

FIRST-PRINCIPLES MODELLING OF N-DOPED Co_3O_4 G.A. Kaptagay¹, Yu.A. Mastrikov², E.A. Kotomin²¹ Kazakh State Women's Teacher Training University, Almaty, Kazakhstan² Institute of Solid State Physics, University of Latvia

N-doped Co_3O_4 is a promising electrocatalyst. By means of first-principles calculations, various concentrations and spatial arrangements of N_o atoms were modelled. Mutual interaction of the dopant atoms was analysed with respect to single N_o atom. Charge redistribution, caused by doping, was calculated.

Keywords: Co_3O_4 , OER, electrocatalyst

1. INTRODUCTION

Oxygen Evolution Reaction (OER) is the essential process for many rapidly developing applications, such as energy conversion and storage [1]. Water splitting devices, some types of fuel cells as well as rechargeable batteries require an effective OER electrocatalyst. Performance of the catalyst depends on overpotential. Noble metal oxides RuO_2 and IrO_2 with low overpotential demonstrate high performance [2]. The cost of these materials, however, limits their usage. Relatively low overpotential of Co_3O_4 makes it a low-cost alternative of noble metal-based catalysts for OER [3], [4].

Numerous works show that overpotential of oxide catalyst can be reduced by doping [5]–[7]. Our earlier investigation confirms that doping Co_3O_4 by fluorine reduces overpotential, resulting in enhancement of catalytic activity [8]. Recent experimental study [9] demonstrates that doping Co_3O_4 by nitrogen, in the combination with oxygen vacancies, reduces overpotential, improving the overall electrocatalytic activity for OER.

Modelling of the surface reactions requires a preliminary study on the N-doped Co_3O_4 bulk. Analysing interaction energies of N atoms in Co_3O_4 , we predict the most favourable spatial arrangement patterns for the dopant. Calculated electron charge redistribution reveals in detail the interaction between nitrogen atoms and Co_3O_4 .

2. METHOD AND MODEL

Calculations were performed using the DFT method [10], as implemented in the computer code VASP 5.4 [11]. Applicability of the method to the system under study was already tested [8]. Core electrons were substituted by the US potentials with the PAW method [12] applied.

Table 1

US PAW Potentials of Co and O

Element	Free electrons	E_{cutoff} , eV
Co	$4s^13d^8$	267.968
O	$2s^22p^4$	400.000
N	$2s^22p^3$	400.000

Exchange-correlation was described by the PBE functional [13]. The Hubbard correction $U-J=3\text{eV}$ [14] was applied to d -electrons of Co_{tet} as well as Co_{oct} atoms. Spin polarization was implemented in the AAF order, alternating on the Co_{tet} planes. For defects modelling cubic 56-atom supercell model was used. Brillouine zone [15] was sampled with the $2\times 2\times 2$ Monkhorst-Pack [16] scheme. Plain-waive basis set has the kinetic energy cut-off of 550eV. Charge redistribution was analysed by the Bader method [17], as implemented by Henkelmann et al. [18], [19].

Co_3O_4 has a structure of normal spinel, symmetry group 227 [20]. The tetragonal $8a$ sites are occupied by Co^{2+} , and the octahedral $16d$ sites by Co^{3+} . O^{2-} ions occupy $32e$ sites.

Doping by nitrogen was performed by substitution of oxygen atoms. Four concentrations were tested – 1, 2, 4 and 8 N per 32(O+N) atoms. There are five non-equivalent distances between 32 e sites in the supercell – 1–4 and 6NN (32e-32e). Some coordination spheres are split to the sub-spheres with a small deviation in distances as shown in Fig. 1.

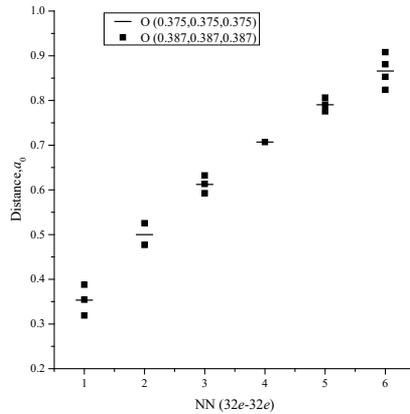


Fig. 1. Nearest neighbours of 32e-32e sites of Co_3O_4 structure, symmetry group 227.

Two N atoms were placed at each sub-sphere of the 1NN coordination sphere. For the 2NN single calculation was performed at the distance of the first sub-sphere. Two N atoms were also placed at the largest possible distance within the model supercell – 6NN, first subsphere. Four N atoms were arranged in three different configurations, as shown in Table 2.

Table 2

12.5% N Concentration Configurations. Distances between N_o in NN (32e-32e)

Conf.1	N_o	N_o	N_o	N_o	Conf.2	N_o	N_o	N_o	N_o
N_o	0	6	4	2	N_o	0	1	4	1
N_o		0	2	4	N_o		0	1	4
N_o			0	6	N_o			0	1
N_o				0	N_o				0

Conf.3	N_o	N_o	N_o	N_o
N_o	0	4	4	4
N_o		0	4	4
N_o			0	4
N_o				0

Nanorod was created, by placing N atoms in line, along the [110]. All N atoms in the same line are the 1NN. The smallest distance between the parallel rods is 3NN (Table 3).

Table 3

25% N Concentration Configurations. Distances between N_o in NN (32e-32e)

	N_o							
N_o	0	1	4	1	4	3	3	4
N_o		0	1	4	3	4	4	3
N_o			0	1	4	3	3	4
N_o				0	3	4	4	3
N_o					0	1	1	4
N_o						0	4	1
N_o							0	1
N_o								0

3. RESULTS

Two N_o atoms, placed at various distances, exhibited predominantly repulsive interaction, except for the smallest possible distance (-0.02eV). The absolute energy values, however, do not exceed 0.1 eV, which characterises the N_o - N_o interaction in Co_3O_4 as neutral (Fig. 2).

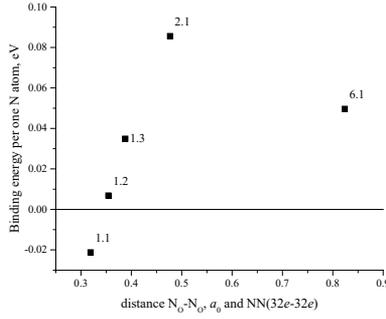


Fig. 2. Binding energy between two N_O doping atoms in Co_3O_4 , per N_O atom, depending on the distance.

The N_O - N_O interaction at higher concentrations strongly depends on a particular configuration of the doping atoms (Fig. 3). The lowest energy of -0.03eV corresponds (Conf. 2, Table 2) to a high number of the N_O - N_O 1NN. The most uniform distribution of N_O (Conf. 3 Table 2) gives intermediate repulsion energy of 0.09eV . The highest binding energy of three calculated configurations of 0.125% is 0.12eV , which can be explained by the presence of the N_O - N_O 2NN bonds (Conf. 1 Table 2) with relatively strong repulsion (Fig. 1).

Aligned in line (Table 3), N_O atoms create stable nano-chains with the binding energy of 0.02eV per atom. Obviously, in such a configuration the primary interaction occurs between the 1NN.

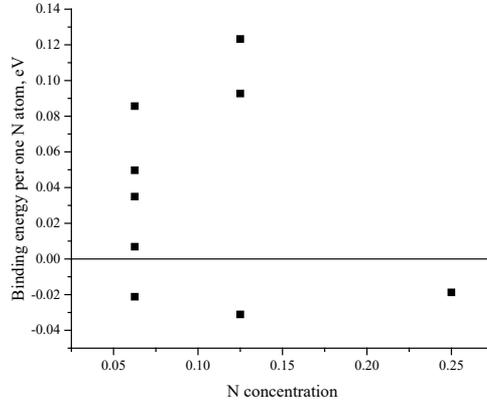


Fig. 3. Binding energy between N_O doping atoms in Co_3O_4 , per N_O atom.

Electron charge redistribution, in comparison with undoped Co_3O_4 , is localised on the nearest to the dopant Co cations. With respect to oxygen anion, nitrogen anion in Co_3O_4 is less negative. Therefore, Co cations become less positive. Configurations with the lowest binding energy values demonstrate relatively high charge transfer (-0.05e) from the N_O - N_O 1NN pairs to the nearest Co_{tet} - Table 4 (N 1.1NN, Table 2 Conf.2, Table 3 Conf.). For the configuration with the strongest repulsion between N_O - N_O (N 2.1NN), the largest charge value -0.07e was observed on Co_{oct} .

Table 4

Electron Charge Redistribution on Co_{tet} and Co_{oct} Cations in e , with respect to the Pure Co_3O_4 . Multiplicity of Co cations is given per N_O atom.

single N		
mult.	N	0.02
1	Co_{tet}	-0.02
3	Co_{oct}	-0.02

N 1.1NN		
mult.	N	0.03
1	Co_{oct}	-0.05
1	Co_{oct}	-0.02

N 1.2NN		
mult.	N	0.03
1	Co_{tet}	-0.02
1	Co_{oct}	-0.02
1	Co_{oct}	-0.02
0.5	Co_{oct}	-0.03

N 1.3NN		
mult.	N	0.02
2	Co_{oct}	-0.02
1	Co_{oct}	-0.02

N 2.1NN		
mult.	N	0.03
2	Co_{oct}	-0.02
0.5	Co_{oct}	-0.07

N 6.1NN		
mult.	N	0.02
1	Co_{tet}	-0.02
3	Co_{oct}	-0.02

Table 2, Conf.1		
mult.	N	0.03
0	Co_{tet}	
2	Co_{oct}	-0.03
0.5	Co_{oct}	-0.05

Table 2, Conf.2		
mult.	N	0.02
0.5	Co_{tet}	-0.06
1	Co_{oct}	-0.01
1	Co_{oct}	-0.03

Table 2, Conf.3		
mult.	N	0.03
1	Co_{tet}	-0.03
3	Co_{oct}	-0.03

Table 3. Conf.		
mult.	N	0.03
0.5	Co_{tet}	-0.06
1	Co_{oct}	-0.04
1	Co_{oct}	-0.02

4. CONCLUSIONS

Small differences ($<0.15\text{eV}$) in interaction energies between various spatial arrangements indicate that in Co_3O_4 oxygen is easily substituted by nitrogen and at room temperature N atoms can be distributed in the material randomly. Repulsive interaction ($<0.13\text{eV}$) between the dopant atoms has been observed for most concentrations and configurations of N_O in Co_3O_4 , except for the 1NN. All structures with dominating 1NN interaction, consistently exhibited energetic stability (-0.02 - 0.03eV), in contrast to other configurations. Binding between two nearest N_O cations is facilitated by an intense electron charge exchange ($0.05e$) with the nearest to both dopant atoms Co_{tet} . Depending on a particular configuration, high charge transfer ($>0.05e$) may show both Co_{tet} and Co_{oct} atoms. The performed calculations create a solid base for the further modelling of OER on N-doped Co_3O_4 surface.

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N-LEĢĒTĀ Co₃O₄ MODELĒŠANA PĒC PIRMAJIEM PRINCIPIEM

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K o p s a v i l k u m s

N-leģētais Co₃O₄ ir perspektīvs elektrokatalizators. Izmantojot pirmā principa aprēķinus, tika modelētas dažādas N_O atomu koncentrācijas un telpiskās struktūras. Piemaisījuma atomu savstarpējā mijiedarbība tika analizēta attiecībā uz mono N_O atomu. Aprēķināts piemaisījumu radītais lādiņa pārdalījums.

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