KINETIC MONTE CARLO MOLECULAR SIMULATIONS FOR FUEL CELL APPLICATIONS AND SURFACE REACTIONS

A Thesis Defense
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Introduction

- This research study focuses on the microscopic behaviors leading to the prediction of macroscopic consequences of the chemicals composing Proton Exchange Membrane (PEM) fuel cells, as well as other chemical reactions on active materials.

- Analysis of microscopic or molecular behaviors is a very important step to understand the phenomenon behind all processes in chemical systems. Each particle is required to be analyzed by the means of one of the realistic simulation methods working in the molecular level.

- The molecular simulation technique used in our conducted research is Kinetic Monte Carlo (KMC) method, where the meso (in the order of $10^{-8}$) scales for time and length apply.
In this research:

- A general purpose Kinetic Monte Carlo (KMC) simulation code has been developed in FORTRAN 90 for fuel cell catalytic and other active material reactions.
- Two of the widely used KMC algorithms: Random Selection Method (RSM) and First Reaction Method (FRM) have been developed for molecular analysis of two-dimensional surface reactions.
- Both Single Active Site Method (SASM) and Multiple Active Sites Method (MASM) have been used depending on the surface reaction types.
- A Quasi-Three Dimensional Approach of RSM by using SASM has been also developed including the molecular and thermal analyses of the cathode surface of PEM fuel cells, with some assumptions.
- A separate algorithm, independent of KMC, has been developed for calculation of fuel cell efficiency.
- Five case studies for catalytic reaction in fuel cells have been performed, each with different type of reactions and compared with those in the literature whenever possible.
- Ten case studies for catalytic reactions on active materials, more complex than fuel cell reactions, have been performed and compared with those in the literature whenever possible.
Existing Literature

- KMC method has been actively developed and used for fuel cells and other active materials by many groups, including University of South Carolina (Mainardi), Pennsylvania State University (Pal), Texas A & M University (Balbuena), Stanford University (Pitsch).

- There are also commercial softwares which use KMC in the analysis of chemical reactions, e.g., CARLOS, MCSim.

- Our work is an implementation of the existing methods in the literature with emphasis on applications to numerous types of reactions and accuracy studies.

- The computer code we developed is general and open ended to include any reactions with multiple reaction steps and material types by adding extra subroutines.
A fuel cell is a mechanism that generates electricity as a result of a chemical reaction.

The reactions that produce electricity take place at the electrodes.

Every fuel cell also has an electrolyte, which carries electrically charged particles from one electrode to the other, and a catalyst, which causes or increases the reaction speed (reduces the activation energy levels of reactions) at the electrodes without itself being affected.
PEM Fuel Cell Operation Diagram

**Hydrogen Fuel**

- **Anode**: H₂ → 2H⁺ + 2e⁻
- **Cathode**: O₂ + 4e⁻ + 4H⁺ → H₂O

**Oxygen, usually from air**

**Load, e.g., electric motor**

**Electrons flow round the external circuit**
Scales Associated with the Simulation Models

- Atomistic
  - Molecular Dynamics
  - Monte Carlo Coarse Grain

- Continuum
  - Micromechanics
  - Finite Element

Length (m):  $10^0$, $10^{-6}$, $10^{-8}$, $10^{-10}$

Time (sec): $10^{-12}$, $10^{-8}$, $10^1$, $10^7$
Kinetic Monte Carlo Methods

- Monte Carlo (MC) method is a computer simulation method intended to simulate the time evolution of some processes taking place in nature.

- Kinetic Monte Carlo (KMC) simulations have recently become progressively more popular methods in order to analyze the behavior of the adsorbed species and their related chemical characteristics on the surface.

- Typically, these are processes which take place with a given known reaction rate, which depends on the flow temperature, the activation energy and the vibrational frequency of chemical reaction. It is essential to realize that these rates are inputs to the KMC algorithm, the method itself cannot foresee them.
Data Flow Chart in Developed KMC Simulations

INPUT DATA
- Chemical reaction model and rates
- Lattice structure and size
- Partial pressure of gasses

SIMULATION PROCESS

OUTPUT DATA
- Concentrations of each species
- Locations of each adsorbed species over the surface
- Time evolutions of species
The Advantages of KMC Methods

- The management of non-equilibrium systems where the conditions change over time is possible.

- Reaction mechanisms for varied catalysis can be simulated.

- These methods are able to simulate simultaneously many different reactions covering trials which extent time scales up to the orders of seconds.

- If reaction rates are not available from real experiments, non-dimensional dimensional time steps are used to obtain time evolution of a system. However, if data are available, the real-time activity of a chemical system can also be simulated with some assumptions.
The Algorithms Used in KMC Methodology

- There are several algorithms performing KMC simulations. The most of the algorithms used in the literature for KMC are the Random Selection Method (RSM), First Reaction Method (FRM), or Variable Step Size Method (VSSM).

- In this thesis, RSM and FRM are performed for molecular simulations, because of their popularity.
Algorithm 1: First Reaction Method (FRM) -- The Gillespie Algorithm

1. First Reaction Method (FRM) can be used for both time-dependent and time-independent reaction rate constants.

2. According to this method, the set of all possible reactions is determined at the given initial configuration of the system.

3. After the required time for the system transition is generated for each reaction, the simulation program again lists all reactions from the one having the smallest occurrence time to the one having the largest occurrence time.

4. Then, the reaction which has the smallest occurrence time is enabled by accordingly changing the configuration, and the simulation time is incremented in that chosen occurrence time.

5. Finally, the set of all possible reactions is generated again according to this new configuration of the system by repeating the procedure until the system reaches the steady state condition.
If a fixed volume $V$ contains a spatially uniform mixture of $N$ chemical species which can interact through $M$ specified chemical reaction channels, then given the numbers of molecules of each species at some initial time, what will these molecular population levels be at any later time?
Assumption: Reactive Collisions

- In general, chemical reaction occurs whenever two or more molecules of appropriate kind collide in an appropriate way.

- The stochastic formulation of chemical kinetics is simply a consequence of taking seriously the fact that collisions in a system of molecules in thermal equilibrium occur in an essentially random manner.

- Reactive collisions, i.e.; collisions which result in chemical alterations of the colliding molecules are always satisfied in the characterization of reaction probabilities.
Algorithm 1: First Reaction Method (FRM) -- The Gillespie Algorithm

- Transition from deterministic reaction rates to stochastic ones (reaction probabilities)

\[
k_i = A \cdot e^{-\frac{E_a}{RT}}
\]

\[
c_i = k_i \cdot N_i
\]

Where \( i = 1,.., M \)

- Calculation of the time increment

\[
\tau = \left(\frac{1}{\sum c_i}\right) \cdot \ln\left(\frac{1}{r}\right)
\]
Algorithm 2: The Random Selection Method (RSM)

- The Random Selection Method (RSM) can be used for both time-dependent and time-independent reaction rate constants.

- In this simulation technique, a single site is selected with a probability of $1/S$, being $S$ the total number of sites, in other words; the number of points on the grid (lattice) representing the active surface.

- Then, the previously set reaction is selected with the probability being proportional to its reaction rate.

- When this reaction is determined to be possible on the selected site by comparing with the randomly generated number by the program, time is incremented by $t$ which is selected also randomly from a fixed distribution.
Algorithm 2: The Random Selection Method (RSM)

- Calculation of the reaction probabilities

\[ k_i = A \cdot e^{-\frac{E_a}{RT}} \]

\[ c_i = \frac{k_i}{\sum k_i} \]

- Calculation of the time increment

\[ t = 1 - \exp\left(-S \cdot \sum k_i\right) \]
Algorithm 3: The Variable Step Size Method (VSSM)

- The Variable Step Size Method (VSSM) can be used for only the time dependent reaction rate constants.

- According to this method, when the system is in an initially given configuration, the set of all possible reactions is determined by the user.

- Rather than calculation of all reaction times for every reaction done in the FRM, this method generates only one time of occurrence for all reactions.

- After the selection of one reaction with a probability being proportional to its rate, the configuration is changed accordingly. Then, the procedure is repeated, respectively.
The cathode side of the PEM fuel cell structure is made of the distributed catalyst (here platinum) particles over the membrane; i.e., the carbon support.

The platinum nano-particles exist in the nature as the three-dimensional cubo-octahedral shaped particles.

One of these particles has eight hexagonal faces which are called as Pt (111) faces (also known as the facets) and six rectangular faces called as Pt (100) (also known as the facets).
Creation of the Lattice Structure

- Definition of the lattice structure in modeling of surface reactions is as important as the interpretation of chemical reactions as well as their orders in the system.

- The main issue in the selection of the lattice, in other words the grid, in the simulation is to maintain the size of the lattice to be fit in the physical distribution of catalytic atoms.

- Our simulations are performed by considering only square type of lattice structure. However, many other lattice structures depending on the nature of the problem are available in the literature.
Creation of the Lattice Structure for Modeling

The structure of (fcc) cubic cell

Square and hexagonal lattice structures in the computational domain

The structure of (hcp) unit cell
For small-scale systems, it cannot be safely assumed that the choice of the boundary conditions has a negligible effect on the properties of the system.

In order to overcome this problem, the general implementation has been performed by all researchers studying Monte Carlo simulation techniques is to use the periodic boundary conditions.

According to this approach to the boundary conditions, the mesh is replicated throughout space to form an infinite lattice.
Two Different Active Site Methods

- Single Active Site Method (SASM)
- Multiple Active Site Method (MASM)

The choice depends on the reaction type and where the reactions take place on a catalytic region, as some catalytic reactions only occur on top site of catalysts, some occur on top, bridge and hollow sites.
In many simulations, SASM is used in the literature as a general trend, and then a unit cell contains only one active site (the tops of active metallic atoms).

As a result, all grid points in the surface mesh represent the top sites of metallic atoms.

Single active site method: linearization of catalyst atoms (representative 4 metallic atoms) and nodal network in the square lattice structure.
Multiple Active Sites Method (MASM)

- In this method, all catalyst atoms in the domain are characterized with their top, hollow and bridge (the sites connecting two metallic atoms) sites.
- Since there is more than single active site per unit cell, then there are different possibilities to model them depending on the substrate and the reactions.

Multiple active sites method: linearization of catalyst atoms (4 metallic atoms) and nodal network in the square lattice structure

Representation of the Pt (111) surface by a hexagonal lattice provided in program CARLOS
The Developed Model

In this model, we only analyze the reactions which take place on Pt (100) catalyst surface with the implementation of the square lattice structure.

Multiple Active Sites Method (MASM) is applied, i.e.; active sites are characterized by the names of top, hollow and bridge sites.

In other words, top sites directly represent the tops of platinum atoms; bridge sites are called as the sites where each atom has a connection with its neighboring atoms; and hollow sites which are empty, but effective sites for some particular reactions.
Before going through the full reaction mechanism on the cathode surface, some important reaction steps are analyzed individually.

Molecular oxygen desorption, adsorption and dissociation elementary reaction steps are evaluated by changing the $O_2$ flow temperature incrementally with the heating rate of 2 K/sec.

In these analyses, 4,096 platinum atoms are considered.

The atomic radius of a single platinum atom is which is used in all fuel cell simulations.
Case Study 1: O₂ Adsorption Reaction

- The intermediate molecular oxygen adsorption reactions on platinum atoms only occur on the bridge sites.

- The corresponding reaction model:

\[
O_2 + b \rightarrow O_2(ads-b)
\]

- First Reaction Method (FRM) is used as the simulation algorithm.
The reaction rate for the adsorption reactions, $k_{ads}$, can be evaluated explicitly.

$$k_{ads} = A \cdot F \cdot S_0$$

- $A$ is the area of a single adsorption site on the surface.
- $S_0$ is the initial (zero coverage) sticking coefficient of the species.
- $F$ is the flow rate of the adsorbed species per unit area according to the classical kinetic theory of gases.

$$F = \frac{P}{\sqrt{(2\pi \cdot M \cdot k_B \cdot T)}}$$

- In this equation, $k_B$ is the Boltzmann’s constant, $M$ is the molecular mass of the adsorbed species (32 g/mol for O$_2$), $P$ is the pressure of adsorbed species, and $T$ is the temperature, respectively.
Case Study 1: O$_2$ Adsorption Reaction

- The vibrational frequency value for the adsorption of O$_2$ is proportional with the sticking coefficient parameter. The sticking coefficient parameter, $S_0$, is also dependent on the temperature as given below.

\[ S_0 = 1.7526 \quad \text{for} \quad T < 100 \, K \]

\[ S_0 = 1.7526 - \left(1.49 \times 10^{-2}\right) \cdot T \quad \text{for} \quad 100 \, K \leq T \leq 111 \, K \]

\[ S_0 = \left(3.12 \times 10^{-2}\right) \cdot \exp\left(\frac{100}{T}\right) \quad \text{for} \quad T > 111 \, K \]

- The analyses of these dependencies are provided for Pt (100) and Pt (111) catalysts.
Case Study 1: $O_2$ Adsorption Reaction

Our Simulation Result

Program CARLOS Result

Temperature (K)

Prefactor ($O_2$ ads)

Reaction Rate (1/sec)

0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
100 150 200 250

Temperature (K)
Case Study 1: $O_2$ Adsorption Reaction

Our Simulation Result
Case Study 2: $O_2$ Desorption Reaction

- The reaction model is written as

\[ O_2(ads-b) \rightarrow O_2 + b \]

- In this case study, the value of temperature is increased from 100 K to 190 K with a heating rate of 2 K/sec.

- For this particular reaction, the value of vibrational frequency is taken as $10^{13}$ sec$^{-1}$ and the activation energy is 0.36 eV.

- The initial configuration is assumed as the all bridge sites are occupied by molecular oxygen.
Case Study 2: $O_2$ Desorption Reaction

Our Simulation Result
Program CARLOS Result
Case Study 2: $O_2$ Desorption Reaction

![Graph showing O2 Concentration over Time (seconds)]
Case Study 3: O$_2$ Reduction Mechanism

- Since this mechanism is the slowest one taking place on the cathode side of fuel cell, it defines the speed of full reaction mechanism, and hence the fuel cell efficiency limit.
- We use Multiple Active Sites Method (MASM) for the definition of lattice structure and Random Selection Method (RSM) as the simulation algorithm.
- The related reaction model, which is based on experimental evidences and initially developed for the hexagonal lattice structure, is given as

\[
\begin{align*}
O_2 \text{ adsorption} & : O_2 + b \rightarrow O_2 (ads - b) \\
O_2 \text{ dissociation} & : O_2 (ads - b) + 2h \rightarrow 2O (ads - h) + b \\
O \text{ diffusion} & : O (ads - h_{hcp}) + h_{fcc} \rightarrow h_{hcp} + O (ads - h_{fcc}) \\
O_2 \text{ desorption} & : O_2 (ads - b) \rightarrow O_2 + b
\end{align*}
\]
Since our identification of surface active sites (due to usage of square lattice) are different from that given in the literature, we ignore the O diffusion step in this case study.

The Pt (100) surface is represented by a two-dimensional square lattice containing 6,400 platinum atoms, and periodic boundary conditions applied in both directions.

In the current study, the cathode surface is assumed empty initially.

The simulation is conducted from 100 K to 200 K temperature range with the heating rate of 2 K/sec and increasing the simulation time by 0.0001 sec.
Case Study 3: \( \text{O}_2 \) Reduction Mechanism

- The reaction rate of molecular oxygen adsorption is calculated according to the adsorption rate equation introduced before, including the implicit calculation of the sticking coefficient and flow rate under the rage of temperature.

- Experimental value of the activation energy for the repulsion event of molecular oxygen is used as 0.36 eV. For the activation energy for the dissociation of molecular oxygen is taken as 0.3 eV from the Density Functional Theory (DFT) on platinum clusters.

- The concentration profiles of the species are obtained under the \( \text{O}_2 \) gas flow pressures of 0.001 and 0.005 Pa as the outcome of this simulation.
Case Study 3: O$_2$ Reduction Mechanism

- Simulation movie
Our Simulation Result for Pt (100)  Program CARLOS Result for Pt (111)
Case Study 4: O$_2$ Reduction Mechanism
On the Poisoned Catalyst

- In this case study, the poisoned catalyst, Pt (100) containing 6,400 platinum atoms at 0.005 Pa O$_2$ gas flow is considered.

- In other words, the active sites are blocked by solution diffused over the catalytic surface, so that the related reaction mechanisms are intently restricted.

- These specific types of analyses are commonly performed by the means of experiments in order to observe the poisoning blockage effect on the reaction efficiency (the percentage of successive reaction steps).

- Hence, the adsorption event of molecular oxygen is gradually avoided.
Case Study 4: $O_2$ Reduction Mechanism on the Poisoned Catalyst
In the presence of an overpotential (loss in potential), the rate of reactions involving electron production and consumption changes according to the *Buttler-Volmer Equation* as

\[
r_i = \nu_i^0 \cdot \exp\left(-\frac{(E_{a0} + \alpha e_0 V)}{K_B T}\right)
\]

- \(e_0\) = elementary charge of an electron
- \(E_{a0}\) = activation energy with no loss
- \(V\) = overpotential
- \(\nu_i^0\) = vibrational frequency
- \(\alpha\) = transfer coefficient
  (0.5 if the reaction consumes \(e^-\) and \(-0.5\) if it produces \(e^-\))
Case Study 5: Full Reaction Mechanism on the Cathode Side of PEM Fuel Cell

1. $\text{O}_2(\text{gas}) + e^- + \text{H}^+ + b \leftrightarrow \text{HO}_2(\text{ads-b})$

2. $\text{HO}_2(\text{ads-b}) + 2\text{h} + e^- + \text{H}^+ \rightarrow 2\text{OH(ads-h) } + b$

3. $\text{O}_2(\text{gas}) + b + e^- \leftrightarrow \text{O}_2^-(\text{ads-b})$

4. $\text{O}_2^-(\text{ads-b}) + 2\text{h} \rightarrow \text{O}^- (\text{ads-h}) + \text{O} (\text{ads-h}) + \text{h}$

5. $\text{O} (\text{ads-h}_{\text{hcp}}) + h_{\text{fcc}} \rightarrow h_{\text{hcp}} + \text{O} (\text{ads-h}_{\text{fcc}})$

6. $\text{O}^- (\text{ads-h}) + \text{H}^+ \rightarrow \text{OH} (\text{ads-h})$

7. $\text{O} (\text{ads-h}) + e^- + \text{H}^+ \rightarrow \text{OH} (\text{ads-h})$

8. $\text{OH} (\text{ads-h}) + t \rightarrow \text{h} + \text{OH} (\text{ads-t})$

9. $\text{OH} (\text{ads-t}) + \text{H}^+ + e^- \rightarrow \text{H}_2\text{O} (\text{ads-t})$

10. $\text{OH} (\text{ads-h}) + \text{H}^+ + e^- \rightarrow \text{H}_2\text{O} (\text{liquid}) + \text{h}$

11. $\text{H}_2\text{O} (\text{ads-t}) \rightarrow \text{H}_2\text{O} (\text{liquid}) + t$
### Case Study 5: Full Reaction Mechanism on the Cathode Side of PEM Fuel Cell

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E_{\text{ar}}(0)$ (eV)</th>
<th>$\nu_i$ (sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.32</td>
<td>1.0</td>
</tr>
<tr>
<td>I-</td>
<td>0.20</td>
<td>$1.0 \times 10^{11}$</td>
</tr>
<tr>
<td>II</td>
<td>0.03</td>
<td>$1.0 \times 10^{8}$</td>
</tr>
<tr>
<td>III</td>
<td>0.30</td>
<td>1.0</td>
</tr>
<tr>
<td>III-</td>
<td>0.36</td>
<td>$1.0 \times 10^{14}$</td>
</tr>
<tr>
<td>IV</td>
<td>0.03</td>
<td>$1.0 \times 10^{6}$</td>
</tr>
<tr>
<td>V</td>
<td>0.13</td>
<td>$2.6 \times 10^{12}$</td>
</tr>
<tr>
<td>VI</td>
<td>0.01</td>
<td>$1.0 \times 10^{5}$</td>
</tr>
<tr>
<td>VII</td>
<td>0.02</td>
<td>$1.0 \times 10^{5}$</td>
</tr>
<tr>
<td>VIII</td>
<td>0.08</td>
<td>$1.0 \times 10^{13}$</td>
</tr>
<tr>
<td>IX</td>
<td>0.01</td>
<td>$1.0 \times 10^{8}$</td>
</tr>
<tr>
<td>X</td>
<td>0.01</td>
<td>$4.7 \times 10^{-2}$</td>
</tr>
<tr>
<td>XI</td>
<td>0.44</td>
<td>$1.0 \times 10^{5}$</td>
</tr>
</tbody>
</table>
Case Study 5: Full Reaction Mechanism on the Cathode Side of PEM Fuel Cell

Concentration of species on Pt (100) catalyst—the solid lines (our simulation results) and Pt (111) catalyst—the dashed lines (program CARLOS results)
Why these differences occur?

- Microscopic reaction rates are proportional to the number of active sites.

- Although we use the same number of platinum atoms (here 4,096), we have different numbers of bridge and hollow sites because program CARLOS is created in order to analyze this reaction mechanism on Pt (111) surface. However, we analyze the mechanism on Pt (100) surface having the square lattice.

- Since we have different number of active sites, we have a different size of the lattice.

- In addition, we cannot apply the oxygen diffusion reaction since \( h_{hcp} \) type hollow sites only involve in the hexagonal lattice.
Applications to Other Catalytic Reactions (Active Materials)

- Kinetic Monte Carlo simulations are also performed for some important cases considering catalytic reactions over active materials for the problems having diverse chemical models.

- In the following case studies, Single Active Site Method (SASM) and Random Selection Method (RSM) are implemented in order to study the non-equilibrium reactions taking place on the surface of a catalyst.
Case Study 6: The Catalytic Reduction of NO with H$_2$ on a Platinum Surface

- The proposed model represents the catalytic reduction of NO with H$_2$ on a Pt surface and involves reaction, adsorption and desorption processes.

- It is assumed that the catalytic surface is surrounded by a gas containing in excess NO with H$_2$ molecules with similar partial densities. In other words, we assume the existence of equal partial pressures (0.5 Pa) of NO and H$_2$ gases surrounding the catalyst.

- A square lattice of finite size involving 1,600 active top sites (platinum atoms), with periodic boundary conditions is used as the catalytic surface.

- This model is used in order to predict the activity endurance of the catalyst before reaching saturation state by reactants and/or products.
Case Study 6: The Catalytic Reduction of NO with H$_2$ on a Platinum Surface

- The diffusion of the particles over the surface are not allowed since the purpose of this study is only to predict the catalytic behavior of reactants where the activity takes place.
- The model is described by the following chemical scheme:

\[
\begin{align*}
&\text{Case Study 6: The Catalytic Reduction of NO with H}_2 \text{ on a Platinum Surface} \\
&\text{The diffusion of the particles over the surface are not allowed since the purpose of this study is only to predict the catalytic behavior of reactants where the activity takes place.} \\
&\text{The model is described by the following chemical scheme:} \\
&\begin{align*}
S &\xrightarrow{k_1} NO \\
NO + S &\xrightarrow{k_2} N + O \\
S &\xrightarrow{k_3} H_2 \\
o + H_2 &\xrightarrow{k_4} S + S \\
N + N &\xrightarrow{k_5} S + S \\
S + S &\xrightarrow{k_3} N + O \\
S &\xrightarrow{k_3} H_2 \\
o + H_2 &\xrightarrow{k_4} S + S \\
N + N &\xrightarrow{k_5} S + S 
\end{align*}
\]
Case Study 6: The Catalytic Reduction of NO with H₂ on a Platinum Surface

- As used generally in the literature, in order to obtain the microscopic reaction rate constants, any reaction event is scaled.

- These microscopic rate constants are considered as the corresponding probabilities given as

\[
\frac{1}{\sum k'} \frac{k_3}{\sum k'} \frac{k_4}{\sum k} \quad \text{and} \quad \frac{k_5}{\sum k}
\]

\[
\sum k = 1 + k_3 + k_4 + k_5
\]

With \( k_4 = k_5 = 1 \)
Case Study 6: Lattice Concentrations for $k_3=0.88$

Our Simulation Result

Kalosakas et al. [26]
Case Study 6: Lattice Concentrations for $k_3=0.93$
Case Study 6: Lattice Concentrations for $k_3=0.93$ with Different Seed Number

Our Simulation Result

nstep = 40000000
seqnc = 0
iseed = 9863

$k_3 = 0.93$

$P_{NO} = 0.5$
The oxidation of CO molecule and the reduction of NO play an important role in order to improve the air quality. For this reason, the researchers in the automotive industry have paid large attention to controlling automotive exhaust emission for catalytic reactors.

In this case study, the CO-NO reaction on a Pt (111) catalytic surface is studied by the implementations of Random Selection Method (RSM) and Single Active Site Method (SASM).

A square lattice structure is used in this analysis as it is also performed in the literature. In order to avoid the edge effects, periodic boundary conditions are also applied, as well.

The reservoir is in contact with a catalytic surface simulated by the means of a 64 x 64 square lattice of dimensions.
For this case, the reaction steps can be written in the following form:

\[
\begin{align*}
\text{CO (g)} + S & \rightarrow \text{CO (ads)} \\
\text{NO (g)} + 2S & \rightarrow \text{N (ads)} + \text{O (ads)} \\
\text{N (ads)} + \text{N (ads)} & \rightarrow \text{N}_2(g) + 2S \\
\text{CO (ads)} + \text{O (ads)} & \rightarrow \text{CO}_2(g) + 2S \\
\text{CO (ads)} + S & \rightarrow \text{S + CO (ads)} \\
\text{N (ads)} + S & \rightarrow \text{S + N (ads)} \\
\text{O (ads)} + S & \rightarrow \text{S + O (ads)}
\end{align*}
\]
The simulation starts by assuming an infinite reservoir comprising CO and NO with the partial pressures of these species.

The equilibrium concentrations of species are measured as a function of the partial pressure of CO.

The computer simulation is run up to 50,000 Monte Carlo (MC) cycles in order to obtain the critical points of reaction mechanism, which give the idea of overall behavior of reaction mechanism for the given initial conditions.

The adsorption probabilities of CO and NO molecules are proportional to their partial pressures.

In this study, all diffusion probabilities are set to unity in order to simplify the process. In other words, the motilities of particles entering reactions are considered without calculation its probability of occurrence. Any particle, which cannot enter any particular reaction, is subjected to move to one of the vacant nearest neighbors.
Case Study 7: CO-NO Reactions on a Pt (111) Catalytic Surface

Final Saturated (Poisoned) State Results by Ignoring Diffusion and CO-CO Repulsion Events

Our Simulation Result

Baloach et al. [28]
Case Study 7: CO-NO Reactions on a Pt (111) Catalytic Surface

Final Saturated (Poisoned) State Results by Ignoring Only CO-CO Repulsion Event

Our Simulation Result

Baloach et al. [28]
Case Study 7: CO-NO Reactions on a Pt (111) Catalytic Surface

Final Saturated (Poisoned) State Results by Introducing CO-CO Repulsion Event

Our Simulation Result

Baloach et al. [28]
The energy considerations provide us the information about the open circuit voltage (OCV) of a fuel cell, and the formulas produced also give key information about how factors such as pressure, gas concentration, and temperature affect the voltage.

Efficiency of a typical PEM fuel cell is normally about 30 to 40 percent which means that only formation of water occurs at these percentage levels, and the cell outputs generally range from 50 to 250 kW capacity depending on the their operating system.

Gibbs free energy is used since the chemical energy is not directly calculated.

\[ \Delta G_f = G_f \text{ of products} - G_f \text{ of reactants} \]

\[ \Delta \bar{g}_f = \left( \bar{g}_f \right)_{H_2O} - \left( \bar{g}_f \right)_{H_2} - \frac{1}{2} \cdot \left( \bar{g}_f \right)_{O_2} \]
The Efficiency Calculation of Fuel Cells

$$\Delta \bar{g}_f = \Delta \bar{h}_f - T \cdot \Delta \bar{s}$$

$$\Delta \bar{g}_f = -2F \cdot E$$

Voltage Drop (Overvoltage) in a Fuel Cell

• Activation Losses
• Fuel Crossover Events
• Ohmic (Resistive-Structural) Loss
• Mass Transport or Concentration Loss

$$V = E - \Delta V_{ohm} - \Delta V_{act} - \Delta V_{trans}$$
The Efficiency Calculation of Fuel Cells

The chart shows the relationship between current density (A/cm²) and operating cell voltage (V). The graph includes data from various sources:

- **Our Simulation Result**
- **General Motors Fuel Cell Stack Research - Test Data**
- **General Motors Fuel Cell Stack Research - Model Prediction**
- **General Motors Fuel Cell Stack Research - Tighter Stack Output Voltage**
- **Pennsylvania State University Research Data**

The y-axis represents the operating cell voltage, ranging from 0 to 1.2, and the x-axis represents the current density, ranging from 0 to 1.
Quasi 3D Approach for PEM Fuel Cell Cathode Side

- Implementation of KMC Simulations:
  - Analysis of reactions via RSM and SASM.
  - Thermal analysis of the surface via steady-state, two-dimensional conduction equation using Energy Balance Method with the finite difference scheme.
  - Obtaining enthalpy and entropy changes resulting from reactions.

- Reaction Model:

\[
\begin{align*}
O_2 & \xrightarrow{k_1} 2O^- \\
H_2 & \xrightarrow{k_2} 2H^+ \\
2H^+ + O^- & \xrightarrow{k_3} H_2O \\
H_2 + O^- & \xrightarrow{k_4} H_2O
\end{align*}
\]
The transition probability for any particle in order to jump from the old state to its new state is calculated considering Lennard-Jones interactions.

The pair-wise atomic interaction energy between two non-bonded atoms can be expressed as a function of inter-nuclear separation, scaling parameter of the length of interaction and well depth of the potential.

The first term on the RHS of the equation describes repulsion and the second term describes attraction.

Interactions between dissimilar particles requires the generation of cross term parameters determined by using the Lorentz-Berthelot mixing rules.
Case Study Conditions:

- There are three square-shaped platinum elements randomly distributed over the domain which consists of 400 cells.
- Each catalyst has randomly located 5 hydrogen ions.
- There are 60 oxygen molecules in the flow over the membrane.
- Diffusion event is allowed for randomly located 4 hydrogen molecules.
- 1000 time steps are run to get the final positions of the particles.
- Initial temperature is assigned as 343 K since efficiently working temperature for the PEM fuel cells is between 70-80 degrees 0C.

Initial distribution of species over the surface
Quasi 3D Approach for PEM Fuel Cell Cathode Side

Distribution of the species at the last time step

Temperature distribution over the surface at the last time step

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Conclusions and Findings

- The KMC program developed during this thesis can be a valuable tool for the designer of different catalytic and other active materials. Using the program, one can obtain the following useful information in material design:
  - Positions of each adsorbed species (reactants and/or products in a particular reaction model) over the surface.
  - Time evolutions of species at constant temperature or voltage.
  - Concentrations of species over surface. This information gives an idea about the efficiency of reaction mechanism which is based on the number, size, geometry and location of distributed catalyst elements as well as the gas flow pressure, temperature and surface voltage.
  - Since the reaction rates are used as the input data in the KMC algorithm and only depend on material characteristics at a constant temperature, one can analyze the efficiency of specific reaction mechanism for different types of catalytic metals at the desired temperature range.
Conclusions and Findings

- Since KMC is a stochastic method, the simulation results depend on the random number generator which is eventually based on the seed number. The results obtained by means of using different seeds become different. However, there is no specific rule in the specification of seed number. This causes difficulties in comparing one’s results with others in the literature.

- If any researcher goes through the literature on KMC simulations, he/she can hardly find any methodology which is generally accepted and applied by all scientists. The common approach in the literature is based on some assumptions as they are illustrated with the case studies.

- The most challenging matter in KMC simulations is to define the intermediate reaction steps in a particular chemical reaction mechanism. For a programmer, this is not the main issue that is needed to be concerned. However, the simulation program, and hence the results are dramatically affected by the definition of reaction mechanisms.

- All two-dimensional simulations should be performed only considering the catalytic regions. Two-dimensional fuel cell case studies are also conducted under this procedure since reacting chemicals cannot sit on the carbon support.
Conclusions and Findings

- Square lattice structure is needed for the analysis of Pt (100) since (100) coded atomic platinum surface has a rectangular shape.
- Hexagonal lattice is a better lattice definition for Pt (111) surfaces since (111) coded atomic platinum surface has a hexagonal shape. Yet, more complicated lattice structure means that more input data are needed in the simulations, which in turn increases experimental efforts.
- The use of multi-catalytic surface, i.e., the catalytic surface containing different catalysts, is not possible to examine realistically by the means of KMC simulations, because the simulation procedures such as the use of periodic boundary conditions and reaction rates narrow our application areas.
Recommendations for Future

- Hexagonal and square lattice structures can be combined together to fully analyze a catalytic region more accurately. A better representation of distributed platinum atoms (the catalytic elements) over the membrane (carbon support) could be to integrate both lattice structures to build cubo-octahedral shaped platinum atoms leading to a 3D model.

- KMC simulations assume that a continuous gas flow has a constant temperature at each simulation run. Since KMC methodology uses this assumption, thermal analysis over the catalytic surface is not possible for two-dimensional analysis due to convection. However, thermal analysis can be applicable with the introduction of the third dimension, i.e., the simulation of gas flow. Quasi 3D model described in the Appendix of this can be used for this purpose.

- If a Quasi 3D model is used, there is no need to assume the constant flow temperature. Heat transfer considerations with the integration of conduction and convection can allow us to make thermal analysis even at the each step for a particular simulation. However, the problem of using accurate reaction rates appears again.
Recommendations for Future

- The Quasi 3D Approach also provides the information about temperature distribution over the surface which allows us to observe the material endurance limits to unexpected high temperatures resulting from improper design of catalytic regions over the membrane, i.e., the number, size, geometry and location of distributed catalyst elements as well as the size of membrane.
- The simulation of the membrane which is also included in Quasi 3D Approach can only be meaningful by including three-dimensional analysis.
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Questions?