Solar Energy Through Better Chemistry

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Solar Energy: Small Piece of the Pie

U.S. energy consumption by energy source (2015)

Total = 97.7 quadrillion Btu

- petroleum: 36%
- natural gas: 29%
- nuclear electric power: 9%
- coal: 16%
- renewable energy: 10%

Total = 9.7 quadrillion Btu

- biomass: 49%
- hydroelectric: 25%
- biofuels: 22%
- biomass waste: 5%
- wind: 19%
- solar: 6%
- geothermal: 2%

Note: Sum of components may not equal 100% because of independent rounding

Source: U.S. Energy Information Administration, Monthly Energy Review, Table 1.3 and 10.1 (April 2016), preliminary data

http://www.eia.gov/energyexplained/?page=us_energy_home
Store Energy in Chemical Bonds

- Fuels from abundant substrates
- Catalysis by earth-abundant metal complexes

Renewable Energy

Catalysts

Chemical Fuels

CO₂

Mn Fe Co Ni Cu

Ru Rh Pd Os Ir Pt

H₂O

H₂ + O₂

N₂

NH₃

Slide from Morris Bullock, PNNL
Electrocatalysts: Energy Storage/Delivery

- Energy is stored in chemical bonds
- Interconversion between electrical energy and fuels requires catalysts
- Catalysts designed to control multi-proton, multi-electron reactions

\[
\begin{align*}
\text{H}_2 & \rightleftharpoons 2\text{H}^+ + 2\text{e}^- \\
\text{O}_2 + 4\text{H}^+ + 4\text{e}^- & \rightleftharpoons 2\text{H}_2\text{O} \\
2\text{H}_2 + \text{O}_2 & \rightleftharpoons 2\text{H}_2\text{O} + \text{electrical power}
\end{align*}
\]

Portions of slide from Morris Bullock, PNNL
Feedback between Experiment and Theory

- Experimental chemists synthesize/characterize catalysts
  - X-ray crystallography and NMR: structures
  - Infrared spectroscopy: vibrations
  - Cyclic voltammetry (CV): reduction potentials
  - $pK_a$ measurements: protonation states
- Theoretical chemists interpret data, make predictions
  - Calculate reduction potentials
  - Assist assignment of CV peaks
  - Calculate $pK_a$’s
  - Determine reaction pathways
  - Predict how to alter pathways, thermodynamics, kinetics

Reduction: $A + e^- \rightarrow A^-$
Protonation: $A^- + H^+ \rightarrow AH$

Rose, Gray, Winkler, JACS 2012
Catalyst Design for H₂ Production/Oxidation

- Design molecular electrocatalysts for H₂ production and oxidation
- Objective: high turnover frequency, low overpotential
- Environmentally friendly, cost effective, earth abundant

Diagram of a catalyst design for H₂ production and oxidation, showing the cathode and metal electrode with molecular structures.
Catalytic Cycle

- Many different steps, often proton transfer (PT) and electron transfer (ET) or concerted electron-proton transfer (EPT)
- Thermodynamics (relative free energies) and kinetics (barriers) important
- Modifying catalysts can change mechanism, thermodynamics, and kinetics
Devised Computational Protocols

*Solis and SHS, Inorg. Chem. 2011*

- Calculate reduction potentials and $pK_a$'s for each ET and PT step
- Generate free energy diagram for all possible mechanisms
- Identify thermodynamically favorable pathway

Cobaloximes produce $\text{H}_2$ from protic solutions at modest overpotentials
Alter Substituents to Tune Thermodynamics

Examine effects of changing R substituents on cobaloximes

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<tr>
<td>σₚ</td>
<td>–0.66</td>
<td>–0.37</td>
<td>–0.27</td>
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<td>–0.01</td>
<td>0.00</td>
<td>0.23</td>
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Electron donating | σₚ | Electron withdrawing

Correlations wrt Cobaloxime Substituents

- All quantities linearly correlated with $\sigma_p \rightarrow$ predict all quantities from $\sigma_p$ or one quantity
- Predict catalysts that follow different pathways and require lower overpotential, weaker acids
- Alter ligands and metals as well as substituents

Solis and SHS, JACS 2011

Ligand non-innocence
Hangman Metalloporphyrins

- Hangman metalloporphyrins shown experimentally to evolve hydrogen
- Initially thought to involve PT from hanging carboxylate to metal
- Calculations suggest an alternative (unexpected) mechanism
- Ligand non-innocence → PT to meso carbon to form phlorin

Solis, Maher, Honda, Powers, Nocera, SHS, ACS Catalysis 2014
Solis, Maher, Dogutan, Nocera, SHS, PNAS 2016
Proposed Mechanism for Ni Porphyrins

- Metal-hydride never formed
- Free-base porphyrin catalysts?
Phlorin Detected Experimentally

*Solis, Maher, Dogutan, Nocera, SHS, PNAS 2016*

Spectroelectrochemistry before electrolysis:
-1.3 V without acid
-1.9 V without acid
-1.9 V with phenol

CV simulations (dotted) agree with experimental catalytic peaks (lines)
• CV simulations assume mechanism predicted by theory and calculated thermodynamic/kinetic quantities

CV simulations: no acid, tosic acid, benzoic acid

[3]/[1-H] are Ni catalysts without/with hanging group
Sequential Mechanisms

- Alter mechanisms, thermodynamics, and/or kinetics by modifying substituents, ligands, metal center
Concerted Mechanism

- Concerted mechanism avoids high-energy intermediates → lower overpotential
Proton-Coupled Electron Transfer Theory

Soudackov and Hammes-Schiffer, JCP 111, 4672 (1999)

Sequential: ET-PT or PT-ET
Concerted: EPT
Mechanism determined by relative energies and couplings
Off-diagonal states much higher in energy → concerted EPT
Theory for Concerted PCET

- Derived analytical expressions for PCET rate constants in various well-defined regimes and applied to solution/enzyme systems
- Derived expressions for electrochemical rate constants and current densities and applied to electrochemical systems

Soudackov and SHS, JCP 2000; 2005
Venkataraman, Soudackov, SHS, JPC C 2008

H₂ oxidation/production
Hydrogenase Enzymes: Biomimetic Models

Design catalysts that mimic hydrogenase active site

Rauchfuss and Hammes-Schiffer groups: designing biomimetic models
Ni catalysts with pendant amines: high turnover frequencies (DuBois)

Biomimetic: modeled after hydrogenase enzymes, which catalyze H₂ oxidation/production

Ni(P₂N₂)₂ Electrocatalysts

Biomimetic: modeled after hydrogenase enzymes, which catalyze H₂ oxidation/production

DOE EFRC: Morris Bullock, Dan DuBois, Michel Dupuis, Simone Raugei, Jim Mayer, Shannon Stahl, Bruce Parkinson, SHS, ...
Ni(P₂N₂)₂ Electrocatalysts

Ni catalysts with pendant amines: high turnover frequencies (DuBois)

Biomimetic: modeled after hydrogenase enzymes, which catalyze H₂ oxidation/production

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Ni(P$_2$N$_2$)$_2$ Electrocatalysts

Ni catalysts with pendant amines: high turnover frequencies (DuBois)

DOE EFRC: Morris Bullock, Monte Helm, Aaron Appel, Dan DuBois, Michel Dupuis, Simone Raugei, Jim Mayer, Shannon Stahl, Bruce Parkinson, SHS, ...

PCET:
PT between Ni and N
ET between Ni and electrode
Enhance Concerted PCET Mechanism

- **Goal**: enhance concerted mechanism to lower overpotential for this step

Average equilibrium Ni-N distance: 3.25 Å

→ thermal fluctuations required for PT

Guiding design principle: pendant amines should be flexible enough to allow motion toward Ni center but still reasonably well-positioned

Validated experimentally: promising catalysts designed by PNNL group

*Horvath, Fernandez, Soudackov, SHS, PNAS 2012; JPCL 2013*
Photosystem II: Key for Photosynthesis

Water splitting: \( 2\text{H}_2\text{O} + h\nu \rightarrow 2\text{H}_2 + \text{O}_2 \)
Photosystem II: PCET at Work

Electron transfer through protein

Proton transport channel

Artificial Photosynthetic Systems

- Design mimics of Photosystem II
- Calculations guiding design
- Theory confirms concerted PCET
- Design proton relay systems with desired oxidation potentials

$E_{1/2} = 1.00 \, \text{V}$

$E_{1/2} = 0.93 \, \text{V}$

$E_{1/2} = 0.62 \, \text{V}$

Mioy Huynh, Ana and Tom Moore, Cliff Kubiak, and others

V vs SCE in MeCN
Summary

• Effective use of solar energy requires design of catalysts
• Catalysts must control movement of electrons and protons
• Biology can inspire catalyst design – hydrogenases, photosynthesis
• Combination of theoretical/experimental chemistry essential
• Theory can provide catalyst design principles
  - alter substituents, ligands, metal
    → change mechanism, thermodynamics, kinetics
  - explore implications of ligand non-innocence: ligand protonation and reduction
  - facilitate concerted PCET mechanism by decreasing proton donor-acceptor distance and enhancing flexibility

Electrical Energy Chemical Energy
(H-H, O-H, N-H Bonds)

Electrocatalyst
Acknowledgments

Alexander Soudackov, Irina Navrotsky, Charu Venkataraman, Michelle Ludlow, Brian Solis, Laura Fernandez, Samantha Horvath, Soumya Ghosh, Mioy Huynh, Aparna Harshan

Experimental collaborators: Tom Rauchfuss, Aaron Appel, Harry Gray, Jay Winkler, Dan Nocera, Ana and Tom Moore, Morris Bullock

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Evidence supporting PT to carbon under weak acid conditions

- PT distance significantly shorter to carbon than to Co
- PT thermodynamically more favorable to carbon by 11.6 kcal/mol
- Calculated free energy barrier for PT in agreement with experimentally determined value

$\Delta G^o_{\text{PT to C}} = -11.6 \text{ kcal/mol}$

$\Delta G^o_{\text{PT to Co}} = -0.2 \text{ kcal/mol}$

Experimental barrier: 8.0 kcal/mol

Solis, Maher, Honda, Powers, Nocera, SHS, ACS Catalysis 2014