Full Length Article

Influence of EDTA in poly(acrylic acid) binder for enhancing electrochemical performance and thermal stability of silicon anode

Sun-Young Lee [a], Yunju Choi [a], Kyong-Soo Hong [a], Jung Kyoo Lee [b], Ju-Young Kim [c], Jong-Seong Bae [a,*], Euh Duck Jeong [a,*]

[a] Busan Center, Korea Basic Science Institute (KBSI), Busan 46742, Republic of Korea
[b] Department of Chemical Engineering, Dong-A University, Busan 49315, Republic of Korea
[c] School of Materials Science and Engineering, Ulsan 44919, Republic of Korea

ABSTRACT

The crucial roles of ethylenediaminetetraacetic acid (EDTA) in the poly(acrylic acid) (PAA)-binder system were investigated for the high electrochemical performance silicon anode in lithium-ion batteries. The EDTA supports the construction of a mechanically robust network through the formation of sbndCOOH linkage with the SiO_2 layer of the Si nanoparticles. The mixture of the PAA/EDTA binder and the conductive agent exhibited an improved elastic modulus and peeling strength. The creation of hydrogen fluoride (HF) was effectively suppressed through the elimination of the H_2O. An H_2O–phosphorous pentafluoride (PF_5) reaction, which is known for its use in the etching of metal oxides including its creation of the solid electrolyte interphase (SEI) layer, generates the HF. A remarkably sound cyclability with a discharge capacity of 2540 mA h g^{-1} was achieved as a result of the synergistic effect between robust mechanical properties and suppression of the HF creation for the stability of the SEI layer.

© 2018 Published by Elsevier B.V.

1. Introduction

High energy density and enabling the long-term operation of lithium-ion batteries (LIBs) is necessary for expanding its application to new fields such as electric vehicles, portable electronic devices and solar/wind plants [1–4]. In addition to the higher reliability, the improvement of cycle and calendar life is a primary target for the development of next-generation LIBs. Silicon (Si) has received the spotlight as the LIBs anode material due to its exceptional theoretical gravimetric capacity ($Li_{15}Si_4$ = 3579 mA h g^{-1} at room temperature) that is approximately 10 times larger than that of graphite ($\sim$ 372 mA h g^{-1} for LiC_6) [3,4]. Unfortunately, despite this advantageous gravimetric capacity, the practical application of the Si anode material is still quite challenging on account of its large volumetric expansion ($\sim$300%) when it is alloyed with Li to form the $Li_{15}Si_4$ phase at room temperature. Such huge volume changes trigger a disastrous fading mechanism such as the pulverization of active materials, a breakage of the electrical contact between the active Si materials and the conductive additives, a film delamination from the current collectors, and a destabilized solid electrolyte interphase (SEI) formation [5–7].

Tremendous efforts have been tried to solve the volume expansion issue, including nano structuring and applying adhesive binder. Among these approaches, nano structuring the Si particles is a promising route to achieve high capacity and acceptable cycle life [8–11]. However, the disadvantage is the fabrication complexity and thus the high manufacturing cost. Another approach is providing mechanically robust and/or adhesive polymers binder because conventional polyvinylidene fluoride (PVdF) is not effective in the supporting of the stable cycling of Si anodes because its weak van der Waals interactions are insufficient for the sustaining of the electrode integrity during large volume changes of Si anode [4,12–14]. More seriously, a low tensile strength of the PVdF can be attributed to its high swellability value [14]. For this reason, mechanically robust and/or adhesive polymers have been studied as a binder because these polymers can accommodate severe volume changes and maintain a good electrical conduction network in the electrode. Recently, the use of poly(acrylic acid) (PAA) [15–17], β-cyclodextrin [4,18–20], pectin [21], agarose [22], alginate [23] and chitosan polymers [14] as advanced binders for the enhancement of the cyclic performance of the Si anodes, for which the hydrogen bonding that forms between the SiO_x native oxide layers of the Si surfaces and the polar-functional groups of the binders has been reported.

* Corresponding authors.
   E-mail addresses: jsbae@kbsi.re.kr (J.-S. Bae), edjeong@kbsi.re.kr (E.D. Jeong).
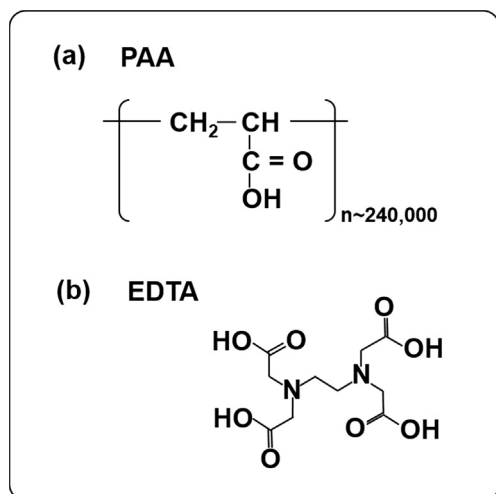
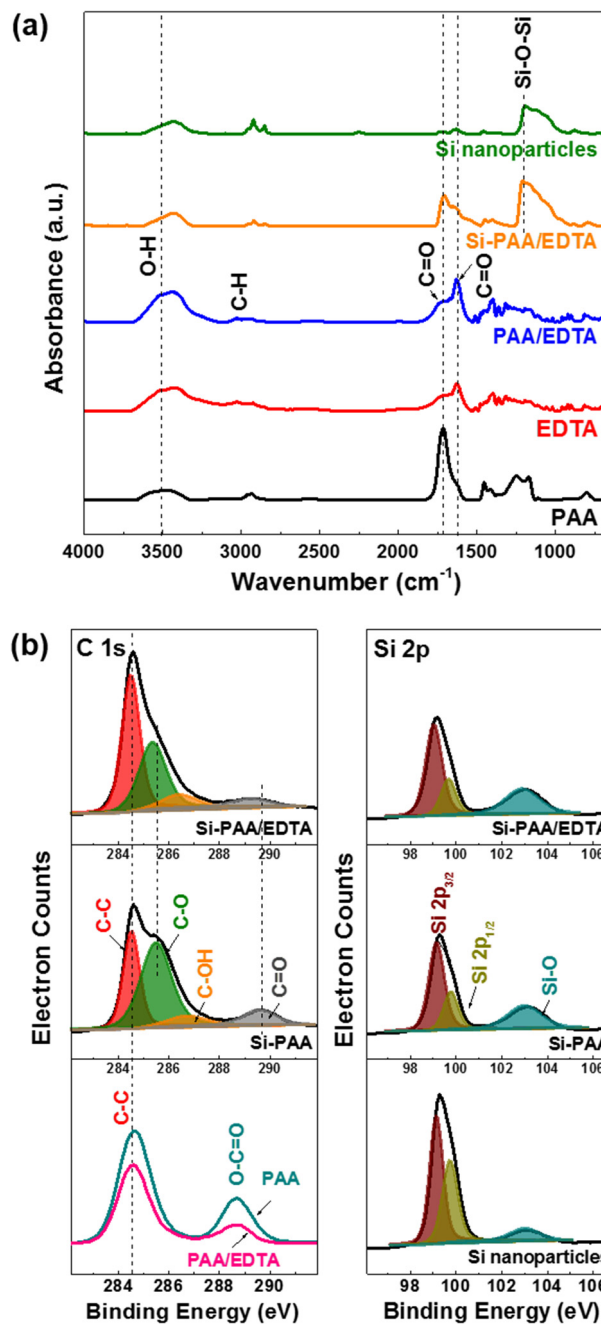Fig. 1. Chemical structure of the (a) PAA and (b) EDTA.

Fig. 2. (a) FTIR spectra of the Si NPs, PAA, EDTA and PAA/EDTA binders, and Si-PAA/EDTA electrode. (b) XPS spectra of the C 1s and Si 2p regions of the Si NPs, PAA and PAA/EDTA binders, the Si-PAA and Si-PAA/EDTA electrodes.

As a linear polymer chain (Fig. 1a), the PAA binder with the previously mentioned a large quantity of —OH and —COOH functional group presented a covalent bond and/or strong interaction of hydrogen bonds between Si particle and binders that is associated with the improved cyclic performance of the Si anode. Nonetheless, the linear chain nature of the PAA polymer binder is susceptible to sliding upon the continual Si volume change during the cycling. Many previous works are confined to volume change issue of Si particle. However, it should be considered that decomposition of electrolyte plays a crucial role in battery aging or capacity fading. The electrolyte lithium salts $LiPF_6$ decomposes into hydrofluoric acid (HF) and POF_3 in the presence of water [24–27]. Such electrolyte decomposition affects LIBs in various ways: The composition of electrolyte deviates from the optimum one, which might worsen the ionic transport property of the electrolyte. In addition, HF might attack anode active materials. Moreover, these problems become remarkable when LIBs with a non-aqueous electrolyte solution are used as secondary batteries in electric automobiles, which must operate reliably at a temperature to 60 °C. In this work, the strong chelating agent ethylenediaminetetraacetic acid (EDTA) was introduced into PAA to suppress the creation of HF and high temperature storage test is carried out. In addition, the interaction of binders with electrolytes, the effect of binders on cycling performance, and the effect of binders on SEI formation on Si particle has been investigated with X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FE-SEM), and transmission electron microscopy (TEM).

2. Experimental

Solution of PAA/EDTA (4 wt.% binder) was prepared. The PAA (Alfa Aesar, 25 wt.% in H_2O, Average M_w = 240000) and the EDTA (Sigma E-4884) with a weight ratio of 9:1 were dispersed in the N-Methyl-2-pyrrolidone/water. The solution was stirred at 40 °C for 12 h. For the working electrode, a slurry of silicon nanoparticles (NPs; Alfa Aesar, APS < 50 nm; Fig. S1) was mixed as follows: carbon black (Denka black 50% compressed; Li-250, Singapore) and binder with a 60:20:20 weight ratio was coated on the Cu current collector using a doctor blade. The coated electrodes were dried in a vacuum drying oven at 110 °C for 2 h. The Si loading density and thickness of the slurry are 0.5–0.6 mg cm^{-2} and ~10 μm, respectively.

The Fourier transform infrared (FTIR) spectra were measured using the Vertex 80 (Bruker) with KBr pellets. For the mechanical properties, polymer films with 50-μm-thick were prepared on slide glasses using a doctor blade. All spectra were collected with 512 scans and spectral resolution of 4 cm^{-1}. For the elastic modulus investigation, the nanoindentation was measured with the three-sided Agilent G200 XP pyramidal diamond Berkovich indenter (maximum depth of indentation = 1200 nm, constant-indentation strain rate = 0.05 s^{-1}). The delithiated electrodes were extracted from cycled cells and rinsed with dimethyl-carbonate five times to remove residual electrolyte and then dried at room temperature in a glove box for ex-situ analysis. The surface and cross-sectional morphologies of the samples were obtained using the Su 70 high resolution scanning electron microscope (Hitachi, Japan) and the JEM 2100F TEM (Jeol, Japan). Ex-situ XPS was