



Conference Paper

First Principles Calculations Study of Lithium-Montmorillonite for Humidity Sensor Application

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Abstract

In this study, we performed calculations on the water molecule adsorbed on lithium montmorillonite using first principles-calculation by means of electronic-structure calculation, with emphasis on approaches based on Density Functional Theory (DFT). The mechanism of water molecule adsorption on the surface of lithium-montmorillonite was investigated from the electronic structure point of view to seek the possibility of using montmorillonite as humidity sensor. The effects of the Van der Waals force to the electronic properties of water molecule on the surface of montmorillonite was also considered and obtained that the structure is more stable energetically. The interaction of water molecule with surface of montmorillonite yields the rotation of the hydrogen atoms of water molecule due to the occurrence of repulsive interaction between two positive ions of hydrogen of water molecule and lithium. From the calculations, lithium-montmorillonite can be considered as a good material for humidity sensor application since there is an electrical change observed even though it is a relatively small that is 0.657 eV.

Keywords: DFT, lithium-montmorillonite, water molecule

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1. Introduction

Interest in research associated with humidity sensor has been growing rapidly in recent years for human comfort. Different kinds of materials including polymer [1], composite [2] and ceramic [3,4] have been applied as humidity sensor. Recently, clay-based mineral such as Montmorillonite (MMT) has been nominated as a good material for humidity sensor since it has a high specific surface area and/or excellent adsorptive capacity [5].

Adsorption of water molecules in the MMT is a great importance for ensuring reliability of MMT as humidity sensor. Fortunately, the water molecules enable easy penetration and separates weakly-bonded layers of MMT. The weakly-bonded layers of MMT are driven by the isomorphic substitution in layers of MMT, which causes the negative charges and subsequently weakens the attraction among the MMT layers [6]. Hence, metal exchangeable cation coordination within the negatively charged MMT is required to neutralize MMT.

The humidity sensitivity of the sensor is also depending on the cationic mobility of the exchangeable cation of MMT. It has been reported that Lithium-MMT in an organic solution has shown good electrical conductivity as compared with other alkali metal exchangeable cations (Li- > Na- > K- > Mg- > Ca- > Sr- > Ba-MMT) [7]. Therefore, in the present study, we focused on the Lithium-MMT and its interaction with water molecule. The mechanism of water molecule adsorption in Lithium-MMT will be described as well as investigation on the structure and electronic properties of water on Lithium-MMT from the atomic scale point of view to get a better understanding on how MMT can be useful for the application of humidity sensor.

2. Computational Method

All electronic properties calculations have been performed using the Density Functional Theory (DFT) within Kohn-Sham formula implemented in Vienna Ab initio Simulation Packages (VASP) [8,9] at an absolute zero temperature. The generalized gradient approximation (GGA) within the Perdew–Burke–Ernzerhof (PBE) functional was employed for the exchange–correlation energy [10]. The Brillouin zone was sampled using 5×5×1 Monkhorst-Pack k-point grid and the cut-off energy was 520 eV. The cut-off energy was chosen based on the high accuracy precision mode applied in the calculation which is giving the following formulation of cut-off energy:

$$E_{cut-off} = 1.3 * ENMAX \quad (1)$$

where ENMAX is the largest pseudopotential file supported in VASP code. Among the O, Si, H, Al, and Mg, the largest ENMAX belongs to the Oxygen atom with the value of 400 eV.

The total energy difference value was set to 0.01 meV giving considerable savings in computational cost and considered to provide high accuracy. Hence, the total energies in this calculation were converged to 0.01meV.

The MMT structure was modelled as one unit cell which consists of 40 atoms and repeated periodically. The isomorphous substitution was taken into account in the alumina octahedral layers by replacing one of Al atom by Mg atom. The Li atom was placed on top of the surface of optimized MMT. A water molecule was then added on top of the optimized Li-MMT. The oxygen atom of a water molecule was initially designed towards the surface of MMT and then the relaxation optimization was started to be calculated. Hence, the total numbers of atom within a unit cell of the H₂O/Li-MMT were 44 atoms. The Van der Waals force correction was included in this calculation using D2 method of Grimme [11].

3. Results and Discussion

In this calculation we compared both structures of MMT and H₂O/Li-MMT. The results of geometry optimization using the DFT calculation for both MMT and H₂O/Li-MMT structures are depicted in Figure 1. In this present study, we only consider to only one

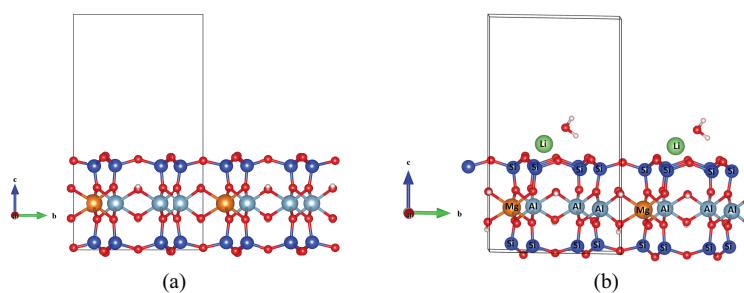


Figure 1: (a) The optimized structure of MMT viewed as a periodic system (1x2x1). A unit cell of MMT is defined as the number of 40 atoms within a frame. (b) The optimized structure of a water molecule adsorbed on Li-MMT viewed as a periodic system (1x2x1). A unit cell of H₂O/Li-MMT is defined as the number of 44 atoms within a frame.

water molecule due to efficient, cost computational reasons, and because we believe it can covered and provides all our investigations needed.

Figure 1a corresponds to the optimized structure of MMT viewed as a periodic system (1x2x1). Despite the fact that Li atom might be trapped in the cavity of alumina octahedral layer, however, due to hydration environment, the Li atom may locate in the cavity of silicate tetrahedral layer of MMT. Therefore in this calculation, we initially located Li atom on top of the MMT surface as shown in Figure 1b. Figure 1b corresponds to the optimized of H₂O/Li-MMT structure viewed as a periodic system (1x2x1). Due to the fact that the water molecules are able to penetrate and then separate weakly-bonded layers of MMT, hence in this calculation, a water molecule is also located on top of the MMT surface. Each slab of MMT is separated by a vacuum at around 10 Å from the MMT surface.

As shown in Fig. 1b, Li atom is facing towards the oxygen atom of a water molecule. This is positively due to the highest electronegativity possessed by oxygen atom of a water molecule. The attraction interaction between the Li atom and a water molecule creates a transfer of charge and a weakly Li-H₂O bonding. The response of the Li-MMT based-sensor to a water molecule is therefore indicated by the change in its electronic properties of Li-MMT. As it is well known that Li-MMT is an insulator like behavior, adsorption of a water molecule will eventually change the electronic properties of Li-MMT either to semiconductor or to metallic behavior or even not to change at all. Although most commonly known that the Li atom can burn the oxygen atom of a water molecule causing a fire in the case of Li battery application, the need of material supported for preventing fire for sensor application should be invented as well.

In our previous calculation, through the density of states analysis, we found that the H₂O/Li-MMT structure is still having an insulator behavior but with the smaller band gap (change from 4.13 eV to 3.88 eV) [12]. The density of states gives the number of allowed electron (or hole) to occupy states per volume at a given energy. The band gap was determined from the conduction and valence bands edge near the Fermi level.

In the case where the Li atom is located at the alumina octahedral layer, the orientation of the OH groups of MMT is changed due to the strong interaction between Li and H atom of the OH groups [13]. However, in the case where the Li atom is located at the MMT surface or in the cavity ditrigonal of silica tetrahedral layers, the OH groups

do not change significantly but still perpendicular with the *b*-axis of this figure instead. This is because the Li atom is preferred approaching a water molecule than moving to the alumina octahedral layer. The water molecule is responsible for the lifted Li atom from the MMT surface. This is also due to the electronegativity of an Oxygen atom of a water molecule which is higher than the Li atom, making the Li-O bond is stronger. Furthermore, the interaction of water molecule with surface of MMT yields the rotation of the H atoms of water molecule due to the occurrence of repulsive interaction between two positive ions of H of water molecule and Li.

In this study, we considered the Van der Waals force correction in the calculation to obtain better results and we found that the band gap of the total density of states is 3.473 eV which is 0.407 eV smaller than calculation without considering the Van der Waals force correction. The total density of states of H₂O/Li-MMT as depicted in Figure 2 is clearly showing that the structure has an insulator behavior. Although humidity sensor requires the high sensitivity of Li-MMT, meaning that Li-MMT is expected to be changed from insulator to semiconductor after a water molecule adsorption, we still consider it as a good material for humidity sensor application since the electrical change was still observed even though it is a relatively small that is 0.657 eV.

Aside of an electrical property analysis, it is important as well to investigate the total energy of H₂O/Li-MMT to determine reactivity of the water adsorption on Li-MMT. In this calculation, we found that the total energy is more stable (-313.93 eV) than calculation without the Van der Waals correction based on reference no. 12 that is -294.60 eV. The negative value of the total energy corresponds to the spontaneous reaction between Li and a water molecule. If we compare previous calculation [12], the Van der Waals correction gives results to the higher reactivity than without applying such correction. Therefore, for the purpose of humidity sensor application then the Van der Waals correction is a great deal importance.

4. Summary

In this study, we performed DFT calculations on the water molecule adsorbed on Li-MMT. The purpose of this study is to determine the possibility whether the Li-MMT can have a chance as a good material for humidity sensor application. The water molecule involved in a unit cell of MMT is only one due to efficient, cost computational reasons, and because we believe it can covered and provides all our investigations needed.

The interaction of a water molecule with surface of MMT yields the rotation of the Hydrogen atoms of water molecule due to the occurrence of repulsive interaction between two positive ions of Hydrogen of water molecule and Lithium. In this study, the change electrical property of Li-MMT was observed through the density of state analysis. The band gap of 3.473 eV was obtained through the density of states which is indicating that H₂O/Li-MMT is an insulator. A relatively small band gap change was confirmed that Li-MMT is able to detect a water molecule in a relatively low concentration. Therefore, Li-MMT is expected to be a good material for the humidity sensor application.

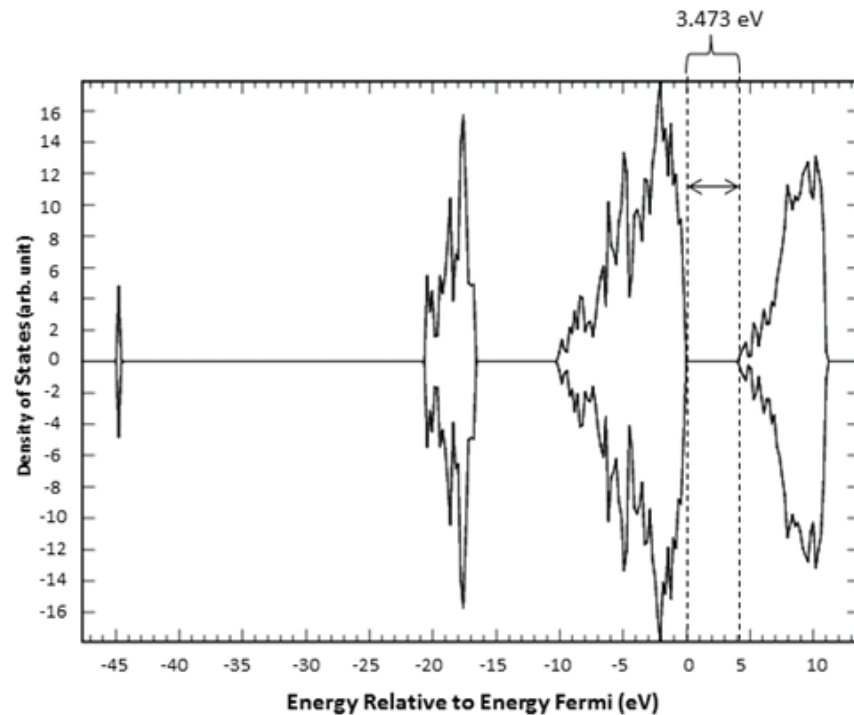


Figure 2: The total density of states of the H₂O/Li-MMT structure. The Fermi energy is set equal to zero. The wide band gap of 3.473 eV value is observed.

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