Mechanisms of the Oxygen Reduction Reaction on Defective Graphene-Supported Pt Nanoparticles from First-Principles

Dong-Hee Lim and Jennifer Wilcox*

Department of Energy Resources Engineering
Stanford University

October 31st, 2011
I. Introduction, Motivation and Goals

II. Review on Oxygen Reduction Reaction (ORR)

III. Computational Methodology

IV. Summary of O$_2$ Adsorption on Pt$_{13}$–Defective Graphene

V. ORR on Free Pt NPs

VI. ORR on Pt$_{13}$–Defective Graphene

VII. Summary and Conclusion
Defect sites of graphene

- Defect sites of graphene
  - Mono-vacancy defect
  - Double vacancy 5-8-5 defect
  - Adatoms

- Serve as starting points for the growth of nanoparticles (NPs)
  - anchoring NPs on the graphene surface

- May enhance the catalytic activity of NPs

Benefits of graphene support

- High surface area (theoretical value of 2630 m²/g)[1]
- High conductivity[2]
- Minimal NP agglomeration (after 5000 CV cycles)
- Tune Pt reactivity

Current catalyst limitations

Oxygen reduction reaction (ORR)

- Taking place at the cathode of polymer-electrolyte-membrane fuel cells (PEMFC)
- The biggest challenge due to its slow kinetics in fuel cells
  - Fuel cell converts energy from a fuel (H₂) into electrical energy
  - Electricity is generated from the reaction between H₂ fuel and O₂ oxidizing agent

Pt catalyst

- Most promising electrocatalyst for ORR
- Expensive
- Carbon black supported-Pt:
  - May aggregate or dissolve from the substrate → decreased activity
- Other types of catalysts:
  → N-doped graphene, Pt₃Co and Pt₃Cr alloys, Pd-Pt alloy, graphene-Pd/Pt, etc

Goal: create surfaces that drive the ORR with high efficiency, i.e., with high rates and low overpotential
Motivation of graphene-supported Pt NPs

Enhanced oxygen reduction activity

- Pt and Pt alloy nanocatalysts supported on graphene, graphene nanoplatelets, or nanoscale graphite
  - Reduction in the high cost of the precious metal
  - Increase in the durability of the Pt support.
- Functionalized graphene-supported Pt nanoparticles enhance the ORR for fuel cells\(^1\) due to increased electrochemically active surface area and less aggregation of Pt NPs.

Previous experimental methods of synthesis

- Irradiation with ions or e\(^-\) has the potential to create vacancies in graphene\(^3\)
- Graphene-metal nanocomposites can be cast as films on carbon fiber electrodes for electrocatalytic applications.

Purpose of study

Few theoretical studies of ORR mechanisms on graphene-supported Pt NPs.

- To utilize defective graphene-supported Pt nanoparticles for the enhancement of the oxygen interaction with the Pt nanoparticle.
- To investigate ORR mechanisms on defective graphene-supported Pt NPs

Tasks:

1) Pt$_{13}$ nanoparticle adsorption on defective graphene
2) Oxygen adsorption on the Pt$_{13}$–defective graphene
3) Oxygen reduction reaction on the Pt$_{13}$–defective graphene
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VII. Summary and Conclusion
1. Two major pathways $^{5,6}$
   
i) *Direct 4-electron pathway*
   \[
   \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} 
   \]
   
   ii) *Series 2-electron pathway*
   \[
   \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2 \\
   \text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O} 
   \]

2. Suggested pathway for Pt and Pt-based bimetallic catalysts

i) **Parallel pathway:** both occurs simultaneously, with the direct as the dominant one

ii) **Series pathway**
   - Markovic et al (2001)$^8$; Grgur et al (Exp_1997)$^{15}$

iii) **Direct pathway**
   - Yeager (1984)$^5$

iv) **Pathway depending on O coverage**
   - Nørskov et al (2004)$^{12}$
   - $\Rightarrow$ At $\theta_O = 0$ (direct), at $\theta_O = 0.5$ (series)

v) **Pathway depending on $O_2$ adsorption configuration**
   - Yeager (1981)$^{13}$
   - $\Rightarrow$ At di-σ structure (direct), at top structure (series)

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I. Model system overview

**Defect sites of graphene**

- Defect sites of graphene
  - Mono-vacancy defect
  - Double vacancy 5-8-5 defect
  - Adatoms

- The presence of carbon vacancies on graphene significantly influences the physical and chemical characteristics and magnetic properties of graphene.[1-3]

- Defective graphene-supported nanoparticles may enhance surface reactivity.[2,4]

- “Magic numbers” $n$ of transition-metal clusters include $n = 7, 13, 15$. The current study has chosen $n = 13$.

- A monovacancy defective graphene consists of 127 carbon atoms.

II. Model system overview

**DFT (VASP software)**
- Periodic density functional theory (DFT)
  - Projector-augmented wave (PAW)
  - Spin-polarized GGA-PBE
- Kinetic energy cutoff: 400 eV
- $k$-point sampling: Monkhorst-Pack scheme $2 \times 2 \times 1$
- Methfessel-Paxton 1st order smearing with 0.1 eV width
- Adsorption energy per nanoparticle ($E_{ads}$):

$$E_{ads} = \frac{1}{N_{cluster}} \left( E_{surf+cluster} - E_{surf} - N_{cluster} \times E_{cluster} \right)$$

where

- $N_{cluster}$: nanoparticle number,
- $E_{surf+cluster}$: total energy (eV) of graphene with nanoparticle,
- $E_{surf}$: total energy (eV) of bare graphene, and
- $E_{cluster}$: total energy (eV) of gas-phase nanoparticle(s).

**Supercell system**
- Orthorhombic supercell $19.74 \times 17.10 \times 32.01 \, \text{Å}$
- Dipole moment correction tested but not included due to its negligible effect

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The expression for the adsorption energy is derived from the total energy of the system with the nanoparticle ($E_{surf+cluster}$), the total energy of the bare graphene ($E_{surf}$), the total energy of the gas-phase nanoparticle(s) ($E_{cluster}$), and the number of nanoparticle(s) ($N_{cluster}$). The equation accounts for the energy cost of adsorbing the nanoparticle on the graphene surface, adjusted for the number of nanoparticles. The diagram illustrates a supercell with dimensions and a nanoparticle adsorbed on a graphene surface.
Free energy (ΔG) of intermediates

\[ \Delta G = \Delta E + \Delta ZPE - T\Delta S \]

- Reaction energy difference
- Difference in zero point energy
- Temperature \times \text{Change in entropy}

\[ \Delta G(A^* + H^+ + e^- \rightarrow AH^*) = \mu(AH^*) - \left[ \mu(A^*) + \mu(H^+ + e^-) \right] = \mu(AH^*) - \left[ \mu(A^*) + \frac{1}{2} \mu(H_2(g)) - eU \right] \]

Simple oxygen reduction

\[ \frac{1}{2} \text{O}_2 + * \rightarrow \text{O}^* \]
\[ \text{O}^* + H^+ + e^- \rightarrow \text{HO}^* \]
\[ \text{HO}^* + H^+ + e^- \rightarrow \text{H}_2\text{O} + * \]

Computational hydrogen electrode (CHE) model by Nørskov et al.\[22]-[25]

- Chemical potential (μ) of (H⁺ + e⁻):
  \[ \mu(H^+ + e^-)_{aq} = \frac{1}{2} \mu(H_2(g)) \]

- Applied potential (ΔG = −eU):
  \[ \mu(H^+ + e^-)_{aq} = \frac{1}{2} \mu(H_2(g)) - eU \]

- Intermediate energy at zero potential:

DFT: geometry optimization and vibrational frequency

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Summary of Pt$_{13}$ adsorption on graphene

**Pt$_{13}$ cluster model**[1]

- D$_{4h}$ symmetry (-54.880 eV)
- $E_B = 3.69$ eV/atom
- Cluster radii = 3.13 and 2.49 Å

**Defective graphene**[2]

**Adsorbed Pt$_{13}$ on defective graphene**[1]

- Top view
- Side view
- $E_{ads} = -7.45$ eV
- $E_B = 3.69$ eV/atom
- Cluster radii = 3.13 and 2.49 Å

**Elevated carbon atom** = 1.33 Å (at maximum)

**Charge difference density ($e/Å^3$)**

- Scale: $\Delta n(r)$ ($e/Å^3$)

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Summary of $O_2$ adsorption on $Pt_{13}$–graphene$^{[1]}$

**$O_2$ adsorption energies**

**A**

- a) $-2.30$
- b) $-1.96$
- c) $-1.80$
- d) $-0.78$

**B**

- a) $-3.92$
- b) $-1.20$
- c) $-1.19$

$E_{ads}$ (eV)

- **A**: a) $-2.30$, b) $-1.96$, c) $-1.80$, d) $-0.78$
- **B**: a) $-3.92$, b) $-1.20$, c) $-1.19$

Excess charge vs. elongated $O_2$ bond

$R^2 = 0.982$

Charge difference density

$\Delta n(r)$ (e/$Å^3$)

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O₂ on Pt₁₃ vs. Pt(111)

Free energy diagram for ORR over Pt₁₃ and Pt(111)[¹]

Applied potential, $U = 1.23$ V

→ The equilibrium potential that the fuel cell can have, allowed by thermodynamics

Common:

- $(H^++e^-)$ steps are uphill
- Relatively stronger binding of O* and HO* on Pt

$E_{ads} (eV)$ on Pt NP:

$O^* (-4.99)$, $HO^* (-3.54$ eV$)$

$E_{ads} (eV)$ on Pt(111):

$O^* (-4.21)$²,
$HO^* (-2.25, -2.31)$³,⁴

O₂ on Pt₁₃ vs. Pt(111)

Free energy diagram for ORR over Pt₁₃ and Pt(111)[1]

Applied potential, \( U = 1.23 \) V

→ The equilibrium potential that the fuel cell can have, allowed by thermodynamics

**Difference:**

- For Pt(111), 1\(^{\text{st}}\) and 2\(^{\text{nd}}\) \((\text{H}^+ + \text{e}^-)\) steps have the same barriers\[22\]
  overpotential \((0.45 \text{ eV})\)

- For Pt\(^{13}\), 2\(^{\text{nd}}\) \((\text{H}^+ + \text{e}^-)\) step is the rate-limiting overpotential \((1.13 \text{ eV})\)

O₂ at bridge vs. top sites

Free energy diagram for ORR over Pt₁₃ at bridge and top sites

- Stronger binding of O* and HO* at bridge than at the top site.
- Stronger binding of O* and HO* require higher overpotential.

- \( E_{ads} \) (eV) at atop site:
  - O* (-4.72), HO* (-3.42 eV)

- \( E_{ads} \) (eV) at bridge site:
  - O* (-4.99), HO* (-3.54 eV)
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Oxygen Reduction Reaction Pathways

Free energy diagrams for ORR over Pt$_{13}$-defective graphene

1) Direct four-electron pathway  \[ \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \]

\[
\begin{array}{cccccccc}
& \text{O} & \text{O} & \xrightarrow{\text{Pt}} & \text{O} & \text{O} & \xrightarrow{\text{Pt}} & \text{OH} & \text{O} & \xrightarrow{\text{Pt}} & \text{H}_2\text{O} & \text{O} & \xrightarrow{\text{Pt}} & \text{H}_2\text{O} & \text{OH} & \xrightarrow{\text{Pt}} & \text{H}_2\text{O} & \text{H}_2\text{O} \\
1 & \text{Pt} & \text{Pt} & & \text{Pt} & \text{Pt} & & \text{Pt} & \text{Pt} & & \text{Pt} & \text{Pt} & & \text{Pt} & \text{Pt} & & \text{Pt} & \text{Pt}
\end{array}
\]

\[
\begin{align*}
\text{O}_2 & \rightarrow \text{O}_2^* \\
\text{O}_2^* & \rightarrow \text{O}^* + \text{O}^* \\
\text{O}^* + \text{O}^* + (\text{H}^+ + \text{e}^-) & \rightarrow \text{O}^* + \text{OH}^* \\
\text{O}^* + \text{OH}^* + (\text{H}^+ + \text{e}^-) & \rightarrow \text{O}^* + \text{H}_2\text{O} \\
\text{O}^* + \text{H}_2\text{O} + (\text{H}^+ + \text{e}^-) & \rightarrow \text{OH}^* + \text{H}_2\text{O} \\
\text{OH}^* + \text{H}_2\text{O} + (\text{H}^+ + \text{e}^-) & \rightarrow 2\text{H}_2\text{O}
\end{align*}
\]
Oxygen Reduction Reaction Pathways

Free energy diagrams for ORR over Pt$_{13}$-defective graphene

1) Direct four-electron pathway

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

Geometry optimization of atomic hydrogen

It is unclear whether $O_2$ dissociation occurs prior to proton/electron-transfer steps

$\Rightarrow$ we postulate that $O_2$ dissociates at the bridge $O_2$ adsorption configuration and proceeds to further proton/electron-transfer steps
Oxygen Reduction Reaction Pathways

Free energy diagrams for ORR over Pt$_{13}$-defective graphene

2) Series two-electron pathway

\[ O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \]
\[ H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \]

\[ \begin{array}{cccccccc}
\text{O–O} & \xrightarrow{} & \text{O–O} & \xrightarrow{} & \text{H–O} & \xrightarrow{} & \text{OH} & \xrightarrow{} & \text{H}_2\text{O} \\
\text{Pt} & \text{Pt} & \text{Pt} & \text{Pt} & \text{Pt} & \text{Pt} & \text{Pt} & \text{Pt} & \text{Pt} \\
1 & 2 & 3 & 4 & 5 & 6 & 7
\end{array} \]

\[ O_2 \rightarrow O_2^* \quad (1) \]

\[ O_2^* + (H^+ + e^-) \rightarrow \text{HOO}^* \quad (2) \]

\[ \text{HOO}^* \rightarrow O^* + \text{OH}^* \quad (3) \]

\[ O^* + \text{OH}^* + (H^+ + e^-) \rightarrow O^* + H_2O \quad (4) \]

\[ O^* + H_2O + (H^+ + e^-) \rightarrow \text{OH}^* + H_2O \quad (5) \]

\[ \text{OH}^* + H_2O + (H^+ + e^-) \rightarrow 2H_2O \quad (6) \]
Oxygen Reduction Reaction Pathways

Free energy diagrams for ORR over Pt\textsubscript{13}-defective graphene

2) Series two-electron pathway

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

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

Geometry optimization of atomic hydrogen

It is unclear whether \text{O}_2 dissociation occurs prior to proton/electron-transfer steps

\[ \Rightarrow \text{we postulate that \text{O}_2 forms HOO}^* \text{ species at the atop site.} \]
Direct 4e pathways (Pt$_{13}$-graphene)

Comparison between more and less stable intermediates

- The stronger binding of intermediates, the higher desorption energy
- The rate-limiting steps:
  - ‘more stable’ = 1.68 eV (at Step 6 $\rightarrow$ 7)
  - ‘less stable’ = 0.78 eV (at Step 4 $\rightarrow$ 5)
- The stability of O* and HO* serves a key role in the activity of Pt NPs.
Direct 4e pathways (free vs. supported Pt$_{13}$)

Comparison between supported and unsupported Pt$_{13}$ NPs

Relative free energy (eV)

\[ \text{TS1} = 0.16 \text{ eV} = 3.67 \text{ kcal/mol} \]
\[ \text{TS2} = 0.37 \text{ eV} = 8.52 \text{ kcal/mol} \]

- It suggests a capability of tuning of the Pt NP reactivity
Direct 4e pathways (free vs. supported Pt₁₃)

**Free energies of activation for O₂ dissociation (TS1 vs. TS2)**

- **Supported Pt₁₃**: TS₁ = 0.16 eV, Elongated O₂ = 1.44 Å, Excess O₂ charge = 0.65e
- **Free Pt₁₃**: TS₂ = 0.37 eV, Elongated O₂ = 1.40 Å, Excess O₂ charge = 0.62e
- **Pt(111)**: Ranging 0.69 – 0.90, 0.44, 0.15–0.30 eV

- All consistent one another, except for O₂ adsorption energies
  
  - Supported Pt₁₃ (−2.30 eV) vs. Free Pt₁₃ (−3.92 eV)

- Generally, the stronger O₂ adsorption on flat metal surfaces, the lower O₂ dissociation barrier energies

- The stability of O₂–free Pt₁₃ is attributed to a significant geometry distortion of the free Pt₁₃ upon O₂ adsorption ($E_{ads}$ with fixed Pt₁₃ = −1.14 eV).

Comparison of d-band centers

- **Pt\textsubscript{13}:** -1.89 eV
- **Pt\textsubscript{13}-defective graphene:** -1.98 eV
- The position of the d-band center is a measurement of the relative reactivity of a given surface\cite{1,2}
- The weaker binding of O\textsubscript{2} and its intermediates
  ➔ resulting in the lower energy barrier of the rate-limiting step for the supported system.

Series 2e pathways (Pt$_{13}$-graphene)

On Pt surfaces
- $E_a$ of –OOH < $E_a$ of $O_2$ dissociation
  $\rightarrow$ –OOH is an initial step of ORR:
  [6, 14, 17, 10, 16]

On Pt$_{13}$-graphene
- $E_a$ of –OOH > $E_a$ of $O_2$ dissociation
  $\rightarrow$ $O_2$ dissociation may be an initial step of ORR
Series 2e pathways (Pt\textsubscript{13}-graphene)

On flat Pt surfaces
Wang and Balbuena\textsuperscript{[1]} shows that $E_a$ of –OOH < $E_a$ of O\textsubscript{2} dissociation:
- A preferred O\textsubscript{2} adsorption configuration $\rightarrow$ a canted HOO* at an atop site.

On Pt\textsubscript{13}-graphene
$E_a$ of –OOH > $E_a$ of O\textsubscript{2} dissociation
$\rightarrow$ O\textsubscript{2} dissociation may be an initial step of ORR

Decomposition precursor of HOO*
Elongated O–O bond (1.48 Å) and shortened Pt –O distance (1.94 Å)
$\rightarrow$ Decomposes to O* and HO* with a small barrer energy of 0.06 eV\textsuperscript{[1]}

Electronic properties

- Charge is transferred from Pt NPs to both $O_2$ and defective graphene

$$\Delta n(r) = n_{\text{surf} + \text{cluster}}(r) - [n_{\text{surf}}(r) + n_{\text{cluster}}(r)]$$
Summary and Conclusions

- **Graphene vacancies** serve to anchor Pt$_{13}$ nanoparticles showing strong adsorption energy of −7.34 eV, which may prevent sintering of the catalyst.

- Benefits of defective graphene supports include:
  - Lowers the O$_2$ dissociation activation energy from 0.37 to 0.16 eV
  - Decreases the energy barrier of the rate-limiting step (HO* intermediate).

- The direct pathway: O$_2$ dissociation activation energy (**0.16** eV)
  - The series pathway: minimum energy barrier for HOO* formation (**0.29** eV)
    - The direct pathway may be preferred at the initial step of the ORR on defective graphene-supported Pt$_{13}$ NPs.

- Pt$_{13}$ NPs serve as a charge donor to both defective graphene and the intermediate species.
First-Principles Investigation of Phase Stability of Complex Hydrides

Dong-Hee Lim and Jennifer Wilcox*

Department of Energy Resources Engineering
Stanford University
Introduction

Magnesium hydride (MgH₂)

- High gravimetric (7.6 wt. % H₂) and volumetric (111 kg H₂/m³) storage capacity
- High temperature required to release H₂
  → can be overcome by adding Si

\[ 2\text{MgH}_2 + \text{Si} \rightarrow \text{Mg}_2\text{Si} + 2\text{H}_2 \]

- Hydrogenation reaction does not readily occur, even at 100 bar of H₂ / at 150 °C
  → due to kinetically unfavorable H₂ dissociation on the Mg₂Si surface

Complex hydrides including alanates ([AlH₄]⁻)

- NaAlH₄, LiAlH₄, KAlH₄, Mg(AlH₄)₂, Na₃AlH₆, Li₃AlH₆, Na₂LiAlH₆, etc
- Known to release H₂ upon contact with water
- Mg(AlH₄)₂ can exothermically dehydrogenate at 163 °C.

\[ \text{Mg(AlH}_4\text{)}_2 \rightarrow \text{MgH}_2 + 2\text{Al} + 3\text{H}_2 \]

- Rehydrogenation is not thermodynamically favorable
Another similar example,

\[
\text{LiAlH}_4 \rightarrow \frac{1}{3} \text{Li}_3\text{AlH}_6 + \frac{2}{3}\text{Al} + \text{H}_2
\]

- Dehydrogenation with \(\Delta H\) of \(-10\) kJ/(mol of \(\text{H}_2\))
- Rehydrogenation with \(\Delta H\) of 9 kJ/(mol of \(\text{H}_2\))

To overcome the irreversible hydrogenation process

- Alanates can be doped with titanium
- Nanostructuring, e.g.,
  - [DFT] As the MgH\(_2\) cluster size decreases below 19 Mg atoms, MgH\(_2\) becomes more destabilized, resulting in a significantly lower hydrogen desorption energy.
  - [Exp] Upon size restriction of nanoparticles of NaAlH\(_4\), LiAlH\(_4\), and LiBH\(_4\), a drastic enhancement of the hydrogen desorption properties can be achieved.
Purpose of Study

“Predicting what phases would be more stable as a function of nanoparticle size would contribute to nanostructuring the complex hydrides for hydrogen storage.”

Proposed study

- To construct a phase stability diagram of the nanoparticle of Mg(AlH$_4$)$_2$ depending on its size as a function of temperature and composition.
- To complete this,
  1) First-principles calculations for total energies of a series of configurations of nanoparticles of Mg(AlH$_4$)$_2$
  2) Cluster expansion parameterized by the total energies, which enables the total energy calculations of any arrangements of Mg(AlH$_4$)$_2$.
  3) Monte Carlo simulations equipped with the cluster expansion to calculate thermodynamic properties and equilibrium phase boundaries.
Acknowledgements

• Support from the Center on Nanostructuring for Efficient Energy Conversion (CNEEC) at Stanford University, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001060

• Super computer facilities from the Texas Advanced Computing Center (TACC) at The University of Texas at Austin supported from the National Science Foundation (NSF)
Supplemental Information
### 3. Views regarding the first electron-transfer step

\[
\begin{align*}
O_2 + \text{Pt} & \rightarrow \text{Pt}–O_2 \\
\text{Pt}–O_2 + H^+ + e^- & \rightarrow \text{Pt}–\text{OOH}
\end{align*}
\]

- Proton is not involved in the rate-limiting step: Yeager (1984)\(^5\)
- The first electron transfer step is rate-limiting step
  \[\rightarrow\] proton is involved in the rate-limiting step \(^{14}\)
- –OOH is initial step of ORR: \(E_a\) of –OOH < \(E_a\) of \(O_2\) dissociation
  Wang and Balbuena (2005)\(^10\); Anderson and Albu (2000)\(^16\)

### 4. Fate of -OOH

- –OOH easily dissociates with 0.06 eV activation barrier to form adsorbed O and OH: Sidik and Anderson (2002)\(^14\)
- Decomposition of –OOH takes place with a rather small barrier \(\rightarrow\) adsorbed O and OH: Wang and Balbuena (2005)\(^10\)

See the list of References
**O₂ dissociation barriers on free Pt₁₃**

**O₂ dissociation barrier on free Pt₁₃ (E_a) = 0.39 eV**

![Reactant and Transition state](image)

**Reaction coordinates**

<table>
<thead>
<tr>
<th>Ea (eV)</th>
<th>Method</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.32</td>
<td>Experiment, Pt(111), gas</td>
<td>[27]</td>
</tr>
<tr>
<td>0.24~0.76</td>
<td>DFT, Pt(111) depending on θ, gas</td>
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</tr>
<tr>
<td>0.7~1.0</td>
<td>DFT, Pt(111), Pt(211) step &amp; near step, gas</td>
<td>[28]</td>
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<tr>
<td>0.44~0.51</td>
<td>DFT, Pt(111) depending on θ, gas</td>
<td>[29]</td>
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<tr>
<td>0.3~0.9</td>
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<tr>
<td>0.15~0.30</td>
<td>DFT, Pt(111), gas</td>
<td>[31]</td>
</tr>
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</table>

# O₂ dissociation barriers on Pt

$E_a$ of free Pt$^{13}$ = 0.39 eV

<table>
<thead>
<tr>
<th>$E_a$ (eV)</th>
<th>Method</th>
<th>O-O (Å)</th>
<th>TS O-O (Å)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.32</td>
<td>Experiment, Pt(111), gas</td>
<td></td>
<td></td>
<td>27</td>
</tr>
<tr>
<td>0.47</td>
<td>$\theta_{O_2}$=0.12 ML, DFT, Pt(111), gas</td>
<td></td>
<td></td>
<td>27</td>
</tr>
<tr>
<td>0.24</td>
<td>$\theta_{O_2}$=0.25 ML, DFT, Pt(111), gas</td>
<td></td>
<td></td>
<td>27</td>
</tr>
<tr>
<td>0.76</td>
<td>$\theta_{O_2}$=0.50 ML, DFT, Pt(111), gas</td>
<td></td>
<td></td>
<td>27</td>
</tr>
<tr>
<td>0.9</td>
<td>Bridge site, DFT, Pt(111), gas,</td>
<td></td>
<td></td>
<td>27</td>
</tr>
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</table>

Other important factors not considered in the current study

- The effect of water layers on the stability of O* and HO*
  
  Interaction strength\[^{[24]}\]:
  
  O* \( \rightarrow \) H\(_2\)O < HO*\( \rightarrow \)H\(_2\)O (or HOO*\( \rightarrow \)H\(_2\)O)

- pH correction\[^{[22]}\]–\[^{[25]}\]
  
  \[ \Delta G(pH) = -kT \times \ln[H^+] = kT \times \ln10 \times pH \]

- The effect of oxygen coverage on binding energies of intermediates

- Field effect from electrochemical double layer

- O\(_2\) dissociation
  
  (according to the simple ORR model)

Justification of fixing graphene surface

O₂ adsorption energy ($E_{O2}$) and change in atomic positions ($\delta_p$)

- Change in atomic positions ($\delta_p$, in Å)
  $$\sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2}$$

where subscripts 1 and 2 represent the atomic positions before and after adsorption, respectively.

Fixed: 83 atoms

Relaxed: 44 atoms
Direct 4e pathways (free vs. supported Pt$_{13}$)

Table 1. O–O bond lengths, activation energies of O$_2$ dissociation ($E_a$), and Pt–O and Pt–OH bond lengths of the free Pt$_{13}$ nanoparticle (Pt$_{13}$) and Pt$_{13}$–defective graphene systems (Pt$_{13}$/G) of direct and series pathways. Steps (1)–(6) correspond to images of Figure 3 and 4 (*indicates average lengths with ± less than 0.007 Å).

<table>
<thead>
<tr>
<th>Step</th>
<th>O–O (Å)</th>
<th>$E_a$ (eV)</th>
<th>Pt–O (Å)</th>
<th>Pt–OH (Å)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Direct Pt$_{13}$</td>
<td>Direct Pt$_{13}$/G</td>
<td>Series Pt$_{13}$</td>
<td>Series Pt$_{13}$/G</td>
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<td>1.23</td>
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<td>1.93</td>
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