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Review

Critical roles of binders and formulation at multiscales of silicon-based composite electrodes

D. Mazouzi [a], Z. Karkar [a, d], C. Reale Hernandez [d], P. Jimenez Manero [a, b], D. Guyomard [a, b, c], L. Roué [d], B. Lestriez [a, b, c, *]

[a] *Institut des Matériaux Jean Rouxel (IMN), CNRS UMR 6502, Université de Nantes, 44322 Nantes Cedex 3, France*
[b] *Réseau sur le Stockage Electrochimique de l'Energie (RS2E), FR CNRS 3459, France*
[c] *ALISTORE-ERI, FR CNRS 3104, France*
[d] *INRS-Centre Énergie Matériaux Télécommunications, 1650 Boulevard Lionel Boulet, Varennes (QC) J3X 1S2, Canada*

HIGHLIGHTS

- All scales of electrode architecture must be optimized for better cyclability.
- Molecular or nanometric scale depends on binder and silicon surface chemistries.
- Binder critically plays on slurry properties and electrode micrometric architecture.
- Carbon additive smoothes mechanical stress at microscopic scale.
- Current collector texture must be designed for macroscopic adhesion of electrode film.

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ABSTRACT

In this review we try to shed a comprehensive understanding on the influence of the different parameters of the formulation of silicon-based composite electrode on its cyclability, i.e. the binder, the conductive additives, the current collector, the electrode porosity and solid loading, in view of a more rational assessment of the relevancy of these parameters for the battery technology. The reasons of the better efficiency of carboxymethyl cellulose and alternative new binders than PVdF are first addressed into details. The critical effects of the active mass loading and porosity on the cyclability are highlighted. Then the influence of the conductive additive type and current collector texture are discussed. Putting everything together shows that it is required to meticulously optimize all the different scales of the composite electrode to hopefully raise the performance of silicon-based electrode above that of graphite commercial ones.

1. Introduction

Over the last few years, silicon (Si) has attracted considerable attention since it has potentially about 10 times the gravimetric capacity of conventional graphite anodes (3578 mAh g^{-1} *vs.* 372 mAh g^{-1} for graphite) [1]. Solving the large capacity fading observed during cycling of silicon electrodes is, however, a complex issue. Two distinct causes, which find origin in the huge volume variation during lithiation and delithiation processes of this material (270%), explain this fading: *(i)* disintegration of Si grains and of the composite electrode architecture and further loss of electrical contact with the current collector of the active mass [2,3]; *(ii)* unstable solid electrolyte interphase (SEI) resulting in continuous liquid electrolyte degradation at the surface of the Si phase [4,5].

Several strategies have been undertaken to solve these problems, among which:

(i) Use of small sized materials (nanoparticles, hollow nanospheres, nanowire arrays, nanotubes, porous structures and thin films) that can effectively withstand the stress induced by heterogeneous changes in the volume of Si electrodes

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[*] Corresponding author. Institut des Matériaux Jean Rouxel (IMN), CNRS UMR 6502, Université de Nantes, 44322 Nantes Cedex 3, France.
E-mail address: Bernard.lestriez@cnrs-imn.fr (B. Lestriez).

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without fracturing and can therefore overcome pulverization. However, the tap density of nanostructured Si electrodes is usually low, resulting in a lowered volumetric capacity of the electrode and the whole cell. Moreover, commercial fabrication of these nanomaterials is likely to be quite costly. Thus, the overall performance is impaired quite severely by using nanostructures [6,7].

(ii) Use of capacity constraint limitations to minimize volume changes.

(iii) Construction of composites, which consists of silicon and other components. The composites act as a buffer to alleviate the stress and accommodate the volume change led by lithium insertion/extraction. An incredible variety of composites with active/inactive materials have been designed and reported in the latest few years [6,7].

(iv) Use of modified electrolyte by film-forming agents such as fluoroethylene carbonate (FEC) or vinylidene carbonate (VC). These ones are mandatory to achieve long cycle lifs [8]. Use new lithium salts [9–11].

(v) To design of the composite electrode formulation, *i.e.* selection of binder chemistry, conductive additive shape, current collector texture, porosity, etc.

More than for any other active material for lithium battery, silicon has stressed the importance of carefully addressing these latter aspects (v), i.e. the formulation and the engineering of the composite electrode. In this review we tried to shed a comprehensive understanding on the influence of the different parameters (binder, conductive additive, current collector, porosity and solid loading) of the formulation of silicon-based composite electrode on its cyclability. Our goal is to help in a more rational assessment of the relevancy of these electrode formulation parameters for the battery technology.

1.1. *Searching for the reasons of the CMC binder efficiency compared to PVdF*

The role of binders is very critical for Si electrodes to maintain the electrode structure and thereby to achieve repeatable LIB operation [12]. Most studies have involved the use of carboxymethyl cellulose (CMC) and poly vinylidene fluoride (PVDF) binders. The more conventional binder PVDF used for the batteries is likely attached to Si particles via weak Van der Waals forces (between its fluorine atoms and hydrogen atoms) [13]. It fails to accommodate large changes in spacing between the particles during battery cycling and becomes quickly incompetent in keeping the particles together and maintaining electrical conductivity within the anode. Noteworthy amounts of data have been achieved for CMC binder, which typically displays a better performance and could be considered to be the state of the art in this field until recently. Historically, Buqa et al. and Liu et al. reported that the cycle life of Si-based electrodes was improved by using an aqueous binder containing the elastomeric styrene butadiene rubber (SBR) and CMC [14,15]. However, Li et al. showed that the use of the stiffer CMC binder resulted in better capacity retention than the SBR + CMC combination and PVdF (Fig. 1a) [16]. Such a result was in strong contradiction with the common belief and intuitive interpretation that a soft binder with large reversible stretching capabilities would better endure the large volume variations of the active material (AM) particles and better keep the mechanical integrity upon cycling of the Si-based composite electrode. Fig. 1b shows the stress *vs.* strain for CMC, PVDF, and SBR–CMC films. Bulk CMC films are very stiff and can only be extended to about 5–8% before breaking. Considering that the volume change of Si particles upon lithiation can be up to 300% and is about 100% for the 1200 mAh g^{-1} capacity delivered in Fig. 1a, the CMC binder should break during the cycling process, based on its mechanical properties as bulky material. Both the SBR–CMC and PVDF are less brittle than CMC. However, they give far inferior charge–discharge cycle life than CMC (Fig. 1a).

It was then shown that CMC favours both *(i)* a much more homogeneous distribution of the carbon black conductive additive particles, by playing the role of a dispersant, and *(ii)* an efficient networking process of the carbon black and Si particles in the composite electrode slurry, due to its extended conformation in solution that enables the formation of bridges between particles (bridging model) (Fig. 2) [17]. Moreover, it was discovered at that time that adjusting the processing conditions with use of a buffered water solution at pH 3 resulted in very significant performance improvement in the case of micro-Si based electrodes.

Hochgatterer et al. showed that compared to the flexible PVdF-co-hexafluoropropylene (HFP), hydroxyethylcellulose (CH_2CH_2OH is the substitution group) also significantly improves cyclability, but to a lesser extent than CMC. They demonstrated the formation of a chemical bond between the carboxylate function (COO^-) of the binder and silicon dioxide layer present at the surface of a silicon wafer (Fig. 3), and suggested that the setup of a chemical bond between the binder and the active masses could be the major claim leading to long-lasting reversibility of lithium uptake/release for Si–C-composite anodes. They also found that the electrode's cycling stability is influenced by the degree of substitution on the CMC-molecule, a higher degree of substitution (a higher concentration of COO^-) being more favourable [18]. In two independent studies, Ding et al. and Mazouzi et al. emphasized the role played by

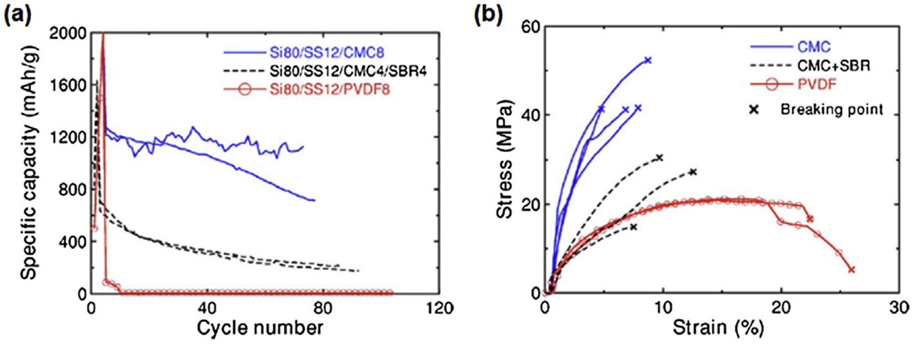

Fig. 1. (a) Specific capacity vs. cycle number for two cells each having Si80/CB12/CMC8, Si80/CB12/SBR4CMC4, and Si80/CB12/PVDF8 electrodes (7–8 μm Si powder, active mass loading ~1.4 mg cm^{-2}, 150 mA g^{-1} between 0.17 and 0.9 V, LiPF$_6$ in EC-DEC). (b) Stress vs strain for CMC, CMC–SBR, and PVDF films. The × at the end of each curve indicates the breaking point. Reprinted with permission from Ref. [16]. Copyright [2007], The Electrochemical Society.