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First-principles Kinetic Monte Carlo Simulation for Catalysis: Application to the PEM Fuel Cells

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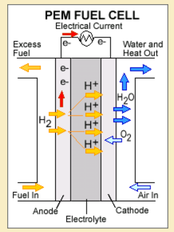
Fuel Cells



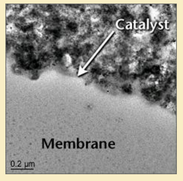
Fuel Cells – New Generation Energy Sources

- Fuel cells are electrochemical energy conversion devices that convert the energy of a chemical reaction directly into electricity.

PEM (Proton Exchange Membrane) Fuel Cells

- PEM fuel cells use a solid polymer as an electrolyte and porous carbon electrodes containing a platinum catalyst.
- PEM fuel cells need hydrogen fuel and oxygen from the air to produce electricity.
- PEM fuel cells are used primarily for transportation applications. Major automotive manufacturers have a fuel cell vehicle in development - including Honda, Toyota, GM, Ford, Hyundai and Volkswagen.

Catalyst



- A noble metal (typically platinum) is used as catalyst to speed up the reaction of oxygen and hydrogen in fuel cell.
- The platinum catalyst is very expensive and extremely sensitive to CO poisoning, making it necessary to explore new materials.

Objectives

Motivation:

- To develop a computer program in order to simulate surface reactions on fuel cell catalyst.
- To understand reaction kinetics in molecular level in order to increase the fuel cell efficiency.

Methodology:

- First-principle Kinetic Monte Carlo (KMC) Molecular Simulation Technique
- Quantum mechanics

Implementation:

- Oxygen Electro-Reduction Mechanism on the Cathode Side of PEM Fuel Cells

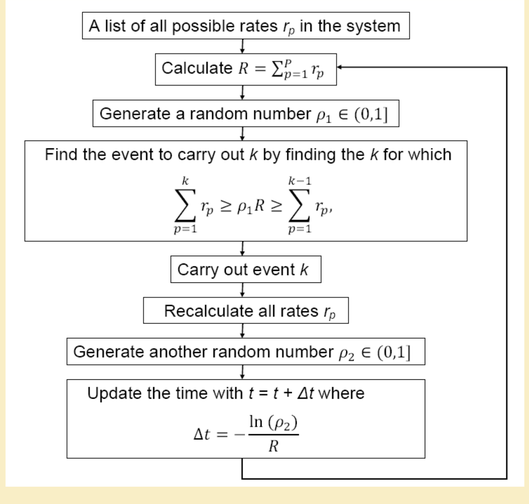
Reaction Mechanism on the Cathode Surface

1. O_2(gas) + e$^-$ + H$^+$ + b ↔ HO_2 (ads-b)
2. HO_2 (ads-b) + 2h + e$^-$ + H$^+$ → 2OH(ads-h) + b
3. O_2(gas) + b + e$^-$ ↔ O_2^-(ads-b)
4. O_2^-(ads-b) + 2h → O^-(ads-h) + O (ads-h) + b
5. O (ads-h_{hcp}) + h_{fcc} → h_{hcp} + O (ads-h_{fcc})
6. O^-(ads-h) + H$^+$ → OH (ads-h)
7. O (ads-h) e$^-$ + H$^+$ → OH (ads-h)
8. OH (ads-h) + t → h + OH (ads-t)
9. OH (ads-t) + H$^+$ + e$^-$ → H_2O (ads-t)
10. OH (ads-h) + H$^+$ + e$^-$ → H_2O (liquid) + h
11. H_2O (ads-t) → H_2O (liquid) + t

– ads = adsorbed species
– t = top site
– b = bridge site
– h = hollow site

First-principles KMC Simulations

- First-principles statistical mechanics provides atomic-scale understanding of the steady-state catalytic reaction by explicitly considering the detailed statistical interplay of all elementary processes.
- First-principles method provides efficiently and accurately approach to simulate chemical systems of reactions.
- At each configuration, all possible elementary processes *p* and the rate r_p at which they occur are evaluated. KMC simulation proceeds by generating a sequence of system configurations as follows:



Reaction Rates

- The density-functional theory (DFT) together with transition-state theory (TST) is employed to accurately obtain the reaction rates need for a First-principle KMC simulations.

Adsorption Rates

$$r_{st,i}^{ad}(T,p_i) = \tilde{S}_{st,i}(T)\frac{p_i A_{uc}}{\sqrt{2\pi m_i k_B T}}$$

$$\tilde{S}_{st,i}(T) = f_{st,i}^{ad}(T)\left(\frac{A_{st,i}}{A_{uc}}\right)exp\left(-\frac{\Delta E_{st,i}^{ad}}{k_B T}\right)$$

$$f_{st,i}^{ad}(T) = \frac{q_{TS(st,i)}^{vib}}{q_{gas,i}^{tran,2D} q_{gas,i}^{int}}$$

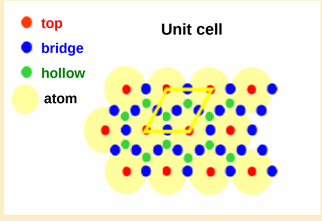
$$q_{gas,i}^{tran,2D} = A_{uc}\left(\frac{2\pi m_i k_B T}{h^2}\right)$$

Desorption Rates

$$r_{st,i}^{des}(T) = f_{st,i}^{des,TST}(T)\left(\frac{k_B T}{h}\right)exp\left(-\frac{\Delta E_{st,i}^{des}}{k_B T}\right)$$

$$f_{st,i}^{des}(T) = \frac{\left(\frac{A_{st,i}}{A_{uc}}\right)q_{TS(st,i)}^{vib}}{q_{st,i}^{vib}}$$

Simulation Model

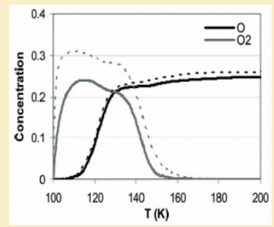


- The catalytic reactions over Pt (111) surface with the implementation of hexagonal lattice structure is simulated.
- Active sites are characterized by the names of top, hollow and bridge sites.

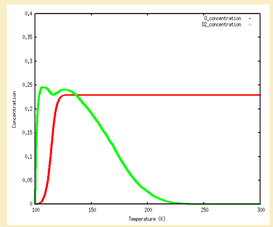
Top site	=	platinum atom
Bridge site	=	site connecting two atoms
Hollow site	=	empty site

- Each platinum atom on (111) surface is represented by one top site, three bridge sites, and two hollow sites (fcc and hcp hollow site).

Oxygen Concentration Profiles



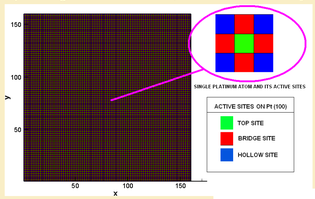
Published Results



KMC Results

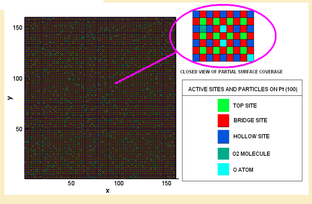
Distribution of Species over a Catalytic Surface of 6,400 Pt Atoms

(Ersungur's MS Thesis, Purdue University/IUPUI, August 2007)



Initial Distribution of species over the surface

Distribution of species at the last time step



Work in Progress

- Quantum molecular dynamics models are studied to accurately obtain the energetic of the relevant processes and the results will be compared with experimental results. A popular package called VASP is used for performing ab-initio quantum-mechanical molecular dynamics calculations.
- After the KMC code is developed successfully for the study of surface reaction on Pt (111) surface, the same approach will be applied to the study of surface reaction on other materials such as platinum alloy.
- Parametric studies will be conducted by KMC simulation method in order to evaluate the fuel cell efficiency.
- Molecular level results will be coupled with the continuum model in order to conduct multi-scale analyses.