Hierarchical columnar silicon anode structures for high energy density lithium sulfur batteries

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HIGHLIGHTS

- Columnar silicon anodes reach area capacities up to 7.5 mAh cm^{-2}.
- Electrode deformation during lithiation hinders the application.
- Structuring by a pulsed laser can avoid the deformation effects.
- Lithiated silicon anodes enhance the volumetric energy density of Li/S cells.

ARTICLE INFO

ABSTRACT

Silicon is a promising anode material for next generation lithium secondary batteries. To significantly increase the energy density of state of the art batteries with silicon, new concepts have to be developed and electrode structuring will become a key technology. Structuring is essential to reduce the macroscopic and microscopic electrode deformation, caused by the volume change during cycling. We report pulsed laser structuring for the generation of hierarchical columnar silicon films with outstanding high areal capacities up to 7.5 mAh cm^{-2} and good capacity retention. Unstructured columnar electrodes form a micron-sized block structure during the first cycle to compensate the volume expansion leading to macroscopic electrode deformation. At increased silicon loading, without additional structuring, pronounced distortion and the formation of cracks through the current collector causes cell failure. Pulsed laser ablation instead is demonstrated to avoid macroscopic electrode deformation by initial formation of the block structure. A full cell with lithiated silicon versus a carbon-sulfur cathode is assembled with only 15% overbalanced anode and low electrolyte amount (8 µl mg$_{sulfur}^{-1}$). While the capacity retention over 50 cycles is identical to a cell with high excess lithium anode, the volumetric energy density could be increased by 30%.

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1. Introduction

The global market growth of electric vehicles and urgent need for customer-driven desire of range extension causes currently a massive demand on high energy density lithium batteries [1,2]. Silicon based anodes have the potential to raise the cell energy density owing to its high theoretical capacity of 3579 mAh g^{-1} in the fully lithiated state at room temperature (Li$_{3.75}$Si) compared to 372 mAh g^{-1} for commercial graphite anodes [3,4]. By considering the limited space for battery energy storage in automobiles, a further key advantage is the volumetric capacity of silicon (8303 mAh cm^{-3}) [5]. This is nearly the fourfold compared to lithium (2047 mAh cm^{-3}) and tenfold vs. graphite (837 mAh cm^{-3}) [6]. However, this comparison essentially ignores the 300% volume expansion of silicon during lithiation, which lowers the volumetric capacity to about 2000 mAh cm^{-3} [7]. However, one should take into account that a pure lithium anode has to be used with excess because of active material loss through dendrite formation [8,9]. Then, silicon is the anode material with the highest volumetric

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capacity.

The volume change during cycling is the major technical challenge of silicon anodes leading to low cycle stability, due to pulverization of silicon and lithium-loss caused by the instability of the solid electrolyte interface (SEI) [10,11]. Especially nanostructures such as nanoparticles [12,13]/hollow nanospheres [14,15], nanowires [16,17]/nanotubes [18,19] and compact [20,21]/porous [22,23] thin films have been suggested to avoid these problems. The developed electrode structures show mostly good capacity retention, cycle life and are able to compensate the volume change. However, such silicon electrodes typically do not fulfill the following needs for high energy density lithium batteries [7,13]:

- area capacities above 2.0 mAh cm^{-2}, to compensate the weight of the current collector
- adequate gravimetric electrode density, to compete with the volumetric capacity of graphite anodes
- high initial coulombic efficiency (CE) over 90% for low lithium loss by SEI formation
- and finally rate, temperature capability, safety, scalable production.

Silicon nanostructures like nanoparticles and nanowires suffer from high lithium losses in the first cycle by SEI formation caused by their high specific surface area [24]. Efforts have been reported to overcome this issue by implementation of additional lithium sources in the cell [25,26], silicon prelithiation before cell assembly [27,28], or reduction of the surface area by encapsulation [29,30] or an interconnected structure [31,32]. Even if some of these suggested methods are promising, they cause extra processing and/or handling of highly reactive lithiated silicon [33]. Compact silicon film anodes combine excellent gravimetric density and low surface area for high initial coulombic efficiency. But films with thicknesses over about 200 nm show a formation of crack patterns caused by the volume expansion [34]. A further increase in film thickness results in a rapid capacity fade, caused by contact loss from current collector [35]. Therefore capacity loadings of practical relevance cannot be realized with compact silicon films.

Columnar silicon films with integrated porosity and good surface to volume ratio for high initial CE were developed at specifically treated current collector foils [36–38]. Capacity loadings up to 4 mAh cm^{-2} were discussed [39], but the electrode structure after cycling was presented only for electrodes with low loadings or capacity limitation. Often, a block-wise structure was observed which can provide the space for the enormous volume expansion, when the initial columnar films have not enough porosity [39,40]. This structure must lead, especially for electrodes with high silicon loading, to a macroscopic electrode deformation like wrinkling, which is normally not alluded [41,42]. A wet chemical etching method was suggested to tailor the free space between silicon columns [43]. But the positive effect was only shown for very thin silicon films with no practical relevance for high energy density lithium batteries.

The pairing of a sulfur cathode with metallic lithium anode offers an outstanding high specific capacity (1672 mAh g$_{sulfur}^{-1}$) and the possibility to exceed an energy density of 400 Wh kg^{-1} [44,45]. A further factor, that support the practical relevance of this system is the environmental friendliness of sulfur, due to high abundance in nature and the non-toxicity [46,47]. However, the use of a metallic lithium anode is a major impediment for the commercialization of lithium sulfur batteries [48]. Pure lithium causes safety issues and its use in excess lowers the energy density [49]. Silicon is considered as alternative anode material for lithium sulfur cells [33,50–52]. Cui et al. reported a combination of an unlithiated silicon nanowire anode with a Li$_2$S cathode [53]. Due to the instability of Li$_2$S in air, low capacity retention and high lithium loss by SEI formation at silicon in the first cycle, a concept based on a lithiated silicon anode and sulfur cathode (SLS) was proposed [54]. However, until now only low active material loadings, high excess of electrolyte and a significantly overbalanced anode were applied in this cell type.

Here, we present the performance of hierarchical columnar silicon anodes with areal capacities up to 7.5 mAh cm^{-2} never reached before, and good capacity retention. We avoid the deformation of columnar silicon film electrodes with high thicknesses and their impact to the low capacity fade. We show that a pulsed laser ablation process can be used to generate hierarchical block-wise structures in the unlithiated state before cycling. Hereby it is possible to tune the free space needed for volume expansion and to avoid the macroscopic deformation at practically relevant capacity loadings. To demonstrate the advantages in terms of volumetric energy density, we have assembled a balanced full cell of lithiated silicon versus carbon-sulfur cathode (SLS type cell [54]) with low lithium excess of 15%. The cell showed an excellent cycling stability comparable to a cell with a high excess lithium anode.

2. Experimental section

2.1. Preparation of electrodes

Anode preparation: Silicon were deposited in a roll to roll process by DC magnetron sputtering at argon pressure of 0.7 Pa (labflex® 200, Fraunhofer FEP) from silicon target (n-type; 99.995%) onto 10 μm thick copper foil (SE-Cu 58, Schlenk Metallfolien GmbH & Co. KG). The current collector foil features a roughened layer of copper dendrites that leads to the formation of columnar structures and ensures the adhesion of silicon [55]. A femtosecond-laser (10 W) with 1064 nm wavelength and 163 mm focal length was used for the partial ablation of silicon. The laser power and feed rate was varied between 10 and 100% and 50–800 mm s^{-1}, in order to identify best processing parameter to generate a block-wise structure.

Cathode preparation: The cathode preparation was carried out in slightly adjusted procedure, as published before from Bauer et al. [56]. A composite of sulfur (Sigma Aldrich, ≥ 99.5%) and carbon black (Printex XE-2B, Orion Engineered Carbons) was mixed in a ratio of 12:5 and melt infiltrated at 155 °C for 12 h in air. The composite was transformed to a slurry by adding carboxymethyl cellulose (CMC, Sigma Aldrich)/styrene-butadiene rubber (SBR) (1:1 m:m) as binder and Multiwall Carbon Nanotubes (MWCNT, Nanocycl NC 7000, 90%) in a weight ratio of 85:5:10 in deionized water. The slurry was coated in a roll to roll process onto a 15 μm thick aluminum foil (MTI Corp., >99,9%) with a comma bar coating technique (FMP Technology) followed by a drying at 200 °C. The cathode had a loading of 2.8 mg cm^{-2}. With regard to the sulfur ratio of 60% in the cathode, this corresponds to 1.7 mg$_{Sulfur}$ cm^{-2}. The cathode thickness was determined to be 60 μm, leading to an electrode density of 0.43 g cm^{-3}. The cathode was dried in vacuum oven at 50 °C for 1 h prior to cell assembly.

2.2. Electrochemical characterization

Half cells: All test electrodes were punched in 12 mm diameter disks and assembled in an argon atmosphere glovebox (MBraun, < 0.1 ppm O$_2$ and H$_2$O) in coin cells (MTI Corp., CR2016) versus lithium reference electrode (MTI Corp., 99.0%, diameter: 15.6 mm, thickness: 250 μm), separated by a polypropylene separator (Celgard 2500). For silicon half cells, 30 μl of 1 M lithium bis(trifluoromethylsulfonyl) imide (LiTFSI, Sigma Aldrich, 99.95%), 0.25 M lithium nitrate (LiNO$_3$, Alfa Aesar, 99.98%, anhydrous) in 1,2-