



Surface Area Increase of Silicon Alloys in Li-Ion Full Cells Measured by Isothermal Heat Flow Calorimetry

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Li-ion pouch cells utilizing a negative electrode formulated with 15 wt% of an engineered Si alloy in a graphite composite electrode were cycled in an isothermal heat flow calorimeter against a LiCoO₂ positive electrode. Two different electrolytes were investigated: a blend of ethylene carbonate and ethyl methyl carbonate (3EC:7EMC) and a blend of ethylene carbonate, ethyl methyl carbonate and 1-fluoro ethylene carbonate (27EC:63EMC:10FEC). Both electrolytes were 1 M in LiPF₆ salt. The parasitic thermal power and coulombic efficiency was derived from isothermal heat flow measurements and high precision current-source meters. Cells without FEC showed high parasitic thermal power which increased with cycle number indicative of a surface area increase which was confirmed by post-cycling scanning electron micrographs and surface area measurements. Cells with FEC showed relatively stable parasitic thermal power. These measurements demonstrate the surprising function of FEC in controlling or attenuating the evolution of surface area in Si alloys. Vinylene carbonate was also found to be effective at controlling the increase in alloy surface area.

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Meeting the promise of silicon or Si alloys to increase the energy density of Li-Ion cells has been the subject of a great deal of research and development. To date the full commercial impact of this materials technology has not been met owing to the difficulties found with silicon.¹⁻⁶ In general the high capacity fade often found in Li-ion cells containing Si has 3 main causes: 1) mechanical or electrical disconnect of the alloy particles in the composite electrode owing to large volume changes¹⁻⁴ 2) crystallization effects, mainly the formation of the Li₁₅Si₄ phase, which shows hcity(cc)Ceiven4w3(e)[(I)-0.44Ih96647iayIh96647iayIh9664-288.rg[(v)TJ-288.Nhctrodeio8(dif997iayI)t0.1[i]2887ll50

The 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, no charge was applied during standing.

The base electrolyte used in this work was 1 M LiPF₆ in a 3/7 (w/w) blend of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) obtained from BASF and used as received. VC (Novolyte) and FEC (BASF) were also used as received. All solvents, salts and blends were stored in a dry box located within a dry room.

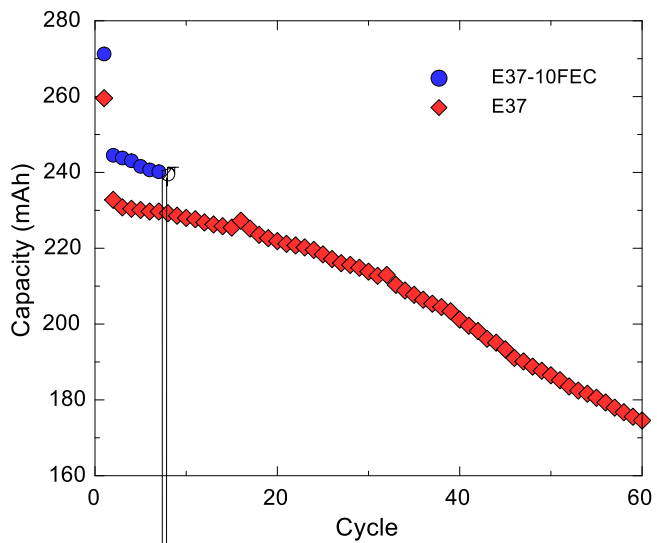
Current source.—Keithley 2602A source-measure units were used to charge and discharge the cells. This equipment is capable of supplying currents in the 10 mA to 100 mA range with an accuracy of $\pm 0.03\% + 6 \mu\text{A}$ with a resolution of 200 nA. The voltage measurement accuracy is $\pm 0.015\% + 1 \text{ mV}$ with 10 μV resolution in the 6 V range. Time resolution is < 1 sec. This precision allows the measurement of the coulombic efficiency to within $\pm 0.02\%$.

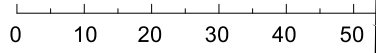
Isothermal heat flow calorimeter.—The heat flow calorimeter is a TAM III (Thermally Activated Module, TA Instruments) in which 12 calorimeters were inserted. The temperature used throughout this work was 37°C. The TAM III is capable of controlling the bath temperature to within a few micro-degrees centigrade. Reference 13 describes the method and modifications made to the TAM III to allow in-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 14.

Cycling protocol.—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.¹⁴ 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.

We have reported on this cycling protocol previously in a study of electrolyte chemistry of graphite//LiCoO₂ cells.¹³ In the present work, where two materials with distinctly different voltage versus capacity characteristics are considered (i.e. Si and graphite), the lithiation and delithiation does not occur uniformly for both materials under all voltage segments. This is discussed below.

Methods.—







0 40 80 120 160 200

and contraction leads to the exposure of fresh non-passivated surfaces which continually drive the additive consumption.

Summary

The electrolyte induced cycle life failure of Gr:Si-alloy//LiCoO₂ cells was shown by calorimetric and precision cycling methods to be an expansion of effective surface area where the formed SEI likely contains active electrochemical surfaces. FEC, used ubiquitously as an additive to improve the cycle life of Si-containing cells was shown to greatly attenuate the surface area expansion most likely through the formation of a denser and more resilient SEI. Sudden capacity failure, observed after FEC has been consumed was also shown to be accompanied by surface area expansion.

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