

A Polymeric Coating on Prelithiated Silicon-Based Nanoparticles for High Capacity Anodes used in Li-ion Batteries

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Abstract

Silicon is a promising candidate anode material for lithium ion batteries due to its high theoretical specific capacity of 4,200 mAh g⁻¹ and low discharge potential. However, a high irreversible capacity loss due to a solid electrolyte interphase formation on the surface of Si anodes during the 1st cycle limits its practical applications. Prelithiation is considered an attractive method that can be used to compensate for the active lithium losses during the 1st cycle. Surface oxidation to Li₂O when the material comes into contact with moisture and oxygen during electrode fabrication is a main obstacle, leading to poor electrochemical stability. In this work the surface stability of prelithiated Si-based nanoparticles was modified via a polymeric nano-coating method. The results demonstrate that coating with 1-fluorooctane is an effective strategy to mitigate irreversible capacity loss and provide electrochemical stability for high performance next generation lithium ion batteries.

Keywords: Lithium ion batteries, Silicon, Prelithiation

1. Introduction

Lithium ion batteries (LIBs) are playing an essential role in the development of electric vehicles (EVs) and grid energy storage technologies owing to their high energy density, low self-discharge, and long cycle life (Kennedy, Patterson, & Camilleri, 2000; Tarascon & Armand, 2001). Silicon (Si) represents an attractive candidate anode material to replace commercial graphite as a way of improving the energy density of LIBs. This is due to its high theoretical specific capacity of 4,200 mAh g⁻¹ (through the formation of a Li_{4.4}Si alloy). This is ten times higher than that of commercial graphite anodes with a relatively low electrochemical potential (370 mV) (Kasavajjula, Wang, & Appleby, 2007; Yin, Wan, & Guo, 2012). However, practical applications that achieve a satisfactory high capacity and stable cycling performance have not been realized since a large volume change (>400%), (Hui

Wu & Cui, 2012) causes mechanical stress within the electrode leading to its rapid structural failure and poor electrical contact with the active material (Beaulieu, Eberman, Turner, Krause, & Dahn, 2001; Domi, Usui, Iwanari, & Sakaguchi, 2017).

Therefore, novel nanostructural designs of silicon-based electrode materials have been utilized to mitigate the volume expansion of the silicon structure and improve its cycling performance (N. Liu, Li, Pasta, & Cui, 2014; N. Liu et al., 2014; Son et al., 2015; Hui Wu & Cui, 2012). This can be facilitated by effective diffusion of active lithium and electrons (Y. Wang, Li, He, Hosono, & Zhou, 2010). However, a drawback to this approach is that the high surface area of these nanostructured materials significantly increases solid electrolyte interphase (SEI) formation during the first cycle (Aurbach, 1994). SEI formation on silicon anodes during the first cycle causes highly irreversible

capacity losses of 50-80% and can result in low Coulombic efficiency (CE) (DiLeo et al., 2013; Hu et al., 2013; H. Wu et al., 2013; X. Wu, Wang, Chen, & Huang, 2003) depending on the structure of the silicon and the composition of the anode composite. The irreversible loss of active lithium anode material during the first cycle can be mitigated by prelithiation, which has been previously achieved. Experimentally, the commercial prelithiation reagent used is stabilized lithium metal powder (SLMP). It can be drop-cast onto an electrode material serving as an anode, such as graphite, SiO₂, Si or CNT-based electrodes (Forney, Ganter, Staub, Ridgley, & Landi, 2013; Z. Wang et al., 2014). However, SLMP is hard to synthesize and is inhomogeneously distributed within the electrodes. Another approach is to use mechanical stirring of the Si anode material with Li metal at high temperatures to form Li_xSi NPs (Yom, Seong, Cho, & Yoon, 2018; J. Zhao et al., 2014; J. Zhao et al., 2018). The resulting material suffers from surface oxidation that forms a Li₂O passivation layer when in contact with moisture and oxygen converting Li_xSi to Li_xSi–Li₂O NPs with a rather low potential and high capacity. These Li_xSi NPs anode materials with fine structures typically show improved electrochemical performance and worsened stability on exposure to air with high relative humidity (RH) (J. Zhao et al., 2015). Therefore, surface coating may be an appropriate alternative to improve stability and yield higher capacities. For example, Li_xSi NPs mixed with poly(styrene-butadiene-styrene) (SBS) polymer and graphene can be used as an anode (J. Zhao et al., 2017a). Also, Li_xSi NPs can be protected by an artificial solid electrolyte interphase (Y. Liu et al., 2017; J. Zhao et al., 2015; J. Zhao et al., 2017b). These coatings are effective to some extent and it is still necessary use them in a dry room.

This work proposes a polymeric-coating on the surface of prelithiated Si-based NPs (Li_xSi NPs). They are made using a prelithiation method to fabricate electrode materials that compensate for first-cycle capacity losses and reduce the unwanted reactions encountered by Li_xSi NPs exposed to air or other reactive environments. These materials are prepared using a thermal prelithiation forming a polymer shell around the NPs in a reaction of Li_xSi NPs with 1-fluorooctane, thereby producing a continuous and dense coating over the Li_xSi NPs. The 1-fluorooctane was selected because of its excellent chemical behavior in nonpolar solvents

such as cyclohexane. It is highly reactive with Li_xSi NPs (J. Zhao et al., 2014). The LiF and other lithium compounds with long hydrophobic carbon chains effectively protect the reactivity of Li_xSi NPs when exposed to an ambient environment though the formation of a dense outer coating (J. Zhao et al., 2015). It is of great importance to develop relatively stable coated-Li_xSi NPs, which can be easily handled during the process of battery assembly.

2. Experimental

2.1 Materials preparation

40 and 80 μL aliquots of 1-fluorooctane (CH₃(CH₂)₇F, Sigma Aldrich) were each mixed in 20 ml of anhydrous cyclohexane and then stirred at 60 °C for 2 h. Next, Li_xSi NPs (200 mg) were synthesized via a modified hydride destabilization method (Vajo, Mertens, Ahn, Bowman, & Fultz, 2004). These Li_xSi NPs were dispersed in anhydrous cyclohexane (Sigma Aldrich) with vigorous stirring for 1 h to obtain a suspension with 5 mg ml⁻¹ of Li_xSi NPs. The 40 μL 1-fluorooctane solution and the Li_xSi NP suspension were homogeneously mixed at room temperature inside a glovebox under an Ar atmosphere for 1 h with vigorous stirring. After mixing, the coated-Li_xSi NPs were washed with cyclohexane and centrifuged to remove unreacted 1-fluorooctane and then dried under a vacuum. This process was repeated using the 80 μL 1-fluorooctane mixture. The samples made up with 40 and 80 μL aliquots of 1-fluorooctane are referred to as the coated-40 and coated 80 samples, respectively.

2.2 Structural and Morphological characterization

X-ray diffraction (XRD) (PANalytical, Empyrean) was performed to examine the crystal structure of the experimental samples using Cu-Kα radiation with a step size of 0.01° and over a 2θ range of 10°-80°. Transmission electron microscopy (FEI, TECNAI G220) was used to investigate the microstructural properties of the Li_xSi-coated NP materials.

2.3 Electrochemical testing

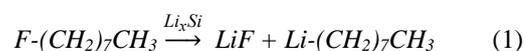
Swagelok type cells were assembled in an Ar-filled glove box to evaluate the electrochemical properties of these materials. The Li_xSi or coated-Li_xSi NP materials were mixed with carbon black (Super P, Alfa Aesar) and polyvinylidene fluoride (PVDF-Kynar 2801, Arkema) (65:20:15 by weight)

in a 1,3 dioxolane (DOL, Sigma Aldrich) solvent, which was then mechanically stirred to form a slurry. The resulting slurry was coated on copper foil using a doctor blade and then dried under a vacuum at 80 °C overnight. The Swagelok type cells consisted of discs of the prepared anode and a Li metal foil (Alfa Aesar), used as counter and reference electrodes, respectively. A 1.0 M LiPF₆ solution in a 1:1 w/w ratio of ethylene carbonate (EC) and dimethyl carbonate (DMC), 1 vol% of vinylene carbonate and 2 vol% of fluoroethylene carbonate was used as an electrolyte with a Celgard 2400 (MTI) separator. Galvanostatic charge/discharge tests were done between 0.01-1.2 V at a C/20 rate (1C = 4.2 A g⁻¹) using a multi-channel tester (BST8 MA, MTI).

3. Results and discussion

The Li_xSi NPs were synthesized via a modified hydride destabilization method using commercial Si, which exhibits surface oxidation that forms a Li₂O passivation layer when in contact with moisture and oxygen during the synthesis of Li_xSi NPs. This leads to poor electrochemical stability. Therefore, modifying the surface of Li_xSi NPs was done via a polymeric nano-coating with the reduction of 1-fluorooctane in cyclohexane, as depicted in Figure 1a, to prevent further oxidation. The morphology of the Li_xSi NPs with a size range of 10 to 20 nm and

of the coated-40 and coated-80 samples are respectively shown in Figure 1b-d. Generally, the surfaces of Li_xSi NPs consisted of lithium fluoride (LiF) and other lithium compounds such as lithium alkyl carbonates with long hydrophobic carbon chains. This is similar to the reaction mechanism employing butyllithium (Wilke, 2003; J. Zhao et al., 2015). Li_xSi NPs transfer a single electron to a C–F bond in 1 fluorooctane forming a C radical and F⁻, and a second electron transfer converts the C radical into a carbanion (reaction 1). Additionally, O₂ and CO₂ in the glovebox may react with alkyl lithium to form a complex mixture of lithium compounds (reaction 2).



The XRD patterns of all the uncoated and coated samples are shown in Figure 2. The coated and uncoated samples at 0 h of exposure to ambient air exhibited quite similar XRD patterns, showing diffraction peaks of the Li₂₂Si₅ (PDF No. 01-073-2049), Li₁₂Si₇ (PDF No. 00-040-0942), Li₂O (PDF No. 01-073-0593), and LiOH phases (space group P4/nmm with PDF No. 01-076-0911, and P4/mmm

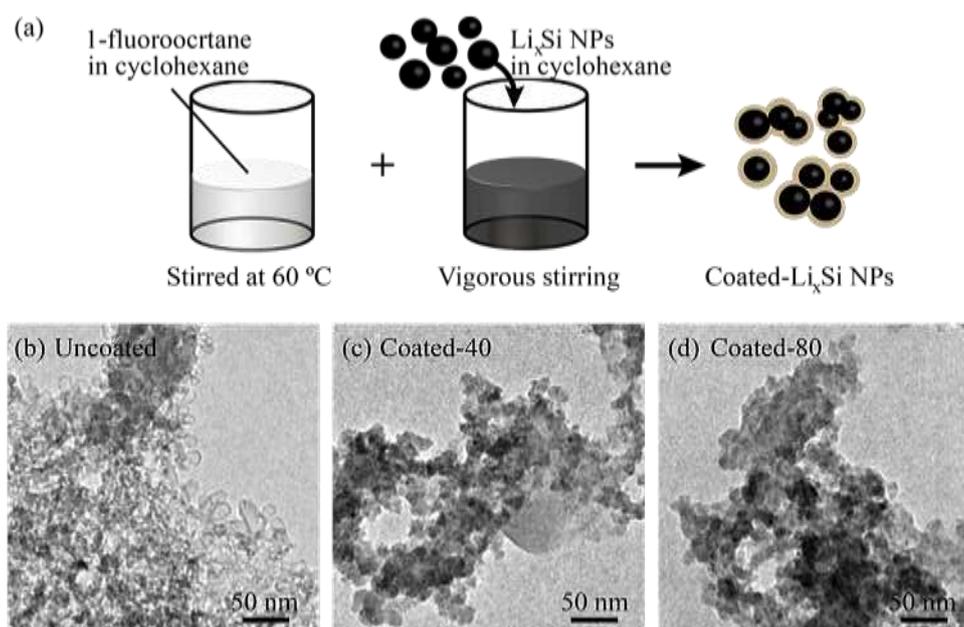


Figure 1. (a) Schematic diagram of the coated Li_xSi NPs passivation layer formed by chemical reactions via 1-fluorooctane. (b-d) TEM images of the Li_xSi NPs, coated-40 and coated-80 samples, respectively.

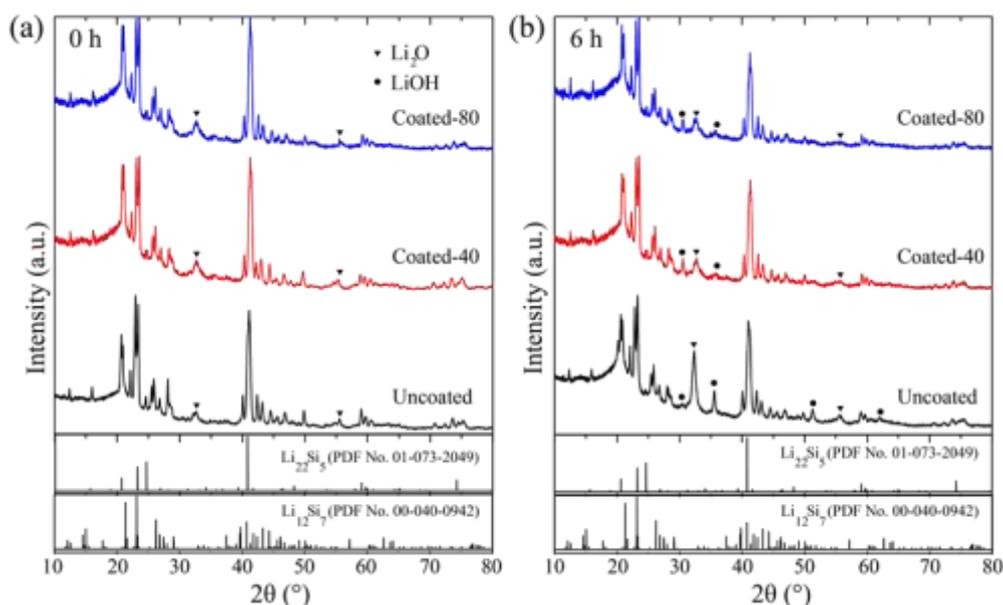


Figure 2. XRD patterns of the uncoated, coated-40 and coated-80 samples after (a) 0 h and (b) 6 h of exposure to ambient air with $20\pm 2\%$ RH.

with PDF No. 00-001-1021) as given in Figure 2a. The $\text{Li}_{22}\text{Si}_5$ and $\text{Li}_{12}\text{Si}_7$ phases are formed as a result of the pre-lithiation process, while the Li_2O and LiOH phases are formed due to reactions with O_2 and water vapor in the ambient environment. The coated and uncoated samples at 6 h of exposure to ambient air with $20\pm 2\%$ RH showed different amounts of Li_2O and LiOH phases compared to those with 0 h of exposure. After exposure to ambient air for 6 h, the XRD pattern of the uncoated sample showed significantly higher peak intensities of the Li_2O and LiOH phases. However, the XRD patterns of the coated samples showed similar peak intensities of these phases. The coated-80 sample showed slightly lower amounts of Li_2O and LiOH phases than that of the coated-40 sample due to a thicker surface coating. This indicates that our method using polymeric coating can effectively protect pre-lithiated Li_xSi NPs and prevent further surface oxidation for at least 6 h. This polymeric coating method is effective because both LiF and lithium alkyl carbonate with long hydrophobic carbon chains can serve to form an effective passivation layer on the surfaces of Li_xSi NPs, retarding reactions of metallic lithium with O_2 and water vapor in an ambient environment (Stubblefield & Bach, 1972; J. Zhao et al., 2017b).

A study of the electrochemical properties of the initial Li_xSi NPs and coated- Li_xSi NP materials (coated-40 and coated-80 sample) at $20\pm 2\%$ RH

after 0 h, 6 h, and 24 h exposure to ambient air was carried out using Swagelok type cells. All samples were fabricated using Li metal as counter electrodes. The electrolyte solution consisted of 1.0 M LiPF_6 in a 1:1 w/w ratio of ethylene carbonate (EC) and dimethyl carbonate (DMC), 1 vol% of vinylene carbonate and 2 vol% of fluoroethylene carbonate with a Celgard 2400 disc as a separator. All the specific capacities and current densities are reported based on the weight of active material in the anodes. The electrochemical behaviour of the initial Li_xSi NPs and coated- Li_xSi NP anodes was evaluated using galvanostatic charge/discharge measurements during their first cycle (Figure 3a-c). The samples after 0 h of exposure showed first charge capacities of about 1,395, 1,371 and 1,091 mAh g^{-1} for the uncoated, coated-40 and coated-80 samples, respectively. After exposure to an ambient environment with $20\pm 2\%$ RH for 6 h, the uncoated sample showed negligible capacity, while the coated-40 sample retained 839 mAh g^{-1} and the coated-80 sample retained 1,025 mAh g^{-1} . This indicates that the coated-40 sample showed a capacity decay of 39% while the coated-80 sample lost less than 6% of its capacity. After 24 h of exposure to the ambient environment, the coated 40 sample exhibited a capacity of 405 mAh g^{-1} , which is a capacity decay of 70% of its initial capacity. The coated-80 sample still delivered a stored capacity of 677 mAh g^{-1} , which is a capacity decay of 38% of its

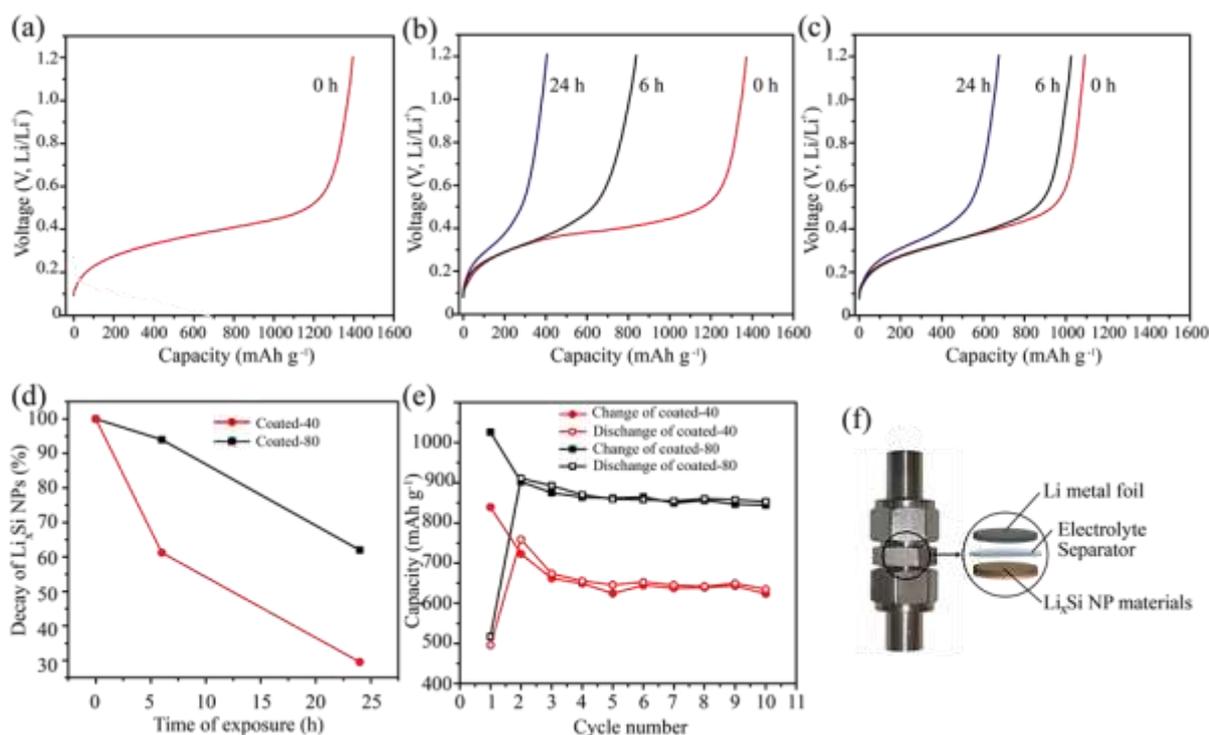


Figure 3. Voltage profiles during first charging cycle of (a) uncoated (b) coated-40 (c) coated-80 samples under ambient conditions for various durations ($20 \pm 2\%$ RH) (d) the change in capacity of the coated anodes as a function of exposure time, (e) the cycling stability of the electrodes prepared from the 6 h air exposed coated-40 and coated-80 samples at a $C/20$ rate ($1C = 4.2 \text{ A g}^{-1}$) (f) the Swagelok type cell for electrochemical testing.

initial capacity. This indicates that even though the coated-80 sample was protected from further surface oxidation for about 6 h, the coating thickness needs to be optimized to prevent reactions of metallic lithium with O_2 and water vapor in an ambient environment for longer exposure times. This topic will be our focus in future experiments. Figure 3d summarizes the results of effect of air exposure.

Figure 3e shows the cycling performance of the electrodes prepared from the coated-40 and coated-80 samples after 6 h of exposure to ambient air. It is noteworthy that the cycling stability of the 6 h air exposed coated-40 sample was quite similar to that of the coated-80 sample. However, the absolute discharge capacity after 6 h at $20 \pm 2\%$ RH of the coated-80 sample was higher than that of the coated-40 sample. The discharge capacities after 10 cycles were ~ 860 and $\sim 630 \text{ mAh g}^{-1}$ for the coated-80 and coated-40 samples, respectively. This shows that the discharge capacity of the coated samples was a function of the concentration of the 1-fluorooctane used in forming the coating. A thicker coating is more effective in preventing reactions with O_2 and

moisture resulting in superior electrochemical performance.

4. Conclusions

We successfully developed a polymeric coating method for pre-lithiated Li_xSi NPs, with a size range of 10-20 nm, using a chemical reaction involving 1-fluorooctane. LiF and lithium alkyl carbonate compounds with long hydrophobic carbon chains can serve as an effective passivation layer on the surfaces of Li_xSi NPs. This polymeric coating layer can retard reactions of metallic lithium with O_2 and water vapor inhibited negative reactions under ambient conditions, improved electrochemical performance, and improved the ease of electrode fabrication. The coated-40 and coated-80 samples showed similar capacity decays in an ambient environment at $20 \pm 2\%$ RH after 6 h, but the coated-80 sample had higher capacities after 10 cycles. This indicates that polymer coating methods are potentially useful in industrial battery fabrication. Thus, application of polymeric coatings on the surfaces of lithium containing anode materials is a promising approach that may facilitate prelithiation

methods for high performance next generation lithium ion batteries.

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