Ab initio MD Simulation of Oxygen Electrocution on Pt(111) in Protonated Water

Project Report for ME346: Introduction to Molecular Simulations
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Chapter 1

Project Overview

1.1 Objectives

In this project, we sought two goals: first, getting a deeper understanding of ABMD methods and familiarizing ourselves with one of the most popular ABMD codes: CPMD. Second, applying our knowledge about CPMD to investigate the specific problem of electroreduction of oxygen in the cathode of a PEM fuel cell. In the following we report the results from our project. We begin by briefly describing the operating principles of PEMFCs, electroreduction of oxygen on platinum, and the idea behind ab initio methods.

1.2 PEM Fuel Cells

The invention of fuel cells goes back to the work by Sir William Grove in the 19th century. The development of fuel cells was not pursued because of the availability of other inexpensive sources of power. However, nowadays fuel cells are receiving a considerable attention both in the industry and the academia alike, due to many recent issues such as a rapid increase in electrical energy demand, shortage of conventional fuels and environmental issues [1].

Of the different fuel cell technologies, Polymer Electrolyte Membrane Fuel Cells (PEMFCs) are favored for near term commercialization, especially for vehicular applications, distributed power generation, and the portable devices industry. PEMFCs use a proton exchange membrane as their electrolyte, which lets only protons to pass through it. They operate in the temperature range of 75-105 °C which is lower than most other kinds of fuel cells. Low operating temperatures make PEMFCs a favorable power source in a wide range of applications, from car batteries to portable devices (Fig. 1.1). The product of a PEMFC is potable water which makes this technology environment friendly. This can provide a solution to the pollution problems facing the world today, if the hydrogen used in PEMFCs is produced from renewable sources such as solar, wind, hydro power, etc. Other advantages include structural modularity, quiet operation, and quick start-up.
The main features of a PEMFC are shown in Fig.1.2. Half cell reactions and the net reaction of the PEM fuel cell are presented below. The half-cell reactions exhibit the standard potentials of 0.0 V for the hydrogen oxidation and 1.23 V for the oxygen reduction, respectively. This results in a standard reversible cell potential of 1.23 V (standard potentials are based on the standard hydrogen electrode, SHE, i.e., pH = 0, T = 298 K, P(reactant) = 1 bar).

\[
\begin{align*}
\text{anode reaction} & \quad \text{H}_2 \rightarrow 2\text{H}^+ + 2e^- \quad E^0_{\text{H}_2/\text{H}^+} = 0.0V \\
\text{cathode reaction} & \quad \frac{1}{2}\text{O}_2 + 2e^- + 2\text{H}^+ \rightarrow \text{H}_2\text{O} \quad E^0_{\text{O}_2/\text{H}_2\text{O}} = 1.23V \\
\text{total reaction} & \quad \text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} \quad E^0_{\text{cell}} = 1.23V
\end{align*}
\]

Electrical and heat energy are produced by the cathode reaction. Theoretically, the Gibbs energy of the reaction is available as electrical energy and the rest of the reaction enthalpy is released as heat. In practice, a part of the Gibbs energy is also converted into heat via different loss mechanisms.

Two sets of gas diffusion layer and electrode are separated by a layer of polymer, called the ‘proton exchange membrane’. At the anode side, hydrogen gas is fed to be in contact with the catalyst, platinum. Hydrogen molecules dissociate and are ionized by Pt catalyst according to the following net reaction:

\[
\text{H}_2 \rightarrow 2\text{H}^+ + 2e^-
\]

The chemical structure of the membrane [2] is such that it only allows protons to pass through and blocks the electrons. The electrons on the other hand, are forced to choose the outer circuitry to complete their travel to the cathode side, thereby generating an electric current. On the cathode side, oxygen molecules reduce from the gas phase and combine with the available protons to produce water. As it is seen, in addition to the fundamental chemical processes like adsorption and diffusion that are present throughout the whole system, there exist electrochemical processes, in which one or more electrons are exchanged. This particular combination of chemical and electrochemical phenomena makes fuel cell a challenging area of research. It is important to fully understand these phenomena to achieve required performance goals.
1.3 Performance of a PEMFC

Performance of fuel cells is typically presented as a V-I curve, where the output cell voltage is plotted as a function of the current density. Figure 1.3 shows the V-I curve of a typical PEMFC (the black solid line). If the cell behaved ideally, it would have a constant thermodynamic voltage $\Delta U_o$, (the flat solid line), which is about 1.23 volts, as explained above. In fact, due to various irreversibility of electrochemical phenomena taking place at micro scales, the output voltage is not constant at its ideal value but drops because of three different loss mechanisms. These regions are identified on the actual V-I curve, in each of which the voltage-drop from the ideal case is due to a certain effect, namely: kinetic, ohmic or mass transport losses. In the first region, a huge drop is observed because of low reaction rates of electrochemical reactions. As the curve depicts, this voltage drop remains till the end. Therefore, any improvement in the first region will shift the curve upward, leading to an overall improvement in the whole performance. The output power of a fuel can also be improved once the reactions happen at higher rates. Experiments suggest that the electroreduction of oxygen is the rate limiting step among all present reactions $[3, 4]$. Schematic of a PEM cathode can be seen in Fig. 1.4 where all the reactants meet to form water:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

The catalyst particles of platinum, which are about 2-5 nm in size, are held by carbon grains. Most of the platinum particles have a cubo-octahedral geometry, which has been observed to have a more stable structure than other shapes. In order for the above reaction to happen, three phases should be present and in contact with each other: gas phase (oxygen), liquid phase (water and proton) and solid phase (electrons). It has been shown that the rate of reactions in cathode scales with size of the triple phase, revealing the crucial role of the triple phase region $[5]$. 

Figure 1.2: Salient parts of a PEMFC. The series of chemical and electrochemical reactions taking place at the catalyst/membrane interface causes the cell to develop a voltage difference between its electrodes.
Figure 1.3: Different loss regimes in a fuel cell. Losses in the leftmost regime are due to slow electrochemical reactions.

Figure 1.4: Simplified structure of a PEMFC cathode. The Pt nanoparticles are supported on carbon particles. These catalyst particles are very spread out so that a high proportion of the catalyst surface area is in contact with the reactants.
1.4 Electroreduction of Oxygen

Among several reactions in a PEM fuel cell, the electroreduction of $O_2$ at cathode is believed to be the slowest step [6]. Many researchers have investigated this step using both theoretical and experimental techniques [7, 8]. The electroreduction of oxygen at the cathode involves several intermediate steps:

\[
\begin{align*}
\text{Pt} & \quad \text{Pt} - \text{O} \\
+ \text{O}_2 & \quad \xrightarrow{\text{\vphantom{1.1}}} \\
\text{Pt} & \quad \text{Pt} - \text{O} \\
\end{align*}
\]  

\[
\begin{align*}
\text{Pt} - \text{O} & \quad \text{Pt} - \text{OH} \\
| & \quad + \text{H}_3\text{O}^+ + e^- \quad \xrightarrow{\text{\vphantom{1.1}}} \\
\text{Pt} - \text{O} & \quad \text{Pt} - \text{O} \\
\end{align*}
\]  

\[
\begin{align*}
\text{Pt} - \text{OH} & \quad \text{Pt} - \text{OH} \\
| & \quad \xrightarrow{\text{\vphantom{1.1}}} \\
\text{Pt} - \text{O} & \quad \text{Pt} - \text{O} \\
\end{align*}
\]  

\[
\begin{align*}
\text{Pt} - \text{O} & \quad + \text{H}_3\text{O}^+ + e^- \quad \xrightarrow{\text{\vphantom{1.1}}} \\
\text{Pt} - \text{OH} & \quad + \text{H}_2\text{O} \\
\end{align*}
\]  

\[
\begin{align*}
\text{Pt} - \text{OH} & \quad + \text{H}_3\text{O}^+ + e^- \quad \xrightarrow{\text{\vphantom{1.1}}} \\
\text{Pt} - \text{OH}_2 & \quad + \text{H}_2\text{O} \\
\end{align*}
\]  

\[
\begin{align*}
\text{Pt} - \text{OH}_2 & \quad \xrightarrow{\text{\vphantom{1.1}}} \\
\text{Pt} & \quad + \text{H}_2\text{O},
\end{align*}
\]

where $\text{Pt} - X$ stands for a chemisorbed $X$ on the platinum surface. The electrochemical mechanism shows that the reduction of oxygen takes place in the presence of protonated water molecules. The first two steps in this mechanism were the focus of this project, and were studied using ab-initio molecular dynamics.

1.5 Ab-initio Molecular Dynamics

Molecular Dynamics (MD) is a powerful tool to investigate many-body condensed matter systems. At the heart of any MD scheme is the description of the interatomic forces. The traditional approach is to determine the potential energy functions in advance and use them in the actual computations. There are several model potentials developed over the years to model the atomic interactions. Some of them shown to give good results in certain applications. In spite of numerous successes with using fixed-potential, there are difficulties with systems in which there are many
different atoms present. Different atoms demands parameterizing various interatomic interactions, dealing with electronic structure, bond formation and breakage, and so on. The traditional MD method was greatly boosted by using the so-called ab-initio methods. The principle idea behind any ab initio MD method is to compute the forces acting on the nuclei from electronic structure calculations at the same time that the MD trajectory is generated. Here, the electronic variables are not integrated out beforehand, but are considered as active degrees of freedom. This means that, given a suitable approximate solution of the many electron problem, “chemically complex” systems can also be handled by MD methods. On the other hand, the approximation is shifted from the level of selecting the model potential to the level of selecting a particular approximation for solving the Schrödinger equation [9]. Applications of ab initio MD are widespread in material science and chemistry, especially where one deals with different atoms and bond formation/breakage. Just to name a few applications, one can mention:

- Solids, Polymers, and Materials
  - Semiconductor industry
  - Graphitization on flat and stepped diamond(111) surfaces

- Clusters, Fullerenes, and Nanotubes

- Matter at Extreme Conditions
  - Virtual matter laboratory

- Glasses and Amorphous Solids

- Surfaces, Interfaces, and Adsorbates
Chapter 2

Simulation Details

2.1 Model Geometry

The platinum surface is modeled by a monolayer slab of Pt atoms arranged in a $3 \times 4$ array with (111) configuration (Fig. 2.1). The $O_2$ molecule is represented by two oxygen atoms separated by their equilibrium interatomic distance (1.2 Å). Initially, the $O_2$ molecule is parallel to the surface at a height of 3.5 Å with its center right above the bridge site (the middle point between two atoms). The hydronium ion ($H_3O^+$) is attached to two water molecules to account for the effect of bulk water on the process [6]. One of the $H$ atoms of the hydronium is placed at a distance of 2.55 Å vertically above the center of the $O_2$ molecule. The plane of the hydronium ion is perpendicular to the $O_2$ axis as shown in Fig. 2.1. The simulation cell is an orthorhombic supercell with $9.59 \times 8.30 \times 13.0$ Å dimensions in x, y and z directions, respectively. The amount of vacuum along the z axis ensures a negligible interaction between the simulation cells in the vertical direction. Periodic boundary conditions are applied to the supercell and the periodicity of the whole geometry was visually verified in MATLAB before running the actual calculations. The CPMD code, which is a very popular code in the ABMD field, was used to compute the energy and path trajectories.

2.2 Algorithm Outline

Ab initio Molecular Dynamics (ABMD) method pioneered by Car and Parrinello in 1985 is probably the most effective technique to compute the properties of materials from electronic structure equations. It has revolutionized the way theory treats real materials (molecules, solids, liquids, etc.) including the thermal motion (molecular dynamics) with forces derived from the quantum behavior of electrons in the system through DFT calculations. Four important advances of the method are:

- Optimization methods instead of variational equations
- Equation of motion (instead of matrix diagonalization)
Car and Parrinello combined these features into a unified algorithm for electronic states, self-consistency and nuclear movement [10, 11]. The temperature of the system is kept constant by the Nose-Hoover algorithm [12, 13] at about 350 K, which is the typical working temperature of a PEM fuel cell. The Nose-Hoover algorithm introduces additional degrees of freedom into the system’s Hamiltonian, for which the equations of motion can be derived. These equations for the additional degrees of freedom are integrated together with “usual” equations for spatial coordinates and momenta. The idea of the method proposed by Nose was to reduce the effect of an external system, acting as heat reservoir, to an additional degree of freedom. This heat reservoir controls the temperature of the given system, i.e., the temperature fluctuates around the target value. Actually, the thermal interaction between the heat reservoir and the system results in exchange of kinetic energy between them [14]. All the simulations were performed on a Linux/Xeon machine (2.4 GHz) for about 1 ps with a time step of 6 a.u. (about 0.12 fs).
Two simulations were performed for the system described above. The parameter varied was the initial distance ($\delta$) between \( H \) atom of the hydronium complex that was closest to the oxygen molecule. The variables of interest are the Kohn-Sham energy and the distances of the oxygen atoms from the Pt surface ($d_1$ and $d_2$), and between themselves ($d_3$). In the first case $\delta$ is 2.55 Å. The evolution of the total energy and the temperature for this simulation is shown in Fig. 3.1. It can be seen that the solution is converged and the system temperature fluctuates about 350 K, as desired. Results for this case, namely, the Kohn-Sham energy and the important reaction coordinates (interatomic distances) are shown in Fig. 3.2.

In this case, the presence of the hydronium+water complex does not seem to have a marked effect on the fate of the oxygen molecule, which, during the course of the simulation moves closer to the Pt surface and ultimately dissociates. In steady state, the oxygen atoms occupy the hollow sites (centroid of the atoms). A snapshot from the steady state is presented in Fig. 3.3. Steady state values of important outputs of the simulation are summarized in Table 3.

In the second case we brought the hydronium+water complex closer to the oxygen molecule
Figure 3.2: Simulation 1: Reaction coordinates and the Kohn-Sham energy. Due to a large enough distance between the oxygen molecule and the hydronium complex, no direct interaction is observed. The sharp drop in the energy plot, from -4 to -7 eV, corresponds to the O-O bond cleavage.

Figure 3.3: Snapshot of the steady state. The O atoms, after dissociation, settle over the hollow sites on the Pt surface.

(here $\delta$ is 1.8 Å). Results are shown in Fig. 3.4. Interestingly, we find that one of the $H$ atoms from the hydronium attaches to one of the oxygen atom from the oxygen molecule (left figure in Fig. 3.5). This $O_2H$ intermediate then moves closer to the surface, with a simultaneous increase in $d_3$, ultimately leading to the breakage of the $O$ – $O$ bond. At steady state, the $O$ and $OH$ are stably adsorbed on hollow sites on the Pt surface (figure on the right in Fig. 3.5). The results are summarized in Table 3.

Assuming that the proton transfer to the oxygen molecule is an activated process, we can say that the two simulations presented above lie on opposite sides of the saddle point. A few more similar simulations can be used to get the saddle point. Although, our results are roughly in agreement with the work of Wang et al. [15] (Fig. 3.6), our predictions for the adsorption sites of the dissociated species are different. While Wang et al. find atop sites as the stable locations for the dissociated species, our simulations predict the hollow sites as the favored spot. A number of
Figure 3.4: Simulation 2: Reaction coordinates and the Kohn-Sham energy. Upon reducing the distance between the oxygen molecule and the hydronium complex, an H atom gets transferred to the O$_2$ molecule. This causes the descent of the two O atoms to be out of phase. The O atom to which the H atom is bonded, comes to the surface more slowly as compared to the other O atom. In the energy plot, the first drop from 0 to -1 eV corresponds to the proton transfer. This was concluded based on the position of the proton as a function of time. The second rapid drop from -1.5 to -5.5 eV is the dissociation of the O-H bond.

Figure 3.5: Snapshots from the simulation. (Left) Transfer of an H atom from the hydronium complex to the oxygen molecule. (Right) Steady state: On Pt(111) surfaces, hollow sites are the preferred locations for adsorption of the dissociated species.
<table>
<thead>
<tr>
<th>Reaction Coordinate</th>
<th>Steady state value (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta = 1.8 \text{ Å}$</td>
</tr>
<tr>
<td>$d_1$</td>
<td>1.6</td>
</tr>
<tr>
<td>$d_2$</td>
<td>1.6</td>
</tr>
<tr>
<td>$d_3$</td>
<td>3.2</td>
</tr>
</tbody>
</table>

**Table 3.1:** Steady state results. Variables used: $d_1$, $d_2$ are the distances of the O atoms from the Pt surface; $d_3$ is the distance between the O atoms of the oxygen molecule.

**Figure 3.6:** Evolution of the reaction coordinates from a similar study done by Wang et al. Results from this project (Fig. 3.4) were found to be in qualitative agreement with those of Wang et al.

Experimental studies have suggested the hollow sites as the destination of the adsorbed species [16]. More comprehensive simulations involving 3 or more slabs of Pt atoms, and more Pt atoms per slab are needed before any conclusive statement can be made from studies as done here.
Bibliography


