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Threshold-like dependence of silicon-based electrode performance on active mass loading and nature of carbon conductive additive

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ABSTRACT

Silicon-based electrodes of various areal capacities, from about 1.5 to 15 mAh.cm^{-2}, were prepared with different conductive additives (carbon black, carbon nanofibers, and carbon nanoplatelets). The sensitivity of the cycling performance to the active mass loading is significant, with a major decrease of the capacity retention with increasing the loading in all cases. There is moreover a critical loading value above which the capacity retention abruptly drops. This critical loading depends on the conductive additive (~1.75 mg cm^{-2} for carbon black, ~2.25 mg cm^{-2} for carbon nanofibers and ~3 mg cm^{-2} for carbon nanoplatelets). The lower capacity retention capability for thicker electrode is attributed to (i) higher mechanical stresses within the electrode films and at the interface with the current collector and to (ii) poorer cohesion of electrodes with higher active silicon loading. Better capacity retention of electrodes with carbon nanoplatelets is attributed to (i) higher initial cohesion of the electrodes and to (ii) good ability of the electrode architecture to reversibly expand/contract upon cycling as shown by in situ electrochemical dilatometry. The efficiency of carbon nanoplatelets as conductive additive allows decreasing its amount in the electrode formulation to 6 wt% without sacrificing cycling performance. Contribution of carbon additives to the mechanical properties of the electrode is as important as their contribution to the electrical properties for silicon.

1. Introduction

Silicon is a promising anode material for next-generation Li-ion batteries due to its high theoretical gravimetric capacity of 3579 mAh g^{-1} in comparison to the 372 mAh g^{-1} of graphite [1–4]. However, it is very challenging to obtain a commercially viable Si-based electrode due to the huge volume change (up to ~300%) of silicon during its lithiation/delithiation, which induces electrical disconnections and instability of the solid electrolyte interphase (SEI) [5].

Over the last ten years, considerable effort has been devoted to solve the poor cycle life of the Si anodes, especially by using nanosized Si materials (nanoparticles, nanowires, nanopillars . . .) which are able to accommodate large strain without extensive cracking [6]. However, the high surface area (exacerbating SEI formation), low compactness (inducing low volumetric capacities) and complex synthesis/processing/handling (resulting in high production cost) of such Si nanomaterials are major drawbacks for their commercial implementation [7].

We have recently shown that low-cost and high-performance silicon-based anodes can be achieved by combining *(i)* the use of high-energy ball-milling as a cheap and easily scalable process to produce nanocrystalline silicon powder favorable to a smooth lithiation, *(ii)* the processing of the electrode with carboxymethylcellulose (CMC) binder at buffered pH 3, which promotes the covalent grafting of the CMC to the Si particles; *(iii)* the use of fluoroethylene and vinylene carbonates (FEC/VC) electrolyte additives resulting in a more stable SEI [8]. As a result, the electrode is able to maintain a capacity of 1200 mAh g^{-1} Si for 900 cycles with a coulombic efficiency above 99% for an active mass loading of about 1 mg cm^{-2}. However, its areal capacity of ~1 mAh cm^{-2} is insufficient to achieve a volumetric energy density improvement over the use of conventional graphite anodes [9].

Obtaining stable Si-based electrodes with commercially relevant areal capacities (*i.e.* $\geq$ 5 mAh cm^{-2}) is very challenging. Indeed, the increase of the areal capacity means an increase of

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the electrode mass loading and thickness, which accentuates the mechanical strain generated by the Si volume change. Although this phenomenon is well known for Si thin-film electrodes [10–12], it has rarely been studied for Si-based composite electrodes containing binder and carbon additives. As for silicon thin-film electrodes, the cycle life of the Si-based composite electrodes dramatically decreases as the active mass loading increases [13–15]. Actually, Si-based electrodes with high areal capacity require careful design of their formulation at different scales, and in particular a special attention must be paid to the tailoring of durable intimate contacts between the active material particles and the conductive additive network so that sufficient electron transfer could be achieved throughout the electrode from the copper current collector [16].

In the present study, silicon-based electrodes of various areal capacities, from about 1.5 to 15 mAh cm^{-2}, are prepared with different conductive additives (carbon black, carbon nanofibers, and carbon nanoplatelets). The objective is to establish the influence of the morphological characteristics of the carbon additive on the mechanical stability and resulting electrochemical performance of the electrode. Although the notable effect of type of carbon conductive additive is commonly accepted, due to the many studies done on positive or graphite negative composite electrodes, [17–20] it has rarely been studied for silicon-based electrode. It will be shown that the choice of the conductive additive is of crucial importance for optimizing Si anodes with practical areal capacities. From the many studies done on positive or graphite negative electrodes, it is generally believed that the efficiency of carbon additive relies upon their capability to maintain the electronic wiring percolation within the electrode upon cycling. We however show that their contribution to the mechanical properties of the electrode is at least as important as their contribution to the electrical properties in the case of Si-based composite electrodes.

2. Experimental

2.1. Materials

Nearly millimetric silicon (99.999%, 20 mesh, Materion) was used as a precursor to prepare the active material. The Si powder was milled under argon atmosphere for 20 h using a SPEX 8000 mixer with a ball-to-powder mass ratio of 5:1. Details on the morphological, structural and chemical characteristics of the ball-milled Si powder are presented elsewhere. [8] Three commercial carbon materials were used as conductive additives (see SEM images in Fig. 1): *(i)* Super P carbon black (CB, particle size ~40 nm, $S_{BET} = 59\ m^2\ g^{-1}$, Timcal), *(ii)* vapor-grown carbon fibers (VGCFs, diameter ~80 nm, length ~10 μm, $S_{BET} = 21\ m^2\ g^{-1}$, Showa Denko), and *(iii)* ultrathin platelets of graphite consisting of short stacks of graphene sheets (GM15, length ~15 μm, width ~5–10 nm, $S_{BET} = 74\ m^2\ g^{-1}$, XGSciences). Carboxymethyl cellulose (CMC, DS = 0.9, Mw = 700 000, Sigma-Aldrich) was used as binder. Citric acid and KOH salts (Sigma-Aldrich) were used to prepare the pH3 buffer solution (0.17 M citric acid + 0.07 M KOH) as slurry media.

2.2. Electrode preparation

The slurries were prepared from a mixture of 200 mg of 80 wt.% silicon, 8 wt.% CMC binder and 12 wt.% conductive additive added in pH 3 buffer solution. The solid loading in the slurry was 30%. Mixing was performed at 500 rpm for 1 h using a Fritsch Pulverisette 7 mixer with 3 silicon nitride balls (9.5 mm diameter). The slurry was tape cast by using a doctor blade onto a 25 μm thick copper foil and dried 12 h at room temperature and then 2 h at 100 °C in vacuum to remove the water. Citric acid and KOH salts, which are not eliminated by this vacuum treatment, contribute to the mass of the electrodes. Taking into account the volume of pH3 solution used, the Si/conductive additive/CMC/(citric acid + KOH) wt.% composition of the electrodes was 73/11/7/9. The Si mass loading was varied from 0.5 to 4.2 mg cm^{-2}.

2.3. Characterization

The rheological properties of the electrode slurries were measured at room temperature on a controlled-stress rotating rheometer (Anton Paar, MCR 101) with a 50 mm diameter plane-and-plane geometry and the sample gap between the Pelletier plane and the geometry was fixed at 0.6 mm. Several types of rheological measurements were carried out: *(i)* two measurements were done with continuous shear: a rate sweep measurement from 0.1 to 1000 s^{-1} to determine the viscosity and a frequency sweep from 0.1 to 10 Hz to obtain information on the behavior of the suspension in the linear domain; *(ii)* then we followed the evolution with time of the moduli at a frequency of 1 Hz and a strain of 0.4% after a preshear at 50 s^{-1} for 60 s to simulate the behavior after casting.

The crystalline structure of the conductive additives (see Supplemental Information) were determined by X-ray diffraction (XRD, using a Bruker D8 diffractometer) with Cu-Kα radiation (λ = 1.5418 Å). Their specific surface area was determined by the Brunauer–Emmet–Teller (BET) method from krypton adsorption isotherm collected at 77 K using a Quantachrome Autosorb analyzer. The Si particle size distribution was determined by laser scattering method using a Mastersizer 2000 Malvern analyzer. The morphologies of the as-received carbon additives and pristine and cycled composite electrodes were observed by scanning electron microscopy (SEM) using a JEOL JSM 7600F microscope.

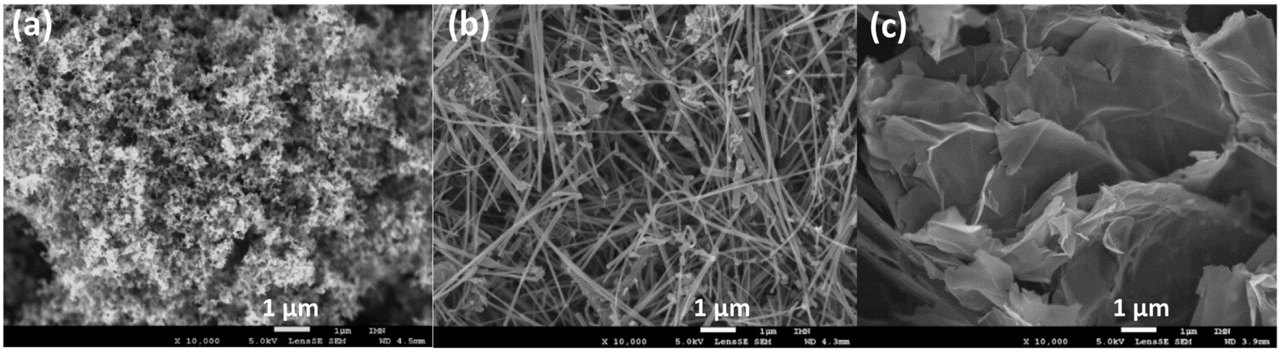

Fig. 1. SEM images of the conductive additives: (a) CB, (b) VGCFs and (c) GM15.