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# DFT study of lithium adsorption on silicon quantum dots for battery applications

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# ABSTRACT

Understanding lithium (Li) adsorption in silicon quantum dots (SiQDs) is crucial for optimizing Li-ion battery (LIB) anode materials. We systematically investigated Li adsorption in ten hydrogenated SiODs ( $Si_{10}H_{16}$ ,  $Si_{14}H_{20}$ , Si<sub>18</sub>H<sub>24</sub>, Si<sub>22</sub>H<sub>28</sub>, Si<sub>26</sub>H<sub>30</sub>, Si<sub>30</sub>H<sub>34</sub>, Si<sub>35</sub>H<sub>36</sub>, Si<sub>39</sub>H<sub>40</sub>, Si<sub>44</sub>H<sub>42</sub>, and Si<sub>48</sub>H<sub>46</sub>) across five adsorption sites (bridge(B), on-top(T), hollow-tetrahedral inner(Td<sub>inner</sub>), hollow-tetrahedral surface(Td<sub>surface</sub>), and hollow-hexagonal(Hex)), utilizing density functional theory (DFT) with the M06-2X hybrid functional and 6-31G+(d) basis set. Findings identify Td<sub>inner</sub> as the most favorable adsorption site, with a binding energy (E<sub>bind</sub>) of 0.80–1.00 eV, dependent on SiQD size. The adsorption site exerts a more pronounced impact on E<sub>bind</sub> than the cluster size. Multiple adsorptions in SiQDs show increased Ebind per Li atom with Li atom number. Molecular volume changes, independent of Li atom number but site-dependent, exhibit a maximum of 2.51 %. SiQD energy gap, influencing conductivity, varies with size, larger SiQDs being more conductive, especially with Li adsorption. Conclusively, our study recommends large-sized SiQDs as optimal LIB anode materials, offering high capacity, minimal volume expansion, and reasonable conductivity. This research addresses a theoretical gap, illuminating the impact of Li adsorption on SiQD molecular volumes and electronic structures, aiding in the design of enhanced capacity silicon anodes for LIB.

## 1. Introduction

Lithium-ion (Li-ion) batteries (LIB) are the most mature battery technology due to their long cycle life, high energy, and power density, which can be found in several applications such as cameras, mobile phones, laptops, electric vehicles, etc. Current research on LIB has been aimed at their applications in electric vehicles which required high capacities of batteries (>200 mAhg $^{-1}$ ) [1–3]. Beyond advancements in Li-ion technology, the landscape of energy storage is undergoing a transformative phase with the exploration of post-LIB technologies. Innovations such as aluminum-ion, potassium-ion, calcium-ion, sodium-ion, and zinc-ion batteries are poised to revolutionize the field, offering unique advantages and addressing challenges associated with conventional LIBs [4-6]. Traditionally, the most commercialized LIB uses graphite-based anodes that have theoretical capacities of 372 mAhg<sup>-1</sup>. The silicon (Si)-based electrode which has a high theoretical capacity of 4200 mAhg<sup>-1</sup> —approximately ten times greater than their graphite counterparts, has been suggested for the anode of LIB. Besides, Si is environmental-friendly, non-toxic, low-cost, and most importantly the second most abundant element in the earth's crust [7–9]. However, there are still several challenges for Si anodes such as the change of volume during intercalation, low electronic conductivity, and slow Li diffusion [10]. Controlling the geometrical structure on the nanoscale with a variety of structures such as nanoparticles, nanowires, nanotubes, nanosheets, and nanopores might be one of the solutions for Si anodes. Since these structures provide large surface area, short diffusion length, and fast diffusion rate [11-13].

Silicon Quantum Dot (SiQD) is a Si nanocluster ranging from 1 to 10 nm in size which holds great applicative potential as nanoscale electronic and optical devices. SiQD is also a low-toxic material exhibiting considerable potential for various biological applications, particularly in bioimaging [14-16]. Reducing the size of Si nanomaterials to the quantum dots scale can significantly increase electrochemical performance. SiQDs also offer short Li diffusion distances which improve rates

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and cycling performances of the battery. Aghajamali et al. [17] observed the electrochemical properties of several nanocomposites of Si crystal with different sizes, i.e. 3, 5, 8, and 15 nm. They reported that the cycling stability of annealed Si nanocrystal composites can be increased significantly when decreasing the size from 15 to 3 nm due to the stress/strain tolerance. Choi et al. [18] proposed  $\pi$ -conjugated molecule bridge SiQDs cluster as an anode material. The electrochemical performance of this material can be enhanced by modifying the organic structures and introducing different functional groups. Using density functional theory (DFT), Xu et al. [19] suggested Si<sub>10</sub>H<sub>16</sub>, Si<sub>14</sub>H<sub>20</sub>,  $Si_{18}H_{24},\,Si_{22}H_{28},\,Si_{26}H_{30},\,Si_{30}H_{34},\,Si_{35}H_{36},\,Si_{39}H_{40},\,Si_{44}H_{42},\,\text{and}\,\,Si_{48}H_{46}$ for stable structures of SiQDs. These ten structures of SiQDs can represent stable Si nanostructures. Using the ten structures, Li et al. [20] investigated the effect of size on the electronic properties of SiQDs. They found the decrement of the HOMO-LUMO energy gap of SiQDs with the increment in the number of Si atoms.

The adsorption of Li atom/ion on the anode material is a key process for charging/discharging in LIB. Harismah et al. [21] and also Pattarapongdilok and Parasuk [22] in their studies investigated the adsorption of Li atom/ion on graphene quantum dots (GQDs). Both parties agreed that the Li atom/ion prefers to adsorb on the center of the hexagonal carbon ring of the GODs (hollow site). Zheng et al. [23] who studied the Li insertion and adsorption on the graphene sheets also reported that Li favors to be adsorbed on the center of the carbon ring, and there are charge transfers from Li to the graphene surface. Wan et al. [24], carried out DFT calculations using the generalized gradient approximation (GGA) functional with projector augmented wave (PAW) pseudo-potentials and plane wave basis set to study Li insertion in bulk Si and found two main adsorption sites, tetrahedral and hexagonal. Zhang et al. [25] investigated single Li atom insertion in various silicon nanowires (SiNWs) with different diameters, growth directions, and adsorption sites (surface, intermediate, and core). They concluded that the E<sub>bind</sub> of Li increases as the diameter grows. The adsorption at the surface site has the highest  $E_{\mbox{bind}}$  while the binding at the intermediate site, the region between the surface and core site, is the lowest. Tritsaris et al. [26,27] studied the diffusion of Li in bulk amorphous Si and a layered Si (silicene) surface. They reported that in bulk amorphous Si,

the energy barrier for diffusion is one factor that controls the diffusion process. For the layered Si, a smaller structural change during lithiation and delithiation and a lower volume change (<25 %) were observed when compared with crystalline Si. Xu et al. [28] investigated the adsorption of Li on single-layer silicene. They noticed that the adsorption in the hollow site is the most stable and van der Waals interaction does not play a crucial role unlike that on the single-layer graphene. Gonzalez et al. [29] carried out the DFT calculations to investigate the effect of Li insertion on the electronic properties of porous Si (pSi). They showed that the presence of Li alters the electronic structure of pSi. Also, they suggested three models of adsorption sites for Li in pSi, i.e. tetrahedral-inner, hexagonal, and tetrahedral-surfaces which is the most stable state.

Addressing a crucial gap in theoretical exploration, this project aims to investigate Li adsorption on SiQDs in LIB anodes. We hypothesize that the adsorption site and Li quantity significantly impact the binding energy (E<sub>bind</sub>) between Li and SiQDs, with expectations of a proportional decrease in SiQD molecular volume as size increases. Employing DFT calculations on ten SiQD models, our novel study explores Li adsorption intricacies and its effects on molecular volumes and electronic structures. Unprecedented in prior theoretical investigations, our work provides valuable insights for designing superior Si anodes in LIB, enhancing capacity and cycle life.

# 2. Computational details

Ten models of SiQDs:  $Si_{10}H_{16}$ ,  $Si_{14}H_{20}$ ,  $Si_{18}H_{24}$ ,  $Si_{22}H_{28}$ ,  $Si_{26}H_{30}$ ,  $Si_{30}H_{34}$ ,  $Si_{35}H_{36}$ ,  $Si_{39}H_{40}$ ,  $Si_{44}H_{42}$ , and  $Si_{48}H_{46}$  which were adopted from Xu et al. [19] and Li et al. [10] were used in this study, Fig. 1. Three types of adsorption sites, i.e., bridge (B), on-top (T), and hollow were investigated. Especially for the hollow site, we followed previous suggestions by Gonzalez et al. [29] who classified hollow/interstitial sites as hollow-tetrahedral-inner (Td<sub>inner</sub>), hollow-tetrahedral-surface (Td<sub>surface</sub>) and hollow-hexagonal (Hex). Illustrations for adsorption sites were displayed in Fig. 2. In addition, apart from single Li atom adsorption double and triple adsorptions by Li atoms were also considered. All calculations were performed based on the DFT with M06–2X hybrid



Fig. 1. Ten models of SiQDs.



Fig. 2. Three adsorption sites, (a) bridge, (b) on-top, and hollow: (c) Td<sub>inner</sub> (d) Td<sub>surface</sub>, and (e) Hex.

functional and 6-31G+(d) basis set using the Gaussian16 software program [30].

DFT is a foundational methodology in our exploration of battery materials, providing insights into diverse battery systems, encompassing structural stability, reaction voltage, capacity prediction, electronic structures, and adsorption kinetics [31]. The selection of the M06-2X functional level for investigating Li adsorption on GQDs is validated through comparisons with MP2 and CCSD(T) methodologies [32]. The M06-2X method, distinguished for excellence in main-group thermochemistry, kinetics, and noncovalent interactions, is chosen based on Truhlar's endorsement [33]. The 6-31G+(d) basis set, renowned for its adaptability, incorporates crucial diffuse functions for studying Li adsorption on SiQDs and related computations involving the adsorption of the tetrachloroaluminate ion on GQDs [6]. In solvent considerations, Yang-Xin Yu's 2018 study using DFT calculations found minimal impact on Li adsorption with solvents like 1,2-dimethoxyethane (DME), acetonitrile (ACE), and dimethyl sulfoxide (DMSO) [34]. However, our gas-phase calculations exclude solvent effects.

## 3. Results and discussion

# 3.1. Binding of Li to SiQDs

We performed geometry optimization for Li adsorption in the bridge (B), on-top (T), and hollow (Td<sub>inner</sub>, Td<sub>surface</sub>, and Hex) sites for ten SiQD structures. The  $E_{bind}$  was calculated according to:

 $E_{bind} = E_{Li} + E_{SiQDs} - E_{Li-SiQDs}$ 

After geometry optimization, 43 adsorption complexes were obtained. The complexes were classified according to the adsorption sites listed in Table S1. Together in the Table, their  $E_{binds}$  were reported. The

43 adsorption complexes are comprised of  $10 \text{ Td}_{inner}$ ,  $10 \text{ Td}_{surface}$ , 9 Hex, 7 B, and 7 T. Comparing between hollow, bridge, and on-top sites, the adsorption at the hollow sites gives the stronger binding for the same SiQD in agreement with previous studies [24,25]. Therefore, we focused our results on the hollow sites.

 $E_{binds}$  of single Li adsorption in the hollow site of SiQDs are between  $-0.57\,$  and  $+1.00\,$  eV as shown in Table 1 and Fig. 3. The adsorption energy above 0.5 eV was categorized as "strong" interaction, while those between 0.2 and 0.5 eV as "weak" interaction. Those with negative values were classified as "unstable" binding, meaning the system becomes less stable after the Li insertion. Thus, it is unlikely for Li to adsorb in that site. From Fig. 3, the adsorption of Li on Td<sub>inner</sub> is above 0.75 eV and that on Td<sub>surface</sub> is lower than 0.5 eV but remains positive for all SiQDs. While for the same SiQDs, the adsorption in Hex has negative binding. It could be concluded that the Td<sub>inner</sub> site gives strong

Table 1	
Binding energy of single and multiple Li adsorption on SiQDs.	

Si number	E <sub>bind</sub> (eV)				
	Li- Td <sub>inner</sub>	Li-Hex	Li-Td <sub>surface</sub>		
			Li	2Li	3Li
Si10H16	0.95	-	0.22	0.65	0.74
Si14H20	1.00	-0.57	0.22	0.65	0.98
Si <sub>18</sub> H <sub>24,</sub>	0.81	-0.51	0.26	0.65	0.78
Si22H28	0.83	-0.47	0.26	0.65	0.78
Si <sub>26</sub> H <sub>30</sub>	0.81	-0.44	0.25	0.60	0.97
Si <sub>30</sub> H <sub>34,</sub>	0.80	-0.40	0.26	0.62	0.72
Si35H36	0.86	-0.41	0.28	0.61	1.05
Si39H40	0.97	-0.42	0.18	0.62	1.12
Si44H42	0.89	-0.33	0.30	0.61	1.11
Si <sub>48</sub> H <sub>46</sub>	0.90	-0.35	0.23	0.61	1.07



Fig. 3. Binding energy of single Li adsorption for three adsorption sites:  $Td_{inner}$ ,  $Td_{surface}$ , and Hex.

adsorption, while Li,  $Td_{surface}$ , and Hex give weak and unstable adsorption, respectively. Thus,  $Td_{inner}$  is the most preferred adsorption site for Li in all SiQDs. Another interesting note is that the  $E_{bind}$  of Li to SiQDs varies with the adsorption position, but not with the cluster size.

We are also interested in multiple adsorptions of Li on SiQDs. Since this property reflects the charge density or capacity of SiQDs which tells how much charge can be stored in the battery. The double (2Li) and triple (3Li) adsorptions of Li were studied by adding second and third Li atoms to the single Li adsorption complexes and performing geometry optimization. Only adsorptions in the  $Td_{surface}$  site were reported here for the multiple adsorptions. Because only the adsorption in this site was obtained after geometry optimization.  $E_{binds}$  for double and triple adsorptions of Li were then compared to the corresponding single Li adsorptions. For comparison, the  $E_{bind}$  per Li atom was calculated according to:

$$E_{bind} = \frac{nE_{Li} + E_{SiQDs} - E_{total}}{n_{Li}}$$

Ebinds for double and triple Li adsorptions of various SiQDs were given in Table 1. The double Li adsorption has Ebinds around 0.60 eV, while they are between 0.72 and 1.11 eV for the triple Li adsorption. Thus, the Ebind increases when more Li atoms are adsorbed on SiQDs. Hence, multiple Li adsorptions increase the structures' Ebind and stability. The highest E<sub>bind</sub> was found for the triple Li adsorption in Si<sub>39</sub>H<sub>40</sub>, Si44H42, and Si48H46. Pattarapongdilok and Parasuk [12] studied the multiple adsorptions of Li in GQDs, They reported that the binding of Li atom to GQDs become weaker as more Li atoms are added. Also, the study of Hu and Zhou [35] revealed that the average E<sub>bind</sub> for multiple adsorptions on GQDs is smaller than that of single Li atom adsorption. Our study suggested that as an anode material SiQDs can provide a higher charge density as compared to the graphene-based anode. For single Li adsorption, the Td<sub>inner</sub> site is the most preferred. However, the Td<sub>surface</sub> site becomes more advantageous when more Li atoms are deposited. Since our largest Si cluster is composed of 48 Si atoms only, which might not have enough space to accommodate a lot of Li atoms inside. Thus, Li prefers to adsorb on the surface (outside) in case of multiple adsorptions. It is possible that the very large SiQD could comfort more Li atoms inside the cluster and the  $\mathrm{Td}_{\mathrm{inner}}$  site would be favored.

In our study, we focused on investigating the adsorption behavior of Li atoms on SiQDs used in LIB anodes. The primary objective was to analyze the influence of adsorption sites and the number of Li atoms on the E<sub>bind</sub> between Li and SiQDs, as well as their molecular volumes and electronic structures. While our study primarily delves into adsorption phenomena, it is essential to acknowledge that the overall behavior in a real LIB system can be complex. Both adsorption and intercalation mechanisms can contribute to the overall performance of the anode. The role of the electrolyte is crucial in determining the predominant mechanism, as it influences the interaction between Li ions and the SiQD anode. In the real LIB, the choice of electrolyte, solvent properties, and the nature of Li salt can significantly impact the interfacial processes. Adsorption and intercalation processes are not mutually exclusive, and their relative contributions may vary based on the specific conditions of the battery system. Further studies and experimentation specifically addressing these aspects are warranted to comprehensively elucidate the interplay between adsorption, intercalation, and the influence of the electrolyte in practical LIB.

## 3.2. Effect of Li adsorption on the volume of SiQDs

The adsorption of Li on the anode material could induce volume expansion which affects the performance and cycle life of the batteries, which is the challenge for the Si anode. To see whether there is volume expansion after Li adsorption, we monitored the molecular volume of SiQDs before and after lithiation. Molecular volumes (van der Waals volume) for ten bare SiQDs (Si<sub>10</sub>H<sub>16</sub>, Si<sub>14</sub>H<sub>20</sub>, Si<sub>18</sub>H<sub>24</sub>, Si<sub>22</sub>H<sub>28</sub>, Si<sub>26</sub>H<sub>30</sub>, Si<sub>30</sub>H<sub>34</sub>, Si<sub>35</sub>H<sub>36</sub>, Si<sub>39</sub>H<sub>40</sub>, Si<sub>44</sub>H<sub>42</sub>, and Si<sub>48</sub>H<sub>46</sub>) and those with Li adsorption at three sites, i.e., Td<sub>inner</sub>, Hex, and Td<sub>surface</sub> were calculated. The percentage change in molecular volume ( $\Delta MV$ ) was used to justify the volume change of SiQDs after Li adsorption. This value was evaluated according to:

$$\Delta MV = \frac{[MV_{Li-SiQD} - MV_{SiQD}]}{MV_{SiQD}} \times 100$$

The percentage change in molecular volume after Li adsorption of various SiQDs were shown in Fig. 4. For single Li adsorption, we observed the percentage change in molecular volume of SiQDs between 0.42 and 2.15 % for the adsorption in Td<sub>inner</sub> and Hex sites. However, much smaller changes were noticed for the adsorption in the Td<sub>surface</sub> site, in which percentage changes in the volume of SiQDs between 0 and 0.29 % were reported. Interestingly, the percentage change in volume does not vary with the number of Li adsorption for this site. For the Li adsorptions in Td<sub>inner</sub> and Hex, the percentage was observed for the size of SiQD, and the larger volume change was observed for the



Fig. 4. The percentage change in molecular volume of SiQDs after Li adsorption.

smaller sized SiQDs, 2.15 % for Si<sub>10</sub>H<sub>16</sub> and 0.42 % for Si<sub>48</sub>H<sub>46</sub>. Thus, the adsorption in Td<sub>surface</sub> causes less volume change than those on Td<sub>inner</sub> and Hex. This observation could be explained. The Td<sub>inner</sub> and Hex sites are inside the SiQD cluster. Li atoms would require space to be included inside the cluster and that causes the expansion of the molecular framework. There is a larger space inside for the larger cluster. Thus, there would be less volume expansion for the adsorption in the large cluster. For Td<sub>surface</sub>, the adsorption takes place outside and has a very limited effect on the molecular framework. Therefore, a very small volume expansion was observed, and this expansion does not depend on the cluster size and the number of Li adsorptions.

Therefore, we recommended large-sized SiQDs for anode materials of LIB. Since the integrity of their structures can be maintained upon Li deposition (no significant volume change should be realized).

### 3.3. Effect of Li adsorption on the energy gap

One of the disadvantages of Si anode is the electrical conductivity of the material as compared to the carbon-based anode. By nature, Si crystal is a semi-conductor with a band gap of around 1.2 eV [36] whereas graphite is a conductor. The band gap is normally used as a measure of the conductivity of the material. For non-periodic system, the energy difference between the highest occupied molecular orbital ( $E_{HOMO}$ ) and lowest unoccupied molecular orbital ( $E_{LUMO}$ ) is used to estimate the energy gap ( $E_g$ ), which addresses the conductivity for this kind of material instead of the band gap.

Energy gaps of un-adsorbed and Li-adsorbed SiQDs were displayed in Fig. 5 (see also in Table S2). The un-adsorbed SiQDs have an Eg between 5.95 (Si<sub>48</sub>H<sub>46</sub>) and 8.09 (Si<sub>10</sub>H<sub>16</sub>) eV and the  $E_g$  varies with the cluster size, where the larger SiQDs have a smaller Eg. One should notice the difference for Eg of 2.34 eV between the smallest and the largest values. After Li adsorption, the Eg is greatly reduced as shown in Fig. 5. In other words, SiQDs becomes more conductive after the Li adsorption. For single Li adsorption, the  $E_g$  was found between 2.33 and 4.12 eV. Thus, a reduction of around 4 eV was observed. For Li-adsorbed SiQDs, in addition to cluster size, the Eg also depends on adsorption sites as well as the number of adsorbed Li atoms. However, differentiation of the energy gap between various adsorption sites and between the number of Li adsorptions are not as significant. Comparing different adsorption sites, SiQDs with Li adsorption on Tdinner have the largest Eg followed by Td<sub>surface</sub> and Hex, respectively. For the adsorption in Td<sub>surface</sub>, the double Li adsorption increases  $E_g$  of SiQDs from 0.05 to 0.35 eV depending on the cluster size, while the triple Li adsorption causes the reduction of Eg



Fig. 5. Energy gaps of various sizes of un-adsorbed and nLi-adsorbed SiQDs.

for small SiQDs (n = 10–30) from -0.66 to -0.11 eV and the increment for medium to large SiQDs (n = 34–46) from 0.48 to 1.03 eV. Thus, the Li adsorption whether single or multiple affects  $E_g$ . This phenomenon proves that SiQDs as semiconductor materials have the capability to accept and release electrons, which is in line with previous studies [24, 25].

To understand how the Li adsorption affects the electronic structure of SiQD, we monitored HOMO and LUMO energies of un-adsorbed and Li-adsorbed SiQDs and displayed in Fig. 6. The Fig. 6a showed energies of HOMO and LUMO of un-adsorbed and Li-adsorbed SiQDs in various sites. The Fig. 6b demonstrated the effect of single, double, and triple Li adsorption on HOMO and LUMO energies of SiQDs.

From Fig. 6, while LUMO energies are unaffected by Li adsorption, HOMO energies of Li-adsorbed SiQDs significantly increase by the adsorption. As a result, the energy gap decreases with Li adsorption. Thus, the drastic reduction of the energy gap is the result of the increment of HOMO energies with the adsorption. HOMO energies for unadsorbed SiQDs are between -10 and -7.5 eV, while those for Liabsorbed SiQDs are around -5 eV. The HOMO energy for the Li atom is -4.16 eV. Thus, the increment of HOMO energies is probably due to the charge transfer from Li to SiQD. The increase in HOMO energies is site- but not size-dependent. It changes the most for Td<sub>surface</sub> and Hex, and to a lesser extent for Td<sub>inner</sub>. From Fig. 6b, the adsorption of 2nd and 3rd Li atoms does not vary the HOMO energy greatly. Therefore, multiple adsorptions should not affect the energy gap of Li-adsorbed SiQDs. Thus, from our study, we can conclude that large-sized SiQDs are good anode materials for LIB due to their high Li adsorption capacity and less volume expansion with reasonable conductivity.

#### 4. Conclusions

We have investigated Li adsorptions in ten hydrogenated SiQDs: Si10H16, Si14H20, Si18H24, Si22H28, Si26H30, Si30H34, Si35H36, Si39H40, Si<sub>44</sub>H<sub>42</sub>, and Si<sub>48</sub>H<sub>46</sub>, as well as their structural and electronic properties. For Li adsorptions, five sites, i.e., bridge (B), on-top (T), hollowtetrahedral inner (Td<sub>inner</sub>), hollow-tetrahedral surface (Td<sub>surface</sub>), and hollow-hexagonal (Hex) were considered. For the same SiQD, the Li atom binds more strongly in Td<sub>inner</sub> and Td<sub>surface</sub> than in the other sites. For different sizes of SiQDs, the  $E_{\rm bind}$  varies very little. Thus, the binding depends on the adsorption site. The stronger binding was observed for Td<sub>inner</sub> with E<sub>bind</sub> between 0.80 and 1.00 eV, while the adsorption in Td<sub>surface</sub> gives a weaker binding with energies between 0.18 and 0.30 eV. Interestingly, the binding of Li in the Hex site is negative (unstable) for all SiQDs. Therefore, Td<sub>inner</sub> is the most preferred adsorption site for any SiQDs. Furthermore, we found the E<sub>bind</sub> to increase as more Li atoms are added to SiQDs. This suggests that SiQD could accommodate more Li atoms per structure and the anode which makes from SiQDs could provide high capacity. To address the life cycle problem of a Si anode, the change of molecular volume of various SiQDs after Li adsorption was evaluated. Our results showed that the change in volume does not vary with the number of Li adsorption, but it depends on the adsorption site and cluster size. The larger size SiQD tends to have a smaller volume change. Moreover, there is less variation in the percentage change in volume for the adsorption in  $Td_{surface}$  (at the most 0.29 %) when compared to that in Td<sub>inner</sub> and Hex (at the most 2.15 %). To avoid the volume expansion owing to Li adsorption, a large SiQD is then recommended. The effect of Li adsorption on the electronic properties (energy gap) of SiQDs was monitored. The energy gap of un-adsorbed SiQDs decreases with the cluster size ranging from 5.95 to 8.09 eV. With Li adsorption, the energy gap is reduced by roughly 4 eV from its corresponding un-adsorbed SiQD value, remaining size dependent. Thus, SiQDs become more conductive after adsorption. The dependency on the adsorption site as well as the numbers of Li adsorption is less pronounced. By monitoring HOMO and LUMO energies, we found ELUMO to be unaltered by the adsorption, while E<sub>HOMO</sub> is raised by around 4 eV for all sites, cluster sizes, and numbers of Li adsorption. Therefore, large-



Fig. 6. HOMO, LUMO energies (eV) of SiQDs, (a) single and (b) multiple Li adsorbed on SiQDs (Li-SiQDs and nLi-SiQDs).

sized SiQDs are good anode materials for LIB since they could provide high capacity, minimal volume expansion, and reasonable conductivity.

## CRediT authorship contribution statement

Fadjar Mulya: Writing – original draft, Investigation, Formal analysis, Data curation. Thanawit Kuamit: Visualization, Software, Methodology. Pavee Apilardmongkol: Visualization, Software, Methodology. Vudhichai Parasuk: Writing – review & editing, Supervision, Resources, Conceptualization.

## Declaration of competing interest

We declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

No data was used for the research described in the article.

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## Appendix A. Supplementary data

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#### F. Mulya et al.

#### Physica E: Low-dimensional Systems and Nanostructures 164 (2024) 116060

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