THEORETICAL INVESTIGATION OF STRUCTURAL AND ELECTRONIC PROPERTIES OF MOLYBDENUM DICHALCOGENIDES MONOLAYERS AND LITHIUM ADSORPTION ON THEIR SURFACES

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INTRODUCTION

It is important to improve the high-efficient anode materials for Li batteries, which require large capacity, high stability and mobility. The research carried out in this study mainly concerns the transition metal dichalcogenide anode $\mathbf{MoX_2}$ (X=S, Se, Te). Structural, electronic and thermoelectric properties of MoX2 monolayers have studied using DFT method. In this regard, it concluded from the calculation of the cohesive energy that the level of stability increases from $\mathbf{MoTe_2}$ to $\mathbf{MoSe_2}$ also from $\mathbf{MoSe_2}$ to $\mathbf{MoS_2}$. All three compounds are semiconductors with direct band gaps in the range of 1 to 1.8 Ev. We have studied the adsorption behavior of lithium on the three different transition-metal dichalcogenide monolayers $\mathbf{MoX_2}$ (X=S, Se, Te). We found that Li adsorbed more stronger on MoS2 than on the other considered MoX2 materials. We also studied the effect of the increasing number of adsorbed Li atoms, and we determined the most stable adsorption sites for the Li atom. Our results indicate that these materials can be a promising anode material for high-performance Li-ion batteries.

METHODS

Our calculations are based on the first principles of the plane wave method within density functional theory (DFT) using pseudopotentials. The exchange-correlation (XC) function is approximated from the Perdew-Burke-Ernzerhof (PBE) function of the generalized gradient approximation (GGA). All numerical calculations are performed using Quantum ESPRESSO software. In self-consistent field (SCF) calculations, the Brillouin zone (BZ) is sampled using a special 4×4×1 k-point Monkhorst-Pack mesh. All atomic positions and lattice constants are optimized using the BFGS method, where total energy and atomic forces are minimized. The convergence for the cutoff energy was chosen to be 55 Ry (748 eV),

RESULTS- $\mathbf{MoX_2}$ (X=S, Se, Te) PROPERTIES

CONVERGENCE AND STRUCTURAL PARAMETERS

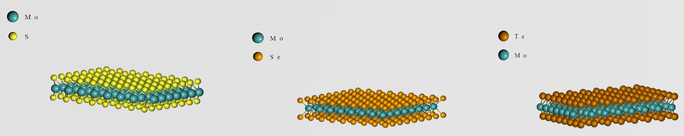


Fig-1 MoX2 monoloyer

The quantity calculated to evaluate the convergence is the total energy of each system studied. For each value of the cutoff energy parameter Ecutoff, a relaxation of the atoms is carried out without modifying the size of the lattice unit cell.

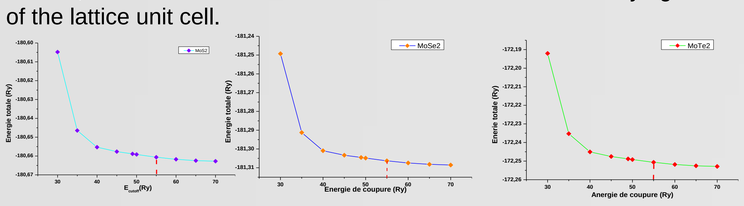


Fig-2 convergence, the total energy stabilizes above a cutoff energy value of 748 eV (55 Ry)

Table-1 Structural Parameters

Structures	d_{Mo-X} (Å)	d_{X-X} (Å)	d_{X-X} (Å)	θ_{X-Mo-X} (deg) -
$MoSe_2$	2.41	3.127	3.13 [2]	80.86
MoS_2	2.54	3.34	3.35 [2]	82.24
$MoTe_2$	2.74	3.62	3.62 [2]	82.71

ELECTRONIC PROPERTIES

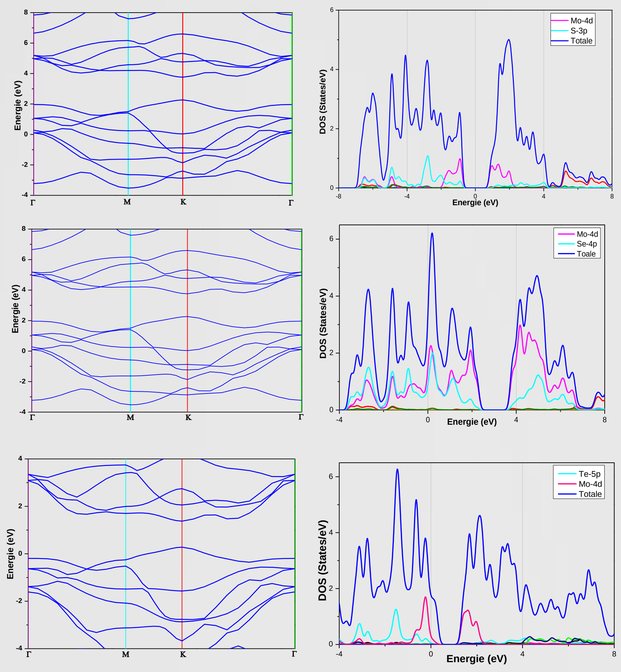


Fig-4 Energy Bandes & DOS of $\mathbf{MoS_2}$
Gap Energy =1.7181 eV

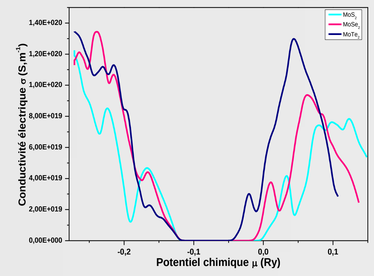
Fig-5 Energy Bandes & DOS of $\mathbf{MoSe_2}$
Gap Energy =1.5025 eV
$E_F = -2{,}9699\ eV$

Fig-6 Energy Bandes & DOS of $\mathbf{MoTe_2}$
Gap Energy =1.0948 eV
$E_F = -0{,}9163\ eV$

All the monolayers, MoS2, MoSe2 and MoTe2, are a direct gap semiconductors at K-K point at 1.7181 eV, 1.5025 eV and 1.0948 eV, respectively.

THERMOELECTRIC PROPERTIES

The BoltzTraP code based on the semi-classical Boltzmann equation was used combined with the obtained electronic structure results.



$MoTe_2$ exhibits greater electrical conductivity compared to other compounds

$MoTe_2$ exhibits higher thermal conductivity than the other two structures

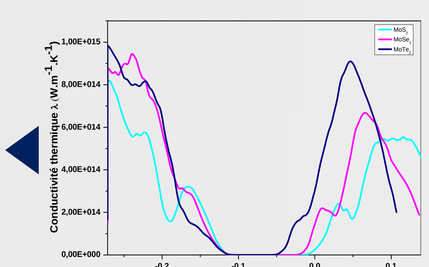


Fig-7 Electrical and thermal conductivity as a function of chemical potential

RESULTS- Li ADSORPTION ON $\mathbf{MoX_2}$ (X=S, Se, Te) SURFACES

To study lithium adsorption on optimized monolayer TMD systems we build a (2×2) supercell. The supercell is then optimized after inserting the lithium atom.

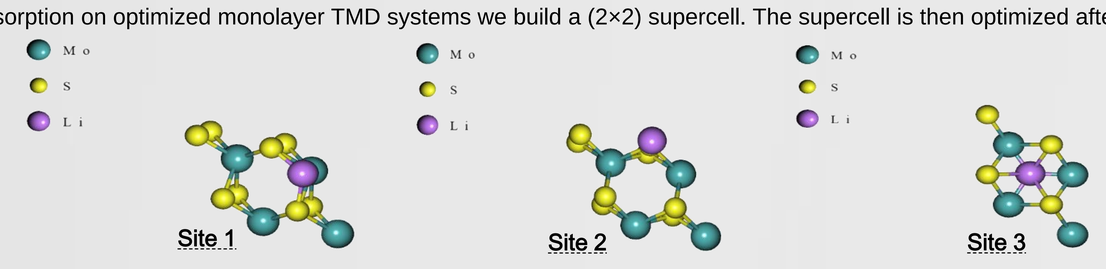


Fig-8 Possible sites of lithium adsorption

Li ADSORPTION ON MoX2 MONOLAYER

Table-2 Adsorption energy

	Energie d'adsorption (eV)			Chalcogène	Electronégativité
	Site 1	Site 2	Site 3		
MoS_2	-0.838	3.102	-0.72	Soufre S	2.58
$MoSe_2$	-0.851	-0.48	-0.783	Sélénium Se	2.55
$MoTe_2$	-1.038	1.53	-0.847	Tellure Te	2.1

STRUCTURAL PARAMETERS AFTER Li ADSORPTION

Table-2 Structural parameters after Li adsorption

MoX_2	d_{Mo-X} (Å)	d_{X-X} (Å)	θ_{X-Mo-X} (deg)
MoS_2	2.43	3.09	79.59
$MoSe_2$	2.57	3.32	81.11
$MoTe_2$	2.741	3.56	81.05

ELECTRONIC PROPRETIES AFTER Li ADSORPTION

All systems become metallic with the adsorption of Li, as will be seen in the calculated energy bands structures. The Fermi level enters the conduction band and a semiconductor-metal transition is made. It can be said that the resistivity of MoX2 systems is reduced by increased conductivity favoring their use in Li batteries as anode material.

Fig-11 Energy Bandes & DOS of $\mathbf{MoTe_2}$
Gap Energy=0,31 eV

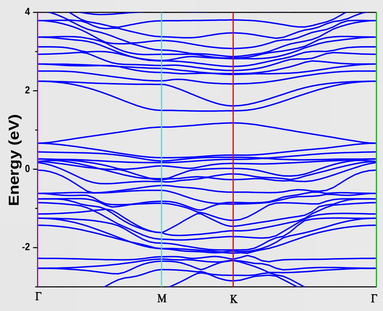


Fig-12 Energy Bandes & DOS of $\mathbf{MoSe_2}$
Energie de Gap=0,068 eV

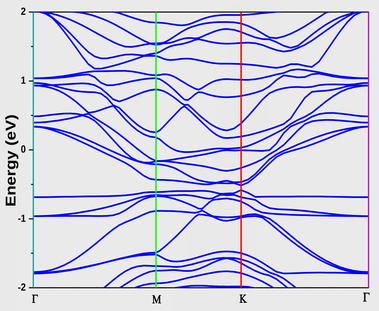
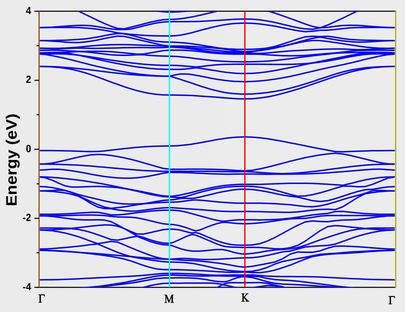


Fig-13 Energy Bandes & DOS of $\mathbf{MoS_2}$
Energie de Gap=1.098 eV



The adsorption of a single lithium atom makes it possible to modify the semiconductor properties exhibited by the MoX2 compounds in their monolayer form. Thus all the compounds studied after adsorption have similar conductive properties with a direct band gap at the same symmetry point K.

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