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COMPUTATIONAL DENSITY FUNCTIONAL THEORY (DFT) APPROACH ON SMART CATALYSTS UTILIZED IN FUEL CELL TECHNOLOGY

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ABSTRACT

Concepts of nanotechnology are utilized in numerous fields. Sustainable or non-conventional source of power is one area in which this smart technology is widely applied. The catalytic property of nanomaterials in Fuel Cell Technology (FCT) is worth mentioning as it would increase efficiency to a great extent. In this work, Monte-Carlo calculations are carried out to check the adsorption of OH⁻ molecule on various platinum catalysts doped with Ru, W, Co and Pd. The catalyst was then made to adsorb on two separate amorphous carbon blocks that acted as cathode and anode respectively. The Membrane Electrode Assembly (MEA) of the fuel cell was made with nafion membrane and Co-doped Pt electrodes. Adsorption of OH⁻ molecule on the final restructured MEA of the fuel cell was studied.

INTRODUCTION

The emergence of fuel cell innovation has made another instrument for the era of cleaner, higher productivity elective vitality for individuals. Various types of fuel cells such as alkaline fuel cell (AFC), polymer electrolyte fuel cell (PEMFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC), and solid oxide fuel cell (SOFC) [1] are available for various applications. PEMFCs are found to be suitable for transportation applications, i.e., buses [2], which utilize packed hydrogen for fuel and can work at up to efficiency of 40%. One major impediment for commercializing such fuel cell is the high cost of precious-metal catalysts which are used for the oxygen reduction reaction (ORR) in PEMFC Fuel Cell [3]. For fuel cell energy production various materials of electro-catalysts for catalyzing can be used. There were two stages for catalyzing the material: the Pt content can be reduced [4] by using the nanostructured engineering and composite material which will increase the mass specific activity and by using the alternative non-noble metal catalyst [5] that provides acceptable catalyst performances for fuel cell applications.

In heterogeneous catalyst, the catalysis event happens on the surface of the particle [6]. It typically consists of crystallites, with an extensive variety of sizes (1-100 nm), irregular shapes and variable creations. In the actual working of a catalyst this complexity can further increase during numerous cycles of a catalytic reaction [7]. The performance (activity, sensitivity, solidness) of a working catalyst is intended by the aggregate behavior of individual active destinations. active sites can be controlled in better manner, which depends on the particle shape, size and the arrangement of surface atoms, may give important relationships between the detected catalytic execution and the atomic or nanoscale structures of the catalyst.[8] The Pt surface area and its natural activity per site can be expanded by utilizing a few methods. One of such strategies is the utilization of Pt based catalysts [9]. For long time Pt compound electro catalysts have been receiving much thought [10]. The ORR action can be upgraded by utilizing a consolidated Pt surface layer of lattice compression. However the lattice withdrawal diminishes the coupling quality. Binding strength is a variable that can be found by utilizing Density Functional Theory (DFT) counts [11] and can be utilized to upgrade the catalytic activity relying upon the adsorption of intermediates of response. As indicated by dynamic analysis [12], desorption of O and OH⁻ are observed to be the rate-constraining steps for the ORR at high possibilities on Pt (111) and Pt nanoparticles. To reduce the greater chances of ORR it is necessary to reinforce a base metal M with Pt to produce Pt-M bimetallic catalyst. Improved ORR energy on these bimetallic catalysts as contrast with Pt is broadly reported [13]. Pt alloying with different metals can enhance the catalytic activity [14] and can likewise enhance its strength and durability [15].

Transition metal based elemental surfaces and bimetallic alloys are evaluated as PEM fuel cell anode catalysts. Trends in surface reactivity are identified. The adsorption energies of O₂ and OH⁻ are used as reactivity descriptors. A procedure is developed for screening for bimetallic alloys of enhanced performance.

OH⁻ bonds firmly to platinum surface particles, leaving less space for O₂ to adsorb onto Pt dynamic sites. Since hydroxide blocking species don't have an active part in reduction of oxygen atoms, their presence generously hinders the rate of cathodic reaction. Pt alloy with metallic particles have an adjusted electronic structure, which changes diverse adsorption properties of Pt. Thus, interaction between OH⁻ particles and Pt is weaker compared to that of the pure Pt catalysts, and surface is less secured by

KEY WORDS

Fuel Cell Technology (FCT); catalyst; Density Functional Theory (DFT); adsorption; cathode; anode; Membrane Electrode Assembly (MEA)

Received: 12 Dec 2017
Accepted: 05 Jan 2018
Published: 9 Jan 2018

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blocking species, leaving more Pt destinations active for adsorption of OH⁻. The general impact creates an increase in particular activity for cathodic response: 10 times more dynamic than the Pt surface and 90 times more dynamic than state-of-the-art Pt catalysts used now as part of fuel cells.

The Pt surface has an abnormal electronic structure (d-band focus position) and arrangement of surface particles in the close-surface region. Under working conditions significant to fuel cells, its near-surface layer shows a very organized compositional. This causes exhaustion of the bonds between the Pt surface atoms and the OH⁻ particles. The weakening builds the quantity of dynamic sites available for O₂ adsorption. As the energy of O₂ reduction is determined by the quantity of free Pt sites accessible for the adsorption of O₂, the inherent catalytic action of Pt alloyed material has been observed to be 10 times more dynamic than the relating Pt. The observed catalytic activity for the ORR on Pt is the highest ever seen on cathode catalysts [16].

In the current paper a physical model of Pt doping with various metals like Ru, W, Co, Pd, Ag and Au is developed. Band-gap and electrical conductivity are calculated. Pt doped with Ru, W, Co and Pd show improved catalytic activity compared to that with other dopants.

COMPUTATIONAL METHOD

The adsorption of OH⁻ molecule on various catalysts was studied using Monte-Carlo simulations. Adsorption finds a feasible adsorption configuration by using Monte-Carlo searches of the configurationally space of the substrate - adsorption system as the temperature is slowly decreased (simulated annealing). It finds the highest stable adsorption sites for wide range of materials, including zeolites, carbon nanotubes and activated carbon [17]. The total energy of configuration *m* is calculated as

$$E_m = E_{mAA} + E_{mAS} + U_{mA}$$

Where E_{mAA} is the intermolecular vitality between the adsorbate atoms, E_{mAS} is the communication energy between the adsorbate particles and the substrate, and U_{mA} is the aggregate intra-molecular vitality of the adsorbate atoms. The intra-molecular vitality of the substrate is excluded as its structure is fixed all through the simulation. The standard outfit is portrayed in the generation of substrate-adsorbate setups subject. The likelihood of an arrangement in this group is given by

$$P_{mn} = \min \{1, \exp[-\beta (E_n - E_m)]\}$$

Where β is the reciprocal temperature and E_m is the total energy of configuration *m*. In other words, transitions to a configuration of lower energy ($E_n < E_m$) are always accepted, but transitions to high energy configurations ($E_n > E_m$) are only accepted with a probability which decreases exponentially with the difference in energy to zero [18].

At high temperatures, the molten material is disordered because the kinetic energy forces atoms to explore higher energy states, such as substitution or defect sites. The system is cooled very slowly such that, at any given time, it is approximately in thermodynamic equilibrium. A slow rate of cooling increases the probability that the atoms will find configurations with lower energy, corresponding to more regular positions in the crystal lattice. As cooling proceeds, the system becomes more ordered and finally freezes into a ground state [19].

In the physical model developed platinum electrode is prepared by cleaving the surface to <111> direction and then doped with various metals. Using Adsorption module the OH⁻ molecules are made to adsorb on the various catalysts and the density was calculated in each case [20].

RESULTS AND DISCUSSION

Adsorption of OH

To analyze the catalytic activity of Pt it was doped with Ru, Co, Pd and W and then OH⁻ molecules are made to adsorb on the electrode using adsorption locator. Configurations of the adsorbed OH⁻ on various catalysts are shown in [Fig. 1]. At the right side of each figure, density scale is indicated to represent the level of OH⁻ molecule adsorption. The red color indicates lowest OH⁻ density adsorption and blue color highest.

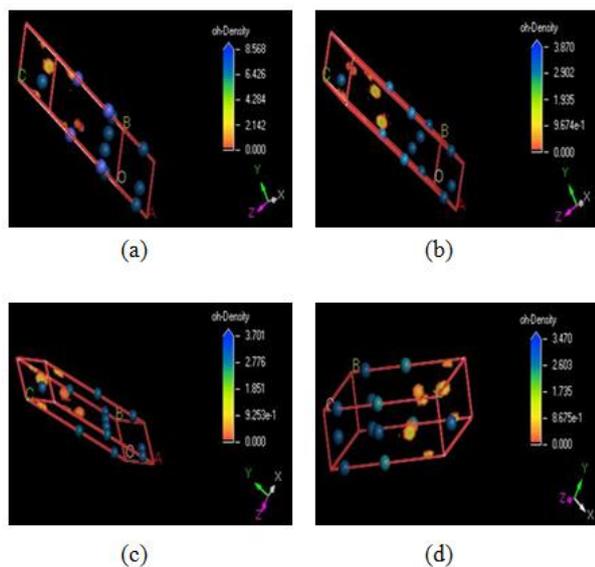


Fig. 1: Adsorption of OH- on: (a) Co doped Pt; (b) W doped Pt (c) Pd doped Pt (d) Ru doped Pt

The maximum density of OH- molecule adsorption on different catalysts is shown in [Table 1]. The maximum density of OH- molecule adsorption is exhibited by Co doping.

Table 1: Adsorption of OH- molecule on various catalysts

Catalyst type	Density of OH ⁻ molecule
Pt/Ru	3.470
Pt/Pd	3.701
Pt/W	3.870
Pt/Co	8.568

Membrane Electrode Assembly (MEA)

[21]Membrane electrode assembly (MEA) is a sandwiched assembly of proton exchange membranes (PEM) and the catalyst doped carbon blocks. In PEM the electrodes were electrically insulated by each other. These electrodes act as anode and cathode. The PEM has a insulator barrier which allows the protons to transport form anode to cathode through membrane [22].

In the current work, nafion is used as the membrane. It has very good thermal and mechanical stability and hence, is used in PEM. The nafion will allow only the cations through the membrane but will not allow the anions or electrons to pass through [23].

The anode /membrane/cathode assembly is shown in [Fig. 2]. Pt/Co catalyst is embedded into the carbon block of anode and cathode with a view of increasing the catalytic activity. The final structure is tested for OH- adsorption and the corresponding maximum density values were noted as 3.974.

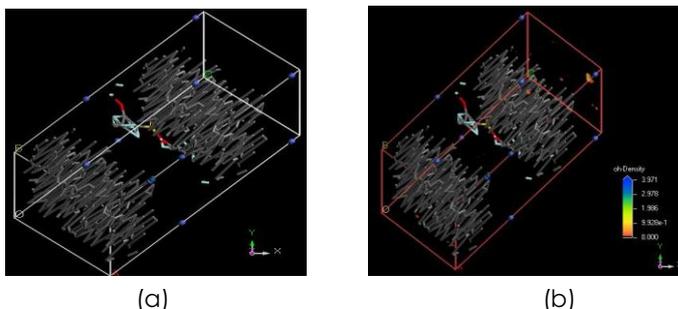


Fig. 2: Final Structure of Membrane Electrode Assembly: (a) Normal Structure of MEA; (b) After the adsorption of OH- on MEA

CONCLUSION

Based on the results obtained in the present work the following conclusion can be drawn:

1. Co doped Pt showed the best OH- adsorption density and hence, was chosen as the catalyst for the preparation of Membrane Electrode Assembly (MEA).
2. The MEA is assembled utilizing the Nafion membrane and catalyst (Co doped on Pt) embedded carbon blocks that serve as cathode and anode respectively. This MEA structure shows greater OH- adsorption density.

CONFLICT OF INTEREST

There is no conflict of interest.

ACKNOWLEDGEMENTS

None

FINANCIAL DISCLOSURE

None

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