



# The effects of cross-linking cations on the electrochemical behavior of silicon anodes with alginate binder

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## ABSTRACT

Silicon is one of the most promising anode candidates for the next generation Li-ion batteries. Polymer binders play a crucial role as they are very essential to keep mechanical integrity of the electrodes and affect the solid electrolyte interphase (SEI) properties. Alginate appears to be the best binder system for Si electrode and it is able to form three-dimensional (3D) conductive polymeric network through in-situ inter-chain cross-linking by divalent cations. Herein, the effects of different cross-linking cations ( $\text{Cu}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Ni}^{2+}$ ) on the electrochemical behavior of silicon nano-sized particle anodes with alginate binder are investigated. It is found that all the alginate networks bridged by the transition metal cations are able to tolerate the volume change of silicon and effectively restrict the volume expansion of the Si particles. The overall electrochemical properties of the Si anode with Ni cations cross-linked alginate exhibit the highest reversible capacity, extraordinary cycleability and superior rate capability. The main reason for the electrochemical enhancement is explained by the improved stability of SEI film on the Si surface.

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## 1. Introduction

Lithium-ion batteries (LIBs) of high energy and power density, improved cycle life and safety are urgently required for electric vehicles (EVs) and energy storage systems (ESSs) [1,2]. Commercial graphite materials used in the state-of-the-art LIBs have only a limited reversible capacity of  $372 \text{ mAh g}^{-1}$  (theoretical value). New electrode materials with high lithium storage capacities are very essential to boost the energy density of LIBs in the future. Silicon has very high theoretical specific capacity of  $4200 \text{ mAh g}^{-1}$ , which is the top over all the other anode materials. Moreover, Si anodes show moderate lithium intercalation and deintercalation potential ( $-0.4 \text{ V vs. Li/Li}^+$ ), which could effectively avoid the safety concern of lithium deposition upon overcharge of the cell. However, the notoriously poor cycleability arising from severe volume change (ca.300%) in the electrochemical processes is hindering its practical

applications into lithium ion battery industry.

To date, there are three main approaches to solving the poor behavior of Si anode, namely: forming composite materials in which Si nano-particles are finely dispersed in an inactive or active solid matrix [3–7]; surface coating using thin film technology [7–9]; adopting functional binders to maintain the physical integrity of the electrode upon lithiation/delithiation processes. While a variety of electrode structures and active phases have been developed to mitigate the severe volume expansion, polymeric binder has turned out to be very critical in maintaining electrode structure and consequently the cycling stability. Actually, the development of functional polymeric binders has been proved to very effective inhibiting the capacity-fading by alleviating mechanical strain and prevent pulverization of Si particles [10–12]. The Si anode with conventional PVDF binder exhibits poor cycling performance as the binder possesses very weak van der Waals interactions with Si surfaces. An ideal electrode binder needs to possess two critical functions. Firstly, there exist strong chemical interactions (hydrogen bonds or covalent bonds) between the binder and the Si surface instead of weak van der Waals forces. Secondly, three-dimensional (3D) network developed by robust chemical bonds is important to provide superb mechanical

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strength to tolerate the severe volume change.

In recent years, various water-based binders such as alginate [13], polyacrylic acid (PAA) [14,15] and carboxy-methyl cellulose (CMC) [16,17] have been widely examined as binders for Si-based anodes. They all contain abundant carboxylic and hydrogen groups which provide strong bonding with the hydroxylated Si surface. Among the polysaccharide polymers, alginate appears to be the most appropriate binder system for Si anode. Alginate is a natural polysaccharide, a linear copolymer of (1 → 4)-linked β-D-mannuroate (M) and α-L-gulonate (G) residues, which has different physical and biological properties due to the varying G/M ratio. Alginate has ability to bind divalent cations, such as alkaline earth metals and heavy metals and to form gels. Rees et al. proposed the “egg-box model”, which has been generally accepted [18–20]. The model indicates that the G blocks along alginate chain adopt a 2/1 helical conformation, setting up a bridge between adjacent alginate chains (Fig. S1†a, region I). A 3D cross-linked polymeric network architecture is therefore obtained. The dramatically enhanced mechanical property resulting from robust chemical bonds can effectively confine the severe volume change of the Si particle. Moreover, alginate binder is also very helpful in building a stable passivating SEI layer to stabilize the Si particle during long-term charge-discharge cycles.

Previously, we have developed a facile and self-assembly strategy to in-situ construct a 3D cross-linked polymeric network with Ca cations and Si nano-particles exhibit significantly improved reversible capacity, superior rate capability and much prolonged cycle life [21]. It is known that alginate chains can be easily interconnected by adding various divalent cations including Cu, Ni, Fe, Co, etc., whereas, the effects of cross-linking cations on the electrochemical behavior of silicon anodes with alginate binder have not been investigated. The cross-linking cations not only play a significant role affecting the mechanical strength of the polymeric network, but also contribute to a different SEI mechanism on the Si surface. A comparison between different cross-linking cations for the alginate binder may represent a new avenue for practical applications of Si anode in the future.

In this work, the electrochemical behavior of a silicon anode with alginate binder cross-linked by using different divalent cations including Cu, Ca, Fe, and Ni is compared. Although all the alginate networks bridged by the transition metal cations are able to effectively restrict the volume expansion of the Si particles, long-term cycling performance of the anodes manifest a distinctive difference. The overall electrochemical properties of the Si anode with Ni cations cross-linked alginate exhibits much improved reversible capacity, extraordinary cycleability, and superior rate capability compared to those with other cations cross-linked alginate. A high reversible capacity of 3026 mAh g<sup>-1</sup> after 500 cycles with a capacity retention ratio of 83.1% was obtained by using the Ni cations cross-linked alginate binder. Even at 10C rate, the Si anode is still able to deliver a capacity of 2411 mAh g<sup>-1</sup>. The main reason for the electrochemical enhancement is explained by the effect of Ni cations cross-linked alginate in stabilizing the SEI on the Si surface.

## 2. Experimental section

### 2.1. Materials and methods

The spherical silicon nano-particles adopted in this study were purchased from Shenzhen Kejin Star Technology Co., Ltd. China. The SEM image of the Si powder is shown in Fig. S2†. Mono-dispersed Si nano-particles of ~100 nm diameter are observed. Sodium alginate (CAS no.9005-38-3) with medium viscosity and the inorganic salts (NiCl<sub>2</sub>, FeCl<sub>2</sub>, CuCl<sub>2</sub>, CaCl<sub>2</sub> and CoCl<sub>2</sub>, analytical grade) were

obtained from Sigma-Aldrich Co., Ltd. Super P carbon black with an average particle size of 40 nm was acquired from TIMCAL Graphite & Carbon (Switzerland).

The 3D alginate binders cross-linked with different divalent cations were prepared by introducing a certain amount of the inorganic salt solution (NiCl<sub>2</sub>, FeCl<sub>2</sub>, CuCl<sub>2</sub>, and CaCl<sub>2</sub> grade) into the 3 wt% alginate solution. Specifically, 1.5 g sodium alginate is dissolved into 48.5 g Milli-Q water (Millipore, USA), and the mixture is agitated with a magnetic stirrer at room temperature overnight to form a homogeneous solution. Afterwards, a certain amounts of the inorganic salt solution were added dropwise into the sodium alginate solution. Upon adding the divalent cations, alginate chains were immediately cross-linked, resulting in a viscous gel. To ensure a uniform distribution of the divalent cation in the solution, the viscous gel was vigorously stirred for another 12 h prior to use.

### 2.2. Electrode preparation and electrochemical tests

Silicon electrodes were prepared by mixing the nano-silicon particle, acetylene black (battery grade), and the prepared alginate gel cross-linked with different molar fractions of the divalent cations by a weight ratio of 70:15:15 in an adequate amount of Milli-Q water. The mixture was stirred using a high shear dispersing emulsifier (FlukofA25, Germany) at 3000 rpm for 30 min and a homogeneous slurry was obtained. The slurry was then cast onto a 15 μm-thick copper foil (99.99% purity). Through varying the height of the blade, the silicon electrode was controlled to have identical mass loading of around 0.45 mg cm<sup>-2</sup>. As a reference, the electrode using alginate binder without divalent cations was prepared according to the same procedure. After drying for 6 h, all the electrode laminates were calendered and punched out into electrode discs of 13 mm diameter. The electrode discs were further dried at 120 °C in vacuum for 16 h and immediately transferred to a glove-box prior to use.

The electrochemical performances were measured with CR2032-type coin cells assembled in an argon-filled glove box (<0.5 ppm of oxygen and water, OMNI-LAB, VAC). Lithium foil was employed as the counter electrode. The electrolyte is composed of 1 mol L<sup>-1</sup> LiPF<sub>6</sub> salt in a mixture of ethylene carbonate (EC), diethyl carbonate (DEC) and Fluorinated ethylene carbonate (FEC) (volume ratio: 7:7:2) (Novolyte Technologies). Galvanostatic charge-discharge cycling was performed on a Maccor S4000 (Maccor Instruments, USA) between 10 mV and 1 V. The C rates were calculated according to the theoretical capacity of Si (4200 mAh g<sup>-1</sup>). For the rate capability test, all the electrodes were discharged (lithiation) and charged (delithiation) at the same rate till 2C (8.4 A g<sup>-1</sup>), and then the discharge rates were kept at 2C and the charge rate was varied from 2 C to 20 C.

In order to examine the cycling stability of the Si anode with alginate binder cross-linked with different divalent cations, long-term cycling test of the electrodes was carried out after the cell formation with 0.2C charge/discharge rates at room temperature for 500 cycles. Cyclic voltammetry of the Si anode in the potential window of 10 mV and 2 V at a rate of 0.05 mV s<sup>-1</sup> was performed on an Autolab potentiostat (Autolab Instruments, Switzerland). Electrochemical impedance spectroscopy (EIS) measurements were performed on a Zahner Elektrik IM6 electrochemical work station over the frequency range of 10<sup>-2</sup> to 10<sup>5</sup> Hz with an alternating voltage of 5 mV. All impedance measurements were carried out at 60% DOD (depth of discharge). Before each test, the cell was held at 60% DOD for at least 4 h at 30 °C to attain a condition of sufficiently low residual current.

### 2.3. Material characterizations

Morphologies of the silicon electrodes with the cross-linked

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