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# BES025. Metal dissolution mechanisms in Pt-based alloys: Ideas for advanced PEM cathode design

Perla B. Balbuena  
Texas A&M University  
3122 TAMU  
College Station, TX 77843  
Phone: (979) 845-3375; Fax: (979) 845-6446  
E-mail: balbuena@tamu.edu

DOE Program Officer: Dr. Raul Miranda  
Phone: (301) 903-8014  
E-mail: Raul.Miranda@science.doe.gov

## Objectives

We aim to develop new understanding that can foster the development of better catalyst materials for proton-exchange membrane cathodes. To achieve this goal, we focus on answering these questions: 1) How the catalytic surface and its environment change as the reaction takes place; 2) What are the effects of the dynamics of the catalyst and that of the surrounding medium on the catalytic activity and stability; 3) What is the effect of important side reactions on the catalytic process.

## Technical Barriers

One of the main problems of current alloy cathode electrocatalysts is their strong dissolution trend especially when platinum is combined with less “noble” transition metals. Upon dissolution, metal ions cause other problems such as membrane degradation, or upon ion reduction, particle agglomeration. In this study, we determine the mechanisms that trigger metal dissolution and analyze possible alternative materials that may help mitigate the problem.

## Abstract

We present results from a systematic density functional theory study of core-shell alloy surfaces, with monometallic cores of the 3d, 4d, and 5d groups. The analysis reveals that all the 4d and 5d pure cores may serve as relatively stable cores, and their beneficial effect on the Pt monolayer may be further tuned by alloying them to another element, here chosen from 3d or 5d groups. The Pd<sub>3</sub>X cores enhance the stability of the surface Pt atoms both in vacuum and under adsorbed oxygen; however, the high oxygen-philicity of some of the X elements induces their surface segregation that

may cause surface poisoning with oxygenated species and metal dissolution in acid medium.

Based on the above DFT studies, we introduce a new class of catalytic materials with enhanced activity and high stability of the surface *and* core atoms against dissolution in acid medium. The significant stability improvement found in the new material is due to the addition of a small-radius species that locates in the interstitial sites of the top subsurface layers locking the core transition metal atoms in their positions, thus avoiding their segregation to the surface and posterior dissolution, which is driven by the oxidative acid environment. We illustrate our findings by a detailed analysis of the durability and activity enhancement for the platinum/iron-carbon/iridium system.

## Progress Report and Future Directions

**1. Surface stability of Pt-monolayers on pure cores.** Calculated electrochemical potential shifts (DU) for surface Pt atoms on top of pure 4d and 5d transition metal cores show that the core elements have little tendency to segregate to the surface, and in some cases (Ir and Rh) they have large antisegregation energies. It is interesting that DU decreases as the difference of charges between the surface and the subsurface becomes smaller, indicating that a large charge transfer between the top surface and the subsurface has a stabilizing effect on the surface Pt atoms. We concluded that in principle, these systems could be *stable* core candidates. Our calculations indicate that the difference in binding energies  $BE_{OH} - BE_O$ , that correlates with previous reports on activation energy for OH formation,<sup>1</sup> follows the order  $Ag > Au > Pd > Pt > Rh > Ir$ . On the other hand, the O binding energies follow the core order  $Rh < Ir < Au < Pd < Pt < Ag$ ; this order is the opposite to that of the reported ORR currents:  $Pd > Au > Rh > Ir$ ; thus, Pt/Pd having an intermediate strength for O adsorption and for OH formation yields the highest ORR activity.<sup>1</sup> It is interesting that the OH adsorption energies (that we shown to be driven by *both* electronic and geometric effects) follow the core order  $Ag < Au < Rh < Ir < Pd$ , and all of the Pt-skin surfaces yield OH adsorption energies weaker than those on Pt(111). In summary, the analysis of stability and activity of the pure cores suggests that combining 4d or 5d elements with 3d elements would provide alternative formulations for core-shell alloys. According to our results, the group of 4d and 5d metals yield weaker O and OH energies, indicating good ORR activities, and their positive DU suggests that if these cores are alloyed with 3d elements

having a large negative d-band center value (such as Co, Ni, Cu), beneficial activity effects may be enhanced.

**2. Surface stability of Pt-monolayers on alloy cores.** Analysis of segregation trends of Pd and X from the core to the surface as functions of the electronic charge of the atom X in the subsurface for Pt/Pd<sub>3</sub>X alloys indicate that the strength of antisegregation of X towards the surface increases with the degree of oxidation of the atom X in the subsurface. On the other hand, Pd has a slight tendency to segregate to the surface that increases with increasing oxidation degree of X in the subsurface. The Pd-segregation data shows two groups: one including elements of the period 6 (Ir and Re), and the other with elements of period 4 of the periodic table. In both cases the less positively charged Pd atoms tend to migrate to the surface, whereas X atoms tend to remain in the core, thus establishing an attractive electronic interaction with the Pt surface atoms bearing slightly negative charges. This polarization of the metal overlayer/transition-metal substrate has been discussed by other researchers based on experimental and theoretical evidence.<sup>2-3</sup> Under 0.25 ML of O, the Pd segregation trend is not very different from that found on the clean surface, but a strong segregation pattern is found for Ir, Cr, V, Ti, and Re, and weaker for Co and Fe. We found that the Ir segregation trend changes drastically from that found in the pure Ir core, since the cohesive properties of the pure Ir system are lost in the alloy. Given our findings respect to segregation trends, it is of interest to analyze the stability of Pt atoms against dissolution when Pt is on the surface of these alloys. These trends reveal a clear correlation of the stability of the Pt atoms on the surface and the degree of oxidation of the atom X in the subsurface, reinforcing our earlier conclusion that a strong attractive electronic interaction may be established between the Pt monolayer and the subsurface alloy layer. The calculated binding energies per Pt atom of the monolayer to the core increase in the order Ir < Co < Fe < Re < V < Ti < Cr, that follows (except for Cr) the order shown by the stability of Pt atoms, both for a clean surface and under adsorbed O. Thus the presence of a relatively small concentration of the X elements in the Pd<sub>3</sub>X core enhances the stability of Pt atoms on the surface of the core-shell alloys. This result is in agreement with previous XPS binding energy shifts<sup>3</sup> and DFT analysis<sup>2</sup> of a metal adlayer on a transition metal substrate revealing heterometallic bond formation attributed to orbital rehybridization effects. With respect to reactivity, although the O binding energies on the Pt-skin surfaces are relatively weak compared to that on Pt(111), these energies increase under segregation of Pd and in some of the surfaces there is a strong increase under segregation of X,

especially for Ti, V, Cr, and Re that are known to have strong affinity for oxygen.

Although we have shown that these cores impart high stability to the surface Pt atoms, another factor to evaluate is the trend of the X core elements to dissolve in acid medium inferred from their experimental redox potentials. It is clear that all the elements would dissolve at more negative potentials than pure Pt (1.18 V). In addition, as remarked by Greeley and Nørskov<sup>4</sup> dissolution tendencies follow trends in segregation energies. Based on this, we remark that our calculated segregation trends add significant information regarding dissolution of core elements under oxidation conditions. With respect to the ORR activity of the group of Pt/Pd<sub>3</sub>X alloys, all the O binding energies are much lower than those on Pt/Pd, following the order Re < V < Ti < Co < Fe < Ir = Cr, the same order is approximately followed by the strength of O adsorbed when Pd segregates. However, on surfaces where the X element has segregated, the binding energies of O to these elements is significantly higher, with the order being changed to Co < Fe < Ir < Cr < Ti < V < Re, that except for small differences is the same order that is followed by the OH binding energies. Thus, within this formulation, Pt/Pd<sub>3</sub>Co and Pt/Pd<sub>3</sub>Fe stand out as promising alloys in both activity and stability aspects. However, the present analysis also suggests that Pt/Pd<sub>3+y</sub>X<sub>1-y</sub> alloys with 0 < y < 1 are excellent candidates for ORR catalysis.

**3. Design of a core/shell material with an active and durable Pt surface.** Based on the above analysis, we inferred that an active surface that is also resistant to dissolution in acid medium requires a stable core that in addition is able to alter the Pt electronic structure increasing its ORR activity. Thus, we investigated a new class of core-shell materials composed by a platinum monolayer over a composite core where an extra element has been added to the transition metals in order to anchor them to the core, thereby retaining their beneficial properties towards the surface atoms and enhancing the stability of the catalyst against dissolution.<sup>5</sup> We demonstrated the properties for the composite system Pt/Fe-C/Ir depicted in Figure 1.

We first evaluated the effect of the presence of subsurface interstitial carbon on the surface electronic

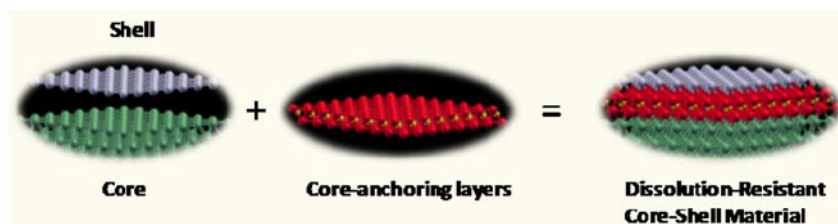


FIGURE 1. Schematic illustration of the proposed new catalytic design.

and geometric properties of the Pt monolayer. We determined oxygen adsorption energy strength (signaling catalytic activity),<sup>6</sup> segregation energy of the subsurface metal atoms on the clean surface and under 0.25 ML of adsorbed oxygen (related to surface stability and activity),<sup>4</sup> electrochemical potential shift on clean surface and under 0.25 ML of adsorbed oxygen (onset of Pt dissolution),<sup>7</sup> and binding strength (per Pt atom) of the top surface to the core (a measure of surface stability). We noted that the largest electrochemical potential shift corresponds to the alloy core in absence of carbon; however this structure has a significant iron surface segregation trend which affects the catalyst durability.<sup>8</sup> Instead the structure where carbon fills the subsurface shows an optimal combination of activity and stability properties.

One of the best characteristics of the proposed composite core-shell material is the antisegregation of transition metal atoms toward the surface even in presence of adsorbed oxygen; this feature is explained from the analysis of the electronic structure as given by the Bader electronic charges.<sup>5</sup> Without carbon, the geometric stress introduced by the Pt overlayer on the core generates a charge transfer that results in an excess of electrons in the surface and a deficit in the first subsurface layer, as found in previous experimental and theoretical studies.<sup>2</sup> A similar charge transfer effect occurs between the Ir and Fe atoms of the 4<sup>th</sup> and 5<sup>th</sup> layers. In presence of carbon, the iron atoms transfer charge not only to Pt and Ir but also to carbon, as revealed by the increase of the positive charges on Fe as the C concentration increases. The charge transfer Fe-C denotes their strong affinity and bonding resulting from orbital hybridization, which prevents iron segregation towards the surface, even under adsorbed oxygen. The increased stability is also associated with the polarization of the first two layers, which determines the high binding of the overlayer to the core.

In summary, we have demonstrated the potential durability and activity properties of a new class of core-shell composite materials. The enhanced durability arises from the use of carbon in the interstitial sites of the subsurface that anchors the transition metals in their positions impeding their segregation to the surface while keeping their beneficial properties that favor ORR activity on the top platinum monolayer. We are currently exploring other core-shell designs that may offer similar catalytic and extended durability properties and we expect to address other challenges such as the presence of surface defects on the performance of the new material. Interesting systems include the use of a Pd monolayer (instead of Pt), although Pd dissolution may happen at lower potentials than those of the Pt monolayer, according to the trend of their redox potentials.

## Future Directions

We are extending our design of dissolution-resistant catalysts to other core combinations. This extended study will allow us to optimize the cost and feasibility of fabrication. We have been discussing possible fabrication of our proposed new catalytic design with experimental groups and we have some ideas for making the systems more realistic keeping the same basic beneficial features. In addition, we are developing and implementing a kinetic Monte Carlo (KMC) technique to evaluate the evolution of the surface as a function of time, under reaction, and under applied potential. The KMC program requires as input the rates of the diffusion and migration processes from the subsurface and on the surface that we have already obtained in our previous and current DFT analysis.

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