



Contribution ID: 124

Type: Poster

Modeling of the synergistic behavior of adjacent Pt{111} and Pt{100} nanorod model facets – A DFT study

Introduction

The oxygen reduction reaction (ORR) is particularly interesting, especially in the context of fuel cells and metal-air batteries [1,2]. The loss in cell potential at low current densities accounts for over 67% of the total potential loss and is primarily attributed to slow ORR kinetics [3]. When modelling the overall ORR activity over multifaceted Pt nanocrystallites, it is generally assumed that the different surface regions, i.e. terraces, edges and corners, are kinetically isolated and can therefore be modelled independently [4-5].

A range of ORR mechanisms have been proposed and the corresponding energetics, i.e. reaction and activation energies, have been calculated and reported [6-8]. A closer look at the reaction mechanisms and energetics shows that (1) O and OH removal over a Pt{111} and Pt{100} surface, respectively, is the most energetically hindered step, [6-8] and (2) facilitating an OH/O exchange between the Pt{111} and Pt{100} facets may result in improved ORR specific activity. Therefore, this study investigates the extent of O and OH cross-surface diffusion between the Pt{111} and Pt{100} facets of a pure Pt nanorod model. Furthermore, the cross-surface diffusion of OH on modified Pt nanorod models is reported.

Materials and Methods

Reaction and activation energies were calculated with periodic Density Functional Theory (DFT), using the Vienna Ab Initio Simulation Package (VASP) [9,10]. The Perdew, Burke and Ernzerhof (PBE) exchange-correlation functional together with the projector augmented wave (PAW) potential method was used. All calculations were spin polarized and corrected for dipole moment. A plane wave basis set cut-off energy of 400 eV was also used.

The potential energy surface for OH and O diffusion between a Pt{111} and Pt{100} facet was calculated by considering a rhombic nanorod model with alternating {111} and {100} facets separated by a pristine edge atomic row. Each surface of this nanorod model consists of 10 Pt atoms, and along the nanorod axis (y-direction) the nanorod is periodic with two Pt atoms per atomic row per cell. A gamma-centered Monkhorst-Pack k-point grid of 1x5x1 was used for all nanorod calculations. The pure Pt nanorod model, Pt_NR, (Figure 1) was modified by substituting the edge Pt atomic row with silver or gold atoms. The latter nanorod models are denoted Pt_NR/silver and Pt_NR/gold respectively.

Results and Discussion

The local nature of the edge effect is confirmed for atomic O. Atomic O cross-surface diffusion over the edge is also investigated and found to be significantly faster ($\times 103$ and $\times 107$ towards the Pt{100} and Pt{111} facet, respectively) at high edge O coverage than at moderate and low coverage. This improvement in the rate constant of diffusion is attributed to the lowering of the activation energy for diffusion of adsorbed O away from the edge, which occurs concomitant with a flattening of the potential energy surface, a result of strong repulsive lateral interactions at high coverage. This brings into question the assumption that different terraces are kinetically isolated.

Although there may be a kinetic connection through atomic O diffusion, the generation of O over Pt{100} is much faster than that over a Pt{111} facet. Furthermore, the hydrogenation of O over Pt{111} is much slower than that over Pt{100} [6-8]. Therefore, facilitation of interfacet diffusion of OH could have a significant impact on the overall rate. Figure 1 (attached) shows the diffusion barriers of OH over an edge and the effect of edge modification with gold and silver atoms. Over an unmodified Pt nanorod (Pt_NR), the rate constant of diffusion of OH from the edge site towards the Pt{111} terrace is 0.09 s⁻¹. We demonstrate that this rate constant of diffusion can be improved via modification of the edge atomic row with gold or silver atoms.

Significance

Facilitating the cross-surface diffusion of OH may improve the kinetic rate over a crystallite with alternating Pt{111} and Pt{100} facets. This work explores an alternative pathway for oxygen reduction over multifaceted platinum crystallites. Moreover, the kinetic data generated is used to develop more accurate microkinetic models to predict the overall ORR activity over multifaceted crystallites.

References

1. A. A. Gewirth, A. A. and Thorum, M. S. Inorg. Chem. 49, 3557 (2010).
2. Nie, Y., Li, L. and Wei, Z. Chem. Soc. Rev. 44, 2168 (2015).
3. Gasteiger, H. A., Kocha, S. S. et al. Appl. Catal. B Environ. 56, 9 (2005).
4. Tripković, V., Cerri, I. et al. Catal. Letters. 144, 380 (2014).
5. Nesselberger, M., Ashton, S. et al. J. Am. Chem. Soc. 133, 17428 (2011).
6. Li, K., Li, Y. et al. J. Mater. Chem. A. 3, 11444 (2015).
7. Duan, Z. and Wang, G. J. Phys. Chem. C. 117, 6284 (2013).
8. Ford, D. C., Nilekar, A. U. et al. Surf. Sci. 604, 1565 (2010).
9. Kresse, G. and Hafner, J. Phys. Rev. B. 47, 558 (1993)
10. Kresse, G. and Furthmüller, J. Phys. Rev. B. 54, 11169 (1996)

Presenter Biography

I am a chemical engineer by training and have obtained both BSc and MSc from the University of Cape Town. My current research involves the application of computational chemistry methods, ab initio density functional theory (DFT), classical molecular dynamics (MD) and microkinetic analysis, to study catalytic systems. The main focus of my current PhD research is the understanding of the oxygen reduction reaction (ORR) mechanism over multi-faceted Pt-based nanomaterials.

I am also interested in methane activation and oxide materials as fuel cell and electrolyser supports.

Primary author: GAMBU, Thobani (Catalysis Institute, University of Cape Town)

Co-authors: VAN STEEN, Eric (Catalysis Institute, Department of Chemical Engineering, University of Cape Town); Dr PETERSEN, Melissa (University of Cape Town)

Presenter: GAMBU, Thobani (Catalysis Institute, University of Cape Town)

Session Classification: Poster session

Track Classification: Computational Chemistry