African Scientific Reports

Screening of Metal-Ion Intercalated Yttrium Carbide and Nitride MXenes for Energy Storage Applications via Density Functional Theory

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Abstract

Rechargeable batteries and energy storage devices play a major role in many facets of human endeavour due to their efficiency and portability. In this work, we investigated the suitability of single-layer intercalated Yttrium-based MXenes Y_2CT_2 (T= Li, Mg, Al) and Y_2NLi_2 as potential energy storage materials using the first principle calculation within the framework of the density functional theory approach. Upon intercalation, the lattice constants of the MXenes expand due to the size of the intercalating species and the electrostatic repulsion. We obtained the theoretical gravimetric capacities, open circuit voltages and adsorption energies. The obtained open circuit voltages for Y_2CT_2 (T= Li, Mg) and Y_2NLi_2 falls within the voltage window of $0 - 1.0V$ which has been found to eliminate dendrites formation caused by alkaline metals during the discharge-charge cycle. The adsorption energies indicate the stability of the intercalating ion on the MXenes surfaces except for Al cation. The results are consistent with other studies on similar MXene families in the existing literature. The work may aid the understanding of the electrochemical properties of 2D materials and we recommend Y_2CLi_2, Y_2NLi_2, and Y_2CMg_2 for future investigation as potential materials for rechargeable batteries.

Communicated by: Wasiu Yahya

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1. Introduction

Electrochemical energy storage materials applications have grabbed the curiosity of many researchers and commercial companies in recent years given their advantages over fossil fuels. Generally, energy storage devices may be employed in many applications such as rechargeable batteries, phones, laptops, wrist watches, powering automobiles and so on. Owing to their efficiency and portability, efforts have been put into research to determine and synthesize suitable and low-cost materials for energy storage device applications. The methods employed in determining the energy storage materials are experimental and theoretical techniques. A theoretical method such as the first principle approach [1–4] has been used to simulate the electronic structure, mechanical properties [5, 6], thermoelectric properties [7–9] energy storage [10–17] and others. This method has been implemented into various computing codes such as VASP [18], CASTEP [19], QUANTUM ESPRESSO [20, 21], WEIN2K [22] and so on. The codes offer the advantage of being low-cost and can be used to simulate the artificial properties of materials. Such simulation results may be compared to experimental data and also help the experimentalist in making decisions during the fabrication process. Materials for energy storage have drawn the attention of the material science community in recent decades. To this end, two-dimensional (2D) materials such as Graphene [23, 24] and MXenes [10, 11, 25] have been explored due to their unique quality in retaining electrochemical energy.

The MXenes family belongs to a large group of 2D systems due to the combination of different chemical elements and structural arrangements. The MXenes possess chemical formula $M_{n+1}X_nT_2$ and are derived from the 3D parent ternary compounds known as MAX phases ($M_{n+1}AX_nT_2$) through acid (HCl and HF or both) etching of the A elements [10]. The respective elements M, A, X and T represent early transition metals (Ti, Ta, Nb, Y, W, Sc, V, Mo Zr), group 13 or 14 elements, Carbon and or Nitrogen and surface termination groups. The chemical acid synthesis has Oxygen (O), Fluorine (F) and hydroxyl elements as the as-prepared functional groups. Other surface groups (FH, H, Br, ClH and so on) have been derived [26] and found to be chemically stable on the bare MXenes. A few double transition metal MXenes have been synthesized [27–29] with many others predicted theoretically [30–34]. The structural configurations and wide range of chemical elements make the MXenes material a large family of 2D materials comparable to the Perovskites, metal oxides/hydroxides, transition metal dichalcogenides, graphene and its derivatives [35]. The structural arrangements, the nature of the transition metals and surface terminations elements give rise to different electronic structures such as metallic, semi-metallic, semiconductor, insulator and magnetic ordering. These properties have been explored in electrochemical energy storage [10, 11], thermoelectric applications [26, 36–42], water purification [43–45], triboelectric devices [46], sensors [47–50] and telecommunications [51]. The most relevant application to our work is in energy storage where many authors have explored using both theoretical and experimental methods [52–60].

The motivation in this current work is two-fold. (a) To use the density functional theory (DFT) approach to predict potential energy storage properties for new MXene systems as alternatives to existing materials. (b) In a recent work [25], the screening of many MXenes materials for potential energy storage applications has been investigated theoretically. However, we are proposing new MXenes not included in [25]. We studied the theoretical gravimetric capacity and open-circuit voltage of mono-layer Y_2CLi_2, Y_2NLi_2, Y_2CMg_2 and Y_2CAl_2 MXenes using the DFT approach. The organization of the remaining part of the paper is as follows: in section two, we will present the theoretical method of computation. Section three contains the discussion of the results and in section four we will give the conclusion.

2. Materials and Method

We considered the screening of mono-layer MXenes materials for battery applications by intercalating metal ions such as Li^+ Mg^{2+} Al^{3+} into the MXene layers using first principles calculation within the framework of the DFT approach. We used Yttrium-based MXenes as case studies. In particular, the following MXenes Y_2CT_2 (T= Li, Mg, Al) and Y_2NLi_2 are treated with the augmented plane wave method as implemented in the QUANTUM ESPRESSO package [15, 16]. For the structural optimization, we used a $12 \times 12 \times 1$ Monkhorst and Pack [61] k points grids for the Brillouin zones integration. We employed the generalized gradient approximation (GGA) of Perdew Burke and Ernzenhof (PBE) for the exchange-correlation functional [62] and utilized a plane-wave cutoff kinetic energy of

105Ry for the wave function. Furthermore, we used a cutoff of 630Ry for the charge density and potential. The total energy convergence threshold was set at 1×10^{-10}Ry. We used the Methfessel-Paxton smearing scheme [63] with a smearing width of 0.011Ry. As for the bare MXenes, we used $10 \times 10 \times 1$ Monkhorst and Pack k points grids to sample the Brillouin zones. The plane-wave cutoff kinetic energy of 80Ry and a cutoff of 480Ry were used for the wave function and the charge density respectively. The density of state calculations was obtained using a $30 \times 30 \times 1$ k-points grid with the tetrahedron method [64]. To circumvent any interaction between a monolayer and its periodic images we set a vacuum space of 20 Å along the c axis. The 2D MXenes possess a hexagonal crystal structure with symmetry P-3m1 and space group number 164. The symmetry points for the Brillouin zone are $\Gamma(0,0,0)$, M(1/2, 0,0) and $K\left(\frac{1}{3}, \frac{1}{3}, 0\right)$. The structure of the bare MXene before and after metal ion intercalation is presented in Figure 1. The relaxed atomic positions were then used to calculate the total energies of the intercalated and bare MXenes. The chemical potential of the intercalating ion was also determined. We calculated the quantities such as the theoretical gravimetric capacity, adsorption energies and the open circuit voltages (OCV). Using M as an intercalant, we can represent the following general chemical reaction as

$$Y_2C + 2M \rightarrow Y_2CM_2. \tag{1}$$

The adsorption energy of intercalated species can be obtained as

$$E_{\text{ad}} = E[Y_2CM_2] - E[Y_2C] - 2\mu[M] \tag{2}$$

where $E[Y_2C]$, $E[Y_2CM_2]$ and $\mu[M]$ are the respective total energies of pristine, intercalated MXene and the chemical potential of the intercalants.

The theoretical gravimetric capacity and OCV are given by the respective equations [25, 65]

$$Q_g = \frac{xnF}{m} \tag{3}$$

$$V = \frac{E[Y_2C] + x\mu[M] - E[Y_2CM_2]}{xne} \tag{4}$$

where n represents the valence state of fully ionized cations from the electrolyte [65], specifically, $n = 1$ for Li, $n = 2$ for Mg and $n = 3$ for Al. We used the concentration ($x = 2$) for the intercalated MXenes monolayers. In equation (3), F, e and M represent the Faraday constant ($26801 \text{mA}hg^{-1}$) electronic charge and the molar mass or chemical weight of the intercalated MXene sheets.
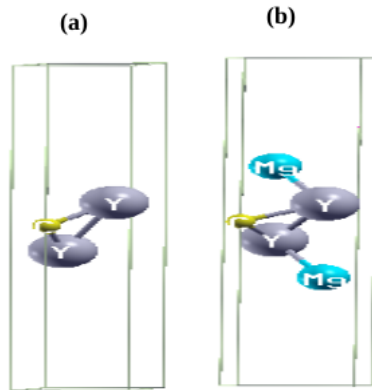

Figure 1. (a) Mono-layer of bare Yttrium carbide MXene (Y_2C) (b) Intercalation of Yttrium carbide MXene with Mg-ion (Y_2CMg_2).
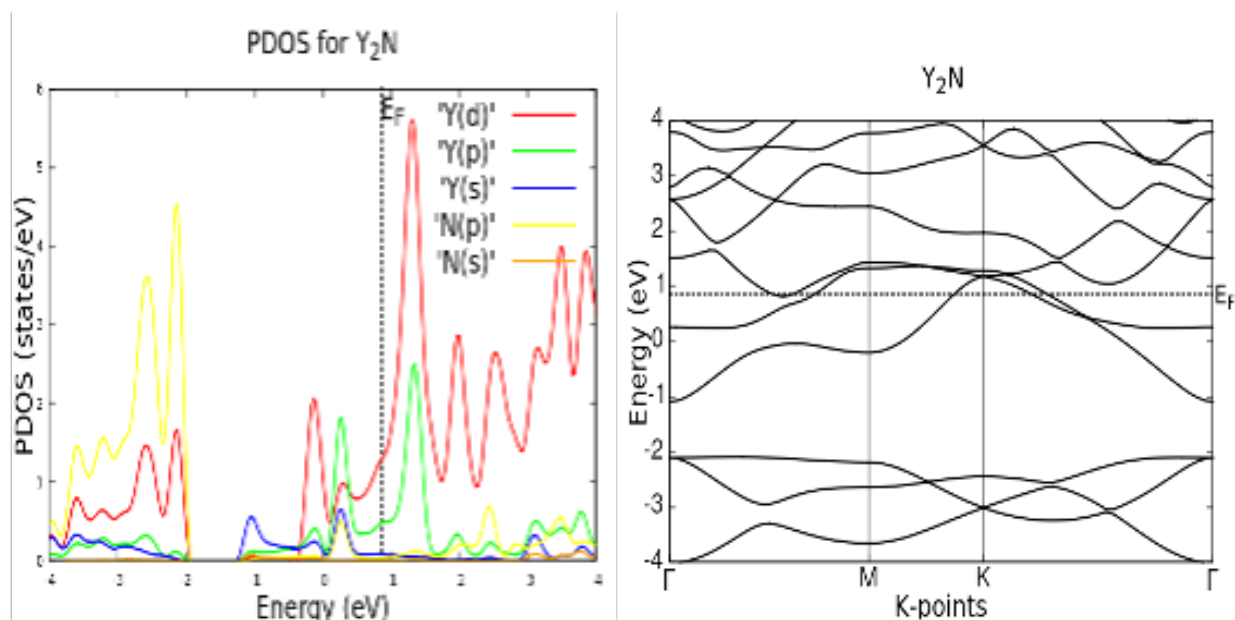
Figure 2. (a) Projected density of states. (b). Energy band diagram of bare Y_2N.

Table 1. Open circuit voltage, adsorption energy and theoretical gravimetric capacity of intercalated Yttrium carbide/nitride-based MXenes

MXene	Open circuit Voltage(V)	Theoretical gravimetric Capacity (mAh/g)	Adsorption energy (eV)
Y_2CLi_2	0.06	263.138	-0.12
Y_2NLi_2	0.08	260.585	-0.16
Y_2CMg_2	0.02	449.619	-0.07
Y_2CAl_2	-0.43	659.909	2.60

3. Results and Discussion

The lattice parameter of the bare MXenes changes when metal ions are diffused into their surfaces. For the bare MXene Y_2C, the lattice parameter is found as 3.60A. After intercalation with Mg, Al and Li ions, the lattice constants expand by 19.44% for Y_2CMg_2, 13.89% for Y_2CAl_2 and Y_2CLi_2. The changes in the lattice parameters have been linked to the ionic radius of intercalating species and lateral electrostatic repulsion after ion intercalations [25]. The bare MXenes Y_2C (see Ref [26]) and Y_2N (see Figure 2) are metallic with the 3d electrons of Y-atom majorly contributing to electrical conductivity. The metallic nature of the bare MXenes indicates that they have an intrinsic advantage for high-performance electrode materials [65]. In Table 1, we presented the theoretical gravimetric capacities, open circuit voltages and adsorption energies for the Y_2CLi_2, Y_2NLi_2, Y_2CMg_2 and Y_2CAl_2 MXenes with Al and Mg intercalated MXenes having the highest values of 659.909mAh/g and 449.319mAh/g respectively. The high values compared to the lithiated MXenes can be attributed to the multivalence states of the Mg and Al ions. The theoretical gravimetric capacity of Y_2CLi_2 MXene is slightly higher than that of Y_2NLi_2 due to its lighter molar weight. The respective OCVs and the adsorption energies are positive and negative for Y_2CLi_2, Y_2NLi_2, Y_2CMg_2 which may be an indication of a favourable condition for battery applications. The nitride-based MXene has a higher OCV than the corresponding carbide MXene due to the extra electron of the nitrogen atom and higher adsorption energy. For the Y_2CAl_2 MXene, the respective OCV and adsorption energy is negative and positive making the MXene system unsuitable for energy storage application. Generally, the OCVs increase with a decrease in the theoretical gravimetric capacities for all MXenes. Also, the intercalated bare MXenes have been found in [25] to have open circuit voltage characteristics of $0 - 1.0V$ which is consistent with the present results. This low voltage window has been found to prevent dendrite formation by alkaline metals during the discharge and charge processes [65, 66].

4. Conclusion

We have presented a study on the screening of intercalated bare MXenes for possible application in metal ion batteries. We used the DFT method to determine the total energies of the MXenes Y_2C and Y_2N, Y_2CLi_2, Y_2NLi_2, Y_2CMg_2 and Y_2CAl_2. The bare MXenes are metallic which allows their usage for high-performance electrode materials. We found a linear correlation between the calculated theoretical gravimetric capacities and the OCVs. The obtained OCV falls within the range of $0 - 1.0V$ which have been reported to eliminate dendrite formation by alkaline metals during the discharge and charge process. The results revealed that the metal ion and the X sites of the MXene materials is responsible for the OCV characteristics. Furthermore, our results are consistent with the works reported in existing literature [25, 65] where the authors studied similar MXene materials. These findings may contribute to the understanding of electrochemical properties of 2D material and we recommend Y_2CLi_2, Y_2NLi_2, and Y_2CMg_2 for future investigation as potential materials for rechargeable batteries.

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