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ENERGY EFFICIENCY OF THE FLUORINE-DOPED Co_3O_4 (100) SURFACE FOR WATER DISSOCIATION

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We report the results of theoretical investigations of water adsorption on undoped and fluorine-doped Co_3O_4 (100) surface by means of the plane-wave periodic density functional theory (DFT) calculations combined with the Hubbard- U approach and statistical thermodynamics. We discuss the effect of fluorine-doping of the Co_3O_4 (100) surface and calculated oxygen evolution reaction overpotential based on the Gibbs free-energy diagram of undoped and F-doped surfaces.

Key words: Co_3O_4 , spinel oxide, water sorption, free-energy diagram, surface

Introduction

Today, we observe worldwide significant progress in the development of the transition to "green" energy. Such development in the countries is connected not only with the strongest negative impact on the environment from emissions, but also with the advanced strategic development of the economies of these countries in this area. Possession of such technologies makes the country's economy more attractive to investments in the energy sector.

Consuming growth not - renewable fossil energy resources of which "thermal pollution", bursts in the atmosphere of products of burning and fast exhaustion of power sources is result do perspective creation of highly effective technologies of use of sustainable that first of all includes development of methods of conversion of solar energy.

Process splitting of water takes place with energy absorption as a result of which the free energy of Gibbs increases by 237 kJ of mole⁻¹. This additional energy necessary for photocatalytic and photoelectrochemical decomposition of water is provided by means of energy of sunlight. For this purpose in photoelectrochemical cells as the cathode noble metals on which there is a restoration of the hydrogen formed in the course of water expansion, and as the anode on which there is a decomposition of water under the influence of sunlight are used, semiconductors in which under the influence of sunlight are excited an electron - hole couples are used. These excited charge carriers in the process of a relaxation are transferred to surface-active parts where participate in water splitting process. For achievement of the greatest efficiency process of diffusion of photoexcited charge carriers on the surface of the catalytic agent shall prevail over process of a recombination an electron - hole couples. Besides, the semiconductor anode shall absorb an electromagnetic radiation in a visible part of a range to be effective for sunlight absorption. Taking into account the specified requirements one of perspective semiconductors for practical application as material of the anode are oxides of transition metals. One of such stable and cheap materials is the cobalt oxide having, in addition, the narrow width of the forbidden band.

Co_3O_4 -based materials are widely used for Lithium-Ion Batteries [1], Zink-Air Batteries, treatment of waste gases [2,3] and other energy applications. In particular, Co_3O_4 is known as a low-cost high-performance catalyst for Oxygen Reduction Reaction (ORR)[4] and Oxygen Evolution Reaction (OER) [5].

Co_3O_4 is easily available and thermodynamic stable oxide in a wide interval of temperatures and conditions with rich concentration of oxygen. Crystal Co_3O_4 has structure of spinel (space group) with the half-filled sites in an octahedral environment of Co^{3+} , and cobalt ions in a tetrahedral environment of Co^{2+} .

Ion Co is the transition element having incomplete configurations of d-orbitals. For the transition elements existence of a set of the connections having a number of physical and chemical properties is peculiar. It is caused by presence at the transition elements of incomplete d-electron shells, and, as a result, a wide set of the valence states of atoms. A specific place among all compounds of d-metals is held by oxides and complex connections on their basis. Ability of the transition elements to change the valence state, presence of the lone couples of electrons at oxygen atoms, ease of exchange of oxygen with the environment,

different impurity centers create variety of defects which, forming the discrete levels in the forbidden band, significantly influence physical and chemical properties of the considered substances [6].

Oxygen Reduction Reaction and Oxygen Evolution Reaction also are main stage of the catalyst processes in metal-air membranes and water splitting. Numerous attempts have been made in order to decrease the energetic efficiency of these reactions maintained on the different catalysts by various dopants. Obtained data are in a good agreement with experimentally obtained results [7]. Another promising doping material for Co_3O_4 is nitrogen. Xu et.al in their experimental work discuss production of N-doped Co_3O_4 nanosheets [8]. Increased surface area in combination with oxygen vacancies lead to enhancement of electrocatalytic activity for OER.

Method and Surface Model

Computational Methodology and Thermodynamic Description

The calculations have been performed using the *ab initio* plane wave computer code VASP [9,10] using the the projector-augmented plane-wave (PAW) formalism [11] in conjunction with PBE (Perdew – Burke - Ernzerhof) GGA exchange-correlation functional [12]. The standard Monkhorst-Pack grid with the $4 \times 4 \times 4$ sampling mesh for the bulk calculations and the $2 \times 2 \times 1$ for the slab calculations was used [13] along with the cutoff energy of 600 eV and the Methfessel-Paxton [14] smearing with $\sigma=0.1$ eV. In performed calculations for the periodic slab model (infinite in two dimensions) the positions of all ions were fully relaxed, to render the net forces acting upon the ions smaller than $1 \times 10^{-2} \text{eV} \cdot \text{\AA}^{-1}$. In order to avoid the interaction between periodically translated images along the direction normal to the surface, we used vacuum gap of 12 \AA.

One unit cell in the bulk contains 2 formula units, i.e. 14 ions. In this study, we focus on the water interaction with the Co_3O_4 (100) surface. The layer was defined by the subset of the ions lying in the same plane perpendicular to the given Miller index in the idealized spinel structure.

We simulated symmetric slabs with an odd number of layers, for which the total dipole moment is zero. As the number of slab layers exceeds seven, the atomic relaxation and the surface energy finally converge. This slab is stoichiometric and symmetric along the surface normal plane. Totally, the 7-plane slabs contain 70 ions. Thermodynamic description of water dissociation process and structure of (100) surface, positions for introduction fluorine atom was explained and schematically was shown in our previous works [15].

Results

Water adsorption. In the present study, we studied the catalytic activity of Co_{2c}^T and Co_{5c}^O sites for H_2O adsorption on the pure and F-doped $\text{Co}_3\text{O}_4(100)$ surface. To investigate the effect of fluorine doping, one 3-fold O_{3c} (with one missing bond to Co^T) surface oxygen atom was substituted by a fluorine ion (the relative $\text{Co}_{2c}^T - \text{F}$ distance are 4.12 \AA and 2.14 \AA for $\text{Co}_{5c}^O - \text{F}$). Therefore, the F dopant concentration was 12.5%. After fluorine doping the slab structure was reoptimized. The calculations predict no essential lattice relaxation around the substitutional F ion: the change of the equilibrium bond length between O and catalytic active cobalt, $\text{Co}_{2c}^T - \text{O}_{3c}$ is larger than $\text{Co}_{2c}^T - \text{F}$ bond by $\Delta l = 0.001$ \AA only. The effective F ion charge was $-1.01e$, slightly larger than $-0.96e$ for the host O ion.

We have investigated a large number of starting geometries of water ad-molecule for detection of the most stable adsorption configuration. The most stable sites for water adsorption were found on the most unsaturated Co ions. For water adsorption simulations molecule was added on the top of Co_{2c}^T and Co_{5c}^O ions at perfect and fluorine doped Co_3O_4 (100) surface.

The adsorption and dissociation energy of water molecules are calculated as

$$\Delta E_{\text{ads}} = E_{\text{adsorbate/surface}} - (E_{\text{adsorbate}} + E_{\text{surface}})$$

where $E_{\text{adsorbate/surface}}$, $E_{\text{adsorbate}}$ and E_{surface} correspond to the total energies of a system formed by the adsorbate at the surface, the isolated adsorbate molecule in gas phase and the bare surface, respectively. In table 1 given basic characteristics of water adsorption process on undoped and fluorine-doped Co_3O_4 (100) $\text{Co}_{0.5}$ -terminated surface. Basic characteristics of water adsorption compared to the analogical dates from ref.[16].

Table 1. Basic characteristics of water adsorption process on undoped and fluorine-doped Co_3O_4 (100) $\text{Co}_{0.5}$ -terminated surface. ΔE_{ads} -adsorption energy; d-dissociative mode; a-associative mode; $d_{\text{Co-O}(\text{H}_2\text{O})}$ -bond length in Å.*denotes present work.

Adsorption Center Co_{2c}^T								
Undoped					F- doped			
$\Delta E_{\text{ads}}/\text{eV}$		Adsorption type		$d_{\text{Co-O}(\text{H}_2\text{O})}$		$\Delta E_{\text{ads}}/\text{eV}$		$d_{\text{Co-O}(\text{H}_2\text{O})}$
*	[16]	*	[16]	*	[16]	*	*	*
-1.6	-1.18	d	d	1.85	1.81	-1.66	a	1.62

The binding energies of O, OH and OOH (ΔE_{O} , ΔE_{OH} , ΔE_{OOH}) and the bond lengths on the undoped and F-doped Co_3O_4 (100) $\text{Co}_{0.5}$ -terminated surface are summarized in table 2. We reveal that the binding energies of O^* , OH^* and OOH^* on the cobalt oxide surface, calculated with PBE+ U , scale according to the relation $\Delta E_{\text{OOH}^*} = \Delta E_{\text{OH}^*} + 3.2$ within ± 0.4 eV as was shown in ref.[17].

Table 2. The binding energies of O, OH and OOH (ΔE_{O} , ΔE_{OH} , ΔE_{OOH} in eV) and bond length on the undoped and F-doped Co_3O_4 (100) $\text{Co}_{0.5}$ -terminated surface. d_x -is bond length in Å, * denotes adsorbate atom.

	ΔE_{O}	$d_{\text{Co-O}}$	ΔE_{OH}	$d_{\text{Co-O}(\text{H})}$	ΔE_{OOH}	$d_{\text{Co-O}}$	ΔE_{O}	$d_{\text{Co-O}}$	ΔE_{OH}	$d_{\text{Co-O}(\text{H})}$	ΔE_{OO}	$d_{\text{Co-O}}$
				$d_{\text{O}^*(*)-\text{H}}$		$d_{\text{O}^*(*)-\text{H}}$				$d_{\text{O}^*(*)-\text{H}}$		$d_{\text{O}^*(*)-\text{O}}$
	Adsorption Center Co_{2c}^T						Adsorption Center Co_{5c}^0					
Undoped	2.23	1.59	-0.11	1.78	3.03	1.81	2.29	1.86	-0.09	1.79	3.26	2.08
				0.97		0.98			0.97			0.98
						1.47						1.45
Fluorine doped	1.81	1.6	-0.54	1.77	2.35	1.81	1.8	1.85	-0.19	1.80	2.75	2.09
				0.97		0.98			0.97			0.98
						1.48						1.47

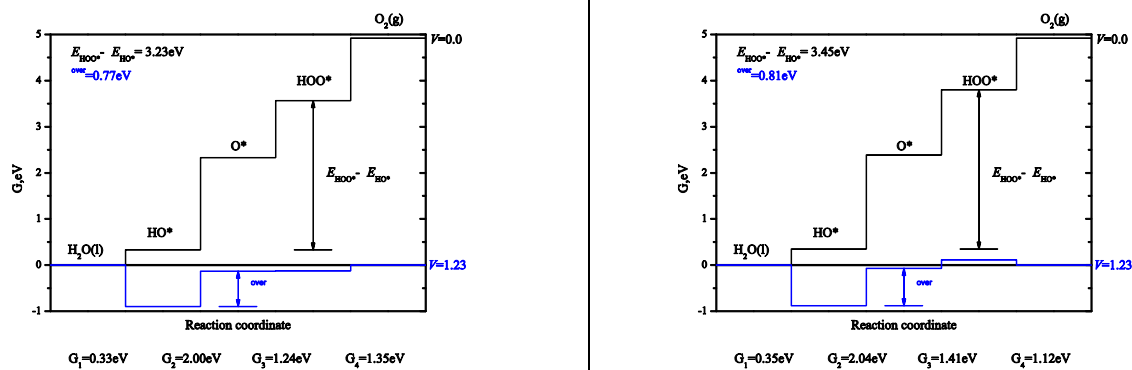
We have calculated the Gibbs free energy changes along the reaction pathway using the computational standard hydrogen electrode (SHE) allowing us to replace a proton and an electron with the half a hydrogen molecule at $V=0$ V vs SHE. The theoretical overpotential is found according to the standard relation

$$\eta = \max[\Delta G_i]/e - 1.23[\text{V}] \quad (2)$$

Undoped surface

a) Co_{2c}^T site

b) Co_{5c}^0 site



Fluorine doped surface

c) Co_{2c}^T site

d) Co_{5c}^O site

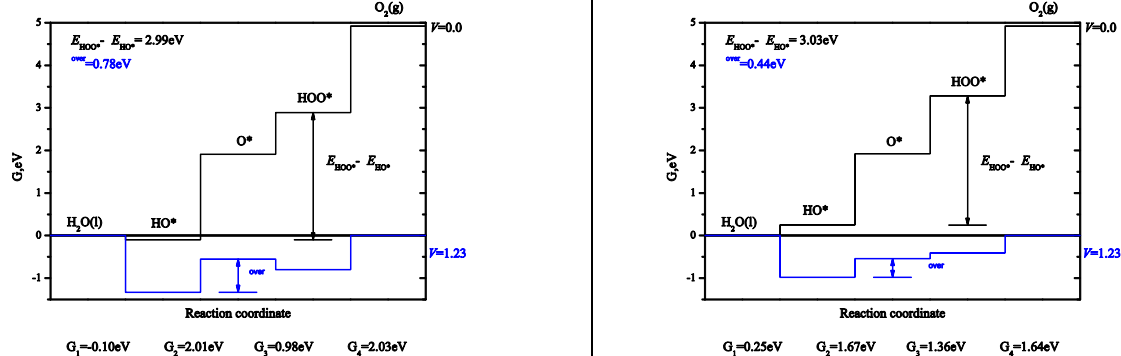


Figure 1. Free-energy diagram at pH=0 and T=298 K for the four steps of the OER at $V=0$ and $V=1.23$ V. Results for the Co_{2c}^T and Co_{5c}^O sites at 0.2ML water coverage for undoped and F-doped surfaces shown; For each case the characteristically difference $\Delta E_{OOH^*} - \Delta E_{OH^*}$ [13,4] and η^{over} are shown.

Figure 1 presents the free energy changes of reactions of adsorption of water molecule and intermediate products of dissociation based on DFT+ U calculations of adsorbed intermediates on the perfect and fluorine-doped $Co_3O_4(100)$ surface at 0.2ML water coverage. The calculations suggest that the theoretical overpotentials for water adsorption on the site Co_{2c}^T on the doped and F-doped surfaces are nearly the same (0.77-0.78 V). In contrast, on Co_{5c}^O site at undoped surface the overpotential is 0.81 V, with the formation of O^* as the determining step. However, at fluorine-doped surface the water adsorption on Co_{5c}^O site shows much smaller overpotential, only 0.44 V, with the same potential determining step as for the undoped surface. In this case the adsorption energy of O^* species is strongly reduced relative to that on undoped surface, which results in decrease of the Gibbs free energy.

Figure 2 shows maps of the total and difference electron density. It is seen from the figures that an electron charge accumulation is observed on the Co in connection with the redistribution of the electron charge in the local environment of the impurity fluorine atom. When fluorine is introduced, most of the charge is distributed to neighboring cobalt ions. In addition, the introduction of fluorine leads to the polarization of neighboring ions. From the surface of the crystal fluorine atom is gained 0.77e.

The change in the adsorption energy on the fluorine doped surface is due to the increase in electrostatic attraction between the adsorbed atoms and cobalt, over which the water molecule and the intermediate dissociation products are adsorbed. Energy of adsorption of intermediate products of splitting upon adsorption on Co_{2c}^T is more stable than adsorption on Co_{5c}^O . For the two ions of cobalt on the fluorine-doped surface, the energy of adsorption increases from 0.1 to 0.52 eV compared to the undoped surface.

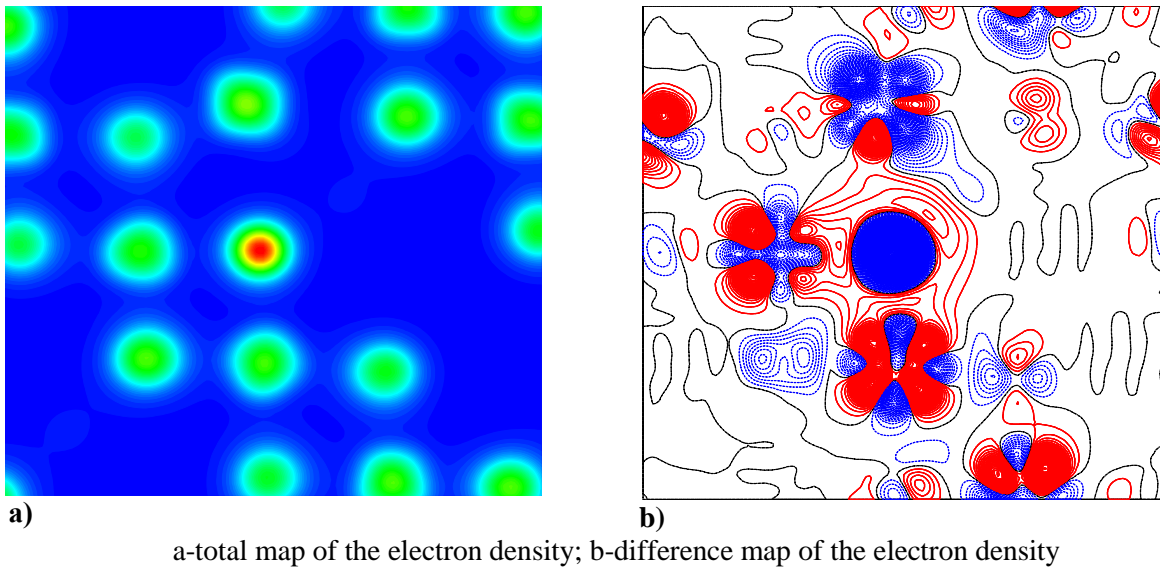
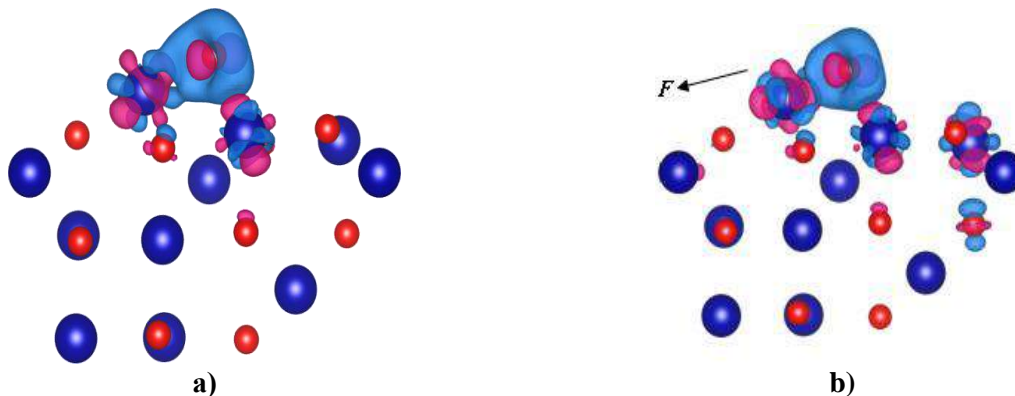


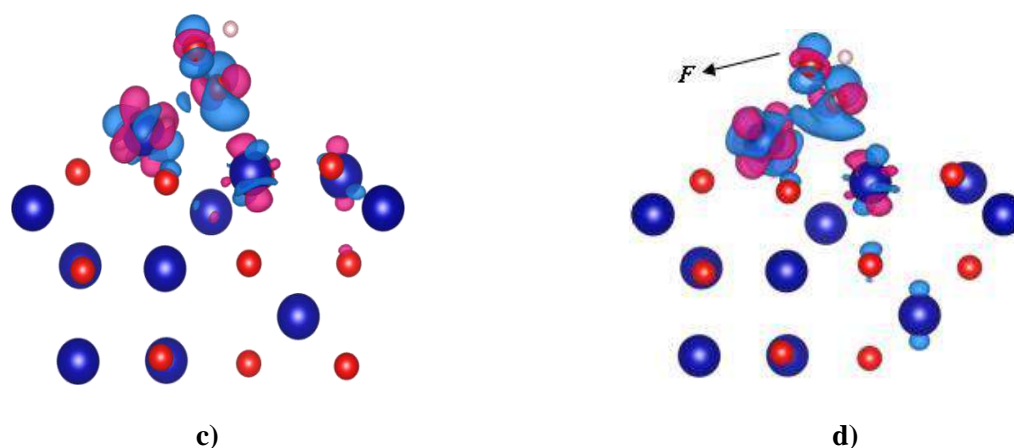
Figure 2 – Map of the electron density distribution of electrons in the introduction of fluorine on (100) surface of cobalt oxide

Note - Blue and red color-excess and lack of electronic density. The difference map was obtained by subtracting the surface density without impurity from the density of the fluorine-doped surface. The increment of density of $0.018 e/\text{\AA}^3$

The analysis of the change of free Gibbs energy in the adsorption of water on the surface (100) showed that the presence of fluorine impurities leads to approximately a twofold decrease in the excess potential compared to the clean surface.

Figure 3 shows the difference map of the electron density in the adsorption of atomic oxygen on a clean and fluorine-doped surface (figure 3a and 3b). Also, the difference map of the electron density in the adsorption of OOH hydroperoxide radical on a clean and fluorine-doped surface (figure 3c and 3d). Difference maps were obtained by subtracting the sum of the density of the adsorbent and adsorbate from the total density. From the figures it is seen that there is an excess charge on Co_{5c}^0 adsorption of atomic oxygen on the ion Co_{5c}^0 on the fluorine-doped surface compared to the clean surface value, there is a slight acquiring of electronic charge of $0.03e$ in connection with the redistribution of electronic charge in the local environment of the impurity fluorine atom. At the same time, during adsorption of the OOH radical, the accumulation of an electronic charge of $0.11e$ on Co_{5c}^0 is greater than in the case of adsorption of O. During the introduction of fluorine, most of the charge is distributed on neighboring cobalt ions.





a - map of the electron density of the surface (100) at adsorption of atomic O; b-map of the electron density of fluorine doped surface (100) at adsorption of atomic O; c-map of the electron density of the surface (100) at OOH adsorption; d-map of the electron density of fluorine doped surface (100) at OOH adsorption

Figure 3 - map of electron density distribution during adsorption of atomic O and radical OOH on pure and fluorine doped surface (100) of cobalt oxide with density increment $0.018 e/\text{\AA}^3$

Conclusions

Using accurate DFT+*U* calculations, we have shown that water can be dissociatively adsorbed on the tetrahedrally coordinated Co^{2+} ions on the Co_3O_4 (100) surface. From the computed Gibbs free-energy changes along the OER, we found that the fluorine-doped $\text{Co}_{0.5}$ -terminated Co_3O_4 (100) surface is catalytically active.

We found also that at the Co_{5c}^0 site on fluorine-doped surface theoretical overpotential on the Co_3O_4 (100) surface is considerably reduced, from 0.81 to 0.44 V. Due to large overpotential, the OER efficiency on the pure Co_3O_4 substrate is expected to be low and thus F doping does improve it. This implies that fluorine-doped Co_3O_4 is active for electrochemical oxidation of water, in full agreement with experimental observations. In the forthcoming paper we will discuss N doping effects.

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ФТОРМЕН ҚОСПАЛАНҒАН Co_3O_4 (100) БЕТІНІҢ СУДЫ ЫДЫРАТУДАҒЫ ЭНЕРГЕТИКАЛЫҚ ТИІМДІЛІГІ

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Мақалада түйіндегі Хаббард жуықтауымен электрон-электрондық корреляцияны ескере отырып тығыздық функционалы теориясы (ТФТ) аясында кобальт оксидінің Co_3O_4 (100) бетінде судың адсорбциялануы мен ыдырауын теориялық зерттеудің нәтижелері баяндалған. Көміртегі қоспасы есебінен болатын беттің катализдік қасиеттерінің өзгеру эффектілері талданған және су молекуласы ыдырауының электрохимиялық реакциясы үшін Гиббстің еркін энергиясының шамасы есептелген. Көміртегі қоспасын енгізудің таза бетпен салыстырғанда асқын потенциалды айтарлықтай азайтатындығы бет иондары мен қоспа атомының арасында заряд тасымалдану арқылы түсіндірілді.

Түйін сөздер: Co_3O_4 , кобальт шпинелі, су адсорбциясы, еркін энергия адсорбциясы, бет

ЭНЕРГОЭФФЕКТИВНОСТЬ ФТОР ДОПИРОВАННОЙ (100) ПОВЕРХНОСТИ Co_3O_4 ДЛЯ РАСЩЕПЛЕНИЯ ВОДЫ

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В статье представлены результаты теоретического исследования адсорбции воды на чистой и фтор допированной пластине Co_3O_4 (100) в рамках теории функционала плотности (ТФП) комбинированной с приближением Хаббарда- U и статистической термодинамикой. Обсуждены эффекты изменения каталитических свойств пластины, возникающие за счет примеси фтора и рассчитаны избыточные потенциалы на основе схемы свободной энергии Гиббса на чистой и фтор допированной пластине.

Ключевые слова: Co_3O_4 , шпинель кобальта, адсорбция воды, диаграмма свободной энергии, поверхность