Electrochimica Acta 245 (2017) 371–378

Contents lists available at ScienceDirect

Electrochimica Acta

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

Research paper

Multiple hydrogel alginate binders for Si anodes of lithium-ion battery

Zhan-Yu Wu[a], Li Deng[a], Jun-Tao Li[a,*], Qi-Sen Huang[c], Yan-Qiu Lu[a], Jie Liu[b], Tao Zhang[a], Ling Huang[b], Shi-Gang Sun[b]

[a] College of Energy, Xiamen University, Xiamen 361005, China
[b] State Key Laboratory of Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China
[c] Contemporary Amperex Technology Co., Limited, No.1 XinGang Road, ZhangWan Town, JiaoCheng District, Ningde 352100, China

ARTICLE INFO

Article history:
Received 29 March 2017
Received in revised form 10 May 2017
Accepted 14 May 2017
Available online 20 May 2017

Keywords:
Lithium-ion battery
Si anode
Binder
Hydrogel alginate

ABSTRACT

A series of hydrogel alginate binders (M-alg, M = Al, Ba, Mn, Zn) for Si anode of lithium ion battery are synthesized by coordinating alginate molecule chains with different cations respectively. Among these binders, Al-alg and Ba-alg both present their Vickers hardness higher than 32.0 HV while other M-alg binders show Vickers hardness less than 25.5 HV. The Ba-alg binder exhibits a viscosity of 30270 mPa s while other M-alg binders only show their viscosities less than 1700 mPa s. The Si anodes with Al-alg or Ba-alg both deliver their capacities near 2100 mAh g^{-1} after 300 cycles at 420 mA g^{-1}, while the electrodes with other M-alg binders show capacities less than 1500 mAh g^{-1}. When the current density is increased to 2100 mA g^{-1} or the Si loading mass is increased to 1.0–1.2 mg cm^{-2}, the electrodes with Al-alg or Ba-alg still have remarkable advantages. Moreover, the ultrahigh viscosity makes Ba-alg strongly adhere with both Si and current collector, so when the electrodes are fabricated with a material mass ratio of 8:1:1 (Si: acetylene black: binder), the electrode with Ba-alg still delivers an outstanding capacity retention of 49.1% after 200 cycles at 840 mA g^{-1}.

1. Introduction

To meet the increasing demand of portable energy storage and electric vehicles, lithium ion batteries (LIBs) are requested to provide higher energy density, lower cost and longer cycle life [1–4]. Various types of materials have been investigated as LIB anodes for replacing the widely used graphite with a relative low capacity, such as Li-alloys based materials and metal oxides [5,6]. Among these materials, Si has been considered as a promising candidate anode for next-generation LIB, due to its ultrahigh theoretical capacity, relatively low Li^+ insertion potential, low cost and nature abundance [7].

However, Si anodes have less successful commercial applications mainly due to the huge volume change (>300%) during lithium alloying/dealloying processes, which causes anode materials pulverized and peeled off from the electrode [2]. Such degradation of electrode brings about two serious problems for their practical applications in LIB. One is the separation of electrical contact between Si particles and current collector that leads to a rapid capacity loss. The other is the continuous formation of the solid electrolyte interphase (SEI) on the Si particle surface, which causes continuous increasing electric resistance and reducing coulombic efficiency [8]. To tackle these challenges, several strategies have been explored [9–18], including the change or modification of binders.

Due to the weak Van der Waals force between binder and Si particles, the traditional polyvinylidene fluoride (PVDF) binder is difficult to buffer the huge volume change of Si particles during the cycling. However, the binders with hydroxyl group (—OH) or carboxyl group (—COOH) could form stronger hydrogen bonds with the silicon oxide thin layer on Si surface. Such kind of hydrogen bonds intensely adhere Si nanoparticles (SiNPs) and the current collector, ensuring an improved electrochemical performance [19]. Along this line, plenty of polymers with —OH or —COOH were applied as the binders of Si anodes in the past few years.

Polyacrylic acid (PAA) and carboxymethyl cellulose (CMC) were demonstrated to play significant positive roles on the electrochemical performance of Si anodes firstly [20,21]. Then, some kinds of natural biopolymers have also been reported. Kovalenko et al. developed sodium alginate (Na-alg) as binder for Si anode.

* Corresponding author.
E-mail address: jtli@xmu.edu.cn (J.-T. Li).

http://dx.doi.org/10.1016/j.electacta.2017.05.094
0013-4686/

The electrode with Na-alg could keep intact better, and result in more stable cycle performance [22]. Ling et al. found that the long chains of Gum Arabic binder could reinforce the Si-based electrode, thus bringing an outstanding cycle performance [23]. Jeong et al. reported that Si particles with Xanthan Gum binder displayed 72.2% capacity retention after 200 cycles [24]. Our research group chose Guar Gum as binder for its high mechanical strength and lithium ion transport ability, and demonstrated that the Si anode with Guar Gum showed low capacity fading even in a lower binder ratio (15 wt%) [25]. Hwang et al. used natural agarose as an alternative binder for both high-performance Si anode and $LiMn_2O_4$ cathode. The full cell with agarose binder exhibited a capacity retention of 87% after 50 cycles [26]. Bie et al. demonstrated that the Si anode with Karaya Gum presented a specific capacity of 2421 mAh g^{-1} at 1.5 A g^{-1} with a capacity retention of 80% after 150 cycles [27].

To further improve the performances, the modifications of binders have been developed. The polyvinyl alcohol (PVA) and PAA cross-linked binder was synthesized by in-situ esterification reaction. A three-dimensional network could be formed and effectively buffer the volume change of Si anode [28]. Ryou et al. prepared mussel-inspired polymer binders through conjugation of

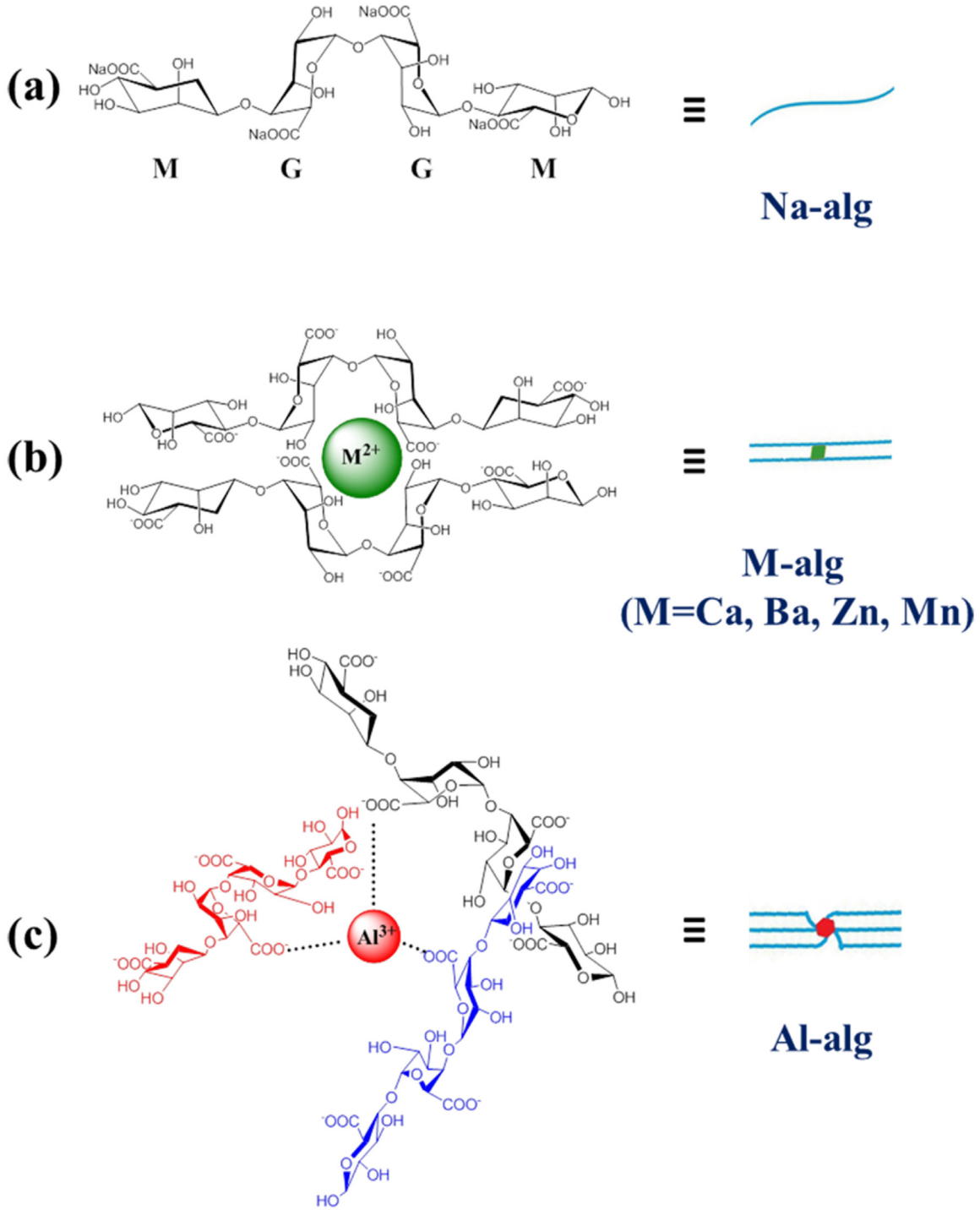

Fig. 1. Schematic of (a) Na-alg, (b) M-alg and (c) Al-alg molecular structures.