Why Is Pt So Unique
A Chemical Physics Approach
Philip N. Ross, Jr.
Materials Sciences Division
Lawrence Berkeley National Laboratory
Berkeley, CA 94708
Outline

• A brief history of electrode kinetics
• Reaction pathway for oxygen reduction
• Effect of pH
• Systematic trends across Periodic Table
• One electron makes a big difference
  \[ d^9s^1 \text{ versus } d^{10}s^1 \]
• Pt at the top of the Volcano Curve
Mechanism of the ORR at metal electrodes

Addition of first electron needed to break O-O bond

Rate limiting step in electrochemical reduction of $O_2$ is 1$^{st}$ electron transfer

\[
O_2 + e^- \rightarrow (O_2^-)_{sol} \quad \text{Outer Sphere} \quad (E^0' = -0.3 \text{ V})
\]

\[
O_2 + e^- \rightarrow (O_2^-)_{ads} \quad \text{Inner Sphere} \quad (E^0' + \Delta G_{ad}/F)
\]

$O_2^-$ adsorption strength related to the electronic properties of the electrode material

Establish general trends across Periodic Table using quantum chemical modeling
Origin of the pH Effect

\[ \text{O}_2,\text{ad} + e^- \rightarrow \bullet \text{O}_2^-\text{ad} \quad \text{(rds)} \]

Because H\(^+\) does not occur in the rds, the rate of this reaction step will not depend on pH. But if we define the electrode potential using the rhe scale, then the overpotential will be pH dependent and thus the polarization curve will shift with pH.

\[ I = kF C_{O_2}\exp(\beta F \eta/RT) \]

\[ \eta = E - 0.059pH - E_o[(O_2/O_2^-)_{ad}] \]

Note that at pH = 14 only weak adsorption of O\(_2^-\) is needed to have reduction in the potential region (rhe) of interest.
Quantum Chemical Modeling Approach

Calculate the interaction of molecular oxygen and the superoxide radical anion ($O_2^-$) with a single metal atom using DFT (B3LYP) LANL2DZ/6-31+G(d)

Obtain the Potential Energy Surface (PES) as a function of ($O_2^-$) distance above the metal atom and the O-O bond extension

Examine the molecular orbital character at various adsorption configurations and plot the correlation diagrams using Hartree-Fock (HF) LANL2DZ/6-31+G(d)
$O_2$ –Pt Potential Energy Curves vs. O-O bond length

![Graph showing potential energy curves vs. O-O bond length for $O_2$–Pt interaction. The graph includes various energy levels and distances, with annotations for activation barrier and electron gains/losses.](image)
(O$_2^-$)-Pt Potential Energy Curves vs. O-O bond length

The graph shows the potential energy curves (in eV) plotted against the (O$_2$)-Pt distance (in angstroms). Various lines represent different O-O bond lengths, labeled with values such as 1.3511, 1.4659, 1.6659, 2.8659, and 3.0659. An activation barrier is indicated at 0.46 eV, and the energy at the activation barrier is $E_a = 0.87$ eV.
Correlation Diagram of the Molecular Orbitals of (O$_2^-$)-Pt

Pt 5d partially filled
Extra electron of O$_2^-$ lift 1$\pi$ close to Pt 5d
\quad Stronger interaction
O$_2^-$ 2$\pi$ above Pt 5d
\quad charge transfer to Pt
(O₂⁻)–Au Potential Energy Curves vs. O-O bond length
Correlation Diagram of the Molecular Orbitals of \((O_2)\)-Pt

Pt 5d levels above \(O_2\) 2\(\pi\)
Charge transfer from Pt to \(O_2\)
\(O_2\) 1\(\pi\) level lower than Pt 5d levels
Weaker interaction between Pt and \(O_2\)
Correlation Diagram of Molecular Orbitals of \((O_2^-)-Au\)
Conclusions from Quantum Chemical Modeling

The strength of interaction of $O_2$ and $O_2^-$ with metals is uniquely related to their electronic structure.

$d^9s^1$ Metal - $O_2^-$ interaction much stronger than $d^{10}s^1$ Metal - $O_2$ interaction

$(d^9s^1)-O_2^- >> (d^{10}s^1)-O_2^-$

$d^9s^1$ Metal - $O_2^-$ interaction much stronger for 5d than 3d orbitals (relativistic effect)

$d^{9-n}s^1$ Metal - $O_2^-$ interaction does not vary as much with n as the $d^{9-n}s^1$ Metal - $O_2$ interaction does (very strong with n>1)

Contribution of adsorption energy of intermediates to the kinetic rate of the ORR can be accurately captured by modern quantum chemical methods.
The Volcano Relation in ORR Kinetics

\[ \Delta G_{\text{intermediate}} (O_2^- \text{ or } OH) \]

Log \( k \)

Exponential term (\( O_2^- \))

Pre-exponential term (1 - \( \Theta_{\text{ad}} \))

\( \Theta_{\text{ad}} \) is mostly \( OH_{\text{ad}} \) not \( (O_2^-)_{\text{ad}} \)

\( H_2O = OH_{\text{ad}} + H^+ + e^- \) or

\( O_2^- + 2 H^+ + e^- = 2 OH_{\text{ad}} \)
ORR on Ag and Au occurs entirely at low coverage by OH\textsubscript{ad}

ORR on Cu affected by strong OH\textsubscript{ad}
Pt at the Top of the Volcano

- Interaction of the electrode with $O_2^-$ requires partially filled d-orbitals with large radial extent
  - Group 1B, 2B, 3B etc. metals have closed d-shells
  - Of Group VIII metals, d-orbitals in first row ($3d^{9-n}$) do not have sufficient radial extent
  - The $5d^{9-n}$ orbitals are the best for forming long bonds
- Interaction of the electrode with $OH_{ad}$ must be relatively weak
  - Of the Group VII metals, Pt has the weakest interaction with $OH_{ad}$