

# DESIGN OF AN OXYGEN REDUCTION CATALYST FOR DIRECT METHANOL FUEL CELLS

Jing Xu, Jinhua Yang, Jim Yang Lee, Mark Saeys  
Department of Chemical and Biomolecular Engineering,  
National University of Singapore, 4 Engineering Drive 4, Singapore 117576

## Summary

First principle calculations were used to screen the activity of oxygen reduction electrocatalysts for direct methanol fuel cells. Density functional theory calculations indicate that the subsurface substitution of Pt by 3d transition metals improves the activity of PdPt catalysts by reducing the oxygen binding energy. Optimal activity close to the maximum of a volcano curve is predicted for PdFe@PdPt and PdMn@PdPt core shell catalysts. To validate the theoretical predictions, a series of the PdM@PdPt catalysts (M=Ni, Co, Fe and Cr) was prepared by a galvanic replacement reaction. Optimal activity and methanol tolerance was observed for a PdFe@PdPt electrocatalyst.

## Keywords

Density Functional Theory; Oxygen Reduction Reaction; Direct Methanol Fuel Cells.

## Introduction.

PdPt bimetallic catalysts have been recognized as promising anode catalysts for direct methanol fuel cells (DMFC) because of their good methanol tolerance. Unfortunately, their activity is less than optimal. To improve the activity of PdPt based catalysts, we propose to replace the subsurface Pt atoms by 3d transition metal atoms, while maintaining the surface PdPt composition. To evaluate the potential effect of subsurface 3d transition metals on the Oxygen Reduction (ORR) activity, Density functional theory (DFT) calculations were performed. The calculations indicate that replacing subsurface Pt by Fe or Mn reduces the barrier for the rate limiting step by 0.1 to 0.15 eV, and brings the ORR activity close to the maximum of a volcano curve.

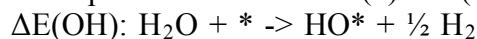
## Computational and Experimental Methods.

Oxygen and hydroxyl binding energies, and O<sub>2</sub> dissociation barriers were calculated using periodic DFT-PW91 as implemented in the Vienna Ab initio Simulation Package (VASP)<sup>1</sup>.

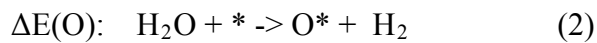
The catalyst was modeled as a (2x2) Pd<sub>3</sub>Pt(111) surface layer and two Pd<sub>3</sub>M subsurface layers, where M is a 3d transition metal. Experimentally, PdM@PdPt (M=Ni, Co, Fe and Cr) core shell electrocatalysts were prepared by a galvanic replacement reaction<sup>2</sup> between PdM alloy nanoparticles with a 70:30 Pt:M atomic ratio and an aqueous solution of PtCl<sub>4</sub><sup>2-</sup>. The composition of the electrocatalyst particles was evaluated using XPS, and confirmed to be consistent with the model used in the calculations.

## Results and discussion.

The ORR activity for different PdM@PdPt electrocatalysts was evaluated computationally using the approach proposed by Nørskov et al.<sup>3</sup> First, hydroxyl and oxygen binding energies were computed from reactions (1) and (2).



(1)



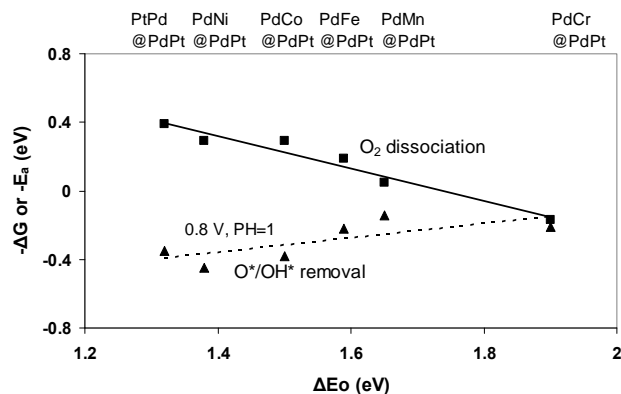
Using formula's from statistical mechanics and electrochemistry, these catalyst properties were then converted to Gibbs free reaction energies,  $\Delta G_{\text{rxn}}(\text{pH}, U)$ , for the removal of  $\text{OH}^*$  and  $\text{O}^*$  from the catalyst surface through protonation. To develop a kinetic model for the ORR,  $\text{O}_2$  dissociation barriers were calculated as well for the different alloys. The calculated  $\text{O}_2$  dissociation barriers and  $\Delta G_{\text{rxn}}$ 's for  $\text{O}^*/\text{OH}^*$  removal are shown in Figure 1 as a function of the oxygen binding energy,  $\Delta E(\text{O})$ . Catalysts to the left of Figure 1 bind  $\text{O}^*$  and  $\text{OH}^*$  too strong, and  $\text{OH}^*$  removal becomes rate limiting. Replacing subsurface Pt by a 3d transition metal reduces  $\text{O}^*$  and  $\text{OH}^*$  binding energies (reactions (1) and (2) become more endothermic), and hence increases the rate of the rate limiting step. However,  $\text{O}_2$  dissociation becomes more sluggish as the oxygen binding energy decreases, and  $\text{O}_2$  dissociation becomes rate controlling for PdCr@PdPt. As shown in Figure 1, the competition between  $\text{O}_2$  dissociation and  $\text{O}^*/\text{OH}^*$  removal leads to a volcano curve. PdFe@PdPt and PdMn@PdPt are predicted to have optimal activity. The change in  $\text{O}^*$  binding energy can be further correlated with the variation in the surface electronic structure using the d-band model.

To evaluate the computational predictions, a series of PdM@PdPt catalysts was synthesized and tested experimentally. The kinetic current density obtained from the Koutecký-Levich equation for PdM@PdPt/C electrocatalysts is shown in Figure 2. A volcano curve is again obtained, with a maximum observed activity for PdFe@PdPt/C. Unfortunately, a PdMn@PdPt electrocatalyst could not be prepared using a galvanic displacement reaction. The PdM@PdPt core shell electrocatalysts were further found to display excellent methanol tolerance when evaluated in the presence of 0.1 M methanol.

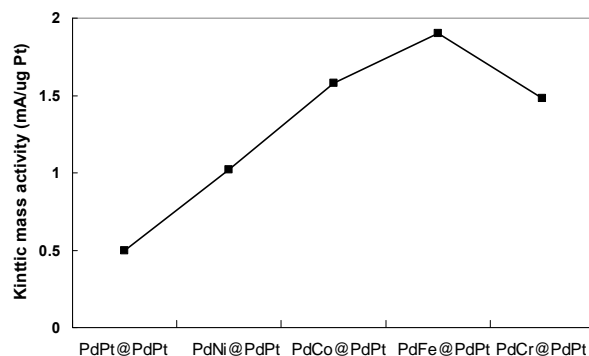
## Conclusion.

The Oxygen Reduction Reaction (ORR) activity for a series of PdPt@PdM core shell electrocatalysts was evaluated using DFT calculations. The calculations indicate that the ORR activity of PdPt catalysts can be improved by replacing bulk Pt atoms by a 3d transition

metal. The optimal catalyst is predicted to have an oxygen binding energy between PdFe@PdPt and PdCr@PdPt. The theoretical predictions were confirmed experimentally; the ORR activity of PdFe@PdPt/C was four times higher than of PdPt/C, yet maintains excellent methanol tolerance.



**Figure 1.** Computational evaluation of the ORR activity of different core-shell catalysts for a cell potential  $U=0.8$  V and a  $\text{pH}=1$ , as a function of the oxygen binding energy,  $\Delta E_{\text{O}}$ .



**Figure 2.** Kinetic mass activity for PdPt/C and PdM@PdPt/C (M=Ni, Co, Fe and Cr) electrocatalysts, measured at a cell potential  $U=0.8$  V RHE.

## References

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