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Screening iridium-based bimetallic alloys as catalysts for direct ethanol fuel cells

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ABSTRACT

Current ethanol oxidation catalysts in direct ethanol fuel cells (typically platinum-based) suffer from low conversion and are susceptible to CO poisoning. We therefore determined to find viable alternative catalysts for ethanol oxidation based on iridium using density functional theory to model bimetallic alloy (1 1 1) surfaces. Iridium was alloyed with another transition metal (from groups 4 through 11), M, in an overlayer (one layer of metal M on top of bulk iridium) or subsurface configuration (M inserted under the first layer of iridium). Segregation energies were calculated and the subsurface configuration was found to be most stable configuration in the majority of alloy cases under vacuum conditions. Select alloys (including Ir–Pt and Ir–Rh) showed a reversal of preferred alloy state (overlayer or underlayer) upon adsorption of CO. CO adsorption was modeled and lower CO adsorption energies were found for many alloys compared to pure Pt, indicating less CO poisoning. Complete oxidation of ethanol is typically limited by the breaking of strong C—C bonds, so any catalyst must lower the barriers for C—C bond breaking. Activation energies for C—C bond breaking (by considering a representative intermediate molecule CHCO) were lowered for the vast majority of the alloys used in an underlayer structure, reinforcing the significance of the underlayer structures or "subsurface" alloys. Finally, we found, based on CO adsorption energy, activation energy for C—C breakage reaction, and metal cost, three important catalyst descriptors, a number of promising catalysts for the ethanol oxidation reaction, such as alloys with M = Zr, Nb, Mo, W, Ru, Os, or Re. Experimental verification (cyclic voltammetry and chronoamperometry for ethanol oxidation) on Ir, Ir–Ru, and Ir–Rh catalysts confirmed the superiority of these Ir-based catalysts compared to Pt. Our results demonstrate that alloys of Ir show promise as more affordable substitutes for platinum group metals.

1. Introduction

The world's energy demand is continually growing, and it is crucial to find alternatives to current fossil fuels. Indeed, more efficient and environmental friendly energy production processes are needed. Numerous solutions are currently being investigated including fuel cells, which may produce energy with low environmental footprint. Polymer electrolyte membrane (PEM) fuel cells have large theoretical efficiency when a fuel, such as hydrogen is supplied to the device, much more than combustion, which is limited by the Carnot cycle efficiency [1]. Nevertheless, the problem of storage currently hinders the use of hydrogen as a fuel. For example, storage may require high pressure tanks operating at 200–700 bar, or a cryogenic tanks working at low temperatures (such as −223 °C) [2,3]. Chemical storage of hydrogen has also being investigated, but is difficult. Other fuels have been considered, including alcohols such as ethanol or methanol. Ethanol is an attractive fuel choice because it is easily stored as a liquid and has high energy density [1,4–6], similar to gasoline's energy density [7]. Ethanol is also relatively non-toxic. Furthermore, ethanol can be produced in important quantities from biomass [5].

Slow kinetics for the ethanol oxidation reaction (EOR) at the anode catalyst limits the efficiency of direct-ethanol fuel cells (DEFCs). For example, over current Pt-based catalysts incomplete oxidation of ethanol produces acetaldehyde and acetic acid which releases only 2 and 4 electrons, respectively [1,4]. Complete oxidation however forms CO_2 and releases 12 electrons [1,4], increasing the available electrical energy, as indicated by the following reactions:

$$CH_3CH_2OH + 3H_2O \rightarrow 12H^+ + 12e^- + 2CO_2 (\text{total oxidation}) \quad (1)$$

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$$2CH_3CH_2OH + H_2O \rightarrow 6H^+ + 6e^- + CH_3COOH + CH_3CHO(\text{partial oxidation}) \quad (2)$$

Current Pt-based catalysts are expensive and also suffer from CO poisoning. It is therefore necessary to find new electrocatalysts that could increase the overall kinetics of the ethanol oxidation reaction and increase the selectivity of the reaction toward CO_2 formation [3]. DEFC anode catalysts have been extensively studied, with much focus on platinum. Various attempts have been employed to reduce the Pt loading, such using alloys or carbon supports or even using other materials like carbides and oxides as anode catalysts. Alloying, by adding another element [3,5,8–10] or by even adding a third element [5], has been a popular method of catalyst development. Different alloy structures have been studied, from metal doping to near surface alloys (NSA) [11] or even core/shell structures [12,13].

The bottleneck for efficient ethanol oxidation is believed to be the breaking of strong C—C bonds [3]. Various C—H, C—O, or C—C scission steps may occur at the catalyst surface, but complete oxidation involves C—C bond breaking, while incomplete oxidation does not. Density functional theory (DFT) calculations are commonly used to identify new potential catalysts and numerous studies have been performed for ethanol oxidation/decomposition [14–17]. Ferrin et al. [18] screened various transitions metals as catalysts for ethanol decomposition using Brønsted–Evans–Polanyi (BEP) correlations to determine the activation barriers for possible intermediates and they have been able to show that, for most transitions metals, including iridium, the rate determining step for C—C cleavage involves a CHCO intermediate being separated into two molecules, CH and CO. Another previous DFT study led by Alcala et al. [15] investigated C—O and C—C cleavage pathways over Pt for ethanol and concluded that C—C scission was also likely to proceed through a ketenyl species (CHCO).

Platinum group metals are well known for their exceptional catalytic properties. Ferrin et al. [18] reported that metals such as Pt, Pd, Ru, Ir or Rh could be interesting candidates for the EOR. Many experimental or theoretical studies can be found in the literature concerning Pt [10,19–21], Pd [6], Ru [22–24] and Rh [3] as catalysts for the EOR but less work has been conducted with Ir. Recent experimental work with Ir and Sn was reported [25] and showed comparable results to that of a Pt_3Sn/C catalyst, currently one of the most efficient anode catalysts for the EOR [10,16]. More recently, Du et al. [4] also showed that Ir (in the form of Ir–Sn–SnO_2) could be a very good catalyst candidate for the EOR, obtaining a high electrochemical activity comparable to a commercial PtSn catalyst. They observed a core–shell structure for the Ir alloy. The same group developed a Ir–Ru alloy [26] which showed enhanced activity compared to Pt or Ir.

Motivated by previous experimental and theoretical work, the reactivity of Ir-based catalysts for the EOR has been investigated, using core–shell-like bimetallic structures made of Ir and another transition metal. Emphasis was placed on C—C bond breaking as a potential rate determining step (CHCO → CH + CO) and in identifying potential catalysts to replace Pt. Our efforts focused on modeling a large number of alloys and screening these alloys for potential ethanol oxidation activity. Accordingly, activation energies were calculated using a previously established BEP correlation [27]. We also examined the resistance of the studied alloys to CO adsorption. The preferred location of alloyed metals (surface or sub-surface) was examined and we determined under what conditions such alloys are stable. Our analysis indicates which alloys would potentially be economically feasible and also catalytically active, suggesting directions for future experimental studies.

2. Methodology

2.1. Computational methodology

2.1.1. Simulation parameters

All calculations were performed using the CP2K code [28,29]. The PBE exchange correlation function was used [30]. CP2K uses the Gaussian and Plane Wave (GPW) [31] method so electron densities were treated by plane wave functions and molecular orbital were represented by double-zeta Gaussian basis functions [32]. Core electrons were represented by Goedecker–Teter–Hutter (GTH) pseudopotentials [33,34]. The current version of CP2K only samples reciprocal space at the Γ point, which could potentially result in simulations errors. Consequently, the slab that we used was rather large so any errors from k-point sampling were minimized. With the exception of Ni, Co, and Fe, which display magnetic properties, all bimetallic structures were modeled as non-spin polarized, similar to previous work [35]. For instance, we calculated the CO adsorption energy over a Au–Ir alloy to differ by only 10^{-4} eV between spin polarized and non-spin polarized calculations.

2.1.2. Surface model

The Ir (1 1 1) surface was modeled using the slab approach, with a 6 × 6 super cell under periodic boundary conditions. Each slab was repeated periodically with at least 30 Å of vacuum between neighboring metal slabs and was three atomic layers thick. The bottom layer of the slab was kept frozen. Two different alloys configurations were used as shown in Fig. 1: the first configuration consisted of replacing the top layer of Ir with another transition metal (overlayer structure), while the second consisted of replacing the middle Ir layer with another transition metal (underlayer structure). Similar alloy structures were used by Greeley and Mavrikakis [11] or by Su et al. [8] in their study of near-surface alloys. Adsorption was allowed only on the top layer of the slab. Transition metals between groups 4 (Ti, Zr, and Hf) and 11 (Cu, Ag, and Au) of the periodic table were all alloyed with Ir.

Adsorption energies were determined according the following formula:

$$E_{\text{adsorption}} = E_{\text{adsorbate/surface}} \text{-} E_{\text{surface}} - E_{\text{adsorbate in gas phase}} \quad (3)$$

where $E_{\text{adsorbate/surface}}$ is the energy of the surface/adsorbate system, E_{surface} is the energy of the clean surface, and $E_{\text{adsorbate in gas phase}}$ is the energy of the gas-phase molecule. We modeled adsorption of CO, CH, and CHCO over the various alloys. As previously mentioned, C—C bond breaking is typically the hardest step in the ethanol oxidation reaction. Work by Alcala et al. [15] showed that C—C breaking of CHCO had the lowest barrier of various possible intermediates over the Pt (1 1 1) surface. Later work by Ferrin et al. [18] expanded to other (1 1 1) surfaces, including Ir. The rate-determining step was found to also involve CHCO C—C scission. Hence, we modeled CHCO adsorption and its derivatives. CO was adsorbed on top sites, which are the most preferred sites over Ir (1 1 1) according to our calculations (see Fig. 3) and previous experimental testing [36]. CH adsorption calculations by Abild-Pedersen et al. [37] reported that CH adsorbs preferentially on threefold sites (hcp or fcc). Previous work also indicated that CH over Pt (1 1 1) prefers hollow sites, with differences in energies between hpc and fcc sites less than 0.1 eV [26,38]. Fig. 2 shows CO and CH geometries. The adsorbed CHCO geometry had the CH group near a hcp site, so only CH in the hcp position was modeled. The initial geometry of adsorbed CHCO we used was based on the work of Alcala et al. [15]. This geometry