



# Manufacturing of industry-relevant silicon negative composite electrodes for lithium ion-cells



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## HIGHLIGHTS

- PAMA dispersant improves the stability of electrodes slurries of Silicon based negative electrode.
- Amount of PAMA must be limited due to competition in adsorption with CMC at the surface of CB particles.
- SBR copolymer latex improves adhesion of the tape to the current collector and increases cycle life.
- Calendaring is detrimental to electrochemical properties.

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## ABSTRACT

In this paper, Poly (acrylic-co-maleic) acid (PAMA) is used as a dispersant to improve the stability of electrodes slurries for large scale processing of Silicon based negative composite electrode. The stability and homogeneity of the slurries are characterized using different techniques. Sedimentation test, electrical measurement, SEM-EDX observations as well as rheological measurements show that a more homogeneous distribution of carbon black (CB) inside the stack of Si particles is reached with presence of PAMA. However, the amount of PAMA is limited due to the competition in the adsorption of PAMA and Carboxymethyl cellulose (CMC) at the surface of the CB particles. Upon cycling with capacity limitation, the optimized electrode formulation at lab scale could achieve more than 400 cycles with surface capacity  $\sim 2.5\text{--}3.3\text{ mAh cm}^{-2}$ . At the pilot scale, the improvement of adhesion of the tape to the current collector by using Styrene-co-Butadiene rubber copolymer latex (SB) helps to maintain long cycle life while calendaring is detrimental to electrochemical properties.

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## 1. Introduction

Nowadays, rechargeable lithium-ion battery is one of the most promising energy storage technologies to enable a various range of clean transportations (hybrid electric vehicles, electric vehicles, Plug-in Hybrid Electric Vehicles). To meet requirements of these automotive applications, it is necessary to find higher capacity electrode materials for Li-ion batteries. The current commercial lithium ion battery is based on the use of graphitic carbon anode which provides a low theoretical capacity of  $372\text{ mAh g}^{-1}$  and energy density ( $779\text{ mAh cm}^{-3}$ ) [1]. Compared with graphite, silicon is a favourable alternative candidate due to a high specific

capacity ( $3572\text{ mAh g}^{-1}$ ) and specific volumetric capacity ( $2081\text{ mAh cm}^{-3}$ ) [2]. However, poor performance of Si electrodes (large capacity fading and low cyclability) is a major issue. This could be explained by two distinct reasons: (i) Silicon exhibits dramatic volume expansion and shrinkage during lithiation and delithiation, respectively. This volumetric variation results in mechanical breakdown of the composite electrode [3,4]. (ii) Formation of unstable solid electrolyte interphase (SEI) causes uninterrupted liquid electrolyte degradation at the surface of silicon [5–7].

Several strategies have been undertaken to overcome these problems. One way is optimising the binder in order to cope at the molecular scale with the expansion and contraction of Si upon alloying and dealloying with Li. Most studies of Si anodes have involved the use of carboxymethylcellulose (CMC) and polyvinylidene fluoride (PVDF) binders. The most conventional binder PVDF used for the batteries is likely attached to Si particles via weak

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Van der Waals forces only (between its fluorine atoms and hydrogen atoms). Moreover, PVdF is significantly plasticized by the liquid electrolyte solvents (carbonates) and becomes an easily deformable material with small resistance to deformations [8]. PVdF thus fails to accommodate large changes in spacing between the particles during battery cycling and quickly becomes incompetent in keeping the particles together and maintaining electrical conductivity within the anode, which is required for battery operation. In the meantime, noteworthy amounts of improvement have been achieved for CMC binders, which typically display a better performance and can be considered to be the state of the art in this field. CMC favours both (i) a much more homogeneous distribution of the carbon black conductive additive particles, (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, and (iii) the establishment of a covalent bond through the esterification of the SiOH surface groups by the COOH functional groups of CMC, which increases the cycle life [9,10]. Since early works on CMC, [11–14] several other works proposed alternative binders to CMC, most of them being polysaccharides and/or bearing COOH functional groups [15–18].

Another way to improve the cycle life is using electrolytes containing a film-forming agent. In the case of silicon, unstable layer is formed in the first cycles without utilising FEC/VC additives and cracks occur on this layer during volume expansion upon Li insertion of the particles which exposes new surfaces leading to additional liquid electrolyte degradation [19–25]. Flexible polycarbonates form in the surface film in FEC and VC-containing solutions, which allows a better ability to accommodate the volume variations of the Si phase, then limiting the contact between the silicon particles and the liquid electrolyte [26]. This results in reduction of the amount of SEI products precipitating and accumulating inside the electrode at each cycle [25].

Besides, electro-conductive additives also display an important influence for the performance of Si-based electrodes. Combining carbon nanotubes (multiwall carbon nanotubes (MWNTs)) and nanofibers (vapor-grown carbon nanofibers (VGCFs)) allows building a hierarchical and resilient 3D conductive network, which strongly improves the cyclability of micron-size Si in Si/C/CMC composite electrodes [27]. In the case of nano-size Si, no improvement was found by using these carbon additives when compared to the standard carbon black (CB). However, by using reduced graphene oxide (rGO) instead of CB as the conductive additive for nano silicon based negative composite electrodes, a

significant improvement of the electrochemical performance was confirmed, whatever the cycling conditions [28,29].

In this work, we aim to design the formulation of nanosilicon-based negative composite electrodes to wind some cylindrical cells. To reach this goal we looked for: (i) homogeneous and stable slurry-state, (ii) suitable mechanical properties for calendaring and battery assembly steps, (iii) long cycle life, for high active mass loadings of about 2.5–3.3 mAh per cm<sup>2</sup>.

## 2. Experimental

**Electrode preparation** – Composite electrodes were made of nanometric Si (particle size 150 nm, specific surface area 14 m<sup>2</sup> g<sup>-1</sup>) as an active material (AM), Super P carbon black (CB, Timcal) as a conductive additive (C), Carboxymethyl cellulose (CMC, DS = 0.9, M<sub>w</sub> = 700.000 g mol<sup>-1</sup> Sigma–Aldrich) and a Styrene-co-Butadiene rubber copolymer latex (SB) as a binder (B) and Poly (acrylic-co-maleic) acid (PAMA M<sub>w</sub> = 3000 g mol<sup>-1</sup> Sigma–Aldrich) as a dispersant (D).

At the lab scale, powders were introduced in a silicon nitride vial according to the electrode formulations given in Table 1. Then, 1 mL of buffer pH 3 0.1 M solution prepared with KOH and citric acid was added to 200 mg of composite electrode material. The solid loading is thus 17 wt%. Three silicon nitride balls (9.5 mm diameter) served as mixing media. A Fritsch Pulverisette 7 mixer was used to mill the slurry at 500 rpm for 60 min. The slurry was tape cast onto a 25 μm thick copper foil and dried for 12 h at room temperature and then at 2 h at 100 °C under vacuum. Citric acid and its salt, which are not eliminated by this vacuum treatment, remain in the composite tape.

At the pilot scale, CMC was dissolved in the buffer pH 3 solution, prepared with KOH and citric acid at 0.1 M. PAMA was added before introducing the conductive additive and the AM. The suspension is then dispersed using a high speed stirrer for 30 min. At the end of the dispersion, the latex is added and the slurry shortly homogenised. The slurries were coated using a semi industrial machine, with a comma bar system and an oven of 1 m length onto a 10 μm thick copper foil at a speed of 0.2 m min<sup>-1</sup>. The transit time in the oven is so around 5 min.

**Sedimentation test** – Small amount (30 mg) of each material (Si, CB) was dispersed in buffer solution pH 3 by using ultrasounds for 15 min. The dispersant quantity was adjusted in order that its concentration (mg mL<sup>-1</sup>) is the same as for electrode preparation. The process of settling was observed visually as a function of time.

**Rheological measurements** – Rheological properties were measured on a controlled-stress rotating rheometer (Anton Paar,

**Table 1**

Composition, porosity, thickness and mean resistivity (measured with 2 probes) of composite electrodes. L and P mean an electrode prepared at the lab scale and at the pilot scale, respectively.

Electrode name	Si (wt%)	CB (wt%)	Latex (wt%)	CMC (wt%)	Buffer (wt%)	PAMA (wt%)	Porosity (%)	Thickness (μm)	Loading (mg Si cm <sup>-2</sup> )	Conductive additive volume fraction <sup>a</sup> (%)	2-probes resistivity with stand. dev. (ohm cm)
La	–	51	–	16	33	–	n.m.	n.m.	n.m.	n.m.	n.m.
Lb	–	49	–	15.7	31.8	3.5					
Lc	–	47	–	15.2	31	6.8					
Ld	–	43.2	–	14.4	29.5	12.9					
L1	67.6	10.1	–	6.8	15.5	–	71–73	66–68	2.6–2.8	3.06	11.6 ± 0.5
L2	65.9	10.1	–	6.8	15.5	1.7	68–70	63–65		3.30	7.6 ± 0.5
L3	64.2	10.1	–	6.8	15.5	3.4	65–68	60–62		3.55	12.7 ± 0.5
P1	65.9	10.1	–	6.8	15.5	1.7	70–71	52–54	2.0–2.1	3.24	11.4 ± 0.5
P2	63.5	9.7	3.6	6.6	15	1.6	68–69	50–51		3.14	9.5 ± 0.5
P3	61.3	9.4	6.9	6.3	14.5	1.6	68–69	52–54		3.01	11.1 ± 0.5
P1	65.9	10.1	–	6.8	15.5	1.7	59–60	41–42	2.0–2.1	4.40	9.4 ± 0.5
P2	63.5	9.7	3.6	6.6	15	1.6				3.97	8.1 ± 0.5
P3	61.3	9.4	6.9	6.3	14.5	1.6				3.85	9.7 ± 0.5

n.m. is for not measured.

<sup>a</sup> The volume fraction is calculated by taking into account the electrode porosity.

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