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# Defected Graphene with Li-decoration for Hydrogen Storage Applications

**S. Seenithurai[1], M. Mahendran[1]*, P. Munieswaran[1], R. Kodi Pandyan[1], S. Vinodh Kumar[1], C. Saranya[1]**

**Smart Materials Lab, Department of Physics, Thiagarajar College of Engineering, Madurai – 625015, India**

**Abstract:** The structural and electronic properties of Li stabilized mono-vacancy graphene (G-MV) have been calculated by employing the Density Functional Theory (DFT). The binding energy of Li on the vacancy site is very strong and thus clustering is hindered in this system. A maximum of four $H_2$ molecules adsorb on Li stabilized G-MV (G-MV-Li) and the hydrogen storage capacity is 7.49 wt% with the adsorption binding energies lying between 0.2-0.6 eV/$H_2$ which is essential for adsorption and desorption of $H_2$ at near ambient conditions. Thus, G-MV-Li could be a potential candidate for onboard hydrogen storage applications.

**Keywords:** Defected Graphene, Li-decoration, Hydrogen Storage Applications.

## Introduction

Hydrogen is considered be an alternative energy fuel because of its high energy content in temrs of mass. In order to realize hydrogen economy, production, storage and transportation are to be realized. Among them, storage of hydrogen is a challenging problem in scientific community. The high pressure storage method and cryogenic storage methods which are conventionally used for many years have potential risk associated with them – outburst during some cataclysmic event. Additionally, cryogenic method requires cooling unit which increases the gravimetric as well as volumetric capacity low. Thus storing hydrogen in a light weight and safe container becomes necessary in current situation.

Recently, carbon-based nanomaterials such as carbon nanotubes and graphene are considered to be the potential candidates for hydrogen storage media because of their light weight, pores structure and high surface area which could accommodate huge hydrogen molecules[1,2]. The interaction between pure carbon nanostructure and the hydrogen molecule is due to the weak van der Waals interaction with binding energies less than 0.1 eV[3,4]. This low binding strength of $H_2$ on pure carbon nanostructures is not sufficient to hold the adsorbed $H_2$ molecule at near room temperature. Thus the interaction has to be increased to the desirable range, 0.2-0.6 eV/$H_2$, in such a way that the desorption of $H_2$ occurs at near ambient conditions[5]. Apart from this, U.S. Department of Energy (DOE) has proposed an ultimate target of 7.5 wt% which is required for a normal vehicle to travel a distance of 500 km before refill[6]. In such effort, carbon nanostructures are doped with boron

or functionalized with metals and metal hydrides[2]. The problem in metals-functionalized carbon nanostructure is that the functionalizing atoms aggregate and forms cluster[7]. This clustering is not desirable because of the reduction in the hydrogen storage capacity. Thus, the interaction binding energy has to be sufficiently increased to prevent the metal clustering[8].

Carbon nanostructures functionalized with Li are widely studied for hydrogen storage applications because of high gravimetric storage capacity owing to the light weight of Li. Metal atoms are found to be stabilized on vacancy sites of graphene with enhanced binding energy compared to pure graphene[9]. In this paper, we analyze the stability of Li on the mono-vacancy site of graphene and subsequently study the hydrogen adsorption characteristics.

### Computational Details

The calculations were performed by using the Density Functional Theory (DFT)-based code DMol[3] as implemented in Materials Studio 4.4[10]. The geometry optimization was performed by using local density approximation (LDA) with Perdew Wang Correlation (PWC) functional. The double numerical plus polarization (DNP) basis sets were used. The geometry optimization has been performed with energy and maximum force of $2\times10^{-5}$ Ha and 0.004 Ha/Å respectively. The core electrons were treated with DFT Semi-Core Pseudo Potentials (DSPPs). A smearing of 0.005 Ha was used to speed up the geometry optimization. The k-points were sampled by 1x1x3 mesh of Monkhorst-Pack special k-point mesh scheme[11].

The average binding energy of $H_2$ adsorption on G-MV-Li is calculated by

$$E_B(H_2) = [E_{TOT}(MV-Li) + E_{TOT}(nH_2) - E_{TOT}(MV-Li-nH_2)]/n \quad (1)$$

Here $E_B$(Li) and $E_B(H_2)$ is the binding energy of Li and $H_2$ on G-MV and G-MV-Li respectively. The $E_{TOT}$ represents the total energy of corresponding structures.
The gravimetric storage capacity of hydrogen is calculated by using

$$C_{gravimetric} = \frac{m(H_2)}{m(host)+m(H_2)} \times 100 \quad (2)$$

Here, $m(H_2)$ represents mass of adsorbed $H_2$ molecules and m(host) denotes G-MV-Li.

## Results and Discussion

### Li-stabilized on Mono Vacancy Graphene

A 3x3 graphene with mono vacancy has been used as a supercell to analyze the interaction with Li. The distance between two layers was set to above 20 Å in order to minimize the interlayer interactions. The structure of mono vacancy graphene is shown in Figure 1(a). In pure graphene, the carbon atoms are bonded with $sp^2$ hybridization. When an atom in the graphene supercell is removed, dangling bonds are formed and this leads to the local distortion. The charge on the edge carbon atoms is found to be -0.035e, -0.064e and -0.035e respectively by using Mullikan charge analysis. The density states corresponding to the mono vacancy graphene is given in the upper panel of Figure 3. Pure graphene is a semi metal or zero gap semiconductor.Due to the removal of one carbon atom, the graphene becomes conducting as evidenced from the non zero density of states at the Fermi energy (E=0 eV).

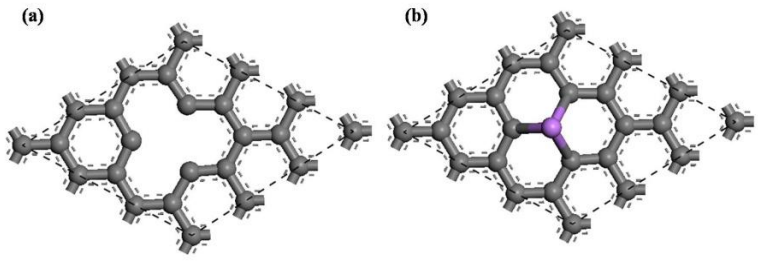


**Figure 1: Optimized structure of mono vacancy graphene. The pure graphene is semimetal or zero gap semiconductor where as mono vacancy graphene is a conductor**

**Li stabilized on Mono Vacancy Graphene (G-MV-Li)**

Experimental studies show that the vacancy sites trap metal atoms with strong binding energy[9]. Thus an Li atom was placed at the carbon vacancy site and the structure was optimized. The Li is highly stable on the vacant site and the optimized structure is shown in Figure 1(b). The Li atom is at a distance of 1.51 Å from the plane of the graphene. Charge on the Li stabilized on G-MV is found to be 0.405e. This positive charge is due to the donation of electron from Li to the G-MV. Through Mullikan analysis, the charge on the carbon atoms on which Li is bonded is found to be -0.169, -0.166 and -0.162 respectively. These negative charges on carbon atoms are due to the charge transfer from the stabilized Li atom.

**Hydrogen adsorption in G-MV-Li**

The hydrogen adsorption configurations in Li-stabilized G-MV are shown in Figure 2. The hydrogen molecules placed nearer to the stabilized Li atom is found to be adsorbed at a distance of 1.949 Å from Li atom. The second, third and fourth $H_2$ molecules were found to adsorb at a distance of 1.979 Å, 2.074 Å and 1.990 Å respectively. The corresponding binding energies were observed to be lie between 0.2-0.6 eV/$H_2$.

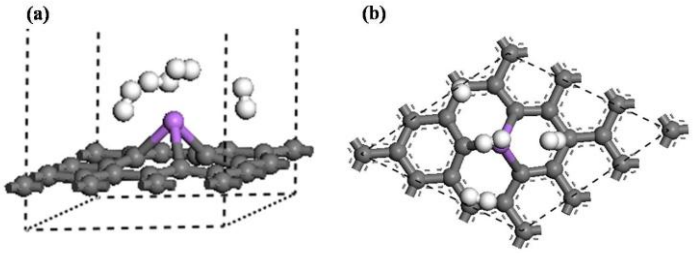


**Figure 2: (a) Side view and (b) top view of optimized structure of Li stabilized mono vacancy graphene with adsorbed hydrogen molecules.**

The interaction between the $H_2$ molecules and the Li-functionalized carbon nanostructures in well understood from previous theoretical calculations. According to them, the interaction between the stabilized Li atom and $H_2$ is due to the polarization of $H_2$ molecule by the positive Li ion. Because of the difference in electronegativity, charge is transferred from Li to the defected graphene sheet, the stabilized atom becomes ion and his lead to an electric dipole. The projected density of states corresponding to the hydrogen adsorbed Li-stabilized mono vacancy graphene is given in Figure 3.

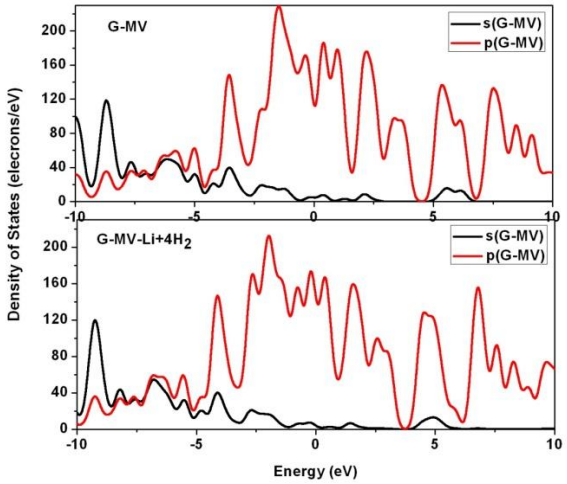


**Figure 3: Density of states of (a) pure mono vacancy graphene and (b) in hydrogen adsorbed Li-stabilized mono vacancy graphene. The enhanced occupied states in the lower panel is due to the transferred charge from Li atom.**

The upper panel shows the s and p states of G-MV. In the lower panel, the s and p states corresponding to G-MV in G-MV-Li+4$H_2$ is given. Here, E=0 eV is set to Fermi Energy ($E_F$) and thus the states below $E_F$ represents occupied states. It is clear from the figure that the additional states are introduced in the mono

vacancy graphene after the Li stabilization. The stable configuration with four $H_2$ molecules adsorbed has a gravimetric storage capacity of 3.35 wt%. If both sides of the graphene is stabilized with Li, a storage capacity of 7.493 wt% could be reached which is equal to the U.S. Department of Energy (US DOE)'s ultimate target for onboard automobile applications. Thus, Li-stabilized mono vacancy graphene could be useful for hydrogen storage applications in onboard vehicles.

The reported results here are based on the DFT which predict the ground state properties at absolute zero temperature only. Since hydrogen storage capacity will be depend on the temperature and pressure, molecular dynamics calculations at room temperature and high pressure is necessary to completely understand this system[8]. If pressure is increased, the hydrogen storage capacity could still be increased further. Recently, different 3-D structures based on carbon nanotubes, graphene and other carbon nanostructures are theoretically proposed[12]. In this study, we report only the gravimetric storage capacity and the volumetric capacity will be depend on the possible realization of 3-D structures experimentally.

## Conclusions

The Li-decorated mono vacancy graphene is the potential candidate for molecular hydrogen storage media. The Li stabilized on the mono vacancy graphene adsorbs up to four H2 molecules and this corresponds to a gravimetric storage capacity of 3.35 wt%. If Li is stabilized on both sides, the hydrogen storage capacity could reach a value of 7.493 wt%. This storage capacity is equal to the ultimate target proposed by the U.S. DOE[6]. The binding energy of H2 adsorption lies in the desirable range and thus Li-stabilized mono vacancy graphene could be useful for on-board hydrogen storage applications.

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