



A DFT STUDY OF THE POISONING EFFECTS OF CO ON $\text{Pd}_x\text{Cu}_{1-x}$ (110) SURFACE

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ABSTRACT

CO contaminants play a significant role in modifying the performance of proton exchange membrane fuel cells (PEMFC). The most common catalyst being used in the PEMFC is Pt. Recently however it has been found that using Pd alloys such as Pd-Cu can increase the fuel cell efficiency versus the pure Pt catalyst. In this work, we examine the adsorption of CO onto $\text{Pd}_x\text{Cu}_{1-x}$ (110) surfaces, with different values of x, in order to improve the CO tolerance. Understanding how molecules interact with such surfaces is one the first steps to understanding catalytic reactions. We use CASTEP, a computational code based on the density functional theory plane-wave pseudopotential method. In the present study, we optimize the surfaces structure of $\text{Pd}_x\text{Cu}_{1-x}$ (110) and then calculated, energy density of states, energies of repulsion and chemisorption for CO on $\text{Pd}_x\text{Cu}_{1-x}$ (110). The results indicate that chemisorption energies of CO on $\text{Pd}_x\text{Cu}_{1-x}$ are highly dependent on the concentration x of the alloy, and the catalyst poisoning arises from the loss of $\text{Pd}_x\text{Cu}_{1-x}$ (d) electrons upon CO adsorption. In addition, density of states analysis indicate that the poisoning effect is a mechanism partially due to the loss of Pd-Cu(d) electrons upon CO adsorption.

Key words: catalysts, poisoning by CO, PEMFC, molecular simulation, DFT Theory.



1. INTRODUCTION

The demand for clean and sustainable energy sources has become a strong challenge in the 21st century. Proton exchange membrane fuel cells (PEMFCs) which convert chemical energy of a fuel into electricity directly with great efficiency are one of the key technologies for enabling generation of clean and sustainable energy [1-3]. However, there are still some technological challenges to be solved. Among those challenges, the development of electrocatalysts tolerant to CO at levels of 50 ppm (with a noble metal loading of 0.1 mg cm⁻² or less) is deemed to be one of the most significant barriers that PEMFCs must overcome to achieve complete commercialization [4]. PEMFCs have several important application areas, including transportation, stationary and portable power, and micro-power.

Nevertheless, at current PEMFC stack operating temperatures of around 80C, the membrane-electrode assemblies (MEAs) within the stack cannot tolerate such high CO levels. Pt-based electrocatalysts are widely utilized as anode due to their outstanding catalytic reactivity toward hydrogen dissociation and oxidation. However, carbon monoxide, which commonly exists in fuel gas, has long been recognized as a source of poison to the Pt-based electrocatalysts and can severely reduce the catalyst efficiency [5,6].

The poisoning effect is especially significant for fuel cells operating at relatively low temperatures, such as proton exchange membrane (PEM) fuel cells [7]. Hence, CO tolerance is of extreme importance in the development of PEM fuel cell anode catalysts since most reformat fuels contain a substantial amount of CO. Two major technical gaps hindering commercialization have been identified: high cost and low reliability/durability. Fuel cell catalysts, such as platinum (Pt)-based catalysts and their associated catalyst layers, are the major factors in these challenges. Although a great deal of effort has been put into the exploration of cost-effective, active, and stable fuel cell catalysts, we have not yet had any real breakthroughs. Therefore, exploring new catalysts, improving catalyst activity and stability/durability, and reducing catalyst cost are currently the major tasks in fuel cell technology and commercialization. In the search for alternative low-cost non-Pt catalysts, researchers have looked at several others, including supported platinum group metal (PGM) types such as Pd-, Ru-, and Ir-based catalysts, bimetallic alloy catalysts, transition metal macrocycles, and transition metal chalcogenides [8,9,10].

On the other hand, Pd [11] or Ru [12] is used as the catalyst for preferential oxidation of CO at low temperature. Among these, the Ru catalyst exhibited high performance for preferential oxidation of CO and long-term stability under a low O₂/CO molar ratio. In any case, considerable amounts of precious metals were used in both a shift converter unit and a CO preferential oxidation unit, resulting in high cost. Moreover, this complicated system containing a CO removal unit led to low efficiency and reliability.

In this work, we study Pd_xCu_{1-x} binary alloy surfaces in order to find an anode less expensive for polymer electrolyte membrane fuel cell (PEMFC) than pure Pt, while improving the problem of poisoning by CO in the catalyst. There is information that replacing Pt by Pd would decrease the

cost by a factor of 5 [13, 14]. Thus we explored other possible alloys [15, 16] of Pd that might lead to higher performance.

Most theoretical studies on the effect of CO poisoning on the catalyst, use clusters of atoms to simulate the catalyst surface and do not take into account its crystal structure. In this work, we use alternative method, the first step for obtaining the results was built bulk alloy of *Pd-Cu* with structure fcc and modeling compositional disorder in the crystal. Disorder was described in terms of a hybrid atom (pseudo-atom) which was putted on atomic sites of the crystal lattice, this description is called mixture atoms description. The x concentration may be used to simulate the case where one atomic site is randomly occupied by two or more different types of atom. In the case of the alloy Pd_xCu_{1-x} , x represents the probability that the site studied is occupied by the atom *Pd*. This method allows create mixtures of different elements, which are a mixture of *Pd*, *Cu-properties*.

The mixture atoms description is the most often used representation of disordered metallic alloys and it can be implemented in virtual crystal approximation [17]. The method was implemented in *Materials Studio* Software [18]. Then the quantum mechanical calculations described here are based on density functional theory (DFT) [19-23] and the BFGS minimize [24], algorithm based on the gradient for the task of optimizing geometric. That is, the BFGS scheme uses a starting Hessian which is recursively updated during optimization. The CASTEP implementation involves a Hessian in the mixed space of internal and cell degrees of freedom, so that both lattice parameters and atomic coordinates can be optimized. For exchange-correlation effects, we use the “generalized gradient approximation” in the form suggested by Perdew, Burke and Ernzerhof, GGA-PBE [25].

The surface calculations were realized using CASTEP of Materials Studio and they start using the optimized structure from the Pd_xCu_{1-x} bulk part. Next, we cleave the bulk for obtaining the surface (110), this is opened a new 2D periodic surface. After, we build vacuum slab. A changing the structure from 2D to 3D periodic and a vacuum is added above the atoms to input the system new in CASTEP.

We show in the present study that the chemisorption energies of CO on Pd_xCu_{1-x} are highly dependent on the concentration x of the alloy and the catalyst poisoning arises from the loss of $Pd_xCu_{1-x}(d)$ electrons upon CO adsorption.

2. METHODOLOGY AND COMPUTATIONAL DETAILS

On this work our goal was to construct a theoretical bi-metal $Pd_{100\%-x}Cu_x$ molecule interacting with carbon monoxide gas-molecules. In the scope to qualify catalytic poisoning on copper palladium metal to those gases we constructed $Pd_{100\%-x}Cu_x$ (110) theoretical surfaces as well as the correspondent (1×1) and (2×1) surfaces. Moreover, the x -value was ranging from 0% to



10% of copper metal considering 2% variation concentrations. This work was achieved using Accelrys Material Studio software for material modeling and simulation applying CASTEP library. With that kind of library it was obtained the geometry optimization of every palladium-copper bi-metal with and without carbon-monoxide presence. Moreover, this job is done by the Material Studio software considering the density functional theory (DFT) model using generalized gradient approximations (GGA) enhanced with 1996 gradient-corrected correlation functional of Perdew, Burke and Ernzerhof [25,26]. With this software, we also calculated the density of states, the number of electrons, up and down number of spins, chemisorption energy for CO on $\text{Pd}_{100\%-x}\text{Cu}_x$ (110).

To achieve this study we followed the next steps. We had to build and optimize every $\text{Pd}_{100\%-x}\text{Cu}_x$ bi-metal bulks and the carbon monoxide molecules through cell primitive optimization and geometry optimization energy; it can be seen, in figure 1, this first step showing a face centered cell (FCC).

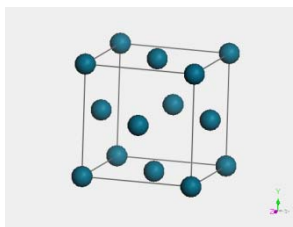


Figure 1 Typical PdCu bi-metal molecule on a FCC structure constructed and geometry optimized.

In particular, to carry out geometry optimization of CO molecules we had to insert them into a simple cubic crystal (CC) lattice. The C-O bond length in the CO molecule can be determined experimentally however, looking into the literature, around 1.12 Å we found a similar bond length value obtained using this modeling software, 1.1539 Å in cartesian coordinates, see next structure on figure 2.

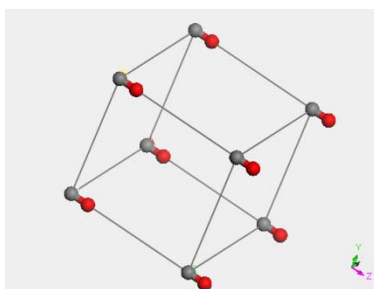


Figure 2 Typical CO molecule into a CC structure constructed and geometry optimized.



The next step was to build $\text{Pd}_{100\%-x}\text{Cu}_x$ (110) surfaces. We had to relax and optimize the $\text{Pd}_{100\%-x}\text{Cu}_x$ (110) surfaces selecting k-points parameters field as 3x4x1 and to calculate Density of States (DOS) for these systems, see figure 3.

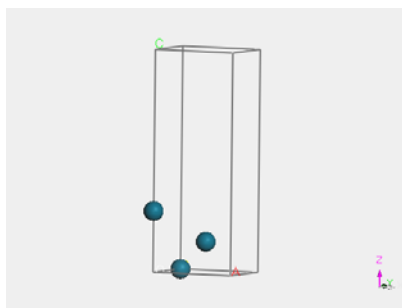


Figure 3 Typical PdCu (110) surface in a crystalline structure which geometry was optimized with no CO molecules around.

Later, we had to add CO molecules to the $\text{Pd}_{100\%-x}\text{Cu}_x$ (110) surfaces and to geometry optimized. These surfaces let us got the (1 x 1) CO on $\text{Pd}_{100\%-x}\text{Cu}_x$ (110) and the (2 x 1) CO on $\text{Pd}_{100\%-x}\text{Cu}_x$ (110) surfaces respectively, we of course optimized the geometry and analyzed the energies and the density of states (DOS) of every obtained crystalline structure, see figure 4 (left) and 4 (right) respectively.

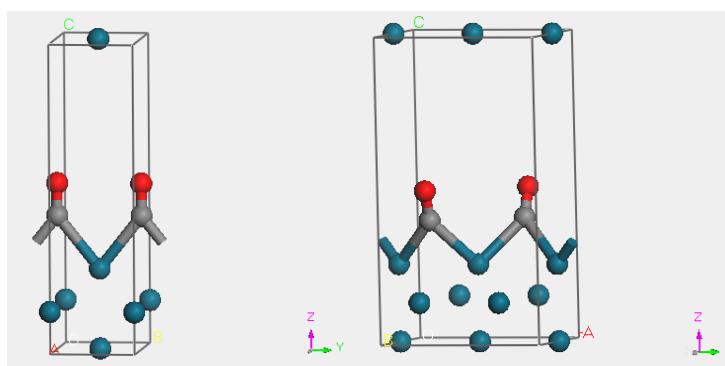


Figure 4 Left: Typical (1 x 1) CO on PdCu (110) surface in a crystalline structure which geometry was optimized. Right: (2 x 1) CO on PdCu (110) surface in a crystalline structure which geometry was optimized

To accomplish this work, we had to use the Supercell tool of the modeling software to change from the 1 x 1 to the 2×1 $\text{Pd}_{100\%-x}\text{Cu}_x$ (110) surfaces. For this structure the k-points parameters had to be modified to 2x3x1 on the geometry optimization analysis. When all the previous

processes were finished we went to calculate chemisorption and repulsion energies using the results given by the material studio software tools.

The average chemisorption energy of CO on Pd-Cu(110) binary alloy surfaces is evaluated using the following equation:

$$\Delta E_{chem} = 0.5E_{(2 \times 1)Pd_xCu_{1-x}(110)} - E_{Pd_xCu_{1-x}(110)} - E_{CO\ molecules} \quad (1)$$

The repulsion energy can be calculated from:

$$\Delta E_{rep} = 0.5E_{(2 \times 1)Pd_xCu_{1-x}(110)} - E_{Pd_xCu_{1-x}(110)} \quad (2)$$

At last we examined the changes in the density of states (DOS). This let us obtain an insight into the bonding mechanism of CO on Pd_xCu_{1-x} (110).

3. RESULTS AND DISCUSSION

The effect of poisoning on various catalyst structures have been widely studied theoretically using both empirical and first-principle methods, most of these consider clusters of atoms of candidate material to catalyst, besides for CO adsorption on the cluster, four possible adsorption modes have been investigated: the on-top site (O), the 2-fold edge (E), the 3-fold hollow site (H), and the side-on configuration on the edge (L). In these studies, upon full geometry optimizations, the H and L modes were found to be unstable. In both cases, the CO molecule migrates to the on-top site [27]. In the present study, we attempt to model the chemistry of CO-poisoning on catalyst by means of interactions between CO with surfaces of Pd_xCu_{1-x}(110). The binary alloy surface provides a useful representation of the active site on-top site, deemed to be essential in many realistic catalytic reactions. The CO molecules were placed on the on-top sites on surfaces of Pd_xCu_{1-x}(110), as shown in Figure 4. The surfaces structure of Pd_xCu_{1-x}(110) remains nearly intact upon structural relaxation.

Figure 5 displays the calculated projected density of states (PDOS) of the CO-molecule, while, figures 6-10 show bare Pd_xCu_{1-x}(110) surfaces and CO-poisoned Pd_xCu_{1-x}(110) surfaces, with x=0.98, 0.96, 0.94, 0.92 0.90. The band structure of CO, without interacting with the alloy presents, below the Fermi level, four bands: three bands filled with s- and p-electrons, centered on the energies 0, -5.0 eV and -20 eV, and a p-band, which is centered on the energy -2.5 eV. For x=0.98, 0.96 and 0.94 (figures 6-8), the band structure of (2x1) Pd_xCu_{1-x} (110) without CO has a single-band below the Fermi level, which is occupied by d-, s-, p-electrons. As the Cu concentration increases, the bands of the Pd-Cu surface, without CO, are elevated from 27 electrons/eV to 55 electrons/eV, and they are filled mostly with d-electrons. In these figures we see that the occupied lowest energy in this band increases from -3.5 eV to -1.8 eV as the concentration x decreases. This means that, Cu transfer more d-electrons to the band of the alloy, and a side effect is to shift the band to energies near the Fermi level, so the greater the

concentration of Cu, the alloy will have it easier to transfer electrons to the band structure of CO, thereby reducing the energy of chemisorption. Figures 5 and 6-11 indicates that d-bands of (2x1) $\text{Pd}_x\text{Cu}_{1-x}$ (110) with CO, below the Fermi level, are enhanced with CO loading on the binary alloy as the CO(σ) orbital donates electrons to the d-band. It is noted that, for concentrations of 0.98, 0.96 and 0.94, three additional bands of s-, p- and d-orbitals are formed below the Fermi level. While at concentrations of 0.92 and 0.90 a fourth band of s-electrons is formed below the Fermi level. These results indicate that as the copper concentration increases, the s electrons of the first band and the p and d electrons of the third band, below the Fermi level, move into an additional band centered around -4.5 eV.

These results indicate that, as copper concentration increases, s- and p-electrons of the bands of CO and d-electrons of Pd-Cu band, nearest to the Fermi level, begin to form an additional band, which is centered around of -4.9 eV for $x=0.92$, and -3.5 eV for $x=0.90$. This mechanism also allowed to have some d electrons available for exchange between CO and Pd-Cu, thereby reducing energy chemisorption. In parallel, the π^* -bands of CO molecules move downward roughly upon receiving back-donation of d-electrons from the $\text{Pd}_x\text{Cu}_{1-x}$ (110) surfaces.

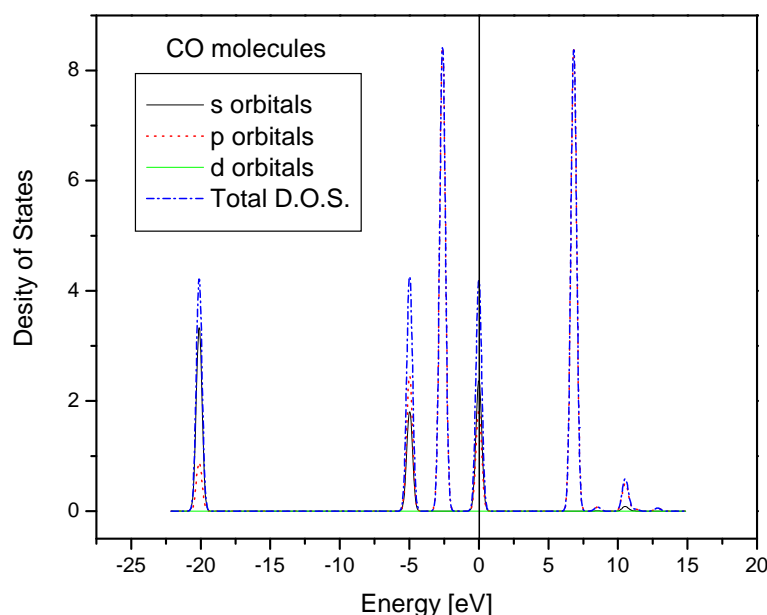


Figure 5 Density of states of CO molecule into crystal.

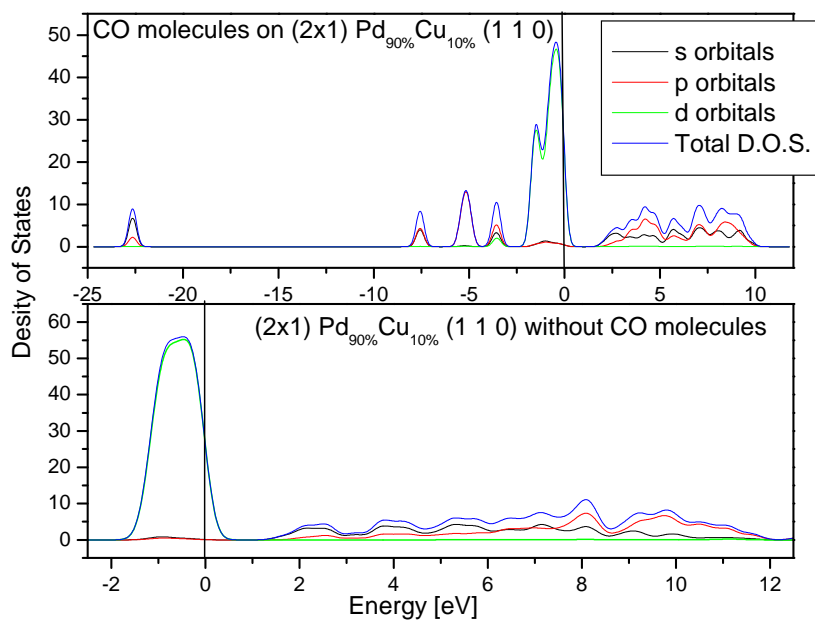


Figure 6 Pd_{0.9}Cu_{0.1}(110) surface projected density of states after and before placing CO molecules.

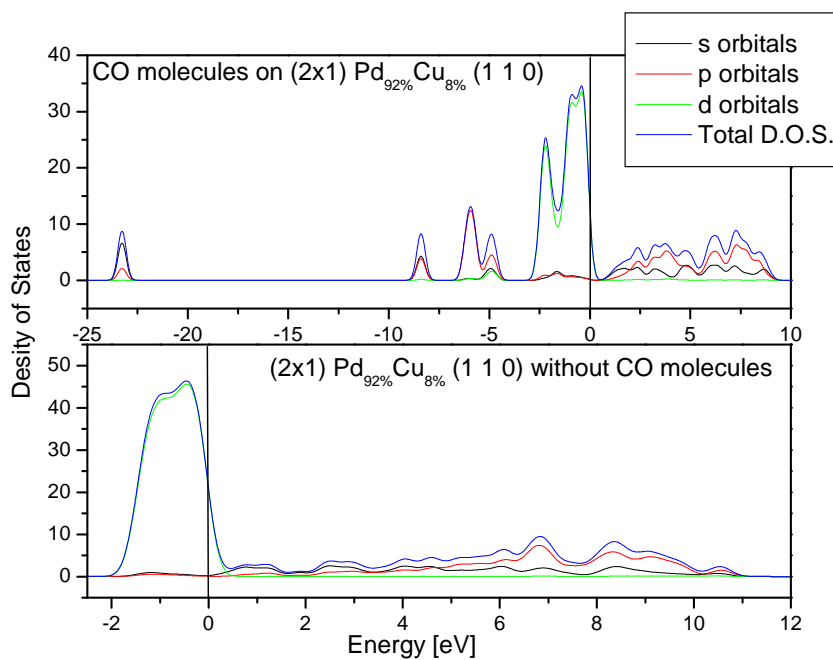


Figure 7 Pd_{0.92}Cu_{0.08}(110) surface projected density of states after and before placing CO molecules.

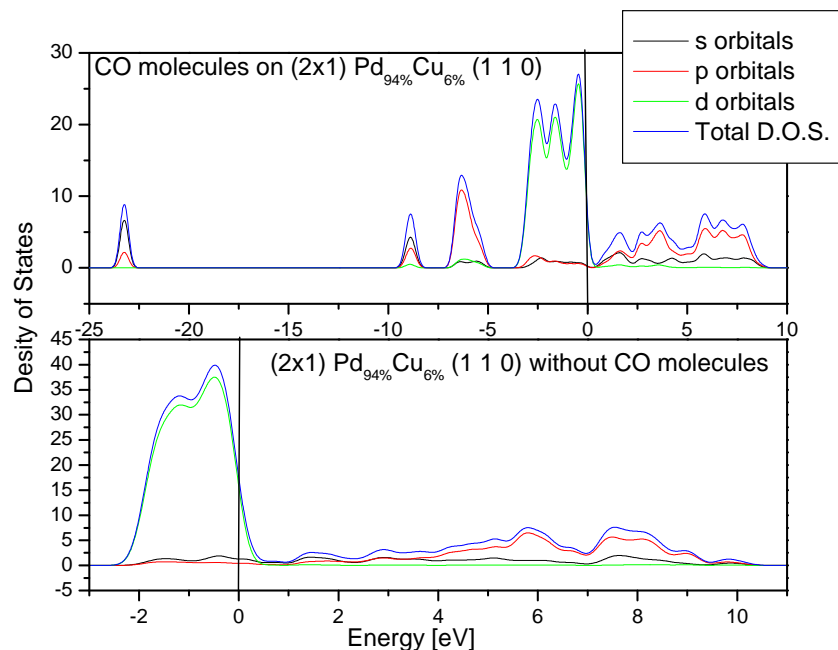


Figure 8 $\text{Pd}_{0.94}\text{Cu}_{0.06}(110)$ surface projected density of states after and before placing CO molecules.

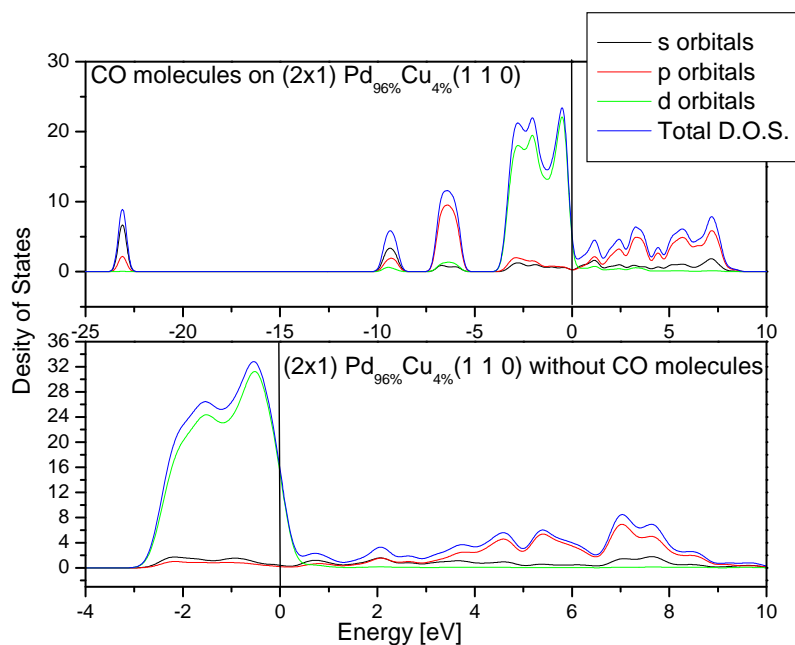


Figure 9 $\text{Pd}_{0.96}\text{Cu}_{0.04}(110)$ surface projected density of states after and before placing CO molecules.

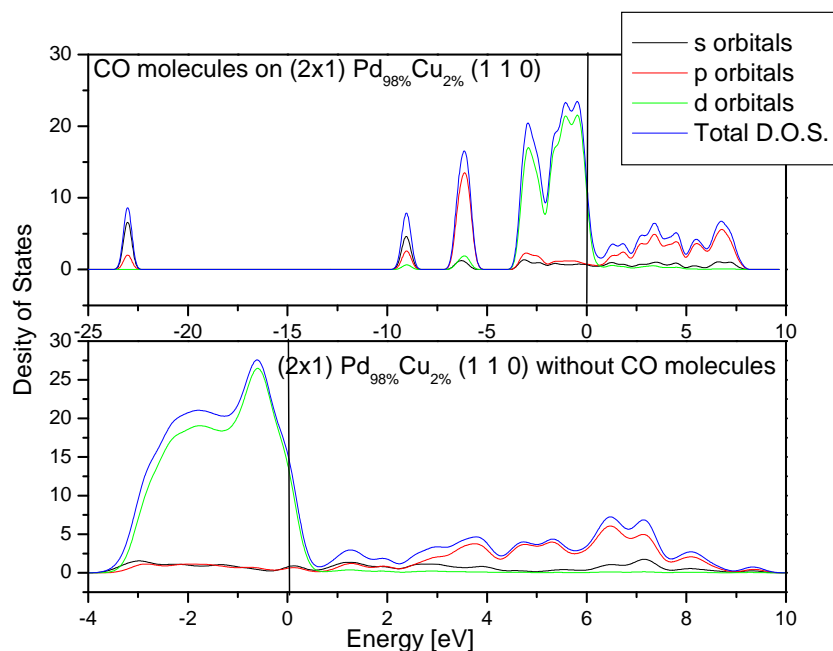


Figure 10 $\text{Pd}_{0.98}\text{Cu}_{0.02}(110)$ surface projected density of states after and before placing CO molecules.

Figure 11 shows the behavior of the energies of chemisorption and repulsion of the CO molecule on the surface (110) of the $\text{Pd}_x\text{Cu}_{1-x}$ alloy. We observe that, as the concentration of Cu increases, the CO molecule binds to the surface with less intensity. This observation indicates that the increase of small amounts of Cu is helping to reduce the effect of CO poisoning, which is in good agreement with some experimental data [28, 29].

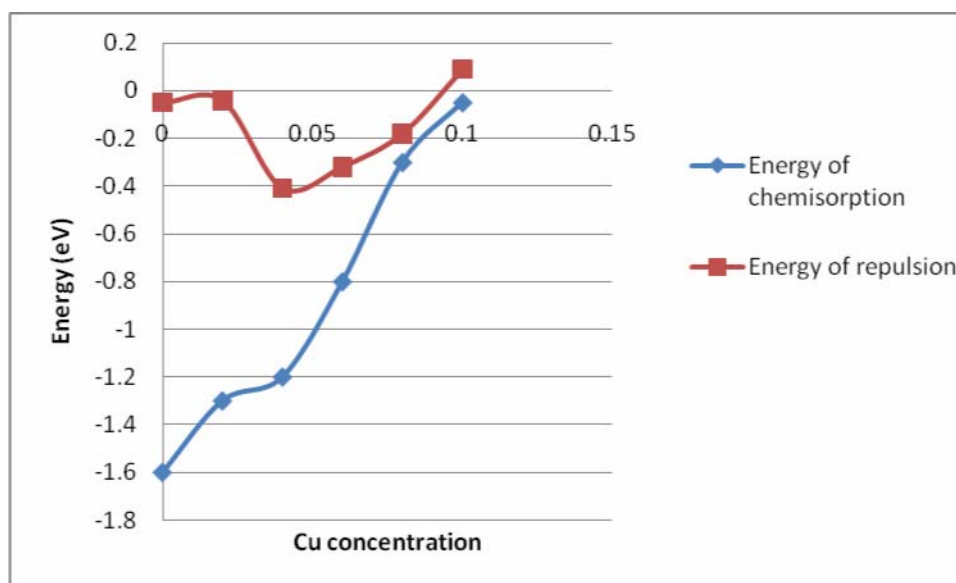


Figure 11 Behavior of the energies of chemisorption and repulsion (eV) of the CO molecule on the surface (110) of the $\text{Pd}_x\text{Cu}_{1-x}$ alloy in function concentration of Cu.

Otherwise, based on the Hirshfeld charge analysis [30], the mechanism can be interpreted as that electron flow from $\text{Pd}_x\text{Cu}_{1-x}$ (d) to CO π^* -orbitals dominates the binding process and the surface (110) of the Pd-Cu alloy acts as an electron donor. The calculated electron loss per CO decreases monotonically as the Cu concentration increases. The electron back-donation from the d-band of the Pd-Cu alloy to the antibonding π^* -orbital of CO gives rise to a looser C-O bond and consequently the C-O bond length is elongated.

To provide a more comprehensive study of poisoning of Pd-Cu catalyst for CO molecules, it is necessary to conduct studies on the effect of temperature and hydrogenation of CO on (110) surface of Pd-Cu alloy. It has been observed experimentally [27] that the CO poisoning effect can be substantially reduced at high temperature. One possible mechanism would be that the H atoms residing near the poisoning sites on $\text{Pd}_x\text{Cu}_{1-x}$ (110) surface could migrate from the metal atoms to attack the C atoms to form surface formaldehyde species, which subsequently desorbs from the surface at a high temperature. To test this hypothesis, we will investigate the hydrogenation of CO on the $\text{Pd}_x\text{Cu}_{1-x}$ (110) surface. We can conclude in this study that low concentrations of Cu in Pd, improve tolerance to CO, so the Pd-Cu alloys can become a promising material for use as anode in PEM fuel cells.

CONCLUSIONS

The catalyst materials play a critical role in many heterogeneous catalytic reactions and in applications such as PEM fuel cells. However, catalyst poisoning by CO has been long recognized as one of the major obstacles to the progress and commercialization of these technologies. In this work, we investigated part of the catalytic processes of poisoning of $\text{Pd}_x\text{Cu}_{1-x}(110)$ by CO by employing calculations based on density functional theory. Our results indicate that the increase of small amounts of Cu is helping to reduce the effect of CO poisoning, which is in good agreement with some experimental data. To find the mechanism of poisoning was necessary to obtain the density of energy states of the Pd-Cu (110) surfaces with and without CO molecules. The mechanism can be interpreted as that electron flow from $\text{Pd}_x\text{Cu}_{1-x}(\text{d})$ to CO π^* -orbitals dominates the binding process and the surface (110) of the Pd-Cu alloy acts as an electron donor. The calculated electron loss per CO decreases monotonically as the Cu concentration increases. The loss of $\text{Pd}_x\text{Cu}_{1-x}(110)(\text{d})$ electron as well as the physically blocked binding sites upon CO poisoning leads to performance degradation of the Pd-Cu catalyst.

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