Tetrachloroaluminate Ion on Graphene Quantum Dots: Towards the Design of Cathode for Aluminum-ion Battery

F. Mulya, V. Parasuk*.

Center of Excellence in Computational Chemistry, Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok, Thailand.

*E-mail: Vudhichai.P@chula.ac.th

Abstract. The adsorption of tetrachloroaluminate, AlCl$_4^-$, on Graphene Quantum Dot (GQD) were studied using Density Functional Theory (DFT). Coronene (C$_{24}$H$_{12}$) and circumcoronene (C$_{54}$H$_{18}$) were used as the model of GQDs. All possible adsorption sites which include hollow, bridge, and on-top as well as three possible standing positions of AlCl$_4^-$ were investigated. AlCl$_4^-$ can be adsorbed on the GQD surface with the adsorption energy of -2.35 to -2.83 eV for the charging condition. The adsorption energy of AlCl$_4^-$ during charging is around 10 times that during discharging. From our study, GQDs can be used as cathode material for Aluminium-ion Battery (AIB) providing higher voltage than graphite. The theoretical voltage for coronene and circumcoronene was found to be 4.3V and 4.0 V, respectively.

1. Introduction

Aluminium-ion battery (AIB) has shown very good potential for use as an alternative energy source, because of its high abundance, high volumetric density, and lower reactivity. AIB also has been viewed as a substitute for lithium-ion battery which has limitations on costly productions and limited resources of lithium. However, AIB also has limitations such as cathode material disintegration, insufficient cycle life, low capacity, and low voltage [1-2]. To solve these problems, many researchers have tried to find suitable cathode materials and electrolytes [3-8]. One of the excellent reports was presented by Lin et.al [9] which employed aluminum metal as anode, carbon-based material (graphite) as cathode, and AlCl$_3$/[EMIM]Cl ionic liquid as electrolytes. They have developed AIB which has high coulombic efficiency, high current density, ultrafast charging, and long cycle life, which was a breakthrough in solving limitations of AIB. Thus, graphite is an excellent material for use as a cathode for AIB. In the electrochemical cell designed by Lin et.al’s, [9] metallic Al and AlCl$_4^-$ are transformed into A$_2$AlCl$_7^-$ at the anode, while AlCl$_4^-$ is intercalated between graphite layers at the cathode during discharging and vice versa during charging condition. Many theoretical calculations have been carried out to study the mechanism for AlCl$_4^-$ intercalation at graphite cathode. [12,13] Nonetheless, it still has important questions to discuss such as the preferred adsorbed orientation of [AlCl$_4$]$^-$ and adsorption sites on graphite. The answers to these questions would help to improve the performance of the aluminium ion battery. Furthermore, searching for alternative cathode materials will also be an interesting research topic.
Graphene Quantum Dots (GQDs), finite-size graphene with the lateral dimension of less than 100 nm in single, double or a few layers, have several advantages such as high conductivity and large specific area. It can be used as a nanostructured material for energy conversion and storage such as photovoltaic cells, supercapacitors, and rechargeable batteries [14-21]. GQDs have attracted tremendous attention owing to its remarkable electronic and physicochemical properties. If the materials can adsorb tetra chloroaluminate ion facilely, GQDs could be used as high-efficient cathode material for AIB. Theoretical studies can help us to understand the insight of the adsorption mechanism and probably predict the theoretical voltage of the aluminium-ion battery. [10-13] In this study, GQDs such as coronene (C_{24}H_{12}) and circumcoronene (C_{54}H_{18}) were examined as a cathode material. Also, the preferred adsorption site for GQDs and standing position (orientation) AlCl_{4}^{-} were investigated. Three patterns of adsorption sites, i.e. bridge, hollow, and on-top, and three types of AlCl_{4}^{-} standing position were considered.

2. Computational Details

Coronene (C_{24}H_{12}) and circumcoronene (C_{54}H_{18}) were used for models of hexagonal-shaped GQDs. Three types of adsorption sites, i.e. bridge (B), hollow (H), and on-top (T) were considered. When considering symmetry, coronene has two, four, and three hollow, bridge, and on-top sites, respectively, Fig. 1. Also from Fig. 1, circumcoronene has three hollow, four bridge, and four on-top sites In addition, the adsorption can be categorized into three zones, central, intermediate, and edge according to Alonso-Lanza et.al. [22] (The zones are marked by color, i.e. blue for central, green for intermediate, and yellow for edge).

![Figure 1](image1.jpg)  
**Figure 1.** Coronene and circumcoronene which the pattern of adsorption sites GQDs, classified based on the area of GQDs: central area (aqua), intermediate area (green) and edge area (yellow).

For AlCl_{4}^{-}, three possible standing positions, I, II, and III where one, two, and three Cl atoms pointing towards the GQD plane as shown in Fig. 2 were as well studied. All calculations were performed based on the density functional theory (DFT) method, with M06-2X hybrid functional [23] and 6-31G+(d) basis set using Gaussian09 software program.
3. RESULTS AND DISCUSSION

3.1 Adsorption on Coronene

All possible patterns of adsorption sites on coronene and standing position of AlCl$_4^-$ for the adsorption during charging and discharging were examined. After performing geometry optimization, we could not obtain stationary points only for some adsorption sites and standing positions. Those sites in which stationary points cannot be found were referred to as “unbind” sites. Interestingly, for some adsorption sites, stationary points can be achieved but they are not the same as the starting configuration. The stationary points for the adsorption of AlCl$_4^-$ on coronene were listed in Table 1. More bound states were observed for the charging condition (27 bind adsorptions) than for the discharging one (13 bind adsorptions). This is quite obvious because coronene has a positive charge in the charging condition. Therefore, it is more attractive for AlCl$_4^-$ than the neutral coronene during the discharging.

In Table 1, the adsorption site T2 (5 times) was most found for the discharging condition, which is followed by sites H1 (3 times), T1 (2 times), B4 (2 times), and H2, respectively. For the charging condition, the frequency of observed adsorption sites is 12, 5, 5, 2, 2, and 1 for H1, B2, T3, B1, B4, and T1, respectively. Interestingly, no adsorption was noticed for the site B3 in both charging and discharging conditions. The standing position III was found in most bind adsorptions. For the charging condition, only the standing position III was observed. This information is in good agreement to the adsorption energy, $E_{\text{adv}}$, displayed in Table 2.
lies that during charging adsorption patterns, H1 from AlCl4⁻ was observed to be between -2.71 to -2.83 eV, while it is between -0.02 and -0.23 eV for the discharging. The vast difference of E_ads for charging and discharging conditions is significant. It implies that during charging AlCl4⁻ can bind to the electrode strongly, while during discharging it can be removed easily. The distance between the coronene surface and AlCl4⁻ (r_S) was found to be between 3.09 and 3.40 Å. This value does not correspond with E_ads since r_S for charging and discharging conditions are in the same range while E_ads of the former case is 10 times stronger. The charge between -0.80 to -0.84 is noticed for the charging condition. These values are higher than the AlCl4⁻ molecular charge, suggesting the charge transfer from AlCl4⁻ to coronene surface. For the discharging condition, the charge between -0.92 to -1.06 was reported. For some adsorption patterns, H1-I, H1-II, and H2-II, AlCl4⁻ charge are more negative than the molecular charge. Thus, coronene donates electrons to AlCl4⁻ instead. This happens only with the electron-rich site such as the hollow site and when the electron density on AlCl4⁻ is weak such standing positions I and II.

Table 1. Optimized structures of [AlCl₄]⁻ coronene in discharging and charging condition

| Sites and Standing | After optimization on discharging condition | After optimization on charging condition |
|-------------------|--------------------------------------------|----------------------------------------|
|                   | I       | II      | III     | I       | II      | III     |
| B1 Unbind         | T2-III  | T1-III  | B2-III  | B1-III  | H1-III  |
| B2 Unbind         | T2-III  | T2-III  | H1-III  | H1-III  | B2-III  |
| B3 Unbind         | Unbind  | Unbind  | Unbind  | H1-III  | T3-III  | T3-III  |
| B4 Unbind         | Unbind  | Unbind  | B4-III  | B4-III  | B2-III  | H1-III  |
| H1 H1-I           | H1-I    | H1-II   | H1-III  | T3-III  | B2-III  | H1-III  |
| H2 Unbind         | H2-II   | T2-III  | H1-III  | H1-III  | H1-III  |
| T1 Unbind         | B4-III  | T1-III  | B4-III  | B1-III  | H1-III  |
| T2 Unbind         | Unbind  | T2-III  | H1-III  | T1-III  | B2-III  |
| T3 Unbind         | Unbind  | Unbind  | H1-III  | T3-III  | T3-III  |

Table 2. Adsorption pattern, adsorption energies E_ads in eV, the distance between coronene plane and AlCl₄⁻ (r_S) in Å and Mulliken charges of AlCl₄⁻ for [AlCl₄]-coronene in charging and discharging conditions.

| Adsorption Pattern | E_ads (eV) | r_S (Å) | Charge of AlCl₄⁻ | Adsorption Pattern | E_ads (eV) | r_S (Å) | Charge of AlCl₄⁻ |
|--------------------|------------|---------|------------------|--------------------|------------|---------|------------------|
| H1-III             | -2.83      | 3.29    | -0.84            | H1-I              | -0.02      | 3.22    | -1.06            |
| B1-III             | -2.78      | 3.31    | -0.83            | H1-II             | -0.10      | 3.35    | -1.02            |
| B2-III             | -2.76      | 3.29    | -0.82            | H1-III            | -0.16      | 3.36    | -0.95            |
| B4-III             | -2.72      | 3.12    | -0.81            | H2-II             | -0.08      | 3.40    | -1.01            |
| T1-III             | -2.75      | 3.33    | -0.82            | B4-III            | -0.22      | 3.21    | -0.93            |
| T3-III             | -2.71      | 3.09    | -0.80            | T2-III            | -0.23      | 3.22    | -0.92            |
|                   |            |         |                  | T1-III            | -0.17      | 3.37    | -0.94            |
The relation between AlCl$_4^-$ charge and $E_{ads}$ is pronounced. For the charging condition, the interaction becomes stronger as AlCl$_4^-$ being more negative. (In this case, the charge of coronene is opposite to that of AlCl$_4^-$.) The discharging condition splits into two cases, where AlCl$_4^-$ charge is less or greater than -1. For less than -1 case, the interaction is stronger as the charge being more negative and vice versa for greater than -1 case. The reverse of the trend is because for that case the charge of coronene is also negative. This suggests that the interaction between AlCl$_4^-$ and coronene surface is electrostatic. It also explains why the standing position III is preferred. The standing position III has three negative charge species pointing towards the positively charged surface.

### 3.2 Adsorption on Circumcoronene

Only the standing position III was considered for this case. Since from the previous section, we found the standing position III to be the most stable standing position for AlCl$_4^-$. Adsorbed sites at standing positions III of [AlCl$_4$] on circumcoronene after geometry optimization were shown in Table 3. For the discharging condition, B4 is the most preferred adsorption site with a frequency of 4. This is followed by H2 (3), T2 (2), T3 (2), T1(1) and H1(1). For charging condition, the most frequent adsorption site is T2 with 4 counts. While adsorption sites B4, T1, T3, H1, and H2 were found 3, 2, 2, 1, and 1 time, respectively. No adsorption is observed for B1, B2, B3, B5, H3, and H4 sites for both discharging and charging conditions. More on-top sites were found for the adsorption of AlCl$_4^-$ than other positions. For the bridge site, only the adsorption at B4 was noticed. This contradicts to the adsorption on coronene, where B4 is the non-favourite position.

| Sites and Standing | After optimization on discharging condition | After optimization on charging condition |
|-------------------|---------------------------------------------|-----------------------------------------|
| B1                | T1-III                                      | T1-III                                  |
| B2                | H2-III                                      | T2-III                                  |
| B3                | T3-III                                      | T3-III                                  |
| B4                | B4-III                                      | B4-III                                  |
| B5                | B4-III                                      | B4-III                                  |
| H1                | H1-III                                      | H1-III                                  |
| H2                | H2-III                                      | H2-III                                  |
| H3                | B4-III                                      | T2-III                                  |
| H4                | B4-III                                      | T2-III                                  |
| T1                | T1-III                                      | T1-III                                  |
| T2                | T2-III                                      | T2-III                                  |
| T3                | T3-III                                      | T3-III                                  |
| T4                | T4-III                                      | B4-III                                  |

Table 4 reported $E_{ads}$, $r_{IS}$, and AlCl$_4^-$ charge of [AlCl$_4$]-circumcoronene complex during charging and discharging. From Table 4, $E_{ads}$ between -2.35 to 2.47 eV and -0.29 to -0.38 eV were listed for the charging and discharging conditions, respectively. $E_{ads}$ of circumcoronene for the charging condition is slightly weaker than those of coronene, whereas those for the discharging condition is stronger. Similar to coronene, the adsorption during charging is around 10 times stronger. Adsorption sites with the strongest $E_{ads}$ are T1 and B4 for charging and discharging conditions, respectively. Unlike coronene, there seems to be no correlation between the results in Tables 3 and 4. This might be because the values of $E_{ads}$ are not much difference between various sites. Like coronene, we found no relation between $E_{ads}$ and $r_{IS}$. The $r_{IS}$ for all sites and conditions are from 3.08 to 3.33 Å.
Table 4. Adsorption pattern, adsorption energies $E_{ads}$ in eV, the distance between coronene plane and AlCl$_4^-$ ($r_{IS}$) in Å and Mullikan charges of AlCl$_4^-$ for [AlCl$_4$]-circumcoronene for charging and discharging conditions.

| Adsorption Site | $E_{ads}$ (eV) | $r_{IS}$ (Å) | Charge of AlCl$_4^-$ | Adsorption Site | $E_{ads}$ (eV) | $r_{IS}$ (Å) | Charge of AlCl$_4^-$ |
|-----------------|----------------|--------------|----------------------|-----------------|----------------|--------------|----------------------|
| H1-III          | -2.45          | 3.27         | -0.90               | H1-III          | -0.31          | 3.31         | -0.96               |
| H2-III          | -2.45          | 3.30         | -0.88               | H2-III          | -0.30          | 3.33         | -0.94               |
| B2-III          | -2.43          | 3.33         | -0.88               | B4-III          | -0.38          | 3.16         | -0.90               |
| B4-III          | -2.44          | 3.20         | -0.83               | T1-III          | -0.30          | 3.31         | -0.92               |
| T1-III          | -2.47          | 3.27         | -0.89               | T2-III          | -0.29          | 3.33         | -0.92               |
| T2-III          | -2.45          | 3.08         | -0.88               | T3-III          | -0.36          | 3.25         | -0.90               |
| T3-III          | -2.35          | 3.08         | -0.83               | T4-III          | -0.36          | 3.20         | -0.91               |
| T4-III          | -2.44          | 3.23         | -0.83               |                |                |              |                     |

The association between AlCl$_4^-$ charge and $E_{ads}$ is once again observed. For the charging condition, $E_{ads}$ is more negative when the charge is more negative. While for the discharging condition the less negative charge results in stronger interaction between AlCl$_4^-$ and circumcoronene. (Since circumcoronene has a negative charge for this case.) We, thus, concluded that the interaction between AlCl$_4^-$ and circumcoronene is electrostatic. The charges of AlCl$_4^-$ between -0.83 to -0.90 and -0.90 to -0.96 were seen for the charging and discharging conditions, respectively. Thus, there is the transfer of electrons from AlCl$_4^-$ to circumcoronene. In circumcoronene, the charge is slightly more negative suggesting fewer electrons being ejected to the surface. This might also explain the weaker $E_{ads}$ when compared to coronene.

### 3.3 Electrode Potential of GQDs

Apart from the adsorptivity of AlCl$_4^-$ on GQDs surface (coronene and circumcoronene), electrode or cell potential is an important property for the metal-ion battery. The theoretical voltage of Aluminum-ion battery using GQDs as the cathode during charging can be determined from the following reaction.

**Cathode:** \[ C_n + [AlCl_4]^-/ = C_n[AlCl_4] + e^- \]

**Anode:** \[ 4Al_2Cl_7^- + 3e^- = Al + 7AlCl_4^- \]

Thus, the theoretical voltage ($E_{cell}$) of [AlCl$_4$]-GQDs system can be computed by

\[
E_{cell} = \left( \frac{3E_{[AlCl_4]Cn} + 4E_{[AlCl_4^-]} + E_{Al}}{nF} \right) - \left( 3E_{Cn} + 4E_{[Al_2Cl_7^-]} \right)
\]

Where $n$ is the number of transferred electrons during the redox reaction, $F$ is the faraday constant (23.061 kcal per volt gram), and $E$ is the energy of each species (kcal/mol). The values of theoretical voltage were given in Table 5 for [AlCl$_4$]-coronene and -circumcoronene.
Table 5. Theoretical Voltage for [AlCl₄]⁻-coronene and -circumcoronene

| Adsorption Site | Adsorption E (kcal/mol) | E_{cell} (V) |
|-----------------|-------------------------|--------------|
| coronene        |                         |              |
| H1-III          | -65.24                  | -4.33        |
| B1-III          | -64.08                  | -4.28        |
| B2-III          | -64.07                  | -4.28        |
| B4-III          | -63.20                  | -4.24        |
| T1-III          | -64.05                  | -4.28        |
| T3-III          | -63.03                  | -4.24        |
| circumcoronene  |                         |              |
| H1-III          | -56.52                  | -3.95        |
| H2-III          | -56.41                  | -3.95        |
| B2-III          | -56.10                  | -3.94        |
| B4-III          | -56.34                  | -3.95        |
| T1-III          | -57.01                  | -3.98        |
| T2-III          | -56.45                  | -3.95        |
| T3-III          | -54.26                  | -3.86        |
| T4-III          | -56.33                  | -3.95        |

Table 5 reported the theoretical voltage between 4.24 to 4.33 V for coronene and 3.86 - 3.95 V for circumcoronene. The cell potential depends on the adsorption energy between AlCl₄⁻ and GQDs, but not sensitive to the adsorption site. The smaller GQD has stronger adsorption energy and hence the higher voltage. Using similar methods, Bhauriyal et.al. [14] reported theoretical voltage in the range of 1.58 to 3.91 V. Our result is in good agreement with their work. One of the problems for aluminum-ion battery is the low voltage. Currently, the best voltage for aluminum-ion battery is 2.45 V as reported by Lin et.al. [9] Thus, smaller size GQDs could provide a remedy to improve the voltage of AIB.

4. Conclusions
Tetrachloroaluminate ion (AlCl₄⁻) can be adsorbed on the surface of coronene and circumcoronene at hollow, bridge, and on-top sites. But not all possible adsorption sites can accommodate AlCl₄⁻. The most preferred standing position of AlCl₄⁻ is the position III where three Cl atoms pointing towards the surface of GQDs. For coronene, adsorption energies of -0.02 to -0.23 eV with T2 as the most preferred site and of -2.71 to -2.83 eV with H1 as the most preferred site were observed for discharging and charging condition, respectively. For circumcoronene, adsorption energies of -0.29 - -0.38 eV for discharging and -2.35 - -2.47 eV for charging were found with B4 and T1 as their respective most preferred adsorption sites. Independent of GQDs, the adsorption energy for the charging condition is roughly 10 times stronger than that for the discharging one. For the charging condition, the interaction is weaker for the larger GQD. The distance between AlCl₄⁻ and GQDs is in the range of 3.08 - 3.40 Å for all conditions. No relation between this distance and the adsorption energy. There is the electron transfer between AlCl₄⁻ and GQD, since the molecular charge of AlCl₄⁻ is more negative than that in the complex. Thus, the interaction between AlCl₄⁻ and GQD is electrostatic. The theoretical voltage was computed to be 4.3 V for coronene and 4.0 V for circumcoronene. Larger GQDs has a lower voltage.
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