

Evaluation of the potentiality of phosphorus doped carbon nitride as protective layer of metallic lithium in lithium-sulfur batteries. materials as protective layers for metallic lithium.

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Introduction

High-performance energy storage and conversion devices are an eco-friendly and mitigating method of growing energy demand. Lithium-ion batteries are currently the dominant energy sources in the use of electrical devices, however, these have almost reached their theoretical limit, not being able to satisfy the terms of current storage systems.

Next-generation lithium batteries, within these, lithium-sulfur (Li-S) and lithium-air (or Li-air) are two of the most promising technologies. However, some problems still need to be solved, so that they can become a competitive product in the market. These batteries use metallic lithium as the active material for the anode. Although this material is ideal for rechargeable batteries, there are two essential problems that prevent its development: the excessive growth of dendrites during charge / discharge cycles, and the low coulombic efficiency of the process due to the solid electrolyte interface (SEI) It is not stable. It is proposed to explore, by means of DFT calculations, the potential use of 2D sheets of graphitic carbon nitrides (g-C₃N₄) with different degrees of phosphorus doping, to protect metallic lithium anodes.

Methodology

A systematic study was approached using the Density Functional Theory (DFT) under the formalism of the Quantum ESPRESSO program, using the generalized gradient approach (GGA) with the PBE correlation and exchange functional, under the augmented plane waves method (PAW). Van der Waals interactions were considered by Grimme's DFT-D2 semi-empirical correction. The convergence parameters used were Ecutwfc = 80 and a grid of k points of 3x3x3, the size of the cell used in xy was 2x2 and the vacuum in the perpendicular direction (z) was 20 Å.

All calculations were made taking into account the spin polarization.

The doping energy was calculated from:

$$E_{Dop} = E(PS) - E(DS) + \Delta H_f(X) - \Delta H_f(P)$$

where:

E (PS): Pristine Surface Energy

E (DS): Energy of the doped surface

ΔH_f = Enthalpy of formation, X = C, N₂

Results

A pristine surface of g-C₃N₄ (Fig. 1) has been doped with P atoms, which have replaced N atoms and C atoms, obtaining the systems shown in Table 1, the doping energies for each system are also shown, in the yellow cells N has been replaced by P, in the light blue cells C has been replaced by P.

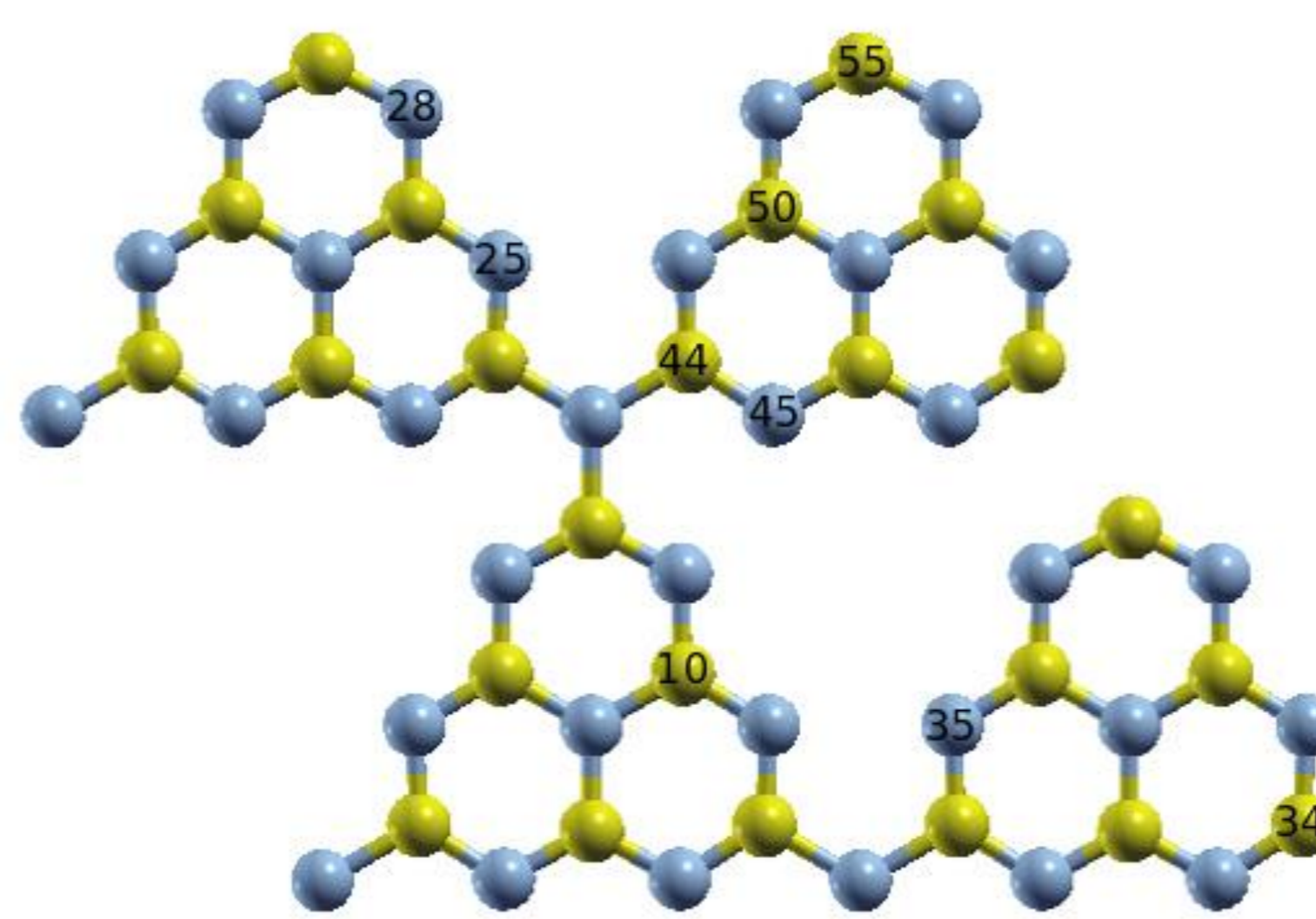


Fig.1. Estructura prístina, en celeste átomos de N, en amarillo átomos de C. Identificación de átomos sustituidos

Table 1. Comparative table of the structures of the different systems and their respective doping energies

Sistema	Estructura	E _{Dop}	Sistema	Energía	E _{Dop}
C3N4		0.00	CP-44		-507,48
NP35		-372,85	CP-50*		-506,48
NP2-25		-746,27	CP2-34		-1014,92
NP2-28		-746,48	CP2-55		-1014,22
NP2-45		-746,16	CP2*-10		-1012,71
NP3-53		-1119,09	CP2*-46		-1013,14
NP3-56		-1118,31			

Future Work

We work at the moment in the determination of the Properties of the different systems, such as obtaining electronic density and electrostatic potential, charge analysis, band diagrams, total and projected density of states with the aim of carrying out a comparative analysis of doping with P substituting N vs C.