Electrochimica Acta 258 (2017) 453–466

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

A comparative study of polyacrylic acid (PAA) and carboxymethyl cellulose (CMC) binders for Si-based electrodes

Z. Karkar [a, b], D. Guyomard [b], L. Roué [a, *], B. Lestriez [b, **]

[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

ARTICLE INFO

Article history:
Received 28 September 2017
Received in revised form
10 November 2017
Accepted 11 November 2017
Available online 13 November 2017

Keywords:
Li-ion batteries
Silicon-based anodes
Binder
Polyacrylic acid
Carboxymethyl cellulose

ABSTRACT

This work is a comparative study on two well-known binder systems for silicon-based negative composite electrodes for Li-ion batteries: polyacrylic acid (PAA) and carboxymethyl cellulose/citric acid (CMC/CA). The electrode slurry rheological properties and the dry electrode morphology and physical properties are studied as a function of the binder content. The electrochemical behavior of the electrodes is also studied as a function of the active mass loading (from 1 to 4.5 mg cm^{-2}). Increasing the binder content from 4 to 12 wt% improves the 1st cycle efficiency, which is clearly related to its contribution as a pre-formed artificial solid electrolyte interphase (SEI) layer. The enhancement of the mechanical strength of the composites with increasing binder content is reflected in the better cyclability of the electrodes with active mass loading higher than 1 mg cm^{-2}. CMC/CA is more efficient as a binder at low content while PAA is more efficient at high content, which could be related to their molecular structure. Finally, for both binders the influence of a post-processing treatment of the electrodes (called maturation) is shown to improve the electrochemical performance. This is however more significant with CMC/CA than with PAA.

1. Introduction

The use of silicon as the active anode material for Li-ion batteries has attracted great attention over the past several years since its theoretical gravimetric capacity is 10 times higher than a conventional graphite anode (3578 mAh g^{-1} vs. 372 mAh g^{-1} for graphite) [1]. However, the integration of Si-based anodes in commercial Li-ion batteries is challenging due to the large volume change of Si during its lithiation (up 270% for $Li_{15}Si_4$), which induces: *(i)* the fracturing of the Si particles and the disintegration of the electrode architecture; *(ii)* the instability of the solid electrolyte interphase (SEI) [2–5]. This results in a rapid capacity decay with cycling and a low coulombic efficiency. To resolve these issues, different strategies have been evaluated, among which are the use of nanostructured silicon materials that are less sensitive to fracturing [6,7], the addition of electrolyte additives enhancing the SEI stability [8,9], the limitation of the lithiation level minimizing the volume change [10,11], and the optimization of the composite electrode formulation and processing (binder chemistry, conductive additive shape, current collector morphology, electrode porosity, etc) [12]. Regarding the electrode formulation, the role of the binder on the Si electrode performance is crucial since it reinforces the mechanical strength of the electrode and thus helps to preserve the electrode architecture upon cycling against the large Si volume change. The possible impact of the binder on the Si surface reactivity and related SEI formation must also be considered. Lastly, its influence on the electrode slurry (ink) properties and resulting electrode homogeneity and porosity is not negligible [13].

Polymer binders that contain carboxyl groups such as polyacrylic acid (PAA) [14,15] and carboxymethyl cellulose (CMC) [16,17] present better electrochemical performance for Si-based anodes than non-functional polymers such as polyvinylidene fluoride (PVDF) and styrene-butadiene rubber (SBR). This is the result of several properties [12]. First, CMC and PAA possess carboxylic functional groups able to strongly bond to the native hydroxyl groups present on the silicon particle surface [12,18–22]. Second, they are not swollen by the liquid electrolyte and thus

---

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

https://doi.org/10.1016/j.electacta.2017.11.082

show no loss of mechanical properties when soaked in it [14]. These two properties allow keeping better cohesion within the composite electrode by locking interparticle contacts. Third, CMC and PAA can form a more or less thin and conformal coating at the surface of the silicon particles and play the role of an artificial SEI [23], thanks to their lithium transport properties where by Li ions hop between the adjacent carboxylic sites [24].

CMC is a linear polymeric derivative of cellulose, consisting of β-linked pyranose monomeric units with commonly 0.6 to 1.2 carboxymethyl ($-CH_2COO^-$) side groups per monomer unit [18,25]. These groups are not evenly distributed along the chain. The predominant functional group on CMC is hydroxyl (3 per monomer unit), which is replaced by the carboxymethyl group during derivatization. PAA is a synthetic linear polymer obtained through the homopolymerization of acrylic acid. It has the same backbone as polyethylene but each monomeric unit has a carboxylic side group. The presence of the carboxymethyl or carboxyl groups is responsible for the aqueous solubility of CMC and PAA relative to insoluble cellulose and polyethylene. Both CMC and PAA are weak polyacids that dissociate in water to form carboxylate anionic functional groups. The cellulose backbone of CMC is a rigid molecular structure due to the nature of the pyranose linkages. In contrast, the polyethylene backbone imparts higher flexibility to PAA. A quantitative parameter that characterizes the chain stiffness is the Kuhn segment length (or persistent length). This parameter is about ten times higher for CMC than for PAA, respectively ~15 and 1.6 nm [26,27]. In the dried and bulk state, these two polymers show a high elastic modulus as a consequence of the intermolecular hydrogen bonding between the side groups. When dissolved in water, both CMC and PAA adopt a stretched molecular conformation because of the electrostatic repulsive interactions between neighbouring ionized carboxy lateral groups, and in the case of CMC because of the backbone rigidity. Changes in pH affect the protonation of the carboxy lateral groups, which in turn impacts its conformation. The neutralization of charges in an acid medium leads to polymer coiling and aggregation through intra- and intermolecular hydrogen bonding between the side groups [28]. However, in the case of CMC, the rigidity of the polymer chain backbone favors the formation of three-dimensional network [29].

Some studies demonstrate the superiority of PAA compared to CMC in silicon based electrodes. For instance, Komaba et al. showed that a SiO-based electrode with PAA binder has a 10 times higher adhesion strength to the Cu current collector than with CMC binder, resulting in a better cycle performance [30]. The superiority of PAA over CMC was attributed to a better covering of the particles and to the cross-linking of the PAA chains by the formation of strong hydrogen bonds between two carboxylic groups and a dehydration reaction of associated carboxylic groups during the drying process at 150 °C. Komaba et al. identified 80% neutralized PAA as the best binder for Si-graphite blends [31]. Bie et al. have also shown that the capacity drops more quickly after 40 cycles with a Si/CMC electrode than with a Si/PAA electrode [32]. Erk et al. also found a better cycling performance for Si/PAA than for Si/CMC based electrodes [33]. Magasinski et al. concluded that the higher concentration of carboxylic functional groups possessed by PAA compared to CMC could explain its superior performance as a binder for Si anodes [14]. However, it must be noted that in all these studies, the CMC was used in a neutral pH solution, which is less favorable to the formation of covalent bonds at the Si/CMC interface [12]. Mazouzi et al. demonstrated the significant effect of the slurry pH on the CMC efficiency for Si-based electrodes. When a pH 3 buffer solution based on citric acid (CA) is used for the slurry preparation, the SiO^- and COO^- groups are neutralized into SiOH and COOH, which favours their grafting esterification upon electrode drying as $Si{-}OH + HO{-}C(O){-}R \rightarrow Si{-}O{-}C(O){-}R + H_2O$ [12]. A few studies display better results for Si/CMC based electrodes. For instance, Koo et al. showed that the first coulombic efficiency (CE) was around 78 and 87%, and the remaining capacity at the 100th cycle was about 800 and 1300 mAh g^{-1} for PAA and CMC, respectively. This was explained by the higher rigidity of the CMC binder which helps to better mitigate the volume expansion of the silicon [21]. Jeschull et al. observed poorer mechanical properties and quicker fading with PAA than with CMC for silicon electrodes, which was attributed to better ability of CMC to establish molecular bridges between silicon and carbon particles [34]. These contradictory results regarding the efficiency of PAA versus CMC suggest that the binder efficiency depends on a large number of parameters related to the electrode formulation (*e.g.* amount of binder relative to the amount/surface area of the active material) and electrode processing conditions (*e.g.* drying conditions), and thus this makes it difficult to compare them.

In this work, we conduct a comparative study on PAA and CMC/CA binders for Si electrodes using a well-defined electrode composition and slurry preparation procedure (acidic conditions). The article is divided in 3 parts. We first study the processing of the electrodes. The rheological properties are studied as a function of the amount (CMC) and type (CMC or PAA) of binder. The dependence of the electrode thickness and porosity as a function of the same parameters and of the tape casting conditions (blade gap) is also quantified in this part. Then the electrode morphology, electrical and mechanical properties are evaluated. In a second part, the electrochemical behavior of these electrodes is studied, as a function of the amount and nature of the binder and of the active mass loading. Finally, in a third part, the influence of a post-processing treatment of the electrodes (called maturation) [35,36] on their electrochemical performance is evaluated.

2. Experimental

2.1. Materials

Ball-milled Si powder was used as active material. It was obtained by high-energy ball milling of nearly millimetric silicon powder (99.999%, 20 mesh, Materion) under argon atmosphere for 20 h using a SPEX 8000 mixer with a ball-to-powder mass ratio of 5:1. The as-milled Si powder consists of micrometric agglomerates (median size ~6 μm, S_{BET} ~12 $m^2\ g^{-1}$) made of sub-micrometric particles more or less welded together [37]. During the slurry mixing (see below), these agglomerates are fragmented into Si particles with a diameter varying from a few tens of nm to a few μm with a median diameter of ~0.2 μm [38]. The conductive additive was ultrathin platelets of graphite consisting of thin stacks of graphene sheets (length 15 μm, thickness 5–10 nm, $S_{BET} = 74\ m^2\ g^{-1}$, GM15 grade from XGSciences). The binders were carboxymethyl cellulose (CMC, DS = 0.9, Mw = 700,000, Sigma-Aldrich) and polyacrylic acid (PAA, Mw = 450,000, Sigma-Aldrich). Citric acid (CA) and KOH salts (Sigma-Aldrich) were used to prepare the pH3 buffer solution (0.17 M CA + 0.07 M KOH) as the slurry medium for the CMC based electrodes.

2.2. Electrode preparation

The electrode slurries were prepared by mixing Si, CMC or PAA and GM15 in deionized water (when PAA is used) or in pH 3 buffer solution (when CMC is used). Note that the pH of the slurry becomes acidic (pH ~2.5) after dissolution of the PAA. The solid mass fraction in the slurry was between 24 and 28% (Table 1a). 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 current