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Effect of Partial Replacement of Pt-Based Catalysts with Fe- and Co- For Oxygen Evolution Reaction in PEM Water Electrolysis: A Combined Theoretical and Experimental Study

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Abstract

The adsorption of Pt_n (n = 1−4) clusters and co-adsorption of Pt_n-Co and Pt_n-Fe on the defect-free anatase TiO_2(101) surface have been studied theoretically at density functional theory (DFT) level. The most stable configurations are observed due to Pt_2 and Pt_3-clusters adsorbed on the titania surface. The electronic structure analyses show that the Fermi level is pinned by Pt, which reduces the band gap from ~3 eV of the clean surface to significantly less than 1 eV for Pt_3. For the co-adsorption of Fe-Pt and Co-Pt, there is a strong bond formation of Fe and Co with the surface O and Ti atoms. In both cases, Fe and Co stay far away from the Pt atom. Due to strong interaction of adsorbed elements with Ti, the co-adsorption energy is larger than the corresponding Pt_3 adsorption energy. The higher stability of the co-adsorption of Fe-Pt_n compared to the Co-Pt_n is in agreement with the electrochemical experimental results which confirm that Fe-containing catalysts deposited on titanium dioxide support (Ebonex) will be higher efficient than Co-containing ones toward oxygen evolution in proton-exchange membrane water electrolysis. The observed effect can be explained with formation of solid solution between the metallic components and a realization of synergetic effect.

Keywords: PEM Water Electrolysis; Quantum-Chemical Calculations; Density Functional Theory; Adsorption and Co-Adsorption; Pt-Based Binary Compounds; Titanium Dioxide.

1. Introduction

The contemporary strong increase in energy consumption, the limited energy resources, and the serious ecological problems in the world make the perspective of replacement of the traditional fossil fuels with hydrogen a near future reality. A promising approach to hydrogen production is electricity induced splitting of water using PEM based water electrolysis [1].

PEM water electrolyser has several advantages compared to the conventional alkaline water electrolysers [2]. Unfortunately, the cost of the hydrogen produced through PEM water electrolysis (PEMWE) is still too high which is the main reason for the limited usage of this otherwise attractive new technology. The use of expensive electrocatalysts (predominately Pt and Pt alloys) is mainly responsible for the high cost [3]. One effective way could be the use of bi- and tri-metallic catalysts in which Pt is partially substituted by a transition metal (Fe, Co, Ni, Cu, Mo and other) and reduce the amount of Pt and at the same time increase the stability of the catalyst impeding the Pt surface mobility and thus, preventing the particles growth and formation of clusters [4-8].

Another way to reduce of price of catalyst is by dispersion of transition metals' intermetallic phases on the active centres of selected catalytic supports and achieving a strong synergetic effect known as strong metal support interaction

(SMSI). In this way it is possible to decrease the amount of the catalysts for a unit electrode surface and to increase essentially the catalytic activity of the composite catalyst [9]. The nature and strength of the interaction between the metal particles (Pt and other transition metals) and the support materials (such as TiO_2) not only govern the growth and stability of the metal clusters but also control the fundamental processes that are critical to the catalytic activity of oxide-supported metal particles [10]. Understanding the nature of the interaction is therefore important to tailor the oxide-metal cluster systems to achieve the desired reactivity and selectivity.

A combination of the contemporary theoretical approaches and the latest developments in nanotechnology may provide the scope of precise prediction, selection, and synthesis of nanostructured electrocatalysts with low Pt content, increased activity, and improved stability.

The objective of this work is to carry out a periodic quantum chemical calculation to study the structure, stability and electronic properties of the model systems with chemical composition similar to those of the experimentally synthesized binary materials (Pt-Fe/Ti_4O_7 and Pt-Co/Ti_4O_7) and the results from these calculations to be compared with experimental results from electrochemical measurement for their catalytic properties toward oxygen evolution reaction (OER) in PEM water electrolysis.

2. Experimental

2.1. Computational Methods

For initial screening and preselection of materials, we have performed periodic quantum-chemical calculations with PWGGA approach where both exchange and correlation functionals are based on PW91 functional [11, 12]. This approach was used as implemented in the crystalline orbital program CRYSTAL09 [13]. The structure, stability and electronic properties for Pt_n adsorption and Pt_n co-adsorbed with Fe and Co on anatase (101) surface are studied. In CRYSTAL, the Bloch functions are linear combinations of atomic orbitals. The quality of the atomic basis sets determines the reliability of the results. Therefore, we have used high quality atomic basis sets obtained from the literature. For titanium an 86-411(d31)G basis and for oxygen an 8-411G* basis were used, which have been successfully applied for electronic properties investigation of stoichiometric, defective and Al and V doped rutile TiO2 [14, 15]. For Pt we have implemented a (8s7p6d)/[6s5p3d]-GTO valence basis set, described in [16] and based on the pseudopotential and basis set from Andrae and all [17]. For Co and Fe, 86-411d41G basis sets were used [18].

A (2×1) supercell of 12 layer slab of (101) surface of anatase TiO_2 was used for the adsorption of Pt_n (n = 1- 4) clusters and co-adsorption of Pt_n and Fe/Co. The models are truly two-dimensional; therefore no vacuum distance between the slabs has to be specified. We have defined the cluster adsorption energy of Pt_n, E_{Ptn}^{ads}, as

$$\mathbf{E_{Ptn}^{ads} = -(E^{Ptn/TiO2} - E^{TiO2} - E_{Ptn})} \qquad \mathbf{(1)}$$

where $E^{Ptn/TiO2}$, E^{TiO2}, and E_{Ptn} are the total energies of the TiO_2 slab with Pt_n, the bare TiO_2 slab, and the free Pt_n cluster, respectively. Similarly, clustering energy of the adsorbed Pt_n clusters was defined as

$$\mathbf{E_{Ptn}^{clu} = -(E^{Ptn/TiO2} - E^{TiO2} - nE_{Pt})/n} \qquad \mathbf{(2)}$$

where E_{Pt} is the total energy of a free Pt atom. Apparently, $E_{Pt}^{ads} = E_{Pt}^{clu}$ for a single Pt adatom on the surface.

2.1. Experimental Methods

The synthesis of the chosen composite catalysts consisted in direct selective grafting of the metals from acetilacetonate precursors (M((C5H7O2)n)m or M-acac (M = Pt, Fe, Co) applying the laboratory procedure described elsewhere [18]. The composition, morphology and surface structure of the prepared materials were studied by bulk and surface analysis, such as EDX, XRD, and SEM [19, 20]. The catalyst are integrated in membrane electrode assemblies with novel carbon-free gas diffusion layers and investigated in relation to their electrocatalytic activity and stability toward the oxygen evolution reaction in PEM water electrolysis using the common electrochemical techniques of cyclic voltammetry and steady state polarization [19-21]

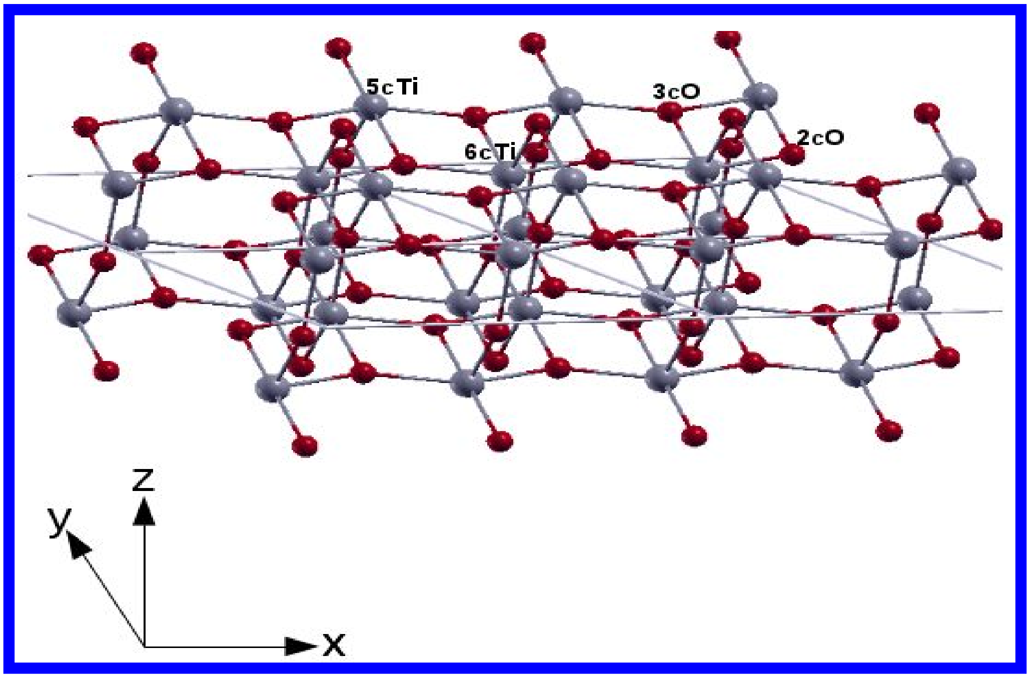
3. Results and discussion:

3.1. DFT Results

3.1.1. Defect Free Anatase (101)

The defect-free anatase TiO_2(101) surface has a stepped structure with the 2- and 3-fold-coordinated oxygen atoms (2_cO and 3_cO) as well as 5- and 6-fold-coordinated Ti atoms (5_cTi and 6_cTi) as shown in Fig. 1. The 2_cO and 5_cTi atoms are unsaturated.

Fig. 1: A 2×2 Supercell of 12 Layer Slab of Anatase (101) Surface, Gray and Red Spheres Represent Ti and O Atoms Respectively

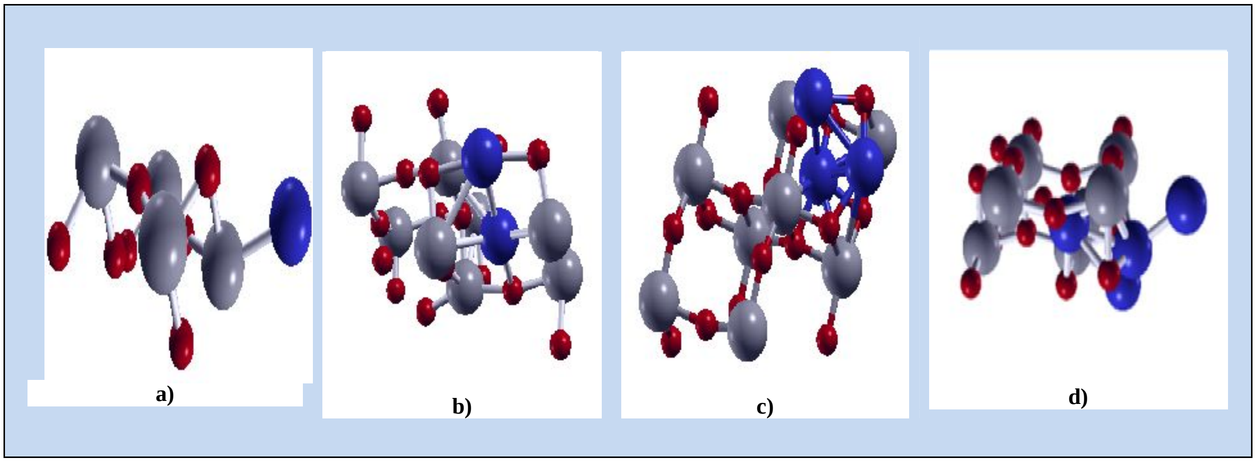


The clean surface shows strong relaxation and reconstruction in the surface layers. The unsaturated 2_cO atoms showed inward relaxation by 0.15 Å and 3_cO atoms showed outward relaxation of about 0.5 Å. The 5_cTi atoms show outward relaxation of 0.05 Å whereas the 6_cTi atoms exhibit larger outward relaxation 0.10 Å. This relaxation and reconstruction also brings the 5_cTi and 6_cTi pair much closer, from 3.10 Å on the bulk-terminated surface to 2.84 Å on the relaxed surface. Due to relaxation, the surface energy is reduced by 0.06 eV/Å^2 with respect to the bulk-terminated structure.

3.1.2. Adsorption of Pt_n on Anatase (101)

Quantum chemical calculations are intended to quantify the observed effect of the electronic and geometric structure of electrocatalysis on their activity. The optimized Pt-adsorption structures for a Pt_1 – Pt_4 atoms are shown in Fig. 2.

Fig. 2: Optimized Structures of Pt_1 – Pt_4 Adsorbed on the Tio_2 (101) Surface



The adsorption energies are calculated for Pt_n (n = 1–4) adsorbed on the TiO_2 (101) surface in different configurations, using equation 1. In Table 1, the calculated adsorption energy, clustering energy and band gap values are compiled for the most stable structures for Pt_n adsorption and compared with available literature data.

Table 1: Adsorption Energy of Pt, Band Gap on the Anatase TiO_2(101) Surface

Model	E-ads, eV	E^t-ads, eV [27]	E-cluster, eV	E^t-cluster, eV [27]	Band Gap, eV
Pt_1	1.92	2.04		-	0.95
Pt_2	1.47	1.95	2.376	2.76	1.11
Pt_3	1.11	1.92	2.311	2.87	0.78
Pt_4	2.36	-	3.181	-	0.522

In case of Pt_1 adsorption, the Pt adatom is attached on top of either a 2_cO or 5_cTi atom leading to the same final Pt_1(O,Ti) structure after relaxation. The adsorption of the Pt atom in this site competes with the surface 2_cO-5_cTi interaction and causes significant elongation of the 2_cO-5_cTi bond, from 1.84 Å on the clean surface to 2.05 Å. The adsorption energy for Pt_1(O,Ti) structure is 1.92 eV which is in close agreement with a previous DFT study of 2.05 eV [22].

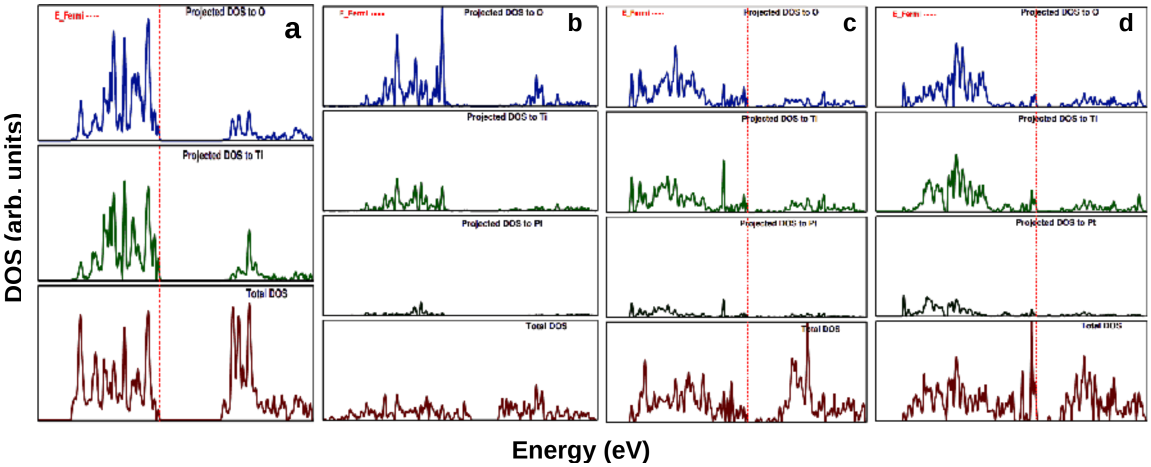
In case of Pt_2 adsorption, both Pt atoms are close to occupy bridging 2_cO-5_cTi sites as in the case of Pt_1(O,Ti) structure (for a single Pt adatom). The modification to the Pt_1(O,Ti) structure is that both Pt atoms are displaced toward each other from the exact bridge site due to the strong Pt-Pt interaction. Consequently, the final structure corresponds to a Pt dimer occupying a hollow site that is formed by the two adjacent 2_cO-5_cTi pairs. The adsorption energy of Pt_2 dimer on anatase (101) surface is 1.47 eV which is smaller than a similar adsorption model (1.95 eV) performed by Han et al. [23]. The heat of adsorption of an additional Pt atom on the existing Pt adatom to form the adsorbed dimer can be estimated as the dimerization energy as presented in Table 2 in the form of clustering energy (calculated using the equation 2). It is observed that the dimerization energy for Pt_2 is 2.38 eV. The large value of dimerization energy indicates that the formation of Pt-Pt bond provides extra stabilization to the adsorbates as compared with the isolated Pt adatoms on the surface. Therefore, bringing a second Pt atom to form a dimer on the surface stabilizes the system.

In Pt_3 adsorption, the triangular plane formed by Pt_3 has tilted toward the surface where the third Pt atom (modification of Pt_2(O,Ti)) forms a bond with the edge 2_cO atom of the upper step. In the finally relaxed structure, the Pt_3 triangular plane is nearly parallel to the surface making it a Pt_3(O,Ti,O) structure. Here the Pt-Pt bond parallel to the 2_cO-2_cO bond becomes shorter than the other two Pt-Pt bonds. The adsorption energy is calculated as 1.1 eV and the clustering energy for Pt_3 is 2.31 eV. Similar to the dimerization energy, the clustering energy of Pt_3 is larger than the adsorption energy of a single Pt adatom. This result indicates that the formation of Pt-Pt bonds in the adsorbed Pt clusters stabilizes the adsorption system. Consequently, adsorbed Pt prefers clustering on the surface.

Pt_4 was adsorbed in a triangular structure, with the open structure of the fourth atom. The calculated values of adsorption energy and clustering energy are higher than those of Pt_2 and Pt_3 (Table 2). Here also the clustering energy of Pt_4 is larger than the adsorption energy of a single Pt adatom, but the relative difference in this case is less than that at Pt_2 and Pt_3. This result indicates that the formation of Pt-Pt bonds in the adsorbed Pt_4 clusters stabilizes the adsorption system too, but to a lesser extent. It is found, that the most stable configurations are the adsorption of Pt_2 and Pt_3-clusters. By more than four platinum atoms, the configuration becomes unstable.

The electronic properties of the clean and Pt_n adsorbed anatase (101) surface were investigated by means of Density of States (DOS) investigation. In Fig. 3, the calculated total DOS and projected DOS figures are compared.

Fig. 3: Projected and Total DOS of Anatase (101) Surface (A), Pt_1 Adsorbed Surface (B), Pt_2 Adsorbed Surface (C) and Pt_3 Adsorbed Surface (D)

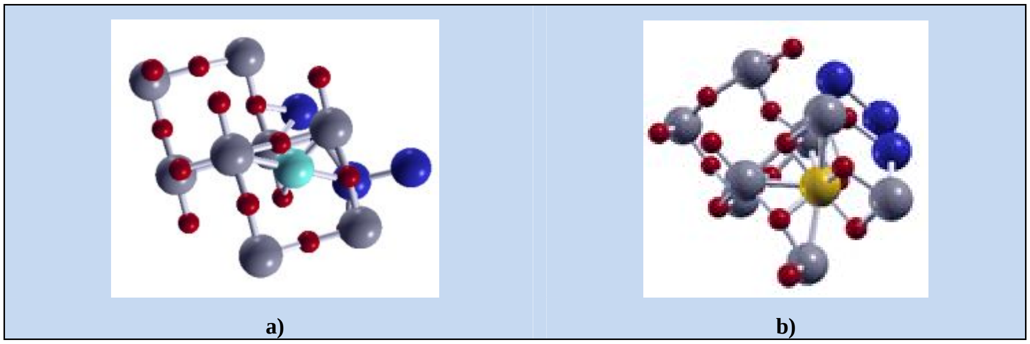


In case of clean anatase (101) surface, both the valence bands (VBs) and the conduction bands (CBs) are mainly composed of O 2p and Ti 3d orbitals. In the case of Pt adsorption on anatase TiO_2 (101), the Fermi level is pinned by Pt, which reduces the band gap from ~3 eV of the clean surface to significantly less than 1 eV for Pt_3. Pt clusters induce local surface relaxations that influence band edges of titanium support and bring a number of band-gap states depending on the cluster size.

3.1.3. Co-Adsorption of Co-Pt_n and Fe-Pt_n on Anatase (101)

Co and Fe are co-adsorbed with Pt_n clusters on the anatase (101) surface in separate investigations. Here we have considered the optimized Pt_3 clusters adsorbed on anatase surface as the starting point (Fig .4).

Fig. 4: Optimized Structures of Co-Pt_3 Co-Adsorption (a) and Fe-Pt_3 Co-Adsorption (b) on the TiO_2 (101) Surface



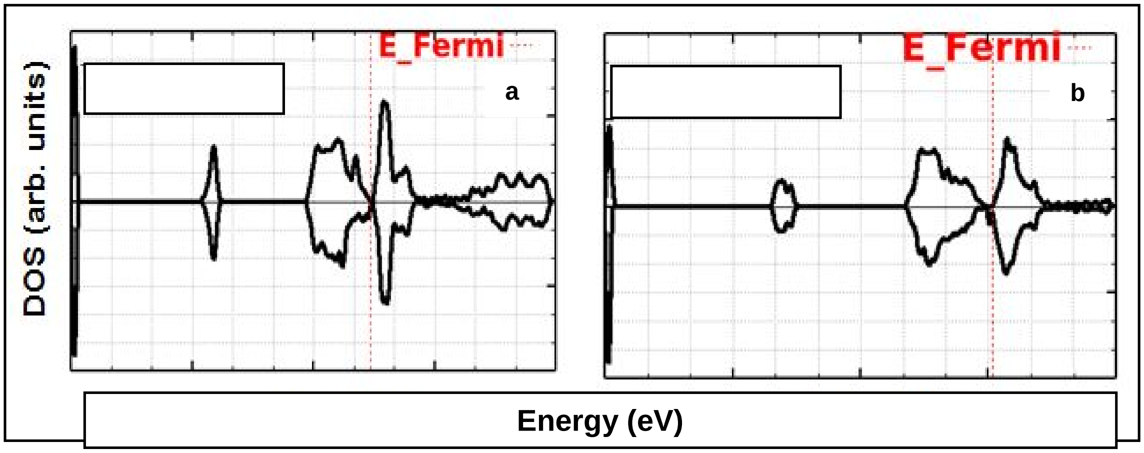
a) b)

Table 2: Adsorption Energy of Co- Pt_3 and Fe-Pt_3, Band Gap and Optimized Structure on the Anatase TiO_2 (101) Surface		
Model	**E-ads, eV**	**Band Gap, eV**
Co-Pt_3	6.06	0.0
Fe-Pt_3	4.05	0.0

In Co-Pt_3 co-adsorption, Co forms strong bonding with the surface O and Ti atoms with Co–2_cO = 2.04 Å and Co–5_cTi = 2.85 Å. It is interesting to note that Co atom lies far from any of the Pt atoms with the smallest Co–Pt distance (3.08 Å). The co-adsorption energy is calculated as 6.06 eV. Due to the absence of strong bond between Co and Pt the structure is unstable and hence the co-adsorption energy is very high. The calculation of electronic properties shows that there are extra states around the Fermi Energy level from Co and Ti atoms which make the system metallic (Fig. 3a).

In Fe-Pt$_3$ co-adsorption, the Fe atom moves far away from the Pt atom. Similar to Co/Pt$_3$ co-adsorption, Fe forms strong bonding with the surface O and Ti atoms with Fe–2$_c$O = 1.85 Å and Fe–5$_c$Ti = 2.37 Å. The co-adsorption energy is calculated as 4.05 eV. The calculation of electronic properties shows that there are extra states around the Fermi Energy level from Fe and Ti atoms which make the system metallic (Fig. 5 b).

Fig. 5: Total DOS of Co-Pt$_3$ co-adsorption (a) and Fe-Pt$_3$ co-adsorption (b) on anatase (101) surface

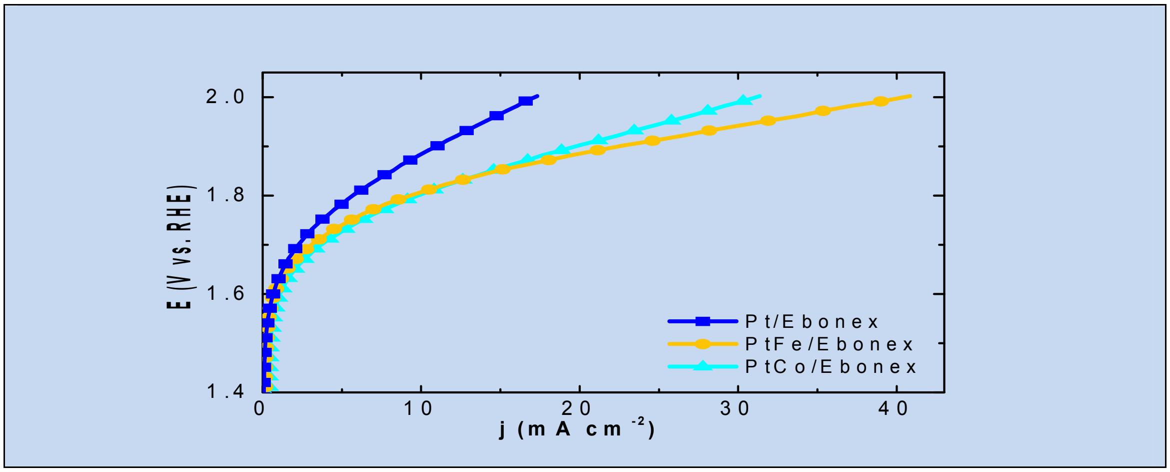


The obtained quantum chemical data are in agreement with the results from our experimental on the relationship between the electronic and geometric structure of Pt mono- and bi-metallic compositions and their electrocatalytic activity [19, 24]. Further study is underway for the consideration of various other adsorption and co-adsorption sites including the increment of n in Co-Pt$_n$ and Fe-Pt$_n$ co-adsorptions.

3.2. Experimental Section

In order to correlate the results from the theoretical calculations with experimental study, we have performed some electrochemical tests such as cyclic voltammetry and steady state polarization. The anodic polarization curves of Fe-Pt/Ebonex and Co-Pt/Ebonex as catalysts toward OER in PEM water electrolysis are presented in Fig 6. This investigation is carried out at the typical PEMWE working temperature of 80°C. The catalysts are integrated in membrane electrode assemblies with novel carbon-free gas diffusion layer [24].

Fig. 6: Polarization curves of Pt/Ebonex, Pt-Fe/Ebonex and Pt-Co/Ebonex at 80°C and scan rate 1 mV.s^{-1} [24]



The results obtained show that the anodic reaction of oxygen evolution proceeds faster on the bimetallic catalysts as the process is most intensive on Pt-Fe/Ebonex.

The effect was prescribed on the one hand to occurrence of hypo-hyper-d-electron interaction between Pt and Fe/Co, leading to changes in the electron density of Pt d-orbital [25]. The enhanced catalytic activity of Fe- and Co- containing Pt-compounds can be explained with the formation of solid solution between the metallic components. The alloying proven by the XRD data causes some structural effects such as reduction of the lattice parameter and the crystallite size which in turn, also resulted in to an increase in the surface area and, accordingly, the catalytic activity [19].

On the other hand the realization of synergetic effect as a result of hypo-hyper-d-electronic interactions between catalyst and support further increases the catalytic effect [19].This shows that the magneli phases serves not only as a supporting material with stable behavior and good corrosion resistance at the high anodic potentials, but also contribute to the efficiency of the composite catalyst.

4. Conclusions

The adsorption of Pt_n (n = 1−4) clusters and co-adsorption of Co-Pt and Fe-Pt on the defect-free anatase TiO_2(101) have been investigated with density functional method. The defect-free anatase TiO_2(101) surface has a stepped structure containing 2- and 3-fold-coordinated oxygen atoms (2_cO and 3_cO) as well as 5- and 6-fold-coordinated Ti atoms (5_cTi and 6_cTi). The adsorption of Pt_n shows that the most stable configurations are the adsorption of Pt_2 and Pt_3-clusters.The preference of Pt_n to the coordinately unsaturated 2-fold-coordinated oxygen sites indicates that these sites may serve as nucleation centers for the growth of metal clusters on the oxide surface.

For the co-adsorption of Fe-Pt and Co-Pt, there is a strong bond formation of Fe and Co on the surface O and Ti atoms. In both cases, Fe and Co stay far away from the Pt atom. Due to strong interaction of adsorbed elements with Ti, the co-adsorption energy is larger than the corresponding Pt_3 adsorption energy. The electronic properties investigations show that a significant band gap narrowing occurs upon Pt_n adsorption on the anatase surface due to adsorbate driven states on the bulk terminated surfaces. The band gap disappears by the co-adsorption of Co-Pt_n and Fe-Pt_n on the TiO_2 (101) surface.

The results of the theoretical calculations are compared with the experimental data on the catalytic efficiency of the bimetallic Pt-containing compounds supported on nonstoichiometric titanium oxide (Ebonex) and integrated in anode with a carbon-free GDL toward OER in PEMWE. Our theoretically observed higher stability of the co-absorption of iron with platinum is confirmed with the experimental data. Therefore, we conclude that the Fe-containing catalysts would be highly efficient for PEM water electrolysis.

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