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Title: Modeling of Non-Precious Metal Catalyst Active Sites

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Intended for: Invited Talk

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Modeling of Non-Precious Metal Catalyst Active Sites

***Edward (Ted) F. Holby* and Chris Taylor**

Los Alamos National Lab

Energy Technology Seminar

September 10th, 2012

Talk Outline

- **Background and Motivation**
- **Monte Carlo Search**
- **Insights from Density Functional Theory**
 - Vibrational spectra comparison with experiment
 - Defected graphene nanoribbon stability
 - Oxygen reduction reaction pathways
- **Conclusions and Future Work**

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Why Fuel Cells?

■ Low temperature fuel cells (PEFC)

- Replacement for internal combustion engine (ICE)
- Potentially removes need for fossil fuels
 - Reduction of energy imports
 - Enables renewable technologies
- Highly efficient (~2x ICE), high power density
- Clean point-of-use
 - No smog, GHG, NOX, etc.

www.hydrogen-fuel.org/Chevrolet-Sequel-Hydrogen-Fuel-Cell-Vehicle.htmf

Slide 4

How a Fuel Cell Works

The Problem with Platinum

- Pt and Pt based alloys – main ingredient in state of art ORR catalysts
- Issues with Pt: cost, supply, and durability

Fuel Cell Cost Breakdown
(at Pt price of \$1,100/oz)

ca. 45% at ~\$1,500/oz today

Ferreira, et al., *J. Electrochem. Soc.* (2005).

James, et al., 2010 DOE Hydrogen Program Review
(2010). Revised P. Zelenay

Solutions for Platinum Problems

■ Solutions:

- Use less Pt
- Find Pt replacement

■ Non-precious metal catalysts (NPMCs) -- earth-abundant materials to catalyze ORR

- Chalcogenides
- Oxides
- Nitrides
- Macrocycles
- M-N/C structures

■ Activity/Stability main issues

■ State of art NPMC developed at LANL (MPA-11)

Wu, *et al.*, *Science* (2011).

How Modeling Can Help

- **Active site structure = rational design principle**
 - Maximize number of active sites / activity
 - Maximize stability
- **What is atomic scale structure of active site?**
 - Amorphous C host (pyrolyzed) with N and transition metal (Fe/Co) dopants – many structures!
- **Is Fe/Co part of active site or simply template?**
 - Active debate ongoing in community
- **Can we do better?**

Proposed Active Sites

- Proposed Fe-N/C structure - Tributsch, *et al.*, *Electrochimica Acta* (2008).

- Proposed Fe-TMPPC structure – Schulenburg, *et al.*, *J. Phys. Chem. B* (2003).

- Proposed Fe-TPTZ structure - Lee, *et al.*, *Electrochimica Acta* (2009).

- Proposed Fe ASC structure - Lefevre, *et al.*, *Science* (2009).

- Proposed M-N/C structures - Tributsch, *et al.*, *Electrochimica Acta* (2008).

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Monte Carlo Search Background

- **Large C/vacancy/N/Fe search space**
- **Need assumptions to model**
 - Activity increases with graphitization – use graphitic host material
 - Relative concentrations
- **Still many questions**
 - Defect Clustering?
 - Edge vs. Center?
 - Spin/Charge State?
 - Structural Motifs?

Holby, Wu, Zelenay and Taylor, *ECS Transactions*, in press

Monte Carlo Search Method

- High throughput approach using semi-empirical (PM6) potential for fast screening
- Metropolis algorithm Monte Carlo (originally developed at LANL)
 - Start w/ random structure
 - Calculate energy (E_1)
 - Random swap
 - Recalculate energy (E_2)
 - If $E_2 < E_1$, accept swap
 - If $\text{rand} < \exp[(E_1 - E_2)/k_B T]$, accept swap
 - Allows energy minimization and stochastic “uphill” swaps

Holby, Wu, Zelenay and Taylor, *ECS Transactions*, in press

Monte Carlo Search Simulations

- **800 initial structures**
 - 0-5 C vacancies
 - Spread of spin and charge states
- **1000 iterations per structure**
 - Python wrapper with Gaussian '09 code

Holby, Wu, Zelenay and Taylor, *ECS Transactions*, in press

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Slide 13

Monte Carlo Search Results

■ Proper vac. Structure

- Fe 2nd NN clustering with “bridge” atom
- N and vac. cluster with Fe structures
- Preference for edges vs. central positions
- Structure dominant over spin/charge state
- Suggests motifs for higher level theory (DFT)

Holby, Wu, Zelenay and Taylor, *ECS Transactions*, in press

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Slide 14

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DFT – Calculation Details

- Vienna Ab-initio Simulation Package (VASP)
- PBE-GGA exchange and correlation functional
- ~15Å vacuum between GNR images
- Converged to < 1 meV
 - 400eV energy cutoff
 - K point mesh $A \times 1 \times 1$ (GNR)
 - Vibrational by force ($< 0.02 \text{ eV/\AA}$)
- MedeA for vibrational spectra
 - Direct method - Parlinski, Li, and Kawazoe (PRL, 1997)

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Vibrational Spectra and NRVS

- Fe active or temple C/N active site?
- Nuclear resonance vibrational spectroscopy (NRVS) with NO probe ligand (O_2 analog) – first surface Fe specific spectroscopic technique (adapted from biology)
- DFT can calculate Fe spectra for direct comparison

Scheidt *et al.*, *J. Inorg. Biochem* (2005).

NRVS – Findings

New Fe vibrations consistent with Fe-NO ligation upon treatment with $\text{NO}_{(g)}$?

Note: $\text{NO}_{(g)}$ should only be able to access iron sites which are gas accessible (i.e. sites which are also accessible to O_2) – surface sensitive!

DFT – Vibrational Spectra

- 3N-monovacancy edge site agrees with NRVS
- 4N-bivacancy edge site does not agree with NRVS
- Can discriminate atomic scale structure of sites!
 - Fe coordination environment

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DFT – Graphene Nanoribbons

- Use of zig-zag H-terminated graphene nanoribbon (GNR) host – VASP code
- Comprehensive study of defects vs. position
- Defects Considered:
 - Monovacancy (a,c)
 - 3N-monovacancy (d,f)
 - Fe/monovacancy (b)
 - Fe/3N-monovacancy (e)

Holby and Taylor, *App. Phys. Lett.*, (2012).

Graphene Nanoribbons -- Vacancies

- Vacancy formation energy shows preference for 3N-termination (graphene / N₂ ref. state)
- Non-monotonic behavior for 3N-monovacancy

Holby and Taylor, *App. Phys. Lett.*, (2012).

Graphene Nanoribbons – Fe and Vacancies

- Fe/monovacancy has increasing formation energy going from edge to center but decreasing Fe binding
- If separate vacancy and Fe adsorption steps, Fe prefers to bind at center of GNR

Holby and Taylor, *App. Phys. Lett.*, (2012).

Graphene Nanoribbons – Fe, N, and Vacancies

- Fe/3N-monovacancy has increasing formation energy going from edge to center and increasing Fe binding
- With N, Fe defects favorable at edge both from formation and binding

Holby and Taylor, *App. Phys. Lett.*, (2012).

Graphene Nanoribbons -- Findings

- **Data suggests that N has two major effects relevant for catalysis:**
 - Decreased formation energy → More active sites
 - Strong edge preference (despite formation pathway) means active sites at edges/increased accessibility
- **Width of GNR (5-7) made little difference in formation and binding energies ($< 75\text{meV}$)**
- **Edge effects reach into GNR width (300 meV vacancy formation energy difference between center of GNR and “bulk” 2-D graphene)**

DFT – Defect Clustering

- Formation energies from DFT indicate clustering of 3N-monovacancy/Fe defects
 - 5N-2Fe most stable

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DFT – ORR Pathway

- 4 e⁻ pathway → H₂O (desirable)
- 2 e⁻ pathway → H₂O₂ (undesirable)
- **Multiple sub-pathways for 4 e⁻ ORR**
 - “Dissociative Pathway”: O₂ → 2O_{ads}
 - “Associative Pathway”: O₂ → HOO_{ads}

DFT – ORR Pathway

- Mono-Fe (3N-1Fe) GNR edge ASC follows associative pathway
- Multi-Fe (5N-2Fe) GNR edge ASC follows dissociative pathway
- Need more ASCS
 - Requires more computational power
- Effect of solvation? Dispersion?

DFT – ORR Pathway

- Anderson and Nørskov Models of ORR suggests that O binding energy of $\sim 2.38\text{eV}$ is ideal for dissociative pathway
- 5N-2Fe site has binding energy of 2.41eV

Anderson, *Phys. Chem. Chem. Phys.* (2012).

Nørskov et al., *J. Phys. Chem. B* (2004).

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Conclusions

- Spectroscopy/DFT (currently) point toward 3N coordinated Fe site vs. traditional 4N
- DFT/MC shows 3N coordinated Fe sites are favored at GNR edge
- DFT/MC shows 3N coordinated Fe sites cluster at GNR edge leading to 5N-2Fe sites
- DFT shows 5N-2Fe binding energy consistent with high activity and experimental spectra

Future Work

- **More ASCs!**

- Vibrational spectra, formation energies, ORR pathways (thermodynamics + kinetic barriers)

- **Development of vibrational, stability, and activity descriptors – what makes ASCs have certain properties?**

- **Synthesis targets based on stability, selectivity, and activity for rational design**

Thank You!

■ Collaborators

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■ Computation Resources

- LANL IC
- ANL CNM
- XSEDE Network