



Influence of inactive electrode components on degradation phenomena in nano-Si electrodes for Li-ion batteries

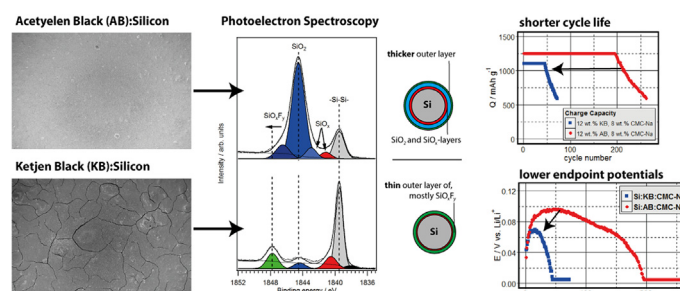
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HIGHLIGHTS

- Electrode components with high surface area lead to poor electrode morphologies.
- Poor morphologies are reflected in short cycle life and fast degradation.
- Differential capacity provides insight to degradation processes of Si electrodes.
- Binder coverage of Si depends on surface areas of the inactive components.
- Binders act as artificial SEI layer and prevent parasitic surface reactions.

GRAPHICAL ABSTRACT



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ABSTRACT

The electrode morphology and electrochemistry of silicon nanocomposite electrodes containing either carboxymethyl cellulose (CMC-Na) or poly(acrylic acid) (PAA) binders are examined in context of their working surface area. Using porous carbon (Ketjenblack) additives, coatings with poor adhesion properties and deep cracks were obtained. The morphology is also reflected in the electrochemical behavior under capacity-limited conditions. Mapping the differential capacity versus potential over all cycles yields detailed insights into the degradation processes and shows the onset of cell failure with the emergence of lithium-rich silicon alloys at low potentials, well before capacity fading is observed. Fading occurs faster with electrodes containing PAA binder. The surface area of the electrode components is a major cause of increased irreversible reaction and capacity fade. Synchrotron-based X-ray photoelectron spectroscopy on aged, uncycled electrodes revealed accelerated conversion of the native SiO_x-layer to detrimental SiO_xF_y in presence of Ketjenblack. In contrast, a conventional carbon black better preserved the SiO_x-layer. This effect is attributed to preferred adsorption of binder on high surface area electrode components and highlights the role of binders as ‘artificial SEI-layers’. This work demonstrates that optimization of nanocomposites requires careful balancing of the surface areas and amounts of all the electrode components applied.

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1. Introduction

Reducing the particle size of an electrode material for lithium-ion battery (LIB) applications to the submicrometer dimension

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has enabled the emergence of some of today's most commonly studied nanomaterials for both positive and negative electrodes [1,2], e.g. lithium iron phosphate (LFP) and silicon [3,4]. It has been shown that nanosized silicon below particle sizes of about 150 nm can better accommodate the strain of the tremendous volume expansion of up to 280% during electrochemical lithiation to $\text{Li}_{15}\text{Si}_4$ [3,5], compared to micron-sized particles. Additional improvements can be gained from tailoring the shape of the nanomaterial [6,7]. Many LIB electrode materials are in fact poor electronic conductors and thus benefit from shorter diffusion pathways and greater inter-particle contact [2].

A major factor in stable cell cycling in LIBs is the stability of the solid-electrolyte interphase (SEI) on the negative electrode, formed as a result of electrolyte decomposition during the first cycles [8,9]. This is true not least for silicon-based battery chemistries. The amount of deposited material is a function of the electrodes' surface area, which may lead to substantial losses of the lithium inventory of the cell [10]. This effect is accompanied by a restricted tolerance to stress. Repeated cracking of this passivating layer induces continuous electrolyte decomposition at the exposed interface. For silicon electrodes especially, the use of electrolyte additives, particularly the combination of vinylene carbonate (VC) [11] and fluoroethylene carbonate (FEC) [12], appear to improve the mechanical properties of the SEI [13]. Furthermore, replacing the common lithium salt LiPF_6 by more benign salts, such as LiTFSI or LiTDL that do not suffer from hydrolysis and HF evolution also contributes to an improved SEI layer [14–18].

The volume expansion of silicon during lithiation leads to particle rearrangements within the electrode, which results in changes in and, ultimately, loss of electronic contact between particle domains [19,20]. Furthermore, a continuous SEI growth decreases the effective surface area and hampers Li^+ diffusion through the porous composite electrode [21]. From an electrochemical perspective, these problems can be approached in two ways: (1) large amounts of conductive additive, as in a silicon:carbon:binder ratio of 1:1:1, and 100% depth of charge (DoC) [20,22] or (2) moderate amounts of silicon (around 80 wt%) and capacity limited cycling to 33–50% DoC [21,23–25], both rendering a lower energy density.

Electrode binders have emerged as a crucial component in silicon electrodes, since the mechanical properties and the interconnectivity of the components of a composite electrode are greatly influenced by the physical properties of the polymer applied [26–28]. Carboxymethyl cellulose sodium salt (CMC-Na) [29–33] (and more general natural carbohydrate-based polymers [34–36]) and poly(acrylic acid) (PAA) [26,37,38] have become the most commonly used binders for the Si system. Because of their low swellability in carbonate-based electrolytes and resiliency, they are more effective in maintaining the electrode morphology and providing a stable electrode-electrolyte interface than the established poly(vinylidene difluoride) (PVdF) binder and its derivatives [26,34,39]. Unfortunately, the overall electrode performance strongly depends on the surface of the silicon particles as a result of different synthetic routes, pretreatments [25,28] or slurry fabrication [40], making comparisons between reported binders problematic. But because of their strategically important location at the electrode interface, polymers can significantly influence the surface reactions and SEI formation, if their functionalities are chosen carefully [39,41,42].

Komaba and co-workers studied PAA and its salts as exfoliation-suppressing binders (or 'artificial SEI' components) in graphite [41,43–46] and silicon:graphite electrodes [47]. Our group also recently reported on the protection of graphite particles in 'aggressive' electrolyte environments (containing large amounts of propylene carbonate) as a more general concept that is attributed to the poor swellability of some polymers, such as CMC-Na and

PAA-Na (poly(sodium acrylate)), in carbonate electrolytes [39,48]. Moreover, localization of the binder in pristine electrodes by energy dispersive X-ray spectrometry revealed a strong preference of PAA-Na for covering the conductive carbon black additive rather than the graphite particles, which have roughly one sixth of the surface area of the carbon black). Therefore, electrodes with low amounts of this binder deteriorated rapidly due to absence of effective protection [48]. In order to further investigate this hypothesis, we here employ the same binders, CMC-Na and PAA, in silicon nanocomposites containing acetylene black (low surface area) and Ketjenblack (high surface area) conductive additive, respectively. It is well known that the silicon system is more susceptible than graphite to the choice in binder [27,31], and hence distinctly different electrode morphologies and electrochemical performance would be expected if preferential binder adsorption takes place on the carbon additives. In this study, we correlate electrode morphology studied by scanning electron microscopy (SEM) with galvanostatic cycling under capacity-limited conditions. For the first time, mapping of the differential capacity over the entire life time of a Si-based cell is presented which gives detailed information on the degradation phenomena. This data is complemented by analysis of the endpoint potentials and internal resistance. These results are then put into context of the surface chemistry of the electrode, which is characterized by synchrotron photoelectron spectroscopy (PES).

2. Experimental

2.1. Electrode preparation and cell assembly

Electrode slurries were prepared according to a formulation of 80 wt% silicon powder (Alfa Aesar, average particle size ~50 nm, surface area: 70–100 m^2/g), 12 wt% conductive additive (acetylene black C-55 (Chevron) or Ketjenblack EC-600 (AkzoNobel)), and 8 wt % binder. In one experiment the silicon:binder ratio of 10:1 was held constant while the content of Ketjenblack in the electrode was changed to 8 wt% (83.6 wt% Si) or 16 wt% (76.4 wt% Si) respectively. The binders, a 35 wt% aqueous solution of poly(acrylic acid) (PAA, $M_w = 250,000$, Aldrich) and carboxymethyl cellulose sodium salt (CMC-Na, Dow Chemicals, d.s. 0.78), were used as received. For electrodes containing altered amounts of binder, the ratio between the carbon and silicon materials remained constant. The solids were dispersed in deionized water (the quantity varied depending on the viscosity of the slurry) and mixed by planetary ball milling for 1 h. The resulting slurry was bar-casted on copper foil (Good-fellow, 22 μm thick). After drying at ambient temperature, the electrodes were punched into 20 mm discs and transferred to an Ar-filled glovebox, where they were first dried under vacuum at 80 °C for 12 h and then subjected to a final drying step over 6 h at 100 °C. The drying temperature was deliberately kept below 125 °C in order to avoid condensation reactions of the binder [38,49,50].

All electrodes were tested in half cells against lithium metal in a pouch cell format with copper current collectors. The porous polyethylene (Solupor, Lydall Performance Materials) separator was dried over night at 80 °C under reduced pressure in an Ar-filled glovebox and was cut into a circular shape, 25 mm in diameter. 1 M LiPF_6 in 1:1 ethylene carbonate:diethyl carbonate (EC:DEC, LP40, Novolyte) was applied as electrolyte. The amount of electrolyte was 75 μL for cells fading before reaching 100 cycles and was increased to 100 μL for cells cycled for longer times. A roughly square piece of lithium foil (125 μm thick, Cyprus Foote Mineral) of $3 \times 3 \text{ cm}$ was used as counter electrode. The lithium excess was doubled by using two pieces of Li foil for cells cycling for more than 100 cycles, due to the high degree of irreversible reactions [22].

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