ISSN 2518-1726 (Online),
ISSN 1991-346X (Print)

ҚАЗАҚСТАН РЕСПУБЛИКАСЫ
ҰЛТТЫҚ ҒЫЛЫМ АКАДЕМИЯСЫНЫҢ
Әль-фараби атындағы Қазақ ұлттық университетінің

# ХАБАРЛАРЫ

# ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
Казахский национальный университет
имени Аль-фараби

# NEWS

OF THE NATIONAL ACADEMY OFSCIENCES
OF THE REPUBLIC OF KAZAKHSTAN
Al-farabi kazakh
national university

## SERIES
## PHYSICO-MATHEMATICAL

**5 (327)**

**SEPTEMBER-OCTOBER 2019**

PUBLISHED SINCE JANUARY 1963

PUBLISHED 6 TIMES A YEAR

ALMATY, NAS RK

**«ҚР ҰҒА Хабарлары. Физика-математикалық сериясы».**

**ISSN 2518-1726 (Online), ISSN 1991-346X (Print)**

Меншіктенуші: «Қазақстан Республикасының Ұлттық ғылым академиясы» РҚБ (Алматы қ.)
Қазақстан республикасының Мәдениет пен ақпарат министрлігінің Ақпарат және мұрағат комитетінде 01.06.2006 ж. берілген **№5543-Ж** мерзімдік басылым тіркеуіне қойылу туралы куәлік

Мерзімділігі: жылына 6 рет.
Тиражы: 300 дана.

Редакцияның мекенжайы: 050010, Алматы қ., Шевченко көш., 28, 219 бөл., 220, тел.: 272-13-19, 272-13-18, http://physics-mathematics.kz/index.php/en/archive

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Типографияның мекенжайы: «Аруна» ЖК, Алматы қ., Муратбаева көш., 75.

**«Известия НАН РК. Серия физико-математическая».**

**ISSN 2518-1726 (Online), ISSN 1991-346X (Print)**

Собственник: РОО «Национальная академия наук Республики Казахстан» (г. Алматы)
Свидетельство о постановке на учет периодического печатного издания в Комитете информации и архивов Министерства культуры и информации Республики Казахстан **№5543-Ж**, выданное 01.06.2006 г.

Периодичность: 6 раз в год.
Тираж: 300 экземпляров.

Адрес редакции: 050010, г. Алматы, ул. Шевченко, 28, ком. 219, 220, тел.: 272-13-19, 272-13-18,
http://physics-mathematics.kz/index.php/en/archive

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Адрес типографии: ИП «Аруна», г. Алматы, ул. Муратбаева, 75.

**News of the National Academy of Sciences of the Republic of Kazakhstan. Physical-mathematical series.**

**ISSN 2518-1726 (Online), ISSN 1991-346X (Print)**

Owner: RPA "National Academy of Sciences of the Republic of Kazakhstan" (Almaty)
The certificate of registration of a periodic printed publication in the Committee of information and archives of the Ministry of culture and information of the Republic of Kazakhstan N 5543-Ж, issued 01.06.2006

Periodicity: 6 times a year
Circulation: 300 copies

Editorial address: 28, Shevchenko str., of. 219, 220, Almaty, 050010, tel. 272-13-19, 272-13-18,
http://physics-mathematics.kz/index.php/en/archive

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Address of printing house: ST "Aruna", 75, Muratbayev str, Almaty

**NEWS**
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
**PHYSICO-MATHEMATICAL SERIES**
ISSN 1991-346X **https://doi.org/10.32014/2019.2518-1726.67**
Volume 5, Number 327 (2019), 126 – 132

UDC 538.972

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# EVALUATION OF ENERGY EFFICIENCY OF THE NITROGEN-DOPED $Co_3O_4$ (100) SURFACE FOR WATER DISSOCIATION

**Abstract:** $Co_3O_4$ is easily available and thermodynamic stable oxide in a wide interval of temperatures and conditions with rich concentration of oxygen. Also $Co_3O_4$ among oxides of transition metals – useful materials for gas sensors, storage systems of energy and materials of anodes of lithium - ion batteries, zink-air batteriesand other energy applications.

For enhancing energy efficiency of decomposition of water molecules on cobalt oxide surfaces was studied effect of various dopants. One of the promising doping materials for $Co_3O_4$ is nitrogen.

In paper we report the results of theoretical investigations of water adsorption on undoped and nitrogen-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 nitrogen-doping of the $Co_3O_4$ (100) surface and calculated oxygen evolution reaction overpotential based on the Gibbs free-energy diagram of undoped and N-doped surfaces. Results of calculations of the overpotentials of water molecule decomposition on the nitrogen-doped (100) surface of cobaltum oxide demonstrate generally the decreased values in comparison withundoped surface with some deviation on considered steps of decomposition.

**Keywords:** $Co_3O_4$, spinel oxide, water sorption, free-energy diagram, surface.

## 1. Introduction

Nowadays, we know that transition to "green" energy perspectival in ecological and economical view. Advantages of technologies of renewable energy make these problems priority for the scientifically research. So, its lead to intensive development of researches for alternative energy resources.

Today, all the talk about hydrogen energy or even a hydrogen economy is the use of hydrogen as the main energy source for various devices.

One of the methods for producing hydrogen is electrolysis. This is a much more expensive way than getting from hydrocarbons, but it is without thermal pollution.

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 renewables that first of all includes development of methods of conversion of solar energy.

Reaction of dissociation ofwater 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 forelectrode material of electrolyze process used different materials.

$Co_3O_4$ 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 (spatial group) with the semi-filled sites in an octahedral environment of $Co^{3+}$, and cobalt ions in a tetrahedral environment of $Co^{2+}$.

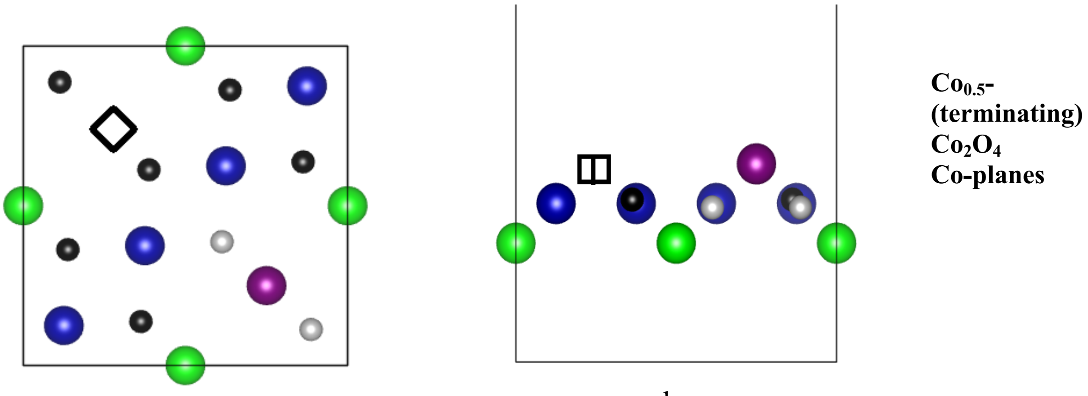
Also $Co_3O_4$among oxides of transition metals – useful materials for gas sensors [1,2], storage systems of energy and materials of anodes of lithium - ion batteries [3],zink-air batteries [4] and other energy applications.

For enhancing energy efficiency of decomposition of water molecules oncobalt oxidesurfaces studied effect of various dopants. One of the promising doping materials for $Co_3O_4$ is nitrogen. Xu et.al in their experimental work discuss production of N-doped $Co_3O_4$ nanosheets [5].

## 2. Method and Surface Model

### 2.1 Computational Methodology and Thermodynamic Description

The calculations have been performed using the *ab initio* plane wave computer code VASP [6] using the the projector-augmented plane-wave (PAW) method [7] in conjunction with PBE (Perdew – Burke - Ernzerhof) GGA exchange-correlation functional [8]. The standard Monkhorst-Pack grid with the $4 \times 4 \times 4$ sampling mesh for the bulk calculations and the $2 \times 2 \times 2$ for the slab calculations was used [9] along with the cutoff energy of 550eV and the Methfessel-Paxton [10] 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 $1 \times 10^{-2}$eV $\cdot$Å$^{-1}$. In order to avoid the interaction between periodically translated images along the direction normal to the surface, we used vacuum gap of 12 Å. As known from our theoretical researches [11] (100) plane was modeled as shown in figure 1.



a b

Figure 1 - $Co_3O_4$ (100) $Co_{0.5}$-terminated surface top view (a) and side view (b). Color coding: $Co^{O}_{5c}$, blue;$Co^{T}_{4c}$, green;$Co^{T}_{2c}$ ,purple;$O_{3c}$ ,black $O_{4c}$, grey; The empty cube indicates Co site.

There are four coordinatively unsaturated 5-fold $Co^{O}_{5c}$, two recessed, fully coordinated 4-fold $Co^{T}_{4c}$, and two protruding 2-fold $Co^{T}_{2c}$. The distance between the nearest $Co^{O}$ ions in a slab is 2.91 Å and the $Co^{T}$ ions are separated by 7.63 Å . There are observed two types of oxygen ions: the 4-fold $O_{4c}$ and 3-fold $O_{3c}$.

### Results.

### Water adsorption

In the present study, we studied water dissociation and adsorption process on the top of $Co^{T}_{2c}$and $Co^{O}_{5c}$ sites on the pure and N-doped $Co_3O_4$(100) surface.

The adsorption and dissociation energy of water molecules are calculated as

$$\Delta E_{ads} = E_{adsorbate/surface} - (E_{adsorbate} + E_{surface}) \quad (1)$$

where$E_{adsorbate/surface}$, $E_{adsorbate}$ 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.Oxygen atoms substituted with nitrogen atoms in four concentrations. There are four concentrations – 1, 2, 4 and 8 N per 32(O+N) atoms. Respectively, nitrogen-doped $Co_3O_4$(100) $Co_{0.5}$-terminated surfaces with four concentration of nitrogen denoted as Configuration 1 ( configuration with 12,5% concentration), Configuration 2 (configuration with 25% concentration), Configuration 3 (configuration with 50% concentration), Configuration 4 (nanorod).

In table 1 given basic characteristics of water adsorption process on undoped and nitrogen–doped $Co_3O_4(100)$ $Co_{0.5}$-terminated surface.

Table 1 - Basic characteristics of water adsorption process on undoped and doped $Co_3O_4(100)$ $Co_{0.5}$-terminated surfaces with different concentration of nitrogen.$\Delta E_{ads}$is adsorption energy; *d* dissociative mode; *a* associative mode; $d_{Co-O(H2)}$-bond length in angstroms

| | **Adsorption Center $Co_{2c}^T$** | | | **Adsorption Center $Co_{5c}^o$** | | |
|---|---|---|---|---|---|---|
| | $\mathbf{\Delta E_{ads}/eV}$ | Adsorption type | $\mathbf{d_{Co-O(H_2O)}}$ | $\mathbf{\Delta E_{ads}/eV}$ | Adsorption Type | $\mathbf{d_{Co-O(H_2O)}}$ |
| perfect | -0.43 | d | 1.84 | -0.47 | a | 2.1 |
| Conf.1 | -0.58 | a | 2.07 | -0.83 | a | 2.04 |
| Conf.2 | -0.39 | a | 2.02 | -0.45 | a | 2.03 |
| Conf.3 | -1.12 | d | 1.90 | -0.28 | a | 1.98 |
| Conf.4 | -0.75 | d | 1.98 | -1.41 | d | 1.95 |

The binding energies of O, OH and OOH ($\Delta E_O$, $\Delta E_{OH}$, $\Delta E_{OOH}$) and the bond lengths on the pure and N-doped $Co_3O_4(100)$ $Co_{0.5}$-terminated surface are given in table 2. We observed that the binding energies of O*, OH* and OOH* on the cobalt oxide surface, calculated with PBE+*U*, scale according to the relation $\Delta E_{OOH*} = \Delta E_{OH*} + 3.2$ within $\pm 0.4$ eV as was shown in ref.[12,13]. In table 2 given the binding energies of O, OH and OOH and bond length on the undoped and N-doped $Co_3O_4(100)$ surface.

Table 2 -The binding energies of O, OH and OOH ($\Delta E_O, \Delta E_{OH}, \Delta E_{OOH}$ in eV) and bond length on the undoped and N-doped $Co_3O_4(100)$ $Co_{0.5}$-terminated surfaces.$\boldsymbol{d_x}$-is bond length in Å, * denotes adsorbate atom.

| | $\Delta E_O$ | $\boldsymbol{d_{Co-O}}$ | $\Delta E_{OH}$ | $\boldsymbol{d_{Co-O(H)}}$<br>$\boldsymbol{d_{O(*)-H(*)}}$ | $\Delta E_{OOH}$ | $\boldsymbol{d_{Co-O}}$<br>$\boldsymbol{d_{O(*)-H(*)}}$<br>$\boldsymbol{d_{O(*)-O(*)}}$ | $\Delta E_O$ | $\boldsymbol{d_{Co-O}}$ | $\Delta E_{OH}$ | $\boldsymbol{d_{Co-O(H)}}$<br>$\boldsymbol{d_{O(*)-H(*)}}$ | $\Delta E_{OOH}$ | $\boldsymbol{d_{Co-O}}$<br>$\boldsymbol{d_{O(*)-H(*)}}$<br>$\boldsymbol{d_{O(*)-O(*)}}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Adsorption Center $\mathbf{Co_{2c}^T}$** | | | | | | **Adsorption Center $\mathbf{Co_{5c}^o}$** | | | | | |
| Un-doped | 2.23 | 1.59 | -0.11 | 1.78<br>0.97 | 3.03 | 1.81<br>0.98<br>1.47 | 2.29 | 1.86 | -0.09 | 1.79<br>0.97 | 3.26 | 2.08<br>0.98<br>1.45 |
| Conf.1 | 1.65 | 1.6 | 0.25 | 1.77<br>0.97 | 2.69 | 1.79<br>0.96<br>1.48 | 2.69 | 1.85 | 0.15 | 1.80<br>0.97 | 3.33 | 2.09<br>0.98<br>1.47 |
| Conf.2 | 1.90 | 1.58 | 0.42 | 1.76<br>0.90 | 3.26 | 1.76<br>0.94<br>1.52 | 2.98 | 1.83 | 0.29 | 1.76<br>0.93 | 3.90 | 2.03<br>0.92<br>1.41 |
| Conf.3 | 1.56 | 1.48 | 0.41 | 1.70<br>0.92 | 2.76 | 1.79<br>0.90<br>1.43 | 2.87 | 1.78 | 0.40 | 1.82<br>0.91 | 2.55 | 1.98<br>0.93<br>1.39 |
| Conf.4 | 1.94 | 1.50 | 1.08 | 1.68<br>0.89 | 2.61 | 1.72<br>0.87<br>1.35 | 2.82 | 1.75 | 1.08 | 1.75<br>0.93 | 2.71 | 2.07<br>0.91<br>1.47 |

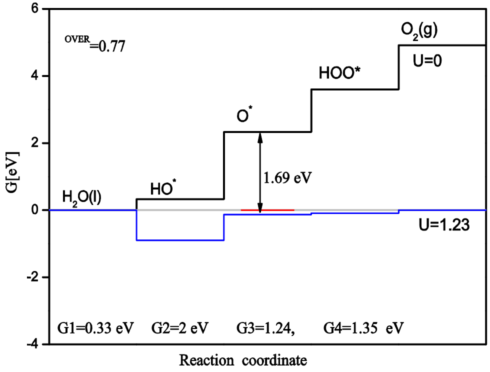
Calculated values of theoverpotentials for each step of water molecule decomposition along the reaction pathway using the computational standard hydrogen electrode (SHE) allowing us to replace a proton and an electron with the half a hydrogen molecule at V=0 V vs SHE according to theory [12,13]for five configurations presented in table 3. The theoretical overpotentialis found according to the standard relation

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

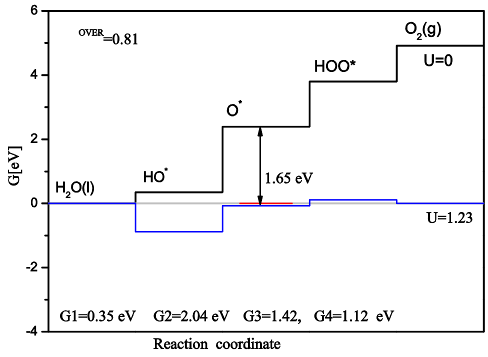
Fig.3 presents the free energy changes of reactions of adsorption of water molecule and intermediate products of dissociation based on DFT+*U* calculations of adsorbed intermediates on the perfect and fluorine-doped $Co_3O_4(100)$ surface at 0.2ML water coverage.

## Undoped surface

a) $Co^{T}_{2c}$site

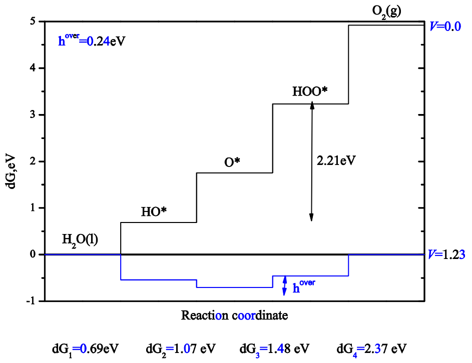


b) $Co^{O}_{5c}$ site

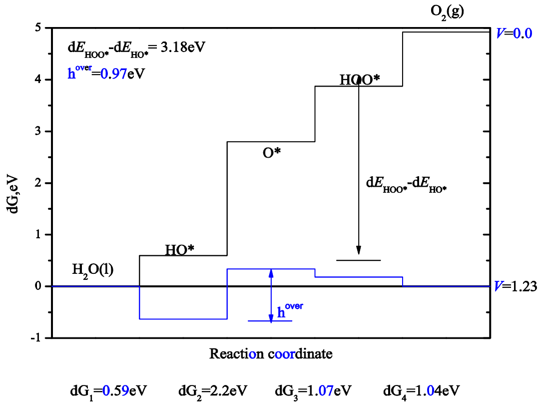


## Configuration 1

c) $Co^{T}_{2c}$site

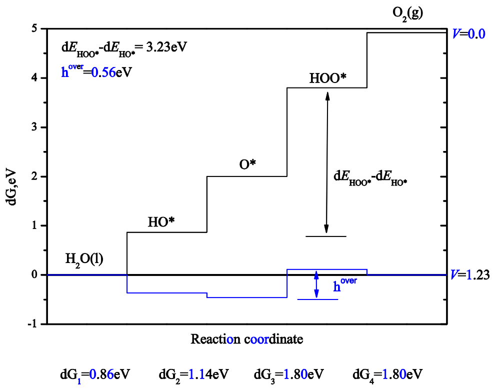


d) $Co^{O}_{5c}$ site

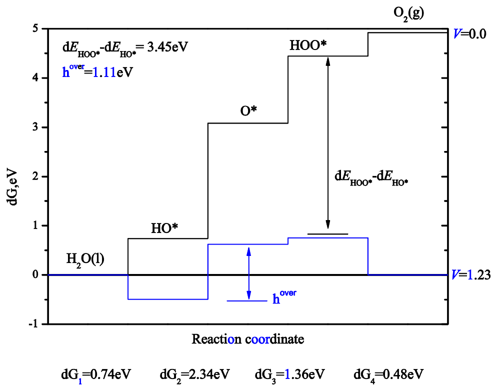


## Configuration 2

e) $Co^{T}_{2c}$site

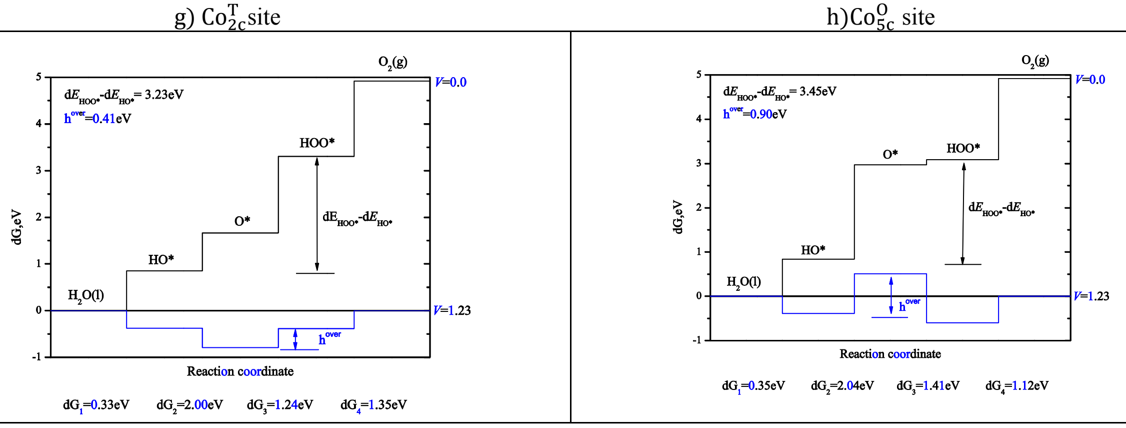


f) $Co^{O}_{5c}$ site



**Configuration 3**

g) $Co_{2c}^{T}$site h)$Co_{5c}^{O}$ site



**Configuration 4**

i) $Co_{2c}^{T}$site j)$Co_{5c}^{O}$ site

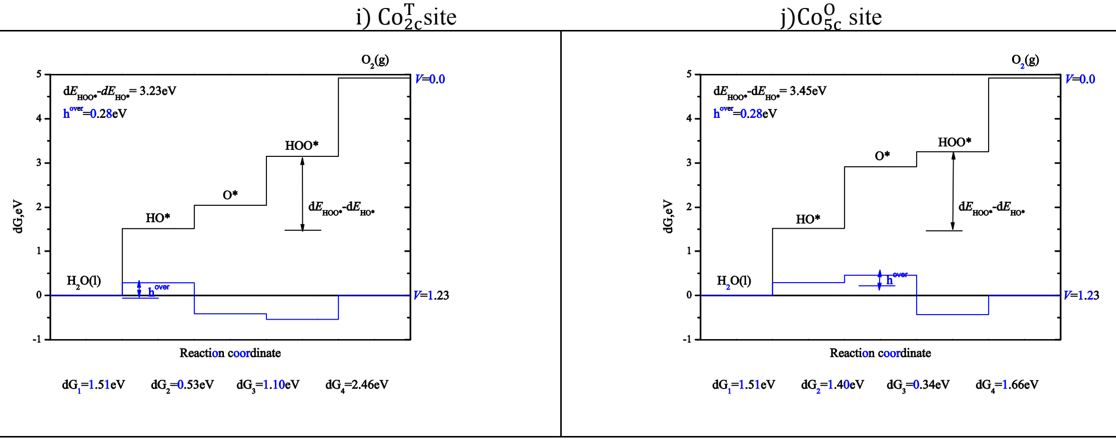


Figure 3 - Free-energy diagram at pH=0 and T=298 K for the four steps of the OER at V=0 and V=1.23 V. Results for the$Co_{2c}^{T}$ and $Co_{5c}^{O}$ sites at 0.2ML water coverage for undoped and 4 Configurations of N-doped surfaces shown; For each case the highest free-energy change is indicated

The calculations suggest that the theoretical overpotentials for water adsorption on the pure surface 0.77 and 0.81 V, respectively $Co_{2c}^{T}$ and $Co_{5c}^{O}$sites. N-doped surfaces demonstrate at $Co_{2c}^{T}$ site decreasing of overpotential (0.56-0.24 V)in comparison$Co_{2c}^{T}$site inundoped $Co_3O_4$surface. For $Co_{5c}^{O}$ site on doped surface values of overpotentialexihibited are nearly the same values as on clean surface (0.90-1.11 V) except for Configuration 4 (0.28 V). In this case of $Co_{2c}^{T}$ site on doped surface reduced values observed with the $OOH^*$ formation as the determining step except Configuration 4.

## Conclusion

It is seen from the figures 3 that an electron charge accumulation lead to strongly reducing overpotentials for $Co_{2c}^{T}$ site in connection with the redistribution of the electron charge in the local environment of the impurity nitrogen atoms. When nitrogenis introduced, most of the charge is distributed to neighboring cobalt ions. In addition, the introduction of nitrogen leads to the polarization of neighboring ions.

The analyzing electron redistribution on the surface by the introducing nitrogen dopants will be described in our forthcoming paper.

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## АЗОТПЕН ҚОСПАЛАНҒАН $Co_3O_4$ (100) БЕТІНІҢ СУДЫҢ ДИССОЦИЯЛАНУЫНА ЭНЕРГЕТИКАЛЫҚ ТИІМДІЛІГІН БАҒАЛАУ

**Аннотация:** Мақалада Хаббард-U жуықтауымен және статистикалық термодинамикамен кіріктірілген тығыздық функционалы теориясының (ТФП) шеңберінде таза және азот қоспаланған $Co_3O_4$ (100) бетіндегі судың адсорбциясын теориялық зерттеудің нәтижелері берілген. Азот қоспасы есебінен пайда болатын беттің каталитикалық қасиеттерінің өзгеру әсерлері талқыланды және таза және қоспаланған пластинадағы азотқа Гиббсеркін энергиясының схемасы негізінде асқын потенциал есептелген.

$Co_3O_4$ оксиді температурамен оттегінің бай концентрациясы жағдайындағы кең интервалда қол жетімді және термодинамикалық тұрақты. Сондай-ақ, $Co_3O_4$ ауыспалы металдар оксидтерінің арасында – газ сенсорларына, энергия сақтау жүйелеріне арналған тиімді материал және литий-ионды аккумуляторларда, мырыш батареяларынан және басқада энергетикалық қолданыстағы анодтық материалдар ретінде кеңінен қолданылады.

Кобальт оксидінің бетінде су молекулаларының ыдырауының энергетикалық тиімділігі нарттыру үшін әртүрлі қоспалардың әсері зерттелген. $Co_3O_4$ үшін перспективалы қоспалаушы материалдардың бірі-азот.

Мақалада Хаббард-U тәсілі мен және статистикалық термодинамика мен үйлескен тығыздық функционалының жазық толқындық теориясын (DFT) есептеу көмегімен таза және азотпен қоспаланған $Co_3O_4$ (100) беттеріндегі су адсорбциясын теориялық зерттеулердің нәтижелері келтіріледі.

$Co_3O_4$ (100) бетін азотпен қоспалаудың және қоспаланған беттердің Гиббсеркін энергия диаграммасының негізінде оттегінің бөліну реакциясының есепті касқын кернеуінің әсері талқыланады. Кобальт оксидінің азотпен легирленге (100) бетінде су молекулаларының ыдырауының асқын кернеулерін есептеу нәтижелері талданатын ыдырау сатыларында кейбір ауытқулармен қоспаланған беттермен салыстырғанда жалпы төмен мәндерді көрсетеді.

**Түйін сөздер:** $Co_3O_4$, оксидшпинелі, суадсорбциясы, еркінэнергиядиаграммасы, бет

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## ОЦЕНКА ЭНЕРГЕТИЧЕСКОЙ ЭФФЕКТИВНОСТИ АЗОТ ДОПИРОВАННОЙ ПОВЕРХНОСТИ (100) $Co_3O_4$ ДЛЯ РАСЩЕПЛЕНИЯ ВОДЫ

**Аннотация:** В статье представлены результаты теоретического исследования адсорбции воды на чистой и азотдопированной 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 азота и рассчитаны избыточные потенциалы на основе схемы свободной энергии Гиббса на чистой и азот допированной пластине.

$Co_3O_4$ является легко доступным и термодинамически стабильным оксидом в широком интервале температур и условий с богатой концентрацией кислорода. Также $Co_3O_4$ среди оксидов переходных металлов - полезные материалы для газовых сенсоров, систем хранения энергии и материалы анодов из литий-ионных аккумуляторов, цинковых батарей и других энергетических применений.

Для повышения энергетической эффективности разложения молекул воды на поверхности оксида кобальта было изучено влияние различных легирующих примесей. Одним из перспективных легирующих материалов для $Co_3O_4$ является азот.

В статье приводятся результаты теоретических исследований адсорбции воды на нелегированной и легированной азотом поверхности $Co_3O_4$ (100) с помощью расчетов плоской волновой теории функционала плотности (DFT) в сочетании с подходом Хаббарда-U и статистической термодинамикой.

Обсуждается влияние легирования азотом поверхности $Co_3O_4$ (100) и расчетного перенапряжения реакции выделения кислорода на основе диаграммы свободной энергии Гиббса нелегированных и N-допированных поверхностей. Результаты расчетов перенапряжений разложения молекул воды на легированной азотом (100) поверхности оксида кобальта демонстрируют в целом пониженные значения по сравнению с нелегированной поверхностью с некоторым отклонением на анализируемых стадиях разложения.

**Ключевые слова:** $Co_3O_4$, шпинель оксида, водная адсорбция, диаграмма свободной энергии, поверхность

## ACKNOWLEDGEMENTS

The project Nr. AP05131211 “First Principles Investigation on Catalytic Properties of N-doped Co3O4” is supported by the Ministry of Education and Science of the Republic of Kazakhstan within the framework of the grant funding for scientific and (or) scientific and technical research for 2018-2020. The authors thank Y.Mastrikov for fruitful discussions and valuable suggestions.

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**ISSN 2518-1726 (Online), ISSN 1991-346X (Print)**

Редакторы *М. С. Ахметова, Т.А. Апендиев, Д.С. Аленов*
Верстка на компьютере *А.М. Кульгинбаевой*

Подписано в печать 10.10.2019.
Формат 60х881/8. Бумага офсетная. Печать – ризограф.
9,6 п.л. Тираж 300. Заказ 5.

*Национальная академия наук РК*
*050010, Алматы, ул. Шевченко, 28, т. 272-13-18, 272-13-19*