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Atomic layer deposited aluminum oxynitride coating for high-performance Si anode in lithium-ion batteries

Hongzheng Zhu a, Mohammad Hossein Aboonasar Shiraz a, Liang Liu a,b, Yue Zhang a, Jian Liu a,*

a School of Engineering, Faculty of Applied Science, University of British Columbia, Kelowna, BC V1V 1V7, Canada
b Automotive Engineering Research Institute, Jiangsu University, Zhenjiang 212013, China

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ABSTRACT

Silicon (Si) has received great attention as a promising anode material for lithium-ion batteries (LIBs) due to its high gravimetric capacity and large abundance. However, the use of Si anodes in LIBs has been hindered by their inferior electrochemical performance, resulting from its vast volume expansion and unstable solid electrolyte interphase (SEI). To address these problems, a novel surface coating material, aluminum oxynitride (AlO\textsubscript{x}N\textsubscript{y}), was developed using a plasma-enhanced atomic layer deposition technique with trimethylaluminum and plasma \textsubscript{N}2/\textsubscript{H}2 as the precursors. The effects of AlO\textsubscript{x}N\textsubscript{y} surface coatings on the electrochemical properties of Si electrodes were investigated. With the optimal AlO\textsubscript{x}N\textsubscript{y} coating (~2 nm), the reversible capacity after 140 cycles was improved from 331 mAh g\textsuperscript{-1} for bare Si electrode to 1297 mAh g\textsuperscript{-1} for AlO\textsubscript{x}N\textsubscript{y}-coated one, and the capacity retention was elevated from 13\% to 72\%. Post-cycling analysis revealed that the AlO\textsubscript{x}N\textsubscript{y} coating significantly suppressed the charge transfer and SEI resistances and maintained the structural integration of Si electrodes by suppressing continuous electrolyte decomposition and electrode delamination from the current collector. This study provides a new perspective on designing advanced functional coating materials for atomic layer deposition for lithium-ion batteries.

1. Introduction

Nowadays, the demand for lithium-ion batteries (LIBs) is increasing in many different fields, such as electronic devices, electric vehicles, and grid storage, due to their relatively high energy density and long lifetime among energy storage technologies available today. However, the ever-increasing need from end-users calls for LIBs with higher energy densities. In current commercial LIBs, graphite is used as the anode and possesses a theoretical capacity of 372 mAh g\textsuperscript{-1}, corresponding to 1-mol Li-ion per 6-mol C atoms. The low specific capacity of graphite results in limited energy densities of current LIBs and becomes one of the main limiting factors towards higher-performance LIBs [1–3]. Besides, present LIBs have serious safety concerns due to potential lithium plating on the graphite surface, and graphite anode needs to be replaced with a better anode with a higher specific capacity and working voltage [4]. Among all anode alternatives, Silicon (Si) has drawn the most attention because of its superior gravimetric capacity of 3590 mAh g\textsuperscript{-1} (Li\textsubscript{15}Si\textsubscript{4}) and high abundance on earth. It provides a tremendous increment to graphite [5–7].

However, Si experiences considerable volume change (~300\%) during the charge and discharge process and thus suffers from severe capacity degradation, unstable solid electrolyte interphase (SEI), and low efficiency. For example, Si active material will pulverize due to the stress-induced by alloying and dealloying, causing rapid material degradation. The pulverization of Si materials also causes detachment and isolation of the Si electrode from the current collector. The successive formation-breaking-reformation procedure of SEI also leads to low Coulombic efficiency (CE), permanent consumption of electrolytes, and severe capacity drop for extended cycling [6,8–16]. All of the issues stem from the volume expansion of different phases of Li\textsubscript{x}Si\textsubscript{y} alloys and side reactions between these Li\textsubscript{x}Si\textsubscript{y} alloys with electrolytes during the lithiation/de-lithiation process. Several methods have been employed to tackle these issues, such as surface coating, nanosizing, and Si/graphite compositing. Utilizing surface coating on nanostructured Si to construct a physical compartment to buffer the volume expansion has been proven as a practical approach [17,18].

Among various surface coating methods, atomic layer deposition (ALD) has been an effective approach to create a protective layer on Si electrodes. ALD provides consecutive, separated, and self-terminating reactions between different chemical precursors and thus excellent...
control over the uniformity and thickness of thin films at an atomic level. ALD enables highly uniform and conformal films on the complex surface due to its surface-controlled nature. The coating material usually serves as an atomic layer deposition (ALD) to deposit AlO\textsubscript{N} coating on the Si electrode for the first time. PEALD has been known as an enabler for a wide range of rapidly gaining applications in popularity. Several merits have been derived from PEALD compared to the thermal ALD. PEALD allows more flexibility in processing conditions and material properties and provides a high reactivity of the plasma species on the deposition surface. We developed AlO\textsubscript{N} coating by PEALD and applied it on the Si electrode in our work. By employing it as a surface modification, the confinement of silicon nanoparticles embedded into the electrode matrix is well achieved, while the kinetics of the charge/discharge process is enhanced due to the unique mechanical and electrical properties of AlO\textsubscript{N} films. The capacity retention of the Si electrode was elevated from 13.3% to 72.3% with the AlO\textsubscript{N} coating. The AlO\textsubscript{N}-coated Si electrode remains a reversible capacity of 1297 mAh g\textsuperscript{-1} after 140 cycles.

2. Experimental

2.1. Materials preparation

Si electrode was prepared by mixing Si nanoparticles (50-nm diameter, Alfa Aesar), Super P, and carboxymethyl cellulose/styrene-butadiene rubber (CMC/SBR) with a weight ratio of 7:2:1 in an aqueous solution to form a uniform slurry. Then the slurry was cast on a copper (Cu) foil and dried overnight in a vacuum oven at 80 °C.

AlO\textsubscript{N} coating was deposited on Si wafer and Si electrodes in a GEMStar XT-P PEALD system (Arradiance, USA). AlO\textsubscript{N} coating was directly applied on Si electrodes, because previous work has suggested that the ALD coating could form continuous protection layers on the whole surface of active material and conductive additives without impeding the electronic conduction network [25]. The deposition of AlO\textsubscript{N} was performed at 150 °C using trimethylaluminum (TMA) and plasma N\textsubscript{2}/H\textsubscript{2} (50/50 sccm, plasma power 300 W) as the precursors. Each ALD cycle consisted of four steps: (1) 0.025 s pulse of TMA, (2) 10 s purge using Ar gas to remove TMA and any byproducts, (3) 10 s pulse of N\textsubscript{2}/H\textsubscript{2} gases with exposure to plasma under 300 W power, and (4) 10 s purge with Ar gas. AlO\textsubscript{N} on the Si substrate was used for growth per cycle (GPC) and X-ray photoelectron spectroscopy (XPS) measurements. The thickness AlO\textsubscript{N} thin film shows a linear dependence on ALD cycles, yielding a growth per cycle (GPC) of 0.73 Å on Si wafer (Fig. SI-1). Si electrode coated with AlO\textsubscript{N} by 10, 30, and 50 ALD cycles were denoted as Si-AlO\textsubscript{N}-10, Si-AlO\textsubscript{N}-30, and Si-AlO\textsubscript{N}-50, respectively. Si wafer was also adopted as the substrate during the deposition for reference.

2.2. Structural characterisations

Morphology and structure of Si electrode and AlO\textsubscript{N}-coated Si electrodes were characterized by using a scanning electron microscope (SEM, Tescan MIRA3 FEG-SEM) and high-resolution transmission electron microscopy (HRTEM, JEOL 2010F). X-ray photoelectron spectroscopy (XPS) was measured on an Axis Ultra DLD (Kratos Analytical).

2.3. Electrochemical characterisations

After AlO\textsubscript{N} coating, the electrode was cut into a round shape with a diameter of 12 mm and loaded into CR2032 cell configuration cells for electrochemical testing. The bare Si electrode and Si electrodes with AlO\textsubscript{N} coatings have been used the cathode, Li metal as the anode, and polyethylene (Celgard) as the separator. The electrolyte was 1.3 M LiPF\textsubscript{6} in ethylene carbonate: diethyl carbonate (EC/DEC, 3:7, v/v) with 10 vol % of fluoroethylene carbonate (FEC) as the additive.

The coin cells were assembled in an Ar-filled glove box with H\textsubscript{2}O and O\textsubscript{2} concentrations below 0.1 ppm. The cycling performance of the coin cells was evaluated in a voltage range of 0.01–1.5 V and with five formation cycles at 0.05 C and subsequent cycles at 0.1 C, on a Neware BTS 4000 battery tester. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were measured on a potentiostat/galvanostat/EIS workstation (SP-150, Biologic).

3. Results and discussion

Fig. 1 shows the structure and composition of Si nanoparticles coated with AlO\textsubscript{N} layer with 100 PEALD cycles. The TEM image in Fig. 1a reveals a uniform and conformal coating of AlO\textsubscript{N} film on the Si nanoparticles. The AlO\textsubscript{N} layer thickness is measured to be about 6.2 nm, slightly thinner than the value (7.3 nm) calculated based on a growth per cycle (GPC) of 0.73 Å on Si wafer substrate (Fig. S1-1). HRTEM observation discloses that the interplanar distance of the Si nanoparticle is 0.31 nm, corresponding to the (1 1 1) plane of Si (JCPDS No. 27-1402), as confirmed by the fast-Fourier-transform image in Fig. 1b inset. The AlO\textsubscript{N} layer on the Si nanoparticle surface possesses an amorphous structure and has no long-range order due to the low PEALD deposition temperature (150 °C). Fig. 1c presents a STEM image of Si nanoparticles with 100-cycle AlO\textsubscript{N}-coating and corresponding EDX mapping of Si and Al elements. STEM and EDX analysis prove the even distribution of AlO\textsubscript{N} coating on the surface of Si nanoparticles, suggesting the benefit of PEALD in achieving high-quality ultrathin layers on electrode materials. X-ray photoelectron spectroscopy (XPS) analysis confirms the existence of Al, O, and N elements from the AlO\textsubscript{N} coating on Si nanoparticles (Fig. 1d). Deconvolution of N1s peak leads to one peak located at 399.5 eV (Fig. 1e), ascribed to the N-Al-O bonding in aluminum oxynitride [26]. Al 2p spectrum is decomposed into one prominent peak at 74.6 eV, which corresponds to the Al-O bond and is verified by the 531.1 eV peak in the O 1s spectrum (Fig. 1e). The deconvolution of the O 1s spectrum resolves another peak centered at 532.1 eV, which could be assigned to the O-H bond. The residual O-H bond could result from incomplete removal of ligands from TMA on the outer surface during the PEALD process. The incorporation of the O element into AlO\textsubscript{N} might occur when the thin films are removed from the reaction chamber and exposed to the air. Previous work has suggested that metal nitrides can be quickly oxidized once direct exposure to air [27,28]. The oxidation of AlN could happen because of exposure to air when the samples were taken out of the ALD reaction chamber. The same phenomena were observed in PEALD TiN, which was proven as TiN\textsubscript{O} due to air exposure [29].

Fig. 2 depicts the effect of AlO\textsubscript{N} coatings (10, 30, and 50 ALD cycles) on the electrochemical performance of Si electrodes as an anode in LIBs. All cells are tested between 0.01 and 1.5 V at 0.05 C in the initial five cycles (formation) and 0.1 C in the subsequent cycles. The AlO\textsubscript{N} coating on Si electrodes was confirmed by EDX mapping under SEM (Fig. S1-2). As seen in Fig. 2 (a), the initial discharge capacity is 3094 mAh g\textsuperscript{-1} for bare Si, and 2108, 2357, and 1624 mAh g\textsuperscript{-1} for the Si electrodes with 10-cycle, 30-cycle, and 50-cycle AlO\textsubscript{N} coating, respectively. The higher discharge capacity of bare Si than the others in
the initial cycles can be attributed to the higher availability of Si particles to react with Li-ion than those of coated ones. In the AlO$_x$N$_y$-coated electrode, Li-ions need to interact with AlO$_x$N$_y$ first to pass through the coating layer and then undergo alloying reactions with Si particles. From the 6th cycle, the Si electrodes with and without AlO$_x$N$_y$ coatings exhibit a dramatic difference in the specific capacity and cycling stability. The discharge capacity of Si-AlO$_x$N$_y$-10, Si-AlO$_x$N$_y$-30, and Si-AlO$_x$N$_y$-50 stabilizes at 1355, 1664, and 1070 mAh g$^{-1}$, respectively, while the specific capacity of bare Si rapidly drops to 937 mAh g$^{-1}$ in the 6th cycle. The bare Si undergoes much more degradation during the initial ten cycles than those with AlO$_x$N$_y$ coatings, probably due to continuous breakdown and formation of SEI layers on Si surface [30]. Among all the samples, Si-AlO$_x$N$_y$-30 maintains the highest specific capacity of 1297 mAh g$^{-1}$ after 140 cycles, in contrast to 331 mAh g$^{-1}$ of bare Si, demonstrating enhanced electrochemical properties of Si electrode using thin AlO$_x$N$_y$ coating (~2 nm thick) by PEALD. The capacity retention of Si electrodes (140th-cycle capacity/2nd-cycle capacity) is elevated from 13% to 72% by using AlO$_x$N$_y$ coating. From Fig. 2a, it can be found that the electrochemical performance of Si electrodes has a strong dependence on the thickness of AlO$_x$N$_y$ coatings. The optimal one is the Si electrode with a 30-ALD cycle AlO$_x$N$_y$ coating (~2 nm). Si electrode with 50-ALD cycle AlO$_x$N$_y$ layer still shows stable cycling stability but experiences a noticeable decrease in its specific capacity compared to Si-AlO$_x$N$_y$-30. The reason could be that AlO$_x$N$_y$ coating is too thick and reduce the diffusion rate of Li ions through the artificial SEI layer, leading to suppressed redox reactions in the Si anode.

CE in the 2nd cycle is calculated as 69.9% and 93.9% for the pristine Si and Si-AlO$_x$N$_y$-30, respectively, implying that AlO$_x$N$_y$ coating reduces the side reaction between the Si electrode and the electrolyte. In general, AlO$_x$N$_y$-coated Si electrodes show improved and stabilized CE over repeated cycling, while pristine Si electrode exhibits high fluctuation in the CE (Fig. 2b). A direct comparison between the charge–discharge curves for pristine Si and Si-AlO$_x$N$_y$-30 is presented in Fig. 2c and d. Pristine Si experiences gradual degradation in the specific capacity and increased polarization, as evidenced by the enlarged charge–discharge plateaus. In contrast, the charge–discharge profiles for Si-AlO$_x$N$_y$-30 have good overlap in the 1st, 2nd, 3rd, 10th, and 50th cycles, suggesting the importance of surface coating in preventing side reactions on the Si surface.

To investigate the improved electrochemical properties of Si electrode by AlO$_x$N$_y$ coating, the CV test was applied on the electrodes at the scan rate of 0.2 mV s$^{-1}$, and the result is shown in Fig. 2 (e) and (f). In the first cycle, it is clear that the reduction curve of bare Si has a shoulder peak at 0.8 V, corresponding to the formation of SEI layer on the non-coated electrode in the initial cycle. This SEI formation is the direct consequence of the electrolyte decomposition and active Si loss, leading to the lower capacity of the pristine Si electrode. In contrast, the AlO$_x$N$_y$-coated electrode shows a significantly suppressed shoulder, indicating the effective role of thin AlO$_x$N$_y$ film to suppress the direct contact of active Si metal with electrolyte while providing a facile Li-ion pathway to react with Si particles in lithiation/de-lithiation. Meanwhile, the separation between oxidation and reduction peaks of Si is reduced with a 30-cycle AlO$_x$N$_y$ coating, indicating better kinetics in the Si-AlO$_x$N$_y$-30 electrode. A better overlapping of oxidation–reduction peaks, especially at the charge/discharge switch point, is observed in Si-AlO$_x$N$_y$-30, suggesting a better kinetic and suppressing thick SEI layer formation.

The electrochemical impedance spectroscopy (EIS) analysis was performed on Si electrodes with different AlO$_x$N$_y$ coatings before and after 100 battery cycles. As shown in Fig. 3 (a), before cycling, the cell displays a single semicircle at the high frequency, corresponding to the charge-transfer resistance of the anode surface and the electrolyte, and a straight line at the low frequency, representing the Warburg resistance. Compared to the pristine Si electrode, AlO$_x$N$_y$-coated Si electrodes show reduced charge transfer and solution resistances (Fig. 3), probably due to the good electrical conductivity of AlO$_x$N$_y$ coating layer. Si-AlO$_x$N$_y$-10 exhibits the smallest charge-transfer resistance of 100 Ω compared to 142 Ω for bare Si electrode (Table 1). 

In Fig. 3(b), all the electrode after cycling shows two semicircles in the high-frequency range, which represent the charge-transfer resistance and SEI resistance, respectively. As seen, AlO$_x$N$_y$ coated Si

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**Fig. 1.** (a) TEM image, (b) HRTEM image, and (c) STEM image with EDX mapping of Si and Al elements for Si particles with AlO$_x$N$_y$ coating deposited by 100 ALD cycles, (d) XPS full survey and deconvolution of (e) N 1s, (f) Al 2p, and (g) O 1s spectra of AlO$_x$N$_y$ thin film on a Si substrate. (Inset in (b) is the Fast Fourier transform (FTT) image of the Si particle.)
Fig. 2. (a) Cycling stability and (b) Coulombic efficiency (CE) of bare Si electrode and Si electrode coated with AlO$_x$N$_y$ layers by 10, 30, and 50 ALD cycles, measured between 0.01 and 1.5 V at 0.05 C during the initial five cycles and 0.1 C in the subsequent cycles; (c, d) charge–discharge profiles and (e, f) Cyclic voltammetry (CV) curves measured at 0.2 mV s$^{-1}$ for Si and Si-AlO$_x$N$_y$-30 electrodes.

Fig. 3. Nyquist plots of bare Si electrode and Si electrodes coated with AlO$_x$N$_y$ layers by 10, 30, and 50 ALD cycles (a) before cycling and (b) after 100 charge/discharge cycles.
electrodes display significantly smaller semicircles in the medium frequency range, suggesting the decreased SEI resistances with AlO$_3$N$_y$ electrodes display significantly smaller semicircles in the medium frequency range, suggesting the decreased SEI resistances with AlO$_3$N$_y$ coating. As a result, we can see, in the coated sample, the artificial SEI coating before and after 100 charge/discharge cycles.

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<th>Electrode</th>
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The Nyquist profiles are fitted by using the equivalent circuit before cycling ($R_s(Q)(R_f Q)(R_{ct} Q)W$) and after cycling ($R_s(Q)(R_f Q)(R_{ct} Q)W$) to obtain EIS parameters (Table 1). $R_s$, $R_f$, and $R_{ct}$ represent the resistance of solution (electrolyte), SEI layer, and charge transfer, respectively. Q and W parameters are constant-phase element and Warburg resistance, respectively.

The compositions of SEI layers on Si electrodes with and without AlO$_3$N$_y$ coating are examined using XPS and the results are presented in Fig. 5. Fig. 5 (a) shows the XPS results of the cycled Si electrode with and without AlO$_3$N$_y$ coating for the Cls peak. The Cls peak can be split into three individual peaks located at Li$_2$CO$_3$ (289.7 eV), C—O (286.2 eV), C—C (284.8 eV). Li$_2$CO$_3$ is a well-known electrolyte reduction product that comes from the irreversible formation of the SEI layer. Poor CE usually occurs with this reduction product [31]. As we can see in Fig. 5 (b), O 1s peak also proves the existence of Li$_2$CO$_3$. Meanwhile, in the Si electrode with AlO$_3$N$_y$ (Fig. 5b), the Li$_2$O component is also detected at 530.5 eV. The signal for LiF in Fig. 5 (c) is considered an electrolyte decomposition product from the LiPF$_6$ salt, which comes from battery cycling over time [32]. The LiF peak is relatively stronger in AlO$_3$N$_y$ coated Si electrode than the bare Si electrode, attributed to the firm SEI layer on the electrode resulting in lower Si exposure. Fig. 5(d) shows the high-resolution XPS spectra of N1s peak from Si electrode without and with AlO$_3$N$_y$ after cycling. For the Si-AlO$_3$N$_y$ electrode after cycling, one peak can be located at Li-N bonding (399.7 eV) [33]. Li-N bonding confirms the presence of Li$_3$N on AlO$_3$N$_y$ coated Si after cycling. Li$_3$N is an ion conductor with very high Li-ion conductivity ($\sigma > 1 \times 10^{-3}$ S cm$^{-1}$), which comes from Li-ion transfer reaction through AlO$_3$N$_y$ coating during cycling [34]. Meanwhile, Fig. 5(e) also confirms the Li-Al-O bonding, a well-known excellent Li-ion conductor [35]. The Li-Al-O comes from the Li-ion reaction with Al-O in AlO$_3$N$_y$ coating. The artificial SEI layer contains Li$_3$N and Li-Al-O, which act as the Li-ion pathway to improve the ion transfers while maintaining the electrode properties and surface morphology of the cycled AlO$_3$N$_y$-coated electrode (Fig. 4 (d)) is strongly attached to the Cu current collector, leading to the stable and excellent electrochemical performance of the AlO$_3$N$_y$ coated electrode due to the confinement effect of AlO$_3$N$_y$ in Si volume expansion.

**Table 1**

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**Fig. 4.** The top-view and cross-section views SEM images of (a, b) pristine Si electrode and (c, d) Si-AlO$_3$N$_y$-30 electrodes (a, c) before and (b, d) after 100 charge-discharge cycles.
mechanical/structural architecture, meanwhile reduces the silicon expansion and lower the interaction of electrode–electrolyte at their interfaces.

For the AlO$_x$N$_y$-coated Si electrode, the reaction of Li-ion and AlO$_x$N$_y$ coating over cycles creates an artificial SEI layer containing Li$_3$N according to the reaction of $4\text{Li} + \text{AlN} \rightarrow \text{Li}_3\text{N} + \text{LiAl}$ [36]. Li$_3$N is an ion conductor with very high Li-ion conductivity ($\sigma > 1 \times 10^{-3}$ S cm$^{-1}$) [37]. The artificial SEI layer improved the coated Si electrode’s capacity and kinetic, meanwhile reducing the silicon expansion and lowering the interaction of electrode–electrolyte at their interfaces. The artificial SEI layer performs as the Li-ion pathway to improve the ion transfers while maintaining the electrode mechanical/structural architecture.

The cycling stability of the Si electrode with and without AlO$_x$N$_y$ coating was further examined at 55 °C, and the results are shown in Fig. 6 (a). The bare Si electrode exhibits higher discharge capacities than Si-AlO$_x$N$_y$-30 in the first three cycles because the AlO$_x$N$_y$ coating layer is less active for Li-ion diffusion at the beginning and requires an “activation process” to become ion conductive. Therefore, the AlO$_x$N$_y$ coating layer impedes the ion conduction in the first few cycles, leading to the reduced reversible capacities of Si-AlO$_x$N$_y$-30. The bare Si
The electrode shows a rapid capacity decay in 50 cycles, which is caused by the severe side reaction between Si and the electrolyte at the raised temperatures. As a result, the un-coated Si has capacity retention of 19.1% after 175 cycles. However, in contrast, Si-AlO$_x$N$_y$-30 exhibits much-improved cycle stability and capacity retention of 51.3% over 175 cycles. Furthermore, Si-30 possesses a relatively stable CE of 98–99% over cycling, while bare Si experiences a more fluctuated state in the CE. These results suggest the durable artificial SEI layers enabled by AlO$_x$N$_y$ coating, which confirm the importance of AlO$_x$N$_y$ coating to Si anode performances at higher temperatures.

4. Conclusions

In summary, Si electrodes were coated with AlO$_x$N$_y$ thin films by PEALD for the first time and applied as the anode for lithium-ion batteries. The electrochemical performance was enhanced due to the electrochemical properties of AlO$_x$N$_y$ film. The capacity retention of the AlO$_x$N$_y$-coated Si electrode was elevated to 72.3%, compared to 13.3% of bare Si electrode. The capacity remained 1297 mAh g$^{-1}$ at 140 cycles, and capacity retention of 51.3% over 175 cycles at 55 °C, indicating promising cycle stability capability of AlO$_x$N$_y$-coated Si electrode. The electrochemical reaction mechanism study and XPS analysis revealed that Li-ion interaction with AlO$_x$N$_y$ coating over cycles led to the formation of an artificial SEI layer containing Li$_2$N and Li-AL-O. The artificial SEI layer performed as the Li-ion pathway to improve the ion transfers while maintaining the electrode mechanical/structural architecture and improved the capacity and kinetic of the coated Si electrode. It also suppressed the silicon volume change and lowered the side reactions at the electrode–electrolyte interfaces. This work might open a new pathway to design high-performance Si electrode materials for Li-ion batteries.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apsusc.2021.151982.

References


