



How silicon electrodes can be calendered without altering their mechanical strength and cycle life



Z. Karkar^{a,b}, T. Jaouhari^a, A. Tranchot^a, D. Mazouzi^c, D. Guyomard^b, B. Lestriez^{b,**}, L. Roué^{a,*}

^a Institut National de la Recherche Scientifique-Centre Énergie Matériaux Télécommunications (INRS-EMT), 1650 boulevard Lionel Boulet, Varennes, QC J3X 1S2, Canada

^b Institut des Matériaux Jean Rouxel (IMN), CNRS UMR 6502, Université de Nantes, 44322 Nantes Cedex 3, France

^c Materials, Natural Substances, Environment and Modeling Laboratory, Multidisciplinary Faculty of Taza, University of Sidi Mohamed Ben Abdellah, Fes, Morocco

HIGHLIGHTS

- The calendering of Si electrodes degrades their mechanical strength and cycle life.
- This is attributed to the rupture of the particle-binder bridges upon calendering.
- The electrode cohesion is restored through an appropriate post-calendering treatment.

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ABSTRACT

The calendering of Si-based electrodes is required to obtain a substantial gain in their volumetric capacity compared to conventional graphite electrode. However, as shown in the present study performed on silicon/carbon nanoplatelets/carboxymethyl cellulose electrodes, their calendering induces a major decrease of their cycling stability. This can be attributed to the rupture of the particle-binder bridges during the calendering, lowering the mechanical strength of the electrode. It is found that these cohesive bonds can be restored through an appropriate post-calendering treatment (called maturation). It consists of storing the calendered electrode in a humid atmosphere for a few days before drying and cell assembly. From in-operando dilatometric experiments, it appears that the volumetric expansion is lower and more reversible than for a standard (not-calendered, not-matured) electrode. As a result, a remarkable improvement of the cycle life is observed. However, when cycled in Si/NMC full cell, a rapid capacity decay is observed because of the SEI instability.

1. Introduction

Developing silicon-based negative electrodes is one of the most promising ways to increase the energy density of the lithium-ion batteries, due to the very high intrinsic gravimetric and volumetric capacities of this material [1]. Its performance as active material is however limited by a poor cyclability in a composite electrode. This is because of the drastic volumetric expansion of silicon up to 270% when it inserts and de-inserts lithium during charge/discharge cycles. This volumetric expansion is detrimental to the electrode performance. Several phenomena can occur, such as the pulverization of the silicon particles, and/or the disintegration of the composite electrode together with its delamination from the copper current collector. Another critical problem is the instability of the solid electrolyte interphase (SEI) layer during cycling. Due to the volumetric expansion, this SEI breaks and is

scrapped from the silicon particles surface, and thus must continuously reform, which quickly leads to the end-of-life of lithium-ion full cells [2–6]. There has been and there is still a huge amount of work trying to resolve all these problems, which is clearly reviewed by Obrovac and Chevrier [1]. As pinpointed by these authors, until now, researches were generally focused on improvements in the cycling performance of silicon in uncompressed electrodes with typically a high porosity of about 60–70%. If such high porous volume allows accommodate the volumetric expansion of silicon-based active materials, which limits electrode deformation and its disintegration and delamination from the current collector [7,8], it can result in volumetric electrode capacities that are much less than a commercial graphite electrode. Thus, in order to use silicon in commercial lithium-ion cells, it is necessary to find a method to compress Si-based coatings to high densities while maintaining good cycling performance.

* Corresponding author.

** Corresponding author.

E-mail addresses: bernard.lestriez@cnrs-imn.fr (B. Lestriez), lionel.roue@emt.inrs.ca (L. Roué).

The state-of-the-art fabrication method of composite electrodes ends up, after the tape casting and drying of the electrode slurry, by a calendaring step under high pressures, which reduces the porosity down to 20–40%. The literature shows that this treatment is essential for obtaining simultaneously high volumetric energy density, high rate and good cycling stability. However an optimal pressure has to be found, which depends on the active material and electrode formulation.

Striebel et al. [9] showed that compression of natural graphite negative electrodes at a moderate range of pressure (0.1–0.3 ton cm⁻²) tended to increase the reversible capacity, reduce the first cycle irreversible capacity loss (ICL) and significantly improved the cyclability of the electrodes at moderate rates. The lower ICL was attributed to an improvement in the electronic conductivity of the electrodes with compression. The improved cyclability was attributed to better adhesion to the current collector, as the unpressed electrodes were observed to delaminate easily after testing from the copper current collector. On contrary, Novak et al. [10] and Gnanaraj et al. [11] found that compression of graphite negative electrodes at a range of high pressure (4–8 tons cm⁻²) degraded the reversible capacity (at low and high rates) and the first cycle efficiency. These were explained by ion transport limitations within the liquid paths as well as particle break-up for the largest pressures. In contrast, application of the same level of pressure to LiCoO₂ electrodes improved the reversible capacity (at low and high rates), which was attributed to improved contacts between the active particles and improved electron transport. Zheng et al. [12] studied Li [Ni_{1/3}Mn_{1/3}Co_{1/3}]O₂ electrodes prepared, as in all the studies mentioned above, with the polyvinylidene difluoride (PVDF) binder. They measured an improvement of the mechanical properties of the electrodes with calendaring, even down to very low porosity values. This cohesion enhancement could be attributed to the plastic flow of the PVDF polymer that can spread between the particles during calendaring [13] and then increases its contact surface area with the active mass and with the current collector surface. This allows the binder/active mass and electrode/collector interfaces to resist a higher level of stress before breaking [14]. In the study of Zheng et al., the cyclability was unaffected by calendaring but the kinetics of the electrode was. An optimum porosity of 30–40% was identified. Calendaring improved the electronic charge transport within the electrode when the porosity was decreased from relatively high values, but increased the charge transfer resistance at electrode/electrolyte interface at relatively low porosities, due to the limitation in the ionic transport within the electrode, which resulted in poor rate capability of the electrode at low porosity. The same conclusions were found in a previous study by Fongy et al. [15] on LiFePO₄ electrodes prepared with the carboxymethyl cellulose (CMC) and butadiene-acrylonitrile copolymer rubber latex binders. The best compromise between electronic limitations at low electrode packing and ionic limitations at high electrode packing was achieved for an optimal porosity in the 30–35% range. Van Bommel and Divigalpitiya [16] clearly showed that calendaring of LiFePO₄-based electrodes prepared with PVDF resulted in a large decrease in contact resistance at the current collector – electrode interface, because the contact surface area at this interface was enlarged, which was critical to improve the electronic wiring of the active mass and to show high rate performance.

Adhesion between the unpressed electrode and the current collector is critical with respect to the calendaring step, as the electrode must not delaminate from the current collector at this time. Porcher et al. [17] studied LiFePO₄-based electrodes prepared with the CMC and styrene-butadiene copolymer rubber latex (SBR) binders. The powders dispersion was varied between coarse (agglomerated) and fine states by using a surfactant. This one affected the maximum calendaring pressure that could be loaded on the electrode and the minimum porosity of the electrode that could be achieved. The coarser was the dispersion state, the more easily the electrode could be densified, *i.e.* a higher compaction could be reached for a lower pressure. This can be understood by considering the ratio between the binder quantity and the apparent surface area displayed by the powders, or the concept of areal density of

connecting chains. Indeed, macroscopic mechanical strength of polymer-based composite materials has been shown to be controlled by the strength of the molecular polymer bridges at the interfaces [18,19], which depends on the areal density of connecting chains that are anchored on both sides of the interface. Back to the study of Porcher et al. [17], a fine powder dispersion means a large surface area developed by the particles and a low areal density of connecting chains, between the particles and at the current collector interface, which translates in lower cohesion, lower adhesion and electrode delamination during calendaring.

Few studies have been reported on the effect of calendaring electrodes comprising silicon or silicon-based materials. Jeong et al. [7] and Dimov et al. [20] have respectively reported that compressing Si₇₅Fe₂₅ (prepared with polyimide binder) or silicon blended with graphite (prepared with the CMC/SBR binders) electrodes considerably shortens their life cycle. However, for Dimov et al., this result was in contrast with their previous data obtained with silicon/graphite blended electrode prepared with the PVDF binder, for which the stronger the calendaring pressure was, the stronger the electrode film and the better the cycle life of the electrode was. Nguyen et al. [21] found that calendaring is detrimental for silicon electrodes prepared with the CMC/SBR binder. The cycle life of half-cells was shortened with a decrease of the electrode porosity. This study also suggested that for the electrode formulation used, even with no calendaring, the contact resistance between the copper foil used as current collector and the composite electrode is negligible in the dry state, contrarily to positive electrodes coated on aluminum foil. Similarly, Kovalenko et al. [22] noticed that when the electrode density was increased from 0.5 to ~0.75 g cm⁻³ (and the total pore volume becomes equal to 2.7 times the volume occupied by Si particles), the silicon electrode (prepared with alginate binder) showed noticeably worse performance.

Du et al. evaluated the effect of calendaring and adding graphite of different particle sizes to composite electrodes comprising a new commercial active/inactive Si-based alloy of 3 M company [23] prepared with the lithium polyacrylate binder [24]. As in the works mentioned above, the calendaring of the electrode resulted in significant detrimental effect on the cycling performance, which was attributed to a degradation of the mechanical wiring of the active mass in the electrode. Indeed, SEM observations showed that the Si alloy micrometric particles were fractured during the calendaring process, resulting in particles fragments not held together anymore by binder bridges. Indeed, silicon and silicon alloys are typically hard and brittle materials and thus could hardly tolerate calendaring [24]. Moreover, it was assumed that particle-binder-particle connections were also deteriorated during calendaring. However, blending graphite with the Si alloy resulted in no particle fracture and clearly improved cycling performance and energy density compared to a pure alloy coating. Such result could be attributed to the lubricating properties of the graphite particles, which platelet-form likely allow alloy particles to slide against each other during densification, instead of fracturing.

In summary, as far as we know, except for the Si-based alloy of 3 M company, which volumetric expansion is mitigated at about 100% by the inactive components in the alloy, no method has been found to compress Si-based coatings to high densities while maintaining good cycling performance. A first likely cause was early on illustrated by Beattie et al. [25]. As the silicon particles volume fraction is increased (here by calendaring), there is dramatic increase of the amount of silicon particles displacement and extrusion out of the electrode film due to expansion/contraction of the active mass during cycling. According to simple geometrical considerations, the largest silicon loading that would still result in good cyclability, was calculated to be 20 vol%, given theoretical expansion of Si (270%) [25]. In such electrode design, the silicon particles do not need to “push” one another during expansion/lithiation; particle rearrangement can be minimized. A second likely cause is that the calendaring step could damage the CMC molecular bridges formed between the silicon and conductive additive

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