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## ARTICLE

# Mass Spectral Molecular Mapping Shows Benefits of Thermal Evaporation in Prelithiated Silicon-Based Electrodes

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Silicon based composites have become increasingly popular as potential anodes for lithium-ion batteries due to their large storage capacity and potential ability to generate batteries with energy densities greater than 350 Wh/kg. These anodes often see reduced initial coulombic efficiency (ICE) due to disruptive volume expansion up to 300% and continuous solid electrolyte interphase (SEI) layer formation. Prelithiation, where an excess reservoir of Li is added to the electrode to compensate for irreversible SEI formation losses during their sample preparation, has proven to solve the issue of immediate capacity loss. Thermal evaporation is a prelithiation technique with limited studies on its effectiveness. In this study, time-of-flight secondary ion mass spectrometry (ToF-SIMS) is used to highlight the benefits of prelithiation via thermal evaporation. ToF-SIMS provides chemical mapping and spatial information in 2D and 3D visualizing the deposition of lithium, identifying  $\text{Li}_x\text{Si}_y$  alloy and  $\text{Li}_x\text{Si}_y\text{O}_z$  silicate formation, and the distribution of lithium passivation into the electrodes. Passivation under different atmospheric conditions, Ar and Ar/ $\text{CO}_2$  highlights the impact of the environment for the passivation effectiveness and formation of  $\text{Li}_x\text{Si}_y$  alloy and  $\text{Li}_x\text{Si}_y\text{O}_z$  silicate. The ToF-SIMS molecular imaging and depth profiling results indicate that prelithiation via thermal evaporation effectively distributes lithium throughout the depth profile length and induces a greater degree of  $\text{Li}_x\text{Si}_y\text{O}_z$  silicate formation over  $\text{Li}_x\text{Si}_y$  alloy. Our ToF-SIMS characterization results indicate the effectiveness of thermal evaporation in producing a more stable electrode and an electrode with an effective lithium reserve that can preserve its capacity.

## Introduction

Lithium-ion batteries (LIBs) are the most developed, widely used energy storage technology across the globe. Improving their capacity, stability, and safety is crucial to expanding their applications and functionality. Traditional LIBs with graphite anodes are matured technologies that demand sophisticated engineering of graphite or the use of alternative materials to meet future energy storage demands.<sup>1-3</sup> Silicon-based anodes are promising alternatives to graphite due to silicon's significantly larger specific energy capacity (up to 4200 mAh/g) compared to graphite,<sup>4</sup> relative abundance, and low cost.<sup>2</sup> However, silicon's large volume swings (~300%)<sup>5</sup> leads to the formation of an unstable solid electrolyte interphase (SEI). These swings lower the structural integrity of the anode, leading to immediate and permanent loss of lithium (as measure by capacity) and initial coulombic efficiencies (ICE).<sup>6</sup> Silicon's sudden capacity loss when cycling is a crucial detriment to its widespread use as an anode material.

Prelithiation, where lithium-containing material is added to an anode during its sample preparation, is a promising

processing method to counteract the capacity and ICE loss during cycling of silicon-based electrodes.<sup>7</sup> Currently, a prelithiation method suitable for use in manufacturing and commercializing silicon-based anodes has yet to be found. Various prelithiation methods have been developed and tested such as prelithiation of the binder,<sup>8-11</sup> electrochemical prelithiation,<sup>12-15</sup> chemical prelithiation,<sup>16-23</sup> and direct contact prelithiation.<sup>24-34</sup> A newly studied prelithiation technique is prelithiation via thermal evaporation.<sup>35-37</sup> Here, a lithium metal source is evaporated onto the anode where the lithium accumulates on the surface and diffuses throughout the anode forming lithium-silicon alloys through solid state diffusion. Thermal evaporation is quick, easy to control, and has been shown to be more uniform along with producing a greater discharge capacity compared to direct contact prelithiation.<sup>36</sup> However, prelithiation via thermal evaporation alone still fails to deter the excess volumetric expansion of silicon-based anodes or the eventual losses of lithium inventory due to deleterious side reactions.<sup>36, 37</sup>

A recently published article covering the thermal evaporation of lithium as a prelithiation technique for silicon-based composites was explored.<sup>37</sup> Uniquely, a fine steel mesh covered the sample electrodes to reduce the strain and volumetric expansion during prelithiation by confining the lithium to

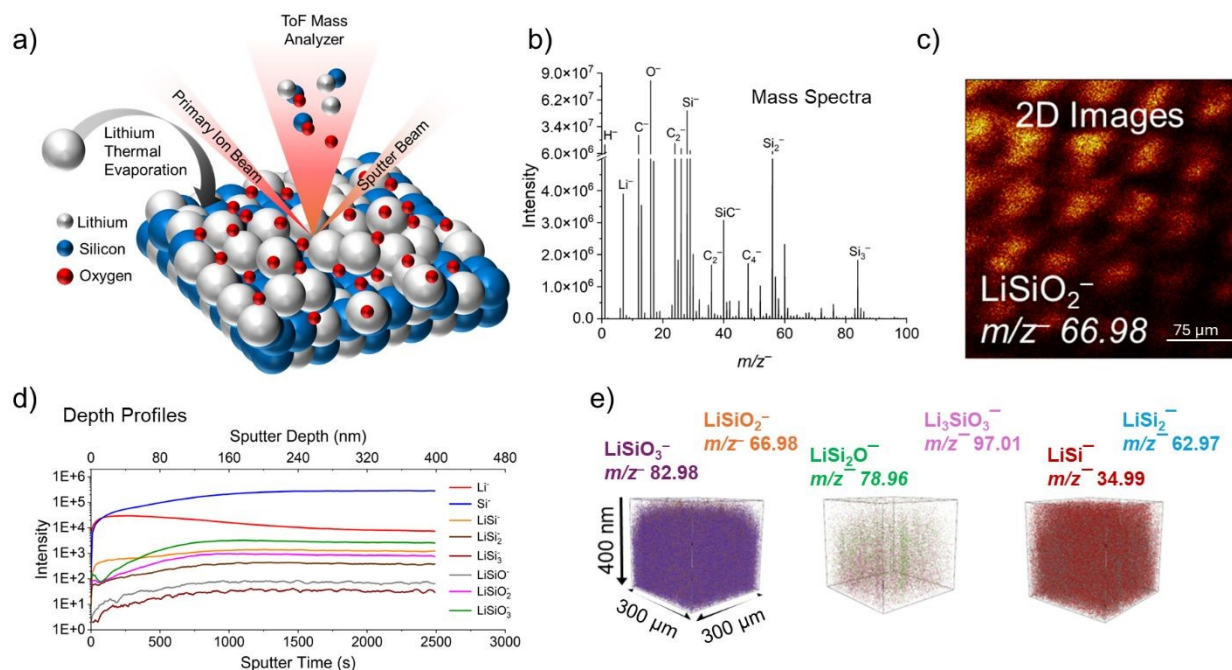
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**Figure 1.** ToF-SIMS schematic (a) providing overview of the battery sample highlighting the silicon anode with lithium passivation and surface oxidation identifying molecules such as  $\text{Li}^-$ ,  $\text{Si}^-$ ,  $\text{Li}_x\text{O}_y^-$ ,  $\text{Li}_x\text{Si}_y^-$ , and  $\text{Li}_x\text{Si}_y\text{O}_z^-$  molecules during analysis. ToF-SIMS collects data such as mass spectra (b), 2D images (c), depth profiles (d) and 3D reconstructions (e) showing the spatial and lateral distributions of interest analytes.

deposit in 'islands.' It was reported that the prelithiated anodes have higher initial coulombic efficiency, but their capacity fade is faster compared to their non-prelithiated samples due to the increased use of silicon and alloy formation that strains the electrodes.

Prelithiation is known to alleviate the problem of reduced ICE in silicon-based anodes, but it also exacerbates the formation of unstable, reactive  $\text{Li}_x\text{Si}_y$  alloy products.<sup>33, 34, 38, 39</sup> Not only does this alloy render the electrodes unsuitable for ambient conditions,<sup>33</sup> but specific alloy phases, like  $\text{Li}_{15}\text{Si}_4$ , create internal stress that reduce the electrodes' structural and cycling stability.<sup>38, 39</sup> Lessening  $\text{Li}_x\text{Si}_y$  alloy presence and instead increasing  $\text{Li}_x\text{Si}_y\text{O}_z$  silicate growth is found to improve the capacity and efficiency of silicon-based anodes.<sup>33, 34</sup>  $\text{Li}_x\text{Si}_y\text{O}_z$  silicates bring about more air stability<sup>33</sup>, moderate volume expansion, and provide more mechanical strength to silicon-based electrodes.<sup>38</sup>

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a highly sensitive surface characterization technique known for its low mass deviation and high lateral resolution.<sup>40</sup> Unlike other analytical instruments such as x-ray photoelectron spectroscopy and scanning electron microscopy, ToF-SIMS offers both chemical and distributional information.<sup>41, 42</sup> Other mass spectrometry techniques such as matrix assisted laser desorption ionization mass spectrometry (MALDI-MS) and differential electrochemical mass spectrometry (DEMS) have been used to study SEI; however, these techniques are limited to the type of information achievable. MALDI-MS typically obtains information regarding polymeric additives of the SEI and DEMS obtains gas evolution information.<sup>43, 44</sup> ToF-SIMS is

the dominant surface analysis technique used in this study to substantiate the effectiveness of prelithiation via thermal evaporation. ToF-SIMS high sensitivity to detect lithium ions and interphase compounds in addition to its mass spectra, depth profiling, surface imaging, and 3D imaging capabilities make it particularly effective at analysing lithiation dynamics.<sup>45, 46</sup> ToF-SIMS is commonly used for cycled electrodes and not commonly for analysis of prelithiation processes.

Here, ToF-SIMS analysis was performed on composite anodes consisting of silicon, polyimide, and carbon black that were prelithiated via thermal evaporation. Depth profiles, molecular images, and mass spectra were collected to map out Li arrangement on the surface, evaluate the dispersion of Li, and identify the presence of key  $\text{Li}_x\text{Si}_y$  and  $\text{Li}_x\text{Si}_y\text{O}_z$  compounds. This ToF-SIMS analysis helps validate the effectiveness of this unique prelithiation method.

## Methods

### Preparation of Electrodes

Detailed sample preparation can be found elsewhere.<sup>37</sup> In brief, silicon composite anodes constructed from 80:10:10 wt.% Si:polyimide (P84):carbon black slurries where silicon is the primary anode material, P84 is the binder, and carbon black acts to enhance the samples' conductivity and as a rheological aid. The silicon was formed by milling silicon chunks in propylene carbonate and the resulting material is oxide terminated. 1-Methyl-2-pyrrolidinone (NMP) was added to the slurry and mixed using a Turbula mixer for 1 hour. This slurry was then doctorbladed onto a Cu foil current collector with a 100μm wet gap, and circular electrodes were punched out providing a 15



mm diameter, 1.77 cm<sup>2</sup> electrode area. The electrodes were cured at 350 deg C for 1 hour under Ar. The electrodes were placed in an Argon-filled glovebox under high-vacuum ( $> 10^{-7}$  Torr) with a tantalum crucible containing lithium. A stainless-steel mesh was placed over the sample electrodes to deposit lithium into 'islands' or pockets on the electrodes' surface. After prelithiation, the mesh was removed to reveal a composite electrode with no surface cracking.<sup>37</sup> To initiate the prelithiation process, the crucible containing lithium was heated and evaporated toward the sample. For passivation, one sample electrode was placed into the vacuum chamber where the vacuum chamber was backfilled with 96% Ar and 4% CO<sub>2</sub> gas environment while the second was passivated in a high purity Argon filled glove box ( $< 1$  ppm H<sub>2</sub>O;  $< 10$  ppm O<sub>2</sub>).

### ToF-SIMS Analysis

Both static and dynamic ToF-SIMS analyses were performed with an IONTOF ToF.SIMS.5-NCS instrument (IONTOF GmbH, Münster, Germany). **Figure 1** displays a schematic of the general ToF-SIMS process and equipment involved. For static ToF-SIMS, a 30 keV Bi<sub>3</sub><sup>+</sup> primary cluster ion beam and with a 0.5 pA current 10 kHz pulse rate, and ion dose density of  $5.11 \times 10^{10}$  ions cm<sup>-2</sup> was used. An electron flood gun was used for charge compensation. The chamber pressure was maintained at  $\sim 8.0 \times 10^{-9}$  Torr during analysis. Static ToF-SIMS spectra were acquired over a 500  $\mu\text{m} \times 500 \mu\text{m}$  area for 60 scans with 256 $\times$ 256-pixel resolution and 100  $\mu\text{s}$  cycle time. Five replicate measurements were acquired for each sample in positive and negative ion modes. Reproducibility plots can be found in **Figs. S1 – S3**.

ToF-SIMS depth profiling was performed with an added 2 keV Cs<sup>+</sup> sputter ion beam with a 600 $\times$ 600  $\mu\text{m}^2$  sputter area and 300 $\times$ 300  $\mu\text{m}^2$  analysis area. Non-interlaced mode was used with 10s sputter time and one analysis frame per scan with a 256 $\times$ 256-pixel resolution. A total of 250 scans were collected. Results from the negative ion mode are presented to study the lithium distributions and verify the presence of lithium-silicon compounds and passivation layers. The results presented include mass spectra, 2D surface images of key ions, depth profile plots, and 3D distribution images of key ions. Additional positive ion mode results are included in the **Supporting Information (SI)**.

ToF-SIMS images provided in this work were acquired using high mass resolution spectrometry mode, not high spatial resolution imaging mode. Mass spectroscopy mode was chosen to study surface chemistry and compositional changes into the bulk of the electrode material. It is worth noting that some ion distribution in the spectroscopy mode may not have the exact distribution as that in the high spatial imaging mode. High spatial resolution 2D images of non-passivated and Ar/CO<sub>2</sub> sample are included in the SI with a 500  $\mu\text{m} \times 500 \mu\text{m}$  analysis region (see **Figs. S12 – S13**).

### ToF-SIMS Data Analysis

ToF-SIMS data was analyzed using SurfaceLab 7.3 software (IONTOF GmbH, Münster, Germany). Mass spectra were calibrated with  $m/z^- 14.02 \text{ CH}_2^-$ ,  $m/z^- 31.99 \text{ O}_2^-$ ,  $m/z^- 43.97 \text{ SiO}^-$ ,  $m/z^- 75.96 \text{ SiO}_3^-$ ,  $m/z^- 160.89 \text{ SiC}_3^-$  in the negative mode and

$m/z^+ 23.01 \text{ LiO}^+$ ,  $m/z^+ 29.03 \text{ CH}_3\text{N}^+$ ,  $m/z^+ 38.96 \text{ K}^+$ ,  $m/z^+ 53.04 \text{ C}_4\text{H}_5^+$ ,  $m/z^+ 176.88 \text{ SiOCs}^+$  in the positive mode. The calibration, spectra analysis, and 2D/3D image reconstructions were done in the SurfaceLab software. The ToF-SIMS depth profiling and mass spectra data were exported as ASCII files and plotted using Origin Pro 2023 (OriginLab, Northampton, Massachusetts, USA). The "search compounds" function of SurfaceLab was used to identify peaks as well as literature cross references.

## Results and Discussion

### ToF-SIMS Spectra Identifies Lithium-Silicon/Silicate Alloys

**Table 1.** Peak identification of the prelithiated anode exposed to inert, Ar gas environment in the negative ion mode.

$m/z^-_{obs}$	$m/z^-_{theo}$	$\Delta M$ (ppm)	Species	Assignment	References
7.0164	7.0166	25.414	Li <sup>-</sup>	Lithium	47
12.0005	12.0005	6.6797	C <sup>-</sup>	Carbon	47
27.9788	27.9775	45.8948	Si <sup>-</sup>	Silicon	48
34.9928	34.9935	20.4321	LiSi <sup>-</sup>	Li <sub>x</sub> Si <sub>y</sub> Alloy	This Work
50.9897	50.9884	25.9407	LiSiO <sup>-</sup>	Li <sub>x</sub> Si <sub>y</sub> O <sub>z</sub> Phase	This Work
62.9712	62.9704	12.0339	LiSi <sub>2</sub> <sup>-</sup>	Li <sub>x</sub> Si <sub>y</sub> Alloy	This Work
66.986	66.9833	40.1563	LiSiO <sub>2</sub> <sup>-</sup>	Li <sub>x</sub> Si <sub>y</sub> O <sub>z</sub> Phase	This Work
78.967	78.9653	21.8536	LiSi <sub>2</sub> O <sup>-</sup>	Li <sub>x</sub> Si <sub>y</sub> O <sub>z</sub> Phase	This Work
82.982	82.9782	45.3584	LiSiO <sub>3</sub> <sup>-</sup>	Li <sub>x</sub> Si <sub>y</sub> O <sub>z</sub> Phase	This Work
90.9477	90.9473	4.1176	LiSi <sub>3</sub> <sup>-</sup>	Li <sub>x</sub> Si <sub>y</sub> Alloy	This Work
97.0131	97.0102	30.0005	Li <sub>3</sub> SiO <sub>3</sub> <sup>-</sup>	Li <sub>x</sub> Si <sub>y</sub> O <sub>z</sub> Phase	This Work

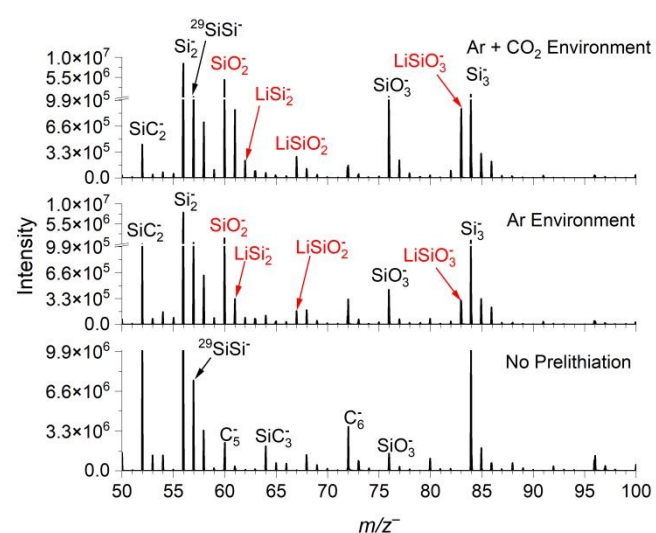
Note:  $m/z^-$  represents the mass-to-charge ratio for negatively charged ions. a  $m/z^-_{obs}$  represents the observed mass to charge ratio. b  $m/z^-_{theo}$  represents the theoretical mass to charge ratio. c  $\Delta M = 106 \times (m/z^-_{obs} - m/z^-_{theo}) / m/z^-_{theo}$ . (expressed in ppm).<sup>49</sup> Peak identification are possibilities identified by SurfaceSpectra software and cross-referenced to literature.

The possible peak identifications are shown in **Table 1** and **Table 2** for the negative ion mode. Peaks with a mass deviation of 65 ppm or less are included. Additional peak identifications are provided in **Tables S1-S6**.

Lithium deposition via the thermal evaporation process onto a Si-based electrode leads to the migration of lithium into the bulk of the electrode forming amorphous Li<sub>x</sub>Si<sub>y</sub> alloys through solid state diffusion due to the high temperatures ( $>400$  °C) of the incoming lithium and the large thermodynamic driving force for lithium alloying reactions with silicon. ToF-SIMS spectra analysis was used to help validate the effectiveness of thermal evaporation as a prelithiation method by identifying lithium-silicon and lithium-silicate alloys.

**Figure 2** shows the ToF-SIMS spectral results within mass range  $m/z^- 50 - 100$  of silicon-based composite electrodes exposed to an Ar/CO<sub>2</sub> environment after prelithiation (a), an inert Ar gas environment after prelithiation (b), and control electrode with no prelithiation (c). The strong presence of silicon and carbon-based compounds in the spectra plots verify the silicon-carbon electrode composition. **Figure 2** highlights spectral peak areas from  $m/z^- 50-100$  showing  $m/z^- 62.97 \text{ LiSi}_2^-$ ,  $m/z^- 66.98 \text{ LiSiO}_2^-$ , and  $m/z^- 82.98 \text{ LiSiO}_3^-$  peaks present in the samples. This mass range shows formation of Li<sub>x</sub>Si<sub>y</sub> alloys and Li<sub>x</sub>Si<sub>y</sub>O<sub>z</sub> phases.





**Figure 2.** ToF-SIMS mass spectra collected in negative ion mode within mass range  $m/z$  50-100 for prelithiated silicon electrodes housed in Ar + CO<sub>2</sub> environment (a), Ar environment (b), and no prelithiation silicon electrode control sample (c). This mass region shows identifications of LiSi<sub>2</sub><sup>-</sup>, LiSiO<sub>2</sub><sup>-</sup>, and LiSiO<sub>3</sub><sup>-</sup> peaks found in the prelithiated samples.

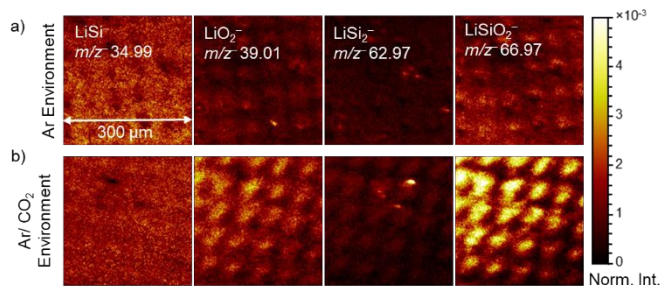
**Table 2.** Peak identification of the prelithiated anode exposed to Ar/CO<sub>2</sub> gas environment in the negative ion mode.

$m/z$ <sub>obs</sub>	$m/z$ <sub>theo</sub>	$\Delta M$ (ppm)	Species	Assignment	References
7.0166	7.0166	0.1463	Li <sup>-</sup>	Lithium	47
12.0007	12.0005	9.7492	C <sup>-</sup>	Carbon	47
27.9785	27.9775	37.0930	Si <sup>-</sup>	Silicon	48
34.9931	34.9935	11.1301	LiSi <sup>-</sup>	Li <sub>x</sub> Si <sub>y</sub> Alloy	This Work
50.9907	50.9884	46.1284	LiSiO <sup>-</sup>	Li <sub>x</sub> Si <sub>y</sub> O <sub>z</sub> Phase	This Work
62.9720	62.9704	25.4692	LiSi <sub>2</sub> <sup>-</sup>	Li <sub>x</sub> Si <sub>y</sub> Alloy	This Work
66.9891	66.9833	86.9175	LiSiO <sub>2</sub> <sup>-</sup>	Li <sub>x</sub> Si <sub>y</sub> O <sub>z</sub> Phase	This Work
78.9689	78.9653	45.9164	LiSi <sub>2</sub> O <sup>-</sup>	Li <sub>x</sub> Si <sub>y</sub> O <sub>z</sub> Phase	This Work
82.9836	82.9782	64.3833	LiSiO <sub>3</sub> <sup>-</sup>	Li <sub>x</sub> Si <sub>y</sub> O <sub>z</sub> Phase	This Work
90.9488	90.9473	16.2503	LiSi <sub>3</sub> <sup>-</sup>	Li <sub>x</sub> Si <sub>y</sub> Alloy	This Work
97.0165	97.0102	64.6421	Li <sub>3</sub> SiO <sub>3</sub> <sup>-</sup>	Li <sub>x</sub> Si <sub>y</sub> O <sub>z</sub> Phase	This Work
120.0143	120.0212	56.9265	Li <sub>4</sub> SiO <sub>4</sub> <sup>-</sup>	Li <sub>x</sub> Si <sub>y</sub> O <sub>z</sub> Phase	This Work

Note:  $m/z$  represents the mass-to-charge ratio for negatively charged ions. <sup>a</sup>  $m/z$ <sub>obs</sub> represents the observed mass to charge ratio. <sup>b</sup>  $m/z$ <sub>theo</sub> represents the theoretical mass to charge ratio. <sup>c</sup>  $\Delta M = 10^6 \times (m/z$ <sub>obs</sub> -  $m/z$ <sub>theo</sub>) /  $m/z$ <sub>theo</sub> (expressed in ppm).<sup>49</sup> Peak identification are possibilities identified by SurfaceSpectra software and cross-referenced to literature.

The control sample, **Figure 2c**, with no prelithiation has negligible or undetected Li<sup>-</sup>, LiSi<sub>2</sub><sup>-</sup>, LiSiO<sub>2</sub><sup>-</sup>, and LiSiO<sub>3</sub><sup>-</sup> peaks in the negative mode. Spectra comparison in the positive ion mode of Ar/CO<sub>2</sub> environment after prelithiation and no prelithiation samples is included in the **Figures S5-S7**. The prelithiation under Ar/CO<sub>2</sub> gas environment, **Figure 2a**, shows higher intensity values for Si<sub>x</sub>O<sub>y</sub><sup>-</sup>, Li<sub>x</sub>Si<sub>y</sub><sup>-</sup>, and Li<sub>x</sub>Si<sub>y</sub>O<sub>z</sub> compounds compared to prelithiation under Ar gas environment, **Figure 2b**. Species such as LiSi<sub>2</sub><sup>-</sup>, LiSiO<sub>2</sub><sup>-</sup>, and LiSiO<sub>3</sub><sup>-</sup> show intensity values of 90024, 270280, and 880891, respectively, for Ar/CO<sub>2</sub> environment which are increased from the same species observed in the inert Ar environment which show intensity values of 89156, 172770, and 312155 for LiSi<sub>2</sub><sup>-</sup>, LiSiO<sub>2</sub><sup>-</sup>, and

LiSiO<sub>3</sub><sup>-</sup> respectively. However, the formation of silicon carbide, SiC<sub>2</sub><sup>-</sup> has a higher intensity value, 1022745, in the Ar environment compared to the Ar/CO<sub>2</sub> environment intensity value of 428892. More counts of silicon carbide could indicate shallow lithium passivation into the electrode or reactivity of the Si and carbon within the electrode or the reaction with silicon during milling with propylene carbonate to form small domains of Si-C. Whereas the high intensities of the lithium-silicates and lower SiC<sub>2</sub><sup>-</sup> signal could indicate better conditions for lithium-silicate formation leading to higher stability electrodes. The lithium-silicon and lithium-silicate alloys observed within the ToF-SIMS spectra provide chemical information suggesting the penetration of lithium into the silicon electrode. Formation of Li<sub>x</sub>Si<sub>y</sub> alloys may correlate with Li evaporation thickness<sup>37</sup>.

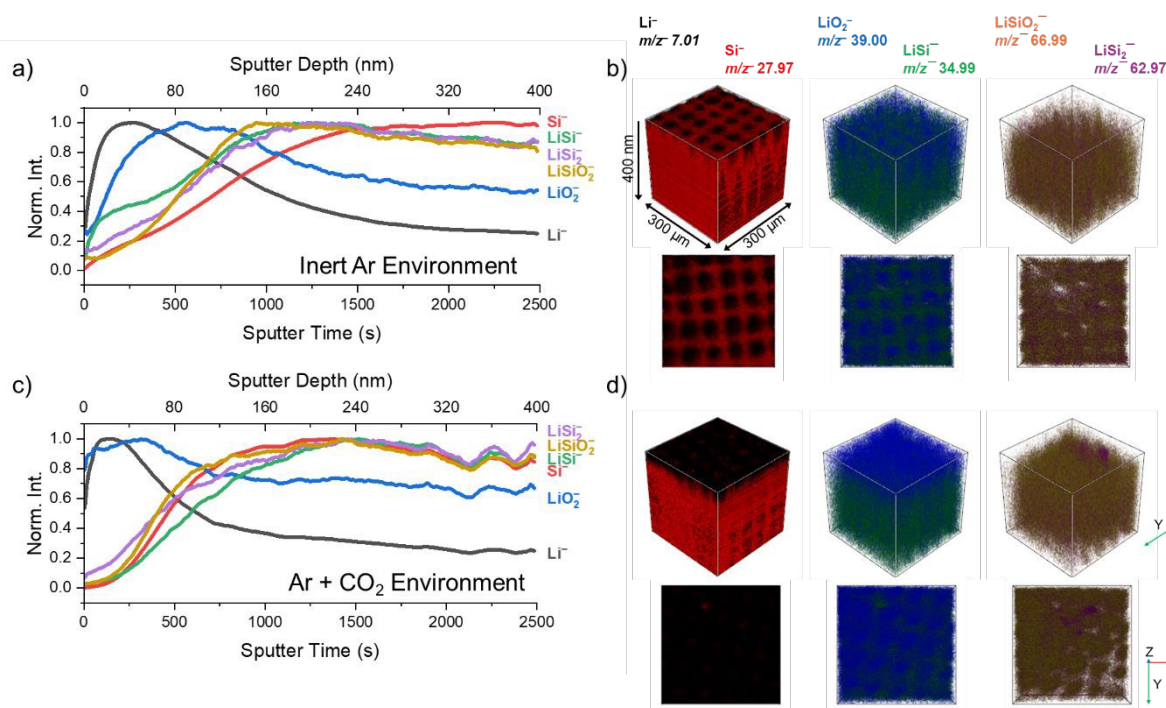


**Figure 3.** Normalized SIMS 2D images in the negative ion mode of prelithiated electrodes after exposure to inert Ar gas (a) and Ar/CO<sub>2</sub> gas (b). The analysis area was 300 µm x 300 µm.

The atmospheric conditions for sample preparation can provide influence over the chemical reaction formation of the Li<sub>x</sub>Si<sub>y</sub> and Li<sub>x</sub>Si<sub>y</sub>O<sub>z</sub>. CO<sub>2</sub> has been shown to have reaction combination properties influencing side reactions on anodes<sup>50-52</sup>. The increase in silicate (Si<sub>x</sub>O<sub>y</sub>) and lithium silicate (Li<sub>x</sub>Si<sub>y</sub>O<sub>z</sub>) formation in **Figure 2a** could be a direct result from the CO<sub>2</sub> in the environment. Silicate formation has been found previously on the surface of silicon anodes when introduced to a CO<sub>2</sub> environment leading to increasing reaction chemistry at the surface of the electrode when the lithium passivates the surface of the anode<sup>38, 53, 54</sup>. The presence of the lithium silicates in **Figure 2b** is an indicator of O<sub>2</sub> presence within the system contributing to the formation of Li<sub>x</sub>Si<sub>y</sub>O<sub>z</sub> products or residual oxides from the milling process or stripping O<sub>2</sub> from the CO<sub>2</sub>. Mitigation of oxygen presence is difficult to fully remove, but the ion intensity comparison shows that the CO<sub>2</sub> is a contributing factor in the increase in peak values observed in **Figure 2a**.

ToF-SIMS spectral plots showing mass range  $m/z$  0-100 can be found within the **Figure S4**. The small  $m/z$  7.01 Li<sup>-</sup> peaks confirm the occurrence of prelithiation as lithium is typically a positively charged ion however, identification of  $m/z$  7.01 Li<sup>-</sup> reflects large amounts of lithium within the sample allowing some lithium to have an electronegative charge. Additional positive ion mode spectra in **SI** provide evidence suggesting lithium penetration and formation of Li<sub>x</sub>Si alloy formation by utilization of the CsM<sup>+</sup> ionization method.<sup>55-57</sup>





**Figure 4.** ToF-SIMS depth profiles (a, c) and overlaying reconstructed 3D SIMS images (b, d) of the prelithiated electrode materials after exposure to an inert Ar gas environment (a, b) and an Ar/CO<sub>2</sub> gas environment (c, d) in the negative ion mode. Total sputtering depth was 400 nm. Sputtering done at 0.16 nm/s. The same colors are used for identified ions in the depth profiles and 3D images. 3D reconstructions were binned by 4 pixels in XY and 4 pixels in Z.

### Depth Profiling and 2D/3D Imaging Provide Insight into Favorable Conditions for Thermal Evaporation

ToF-SIMS molecular imaging reveals ‘island-like’ lithium deposition pattern actively occurred especially for electrodes placed in purely inert, Ar + CO<sub>2</sub> gas environments. **Figure 3** presents the negative ion mode surface images of four key ions of interest:  $m/z^-$  34.99 LiSi<sup>-</sup>,  $m/z^-$  39.01 LiO<sub>2</sub><sup>-</sup>,  $m/z^-$  62.97 LiSi<sub>2</sub><sup>-</sup>, and  $m/z^-$  66.97 LiSiO<sub>2</sub><sup>-</sup> for prelithiated electrodes after exposure to inert Ar gas (a) and Ar/CO<sub>2</sub> gas (b). **Figure 3** showcases a hatch pattern due to a steel mesh grid which was placed over the silicon electrode to protect the silicon anode in the analysis region. The lithium deposit areas are congregated in the mesh grid openings, thus producing ‘island-like’ deposit areas.

**Figure 3a** shows lithium silicon alloy (LiSi<sup>-</sup>/ LiSi<sub>2</sub><sup>-</sup>), lithium oxide (LiO<sub>2</sub><sup>-</sup>), and lithium silicate (LiSiO<sub>2</sub><sup>-</sup>) compound signals across the surface with specific negative regions observed. These negative regions correspond to trapped O<sub>2</sub><sup>-</sup> signal. A red, green, blue overlay showing the oxygen distribution can be found in the **Figure S8**. **Figure 3b** showcases the lithium deposition areas as more concentrated within the areas where the mesh grid was absent. The more intense pockets of LiO<sub>2</sub><sup>-</sup> and LiSiO<sub>2</sub><sup>-</sup> ion signals show the lithium depositing into the holes of the mesh as expected. The results suggest that the CO<sub>2</sub> gas may have helped concentrate the thermal evaporation of lithium. The lithium oxide and lithium silicate phase are more dominant likely due to reactions with the CO<sub>2</sub> gas. Images collected within the positive ion mode can be found in **Figure S9**

corroborating the aforementioned results observed within negative ion mode.

Depth profiles were used to examine the depth of lithium penetration into the silicon electrodes after thermal evaporation of lithium. Depth profiles and 3D reconstruction images of the analysis area for silicon electrodes in Ar/CO<sub>2</sub> and inert Ar environments are reported in **Figure 4**. Depth profiles in positive and negative mode of the no prelithiation silicon electrode control can be found in **Figure S10**. The depth profiles reached a total depth of 400 nm after a total sputter time of 2500 s indicating a sputtering rate of 0.16 nm/s for each sample. **Figure 4a** and **4c** present the depth profiles which highlight thermal evaporation’s ability to effectively disperse lithium throughout the electrodes as we can track molecules such as Li<sup>-</sup>, Si<sup>-</sup>, LiSi<sup>-</sup>, LiSi<sub>2</sub><sup>-</sup>, LiSiO<sub>2</sub><sup>-</sup>, LiO<sub>2</sub><sup>-</sup> etc.

**Figure 4a** corresponds to the prelithiated electrode material exposed to inert Ar gas environment, while **Figure 4c** corresponds to the prelithiated electrode material exposed to an Ar/CO<sub>2</sub> gas environment. Expectedly, the highest concentration of lithium is found on the surface of the electrodes. The increased intensities of both the Li<sup>-</sup> and LiO<sub>2</sub><sup>-</sup> depth profile lines in **Figure 4a** and **4c** followed by the slowly increasing growth of Si<sup>-</sup> intensities show that a layer of lithium forms atop the silicon electrodes where the steel mesh was placed, creating pockets. Despite the layer growth and steel mesh’s restricted areas of deposition the lithium is still dispersed throughout the electrodes as the depth profiling and 3D image data highlight. The formed lithium layer nor steel



mesh are restricting the lithium from randomly diffusing throughout the sample electrodes.

The Ar/CO<sub>2</sub> also has lithium spread laterally across the surface possibly due to CO<sub>2</sub> gas or surface alteration, after the mesh was removed prior to ToF-SIMS analysis. These pockets are observed when examining other ion species (i.e., Li<sub>2</sub>O). Our results substantiate the steel mesh as a beneficial addition to the thermal evaporation process as it reduces the electrodes' strain and volumetric expansion while still enabling effective prelithiation to occur. **Figure 4c and 4d** observe a high intensity in lithium signal followed by a steady decrease as well as a layer of lithium atop the surface for the prelithiated anode under Ar/CO<sub>2</sub> conditions. The point at which the Li<sup>-</sup>/Si<sup>-</sup> cross shows the depth at which the anode material becomes more prominent, observing the interface of the anode and the thermal evaporated lithium. Under Ar/CO<sub>2</sub> conditions, this interface section arrives at 82.4 nm in depth whereas the interface for the inert Ar conditions occurs at 140 nm in depth. However, the lithium overall depletes similar under both conditions. Chemical reaction under Ar/CO<sub>2</sub> conditions allows the formation of lithium silicon (Li<sub>x</sub>Si<sub>y</sub>) and lithium silicate (Li<sub>x</sub>Si<sub>y</sub>O<sub>z</sub>) to form closer to the surface and remain at high intensity levels throughout the sample. Formation of Li<sub>x</sub>Si<sub>y</sub> and Li<sub>x</sub>Si<sub>y</sub>O<sub>z</sub> species closer to the surface can potentially help H<sub>2</sub> storage.<sup>58</sup>

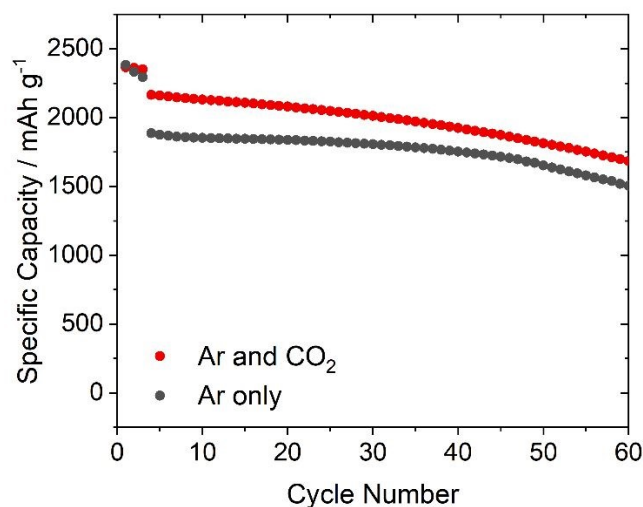
Visualization of the lithium incorporation into the silicon electrode material after prelithiation is made possible by 3D reconstruction as provided by **Figure 4b**, inert Ar gas environment, and **Figure 4d**, Ar/CO<sub>2</sub> gas environment. Both **Figure 4b** and **4d** provide visual evidence of dense distributions of Li<sub>x</sub>Si<sub>y</sub> and Li<sub>x</sub>Si<sub>y</sub>O<sub>z</sub> molecular signals. We observed specific channels of lithium penetration, as shown by Li<sup>-</sup> in black and LiSi<sup>-</sup> shown in green, where the lithium stayed within the path designated by the mesh grid. We also show that the LiO<sub>2</sub><sup>-</sup> distribution was more significant for the inert Ar/CO<sub>2</sub> gas environment versus the LiO<sub>2</sub><sup>-</sup> for the Ar gas environment leaving a uniform layer at the top of the material. This is likely due to lithium readily reacting with the environment to form an oxide layer. The oxide layer stayed mostly at the surface according to the depth profile and reconstructed 3D images as shown in **Figure 4c** and **4d**. LiSi<sub>2</sub><sup>-</sup> is a likely fragment from a larger Li<sub>x</sub>Si<sub>y</sub> molecule. Positive mode depth profiles and 3D images of the inert Ar gas environment and an Ar/CO<sub>2</sub> gas environment can be found in **Figure S11**.

#### Lithium Silicate Tends to Form Over Lithium Silicon Alloys

Although ToF-SIMS is not used to precisely quantify the degrees to which certain compounds form, our results suggest that both Li<sub>x</sub>Si<sub>y</sub> alloy and Li<sub>x</sub>Si<sub>y</sub>O<sub>z</sub> silicate compounds form in more readily under Ar/CO<sub>2</sub> conditions. **Figure 4** highlights LiO<sub>2</sub><sup>-</sup> and LiSiO<sub>2</sub><sup>-</sup>

having greater surface presence in the Ar/CO<sub>2</sub> environment most likely stemming from the presence of the CO<sub>2</sub> decomposing into carbon and oxygen compounds. Each passivation environment shows similar intensities for LiSi<sup>-</sup> and LiSi<sub>2</sub><sup>-</sup> throughout the samples. The stronger presence of Li<sub>x</sub>Si<sub>y</sub>O<sub>z</sub> silicates is further substantiated by the identification of compounds such as Li<sub>3</sub>SiO<sub>3</sub><sup>+</sup>, LiSiO<sup>+</sup>, and Li<sub>3</sub>SiO<sub>2</sub><sup>+</sup> compared to LiSi<sup>+</sup> and Li<sub>2</sub>Si<sup>+</sup> seen in the positive mode depth profiles (**Figure S11**) for the same samples. The greater number of silicate compounds existing at larger or similar intensities to the alloying compounds in **Figure 4b** and **4d** visually show how densely the most prominent silicate and alloy compounds form throughout the depth profiles. The ΔM mass deviation values for our Li<sub>x</sub>Si<sub>y</sub> alloys and Li<sub>x</sub>Si<sub>y</sub>O<sub>z</sub> silicates range up to ± 87 ppm for the negative mode (**Table 1 & 2**) and ± 68 ppm for the positive mode (**Table S4 and S5**). These deviation values along with many of these compounds not being found in the non-prelithiated samples suggest our peak identification is reliable.

Two recent studies found that forming Li<sub>x</sub>Si<sub>y</sub>O<sub>z</sub> silicates contributed to improved capacity retention and ICE in prelithiated silicon electrodes<sup>33, 34</sup>. Both Bai *et al*<sup>33</sup> and Bhat *et al*<sup>34</sup> analyzed prelithiated silicon electrodes after cycling. According to Bhat *et al*, having a prelithiation process tailored to only producing Li<sub>x</sub>Si<sub>y</sub>O<sub>z</sub> silicates in an SiO electrode created electrodes with a high ICE value and capacity retention after 200 cycles. Bhat *et al* highlights that, between the formed silicates, Li<sub>2</sub>SiO<sub>3</sub> and Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> are the most ideal silicates to see under moderate prelithiation amounts. They suggest Li<sub>4</sub>SiO<sub>4</sub> is a possible sign of over prelithiation. Bai *et al* found that prelithiated silicon electrodes which grow an SEI layer consisting of Li<sub>2</sub>SiO<sub>3</sub>, Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>, and Li<sub>4</sub>SiO<sub>4</sub> are more stable and conductive compared to non prelithiated silicon electrodes that normally form Li<sub>2</sub>CO<sub>3</sub> and LiF SEI compounds after cycling. Although our ToF-SIMS results did not find Li<sub>2</sub>CO<sub>3</sub> or Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> compounds in our uncycled samples, our samples may form these desirable silicates under cycling. Our analyses suggest thermal evaporation may be effective in producing stable electrodes.



**Figure 5.** Anode cycling versus specific capacity for Ar/CO<sub>2</sub> anode and Ar only anode, indicating a 14.8% increase in specific capacity observed when cycling after solid-electrolyte interphase formation.

The silicon for the anode is prepared by milling with propylene carbonate to functionalize the surface. During the milling process, the Si breaks down and forms Si-C bonds at the surface. This covalent bonding is likely the reason behind the SiC observation.<sup>59</sup> The increase in SiC<sub>2</sub><sup>-</sup> peak observed for the Ar environment and No-prelithiation environment in **Figure 2** is due to the lack of Li<sub>x</sub>Si<sub>y</sub> and Li<sub>x</sub>Si<sub>y</sub>O<sub>z</sub> formation. The Ar/CO<sub>2</sub> environment sample has these molecules closer to the surface, potentially reducing the amount of ionizable SiC at the surface. Additional evidence is depicted in **Figure 4**. Li<sub>x</sub>Si<sub>y</sub> and Li<sub>x</sub>Si<sub>y</sub>O<sub>z</sub> molecules are detected at approximately 80 nm in the Ar/CO<sub>2</sub> environment depth profiles compared to 140 nm in those of the inert Ar environment. Formation of the Li<sub>x</sub>Si<sub>y</sub> and Li<sub>x</sub>Si<sub>y</sub>O<sub>z</sub> molecules closer to the surface may have impact on the cycling stability and specific capacity of the anodes.

**Figure 5** shows the specific capacity comparison after cycling for Ar/CO<sub>2</sub> and Ar only anode. The result reveals a 14.8 % increase in specific capacity when cycling after SEI formation. This is possibly due to the fact that available lithium reacts with surface molecules before cycling of the Ar-only anode. In contrast, CO<sub>2</sub> may passivate lithium, allowing for the formation of the Li<sub>x</sub>Si<sub>y</sub> and Li<sub>x</sub>Si<sub>y</sub>O<sub>z</sub> molecules. When preparing these anodes, CAMP Si (2.0 mAh cm<sup>-2</sup>) was paired with NMC 811 to give a N/P of 0.8. The electrolyte was GenF3 and separator was Celgard 2325.<sup>60</sup> Cycling was done at a C/20 rate for 3 cycles to enable SEI formation before subsequent C/3 cycling. Identification of the Li<sub>x</sub>Si<sub>y</sub> and Li<sub>x</sub>Si<sub>y</sub>O<sub>z</sub> molecules closer to the surface and the higher specific capacity observed for the Ar/CO<sub>2</sub> anode provide strong evidence for a more stable Si anode.

## Conclusions

Through ToF-SIMS analysis and particularly its visual recreations, thermal evaporation was shown to uniformly prelithiate samples with a steel mesh confining the lithium deposition to ‘pockets.’ The prelithiated samples had strong lithium presence throughout their depth profiles and visually showed homogeneous dispersions of interphase Li<sub>x</sub>Si<sub>y</sub> and Li<sub>x</sub>Si<sub>y</sub>O<sub>z</sub> compounds. Restricting prelithiation to specific channels still allows uniform distributions of lithium while alleviating the electrodes’ volumetric expansion from prelithiation. Our results suggest that future thermal evaporation prelithiating process should incorporate steel meshes or similar confining tools to mitigate the volumetric expansion. Our results also suggest that Ar/CO<sub>2</sub> environment may have helped create a prosperous environment for Li<sub>x</sub>Si<sub>y</sub> alloy formation. Further experiments are necessary to determine which other gas environments could provide beneficial results.

ToF-SIMS proves to be an effective characterization tool for studying prelithiation dynamics. Our ToF-SIMS results provided a unique angle for evaluating the viability of prelithiation via thermal evaporation. Our 2D images were able to spatially

resolve specific features like the ‘pockets’ where prelithiation occurred and where silicon was less impacted under the grids. We also identified the formation of various Li<sub>x</sub>Si<sub>y</sub>O<sub>z</sub> silicates and Li<sub>x</sub>Si<sub>y</sub> alloy compounds and found that the electrodes contained likely higher concentrations of Li<sub>x</sub>Si<sub>y</sub>O<sub>z</sub> silicates overall. Since these silicates are preferable for forming more stable solid electrolyte interphase, our results suggest that thermal evaporation could be an effective prelithiation method for silicon anodes. The passivation depths are comparable between each environment. However, the depth profiling data suggests that the Ar/CO<sub>2</sub> passivation forms alloy and oxide phases closer to the surface and increases the abundance of Li<sub>x</sub>Si<sub>y</sub> alloy and Li<sub>x</sub>Si<sub>y</sub>O<sub>z</sub> phase, which creates a more stable anode. Additional ToF-SIMS studies should be done on cycled electrodes to analyze the performance, SEI layer composition, and electrode composition after cycling. Better understandings of ideal prelithiation levels, alloy concentrations, and silicate concentrations would help guide process modifications.

## Author contributions

G.D.P. provided data curation, formal analysis, investigation, methodology, validation, visualization, writing – original draft preparation, and writing – review and editing; I.M. provided formal analysis, visualization, writing – original draft preparation; A.L.M. provided conceptualization, methodology, resources, writing – review and editing; G.M.V. provided conceptualization, project administration, resources, writing – review and editing; X.Y.Y. provided conceptualization, funding acquisition, investigation, project administration, resources, software, supervision, validation, writing – review and editing.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The authors declare that the data supporting the findings of this study are available within the paper and its supporting information. Should any raw data files be needed in another format they are available from the corresponding author upon reasonable request.

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# Mass Spectral Molecular Mapping Shows Benefits of Thermal Evaporation in Prelithiated Silicon-Based Electrodes

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## Data availability

The authors declare that the data supporting the findings of this study are available within the paper and its supporting information. Should any raw data files be needed in another format they are available from the corresponding author upon reasonable request.

