

Structural and electronic properties of β -MnO₂ nanoclusters

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Abstract. Pyrolusite (β -MnO₂) was investigated for potential use in energy storage devices due to its promising properties for cathode materials in rechargeable lithium-ion batteries. A combination of evolutionary algorithm search techniques and density functional theory techniques were used to determine the structural stabilities of the β -MnO₂ nanoclusters on the energy landscape. However, pyrolusite suffers from some structural defects and impurities that hinder its optimal use. The predicted order of stability for the MnO₂ nanoclusters correlates with isostructural TiO₂. There is an improvement in the stability and electrical conductivity of the nanoclusters as compared to their β -MnO₂ bulk counterparts. The cobalt doped nanoclusters showed a preference toward circular compact bonding patterns. The band-gap energy revealed that the nanoclusters have a metallic characteristic behaviour with narrow band gap energies, indicating their good conductive properties. Cobalt doping was shown to improve the structural properties of the nanoclusters based on the decreased bond lengths and more spherical bond angles. Moreover, it also succeeded in improving the conductivity of the nanoclusters based on the reduced Mulliken and Hirshfeld partial charges. The electronic charge density differences of the cobalt doped β -MnO₂ nanoclusters displayed a prevalence of the weaker ionic bonding instead of the preferred stronger covalent bonding. This shows the limited effectiveness of cobalt as a dopant.

1. Introduction

The emergence of the 4th industrial revolution has brought forth unprecedented demands of electrical power needed to support this automated technological world. This demands have led to high costs in Brent crude oil [1], natural gas for electricity supply in North America [2], coal for electricity supply in most countries worldwide and in South Africa specifically [3]. The increased global demand driven by overreliance on these non-renewable and non-recyclable energy sources has led to the surging prices of these fossil fuels. Moreover, the continuous use of these fossil fuels leads to the unavoidable environmental pollution which in turn causes unfavourable climatic conditions and health threats to human life [4].

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Renewable and recyclable energy is one of the more viable ways to remedy this looming crisis as an alternative energy source, and thus rendering research in this field important.

However, rechargeable batteries for electric vehicles require higher capacities and greater power output. One of the restrictions hindering the performance of secondary batteries from meeting the increasing requirements for performance and energy storage is the development of suitable cathode materials. MnO_2 compounds are encouraging as probable alternative materials in rechargeable batteries due to their low toxicity and financial cost. However, they suffer from some structural defects and impurities that hinder their use [5]. Recent studies have shown that nanostructural refinement can be used to correct the structural defects present in other rutile-type structures of iso-structural TiO_2 [6].

Future battery advancements rely on the creation of multifunctional electrode materials with unique nano-architectures. These endeavours have produced positive results as evident with the production of electric vehicles. Historically, more focus was on the iso-structural rutile- TiO_2 [7]. The stability of TiO_2 nanostructured materials further highlights the potential of rutile polymorphs from transitional metal oxides when used as electrodes in lithium-ion rechargeable batteries [8]. One such polymorph is MnO_2 which has received increased focus in recent years as technological advancements (computational algorithms) have opened new avenues that enable researchers to gain some insight and exploit these materials further. Particularly, nanostructuring has demonstrated the capability to improve the stability and electrochemical performance of rutile MnO_2 in lithium-ion rechargeable batteries. Previous studies successfully investigated the doping of MnO_2 hierarchical nanostructures with cobalt in the quest to enhance their pseudo-capacitive properties hence the use of cobalt used to dope the nanoclusters in this study [9].

This study aims to show that nanostructuring and doping can be used to improve the structural properties and stability of MnO_2 systems for the specific use as cathode in rechargeable batteries. In particular, the effect of cobalt doping on the β - MnO_2 nanoclusters are investigated. Doping with cobalt has shown promising results previously [9].

2. Methodology

The current study employed the Buckingham potential in conjunction with the Lennard-Jones potential in order to avoid the risk of an un-physical "Buckingham catastrophe" at short range when utilised to model charged systems [10]. These refined potentials were previously used successfully to model bulk, surfaces, and nanostructures of other MnO_2 systems [11]. β - MnO_2 belongs to the ditetragonal dipyramidal class (4/mmm - n 4/m 2/m 2/m) with the $P4_2/mnm$ tetragonal space group with a density between 5.04 - 5.19 g/cm^3 . Each manganese atom in the rutile bulk β - MnO_2 lattice has six neighbouring atoms. During calculations the bulk β - MnO_2 crystallizes into a periodic bulk structure with the lattice parameters reported as $a=b= 4.404 \text{ \AA}$, $c = 2.876 \text{ \AA}$ and $\alpha=\beta=\gamma = 90.0^\circ$, with a unit cell volume of 55.79 \AA^3 [12].

Firstly, the interatomic potential (IP) method code; the General Utility Lattice Program (GULP) [13] was used to refine the original system within the interatomic potential scheme. GULP was employed within the Knowledge-Led Master Code (KLMC) [14]. The refined IPs are used to generate and classify the nanoclusters using the genetic algorithm approach.

Secondly, the density functional theory (DFT) based code; Cambridge Serial Total Energy Package (CASTEP) [15] is used to optimise the generated nanoclusters, rank them according to their stability and investigate their charge density differences. A DFT optimisation of the bulk β - MnO_2 structure was evaluated using a 500-eV cut-off energy and a $2 \times 2 \times 4$ k-point set befitting the tetragonal crystal system of the rutile pyrolusite.

Lastly, the molecular dynamics (MD) based code D-Mol³ [16] was employed to evaluate the effect of doping the nanoclusters with cobalt. A flow chart describing the methodology used in this study is summarised in figure 1.

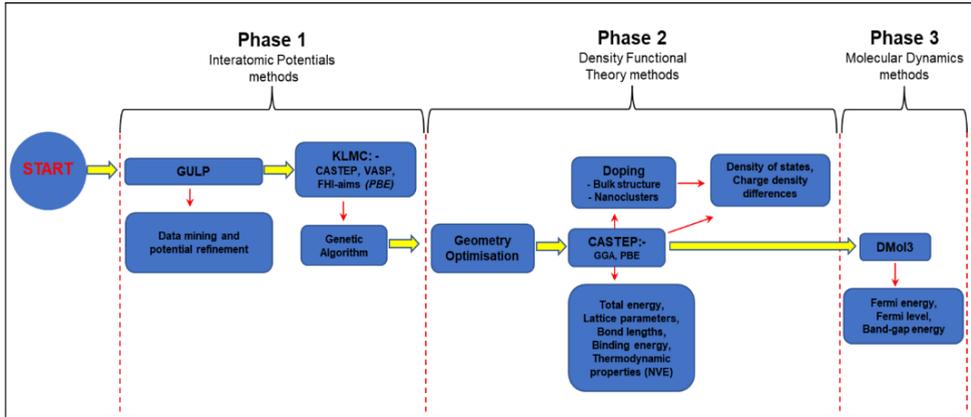


Figure 1: Flow chart of the computational codes used, and the properties measured

Figure 1 illustrates the flow chart of the evolutionary algorithm [17] used to generate the nanoclusters. The chart also displays the codes used and the properties measured.

3. Results and discussions

3.1. Bulk structure optimisation and doping

We report the equilibrium properties and the effect of doping with cobalt doping for both the bulk β -MnO₂ and the resulting nanocluster. This follows from the atomistic study of dopant site-selectivity that was carried out previously and succeeded in enhancing the stability and conductivity of other doped complexes [18].

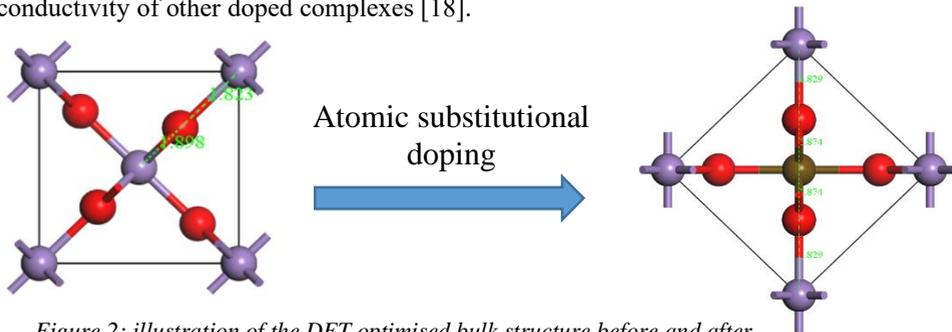


Figure 2: illustration of the DFT optimised bulk structure before and after substitutional doping by cobalt

Cobalt doping produced a more compact structure which is ascribed to the shorter bond lengths (see table 1). The observed shorter bond lengths were obtained when the substitutional doping was performed on the central manganese atom as opposed to the exterior corner manganese atoms with a lesser coordination.

Table 1: Structural properties comparing the pure and the Co doped bulk structures

	Symmetry (Space group)	E_B (eV/at om)	Cell volume (\AA^3)	Density (g/cm^3)	Lattice parameters (\AA)		Bond lengths (\AA)	
					a = b	c	centre Mn/x-O	corner Mn/x-O
Pure β - MnO ₂	P4 ₂ /mnm (D4H-14)	-5.08	53.98	4.99	4.40	2.80	1.90	1.82
Mn/Co	Cmmm (D2H-19)	-5.17	53.62	5.51	4.33	2.86	1.87	1.83

It is clear from table 1 and figure 2, that doping with cobalt stabilizes β -MnO₂ bulk structure. The doped structure is more stable with a lower binding energy (E_B) of -5.17 eV/atom. Furthermore, the structure is more compact since it has a smaller cell volume of 53.62 \AA^3 and lower lattice parameters for a and b . It was also observed that the doped bulk structure has also undergone a migration in the space group from P4₂/mnm (D4H-14) to Cmmm (D2H-19) but preserved the tetragonal symmetry.

3.2. Electronic properties of the MnO₂ nanoclusters

The electronic properties were deduced from molecular dynamics calculations performed using the D-Mol³ [16]. The most stable nanocluster comprised of three manganese atoms and six oxygen atoms (9 atoms in total) was selected for further analysis. This represents an opportunity to investigate the growth of the nanoclusters because the unit bulk structure has six total atoms. An important property of interest in this paper is the band-gap energy which measures the energy difference between the valence and conduction bands.

Table 2: Doping of the most stable n3 nanocluster with the cobalt dopant

	Pure IP n3-01	Pure DFT n3-01	Co-doped n3-01 nanocluster
Fermi Energy eV	-7.21	- 6.49	- 6.30
DFT energy gap eV	0.72	0.42	0.14
valence band eV	-7.21	- 6.49	- 6.30
conduction band eV	-6.49	- 6.07	- 6.16
binding energy (eV/atom)	-3.97	- 4.44	- 4.55

Table 2 compares results calculated using D-Mol³ [16] for nanoclusters generated using IP and those optimized using DFT. This was done to check which structures are more stable. Clearly, the DFT based nanoclusters were more favourable due to their lower binding energy. The cobalt doping was conducted on the most stable nanoclusters (optimized using DFT).

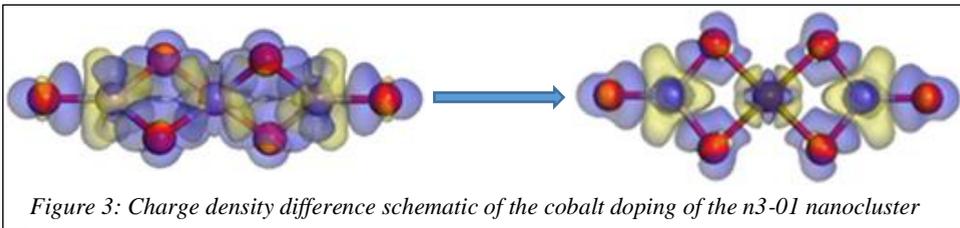
From table 2, it is observed that the undoped DFT optimised nanocluster is a better electrical conductor as it has a decreased band-gap energy from 0.72 eV for the IP generated nanocluster to 0.42 eV for the DFT optimised nanocluster. The binding energy has also improved to -4.44 eV/atom, showing that the DFT optimised nanocluster is more stable and correlates well with results reported by Zhai *et al.* [19]. This proves the efficacy of DFT techniques in improving IP calculations, in good agreement well with previous studies [11].

The Co-doped nanocluster displays further improvements whereby the pure DFT energy gap decreased from 0.42 eV to 0.14 eV after cobalt doping. This further highlights the efficacy of doping on the stability and conductivity of MnO₂ nanostructures.

Table 3: Partial atomic charges of the cations in the most stable n3 nanocluster

Specie	Mulliken	Hirshfeld	Specie	Mulliken	Hirshfeld
Mn1	1.42	0.39	Mn1	1.57	0.40
Mn2	1.49	0.32	Co	0.57	0.19
Mn3	1.42	0.39	Mn3	1.57	0.40
Total	4.33	1.1		3.71	0.99

Table 3 compares the partial atomic charges of the cations in the pure undoped n3 nanocluster and the Co-doped nanocluster. Analysis of the total charges shows that the Co-doped nanocluster has lower net positive charge indicating better electrical conduction in the doped nanocluster system.



The charge density difference analysis in figure 3 shows the weaker ionic bonding in the Co-doped nanocluster as opposed to the stronger covalent bonding in the undoped nanocluster. This is because there are visible gaps between the charge density regions of the Mn and O atoms whereas there is a prevalence of overlapping charge density regions in the pure n3 nanocluster. More importantly, it should be noted that, 100% pure compounds do not exist in nature because all naturally occurring ores contain some sort of impurities, defects, or other foreign elements [20] hence the importance of investigating doping even though doped compounds display some weaknesses when compared with pure compounds.

4. Conclusion

A combination of the Buckingham potential and the 12-6 Lennard-Jones potential was successfully utilised to generate a bulk structure that showed a good correlation with other previous studies. It was also shown that doping was preferential on the central manganese atom which had the higher coordination as compared to the manganese atom at the edge of the bulk structure. The atomistic substitutional method of doping was shown to produce the most stable and compact bulk structure. Cobalt has also shown some promising properties especially the improving the conductivity of the nanoclusters due to the decreased band-gap energy. The electronic charge density profiles however displayed weaker ionic bonding patterns when cobalt was used, hence it is recommended to investigate other dopants such as nickel which has shown positive results in other studies [21]. A combination of other dopants with cobalt at a lower concentration is also recommended to explore the effectiveness of codoping. The use of DFT based techniques is also recommended since it provided results showing enhanced stability and compactness of the nanocluster.

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