating dew point of ~50 °C. The cell filling procedure employed brief, periodic vacuum degassing in order to allow the electrolyte to access all void volume within the cell’s electrodes. The weight before and after the electrolyte filling procedure was recorded in order to ensure the weight of electrolyte added to each cell was consistent. The pouch cells were then sealed under vacuum in a MSK-115A vacuum sealing machine (MTI Corp.) The cells were allowed to stand for 24 hours prior to cycling to ensure complete wetting.

The electrolyte used in this work was 1 M LiPF6 in a 3:7 by weight blend of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) obtained from BASF under the name LP57 and used as received. Fluoroethylene carbonate (FEC) was obtained from BASF and used as received. Diethyl pyrocarbonate (DEPC) was obtained from Sigma Aldrich and used as received. All solvents, salts and blends were stored in a dry box located within a dry room. The introduction of CO2 into the cells was done through the addition of dry ice to the pouch cells as previously described. Briefly, after electrolyte filling and wetting, approximately 5 mg of dry ice was added to the cell. The cell was then immediately sealed without degassing.

Archimedes measurements of pouch cell volume.—Pouch cell volumes were measured using the Archimedes method. Pouch cells were suspended from Mettler Toledo balances into beakers of pump oil. Weight measurements were logged using custom software from the balances and volumes calculated using the oil density. Pouch cells were wired using fine magnet wire to minimize the effect of the wires on the weight measurement. Balances and beakers were in a temperature controlled room held at 22 °C and protected by a shroud to avoid CO2 exposure.
minimize the impact of air currents. In some cases small open-ended polypropylene tubes were included inside the cell to avoid volume changes due to gas, as previously described.¹⁴

**Isothermal heat flow calorimetry.**—Isothermal heat flow calorimetry was conducted using a TAM III (Thermally Activated Module, TA Instruments) in which 12 calorimeters were inserted. The temperature used throughout this work was 37 °C. The TAM III is capable of controlling the bath temperature to within a few micro-degrees centigrade. Reference 6 describes the method and modifications made to the TAM III to allow operando calorimetry measurements on Li-ion cells. Further details for adapting the TAM III calorimeter to parasitic measurements with pouch cells can be found in Reference 7.

**Electrochemical measurements.**—Electrochemical cycling in the context of thermal measurements was performed with Keithley 2602A source-measure units allowing the measurement of the coulombic efficiency to within ± 0.02%. Electrically, electrochemical cycling in the context of Archimedes measurements was performed with a Maccor Series 4000 cycler. Cycle life testing was performed with a Neware BTS3000 cycler having a maximal current of 500 mA. High precision cycling was performed with an ultra-high precision Novonix cycler.

The protocol for cycling cells in the isothermal heat flow calorimeter was as follows: cells were cycled 10 times in each of the voltage segments of 3.0–3.8, 3.5–3.8, 3.7–3.9, 3.8–4.0, 3.9–4.1 and 4.0–4.25 V. The current for all cycles was 20 mA, nominally C/11 for a full voltage range of 3.0–4.25 V. Ten cycles per voltage segment resulted in a nominally stable coulombic efficiency and average parasitic thermal power for a given voltage segment as described in an earlier publication.⁷ The last cycle of each voltage segment was then used to construct a plot of parasitic thermal power versus the average voltage of the segment. We note that in the method we use here, coulombic efficiency, or inefficiency, is simultaneously collected with the thermal data for each voltage segment. Other cycling protocols are described in detail earlier.⁶ Here we briefly describe the methods used in the present work. This method, termed the “integration/subtraction” method, yields an average parasitic thermal power at a given average voltage. Briefly, a total thermal energy is first obtained from the calorimetry data over one cycle. Secondly, the energy loss over one cycle is calculated using the voltage and current (corresponds to the hysteresis area in a voltage-capacity plot). Subtracting the energy loss from the total thermal energy yields a parasitic energy. Dividing the parasitic energy by the cycle time yields an average parasitic thermal power that can be compared across cycles of various durations.

**Wet milling.**—Cathode material HX12Th (Umicore), having the nominal composition Li(Ni0.6Mn0.2Co0.2)O2 (NMC622) with an unknown surface coating, was mixed with N-Methyl-2-pyrrolidone (NMP) in a 1:1 weight ratio. Two kilograms of the mixture were then bead milled using a Netzsch LabStar in a 700 mL chamber with a silicon carbide liner and filled with 0.5 mm Y-stabilized zirconia beads. The zirconia agitator had a speed of 3000 RPM and the flow rate of the mixture was 150 mL/min. The mill was operated in recirculating mode for approximately one hour. Small samples were taken during mill operation to track progress. The final product is coined high surface area NMC622 (HSNMC).

**Particle size distribution and surface area.**—Particle size measurements were performed in water with 1 minute of sonication prior to measurement with a HORIBA LA-950 laser particle size analyzer (HORIBA, Japan). Surface area measurements were performed using a Quantachrome NOVA surface area analyzer.

**Preparation of electrodes and single layer pouch cell assembly.**—The HSNMC was used to make slurries. Table II lists the materials used to make electrodes and Tables III and IV lists the composition of the positive electrodes. NMC622 that was not milled to a high surface area was included as a control at the 2% level.

### Table I. Specifications of the Li-ion pouch cells used in this study.

|          | Negative | Positive |
|----------|----------|----------|
|         | LF129    | LF872    |
| Formulation (w/w) | BTR918/SiAlloy/KS6/SP/LiPAA⁺ | LiCoO₂ | MAGE/SiAlloy/KS6/LiPAA⁺ |
| Coating weight (mg/cm²) | 70.7/15/40/3.10 | 97 | 63/17/10/10 |
| Nominal Porosity (%) | 8.5 | 20.8 | 9.1 |
| Current collector | 30 | 20 | 30 |
| Reversible capacity | 15 μm Cu | 2.6 mAh/cm² (3.0 V – 4.25 V) | 2.6 mAh/cm² (3.0 V – 4.25 V) |
| Balance cutoff voltage | 20 μm Al | 4.35 V | 4.35 V |
| Nominal capacity | 220 mAh | 250 mAh | 250 mAh |

⁺LiPAA-based binder.

### Table II. Materials used to make electrodes.

| ID     | Material                        | Vendor      |
|--------|---------------------------------|-------------|
| UX20P  | LiCoO₂                          | Umicore     |
| PVDF   | Polyvinylidene fluoride         | Arkema      |
| LiPAA  | Lithium polyacrylate            | Sigma Aldrich |
| SP     | Super P                         | Imerys      |
| KS6L   | Synthetic flake graphite        | Imerys      |
| BTR 918II | Synthetic graphite        | BTR New Energy Materials |
| Si Alloy | Si-metal alloy                  | 3M          |

### Table III. Positive electrode compositions of control electrodes.

| ID | LCO | NMC622 | KS6 | SP | PVDF |
|----|-----|--------|-----|----|------|
| P0 | 94% | 0%     | 1.25% | 1.25% | 3.5% |
| P0-2 | 92% | 2%     | 1.25% | 1.25% | 3.5% |

### Table IV. Positive electrode compositions with HSNMC.

| ID | LCO | HSNMC | KS6 | SP | PVDF |
|----|-----|-------|-----|----|------|
| P0.5 | 93.5% | 0.5% | 1.25% | 1.25% | 3.5% |
| P1 | 93.0% | 1.0% | 1.25% | 1.25% | 3.5% |
| P2 | 92.0% | 2.0% | 1.25% | 1.25% | 3.5% |
| P4 | 90.0% | 4.0% | 1.25% | 1.25% | 3.5% |
| P8 | 86.0% | 8.0% | 1.25% | 1.25% | 3.5% |
NMP based slurries with solids as listed in Tables III and IV were mixed in a THINKY ARE-310 planetary centrifugal mixer and coated at 15.6 mg/cm² single sided on 20 μm Al foil with a HIRANO coating machine. Dried electrodes were then calendered to a thickness of 70 μm.

A negative electrode with composition 20% Si alloy / 72% BTR-918II / 3% KS6L / 1% SP / 4% LiPAA by weight was coated with a HIRANO coater at 6.6 mg/cm² single sided on 18 μm Cu foil and calendered to 70 μm. The engineered silicon alloy was as described in previous publications. The experiments involving the blends of LCO and NMC622 used single layer pouch (SLP) electrochemical cells and were assembled by pairing single sided positive and negative electrodes as described above. Two cells were assembled for each pairing. The positive and negative electrodes were separated by a CELGARD 2325 separator and enclosed in an aluminized pouch. The SLPs were assembled in another laboratory for imaging. Cross section imaging was performed with a JEOL JSM-7600F field emission scanning electron microscope (FESEM).

The experiments involving the blends of LCO and NMC622 used single layer pouch (SLP) electrochemical cells and were assembled by pairing single sided positive and negative electrodes as described above. Two cells were assembled for each pairing. The positive and negative electrodes were separated by a CELGARD 2325 separator and enclosed in an aluminized pouch. The SLPs were assembled in a dry room with a dew point of −40°C or less and vacuum dried at 80°C for 24 hrs. They were then filled with 0.48 g of LP57 electrolyte. After filling, the cells were vacuumed to induce wetting, then vacuum sealed using a MSK-115 vacuum sealer. After vacuum sealing the cells were held at 2 V for 24 hrs. They were then filled with 0.48 g of LP57 electrolyte. The LCO (LF129) cells perform much worse than the NMC622 cells even though they have similar negative electrodes, and identical cycling conditions and electrolyte. The performance of both these chemistries can be significantly improved with electrolyte additives, as was shown in a previous publication which used the same LCO (LF129) cells. For example, the cycles to 80% of the LCO cells can be extended from ~60 to ~220 with the addition of 10% FEC. Figure 2b shows that the for the LCO cells, the absence of gas after formation means the volumes with and without tubes are identical, furthermore the volumes increase with decreasing capacity, presumably due to the surface area increase of the Si alloy. Figure 2b also shows that for the NMC622 cells, the gas volume gets gradually consumed and by cycle 50, both cells have equal volumes. Though the cycle life without additives of the NMC622 cells is much better than that of the LCO and without tubes. As explained in a previous publication, the tubes allow differentiation of volume changes caused by solid and gaseous expansion. Cells without tubes show gaseous and solid expansion while cells with tubes only display solid expansion. The difference between the two volume curves therefore corresponds to the gas volume. The negative electrodes are nominally identical with similar amounts of Si alloy and graphite. Cell design details can be found in Table I. All cells had identical LP57 electrolyte (1 M LiPF6 in 3:7 EC:EMC). Cells were cycled between 3 V and 4.25 V with a C/20 formation cycle and CCCV (constant current, constant voltage) cycling at C/3 with a C/20 current cutoff. Figure 1 shows that when a tube is present to contain the gas, the expansion of the NMC622 (LF872) and LCO (LF129) cells are very similar. On the other hand when a tube is not present, the substantial gassing from the NMC622 cells is noticeable. Based on the literature, gas production occurring above 3.7 V is assumed to be primarily CO2. Increased gassing with NMC622 compared to LCO is consistent with the literature. As discussed in Reference 4, the gassing observed in these cells is considerably less than with cells containing only graphite in the negative electrode. Figure 2 shows the discharge capacity and the average volume as a function of cycle number. The LCO (LF129) cells perform much worse than the NMC622 cells even though they have similar negative electrodes, and identical cycling conditions and electrolyte. The performance of both of these chemistries can be significantly improved with electrolyte additives, as was shown in a previous publication which used the same LCO (LF129) cells. For example, the cycles to 80% of the LCO cells can be extended from ~60 to ~220 with the addition of 10% FEC. Figure 2b shows that the for the LCO cells, the absence of gas after formation means the volumes with and without tubes are identical, furthermore the volumes increase with decreasing capacity, presumably due to the surface area increase of the Si alloy. 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**Results**

**Operando archimedes volume measurements.**—Figures 1a and 1b show the voltage and volume respectively of Si alloy containing pouch cells with LCO (LF129) and NMC622 (LF872) cathodes, with and without tubes. As explained in a previous publication, the tubes allow differentiation of volume changes caused by solid and gaseous expansion. Cells without tubes show gaseous and solid expansion while cells with tubes only display solid expansion. The difference between the two volume curves therefore corresponds to the gas volume. The negative electrodes are nominally identical with similar amounts of Si alloy and graphite. Cell design details can be found in Table I. All cells had identical LP57 electrolyte (1 M LiPF6 in 3:7 EC:EMC). Cells were cycled between 3 V and 4.25 V with a C/20 formation cycle and CCCV (constant current, constant voltage) cycling at C/3 with a C/20 current cutoff. Figure 1 shows that when a tube is present to contain the gas, the expansion of the NMC622 (LF872) and LCO (LF129) cells are very similar. On the other hand when a tube is not present, the substantial gassing from the NMC622 cells is noticeable. Based on the literature, gas production occurring above 3.7 V is assumed to be primarily CO2. Increased gassing with NMC622 compared to LCO is consistent with the literature. As discussed in Reference 4, the gassing observed in these cells is considerably less than with cells containing only graphite in the negative electrode. Figure 2 shows the discharge capacity and the average volume as a function of cycle number. The LCO (LF129) cells perform much worse than the NMC622 cells even though they have similar negative electrodes, and identical cycling conditions and electrolyte. The performance of both of these chemistries can be significantly improved with electrolyte additives, as was shown in a previous publication which used the same LCO (LF129) cells. For example, the cycles to 80% of the LCO cells can be extended from ~60 to ~220 with the addition of 10% FEC. Figure 2b shows that the for the LCO cells, the absence of gas after formation means the volumes with and without tubes are identical, furthermore the volumes increase with decreasing capacity, presumably due to the surface area increase of the Si alloy. Figure 2b also shows that for the NMC622 cells, the gas volume gets gradually consumed and by cycle 50, both cells have equal volumes. Though the cycle life without additives of the NMC622 cells is much better than that of the LCO
cells, they do eventually undergo sudden failure and their capacity drop also coincides with an increase in solid volume.

**Impact of cutoff voltages and additives with Si-containing NMC622 full cells.**—Identical LF872 cells with identical LP57 electrolyte were used for this experiment, additives are as noted. Figure 3a shows the normalized capacity (cycle 10) retention of four cells with different lower cutoff voltages (LCV) and upper cutoff voltages (UCV). All cells had the base electrolyte and a C/20 (12 mA) constant current formation cycle followed by CCCV at C/3 (80 mA) with a C/20 current cutoff. Table V(a) lists the capacities at cycle 10 and

| LCV | UCV  |
|-----|------|
| 2.75 | 4.25 |
| 3.00 | 247   |
| 2.75 | 4.35 |
| 3.00 | 264   |

Table V(b) lists the cycles to 80% retention. The absence of additive in these cells is notable, since an additive such as FEC, or CO₂ is normally required to obtain good cycle life with Si-based materials. The LCV and UCV have dramatic effects on capacity retention. All cells have similar fade rates until sudden death occurs, presumably due to a blooming of the surface area on the Si alloy material. The performance of the two cells with a 4.25 V UCV is close to what one would expect for an electrolyte system without additives for Si. Furthermore, the cells with a 2.75 V LCV perform slightly worse, presumably due to the deeper delithiation experienced by the Si alloy. The deeper delithiation leads to increased contraction with possible impacts on mechanical and parasitic losses. Figure 3b shows the voltage capacity curve at cycle 5 for the 2.75 V to 4.35 V cell and the 3.00 V to 4.25 V cell. The voltage curves have been translated for ease of comparison and show that the upper and lower cutoff choices lead to similar variations in capacity.

In traditional full cells, increases in UCV voltages lead to worse coulombic efficiency and capacity retention. It is therefore surprising to see that the cells with 4.35 V UCV perform better than their 4.25 V counterparts by a factor of up to 3.5× in terms of cycles to 80%, this is a phenomenal increase in performance for such a small change in cycling conditions.

To contrast the impact of UCV to that of additives, three cells with additives and cutoffs of 3 V–4.25 V were cycled and compared to a control cell. The first had 2 wt% FEC, the second had CO₂ as dry ice added to the pouch cell as described in a previous publication and the third had 5 wt% DEPC. The DEPC undergoes decomposition to ethylene carbonate and CO₂ during the first charge and is a more convenient way to include CO₂ in cells. The DEPC cells therefore pillowed during their first charge with a similar appearance to the CO₂ dry ice cells. Figure 3c shows that FEC and CO₂ have a large impact on cycling performance. The combination of NMC622 with CO₂ or DEPC is tremendous, raising the retention of the cells to 88% at 500 cycles and above 85% at near 1000 cycles with DEPC. The agreement between the dry ice and DEPC cells confirms the effectiveness of DEPC as a CO₂ release additive. Comparison of Figures 3a and 3b shows that raising the cutoff voltage from 4.25 V to 4.35 V is more effective at extending the cycle life of this Si alloy containing NMC622 cell than the addition of FEC, but not as effective as the addition of CO₂. Of course, the CO₂ cells had the shape of a pillow due to the positive gas pressure.

To further probe the impact of UCV, NMC622 (LF872) sister cells were cycled with base electrolyte in an Archimedes setup with a LCV of 3 V and an UCV of 4.25 V or 4.35 V. The cells were cycled with identical protocols as above with the exception of a C/20 characterization cycle every 50 cycles. The objective of this experiment was to determine if the higher UCV led to measurable gassing and corresponding increase in volume. Figure 4a shows the discharge capacities, once again confirming the positive impact of increased UCV on capacity retention. Figure 4b shows that the volume of the cells is correlated with the capacity fade, remaining essentially...
constant until sudden failure occurs and the volume of the cells starts increasing due to the increase in surface area of the Si alloy, as demonstrated in Reference 4. There is therefore no evidence for increased gas volume during cycling with the 4.35 V UCV cells.

**High precision calorimetry.**—Figure 5 shows the parasitic power and coulombic inefficiency (CIE), calculated as 1-CE, of LCO (LF129) cells and NMC622 (LF872) cells as a function of average voltage and Figure 6 shows the same type of data for NMC622 (LF872) cells only. The methodology is identical to that used in previous publications.3,7 Briefly, after a number of cycles at room temperature, the cells are cycled in an isothermal calorimeter in narrow voltage ranges. The parasitic power and CIE are simultaneously collected on a per cycle basis within the narrow voltage range. After 10 cycles within the narrow voltage range the parasitic power and the CIE have stabilized and the final measurement is reported. Figure 5 shows results for LCO and NMC622 cells with similar numbers of cycles and cycling performed with an UCV of 4.25 V. The LCO cells have much higher parasitics than NMC622 cells even at a low number of cycles, before sudden failure has occurred (see Figure 2). The difference in parasitics is expected to stem from the negative electrode material as the magnitude of parasitic power observed in the LCO case is normally seen only from surface area increase in Si materials3 and not from LCO at 4.25 V. Figure 6 shows results for two groups of cells, the first group has a cycling UCV of 4.25 V and measurements were performed after 42, 81, and 132 cycles at room temperature. The second group had a cycling UCV of 4.35 V and measurements were performed after 45, 87, and 138 cycles. Note the difference in scale with Figure 5. Comparison of the 42 and 45 cycles cells shows that even before sudden fade occurs (see Figure 4a) the 4.25 V cells have higher overall parasitics than their 4.35 V counterparts. As cycling continues and the 4.25 V approach their sudden fade, the parasitics increase, and finally become large after sudden failure. It is notable

**Figure 4.** (a) Discharge capacity and (b) volume with ongoing cycling of LF872 cells with voltage cutoffs as indicated in the legend. Open/closed symbols are sister cells.

**Figure 5.** (a) Parasitic power and (b) coulombic inefficiency of NmC622 (LF872) and LCO (LF129) cells with Si alloy/graphite negative electrodes. Parasitic and coulombic efficiency measurements performed after number of cycles as indicated in the legend. All cells had LP57 electrolyte and were cycled between 3.0 V and 4.25 V.

**Figure 6.** (a) Parasitic power and (b) coulombic inefficiency of LF872 cells having undergone cycling with an UCV and cycle number as indicated in the legend. All cells had LP57 electrolyte.
that the parasitics appear to be a more accurate metric than the CIE, possibly due to the role of the negative electrode overhang. Unlike the 4.25 V cells, the 4.35 V UCV cells remain at the same level of parasitic power and CIE throughout their cycling. This is consistent with the cycle life observed in Figure 4a, where cycling remains excellent beyond the number of cycles tested. Comparing across cells, one can see that parasitic power increases with increasing average voltage, as is universally seen among cell chemistries. The effect of increasing the UCV rather has the impact of shifting the whole curve of parasitic power or CIE, much like the effect of an electrolyte additive such as FEC or CO2.

**Engineered cathodes.**—Wet milling of NMC622.—Figure 7 shows the evolution of surface area and particle size during sizing by wet milling of the NMC622 particles. The starting material had a median diameter (D50) and specific surface area (SSA) of 9.8 μm and 0.23 m2/g respectively and the ending material had a D50 and SSA of 0.47 μm and 11.8 m2/g. The high surface area NMC622 (HSNMC) therefore has ~50x the surface area of the starting material. Figure 8 shows the particle size distribution of the HSNMC compared to the starting material. The HSNMC has a narrow single modal distribution.

Performance of engineered positive electrodes in Si-containing full Cells.—Single layer pouch cells (SLPs) were assembled as described in the experimental section. A total of seven different positive electrodes were tested against an identical negative electrode, two of which were controls (P0 and P0-2) and five of which included the HSNMC. SLPs are named according to the ID of their positive electrode. All cycling occurred at 30 °C in temperature controlled boxes with an ultra-high precision Novonix cycler. Figure 9 shows the voltage capacity curve of the formation cycle. The formation cycle was completed by charging the cells to 4.35 V and discharging them to 2.75 V at 1.8 mA (~C/15). The cells had a nominal reversible capacity of 30 mAh and a nominal areal capacity of 2.5 mAh/cm2. The capacity is plotted per mass of total positive electrode material. All cells had well-behaved voltage curves and the lack of difference shows that the HSNMC is not negatively impacting the performance of the cell. Figure 10 further shows that the HSNMC is contributing to the capacity, indeed the measured discharge capacity compares well to the capacity calculated using the formulations listed in Tables III and IV and reversible capacities of 172 mAh/g and 180 mAh/g for LCO and NMC622 respectively. The conclusion from Figures 9 and 10 is that the milling of the HSNMC has not negatively impacted its electrochemical properties and blending it into an LCO-based cathode has not negatively impacted the LCO. The only electrode which appears to break the trend is the P8 electrode which contained 8% of HSNMC, which indicates that there may be an upper limit up to HSNMC content. During the coating of the P8 electrode, the
A slurry was seen to undergo some gelation, the impact of which is unknown.

Figure 11 shows the cycling performance of the cells at 30°C. Cells were charged at 15 mA (C/2) up to 4.25 V then at 1.5 mA (C/20) up to 4.35 V, then discharged at 15 mA to 2.75 V. It is worth noting once more that these cells contain only LP57 base electrolyte (1 M LiPF6 in EC:EMC 3:7) and do not contain any of the usual additives required for Si-based materials. The inclusion of HSNC has a dramatic impact on capacity retention. The two controls (P0, P0-2) have the worst performance and the performance increases monotonically with HSNC content. The difference in performance is even more dramatic in the CE, the dip at cycle 50 was caused by the cells ending their cycling protocol and needing to be restarted. Figure 11c shows the average discharge voltage. All the cells had similar discharge voltages except the 8% HSNC (P8) which had a lower average voltage, though a much expanded scale is being used and the effect is rather minor in absolute terms. It is not certain what the cause of this is, it may be related to the gelation observed in the slurry, though a possible alternative explanation is that the small particle HSNC may be filling the porosity of the LCO electrode, thereby impacting ion conduction via the electrolyte. The impact is larger than that expected from the difference in average voltage between LCO and NMC.

SEM cross sections.—After 75 cycles the SLPs were discharged and disassembled in a dry room. The electrodes were cross sectioned with an ion beam polisher and the cross sections were imaged with a FESEM. Figure 12 shows the cross sections of the (a) P0-2 and (b) P8 positive electrodes. The SEM of the P0-2 positive electrode, which had 92% LCO and 2% NMC622, shows a LCO single crystal on the left and a NMC622 particle on the right. The SEM of the P8 positive electrode, which had 86% LCO and 8% HSNC, shows that the HSNC is sub-micron, well mixed with the conductive additives (darker gray), and fills the interstitial space between the larger LCO single crystals.

Figure 13 shows the cross section FESEM images of the negative electrodes of the SLPs with positive electrodes (a) P0, (b) P0-2, (c) P2, and (d) P8 as well as (e) a previously published cross section of a Si-alloy containing negative electrode with 75 cycles in the presence of CO2. The only difference in the cycling conditions of the electrodes in Figures 13a–13d is the amount of NMC in the cathode. Indeed, these are negative electrodes from the same coating run, cycled in the same electrolyte, in identical cycling parameters. Figures 13a and 13b show the increase in surface area characteristic of Si-based materials cycle without additives, while Figures 13c and 13d show improved microstructure. Figure 13d displays a Si alloy particle which is composed of 86% LCO / 8% HSNC.
parable to those in 13e after an identical number of cycles. The Si alloy particles in Figure 13e were cycled in the presence of CO$_2$, the best Si alloy additive known to these authors.

Addition of FEC.—Two pairs of SLPs were assembled with the P4 electrode. One cell used the control electrolyte, while 2% FEC was added to the other. The cells were cycled at room temperature with a C/3, 4.35 V, C/20 CCCV charge and C/3, 2.75 V CC discharge. Figure 14 shows the normalized capacity of the cells. The P4 control has a slightly greater number of cycles to failure than the equivalent cell in Figure 11 likely due to cycling at room temperature instead of 30°C. The addition of 2% FEC is seen to increase the cycle life. One can conclude that the benefits of HSNMC and FEC can be combined for Si-based materials.

Discussion

In the first section, the choice of positive electrode material in full cells containing Si-alloy/graphite negative electrodes was shown to have a large impact on performance. LCO and NMC622 were compared, and NMC622 was found to lead to much better performance than LCO. Gassing on formation was also found to be greater with NMC622 than with LCO, in agreement with the literature. According to the literature, CO$_2$ should be the main component of the gas. Archimedes measurements during cycling showed that the gas was consumed with ongoing cycling and that capacity loss was correlated with increase in solid volume in the cells. The impact of cutoff voltage was then explored for NMC622 in Si-alloy containing full cells. Regular cycling. Archimedes measurements, high precision cycling and calorimetry measurements all paint a consistent picture of the UCV having the most impact on cycling life. Increasing the UCV leads to longer cycle life, lower volume expansion, lower parasitics throughout the whole voltage range, and high CE. In fact, increasing the UCV is similar in every respect to adding an additive to improve the performance of the Si alloy. Since it is known that the parasitics at the cathode increase with UCV, it is initially very puzzling to see the parasitics and CIE of the full cell decrease when raising the UCV. This observation leads to the conclusion of an interplay between the positive and negative electrodes. A reaction product at the surface of the NMC622 positive electrode leads to an improvement in performance at the negative electrode containing Si alloy. Indeed this type of behavior has not been noted for cells containing only graphite, in fact the opposite is normally true. Since the reaction is most likely produced at the surface of the cathode material, increasing the surface area of NMC622 should lead to an improvement in full cell performance.

Several different positive electrode materials are used in commercial cells. The choice of positive electrode material is guided by application requirements such as energy density, safety, cost, average voltage, etc... LiCoO$_2$, for example, is particularly well suited for consumer electronics applications where energy density and average voltage (particularly in single cell applications) are more important than cost and safety, though the latter two still need to be acceptable. Energy density is the principal value proposition of Si-based materials. The pairing of LiCoO$_2$ with Si-based materials is therefore particularly attractive for the consumer electronics market. The results of the previous section show that a synergy exists between NMC622 and Si-alloy, and this behavior is expected to be general to all Si-based materials. It is therefore of interest to investigate if the benefits identified with NMC622 can be combined with LCO. Working from the hypothesis that the surface area of NMC is the most important factor, positive electrodes were designed which retained the majority of the electrochemical properties of a LCO positive electrode while having a significant surface area of NMC622 by including high surface area NMC622 (HSNMC). The HSNMC was obtained by wet milling commercial NMC622 (Umicore HX12Th).

As an example, the P4 positive electrode had 90% LCO and 4% HSNMC. The addition of HSNMC is expected to have very little impact on energy density of the electrode since the HSNMC still has capacity, has only a slightly lower average voltage, is able to pack within the interstices of the LCO and is known to perform well as an active material. However, it adds a large amount of NMC622 surface area. Since the absolute surface area of the cathode increases, one can expect the parasitic reactions occurring at the positive electrode surface to increase, however the results in this paper show that these are far outweighed by an increase in performance when using Si in the negative electrode.

The P0-2 control had 2% of regular NMC622 and yet had significantly worse performance than P2 which had an equal amount of HSNMC. These full cells differed only in the surface area of Li(Ni$_{0.9}$Mn$_{0.1}$Co$_{0.2}$)O$_2$. Since the surface area of NMC622 is the key metric helping the performance of the Si, one can compare performance based on the surface area of NMC622 normalized by the Si capacity, this is an intensive variable that does not change with cell capacity. Figure 15 shows the coulombic efficiency at cycle 20 of sister SLPs as a function of the normalized NMC622 surface area, note the agreement between sister cells and the expanded scale allowed by the high precision cycler. Figure 15 shows that the CE has a strong, monotonic dependence on the NMC622 surface area. Figure 15 also shows the surface area that would be obtained in a pure NMC622 positive electrode is already reached with only ~2% of HSNMC. Diminishing returns are also seen with increasing surface area, meaning further increase in HSNMC content beyond 8% is unlikely to result in increased performance.
performance. These results therefore point toward a readily applicable strategy for enabling Si materials in full cells with LCO-based positive electrodes. Indeed, NMC622 is a well-established material already known to cell makers with an existing supply chain.

**Nature of the NMC622 – Si synergy.**—The question of the chemical nature of the synergy between NMC622 and Si is important but difficult to directly answer. Here we propose CO$_2$ as being the main actor, however this is only a hypothesis which will require confirmation with careful study.

In Reference 4 CO$_2$ was shown to have a tremendous impact on the cycling performance of Si-based materials. CO$_2$ was shown to be better than FEC, the gold standard in additives for Si materials, in improving capacity retention and coulombic efficiency, while reducing parasitics at the full cell level. CO$_2$ was also shown to have a synergy with FEC. These results were confirmed in another study showing Li oxalate improves the performance of Si-containing cells via CO$_2$ release. At the same time, studies of gassing in cathode materials have shown that CO$_2$ can be produced at higher voltages, where during formation a gas step at 4.3 V was attributed to CO$_2$ production at the NMC positive electrode. However not all cathode materials produce gas at high voltage in the same way. Indeed, LiCoO$_2$ results in very little gassing during formation, with another study showing complete suppression of high voltage gas evolution. Furthermore, NMC622 is found to lead to increased gassing compared to NMC variants with lower Ni content. Reference 17, which studied NMC111, NMC532 and NMC622, states: “Another interesting finding is that NMC622 cells always generate more gas during formation to 4.4 V or continuous cycling to 4.4 V than cells of the other grades, regardless of the electrolyte additives selected.” The identification of gassing with continuous cycling is a particularly relevant observation to understand the results of this current study. Recent studies from the Gasteiger group with on-line electrochemical mass spectrometry measurements have shown the increased production of CO$_2$ with increasing state of charge and the attribution of CO$_2$ production to oxygen release from the NMC lattice. Released O$_2$ would react with EC to form CO$_2$, CO and H$_2$O. The authors distinguish this type of reaction as “chemical oxidation” as opposed to “electrochemical oxidation” which would only involve the decomposition of electrolyte molecules.

Another recent study attributes the increased gassing found with NMC to the presence of Li$_2$CO$_3$ remaining from synthesis. In this current study, the HSNMC was produced by milling NMC622 in NMP. The NMP/HSNMC slurry resulting from the milling was dried and this is therefore compatible with the capacity retention observed in Figure 14. One can apply the same reasoning to the case of the 2.75 V – 4.35 V NMC622 (LF872) cell in Figure 3, which had ~108 mAh$_{th}$ and ~150 cycles to failure. Adopting the ~0.4 µg/cycle/mAh$_{th}$ from Reference 4, which was averaged over 200 cycles, one estimates that ~147 µmol of CO$_2$ were consumed. The lattice re-arrangement thickness can then be calculated with the 0.23 m$^2$/g of NMC622, 95% NMC622 loading, 18.3 mg/cm$^2$ and 88.4 cm$^2$ resulting in lattice re-arrangement thicknesses of 43 nm or 21 nm for spinel or rocksalt respectively. A lattice re-arrangement of 43 nm would correspond to ~5% of the NMC622, and therefore would be within the range of observed capacity fade.

The dependence of performance on the UCV voltage of the full cell is a strong indication that a reaction product from the positive electrode surface is leading to improved performance with Si. Reference 11 indicates that increased gas production of CO$_2$ started at 4.3 V for NMC442 using Archimedes measurements in NMC/graphite pouch cells. This would point to an explanation for the marked difference in performance between the results obtained with 4.25 V and 4.35 V UCVs. We were unable to identify such increased production in our own Archimedes data during formation cycles, which may be due to the ongoing consumption of CO$_2$ by Si. The rate of consumption of CO$_2$ by Si was shown in a previous publication to be relatively high. Indeed careful study of Figures 1 and 2 show the rapid gas consumption that results from Si. In the case of LCO, the gas is completely consumed before the completion of the formation charge. This makes the quantification of continuous gassing very difficult as the gas may be consumed before exceeding its solubility limit. Despite the careful analysis of cycles for 83 cycles to 4.3 V (~4.4 V vs Li) in LP57, we were unable to identify volume increase at the top of charge due to gas production. In an effort to pinpoint the production of CO$_2$, we assembled symmetric SLPs using only positive electrodes and cycled them in an Archimedes setup. The procedure was similar to previous study though SLPs were used as a format instead of coin cells. We were unable to measure any increase in volume with ongoing cycling with any of the engineered electrodes. This unexpected result points either toward a different mechanism than CO$_2$ production, that CO$_2$ may also be consumed at the positive, or that cross-talk between negative and positive electrodes is necessary for the production of CO$_2$. The cross-talk hypothesis, seems oddly inconsistent with the chemical oxidation of the positive electrode and subsequent CO$_2$ production.

**Chemical oxidation.**—Reference 19 proposed that the chemical oxidation of NMC622 occurred via a re-arrangement of the layered lattice to a spinel or rocksalt configuration according to:

- **Spinel:** $\text{Li}_n\text{MO}_2 \rightarrow \frac{x}{3} \text{Li}_s + \frac{1}{3} \text{M}_s + \frac{1}{3} \text{O}_2 + \frac{1}{3} \text{O}_2$ \[1\]
- **Rocksalt:** $\text{Li}_n\text{MO}_2 \rightarrow (x + 1)\text{Li}_s + \frac{1}{3} \text{M}_s + \frac{1}{3} \text{O}_2 + \frac{1}{2} \text{O}_2$ \[2\]

The released oxygen then reacts with the electrolyte to produce CO$_2$ according to:

$$\text{EC} + 2\text{O}_2 \rightarrow 2\text{CO}_2 + \text{CO} + 2\text{H}_2\text{O}$$ \[3\]

The amount of Li in the conversion is a function of state of charge of the NMC and in this case $x = 0.2$ is used for NMC622 delithiated to 4.35 V in a full cell (~4.45 V vs Li metal). Reference 4 quantified the consumption of CO$_2$ on a per cycle basis as being ~0.4 µg/cycle/mAh$_{th}$ in cells of a similar format and similar negative electrode formulation cycled between 2.75 V and 4.3 V over the course of 200 cycles. However, significant CO$_2$ was consumed on formation and taking the numbers from the first 60 cycles one obtains a consumption rate of ~0.8 µg/cycle/mAh$_{th}$.
symmetric cells with positive electrodes, and furthermore, Reference 19 only observed CO$_2$ production due to lattice re-arrangement above 4.7 V vs Li for NMC622, whereas cells in the current study were only cycled to 4.35 V (~4.45 V vs Li). There is clearly more to be understood. Of particular interest is whether the nature of the negative electrode (Li, graphite, Si, Si-alloy) plays a role in the behavior of the positive electrode.

**Electrochemical oxidation.—** An alternative hypothesis is that the CO$_2$ was produced via electrochemical electrolyte oxidation. This hypothesis is harder to verify quantitatively but is certainly compatible with most of the results, including calorimetry measurements and UCV dependence. Assuming the CO$_2$ originates from EC at a 1:1 molar ratio, the total amount of EC would correspond to 1434 μmol of CO$_2$. As discussed above in the case of the P4 SLP, this is more than two orders of magnitude greater than the expected total CO$_2$ consumption. Therefore EC depletion can be ruled out as a cause of sudden failure and the feature which is the hardest to interpret in the electrochemical electrolyte oxidation hypothesis is the sudden failure of the cells after a given number of cycles. One would expect electrolyte oxidation to continue and to supply the negative electrode with CO$_2$ which would maintain excellent cycling on an ongoing basis. A possible explanation would be that the CO$_2$ production rate gradually decreases as the solid electrolyte interphase (SEI) builds up on the cathode material and thereby reduces its CO$_2$ production rate. Further studies are needed.

Regardless of the mechanism, the results presented above show that the design of the positive electrode and its parasitic activity can have a tremendous impact on the cycling performance and parasitic activity of negative electrode materials, particularly Si-based materials. Furthermore, these differences in behavior can be leveraged to engineer positive electrodes which will enhance the performance of full cells containing Si-based materials. We expect that the interplay between negative and positive electrode will become an increasingly important aspect of full cell design as the battery community continues to further understand their respective parasitic reactions and possible cross-talk.

**Conclusions**

Wound pouch cells with a LiNi$_{0.6}$Mn$_{0.2}$Co$_{0.2}$O$_2$ (NMC622) positive electrode and graphite/Si alloy negative electrode were shown to have significantly better performance than equivalent cells with a LiCoO$_2$ (LCO) positive electrode in the absence of electrolyte additives. Increasing the UCV of Silicon containing NMC622 cells from 4.25 V to 4.35 V led to an improvement in performance. Engineered positive electrode were designed with small amounts (~8 wt%) of high surface area NMC622 added to LCO-based positive electrodes in single layer pouch cells with graphite/Si alloy negative electrodes. The addition of high surface area NMC622 led to improvements in cycling performance and coulombic efficiency. Adding FEC further improves the performance of cells showing the benefits can be combined. High precision calorimetry and cycling, Archimedes volume measurements, and cross-section scanning electron imaging support the hypothesis of interplay between the parasitic reactions at the positive and negative electrodes. The NMC622 positive electrode is proposed to stabilize the Si alloy in the negative electrode via a CO$_2$ release mechanism, though further confirmation of the mechanism is needed. These results provide guidelines for designing positive electrodes that will improve the performance of Si-containing full cells. These results also highlight the need to further understand the parasitic reactions occurring at the surface of positive and negative electrodes and how they may depend on each other. Finally, successful implementation of Si-based materials requires optimization of the complete full cell including positive electrode, electrolyte, additives, and cycling protocol.

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