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**“Mitigation of CO poisoning on functionalized Pt/TiN(001) surface:
A fundamental study of the next-generation fuel cell technologies”**

27th May 2014

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Abstract: It has been previously reported that the system of embedding single Pt atom in the N-vacancy site on TiN(100) surface (Pt/TiN) could be a promising catalyst for proton exchange membrane fuel cells (PEM FCs). The adsorption properties of molecules on Pt/TiN are an important step, when it is incorporated as the anode or cathode of PEM FCs. Utilizing the first principle calculations based on density-functional theory, this proposal systemically investigates the adsorption of several atomic and molecular species on Pt/TiN system, as well as the co-adsorption of these molecular fragments. The favourable binding sites and energies of adsorption of several molecular species, namely carbon dioxide (CO₂), carbon monoxide (CO), oxygen (O₂), hydrogen (H₂), hydroxyl (OH), oxygen atom (O), and hydrogen atom (H) are explored. For each, the formation energies, preferred binding site and their associated vibration frequencies will be studied. Preliminary results of molecular adsorption indicate that these interactions could well be dominant surface interactions under operational conditions. To further study the fundamental impact of surface functional groups on CO mitigation in this catalyst system, the co-adsorption of CO and OH (or H) on the Pt/TiN surface are also investigated. In this proposal, we will attempt to study and explain the fundamental mechanism behind the mitigation of CO poisoning on functionalized Pt/TiN surfaces under both acidic and basic operation conditions in PEM FCs.

Introduction: Recently, we have studied and reported the unique role of titanium nitride supports for single-atom platinum-based catalysts in fuel cell technology using first-principles DFT calculations. We have investigated the adsorption properties of Pt atoms on the pristine TiN(001) surface, as well as the dominant influence of surface defects on the thermodynamic stability of platinized TiN. Optimized atomic geometries, energetics, and analysis of the electronic structure of the Pt/TiN system are reported for various surface coverages of Pt. We find that atomic Pt does not bind preferably to the clean TiN surface, but under typical PEM fuel cell operating conditions, i.e. strongly oxidizing conditions, TiN surface vacancies play a crucial role in anchoring the Pt atom for its catalytic function. Whilst considering the energetic stability of the Pt/TiN structures under varying N

conditions, embedding Pt at the surface N-vacancy site is found to be the most favorable under N-lean conditions. Thus, in-line with reported experimental findings, we propose that the system of embedding Pt at the surface N-vacancy sites on TiN(100) surfaces could be promising catalysts for PEM fuel cells.

Experiment: We employ the projector augmented-wave (PAW) method for the electron-ion interactions and the generalized-gradient approximation (GGA) due to Perdew, Burke and Ernzerhof (PBE) for the exchange-correlation functional in density-functional theory (DFT), as implemented in the Vienna *ab initio* Simulations Package (VASP). With its PAW potentials, VASP combines the accuracy of all-electron methods with the computational efficiency of plane-wave approaches.

Using this computational setup, we study and investigate the chemical effects of simple chemisorbed species on this Pt/TiN surface, and also hope to provide an first-principles based explanation of how these surface functional groups (under both acidic and basic conditions) could help in the mitigation of CO poisoning of this Pt/TiN catalyst system.

Details can be found in the following published papers:

1. R. Q. Zhang, C.-E. Kim, B.-D. Yu, C. Stampfl, and A. Soon, Mitigation of CO poisoning on functionalized Pt/TiN surfaces, *Phys. Chem. Chem. Phys.* **15**, 19450 (2013)

Results and Discussion: In summary, from the first-principles calculations based on density-functional theory, the adsorption of several molecular species – namely CO₂, CO, O₂, H₂, OH, O, and H, on the Pt–TiN system, as well as the co-adsorption of CO with H or OH, were performed and systemically investigated. We find that the molecular adsorbates CO₂, CO and H bind preferentially to the T_{Pt} site, whilst other molecular adsorbates like OH and O prefer the T_{Ti} site. We also find that surface functional groups (e.g. OH or H) in the presence of the CO adsorbate drastically weaken the CO adsorption energy on the Pt–TiN(100) surface. On the basis of these findings, we propose that the acid and base conditions in PEM FCs could well provide a possible way to minimize CO poisoning on these surface-functionalized Pt–TiN surfaces.

List of Publications and Significant Collaborations that resulted from your AOARD supported project:

Published papers in peer-reviewed journals

1. R. Q. Zhang, C.-E. Kim, B.-D. Yu, C. Stampfl, and A. Soon, Mitigation of CO poisoning on functionalized Pt/TiN surfaces, *Phys. Chem. Chem. Phys.* **15**, 19450 (2013)

Conference presentations without papers

1. 9th World Congress of Chemical Engineering (WCCE9), Seoul, Korea (2013)