

## Core-Shell PtOs as an Efficient Catalyst for Oxygen Reduction Reaction

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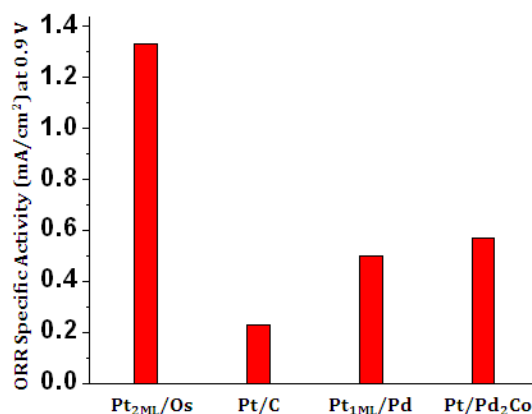
The efficiency of the Oxygen Reduction Reaction (ORR) at the cathode of a Proton Exchange Membrane Fuel Cell (PEMFC) is a critical issue for its commercial application [1-4]. To date, the best ORR catalysts are Pt and Pt-based binary alloys, such as Pt<sub>3</sub>Ni [5] and Pt<sub>3</sub>Co [6]. The exact mechanism responsible for the superior ORR performance of the Pt<sub>3</sub>Ni alloy has not been clearly determined yet. It is realized that in alloyed Pt electrocatalyst, the surface segregation of Pt atoms in which the surface layer is 100% Pt (so-called Pt-skin) whereas the second layer has more than 50% of the alloyed solutes [7] (e.g. Co, Ni), is an important surface property that contributes to the improved ORR catalytic properties [8, 9]. During the ORR process, adsorbates including the O and OH can lead to undesirable leaching of the alloyed solutes to the catalyst surface [10]. For instance, the subsurface Co atoms in the Pt<sub>3</sub>Co catalysts were found to migrate to the surface and dissolved into the electrolyte during extended fuel cell operations [11, 12]. Consequently, the subsurface layers became essentially Co-free, and only Pt atoms were present in the surface regime reflecting a Pt-like electrocatalytic behavior. Similar behavior of Ni leaching has been observed in Pt<sub>3</sub>Ni as well [13].

Using quantum mechanics (QM) calculations, we have studied the segregation energy with adsorbed O and OH for 28 Pt<sub>3</sub>M alloys, where M is a transition metal. The calculations found surface segregation to become energetically unfavorable for Pt<sub>3</sub>Co and Pt<sub>3</sub>Ni, as well as for the most other Pt binary alloys, in the presence of adsorbed O and OH. However, Pt<sub>3</sub>Os and Pt<sub>3</sub>Ir remain surface segregated and show the best energy preference among the alloys studied for both adsorbed species on the surface.

We have selected PtOs systems for our further theoretical and experimental studies. Binding energies of various ORR intermediates for the Pt<sub>3</sub>Os and Pt on the Os substrate were calculated and analyzed. We find that the binding energies of oxygen-containing species, except for O<sub>2</sub>, show the following trend:

$$E_{\text{Pt}_1\text{ML}/\text{Os}} < E_{\text{Pt}_2\text{ML}/\text{Os}} < E_{\text{Pt}_3\text{ML}/\text{Os}} < E_{\text{Pt}} < E_{\text{Os}}$$

Energy barriers for different ORR steps were computed for pure Pt, Os, Pt<sub>3</sub>Os and Pt/Os core-shell catalysts with 1, 2 and 3 layers of Pt on the Os substrate and the rate-determining step (RDS) was identified. It turned out that the RDS barrier for the Pt<sub>3</sub>Os alloy and Pt/Os core-shell catalysts is lower than the corresponding barrier for pure Pt. This result allows us to predict better performance of the Pt/Os system compared to pure Pt, which is in fact observed in experiment. The ORR specific activity is about 7 times higher than that of pure Pt (Figure 1).



**Figure 1.** ORR specific activity of core-shell catalysts. Results for Pt/Pd and Pt/Pd<sub>2</sub>Co core-shell catalysts are from Refs 14 and 15, respectively.

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