Analysis of Oxygen and Proton Reduction Reactions on Pt Catalyst Postprint

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Abstract

The characteristics of the oxygen reduction reaction at the cathode of proton exchange membrane (PEM) fuel cells significantly impact cell performance. This study establishes an oxygen adsorption model on the Pt electrocatalyst surface and a redox reaction model for hydrogen and oxygen on the Pt surface, employs molecular dynamics methods to simulate and investigate the reaction mechanism between hydrogen atoms and oxygen on the Pt surface, and analyzes the influence of temperature on the characteristics of the oxygen reduction reaction. The findings reveal that the initial adsorption of hydrogen and oxygen atoms on the Pt surface constitutes the rate-determining step of the entire oxygen reduction reaction; as temperature increases, the reaction rate of the oxygen reduction reaction accelerates, yet temperature does not affect the product structures in each step of the oxygen reduction reaction. The research results hold significant importance for enhancing the understanding of PEM fuel cell reaction mechanisms and promoting the application of fuel cells.

Full Text

Abstract

Oxygen reduction reaction characteristics at the cathode of Proton Exchange Membrane (PEM) fuel cells significantly impact overall battery performance. This study establishes models for oxygen adsorption on Pt catalyst surfaces and redox reactions between hydrogen and oxygen on Pt, employing molecular dynamics simulations to investigate the reaction mechanism of hydrogen and oxygen atoms on Pt surfaces and analyze temperature effects on oxygen reduction reaction behavior. The findings reveal that the initial adsorption of hydrogen and oxygen atoms onto the Pt surface constitutes the rate-determining step of the entire oxygen reduction process. While elevated temperatures accelerate the reaction rate, temperature variations do not alter the product structures formed

in each reaction step. These results contribute substantially to understanding PEM fuel cell reaction mechanisms and advancing fuel cell applications.

Keywords: PEM; fuel cell; catalyst; reaction mechanism

0 Introduction

Electrode reactions, particularly the cathodic oxygen reduction reaction, critically influence PEM fuel cell performance. With recent advances in PEM fuel cell technology, the oxidation-reduction mechanism in cathode catalyst layers has attracted considerable attention. Platinum represents one of the most commonly used and effective catalysts in proton exchange membrane fuel cells, making redox reactions occurring on Pt surfaces a major research focus.

Current understanding identifies two primary pathways for oxygen and proton reduction at PEM fuel cell cathodes: the four-electron and two-electron mechanisms. In the weakly acidic environment of PEM fuel cells, oxygen reduction predominantly follows the four-electron pathway when Pt contains minimal impurities [1]. In weakly alkaline environments, Miah et al. observed a two-step four-electron redox process using voltammetric cycling techniques [2]. Adzic et al. [3] proposed that PEM fuel cell cathode oxygen reduction proceeds primarily through the four-electron mechanism, with both two-electron and four-electron pathways occurring simultaneously. Markovic et al. [4] argued that the two-electron mechanism is more applicable to Pt and Pt-alloy catalysts, a view shared by Sun et al. [Error! Reference source not found], who concluded that the two-electron pathway is more suitable for oxidation-reduction reactions. Based on energy variation patterns during reaction, Liu et al. [6] investigated the redox mechanism using two-electron theory, finding that the first reaction step releases the least energy while the fourth step releases the most energy relative to the first three steps. Regarding the first electron transfer, Hartnig et al. [7] conducted studies on solvent molecule reorganization and related phenomena.

Ana M. Gómez-Marín et al. [8] identified the reduction of soluble intermediate species as the decision-making step in the overall reaction process. Catalysts accelerate oxygen and proton reduction reactions [9], with catalyst particle size and distribution, temperature, and acidic/alkaline environments significantly influencing reaction rates and mechanisms [10][11]. To enhance PEM fuel cell reaction rates, various catalysts and composite catalysts have been developed and experimentally compared [12][13].

While existing literature primarily focuses on catalyst preparation, catalytic properties, and electrode characteristics, few studies have simulated and analyzed the oxygen reduction reaction mechanism at fuel cell cathodes. Research on oxygen reduction mechanisms under Pt catalysis and their influencing factors remains particularly scarce. This paper employs molecular dynamics and quantum mechanics principles to simulate and analyze the oxygen reduction reaction mechanism on Pt catalyst surfaces, examining how parameters such as temperature affect reaction characteristics under Pt catalysis.

1 Simulation Methodology

The simulations utilize CASTEP software based on Density Functional Theory (DFT). High-temperature PEM fuel cell conditions were modeled at temperatures of 393 K, 413 K, 433 K, 453 K, and 473 K, with an oxygen back pressure of 0.1 MPa, to investigate the cathode catalyst reaction: O + 4H → 2H O occurring on Pt surfaces.

Structural optimization employed the Generalized Gradient Approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional. Medium computational precision was applied with a plane-wave cutoff energy of 300 eV. Self-Consistent Field (SCF) cycles were set to 300, with convergence criteria requiring energy convergence within 2.0×10 eV/atom. Molecular dynamics calculations utilized the NPT ensemble, specifying temperature, pressure, and reaction duration while fixing the unit cell center-of-mass.

The simulation began with structural optimization of the Pt primitive cell. From the optimized cell, a Pt(111) surface was cleaved to construct a four-layer Pt slab with a 2.0 nm vacuum layer, forming a 1×2×1 supercell. The bottom two atomic layers were constrained, and the cell was relaxed to obtain structural parameters: a = 0.570905 nm, b = 0.988836 nm, c = 2.69921 nm, = = = 90°. The O molecule was similarly optimized, yielding an O-O bond length of 0.124014 nm. When placed in the vacuum layer above the Pt(111) surface, O adsorbs onto Pt. Optimizing this adsorption structure produced the lowest-energy stable configuration of O on Pt(111), shown in [Figure 1: see original paper]. The energy variation during adsorption is depicted in [Figure 2: see original paper].

This stable O adsorption structure on Pt(111) served as the initial model for molecular dynamics simulations of oxygen reduction reaction characteristics on Pt surfaces. The calculated Pt lattice constant of 0.40 nm compares favorably with the experimental value of 0.392 nm, confirming that the computational parameters are reasonable and the data falls within valid ranges.

2 Reaction Pathway

In weakly acidic environments, the O reaction pathway follows: O + 4H + 4e → 2H O. On Pt surfaces, the oxygen reduction reaction proceeds through four distinct steps.

The first step involves positioning the first hydrogen atom (H) 0.3 nm above the midpoint between O and O , initiating the reaction: $O + H \rightarrow$ O H → $O +$ OH (where * denotes species adsorbed on Pt), as illustrated in [Figure 3: see original paper]. During the reaction, H gradually approaches O , forming a bond at a distance of 0.1261 nm [FIGURE:3(b)]. Depending on reaction timing, two distinct products can form [FIGURE:3(b) and (c)]. The energy variation over time is shown in [Figure 4: see original paper], revealing a transient energy stabilization period after product A formation. Without sufficient H supply, this

intermediate decomposes to product B, releasing additional energy. However, under actual conditions with continuous and adequate H supply, the first-step reaction proceeds as $O + H \rightarrow$ O H without the $O\,H \rightarrow$ O + *OH decomposition pathway.

In the second step, the second hydrogen atom (H) is introduced, producing the reaction: $O\,H + H \rightarrow$ O H $\rightarrow OH +$ OH. The model, shown in [Figure 5: see original paper], positions H 0.3 nm equidistant from O , H , and O . Molecular dynamics simulations reveal that after H addition, H moves toward O , bonds with it to form $O\,H$, *and ultimately decomposes into two* OH species [FIGURE:5(b) and (c)].

Based on product C from [FIGURE:5(c)], the structure was optimized and a third hydrogen atom was added for the third reaction step: $2OH + H \rightarrow$ OH + H O. The initial model [FIGURE:6(a)] places H 0.3 nm above O . Molecular dynamics simulation shows that after O bonds with H , its connection to Pt atoms breaks, forming a water molecule that desorbs [FIGURE:6(b)].

Since H is continuously and abundantly supplied in actual reactions, product A was structurally optimized to serve as the starting point for the second reaction step. Finally, the product from the third step (E) was optimized, and a fourth hydrogen atom (H) was added to initiate the fourth reaction: *OH + H O + H $\rightarrow$ 2H O. The initial reactant for this step is shown in [FIGURE:7(a)], with molecular dynamics simulation yielding the final product F [FIGURE:7(b)].

3 Temperature Effects

Simulations were conducted at constant pressure, identical Pt surface states, and equivalent H atom placement positions to analyze temperature effects (393 K, 413 K, 433 K, 453 K, and 473 K) on each of the four reaction steps:

1. $O + H \rightarrow$ O H
2. $O\,H + H \rightarrow$ O H $\rightarrow OH +$ OH
3. $2OH + H \rightarrow$ OH + H O
4. *OH + H O + H $\rightarrow$ 2H O

Each subsequent step begins from the product of the previous step, with H atoms added at the same position.

[Figure 8: see original paper] shows the energy variation during the four-step reaction process at 433 K. With equivalent initial H atom positions relative to oxygen atoms, each step requires different durations, with the first step consuming the longest time—approximately 130 fs. The second, third, and fourth steps each require less than 50 fs. This demonstrates that the initial H adsorption onto O on Pt(111) requires the longest duration in the overall reaction, establishing this step as the rate-determining step.

[Figure 9: see original paper] illustrates the reaction rate for this controlling first step as a function of temperature. The data show that as temperature increases, the time required before bond formation decreases, indicating that molecular motion accelerates with temperature. Additionally, the time to reach steady state after bond formation shortens significantly, demonstrating that reaction rates increase with temperature.

summarizes the instantaneous velocity of H atoms at the moment of adsorption and the average velocity before adsorption, the bonding time between O and H , and the optimal bond length of the stabilized structure under various temperature conditions for the rate-determining first step.

The data reveal that as temperature rises, the motion velocity of H atoms both before and during adsorption increases significantly, while the time required for bond formation decreases. However, temperature has negligible effect on the optimal bond length of the product in its stable state.

4 Conclusions

Based on density functional theory, molecular dynamics simulations of O reduction reactions on Pt(111) surfaces yield the following conclusions:

1. In the reaction process between O and H on Pt(111) surfaces with continuous and sufficient H supply, the first step can only proceed as: $O + H \rightarrow$ O H.
2. Throughout the O and H reaction process on Pt(111), the first step—adsorption of H onto O —requires the longest duration and constitutes the rate-determining step of the overall reaction.
3. Elevated temperatures increase H atom motion velocity and shorten the time for O-H bond formation, indicating that temperature increases enhance reaction rates without affecting the structures of products formed in each reaction step.

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Note: Figure translations are in progress. See original paper for figures.