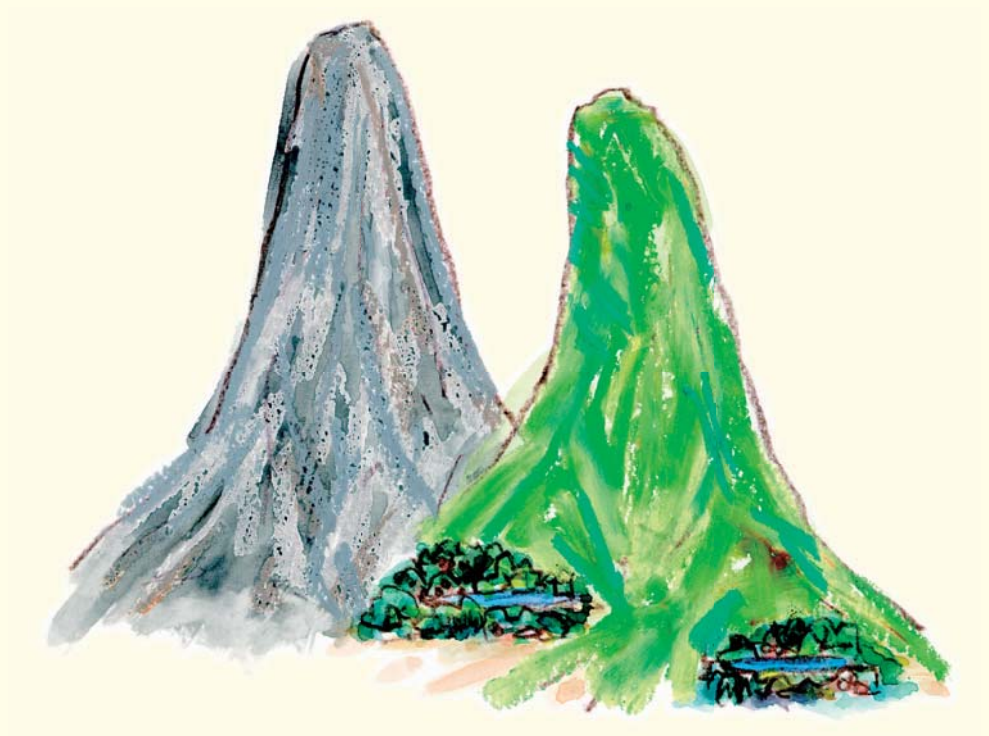


Platinum Catalysts vs. Enzymes and their Models



International Institute for Carbon-Neutral
Energy Research (I²CNER)
Kyushu University



Copyright © 2012 by Kyushu University
Printed in Japan. All rights reserved.

Platinum Catalysts vs. Enzymes and their Models

Seiji Ogo

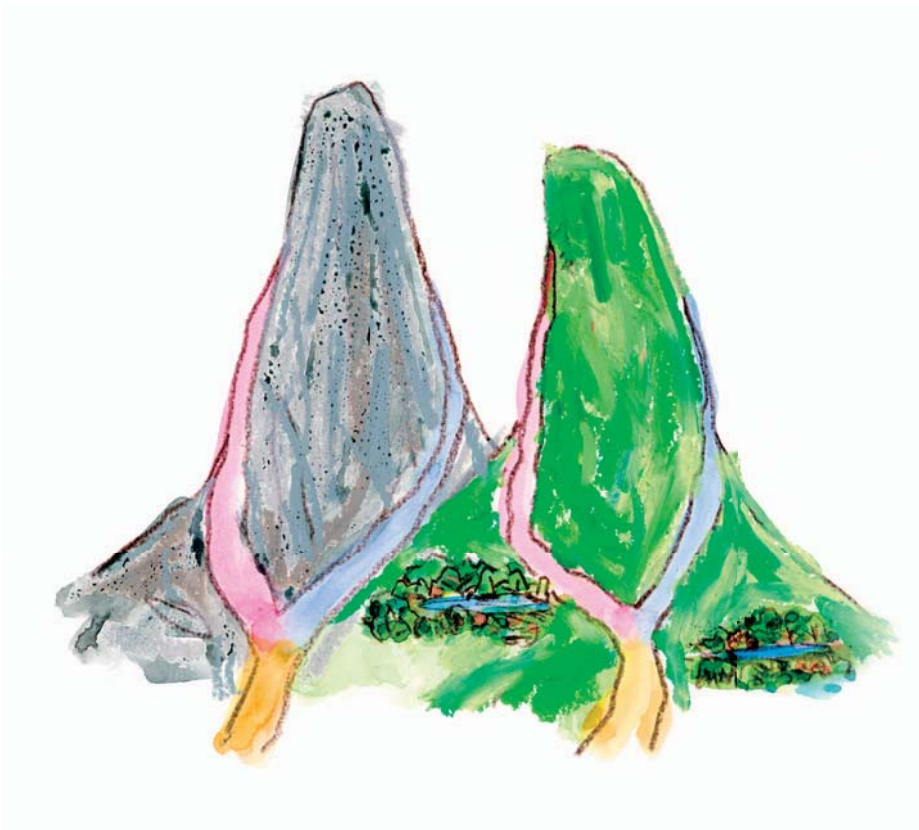
**Illustrated by
Takeshi Ichikawa**

**International Institute for Carbon-Neutral
Energy Research (I²CNER)
Kyushu University**

Contents

The Tale of the Two Genies	1
Scientific Background	27
References	40

The Tale of the Two Genies

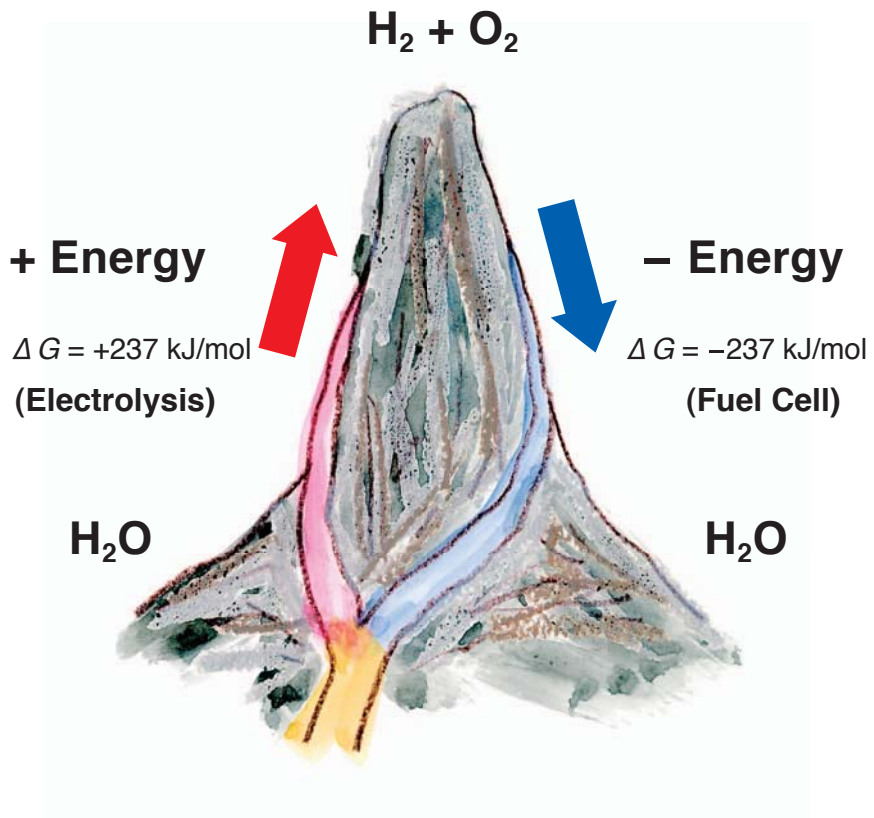


There are two big mountains for energy conversion in the world.

The left mountain represents platinum (Pt) and the right mountain represents enzymes — natural molecules used by living things for performing work in cells. The right mountain is explored by chemists that produce simple molecules that model the workings of enzymes.

In order to utilize hydrogen gas (H_2) and water (H_2O) for energy storage, we have to climb up to the top of either the Pt or the enzyme mountain.

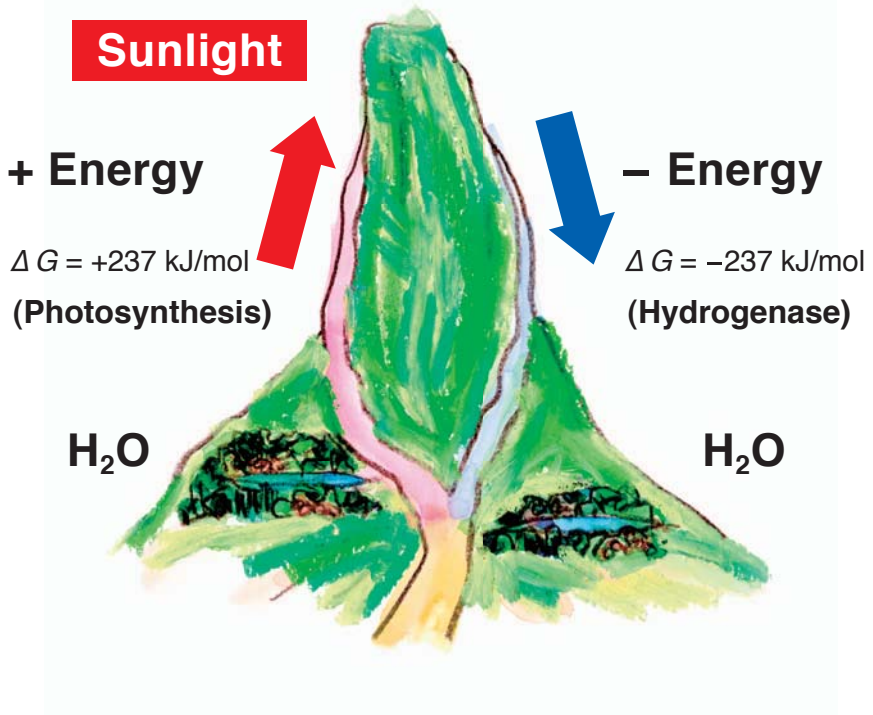
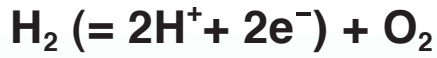
However, the Pt mountain is expensive, and thoroughly explored while the enzyme mountain promises to be cheap and still holds many secrets.



Focusing on the platinum (Pt) mountain, there are two routes: one that goes up and one that comes down.

The harder route, from the bottom to the top, is the way of electrolysis (using electricity) of water (H_2O) to produce hydrogen gas (H_2) and oxygen gas (O_2) by using Pt. In 1800, Anthony Carlisle and William Nicholson first found this climbing route.¹

The route down is the way of building a fuel cell that generates electric energy from H_2 and O_2 . This route was first found by William R. Grove who climbed down from the top in 1839.²



Similarly, the enzyme mountain has a route up and a route down.

The harder, ascending route is the way to oxidize water (H_2O) to produce protons (H^+), electrons (e^-), and oxygen gas (O_2) by photosynthesis. This climbing route has not been discovered yet.

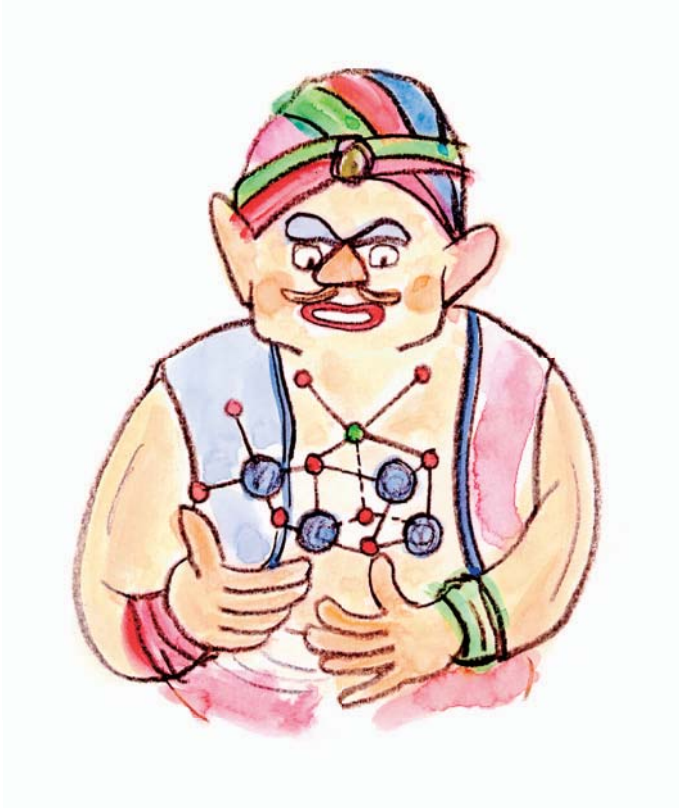
The descending route is the way of building a fuel cell that generates electric energy from hydrogen gas (H_2) and O_2 by using the hydrogenase enzyme or a chemical model. This climbing route was pioneered by Ogo and co-workers in 2011 using a hydrogenase model molecule. They were the first to find the way down from the top of the mountain.³



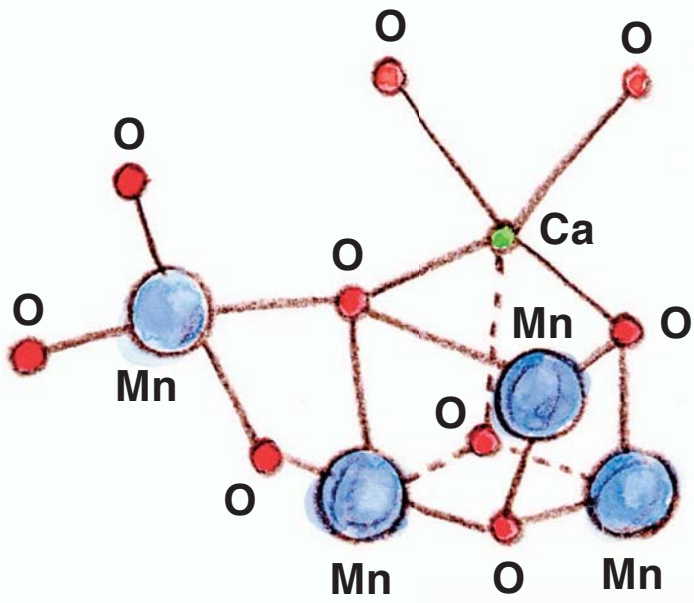
In nature, the fat genie knows the ascending route and he has filled the earth with oxygen gas (O_2) by photosynthesis. He wears a necklace encrusted with four manganese (Mn) atoms. The fat genie likes to store energy in hydrogen gas (H_2).



When the fat genie wants to store energy in hydrogen gas (H_2), he uses his necklace with four manganese (Mn) atoms. He can build a special device that breaks water (H_2O) into H_2 and oxygen gas (O_2) by using his necklace.



He takes off his necklace and then constructs four manganese (Mn) atoms in a certain arrangement to create an enzyme called “photosystem II”. He is able to store energy in hydrogen gas (H_2) starting with water (H_2O).



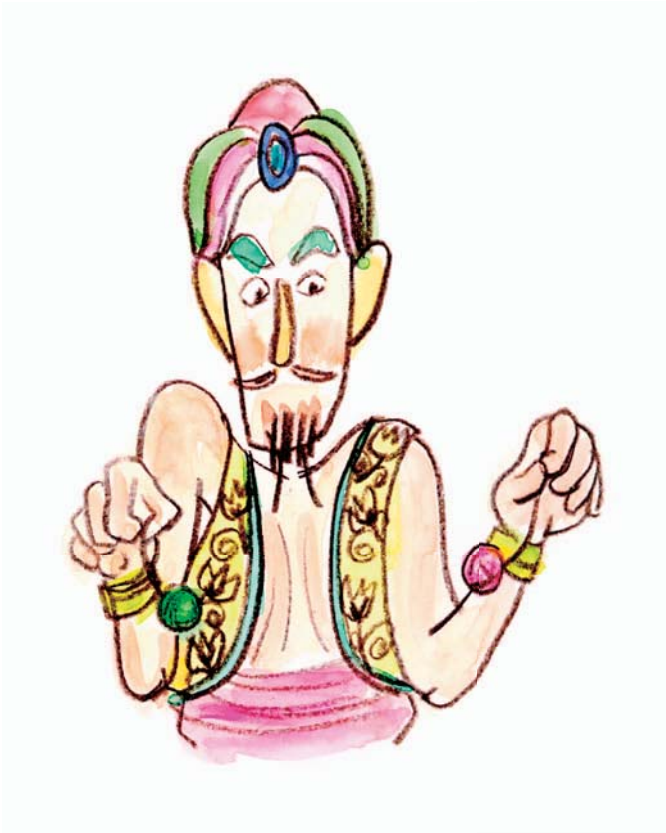
Photosystem II catalyzes water (H_2O)-oxidation to extract electrons (e^-) from H_2O at the oxygen-evolving-center (OEC).

The OEC is constructed of four manganese (Mn) atoms and one calcium (Ca) atom, which are linked by oxygen (O) atoms to make a cubic-type framework. The terminal Mn and Ca atoms are attached to H_2O molecules. In 2011, the exact structure of the OEC was finally revealed by X-ray analysis.⁴

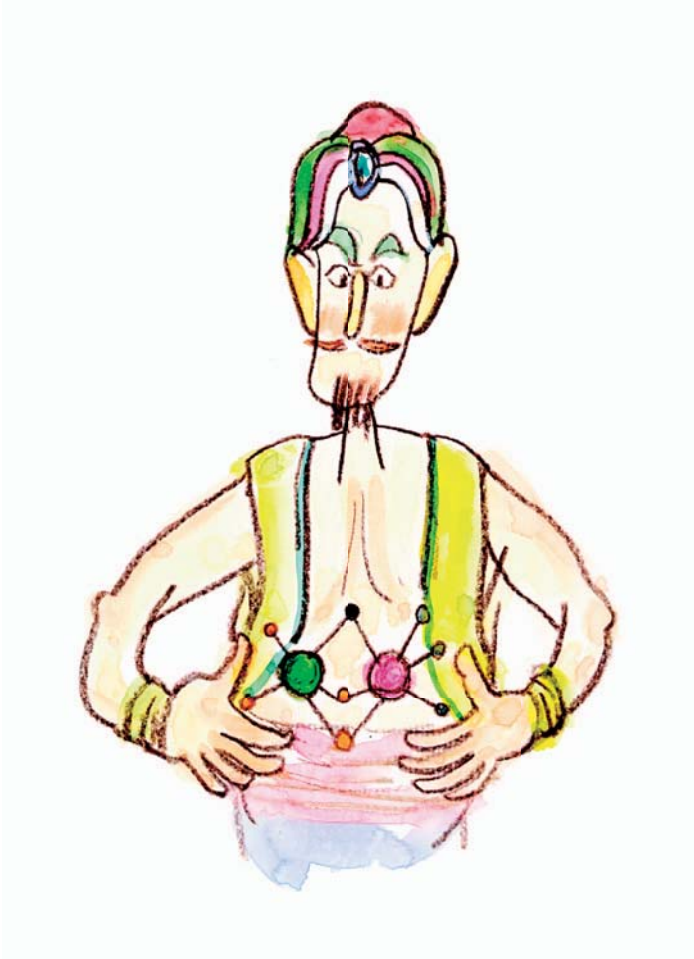
Even now, nobody has discovered how to efficiently oxidize H_2O — only the fat genie knows. This secret should solve the energy issues that threaten the earth. Many researchers are trying to elucidate the secret mechanism.



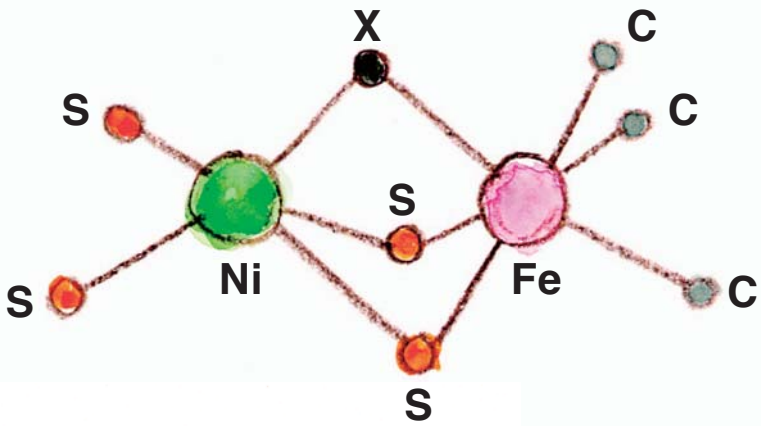
The slim genie knows the descending route from ancient times. He wears earrings decorated with nickel (Ni) and iron (Fe) atoms. The slim genie likes to release energy from hydrogen gas (H_2).



If the slim genie needs energy, he is easily able to get it from hydrogen gas (H_2) by using his earrings. He can make a device with one nickel (Ni) atom and one iron (Fe) atom to release the energy from H_2 .

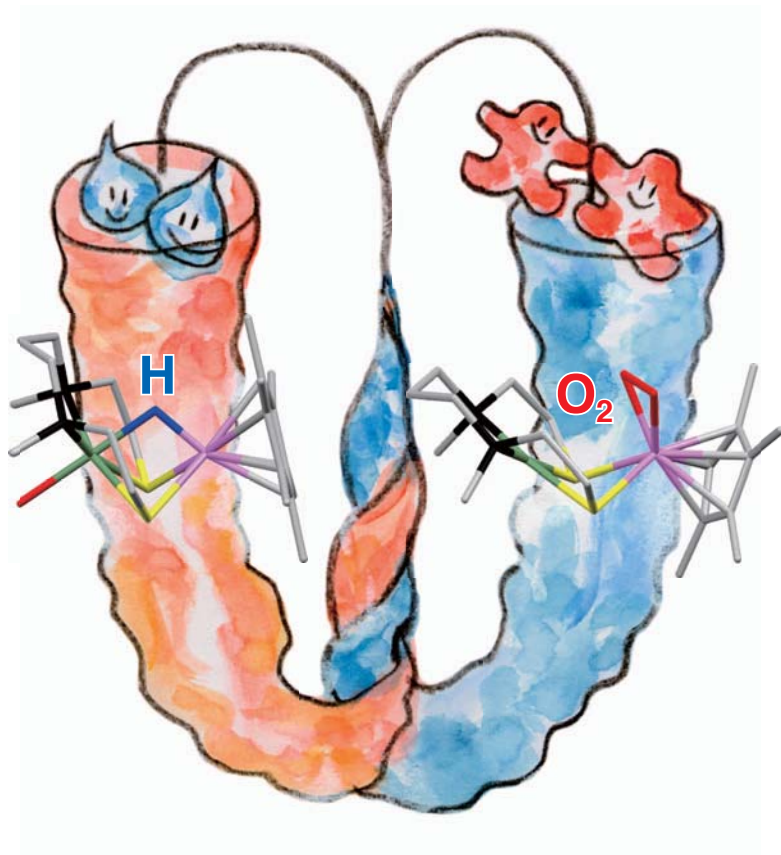


He takes off his earrings and tethers nickel (Ni) and iron (Fe) atoms by special glue to make a framework. Then, an enzyme called “[NiFe] hydrogenase” is built.



This picture depicts the active center of [NiFe] hydrogenase ([nickel-iron]hydrogenase).⁵ The Ni and Fe atoms are bridged by sulfur atoms from cysteine. This active center cuts the H–H bond to extract electrons (e^-) from hydrogen gas (H_2). The mysterious atom “X” is the key atom for cutting the H–H bond.

However, it has long been a mystery how the slim genie can so easily cut the H–H bond to extract e^- .

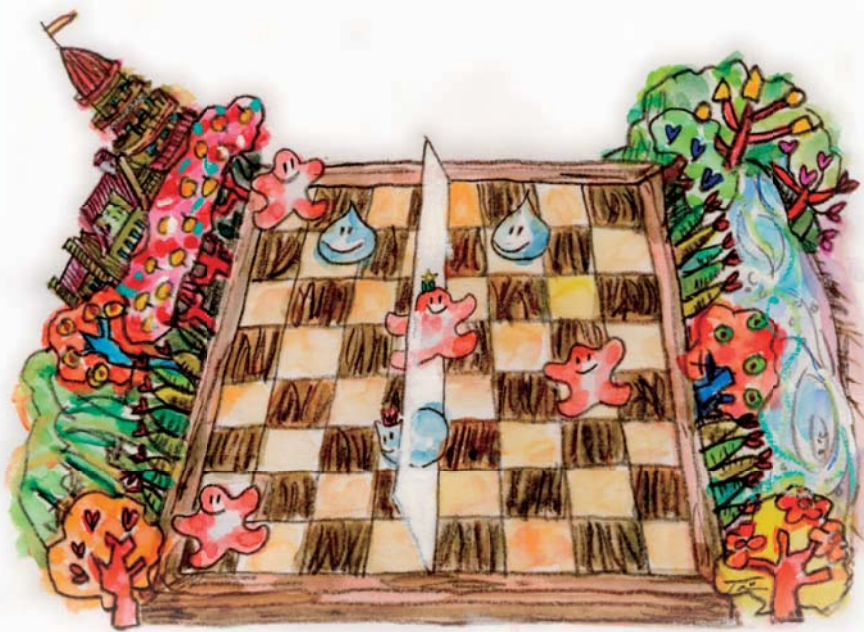


[NiFe]hydrogenase ([nickel-iron]hydrogenase) extracts electrons (e^-) from hydrogen gas (H_2) but they are usually poisoned by oxygen gas (O_2). O_2 -tolerant [NiFe]hydrogenase, however, can protect itself by turning the O_2 into water (H_2O).

Ogo and co-workers made a simple chemical model of the O_2 -tolerant [NiFe]hydrogenase and reproduced these functions.³ At this time, Ogo learned the way down the mountain.

They have now climbed from the top to the bottom of the mountain to achieve the construction of a fuel cell with a hydrogenase model molecule.³

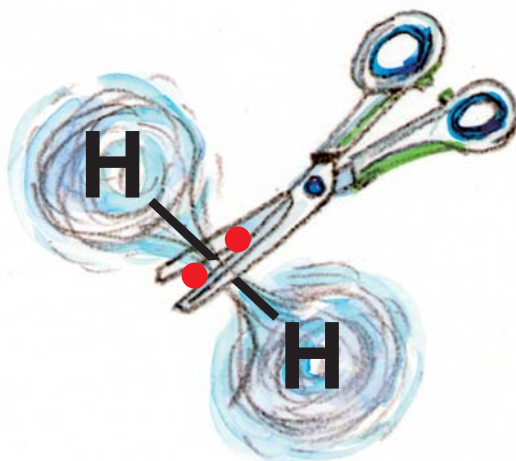
THE END



Scientific Background

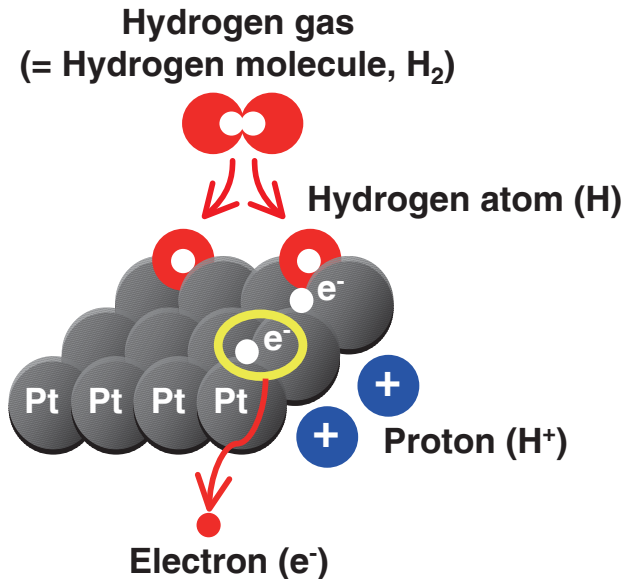
How to Cleave H–H Bond Easily

Hydrogen gas (H_2) has an unexpectedly strong H–H bond. Interestingly, when the dissociation takes place in water, the energy needed to cut the bond decreases dramatically because water's strong solvation assists the bond cleavage of H_2 .

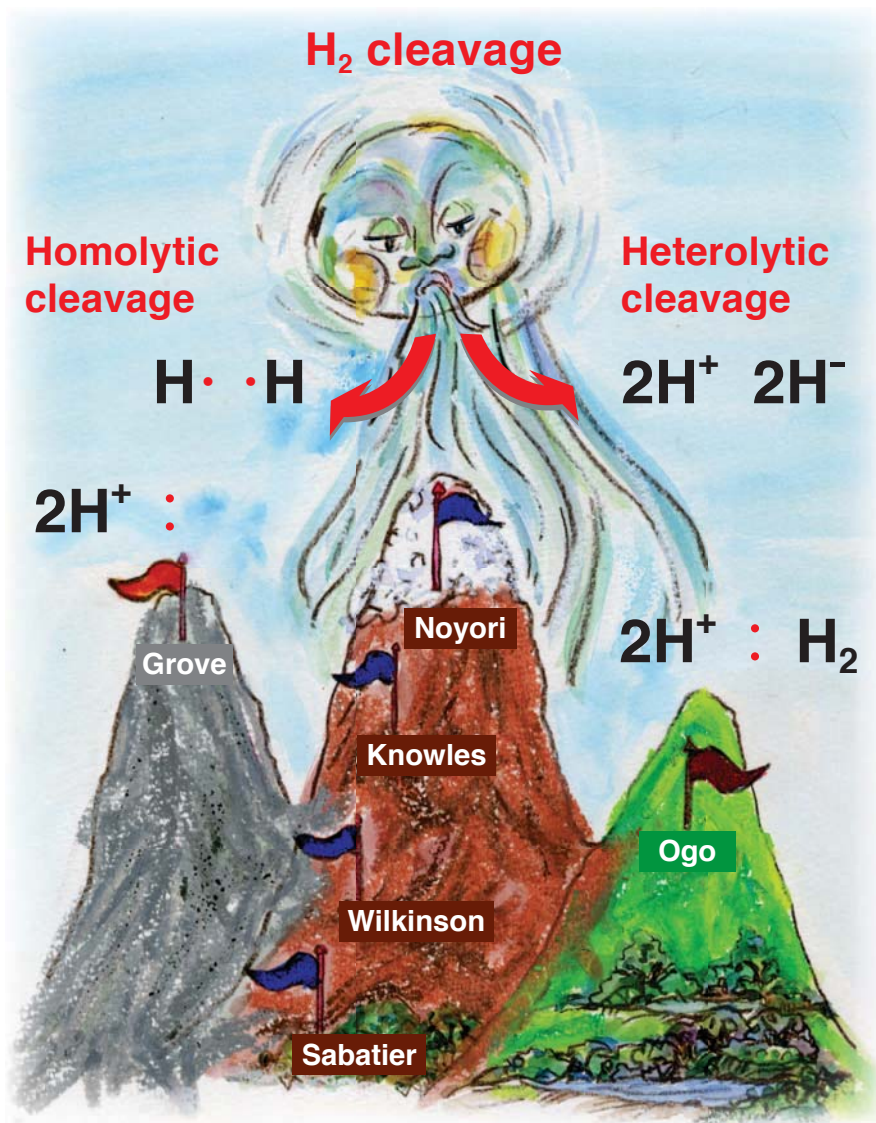


Transition Metal Catalysts

Transition metal catalysts such as platinum (Pt) are very helpful in cleaving hydrogen gas (H_2). To achieve the most efficient H–H bond cleavage, the use of transition metal catalysts and water as the solvent is the best choice.



Three Mountains in Hydrogen Research



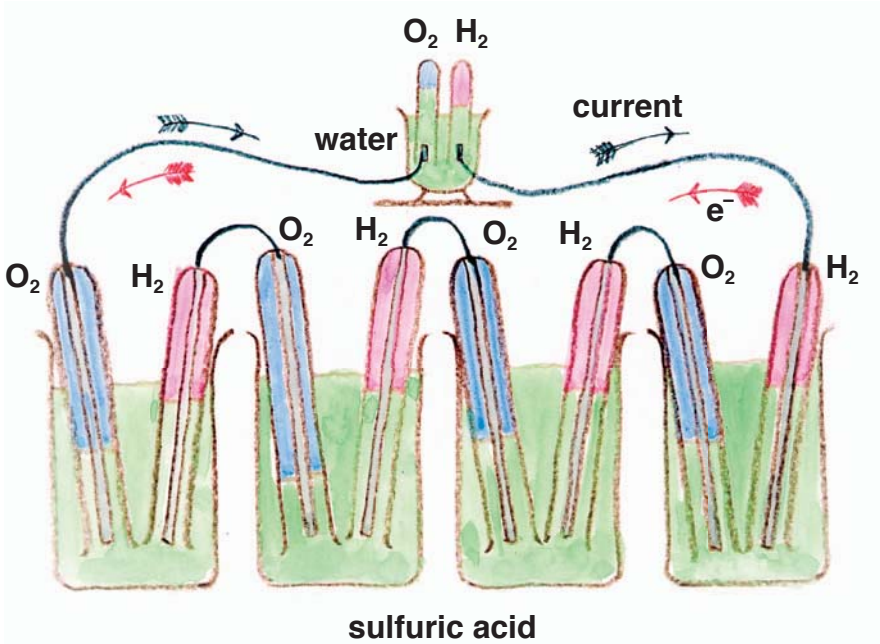
The first gray mountain corresponds to Grove's achievement, in which hydrogen gas (H_2) was homolytically cleaved with a platinum (Pt) metal catalyst and two electrons ($2e^-$) were taken out and transformed to electric current.

The more recent brown mountain is dedicated to Savatier, Wilkinson, Knowles, and Noyori for their achievements, in which H_2 was both homolytically and heterolytically cleaved with transition metal catalysts and the generated H species were used for hydrogenation of chemical compounds.

The newly formed green mountain recognizes Ogo's achievement, in which Ogo's catalyst, using nickel (Ni) and ruthenium (Ru), cleaves two molecules of H_2 heterolytically and the resulting two hydride ions ($2H^-$) are converted to H_2 and $2e^-$.

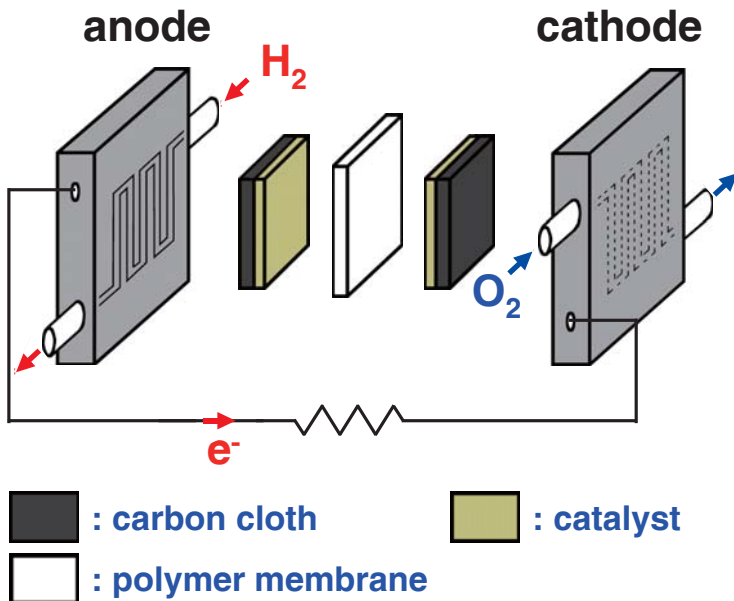
William R. Grove

In 1839, Grove built the first fuel cell. He discovered that immersing the ends of two platinum (Pt) electrodes in sulfuric acid and each of the other two ends in separate sealed containers of hydrogen gas (H_2) and oxygen gas (O_2) cause a constant flow of current.²



Fuel Cell

In fuel cells, the hydrogen gas (H_2) reacts on the anode electrode that converts H_2 into negatively charged electrons (e^-) and positively charged protons (H^+). The protons move to the cathode electrode where they combine with oxygen gas (O_2) and e^- to produce water.

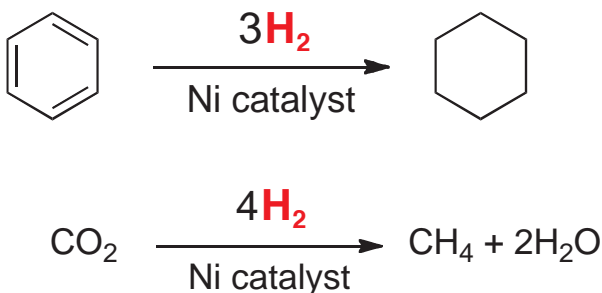


Paul Sabatier

The Nobel Prize in Chemistry 1912

A pioneer of homo- H_2 cleavage on metal
Sabatier's catalyst

Sabatier discovered catalytic hydrogenation of benzene and carbon dioxide (CO_2) using hydrogen gas (H_2) and nickel (Ni) metal powder to produce cyclohexane and methane (CH_4), respectively.⁶ The active species are Ni hydrides generated by homolytic cleavage of H_2 .

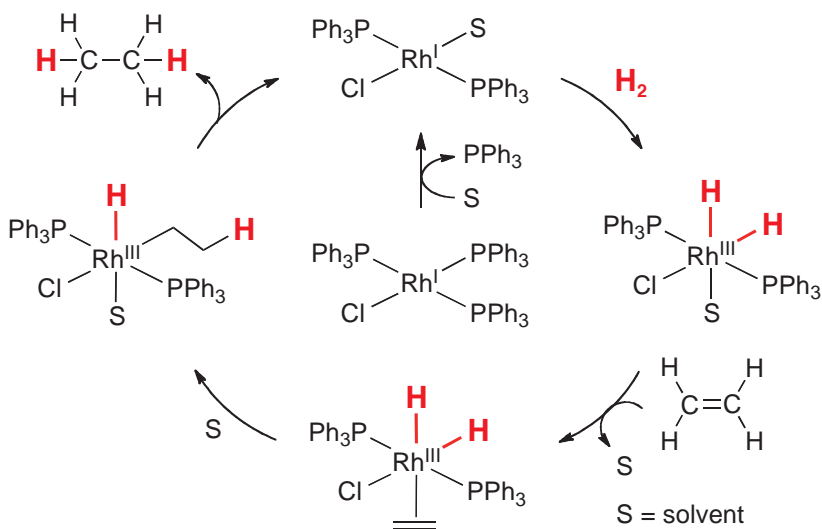


Geoffrey Wilkinson

The Nobel Prize in Chemistry 1973

An important finder of homo- H_2 cleavage
using a molecular catalyst
Wilkinson's catalyst

Wilkinson's catalyst is a rhodium (Rh) complex with three large phosphine ligands coordinated with the metal center, $Rh(PPh_3)_3Cl$. This complex catalyzes homogeneous hydrogenation of ethylene to ethane through homolytic cleavage of hydrogen gas (H_2).⁷



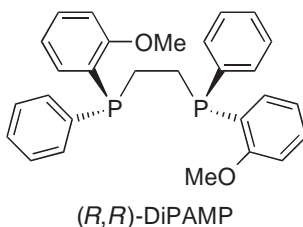
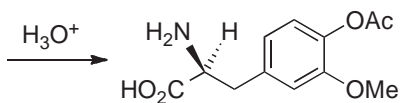
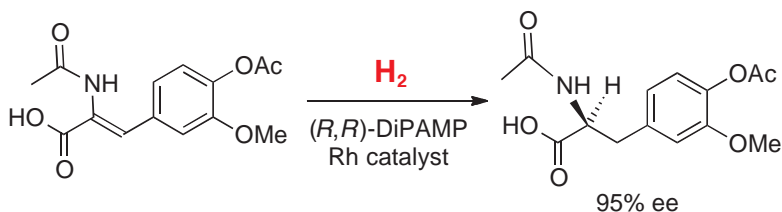
William S. Knowles

The Nobel Prize in Chemistry 2001

An important investigator of homo- H_2 cleavage
for enantioselective drug synthesis

Knowles' catalyst

Knowles discovered a rhodium (Rh) complex with chiral phosphine ligands which catalyzes the asymmetric hydrogenation of olefins to produce medical starting compounds for the remedy of Parkinson's disease.⁸ This catalyst also promotes homolytic cleavage of hydrogen gas (H_2).



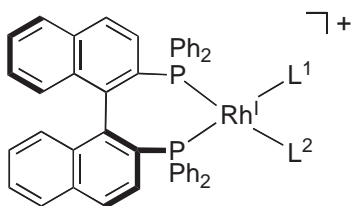
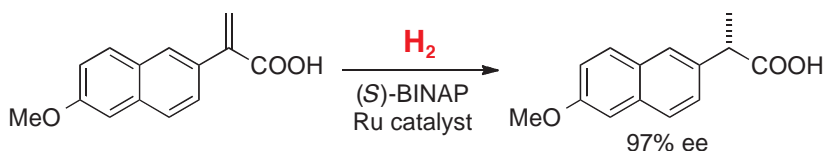
Ryoji Noyori

The Nobel Prize in Chemistry 2001

A great explorer of homo- and hetero- H_2 cleavage for asymmetric organic synthesis

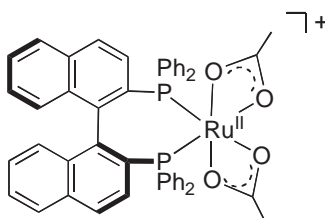
Noyori's catalyst

Noyori developed the asymmetric hydrogenation of β -keto-esters and olefins to produce important pharmaceutical compounds by using enantiomers of rhodium (Rh) and ruthenium (Ru) BINAP complexes and homolytic or heterolytic cleavage of hydrogen gas (H_2).⁹



(S)-BINAP Rh catalyst

$L^1, L^2 =$ tetrahydrofuran
acetone, *etc.*

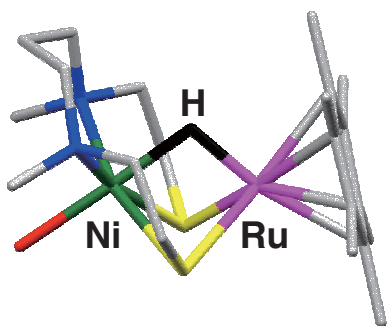


(S)-BINAP Ru catalyst

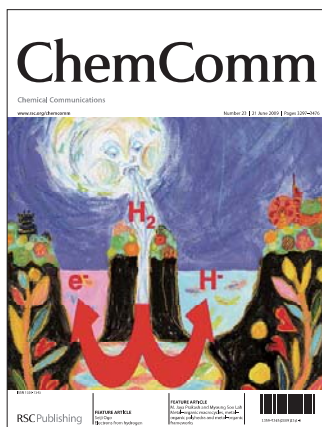
Ogo's Catalyst

– A New Discovery in H₂ Energy

Ogo, of Kyushu University, and his research group have succeeded in extracting electrons (e⁻) from hydrogen gas (H₂) with a nickel (Ni)-ruthenium (Ru) catalyst also known as Ogo's catalyst. This is the world's first molecular catalyst that severs H₂ via heterolytic cleavage and extracts e⁻ in water.^{3a,b}



Science
2007, 316, 585-587



Chem. Commun.
2009, 3317-3325

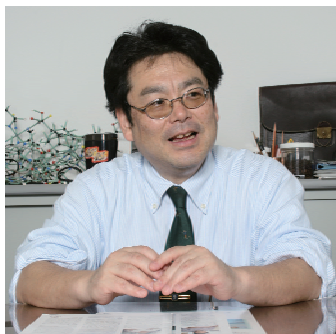
Utilization of Ogo's Catalyst

– Jack of All Trades

Ogo and his research group have successfully developed fuel cells that use molecular catalysts for electrodes.^{3c} A fuel cell based on a single molecular catalyst uses a hydrogenase mimic to catalyze the oxidation of hydrogen gas (H_2) and reduction of oxygen gas (O_2).



Angew. Chem. Int. Ed.
2011, 50, 11202-11205



Seiji Ogo

References

1. Chemistry World, 2003: <http://www.rsc.org/chemistryworld/Issues/2003/August/electrolysis.asp>
2. W. R. Grove, London, *Edinburgh and Dublin Philosophical magazine and Journal of Science*, **1842**, *21*, 417–420.
3. (a) S. Ogo et al., *Science*, **2007**, *316*, 585–587. (b) S. Ogo, *Chem. Commun.*, **2009**, 3317–3325. (c) T. Matsumoto, K. Kim, S. Ogo, *Angew. Chem. Int. Ed.*, **2011**, *50*, 11202–11205. (d) K. Kim, T. Matsumoto, A. Robertson, H. Nakai, S. Ogo, *Chem. Asian J.*, **2012**, *7*, 1394–1400.
4. Y. Umena, K. Kawakami, J.-R. Shen, N. Kamiya, *Nature*, **2011**, *473*, 55–61.
5. (a) A. Volbeda, M.-H. Charon, C. Piras, E. C. Hatchikian, M. Frey, J. C. Fontecilla-Camps, *Nature*, **1995**, *373*, 580–587. (b) A. Volbeda, E. Garcin, C. Piras, A. L. de Lacey, V. M. Fernandez, E. C. Hatchikian, M. Frey, J. C. Fontecilla-Camps, *J. Am. Chem. Soc.*, **1996**, *118*, 12989–12996.
6. P. Sabatier, *Nobel lecture*, **1912**.
7. (a) G. Wilkinson, *Angew. Chem.*, **1974**, *86*, 664–667. (b) G. Wilkinson, *Nobel lecture*, **1973**.
8. (a) W. S. Knowles, *Angew. Chem. Int. Ed.*, **2002**, *41*, 1998–2007. (b) W. S. Knowles, *Nobel lecture*, **2001**.
9. (a) R. Noyori, *Angew. Chem. Int. Ed.*, **2002**, *41*, 2008–2022. (b) R. Noyori, *Nobel lecture*, **2001**.

