



Understanding capacity fade in silicon based electrodes for lithium-ion batteries using three electrode cells and upper cut-off voltage studies



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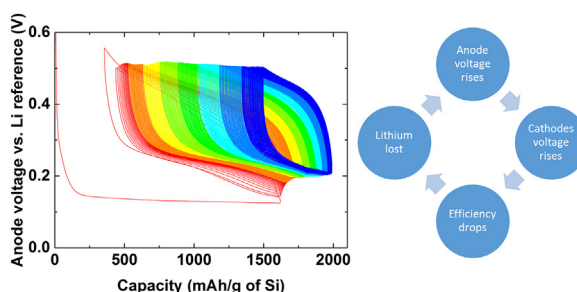
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HIGHLIGHTS

- End of charge voltage drifts more positive as a function of cycle number.
- Voltage at the cathode reaches >4.4 V vs. Li, resulting in capacity fade.
- End of charge voltage dramatically affects cycling efficiency.
- Loss of capacity causes rise in end of charge voltage.

GRAPHICAL ABSTRACT



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ABSTRACT

Commercial Li-ion batteries are typically cycled between 3.0 and 4.2 V. These voltage limits are chosen based on the characteristics of the cathode (e.g. lithium cobalt oxide) and anode (e.g. graphite). When alternative anode/cathode chemistries are studied the same cut-off voltages are often, mistakenly, used. Silicon (Si) based anodes are widely studied as a high capacity alternative to graphite for Lithium-ion batteries. When silicon-based anodes are paired with high capacity cathodes (e.g. Lithium Nickel Cobalt Aluminium Oxide; NCA) the cell typically suffers from rapid capacity fade. The purpose of this communication is to understand how the choice of upper cut-off voltage affects cell performance in Si/NCA cells. A careful study of three-electrode cell data will show that capacity fade in Si/NCA cells is due to an ever-evolving silicon voltage profile that pushes the upper voltage at the cathode to >4.4 V (vs. Li/Li⁺). This behaviour initially improves cycle efficiency, due to liberation of new lithium, but ultimately reduces cycling efficiency, resulting in rapid capacity fade.

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1. Introduction

Silicon (Si) is often studied as an alternative to graphite for negative electrodes in Lithium-ion (Li-ion) battery technology due to its high theoretical specific and volumetric capacity (3579 mAh/g

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and 2190 mAh/cm³ respectively) [1]. Although encouraging theoretically, practical silicon electrodes exhibit relatively low cycle efficiency; capacity retention drops off quickly as a function of cycle number. There are numerous factors which conspire to reduce cycle life in silicon electrodes. Some of the most important factors to consider are:

- 1) Large expansion during lithiation (up to 280%) [1].
- 2) Electrode delamination from the current collector due to large volume changes
- 3) Instability of the Solid Electrode Interphase (SEI) due to large expansion
- 4) Instability of the electrolyte with lithiated silicon

Factors two and three above are strongly dependent on factor one. A popular strategy to cope with the large expansion associated with full lithiation of silicon is to cycle electrodes to less than full capacity [2–8]. This is often achieved using capacity constrained cycling methodologies in half cells vs. a lithium (Li) metal electrode. For example, some authors restrict the Si capacity to ~1200 mAh/g (instead of 3579 mAh/g) [2–8] and then cycle to ~1 V to delithiate the silicon (in half cells). Inevitably, the delithiation capacity is less than the lithiation capacity, due to irreversible capacity loss. As an example, consider cycle *x* where the silicon electrode is lithiated to 1200 mAh/g. During the subsequent delithiation cycle, suppose that 1195 mAh/g of capacity is recovered (e.g. 99.6% efficiency). In this case 5 mAh/g of capacity is lost, due to irreversible processes, causing 5 mAh/g worth of silicon to become unavailable (e.g. due to loss of electrical contact). On cycle *x* + 1, the silicon electrode is again lithiated to 1200 mAh/g. This is possible, because both electrodes have an excess of reactant. There is an excess of lithium from the lithium electrode, and there is an excess of silicon (because the silicon is being cycled to 1200 mAh/g, rather than the full capacity of 3579 mAh/g). For simplicity, assume 5 mAh/g of capacity is lost on every cycle. In this case the silicon electrode will be unable to achieve 1200 mAh/g of capacity after 475 cycles. When plotting cycle number vs. capacity, cycles 1–475 will look perfectly flat, then capacity will quickly fall (with a slope of 5 mAh/g/cycle). This type of behaviour is observed in all capacity constrained cycling results [2–8]. Refer to [1], for a more detailed explanation of this process.

Although capacity constrained cycling produces aesthetically pleasing graphs when capacity is plotted as a function of cycle number, it is easy to underestimate the inefficiencies occurring in the cell. This cycling technique masks the true behaviour of the electrode, and is not useful as a practical screening technique.

Despite the considerations above silicon electrodes are commonly cycled to less than their full capacity [2–8]. One method to achieve a type of constrained capacity cycling is to pair a high capacity silicon electrode with a lower (areal) capacity cathode. The cell is charged to a set voltage (e.g. 4.2 V), liberating a known amount of lithium from the cathode. Typically, sufficient cathode material is used to achieve reversible silicon electrode capacities of ~1200 mAh/g (as above).

Silicon electrodes are often fabricated from polycrystalline or semi-crystalline powders. During the first lithiation cycle crystalline Si is converted to amorphous Si. Room-temperature electrochemical lithiation of silicon does not follow the thermodynamic phase diagram [9], [10]. When cycling strategies use less than the full capacity of the silicon it is important to understand what happens to the silicon electrode as a whole, especially as a function of cycle number and state of charge (SOC). Ideally, the unlithiated silicon is a passive spectator, and is not involved during subsequent cycles. However, the spectator theory is not correct. The silicon electrode undergoes gradual but continuous changes during cycling. The data below will also show that changes at the anode

results in detrimental changes at the cathode. A combination of these factors readily explains the rapid capacity fade observed in silicon-based electrodes.

2. Experimental

Silicon electrodes were prepared in multiple steps, outlined below:

2.1. Stock PAA solution

A solution of Polyacrylic Acid (PAA; Sigma Aldrich, MWT = 450 k, purity ≥ 99.5%) was prepared by mixing 24 g of PAA with 176 g of deionised water (equates to 12 w/w% PAA) in a 500 mL Nalgene[®] beaker. The PAA slurry was mixed using a Primix Homodisper (Model 2.5) at 500 rpm for 120 min, followed by stirring at 250 rpm for a further 120 min with a Primix medium shear impeller blade until the solution was clear.

2.2. Partially neutralised PAA solution

12.4 g of sodium carbonate (Na₂CO₃; Fisher Chemical, purity > 99.5%) was added to the stock PAA solution (described above). This represents a molar ratio of 1.42:1 PAA: Na₂CO₃ and 70% Na neutralization of the PAA. The mixture was stirred by hand, with a spatula, until all of the Na₂CO₃ was dissolved. The partially neutralized Na-PAA solution was left overnight until the Na-PAA solution turned clear. Note that the reaction of the stock PAA solution with Na₂CO₃ was aggressive and excessive foaming occurred.

2.3. Si slurry

10 g of Si (Elkem Silgrain e-Si, d50 3.1 μm, purity 99.7%) was mixed with 1.43 g of carbon black (Alfa Aesar, Acetylene Black purity 99.9+ %, S.A. 75 m²/g), 0.85 g of graphite (Timrex SFG6, purity 99.93%), and 20 g of deionized water in a 250 mL Pyrex[®] vessel. The Si slurry was then placed in a sonic bath (Fisherbrand FB 15060, 150 W, 37 kHz) for 1 h to break down agglomerates. After sonication the slurry was further mixed using medium shear stirring in a Primix Homodisper Model 2.5 for 30 min at 1000 rpm.

15.45 g of partially neutralized Na-PAA solution (described above) was added to the entirety of the Si slurry described above. The composite slurry was impeller stirred (Primix Homodisper Model 2.5) for 30 min. Thirty millilitres of the resulting solution was transferred to a Filmix mixing vessel and subjected to the following mix cycle: two dispersions for 30 s each at 10 m/s then 30 s at 25 m/s. The rest of the slurry receives the same mixing procedure (the solution was broken up into two smaller batches to accommodate the 60 mL volume of the Primix Homodisper Model 2.5).

The above formulation results in electrodes with a dry mass % composition of 70: 14: 10: 6 (Silicon: Na-PAA: carbon black: graphite).

After degassing, anode coatings were cast onto 10 μm thick Cu foil (Oak Mitsui, electrodeposited) using an RK printing applicator applying a partial vacuum on the Cu foil and a doctor blade set at a blade gap of 100 μm. Coated electrodes were dried on a hot plate at 80 °C followed by vacuum drying (7 mBar) for 12 h at 70 °C.

The mass loading on dried Si electrodes was ~20.7 g/m² total and ~14.5 g/m² active (i.e.: ~5.2 mAh/cm² at full Si capacity).

2.4. Cathode

Lithium Nickel Cobalt Aluminium Oxide, LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ (NCA), cathodes were paired with silicon electrodes due to their

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