THE ROLE OF THE CHEMICAL SCIENCES IN FINDING ALTERNATIVES TO CRITICAL RESOURCES

A WORKSHOP SUMMARY

Douglas Friedman, Tina Masciangioli, and Steve Olson, *Rapporteurs*

Chemical Sciences Roundtable

Board on Chemical Sciences and Technology

Division on Earth and Life Studies

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* These members of the Chemical Sciences Roundtable were members of the planning committee for the Workshop on the Role of the Chemical Sciences in Finding Alternatives to Critical Resources but were not involved in the writing of this workshop summary.

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Preface

The Chemical Sciences Roundtable (CSR) was established in 1997 by the National Research Council (NRC). It provides a science-oriented apolitical forum for leaders in the chemical sciences to discuss chemistry-related issues affecting government, industry, and universities. Organized by the National Research Council's Board on Chemical Sciences and Technology, the CSR aims to strengthen the chemical sciences by fostering communication among the people and organizations—spanning industry, government, universities, and professional associations—involved with the chemical enterprise. One way it does this is by organizing workshops that address issues in chemical science and technology that require national attention.

In September 2011, the CSR organized a workshop on the topic, "The Role of Chemical Sciences in Finding Alternatives to Critical Resources." The one-and-a-half-day workshop addressed key topics, including the economic and political matrix, the history of societal responses to key mineral and material shortages, the applications for and properties of existing minerals and materials, and the chemistry of possible replacements. The workshop featured several presentations highlighting the importance of critical nonfuel mineral and material resources in history, catalysis, agriculture, and electronic, magnetic, and optical applications.

This document summarizes the presentations and discussions that took place at the workshop. In accordance with the policies of the NRC, the workshop *did not* attempt to establish any conclusions or recommendations about needs and future directions, focusing instead on issues identified by the speakers. In addition, the organizing committee's role was limited to planning the workshop. The workshop summary has been prepared by the workshop rapporteurs Douglas Friedman, Tina Masciangioli, and Steve Olsen as a factual summary of what occurred at the workshop.

Acknowledgment of Reviewers

This report has been reviewed in draft form by individuals chosen for their diverse perspectives and technical expertise, in accordance with procedures approved by the NRC's Report Review Committee. The purpose of this independent review is to provide candid and critical comments that will assist the institution in making its published report as sound as possible and to ensure that the report meets institutional standards for quality and objectivity. The review comments and draft manuscript remain confidential to protect the integrity of the process.

We wish to thank the following individuals for their review of this report:

Madhav Manjrekar, Vestas Technology, Houston, Texas
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Although the reviewers listed above have provided many constructive comments and suggestions, they were not asked to endorse the content of the report, nor did they see the final draft before its release. The review of this report was overseen by **Ann Maest**, Stratus Consulting, Boulder, Colorado, appointed by the National Research Council, she was responsible for making certain that an independent examination of this report was carried out in accordance with institutional procedures and that all review comments were carefully considered. Responsibility for the final content of this report rests entirely with the author(s).

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APPENDIXES

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Introduction and Overview

Critical elements—and especially rare earths—were in the news in 2011, as a sample of headlines demonstrates:

- "Stable rare earth supply sought," *Daily Yomiuri Online*, September 8.
- "Chasing rare earths, foreign companies expand in China," *New York Times*, August 24.
- "China to reform rare earth exports after WTO," *Reuters*, July 6.
- "China holds the world hostage in rare earth metals," *Business Insider*, June 13.
- "Got Yttrium?" *Time*, March 28.
- "Can Toyota innovate its way out of the Prius's rare earth element problem?" *Christian Science Monitor*, January 19.[1]

Widespread concern over the future availability of critical elements led the Chemical Sciences Roundtable to hold a workshop on September 29-30, 2011, in Washington, D.C., on the role of the chemical sciences in finding alternatives to critical resources. Key topics addressed during the workshop included

- The economic and political matrix for addressing the issue,
- The history of societal responses to key mineral and material shortages,
- The applications for and properties of existing minerals and materials, and
- The chemistry of possible replacements.

"The chemical sciences have not yet been much involved in the national discussion over critical elements," said Patricia Thiel, Division Director for Science and Technology at Ames Laboratory, Distinguished Professor of Chemistry at Iowa State University, and one of three members of the organizing committee for the workshop. Yet historically the chemical sciences have played an essential role in this area. In the early years of the 20th century, fertilizer was so scarce that it was sometimes stolen, and war broke out in South America over one of the world's two main sources of nitrogen, guano from bird droppings (the other main source at the time was sodium nitrate mined in Chile). Then, in 1909, Fritz Haber discovered a way to fix atmospheric nitrogen as ammonia using iron as a catalyst at high pressure, and a few years later Carl Bosch, an industrial chemist at BASF, developed a way to apply this process on an industrial scale. The Haber-Bosch process was born in controversy, since it prolonged Germany's ability to wage World War I without blockaded imports from South America. But the discovery has had "great impact that continues to reverberate today," said Thiel. Most significantly, by facilitating intensive agriculture, it enabled the great and continued expansion of the human population in the 20th and 21st centuries.

The same year that Fritz Haber fixed nitrogen using the precursor to the modern process, chemists produced the first totally synthetic rubber. When the price of natural rubber, which was produced primarily in Asia, increased sharply in 1925, industrial production of synthetic rubber rose substantially. "But the real stimulant to industrial production came in World War II," said Thiel, "when the Axis countries took over the supply fields in Asia and cut off all supplies of natural rubber to the Allies."

In modern times, critical materials are used in many everyday activities. Essentially all electronic devices use a wide variety of these materials, including rare earth elements,

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[1] Roderick Eggert, one of the three members of the workshop organizing committee, listed these headlines in his presentation summarized in Chapter 2.

precious metals, and other rare, expensive elements of the periodic table. For example, the Toyota Prius uses at least eight different critical elements in its design. As described in Chapter 2, in everything from the hybrid electric motor, to the LCD screen in the passenger compartment, to the rechargeable NiMH battery to power the car, to the catalytic converter that cleans the exhaust, critical elements play a primary role in the operation of this modern car.

Those examples "nicely illustrate the role of chemistry in addressing shortages of critical materials," Thiel concluded, "and the chemical sciences continue to have an enormous role to play today."

OVERVIEW OF THE WORKSHOP

After Thiel's introductory remarks, the workshop consisted of five pairs of related presentations and subsequent discussions. These presentations are summarized briefly below and in Chapters 2-6 of this summary.

Chapter 2: Assessments of Criticality

Roderick Eggert, Professor and Director of the Division of Economics and Business at the Colorado School of Mines, presented a framework for assessing the availability of critical elements that was developed by a National Research Council committee that recently examined the issue (NRC, 2008). Elements can be positioned in a two-dimensional array comparing their importance in use and supply risk. Using this framework, the most critical elements are the platinum-group elements, the rare earths, manganese, indium, and niobium. Eggert elaborated on his view that the chemical sciences are essential in finding substitutes for critical elements, enhancing mineral extraction and recovery processes, improving manufacturing efficiency, and enabling better recycling.

Diana Bauer, Director of the Office of Economic Analysis in the Department of Energy's Office of Policy and International Affairs, presented the main findings of the Critical Material Strategy released by the Department of Energy (DOE) in 2010. The report found that "four clean energy technologies—wind turbines, electric vehicles, photovoltaic cells, and fluorescent lighting—use materials that are at risk of supply disruptions in the short term. In the report, five rare earth elements (dysprosium, neodymium, terbium, europium, and yttrium), as well as indium, were assessed as most critical in the short term" (DOE, 2010).

Chapter 3: Critical Materials in Catalysis

James Stevens, Corporate Fellow, Core Research and Development Department, Dow Chemical Company, gave a broad perspective on the use of critical materials, especially platinum-group metals, as catalysts in industry. Various aspects of the catalysis process are more economically significant than the cost of the metals, and many chemical processes have evolved from originally using low-cost metals such as cobalt to much scarcer metals because the high cost of separations and capital expenses overwhelm the difference in the price of the metal. Opportunities exist for further work in the areas of emissions catalysis, hydrosilylation, hydroformylation, and enantioselective catalysis to help address this cost differential.

Jingguang Chen, Claire D. LeClaire Professor of Chemical Engineering and Co-Director of the Energy Frontier Research Center, University of Delaware, presented his research results aimed at reducing and replacing platinum in catalysis. In water electrolysis, for example, monolayer platinum can achieve the same activity as bulk platinum using vastly less precious material. In biomass conversion reactions, a nickel on tungsten carbide catalyst can replace a platinum nickel catalyst for the production of hydrogen. These platinum-free catalysts also are very active in the direct conversion of cellulose from plants to useful chemicals that can be used in our current chemical plan infrastructure.

Chapter 4: Replacing Critical Materials with Abundant Materials

Morris Bullock, Laboratory Fellow and Director of the Center for Molecular Electrocatalysis at the Pacific Northwest National Laboratory, described the development of electrocatalysts based on inexpensive, Earth-abundant metals. Low-temperature fuel cells generally use platinum, but nickel complexes can effectively catalyze the oxidation of hydrogen. Related complexes of cobalt, iron, and manganese are being studied as well, showing that it is possible to rationally design catalysts based on abundant, inexpensive metals as alternatives to the more expensive precious metals.

Christine Lambert, Technical Leader, Ford Research and Advanced Engineering, recounted the 30-year history of using base metals to replace precious metals in three-way automobile catalysts that simultaneously control hydrocarbons, carbon monoxide, and nitrogen emissions in gasoline vehicle exhaust. There is no known combination of base metals that are as active and durable as precious metals. But there has been a general reduction of precious metals use due to the addition of stabilizers to improve catalyst effectiveness over longer mileages, reduction of poisons present in the fuel and oil, and tighter control of engine parameters. Current diesel aftertreatment technologies, which do not use precious metals, also have been undergoing rapid evolution with the development of catalysts that have improved thermal stability and wider operating windows for temperatures and flow rates.

Chapter 5: Optoelectronics and Photovoltaics

Joseph Shinar, Senior Physicist at the Ames Laboratory, Professor and Chair of the Department of Physics and Astronomy, and Professor of Electrical and Computer Engineering at Iowa State University, discussed five critical materials or families of materials in optoelectronic technologies: erbium-doped fiber amplifiers, which are critical components of the repeaters in optical fiber networks; solid-state lasers based on lanthanide dopants in yttrium aluminum garnet, which are used extensively in spectroscopy and laser lithotripsy; indium in various ubiquitous III-V devices; transparent conducting indium tin oxide films, which are currently behind virtually 100 percent of all displays and figure similarly in the emerging organic light-emitting diode (OLED)-based solid-state lighting paradigm; and heavy rare earth elements which are currently critical for efficient OLED-based displays. He described examples highlighting the importance, availability, and estimated amounts of these metals that will be needed as these technologies mature and pervade the world economy in the coming decades.

Ken Zweibel, Director of the George Washington University Solar Institute, discussed the rapidly dropping cost and increasing use of photovoltaic (PV) solar cells and prospects for further expansion of these materials. The most important materials that are needed to produce solar power today include silicon, silver, tellurium, and cadmium. Emerging technologies could require significant quantities of indium, selenium, molybdenum, gallium, germanium, arsenic, and ruthenium. Some of these materials have supply or cost issues, which has spurred interest in developing strategies to reduce the amounts of materials needed to effectively produce electricity. New sources and additional refining capacity will be essential if demand for these materials greatly increases.

Chapter 6: Critical Materials in Large-Scale Battery Applications

David Bradwell, Chief Technology Officer at Liquid Metal Battery Corporation and Visiting Scientist at the Massachusetts Institute of Technology, explained that batteries designed for grid-scale energy storage applications face a unique set of material selection challenges. Whereas many other power technologies can improve performance via enhanced material microstructure or device design optimization, the energy capacity of a battery is directly related to the amount of active material. For broad-scale energy-intensive applications, this means the active materials must be inherently low cost and sufficiently abundant. Interestingly, the cost of the raw active materials is not always the primary cost driver; thus, to more fully evaluate the opportunity for emerging storage technologies, the entire system must be considered. A host of new battery technologies—including a set of liquid metal battery projects—are being pursued at universities, startup companies, and large well-established corporations across the country.

Jay Whitacre, Chief Technology Officer of Aquion and Professor of Engineering and Public Policy at Carnegie Mellon University, looked at battery technologies for energy applications, including lithium-ion and aqueous electrolyte batteries. The adoption of lithium-ion battery technology is, as of this workshop, not constrained by materials. Rather, it is constrained by the way the materials function and the complexity of the device itself. In contrast, low-cost, low-energy-density, and long-lifetime batteries could serve as a feasible and economic means of energy storage.

Chapter 7: General Observations

The final chapter compiles some general observations made by the individual workshop speakers that apply broadly to critical materials and the role of the chemical sciences in addressing these issues.

2

Assessments of Criticality

Two speakers at the workshop described recent efforts to establish levels of criticality for materials and determine where particular elements fall within these levels. Both observed that the supply of and demand for critical materials are constantly changing, which complicates assessments of criticality. But supply and demand can be projected into the future to create scenarios of material availability. Such projections can identify opportunities for the chemical sciences to increase supply (through better extraction or recycling technologies, for example) or decrease demand (through the development of replacement materials and new technologies).

A FRAMEWORK FOR ASSESSING CRITICALITY

Though rare earths have drawn the most attention from the media, the concerns surrounding critical elements are much broader, said Roderick Eggert, one of the three members of the organizing committee. The phrase that some people have used to describe the situation is "the periodic table is under siege." Just a few decades ago, most of the products used in a household or business relied on 20 to 30 elements. Today, as Steven Duclos, Chief Scientist and Manager for Material Sustainability of General Electric Global Research, has said, GE uses at least 70 of the first 83 elements of the periodic table in its products or in the processes used to make these products (Duclos, 2010). "Mineral-based materials are becoming increasingly complex," said Eggert.

This growing complexity could lead to an explosion in demand for some elements now used in small quantities. For example, gallium, indium, and tellurium are important in emerging photovoltaic technologies. Other elements from throughout the periodic table are critical for various energy technologies (Figure 2-1).

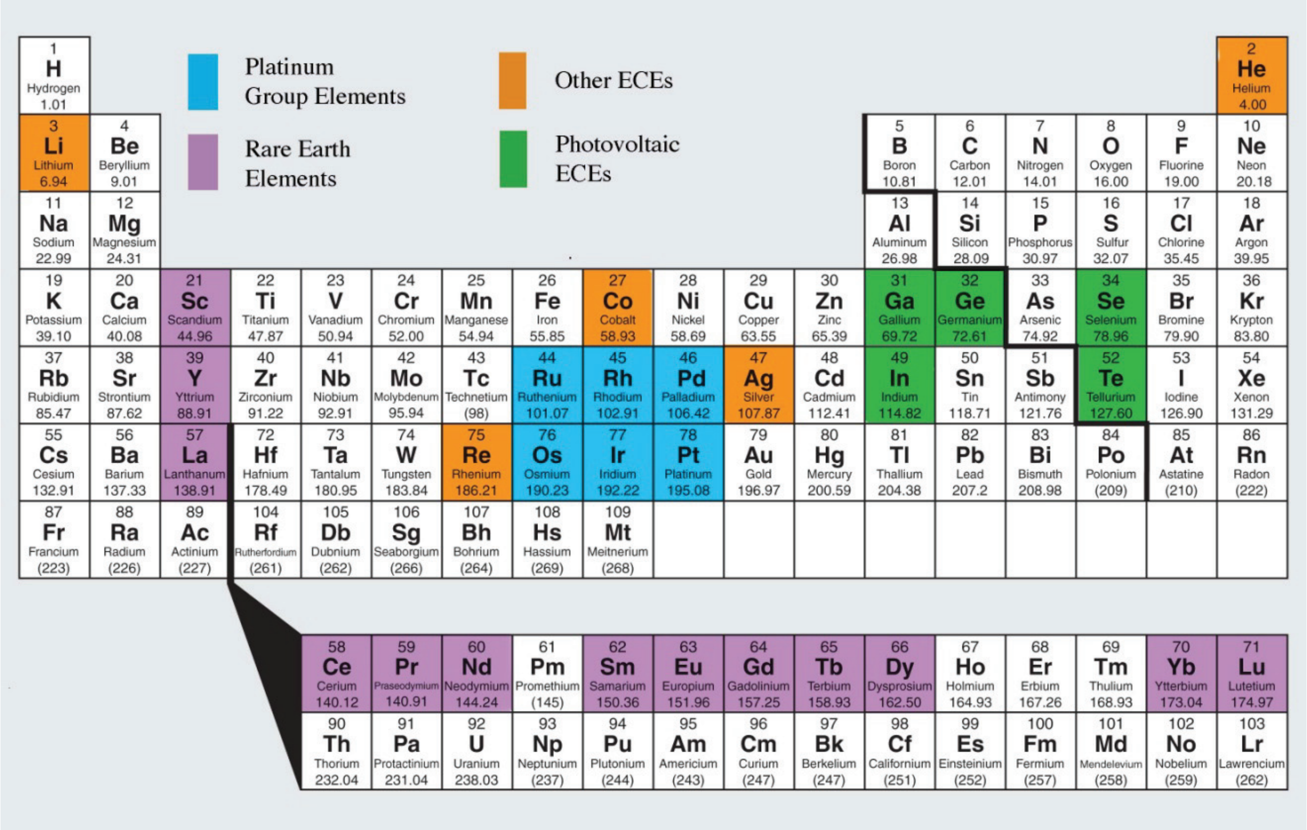
Elements of Criticality

Criticality in element availability has three dimensions, said Eggert.

The first is importance in use. In some cases, the primary concern is physical availability. Will it be possible to get a small amount of an essential element that provides a critical or desired property to a material? In other cases, cost is the essential factor. With photovoltaic thin films, for example, the cost of the gallium, indium, or tellurium is a substantial part of the total cost of the delivered photovoltaic material. The cost of these elements therefore could determine the extent to which thin films are deployed on a large scale. Finally, importance in use relates to the ease or difficulty of substituting another material that can provide the desired properties of a scarce material.

The second dimension is supply risk. Fragile supply chains raise key questions. Will supplies be able to keep up with demand? Will supplies be secure? What are the implications for input costs to products and processes? The threat, said Eggert, is that mineral availability could constrain the development and diffusion of emerging technologies.

The third dimension is time. What is critical today may not be critical tomorrow, and vice versa, said Eggert. The ability to respond to a perceived shortage or supply restriction depends critically on the time period available for response. Adjustments that are possible in the short term—one to a few years—may be constrained by existing production capacity, the nature of capacity, the location of capacity, and existing technologies on either the supply side or demand side. Over the long term—a decade or more—much more significant adjustments are possible. "But these adjustments require investments—time, effort, money—today, with payoffs in the future," said Eggert.



1 H Hydrogen 1.01																	🟧 2 He Helium 4.00
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11 Na Sodium 22.99	12 Mg Magnesium 24.31											13 Al Aluminum 26.98	14 Si Silicon 28.09	15 P Phosphorus 30.97	16 S Sulfur 32.07	17 Cl Chlorine 35.45	18 Ar Argon 39.95
19 K Potassium 39.10	20 Ca Calcium 40.08	🟪 21 Sc Scandium 44.96	22 Ti Titanium 47.87	23 V Vanadium 50.94	24 Cr Chromium 52.00	25 Mn Manganese 54.94	26 Fe Iron 55.85	🟧 27 Co Cobalt 58.93	28 Ni Nickel 58.69	29 Cu Copper 63.55	30 Zn Zinc 65.39	🟩 31 Ga Gallium 69.72	🟩 32 Ge Germanium 72.61	33 As Arsenic 74.92	🟩 34 Se Selenium 78.96	35 Br Bromine 79.90	36 Kr Krypton 83.80
37 Rb Rubidium 85.47	38 Sr Strontium 87.62	🟪 39 Y Yttrium 88.91	40 Zr Zirconium 91.22	41 Nb Niobium 92.91	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	🟦 44 Ru Ruthenium 101.07	🟦 45 Rh Rhodium 102.91	🟦 46 Pd Palladium 106.42	🟧 47 Ag Silver 107.87	48 Cd Cadmium 112.41	🟩 49 In Indium 114.82	50 Sn Tin 118.71	51 Sb Antimony 121.76	🟩 52 Te Tellurium 127.60	53 I Iodine 126.90	54 Xe Xenon 131.29
55 Cs Cesium 132.91	56 Ba Barium 137.33	🟪 57 La Lanthanum 138.91	72 Hf Hafnium 178.49	73 Ta Tantalum 180.95	74 W Tungsten 183.84	🟧 75 Re Rhenium 186.21	🟦 76 Os Osmium 190.23	🟦 77 Ir Iridium 192.22	🟦 78 Pt Platinum 195.08	79 Au Gold 196.97	80 Hg Mercury 200.59	81 Tl Thallium 204.38	82 Pb Lead 207.2	83 Bi Bismuth 208.98	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)
87 Fr Francium (223)	88 Ra Radium (226)	89 Ac Actinium (227)	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (266)	107 Bh Bohrium (264)	108 Hs Hassium (269)	109 Mt Meitnerium (268)									
				🟪 58 Ce Cerium 140.12	🟪 59 Pr Praseodymium 140.91	🟪 60 Nd Neodymium 144.24	61 Pm Promethium (145)	🟪 62 Sm Samarium 150.36	🟪 63 Eu Europium 151.96	🟪 64 Gd Gadolinium 157.25	🟪 65 Tb Terbium 158.93	🟪 66 Dy Dysprosium 162.50	67 Ho Holmium 164.93	68 Er Erbium 167.26	69 Tm Thulium 168.93	🟪 70 Yb Ytterbium 173.04	🟪 71 Lu Lutetium 174.97
				90 Th Thorium 232.04	91 Pa Protactinium 231.04	92 U Uranium 238.03	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)

FIGURE 2-1 Possible energy-critical elements (ECEs).
SOURCE: Dr. Robert Jaffe, APS and MRS (2011).

Eggert recently chaired the National Research Council (NRC) Committee on Critical Mineral Impacts on the U.S. Economy, which released the report *Minerals, Critical Minerals, and the U.S. Economy* (NRC, 2008). That report used a two-dimensional diagram to represent supply risk along the horizontal axis and impact of supply restrictions along the vertical axis (Figure 2-2). Thus, an element farther from the origin (such as A in the diagram) would be more critical than an element closer to the origin (B).

Using this framework, the committee conducted a preliminary analysis of 11 critical elements and element families (Figure 2-3). The platinum-group elements, the rare earths, manganese, indium, and niobium were most critical in this analysis. An important point to draw from this analysis is that criticality is a matter of degree, not an either-or characteristic. “There is a tendency to say, What is the list of critical elements? But it’s not the list [that is important] but where a particular element falls within a range of high or low criticality.” said Eggert.

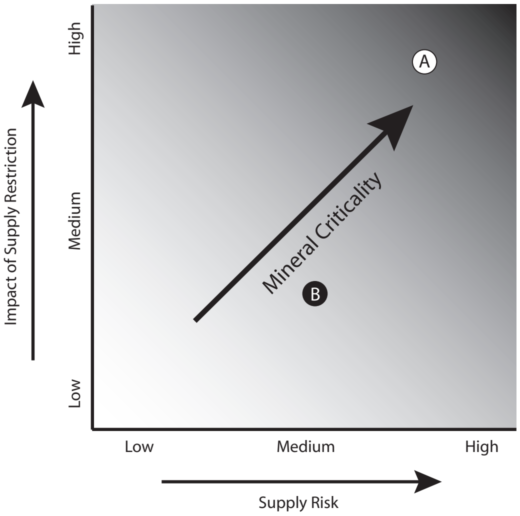


FIGURE 2-2 Mineral criticality depends on both supply risks and the impact of supply restrictions.
SOURCE: NRC (2008).

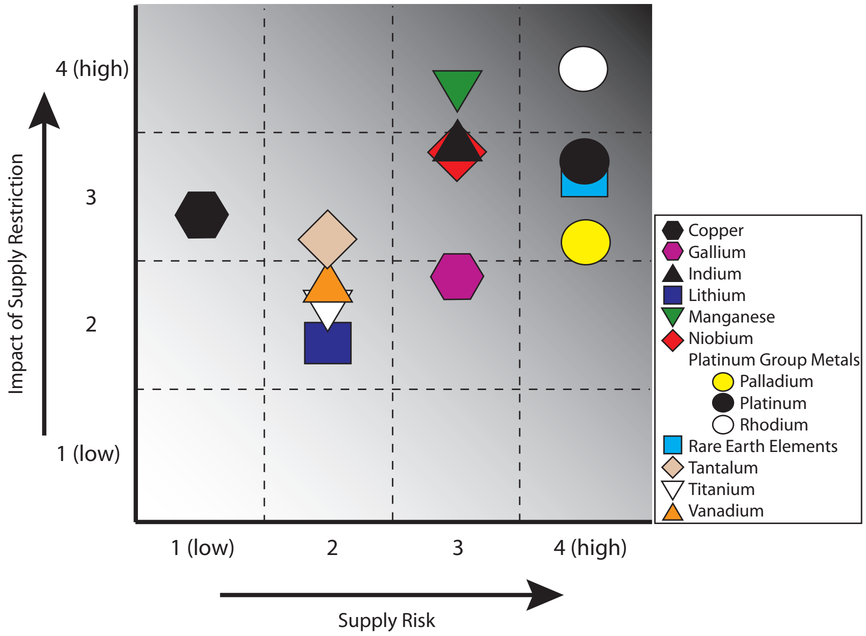


FIGURE 2-3 Within a framework of supply risk and impact of supply restrictions, some elements are more critical than others.
SOURCE: NRC (2008).

Additional Observations

Based on this analysis, Eggert made four additional observations.

First, criticality is in the eye of the beholder. For a Toyota Prius, rare earth elements are critical in a variety of applications, such as permanent magnets in motors throughout the vehicle (Figure 2-4). Other rare earth elements are important in different types of glasses, in the flat-panel display, in the catalytic converter, in the batteries, and elsewhere.

In photovoltaic devices, copper, indium, gallium, selenium, cadmium, tellurium, and other elements can all be critical.

The U.S. military has defined a list of critical elements for national security that includes gallium, lithium, niobium, rare earths, rhenium, and tantalum (Parthemore, 2011).

On the international front, the Japanese government, in partnership with Japanese industry, has stockpiled cobalt, chromium, manganese, molybdenum, nickel, tungsten, and vanadium. It is also considering stockpiling gallium, indium, niobium, platinum, rare earths, strontium, and tantalum.

Thus, different groups have different definitions of critical materials.

Second, each element has its own story, said Eggert. For some elements, production is concentrated in a small number of mines, companies, or countries. All three situations pose risks. Concentration within a country may pose geopolitical risks, as in the case of China. A mine may have technical problems associated with production. A small number of companies with market power may act in an opportunistic way to the disadvantage of users. As an example of a production risk, Europe considers beryllium to be a critical element because its supply originates from only one beryllium mine and it is in the United States.

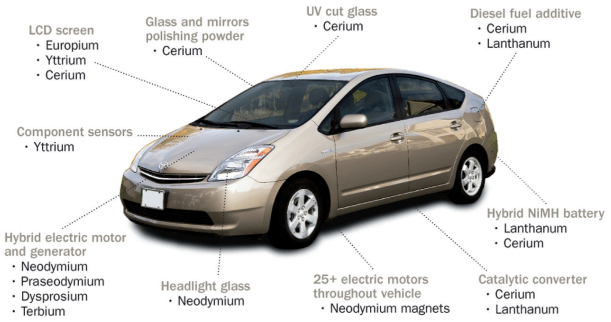


FIGURE 2-4 New hybrid vehicles incorporate many critical elements.
SOURCE: Courtesy of *Science News* (2011) (photo: Owaki/Kulla/Corbis, adapted by Janel Kiley).

For other elements, geological scarcity is a more important factor. Elements occur in different concentrations in the Earth's crust (Figure 2-5). For example, rare earths are not as rare as other elements geologically. Some elements are reasonably abundant on average but tend only rarely to be concentrated to a sufficient degree that they become commercially viable to extract (e.g., germanium, rubidium, strontium, and niobium).

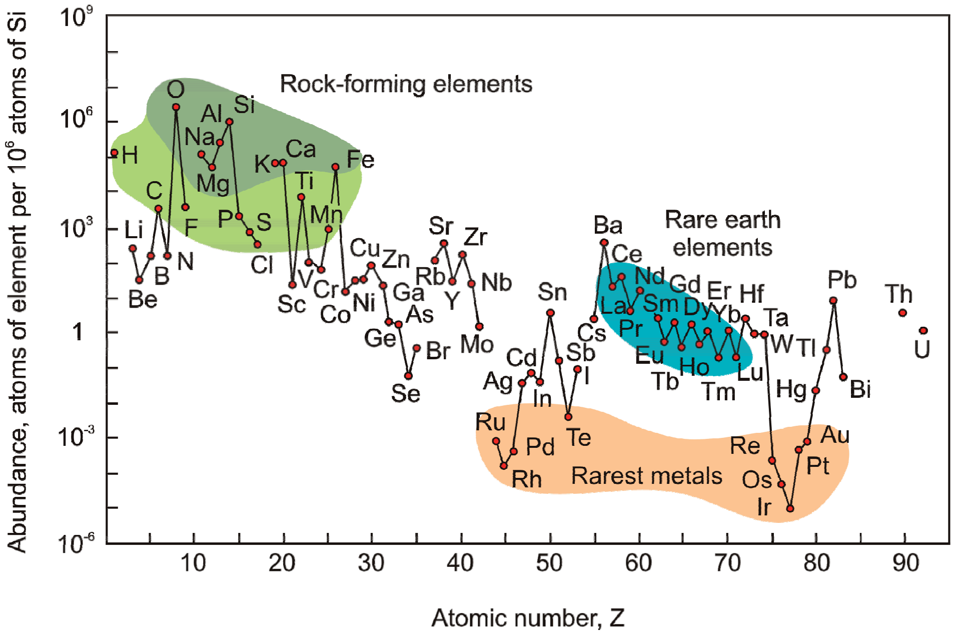


FIGURE 2-5 The abundance of elements in the Earth's crust tends to decline with increasing atomic number, but not uniformly.
SOURCE: Adapted from Haxel et al. (2002, Fig. 4).

Also, an element may be produced only as a byproduct of another element. For example, indium is produced almost exclusively as a byproduct of zinc processing, tellurium is produced almost exclusively as a byproduct of copper refining, and gallium is produced almost exclusively as a byproduct of the processing of bauxite into alumina and ultimately into aluminum. In these cases, the supply of the byproduct may be unresponsive to increases in the price of the byproduct. Thus, if the price of indium increases, the availability of indium may not go up because its availability is determined largely by zinc economics. By the same token, supply may be very responsive to a fall in the price of the main product. If copper production falls because prices tumble, the availability of tellurium could drop.

Finally, environmental and social concerns may produce long lead times and high production costs for some elements.

Eggert's third observation was that markets respond to both supply and demand signals but with time lags. For example, exploration for rare earth elements is booming, with hundreds of exploration projects currently examining rare earth mineralization in deposits around the world. Maybe only three of four of these deposits may become rare earth mines, Eggert said, but markets are responding. Even for elements produced today as byproducts, sufficient demand could lead to the development of mines only for that material.

Markets also respond to supply side signals, such as new extraction technologies, manufacturing efficiencies, and recycling to relax supply constraints. Stockpiles, diversified supplies, sharing arrangements with other users, and strategic relationships with suppliers all can affect supply and demand.

Over the longer term, substitutes can be found for elements. In some cases, an element can be replaced with one less subject to supply risk, though these opportunities are relatively rare, according to Eggert. A more common substitution involves replacing one type of material with another, such as incandescent lighting with first fluorescent lighting and then light-emitting diodes (LEDs).

Eggert's fourth and final observation was that government has an essential role to play. First, government needs to push for undistorted international trade. For some elements, such as the rare earths, trade restrictions could influence availability, the reliability of supply, and cost, and government policy can ease or eliminate these restrictions.

Also, the process of regulatory approval for domestic resource development needs to be improved. "I am not jumping on the bandwagon arguing against regulation generally but rather speaking to the efficiency of regulation," Eggert said. "We have a problem as a society with the process of regulatory approval for all types of major projects. Not that there is not a role for public input into regulatory decision making—there is—but I think we could do it a little more efficiently, not just in mining but throughout the economy."

Government also can facilitate the collection and dissemination of information and analysis. Information is necessary for informed and intelligent decision making, both in the private sector and in the public sector, and government can help provide this information for critical elements.

Finally, government can facilitate research and development, especially at the precompetitive stage. In this early stage of research and development, the benefits are diffuse, uncertain, and far in the future, making them difficult for a private actor to capture. In such cases, government action is justified because of spillover benefits that go beyond private benefits.

The Role of the Chemical Sciences

Eggert concluded his presentation by discussing the role of the chemical sciences in critical resources. The chemical sciences are of course essential for research and innovation, he said. On the demand side, they can enable element-for-element substitution as well as broader system substitutions. The chemical sciences also can relax supply constraints through improvements in extraction and recovery.

In terms of manufacturing, the chemical sciences can improve manufacturing efficiency in response to increased scarcity or availability concerns. For example, when flat-panel displays experienced dramatic growth in production and drove up indium prices a decade ago, the chemical sciences improved the incorporation of indium into the indium tin oxides in the displays from approximately 25 to 30 percent to 70 to 80 percent of the indium purchased.

Finally, the chemical sciences play important roles in recycling, which is essentially another form of extractive metallurgy.

THE DOE CRITICAL MATERIALS STRATEGY

As new energy technologies are developed and widely implemented, the demand for critical elements could soar. To prepare for such a future, the Department of Energy (DOE) recently issued its first Critical Materials Strategy (DOE, 2010). Diana Bauer described the main conclusions of the analysis and briefly discussed an update of the study under way at the time of the workshop.

The analysis looked at four clean-energy technologies: energy-efficient lighting, wind turbines, electric vehicles, and photovoltaics. It examined the full supply chain for the critical elements used in these technologies, including extraction, processing, manufacturing, and recycling. It also looked at materials availability and policies in both materials-producing countries and materials-consuming countries as well as in countries like China that have characteristics of both. The supply of critical materials is complicated by factors like co-production, where the production of one element depends on the production of another, the availability of substitutes, and the geographically uneven distribution of ores from which the elements can be economically recovered.

Another complexity in the picture is the abundance of rare earths are not uniform and it is often not possible to substitute one rare earth for another. Looking at the various deposits and the various rare earth elements, the different deposits have different relative proportions of all the different elements. Current practices could potentially could be overproducing some of them, while underproducing others.

For example, cerium is somewhat abundant relative to the other rare earths, whereas dysprosium, which is needed for magnets, may not be as rare as terbium, but it is significantly more rare than neodymium, which is another component of magnets. This aspect of production is important to consider, as mines may not be producing rare earth elements in the proportions that are required for the actual technologies being developed.

Also, even though more than 95 percent of today's rare earth supply comes from China, new mines are opening in other countries, further complicating the supply picture (DOE, 2010).

Matching Supply to Demand

The DOE analysis looked at 2010 production for a variety of elements and considered potential additions to supply by 2015. Some of the supply additions were from recycling, while others were from new production.

It then estimated the demand for critical elements by the four technologies considered in the study under conditions of high and low market penetration and high and low material intensity. Energy technologies can use critical elements to different extents depending on the specific technology used and supply factors. Nonenergy technologies also create a demand for these materials, which needs to be factored into the analysis. And intellectual property can be a factor, Bauer noted, when a company holds a patent on a key technology, for example.

The result of the analysis was a series of charts projecting supply and demand through 2025 (Figure 2-6). The charts show demand under four different scenarios along with the current and future supply as new mines begin production. "These graphs are not predictions," Bauer emphasized. "We are just trying to show how the different factors interrelate." For example, if research and development were directed toward lowering material intensity, how much would demand have to drop to reach the available supply? Or if a company were considering opening a new mine, what impact will the new production have on global demand and price?

Using the graphs of supply and demand, the DOE analysts assessed criticality using the same approach developed by the NRC committee that looked at critical elements (Figure 2-7). According to this framework, the most critical element was dysprosium, with neodymium, terbium, yttrium, europium, and indium also judged as "critical."

The study then looked at the change in criticality over the short to medium term, which is defined as 5 to 15 years (Figure 2-8). For example, lithium moved from not critical to near critical as projected demand rose during this period, whereas cerium and lanthanum made the opposite transition because of increased supply.

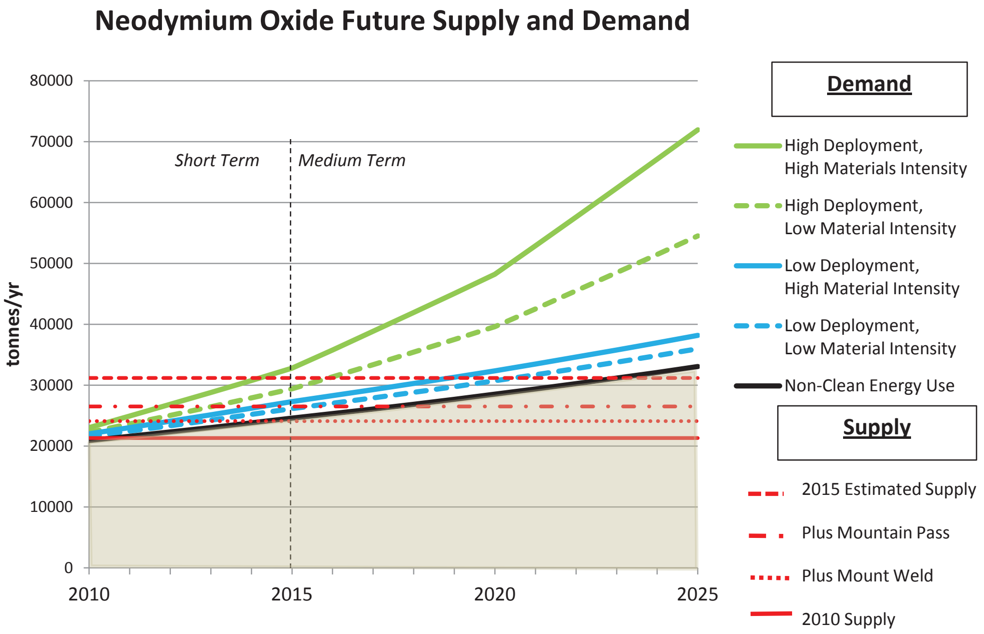


FIGURE 2-6 The demand for neodymium oxide could exceed supply by the year 2015 if new energy technologies undergo high deployment with high materials intensity.
SOURCE: DOE (2010, Fig. 7.2, p. 77).

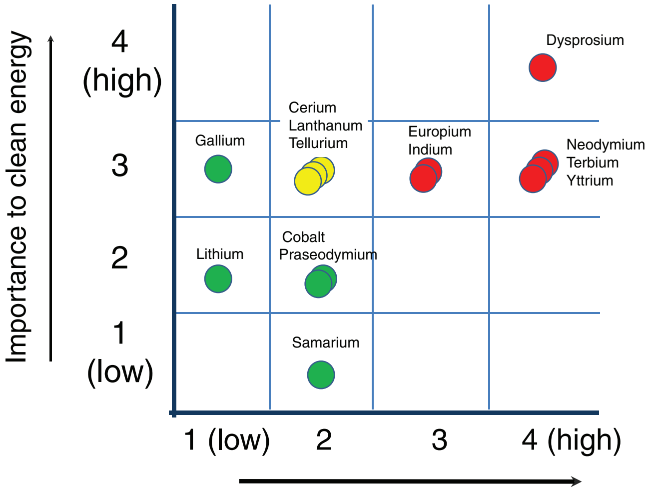


FIGURE 2-7 Five rare earths and indium fall into the critical category in the short term.
SOURCE: DOE (2010, Fig. ES-1, p. 8).

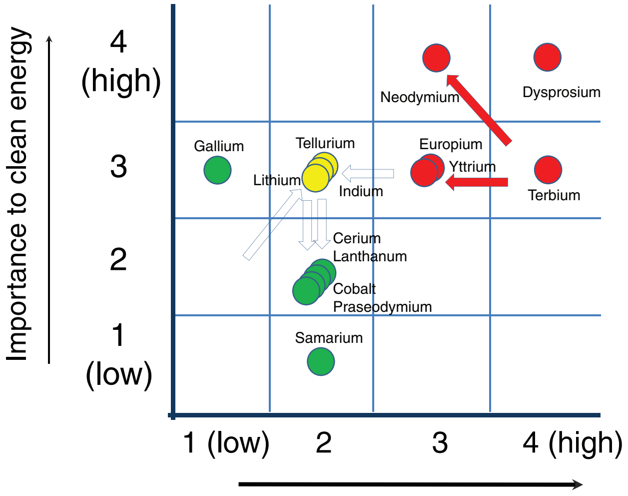


FIGURE 2-8 Between the near and medium terms, several elements change criticality categories.
SOURCE: Adapted from DOE (2010, Fig. ES-2, p. 8).

Program and Policy Directions

Bauer listed a number of program and policy directions presented in the Critical Materials Strategy, including research and development, information gathering, permitting and financial assistance for domestic production and processing, stockpiling, recycling, education, and diplomacy. Not all of these areas are within DOE's core competencies, she noted, but some are.

In particular, DOE's Office of Science, Office of Energy Efficiency and Renewable Energy, and Advanced Research Projects Agency-Energy (ARPA-E) are investing in a variety of promising technologies. Examples include alternatives to motors and generators that do not include rare earths, and magnet formulations that have higher performance with less rare earth content using nanotechnology approaches. DOE also has been sponsoring critical materials workshops and international meetings to help build a global as well as a national research community.

At the time of the workshop, DOE was working on an integrated research plan to be released by the end of 2011. As part of these efforts, the department planned to strengthen its information-gathering capacity and analyze additional technologies, such as the fluid-cracking catalysts used in petroleum refining. DOE will continue to work closely with international partners, interagency colleagues, Congress, and public stakeholders to incorporate outside perspectives into its planning, Bauer noted. Also, a new interagency working group led by the White House Office of Science and Technology Policy has been formed to address critical and strategic mineral supply chains, she said.

DISCUSSION

In response to a question about the role of prices in changing the availability of critical elements, Eggert agreed that price is important but also pointed to other factors. For example, supplies of the platinum-group elements may be more constrained than supplies of rare earth elements. For the past several decades, much of the rare earths used worldwide have come from two mines—the Mountain Pass Mine in California and the Bayan Obo Mine in China. The dramatically higher prices for rare earths over the past year may not have an immediate impact but over the longer term could lead to more geographically diversified mines.

Dennis Chamot of NRC pointed to the potential for relatively inexpensive materials to replace more expensive ones. For example, composites are replacing more and more steel in automobiles. Similarly, biological systems generally cannot afford to use scarce elements in processes such as photosynthesis, so organic chemistry may suggest ways to replace exotic elements.

In response to a question about supply constraints, Eggert said, "We're really not in danger of running out of anything. Human demand relative to what's available in the Earth's crust is relatively small even for the rare elements, and that at least for our lifetimes and probably the lifetimes of our children and grandchildren there are significant opportunities to expand the availability of things like rare earths if we choose to devote effort to those activities."

He also pointed out that the geographic allocation of a resource can be very important. For some critical elements, China plays an important role. At present, China is exercising its market power, which creates, in effect, a two-tiered pricing system, where prices in China to Chinese users of these elements are lower than to users in the rest of the world. However, this is less an issue of geology and more a result of existing production capacity, according to Eggert.

Thiel asked Eggert which elements are most worrisome to him in terms of price and availability. "The simple answer is gallium, indium, and tellurium for photovoltaics," Eggert replied. "That may be biased because my institution is right across the street from the National Renewable Energy Lab, and we've had lots of discussions on these issues. But those elements are relatively rare in a chemical sense in the Earth's crust, they don't tend to be concentrated significantly above average crustal abundance in very many locations, and they are currently all produced as byproducts."

In response to a question about recycling, Bauer noted that the potential varies by technology. For example, wind turbines from 30 years ago will not contain any neodymium, so they cannot serve as a source of that material. But fluorescent lights offer more potential because they have a shorter lifespan, a collection infrastructure is in place, and they contain heavy rare earth elements that will not be produced in much greater amounts from the mines slated to come on line. "That is a good niche type of recycling application to do first," she said.

Bauer also was asked whether actual shortages of critical elements can currently be documented, and she responded that price pass-throughs have been documented in some industries. "Part of the challenge is that a lot of companies don't want to share publicly their lack of ability to get material because that makes them vulnerable within the market to price increases or other disruptions," she said.

Finally, Bauer was asked whether DOE has seen evidence of black markets in critical elements, and she noted that the rare earth situation is special. Because China has export quotas on rare earths, producers in China have incentives to develop black-market channels, "and there is definitely evidence that that has happened and is happening."

3

Critical Materials in Catalysis

A major use of critical materials is in catalysis, which is the subject of both this chapter and the next chapter. Catalysts can be used on a large scale, as is the case with many heterogeneous catalysts, or on a small scale, as is the case with most homogeneous catalysts. A critical element may not be the most costly component of a catalyst, but the availability of that element or sudden changes in cost can disrupt its use. For example, as described in this chapter, platinum-based catalysis and electrocatalysis hold particular promise in several energy technologies, but platinum falls into one of the highest levels of criticality, as described in the previous chapter. Major research efforts are therefore under way to reduce the use of platinum in catalytic processes and to develop replacements for platinum in various applications.

CRITICAL MATERIALS IN CATALYSIS

"Catalysis is a broad topic, one that covers many orders of magnitude, from the 5-million-pound-per-hour scale down to the gram scale," explained James Stevens. However, catalysts can be divided into two main divisions, homogenous and heterogeneous catalysis, each with its own issues for critical materials.

In terms of volume, most catalysts are heterogeneous catalysts. Heterogeneous catalysts are easy to separate from product, and they work at very high temperatures, with alumina and silica catalysts capable of operating at temperatures of 1000°C. Heterogeneous catalysts are challenging to study and afford a poor degree of synthetic control. However, if heterogeneous catalysts could be rationally designed, they could offer tremendous advantages—for example, in emissions control applications.

Homogenous catalysts are more sophisticated chemically and can perform more useful chemical reactions. They are more selective and produce higher reaction rates than heterogeneous catalysts, and it is possible to design complex structures for specific tasks and use high-throughput, combinatorial methodologies to discover new homogenous catalysts and new reaction schemes that use new homogenous catalysts. However, homogenous catalysts are limited to use in lower-temperature chemical reactions.

Homogenous catalysts are by their nature used in very small amounts and produce many moles of product per mole of catalyst, with very high reaction rates. For example, a chiral ferrocynal iridium phosphine catalyst, used in the largest application of asymmetric synthesis to perform an enantioselective hydrogenation as part of an herbicide synthesis, produces over 2 million turnovers per catalyst molecule at a rate of 600,000 per hour (Blaser et al., 1999). Producing 10 million kilograms of product per year requires about 5 kilograms of iridium, assuming that no recycling occurs. This catalyst accounted for about 0.1 percent of U.S. imports of iridium in 2010.

Costs and the Supply Chain

While the 5 kilograms of iridium used per year in this catalyst would cost about $100,000, again assuming that no recycling occurred, that would account for less than 30 percent of the cost of the catalyst (Blaser, 2002). The most expensive components of this catalyst are the ligands surrounding the metal, which is often the case with homogenous catalysts. In addition, although the metal can usually be recycled, the ligands cannot. Other examples showing that ligand costs can dominate catalyst costs include a constrained-geometry titanium catalyst for ethylene co-polymerization; a zirconium catalyst for isotactic polypropylene synthesis (for which the metal accounts for about only 0.5 percent of the total catalyst cost); and a rhodium catalyst for enantioselective hydrogenation (for which the metal accounts for less than 15 percent of the total catalyst cost).

These catalysts are expensive to produce for several reasons. They are made in very small quantities, and small-scale production tends to be expensive. In addition, these catalysts often require multistep syntheses, which add cost.

Even though the metals in homogeneous catalysts are usually not the most expensive component, the cost of these metals can fluctuate wildly. Rhodium prices, for example, increased 20-fold during a four-and-a-half-year period starting in early 2004, jumping from $16,000 to $314,000 per kilogram. Prices then plummeted in a matter of months to under $50,000 per kilogram. Stevens explained that price increases are not necessarily a bad thing for a big chemical company. When prices increase, the metal the company has in storage also increases in value, producing a gain in working capital. When the price plummets, as it did with rhodium, the result is a loss in working capital. Some of these short-term fluctuations can coincide with the startup of a new large chemical process and the purchase of these metals to have in inventory.

The supply chain for these metals is global and involves several players. As an example of how the supply chain operates, Stevens used a hypothetical case in which Dow Chemical developed a new process that required 100 kilograms of platinum. The platinum-group-metal inventory and purchasing manager at Dow would contract with one of the many precious metal brokers to either purchase or rent the necessary platinum, depending on the prevailing market conditions or whether the company wanted to hedge the price of platinum. After acquiring the metal, the company would send it to a catalyst manufacturer who would prepare the catalyst according to Dow's specifications. Once the catalyst was spent, or inactive, it would be sent to a refiner to recover the platinum. Often, the broker, catalyst manufacturer, and refiner are the same entity. For platinum-group metals, loss of metal is on the order of 1 to 2 percent. Small amounts of metal also can be recovered from the reaction vessels and pipes in the chemical plant once the plant is decommissioned.

Cost and Supply Constraints

Catalysts used in refineries, Stevens noted, have particular issues because of the enormous quantities of catalysts used, often on the scale of millions of kilograms. Fluid-cracking catalysts and isomerization catalysts, for example, require very large amounts of metal. Sometimes a process that looks promising becomes impractical because of the amount of metal it would require. In one instance, a superior iridium-based fluid-cracking process would have required more iridium than is available worldwide. These facts point to the enormous potential for catalysts that do not require platinum-group metals.

However, in trying to develop replacements, it is important to keep an eye on the real market drivers. As an example, Stevens cited the enormous effort that went into creating simple metallocene catalysts based on titanium and zirconium to produce isotactic polypropylene with a melting point of around 160°C. This effort took 15 years, cost $500 million, and was successful, but the catalysts are not used commercially, except for one catalyst used to make a very small amount of a specialty material.

One promising area is the development of hydrosilylation catalysts that do not require platinum-based metals. Hydrosilylation is the largest-cost application for homogeneous catalysis. Platinum-based hydrosilylation catalysts are used widely in pharmaceuticals manufacturing, while rhodium- and platinum-based catalysts are used to make siloxanes and silicone rubber. As a result of the catalytic process used to make cured silicones, for example, some 4 to 6 metric tons of platinum per year are "lost" with the product (Figure 3-1). At the current price of platinum, that amount represents $250 million to $377 million worth of metal, a cost industry swallows because of the catalyst's superior properties.

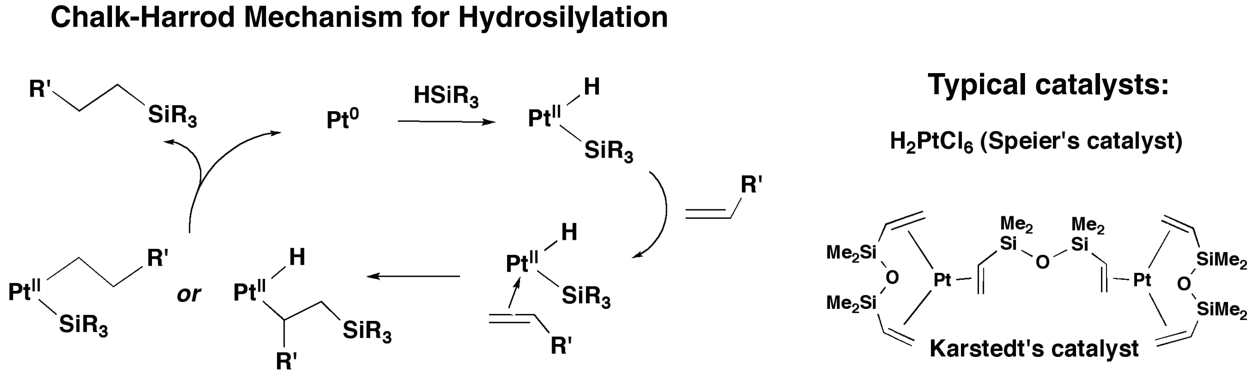


FIGURE 3-1 Current hydrosilylation processes lose some 4 to 6 metric tons of platinum per year.
SOURCE: T. Don Tilley, University of California, Berkeley (Stevens, 2011).

The development of lower-cost catalysts that meet critical performance characteristics could have significant economic benefits. However, the cost of the metal is not the only factor that must be considered. A catalyst that uses an inexpensive metal but expensive ligands could end up costing the same. Stevens elaborated to say that the current platinum-based catalyst is used because it has the desirable cure kinetics that enable the polymer to remain liquid for the time necessary to fill a mold. It also produces regioselectivity and chemoselectivity, resulting in high-molecular-weight polymers, which is a critical parameter.

Potential approaches to meeting these requirements with a lower-cost catalyst include identifying new silane and olefin activation chemistries and new reaction mechanisms that do not require the two-electron redox processes catalyzed so effectively by platinum. The application of new high-throughput catalyst discovery methodologies holds promise for making such advances.

Another promising area is the development of new catalysts for acetic acid production, the second largest use of homogeneous catalysis. In the 1960s, BASF launched an acetic acid process that used a cobalt catalyst, but this was replaced in 1970 with Monsanto's greatly improved rhodium-based catalyst. The new catalyst was more highly selective and required lower pressures, reducing overall costs per pound of acetic acid. Rhodium recovery was also very high.

This catalyst, however, was replaced in the 1990s by an iridium-based catalyst developed by BP. This catalyst, which could be used in the same plant as Monsanto's rhodium-based catalyst, had higher selectivity still and afforded better water use, thereby lowering the capital costs associated with drying columns. The lower capital costs more than made up for the increased cost of the metal used. Iridium, unlike rhodium, is not at the moment considered a critical material because it is not used in significant quantities today. If demand for iridium increases significantly, it could be considered a critical element.

The latest version of this catalyst, introduced a decade ago by Celanese, uses rhodium again but offers better iodine and water management and allows for larger plant construction. This, in turn, lowered the cost per pound of the final product. Though rhodium is a critical material, the amount used by the chemical industry to manufacture acetic acid is relatively small.

Emissions Catalysts

Emissions catalysts, particularly for use in cleaning up diesel exhaust, are significant users of platinum-group metals. Diesel is growing as a percentage of vehicle production worldwide, largely because of the higher fuel efficiency of diesel engines. However, diesel exhaust also has significant emissions problems. Removing NO_x from diesel exhaust requires a reduction catalyst and is difficult using existing catalyst technology, whereas removal of carbon monoxide and unburned hydrocarbons requires an oxidation catalyst (Figure 3-2). Particulates must also be removed from diesel exhaust, and filters contain metal catalysts.

Today, emissions catalysts account for 81 percent of U.S. platinum-group metal imports. Emissions catalysts also use significant quantities of cerium, which acts as an oxygen buffer in NO_x reduction. Looking ahead, new filter structures will require new catalysts, and there are opportunities to develop catalysts that do not use platinum-group metals. Nickel-based catalysts may prove useful, as may copper-based catalysts now that concern over the potential to produce dioxins as a byproduct has been alleviated.

Hydroformylation and Enantioselective Catalysis

The biggest application of homogeneous catalysis, in terms of the amount of product made, is in hydroformylation. The first catalysts were rolled out in the 1940s and used cobalt, a first-row transition element. Cobalt catalysis suffered from the need for high pressures and temperatures,

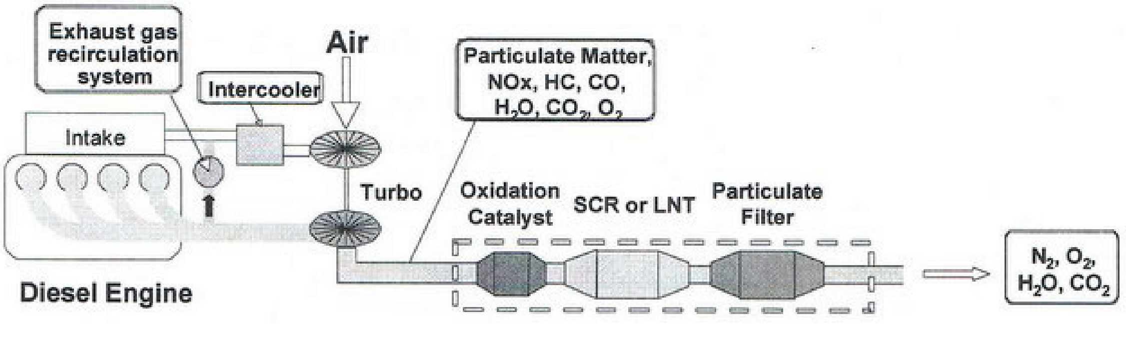


FIGURE 3-2 Removing pollutants from diesel emissions requires several catalysts and filters. SCR: selective catalyst reduction; LNT: lean NO_x trap.
SOURCE: Stevens (2011).

poor conversion and low selectivity, and costly catalyst recovery (Figure 3-3). Poor selectivity was the real problem because it is expensive to separate chemicals, in terms of both energy and capital costs. The major application of this technology was to make linear molecules, either *n*-butanol or derivatives such as 2-ethylhexanol, and copper-based catalysts resulting in normal-to-iso ratios of 3 to 4.

In the 1970s, Union Carbide commercialized a rhodium-based hydroformylation catalyst. While more expensive, this catalyst operated at much lower pressures and temperatures and generated product with a normal-to-iso ratio of 10, reducing capital costs substantially. Union Carbide introduced a more expensive rhodium-based catalyst in 1995 that required still lower temperatures and pressures and generated product with a normal-to-iso ratio of 30. This catalyst is more expensive because it uses phosphite ligands rather than low-cost phosphine. Today, 95 percent of the 7 million metric tons per annum production of 2-ethylhexanol and butanols is achieved using rhodium-catalyzed hydroformylation.

"The challenge in all of these systems," Stevens explained, "is to control the regioselectivity, chemoselectivity, and enantioselectivity, where enantioselectivity refers to making the branched molecule, which has a chiral center, versus the normal molecule, which does not."

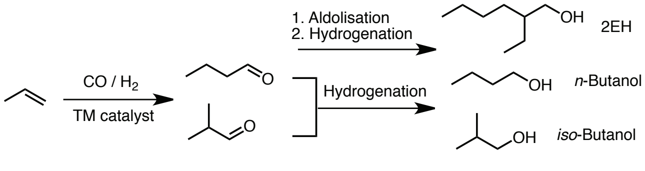


FIGURE 3-3 Cobalt catalysts produced undesirable amounts of *iso*-butanol compared to *n*-butanol.
SOURCE: Stevens (2011).

Today, there is a big push to develop catalysts that make more of the branched, chiral products than the normal products (Figure 3-4). Research has shown that the electronic environment surrounding the rhodium metal controls whether the product is the branched or linear isomer.

Branched aldehydes are incredibly versatile chemical intermediates that can be used to produce a wide variety of compounds, but the key is controlling regioselectivity and enantioselectivity. Today, researchers at Dow and Union Carbide have developed a number of ligands that achieve these requirements, though the application of high-throughput methods could improve catalysts further. These catalysts use rhodium or cobalt, but again, it is the ligands that ultimately determine the selectivity that the catalysts display.

By developing a better understanding of the mechanisms by which the catalysts work, researchers have been able to rationally design ligands to improve catalyst performance. As an example, Stevens discussed how Dow chemists took ligands developed by DuPont and created a new set of ligands that improved catalyst performance. The initial ligand, called DuPhos, showed good enantioselectivity in asymmetric hydroformylation, but the catalysts had poor activity. Dow chemists asked if the activity could be improved by increasing the electron-withdrawing substituents on the ligand, and the answer was yes. The resulting diazophospholane ligands not only improve catalyst activity but also provide the opportunity to fine-tune reactivity because their basic chemical skeleton can be readily modified. They are also easy to synthesize in what is essentially a two-step process that combines an aldehyde, benzoic acid, and hydrazine to make large libraries of molecules.

Today, with the large number of hydroformylation ligands available, it is possible to generate very high branched-to-linear ratios and very high enantioselectivities with high

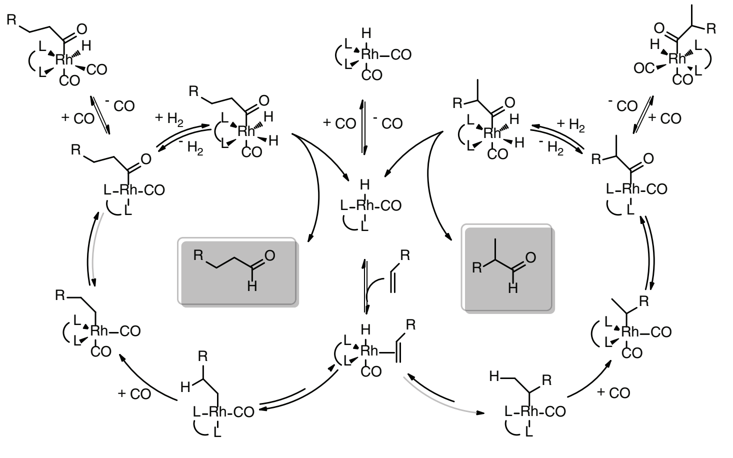


FIGURE 3-4 Hydroformylation can produce linear or branched isomers depending on the ligands surrounding the rhodium catalytic center.
SOURCE: Stevens (2011).

turnover rates and under mild conditions. There is still room, however, to improve the chemoselectivity and functional group tolerance. "The key is to find out the critical performance characteristics needed for commercial viability," said Stevens.

Finally, Stevens noted that there is real need for high-performance catalysts that can provide enantioselectivity around a carbonyl bond. Catalysts now available achieve turnover numbers on the order of 10 to 1,000 $s^{-1}$and function at very low rates.

ALTERNATIVE MATERIALS TO REPLACE PLATINUM IN CATALYTIC AND ELECTROCATALYTIC APPLICATIONS

In the quest for secure sources of energy, the conversion of renewable resources into liquid fuels—biomass into diesel and gasoline, for example, and water into hydrogen—is among the most active areas of research. Platinum-based catalysis and electrocatalysis hold particular promise in producing renewable, domestic sources of transportation fuels and other basic chemicals, but platinum is a strategic, imported metal. In the case of electrocatalysis, said Jingguang Chen, efforts are ongoing to reduce the amount of platinum needed by a factor of 10 to produce hydrogen via the electrolysis of water. For the catalytic conversion of biomass into liquid oxygenates, research is focusing on completely replacing platinum with tungsten in the necessary catalysts.

As has already been highlighted, platinum-group metals are used widely in the chemical and refining industries. In the area of clean energy technologies, platinum is the most promising catalyst for low-temperature fuel cells, electrolyzers, and photoelectrochemical cells, which use sunlight to power electrolysis. These clean-energy catalysts, however, require larger platinum nanoparticles than are needed in traditional heterogeneous catalysts, which would boost platinum use dramatically. Indeed, recent studies, said Chen, suggest that there is not enough platinum in the world to use such catalysts on the scale envisioned to power industrial processes.

The major challenge in replacing platinum with an early transition metal is that the electronic properties are different. Many research teams are attempting to use carbon to modify the electronic properties of tungsten and other metals that, like platinum, are in the 5d group of metals. In particular, metal carbides have many properties desired for industrial heterogeneous catalysts. They have high hardness and wear resistance, are stable at high temperatures, and are excellent electrical conductors. Using theory and model systems, researchers have developed design principles that have enabled them to create new metal carbide catalysts that have platinum-like activity and stability.

Efforts to reduce, rather than eliminate, platinum use are focusing on creating thin-layer or monolayer supported catalysts. This approach takes advantage of the fact that platinum catalysis occurs only on the very top layer of a platinum particle (Figure 3-5).

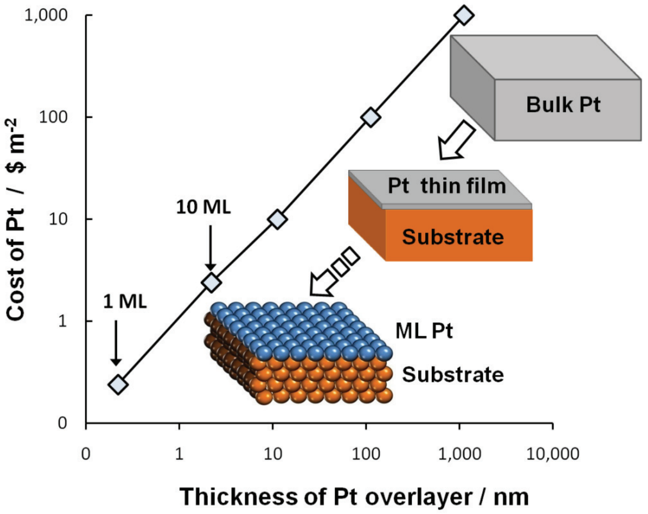


FIGURE 3-5 Thin-film and monolayer catalysts can greatly reduce the amount of platinum needed for catalysis. ML: mono-layer
SOURCE: Esposito and Chen (2011).

Hydrogen Production from Water Electrolysis

One rationale for developing efficient methods of generating hydrogen via water electrolysis is that hydrogen could then be used to store intermittent solar or wind energy. Electrons would be harvested during production and used to electrolyze water, producing hydrogen that would be stored and converted back into electricity using a fuel cell at night or when winds are calm. The major obstacle to this scenario is that large-scale commercialization is impossible because of the demand for and cost of the platinum catalysts now used in electrolysis and fuel cells.

There are two ways to use sunlight to power electrolysis. The indirect method is to use photovoltaic panels to convert sunlight into electricity that then is used to electrolyze water. The direct method is to use a catalyst that generates electrons directly from sunlight and uses those electrons to produce hydrogen and oxygen from water. Both processes require platinum in the cathode.

As part of a concerted effort to develop a monolayer platinum cathode for electrolysis, Chen and his collaborators asked the following questions:

- What is the descriptor responsible for making platinum the optimal catalyst for the hydrogen evolution reaction?
- Does monolayer platinum on a tungsten carbide particle meet such a descriptor for high activity in the hydrogen evolution reaction?

- Is monolayer platinum on a tungsten carbide particle stable under the relatively harsh conditions of the hydrogen evolution reaction?

The key feature of the descriptor comes from research on the binding energy of hydrogen to various metals. These experiments show that the hydrogen binding energy with platinum is –0.46 electron volts (eV). Quantum calculations are used to predict which carbides and monolayer systems would produce a hydrogen binding energy similar to that seen with platinum. Tungsten carbide alone has a predicted hydrogen binding energy of –0.99 eV, but when combined with a monolayer of platinum, the predicted hydrogen binding energy drops to –0.43 eV.

Chen and his collaborators confirmed these predictions experimentally. Tungsten carbide alone, which costs four orders of magnitude less than platinum, is inactive electrochemically. However, electrocatalytic activity increased as the density of platinum on a tungsten carbide electrode increased. When the platinum density reached one monolayer, electrocatalytic production of hydrogen was virtually identical to that seen with pure platinum.

Chen noted that platinum binds very tightly and stably to tungsten carbide. Furthermore, extended electrolysis tests showed that monolayer platinum on tungsten carbide structures was stable. Hydrogen production remained constant, and physical characterization using scanning electron microscopy and x-ray photoelectron spectroscopy confirmed that the platinum monolayer was stable on tungsten carbide under the harsh electrolysis conditions. In fact, said Chen, the platinum monolayer on tungsten carbide material is more stable than the commercial catalyst used today.

Thin films such as these are useful for experimentation and model calculations, but platinum monolayers on supporting particles would perform better in commercial applications. Chen's group is using atomic layer deposition to form platinum monolayers on tungsten carbide particles and to create a commercially viable material after 10 deposition cycles. Electrolysis measurements show that the platinum-on-tungsten carbide particles produced after 10 atomic-layer deposition cycles are just as active as commercial platinum catalyst. However, elemental analysis reveals that these particles contain 10-fold less platinum than the commercial catalyst.

This is not the end of the story. The same binding energy model suggests, as Chen said, that "instead of just using tungsten carbides as a base material, we can actually think about other carbides, such as molybdenum carbides. We can even think about using palladium on metal carbides." He also noted that this approach can be used to design platinum on metal carbide catalysts for other electrochemical devices, including their use as the anode material in direct alcohol fuel cells or the cathode material for oxygen reduction reactions.

Platinum-Free Catalysts for Biomass Conversion

In addition to his work on electrocatalysis, Chen and his collaborators have been developing platinum-free catalysts for converting biomass into oxygenated chemicals. These studies use quantum calculations and model systems to rationally design potential catalysts. Such studies enabled his group to develop a nickel-on-tungsten carbide catalyst that performs better and is more stable than a nickel-on-platinum catalyst for converting glycoaldehyde into hydrogen and carbon monoxide, which then can be combined using standard chemistry to produce a wide range of chemicals.

Though these examples show that it is possible to reduce or even eliminate platinum in industrially important catalysts, several challenges remain for these efforts to have a major impact. One is to increase the surface area of the platinum on metal carbide materials. Currently, high temperatures are needed to make stable metal carbides, but the resulting materials have low surface areas.

A related challenge is to develop new synthetic methods that create metal carbide with high surface areas, which would result in catalysts with much higher activity. Similarly, there is a need for better methods of depositing monolayers of platinum on metal hydrides while inhibiting carbon deposition on the particles, which reduces catalytic activity. A challenge in the electrocatalysis area is to develop platinum-sparing metal carbide materials that have long-term stability over a range of pH values.

DISCUSSION

In response to a question about whether there might be a balance between complete coverage of a metal carbide particle with platinum and somewhere between 25 and 75 percent coverage in terms of cost and stability, Chen said further tests may demonstrate that reduced coverage may be possible to achieve the same results. He explained that his group does not have the facilities to perform hundreds of hours of stability tests to determine the optimal coverage, and he hopes that a commercial vendor will be interested in conducting such tests. Chen also noted that recovering the platinum from these metal carbide materials appears to be easy.

Ernest Chamot, of Chamot Labs, asked if biomimetic approaches might be better than the rational design approach for creating new catalysts for biomass conversion. Chen replied that a biomimetic approach would likely work well for homogeneous catalysis. Such an approach would center on developing better ligands. For heterogeneous catalysts, however, a biomimetic approach is not likely to be successful.

Levi Thompson, Richard Balzhiser Professor of Chemical Engineering at the University of Michigan, and, with Thiel and Eggert, the third member of the workshop organizing committee, noted that his group has observed that the underlying metal carbide can actually dissolve under some conditions. He wondered if the highly oxygenated conditions in a biomass reactor would be conducive for dissolution of the underlying carbide, and he asked if Chen had observed that in his experiments. Chen replied that there is some tungsten dissolution, but only a small amount. The trick to suppressing dissolution, he explained, is to use very high pressures to compensate for oxidation.

In response to a question about the efficiency of biomass-to-chemical processes, Stevens noted that photosynthesis is actually very inefficient, using less than 1 percent of the incident energy. Even with sugar cane in the tropics, which is one of the best plants in terms of turning sunlight into useable materials, efficiency is less than 1 percent. As a result, making 700 million pounds a year of ethylene requires 450 square miles of sugar cane. "The net primary productivity of any plant-based photosynthetic process is a real limitation when you talk about the scale that's required to make chemicals on a big scale."

Stevens also was asked what advice he would give a 22-year-old thinking about picking a research advisor, and he replied that industry is currently having trouble finding chemical engineers with the skills industry needs. He also thought that because the efficiency of photovoltaics is so much greater than the biomass conversion processes, photovoltaics would be the more promising field. Finally, over the next few decades basic research will remain essential for energy issues in areas such as the manipulation of matter on a small scale.

4

Replacing Critical Materials with Abundant Materials

Replacing critical materials with abundant materials, particularly in applications that use large amounts of catalysts, would have many benefits. Abundant materials are cheaper, less susceptible to supply fluctuations, and more environmentally benign. Cheap and abundant metals also can be less selective, less tolerant of functional groups, and use more expensive ligands than rare and expensive metals, but research gradually is reducing these shortcomings.

A particular application discussed in this chapter is the use of precious metals in automotive catalytic converters. The automotive industry is a major user of platinum, palladium, and rhodium in catalytic converters, which has spurred research on the use of other types of materials as catalysts. Although no good alternatives to the use of these materials yet exist, promising approaches are being investigated.

MOLECULAR ELECTROCATALYSTS FOR ENERGY CONVERSIONS USING ABUNDANT METALS

In many important processes powered by a homogeneous catalyst, the cost of the catalyst's metal component is a small part of the overall expense. Nonetheless, chemists are developing novel reaction schemes that use homogeneous catalysts made with "cheap metals," said Morris Bullock, Laboratory Fellow and Director of the Center for Molecular Electrocatalysis at the Pacific Northwest National Laboratory (PNNL). These efforts are centered on using abundant, inexpensive metals—mostly first-row metals, but also molybdenum and tungsten—to replace precious metals.

Even in cases where an expensive metal is a fraction of a catalyst's total cost, creating efficient catalysts from inexpensive metals is likely to produce significant savings, said Bullock. Platinum, on a per mole basis, is approximately 4,000 times more expensive than nickel and 10,000 times more expensive than iron. Similarly, palladium is 3,000 times more expensive than copper, while ruthenium is 2,000 times more expensive than iron.

Palladium-based homogenous catalysis, in particular, is of critical importance in the pharmaceutical and agricultural industries for forming carbon-carbon bonds. The 2010 Nobel Prize in Chemistry was awarded for palladium-catalyzed cross-coupling reactions, which can be used to make virtually any type of carbon-carbon bond needed. The powerful Buckwald-Hartwig carbon-nitrogen bond-forming reactions are another class of palladium-catalyzed chemistries used widely in the pharmaceutical and agricultural industries (Hartwig, 1998; Wolfe et al., 1998). This latter set of reactions, Bullock noted, uses palladium loadings as low as 10 parts per million (ppm), so the expense of the precious metal in this case is not a significant factor.

It is possible, though, to substitute less expensive metals for palladium. A copper iodide/L-proline catalyst, for example, can be used to form carbon-carbon and carbon-nitrogen bonds (Ma et al., 2003). A nickel catalyst can be used to make carbon-carbon bonds with some stereoselectivity, which enables the assembly of fairly complex organic molecules (Harath and Montgomery, 2008). Chemists also have developed iron catalysts in carbon-carbon bond-forming reactions, although the results are not always what they seem. In one case, researchers made the observation that 98 percent pure iron chloride, compared to 99.99 percent pure material, produced higher yields of the desired product. Further study found that the reaction was actually catalyzed by a 10 ppm copper oxide impurity (Buchwald and Bolm, 2009). "There are plenty of other reactions that do get catalyzed by iron, but it highlights something that you have to be careful about in making sure that you can identify the real catalysts in these reactions," said Bullock.

The Pros and Cons of Cheap Metals

In addition to the large price advantage that comes with substituting a prevalent, cheap metal for a rare, expensive metal, cheap metals are often environmentally more benign. Losses of metal are more easily tolerated in an industrial process, which can reduce or eliminate the recycling steps that are almost mandatory with expensive metal catalysts. In the pharmaceutical industry, the Food and Drug Administration may or may not allow trace levels of residual catalyst in a final drug product. As Bullock stated, "How much palladium can you have in a pharmaceutical body compared to how much iron?"

The reasons that more cheap metal catalysts are not widely used today are many, and Bullock listed several of them. One reason is that reactions catalyzed by cheap metals have not been widely studied to date, though they are receiving more attention now. Another reason is that the selectivity of cheap metal catalysts is not as good as is obtained with palladium catalysts, and the scope of the reactions is not as broad. Boosting the activity of cheap metal catalysts can mean using more expensive ligands; for example, catalysts based on aryl iodides are more reactive, but more expensive, than aryl chlorides.

Cheap metal catalysts are often less tolerant of functional groups on the reactants. A reaction that works with an ester moiety present may not work when an alcohol or carboxylic acid functional group is present. In contrast, palladium-based catalysts often work with a wide range of modified starting materials. In addition, cheap metals may require a higher catalyst loading than when palladium is used, negating some of the cost advantage. Bullock added, though, that this may be a result of the fact that cheap metal catalysis has not been studied as exhaustively as has palladium-based catalysis, and that additional research is likely to make headway on this problem.

The final problem facing cheap metal catalysts is one of motivation. For a pharmaceutical company making a high-value-added drug at small scale, and for which catalyst cost is not a major factor in the final price of the drug, there is often little motivation to expend research dollars solving a relatively small problem.

To illustrate some of the challenges in developing cheap metal catalysts, Bullock discussed the fact that reaction mechanisms may not be universal, making the search for new catalysts difficult. For example, an important class of chemical reactions hydrogenate carbon-oxygen double bonds. These carbonyl hydrogenation reactions use ruthenium- and rhodium-based catalysts to convert ketones and aldehydes into alcohols. One such ruthenium catalyst, for which the Nobel Prize was awarded, does not operate via the traditional mechanism for ketone hydrogenation. Normally, the reacting ketone would first coordinate with the metal, after which oxygen inserts itself into a metal-hydrogen bond. With this particular ruthenium catalyst, no coordination or insertion is required. Instead, the reaction occurs through a hydride ion on the ruthenium and a proton from the ligand-attached nitrogen coordinated to the ruthenium. The end result is the same, but the mechanism is completely different than expected (Noyori et al., 2001).

"The overall point I want to make is that if you're trying to develop a new type of catalyst with a different metal, it is going to look a lot different," said Bullock. "You don't want to replace platinum or palladium with iron or copper and try to use the same ligand set. The ligands will almost certainly change." The idea, he explained, is to not try to emulate what precious metals are doing as catalysts. Instead, the intention is to look at the reactivity characteristics of the cheap metals, understand the electronics of the reactions and the energy states, and then build a catalyst around those metals from the ground up using fundamental principles.

As an example, Bullock discussed work done in his laboratory developing a molybdenum-based catalyst for hydrogenating ketones to make alcohols at low temperature and hydrogen pressure and under mild conditions (Bullock and Voges, 2000). This reaction occurs by a different mechanism, one that capitalizes on the reactivity patterns of molybdenum hydrides and involves delivering a proton to the oxygen atom in the ketone first, leaving a metal hydride that then delivers hydride to the carbon atom, creating the saturated alcohol. Fundamental research on the acidity of metal hydrides and both the kinetics and thermodynamics of metal hydride behavior made the development of this catalyst possible.

The same types of basic research studies were done by other researchers to develop an iron-based catalyst that also performs a heterolytic cleavage of hydrogen as the key step in the hydrogenation of carbon-oxygen double bonds (Casey and Guan, 2009). But equally important is the fact that the catalyst is regenerated under low-pressure hydrogen conditions. More recently, another group created an iron-based catalyst that under similarly mild conditions works at very low catalyst loadings of 0.05 mole percent (Langer et al., 2011).

Iron-based catalysts also can be used to hydrogenate carbon-carbon double bonds. Again, this work was based on solid fundamental chemistry research to create redox-active ligands that help drive the reaction. One of these catalysts achieves turnover frequencies of up to 1,800 per hour in the conversion of 1-hexene to hexane (Bart et al., 2004).

High-Volume Applications of Cheap Metal Catalysts

Although the examples cited above show that it is possible to create potent catalysts for the production of the type of low-volume specialty chemicals used in the pharmaceutical and agricultural industries, the impact on the overall demand for expensive and rare metals is not likely to be substantial. An area where a real impact could be had is in the area of renewable energy production, which would require massive amounts of catalyst, as was discussed in the previous chapter.

"We hope that there is going to be a much higher use of solar energy and other types of renewable energy in the future," said Bullock. "What we want to do is store that energy in the form of the chemical bonds in a fuel." Making this conversion, he added, requires "developing electrocatalysts that will convert electrical energy to chemical bonds, largely in the form of molecular hydrogen. Then, when you need the electricity, you can run hydrogen in a fuel cell and get your electricity back."

Research at PNNL is focusing on developing catalysts that do not require platinum for hydrogen oxidation, which releases electrons, and the reverse reaction, proton reduction, that stores electrons. This work is also germane to the broader topic of oxygen and nitrogen reduction, which are more complex reactions given that oxygen reduction to water is a four-electron and four-proton event and nitrogen reduction to ammonia is a six-proton and six-electron event.

The theoretical framework for this research is based on understanding the first and second coordination spheres of nickel, the region where the electronic properties of the ligands surrounding a metal atom have the biggest influence on the metal's catalytic properties (Rakowski DuBois and DuBois, 2009). In particular, Bullock and his colleagues are focusing on the role that phosphine ligands bearing pendant amines play in proton relays when these ligands are built into the second coordination sphere around nickel. Research at PNNL has shown that proton transfer into or away from the metal plays a key role in accelerating intra- and intermolecular proton transfers and stabilizing binding of hydrogen to the metal. These pendant amine-facilitated proton relays also lower the barrier for heterolytic cleavage of hydrogen (DuBois and Bullock, 2011) and facilitate the coupled proton-electron transfers that are important in the reduction of oxygen and nitrogen.

The inspiration for using pendant amines to design nickel hydrogenation catalysts comes from nature, which does not use rare and precious metals in its catalysts. Protein crystallography studies of the structure of an iron-iron hydrogenase enzyme revealed the presence of pendant amines in the coordination sphere surrounding the metal atoms. But rather than building structural mimics of nature's catalyst, the PNNL team is designing functional models that re-create the electronic and energy environment of the enzyme's catalytic center.

Bullock discussed a few early examples of the catalysts developed from this effort. As shown in Figure 4-1, adding two pendant amines to nickel's coordination sphere produced huge positive changes in the hydrogen oxidation activity of the resulting nickel catalyst by reducing the overpotential of the system, which increases the catalyst's energy efficiency. Taking this approach one step further, the PNNL team reduced the flexibility of the pendant amines, essentially locking them into place around the nickel atom. This cut the activation energy nearly in half and increased the turnover frequency from less than 0.5 per second to 10 per second.

Developing a clearer understanding of the mechanism involved in catalytic oxidation of hydrogen played an important role in taking these initial results and creating far superior nickel hydrogen oxidation catalysts. These studies, which relied heavily on nuclear magnetic resonance spectroscopy, showed that moving protons onto pendant amines avoids having the reaction pass through a nickel(III)

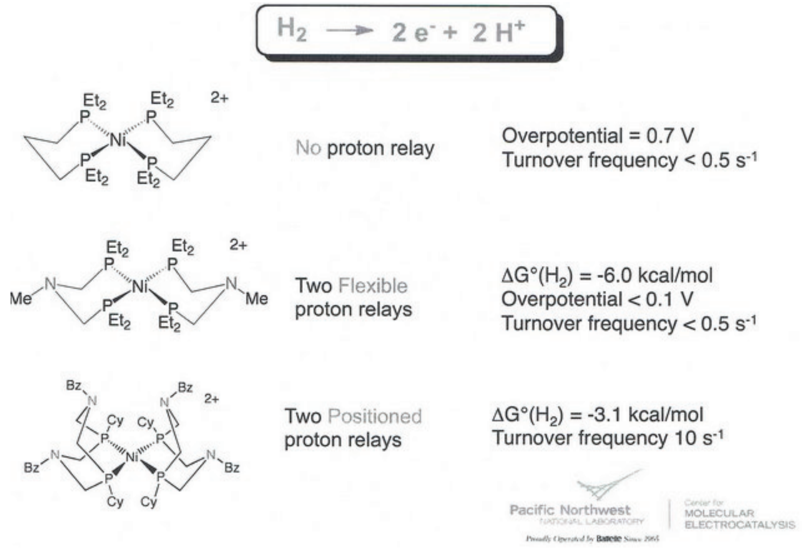


FIGURE 4-1 Nickel catalysts can oxidize hydrogen.
SOURCE: Bullock (2011).

intermediate, which lowers the energy barrier considerably. Based on this mechanistic understanding, the PNNL team created a nickel-based catalyst that produces 50 turnovers per second at one atmosphere of hydrogen (Yang et al., 2010), and another one that was not as good a catalyst for hydrogen oxidation but that was able to mimic the natural hydrogenase enzyme and catalyze both hydrogen oxidation and reduction (Kilgore et al., 2011). This catalyst is the first reported to carry out both the forward and reverse reaction.

One issue that arose in these studies was that protons can become trapped between two pendant amines in the same ligand, reducing catalytic activity. Switching to a ligand that had two phosphorous atoms to coordinate to the nickel core but only one nitrogen, a so-called P_2N_1 ligand, produced a dramatic increase in catalytic activity and resulted in turnovers of over 100,000 per second, which is more than 10 times faster than the iron-based hydrogenase that served as the inspiration for this work (Helm et al., 2011). However, this catalyst still has a high overpotential that needs to be addressed to improve its energy efficiency.

The PNNL also has used rational design principles to create the first iron-based catalyst for hydrogen oxidation. Turnover rates for this catalyst are only about two per second, but this research is still in its infancy.

In addition, working with a team at the University of California, San Diego, Bullock and his colleagues have created a nickel-based electrochemical catalyst that oxidizes formate. This is the first reported instance of a homogenous formate oxidation catalyst, and it is the first example of a formate oxidation catalyst of any kind that does not use platinum-group metals (Galan et al., 2011). These studies are ongoing.

Bullock concluded his presentation by noting that performing homogenous catalysis without precious metals has many advantages. In particular, iron, nickel, and other abundant metals are much less expensive and are often more environmentally benign. He added that, while an increasing amount of research is being done in this area, more fundamental research is needed to drive catalyst design efforts. The notable successes that the field has achieved in finding replacements for palladium in organic synthesis and for platinum in fuel cell and energy applications were all made possible by fundamental organometallic chemistry research, he observed.

NOVEL METALS AND BASE METALS IN AUTOMOTIVE CATALYST SYSTEMS

The auto industry is a major user of both precious- and base-metal catalysts. In automotive applications, catalysts are used to reduce the amount of regulated pollutants in the exhaust from gasoline and diesel vehicles. These pollutants include hydrocarbons, carbon monoxide, nitrogen oxides (NO_x), and particulate matter. Catalysts convert these pollutants into nitrogen gas, carbon dioxide, and water.

The heart of the automotive catalyst system is the catalytic converter, explained Christine Lambert. The catalytic converter is essentially a ceramic honeycomb encased in a metal can attached to the vehicle's exhaust pipe. Within the ceramic honeycomb is a supported metal catalyst that has been wash-coated onto the ceramic support, as shown in Figure 4-2.

The standard catalytic converter on a gasoline-powered vehicle uses a three-way catalyst engineered over many years to be extremely durable, said Lambert. Current versions are designed to meet emissions standards for 120,000 miles. They operate between 350°C and 650°C, the normal operating range of a gasoline engine, but they are durable to over 1000°C. The catalysts operate in near-stoichiometric exhaust gas, which means that the air and fuel fed into the engine is at the stoichiometric ratio needed to burn that fuel and that there is no excess oxygen. Contact time with the catalyst ranges from 60 to 300 milliseconds (Heck and Farrauto, 2001).

As engine control has improved over the years, the pollutant content of the exhaust has fallen into a tighter range of concentrations. As a result, catalysts are now able to handle all three gaseous pollutants simultaneously using what is called a three-way catalyst. Particulates are an issue only with diesel engines, and they are dealt with separately.

Today's three-way catalyst is a complex, multicomponent system. The bulk of the catalyst is made of cordierite, a magnesium iron aluminum cyclosilicate that forms the ceramic honeycomb. γ-Alumina forms the support base, and cerium oxide (ceria) and zirconium oxide (zirconia) are oxygen-storage components to help the catalyst when it is in the high-efficiency stoichiometric window.

In addition to the rare earth mineral ceria, two other rare earth minerals, lanthanum oxide and neodymium oxide, maintain the alumina in its gamma form and play an important role in durability. Barium oxide and strontium oxide also serve as stabilizers and can store NO_x if the engine is running lean, though that is not their primary purpose. A small amount of nickel oxide suppresses the formation of hydrogen sulfide from the relatively high amount of sulfur that is still present in gasoline. Finally, there is a small amount, about 0.5 percent, of the precious metals platinum, palladium, and rhodium (Gandhi and McCabe, 2004).

Summarizing the 30-plus-year history of gasoline catalyst development, Lambert explained that early fundamental research focused on identifying which elements could be good candidates for further development. Gold and silver were eliminated as candidates because of their limited durability and activity. Ruthenium, iridium, and osmium had suitable activity profiles, but they form volatile oxides at elevated temperatures, ruling them out as automotive catalysts. "At that point, the choices boiled down to platinum and palladium," said Lambert.

Platinum and palladium were incorporated into the first catalytic converters when regulations mandated reductions

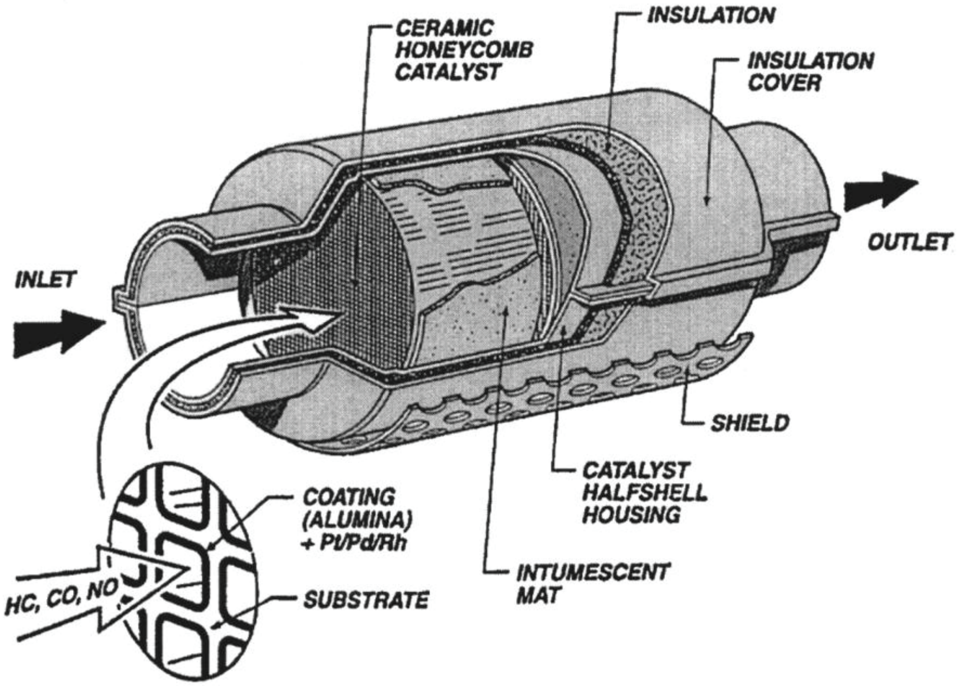


FIGURE 4-2 An automotive catalytic converter contains a catalyst on a ceramic substrate.
SOURCE: Heck and Farrauto (2001).

in hydrocarbon and carbon monoxide emissions. Later, when NO_x standards were added to the regulations, rhodium was incorporated into the catalyst mix. Over the years, the stabilizers were added, as were ceria and zirconia as oxygen stabilizers. When lead was removed from gasoline, platinum was eliminated from the catalyst because palladium then could replace all platinum-based activity. Today's catalytic converters still contain some rhodium because, as Lambert said, there is no acceptable substitute for rhodium when it comes to NO_x reduction. Improvements in the physical design of the catalyst, with platinum-group loadings changing from the front to the back of the converter, have reduced the amount of metal needed in the converter (JM, 2011).

Supply and Demand

The automotive catalyst market is not isolated but sits within a supply chain that serves industrial catalyst manufacturers, jewelry makers, and electrical equipment manufacturers. The catalytic converter supply chain starts with the substrate manufacturers, who send their product to the catalyst coaters who purchase the metals. From there, the coated ceramic goes to the canners, who assemble the finished catalytic converter and ship it to the auto manufacturer. Currently, the automotive catalytic converter market consumes more platinum-group metals than it recycles, a situation that needs to be improved, according to Lambert. Unlike the industrial catalyst market, there is no well-developed internal recycling infrastructure in the automotive market.

Most of the world's platinum comes from South Africa, which supplied over 75 percent of the 6.06 million ounces produced in 2010. Russia supplied just under 14 percent of the total, with the rest coming from other countries. Total demand for platinum in 2010 was 7.88 million ounces, with automobile catalysts requiring 3.125 million ounces, or 40 percent of the total. Recycling was able to make up for the difference between supply and demand.

Russia is the biggest supplier of palladium, producing 3.72 million ounces in 2010, while South Africa produced 2.575 million ounces. Other countries added just under 1 million ounces to the world's available stores of palladium. Recycling added another 1.845 million ounces, but taken together, the world's demand for palladium—some 9.625 million ounces—outstripped supplies by nearly a half million ounces. Automotive catalysts accounted for 57 percent of the demand for palladium (JM, 2011). Lambert added that the automotive catalyst market accounts for most of the world demand for rhodium.

Because the automotive industry is a major user, if not the major user, of these metals, the industry is impacted significantly by the price volatility for these metals. Since 1992, platinum, palladium, and rhodium have all seen one or more price spikes. As a result, catalyst manufacturers have developed several designs that use varying amounts of these three metals in an attempt to mitigate dramatic shifts in costs.

Price volatility also has contributed to the drive to develop catalysts based on less expensive metals such as copper. Though copper prices can spike as well, prices may go from \$1 per pound to \$4 per pound, compared to a spike from \$1,000 per ounce to as high as \$12,000 per ounce for rhodium (Kitco, 2011).

However, a comparison of platinum-group metals with other metals shows that the former are hard to beat when it comes to carbon monoxide and hydrocarbon oxidation activity, particularly in the presence of sulfur at temperatures under 500°C (Kummer, 1980). In the early 1990s, researchers at Ford tested a variety of copper and copper-chromium combinations in catalytic converters installed in an actual car exhaust system. For NO_x conversion, a catalyst comprising 4 weight-percent copper and 2 weight-percent chromium performed the best, but only when operated under rich conditions, which reduced carbon monoxide and hydrocarbon conversion and fuel economy. This study showed, too, that copper catalysts needed to be close-coupled to the engine in order to avoid sulfur poisoning (Theis and Labarge, 1992).

After more than 30 years of research, Lambert concluded, there still are no good options for creating catalysts to treat gasoline engine exhaust that do not use platinum-group metals. The only real advance, she said, was the transition to palladium-rhodium and palladium-only catalysts enabled by the elimination of lead from gasoline.

The Importance of Diesel

As a percentage share of the U.S. market, diesel accounts for about 1 percent of new car sales and under 10 percent of light truck sales. For heavier trucks, such as the Ford F-250 and Dodge Ram, diesel models account for close to 90 percent of new vehicle sales. While diesel car sales are increasing, so, too, are the regulatory demands on diesel emissions. Engine makers have responded by improving catalysts, resulting in a substantial drop in diesel emissions since 1990.

In the mid-1990s, diesel exhaust treatment systems consisted solely of oxidation catalysts. Some diesel exhaust catalysts did not use any platinum-group metals, with ceria and alumina providing just enough catalytic activity to oxidize particulate matter enough to meet emission standards then in force. The introduction of ultra-low-sulfur diesel fuel in 2007 opened new opportunities for diesel exhaust emissions control systems. Particulate filters became standard, as did catalytic converters with high precious-metal content. These new systems operated under lean conditions to control NO_x emissions, and some engine manufacturers added NO_x traps.

In 2010, engine manufacturers added an extra reductant to the vehicles in the form of aqueous urea and turned to a copper catalyst for NO_x control (Figure 4-3). The complete exhaust treatment system now includes a platinum-group metal diesel oxidation catalyst, an aqueous urea tank that is refilled during oil changes, a mixing system that injects the urea into the exhaust stream, a selective catalytic reduction chamber in which a copper-zeolite catalyst converts NO_x and urea into nitrogen gas and water, and finally a particulate filter. Approximately every 500 miles, the temperature in the filter is raised to 500°C to burn off the trapped carbon particles, producing carbon dioxide.

Lambert noted that there is a huge exhaust temperature difference between gasoline and diesel engines. Once a diesel engine is at full operating temperature, exhaust temperatures average about 200°C, whereas a gasoline engine's exhaust runs about 500°C. "It is hard to do catalysis at 200°C under the high space and velocity conditions characteristic of engine exhaust," she said.

An added complication for diesel engine exhaust is that its oxygen content jumps significantly when the engine decelerates. During deceleration, no fuel goes into the engine, so the exhaust stream is just air with about 20 percent oxygen content, making NO_x control under conditions that range from rich to lean challenging. Manufacturers have responded with several systems, including urea-based systems that have a wide temperature window. Other approaches to achieving NO_x control under lean conditions include a hydrocarbon selective catalyst reduction (SCR) system that uses platinum but does not require a regenerating filtration system, lean NO_x traps that use barium to absorb NO_x during lean conditions, and a recently developed system that uses an ethanol-in-silver catalyst that is most useful for off-road diesel engines.

Urea and Zeolite Systems

Urea is a nontoxic commodity chemical produced by fertilizer manufacturers. When heated with water, it produces carbon dioxide and ammonia. It is injected into the exhaust system upstream of the catalyst as an aqueous solution at 32.5 weight-percent, a eutectic mixture with the lowest possible freezing point. In the presence of a suitable catalyst, ammonia reacts with the various nitrogen oxides in the presence of oxygen to produce nitrogen gas and water.

There are a number of non-precious-metal catalysts suitable for NO_x reduction. Copper zeolites are best at low temperatures, whereas iron zeolites perform best at high temperatures. Vanadium-based catalysts, which are very inexpensive, are also effective but are not appropriate for U.S. diesels equipped with particulate filters because of the high temperatures at which those filter systems must operate (Cavataio et al., 2007).

Zeolites, Lambert explained, are made of aluminum oxide and silicon oxides with a crystalline structure. They are found in nature but in most cases are synthesized to achieve the high purity needed for industrial purposes. Zeolites are in widespread use as water softeners, absorbents, and desiccants and in oil refining.

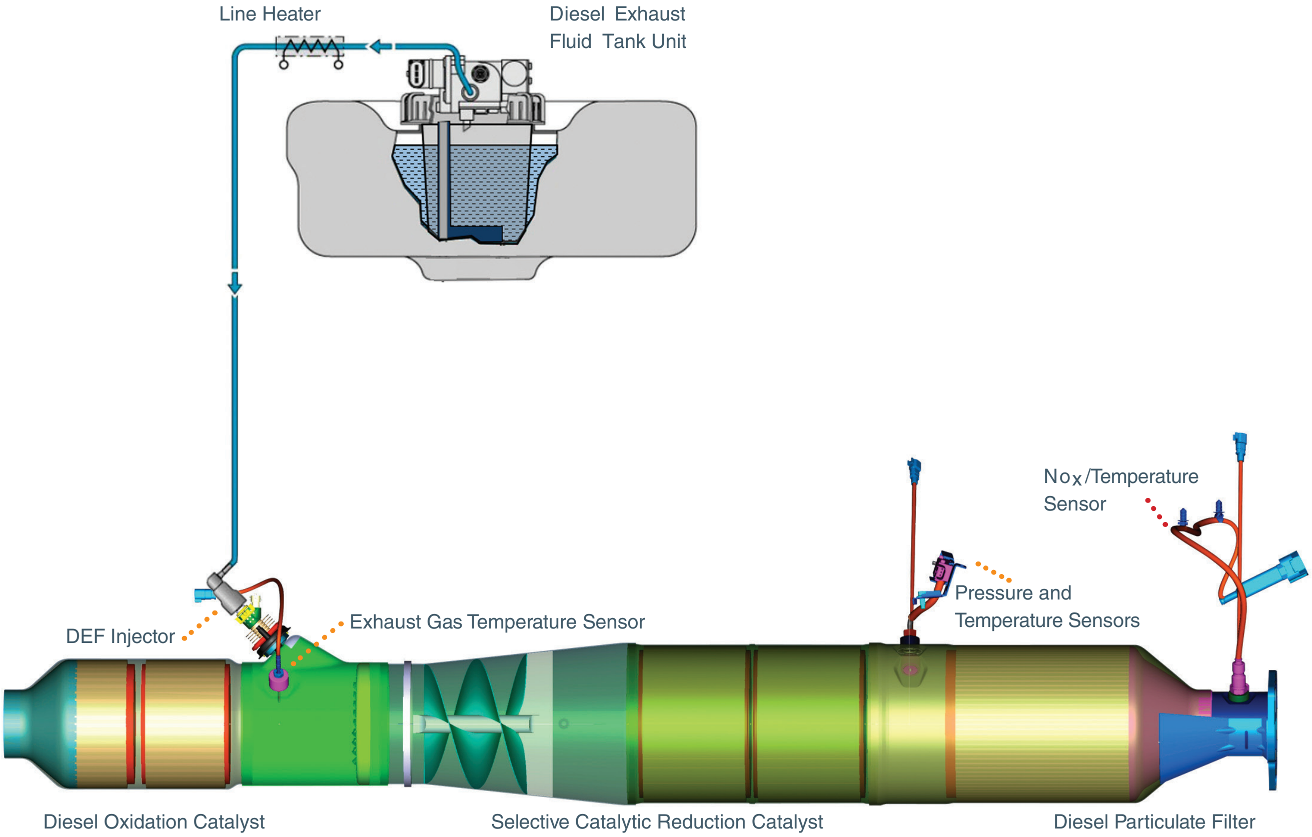


FIGURE 4-3 U.S. diesel exhaust treatment systems have become progressively more sophisticated to reduce emissions.
SOURCE: Ford (2011).

At Ford, Lambert and her colleagues found that a zeolite known as chabazite, which has a very small average pore size, combined with copper is a suitable diesel exhaust catalyst (Kwak et al., 2010; McEwen et al., in press) in an SCR system. Numerous academic studies suggest that copper is located inside the cage of the zeolite structure and that ammonia and NO_x enter the cage, where they react in the presence of copper and oxygen to produce nitrogen gas and water.

There were a number of challenges to overcome to commercialize the SCR system that Ford now uses with its diesel engines. First, Lambert and her colleagues had to stabilize the platinum-based oxidation catalyst that sits in front of the SCR system. They accomplished this task by adding palladium to the catalyst mixture. After working with various ratios of platinum to palladium, they found that a 1:4 platinum-to-palladium mixture resulted in the best combination of hydrocarbon oxidation at cold-start temperatures and stability. The latter is important because volatilized platinum interferes with the NO_x reduction process by poisoning the copper catalyst in the SCR system (Cavataio et al., 2009). Lambert noted that it is important enough to avoid precious-metal contamination of the copper catalyst that the two components are made in separate buildings. Having even a small amount of platinum on the copper-zeolite catalyst turns the latter into an ammonia oxidation catalyst instead of a NO_x reduction catalyst.

Lambert noted that Ford researchers first worked with a beta-type zeolite as the copper support, but that this combination was poisoned by hydrocarbons to some extent. The catalyst could be regenerated by heating it to 500°C, but treatment at this temperature was found to produce melting that destroyed the zeolite's structure. Moving to chabazite solved this problem. She added that chabazite's small pore size prevents larger hydrocarbon molecules from reaching the active copper catalyst, preventing the formation of dioxins in diesel exhaust.

Sulfur can negatively impact copper-zeolite catalyst activity, particularly at temperatures below 300°C. Sulfur can be removed from the catalyst at filter regeneration temperatures, however. In fact, research found that at the now-mandated level of sulfur allowed in diesel fuel—15 ppm or less—the copper-chabazite catalyst can tolerate the amount of sulfur absorbed between 500-mile regenerations and still reduce NO_x levels enough to meet exhaust standards.

The use of aqueous urea filtration is possible because manufacturers and suppliers worked together under the auspices of the U.S. Council for Automotive Research to define product specifications. Aqueous urea is now sold as Diesel Exhaust Fluid™ (DEF™) in amounts ranging from gallon bottles to drums. The cost of DEF ranges from $2.79 per gallon in bulk to $4.65 per gallon in bottles. The Department of Energy created a website, www.finddef.com, to point users to retail locations that sell DEF.

The use of urea-based SCR conversion systems not only has a direct effect on NO_x emissions, but data from the Environmental Protection Agency suggest that it has had an indirect effect on carbon dioxide emissions. Because the SCR systems are performing the bulk of NO_x reduction, diesel engines can now run at higher fuel efficiencies, which reduces carbon dioxide emissions. At light and moderate engine loads, engines equipped with urea-based NO_x control systems will have a greater than 10 percent advantage over engines equipped with other NO_x control systems. Urea-based systems are now used on the majority of diesels sold starting in 2010.

Summarizing the impact of medium-duty diesel vehicles on platinum-group metal utilization, Lambert said that volumes have increased since 2005 because of more stringent emissions standards, but the move in 2010 from an all-platinum catalyst to a palladium-rich catalyst has dropped platinum use close to 2007 levels. Diesel engines still use more platinum than in comparable gasoline-powered medium-duty trucks, but that gap is shrinking.

Looking to the future, Lambert noted that adding an SCR to other lean NO_x catalyst components may enable further advances in the development and adoption of lean-burn technologies for gasoline engines that lower or eliminate the need for platinum-group metal catalysts (Xu et al., 2010). However, adopting SCR technologies for use with gasoline engines will require lowering the sulfur content of gasoline from its current 80 ppm to 15 ppm or developing technology that removes sulfur from the exhaust stream prior to the SCR unit.

Research is also aimed at boosting NO_x oxidation activity of palladium to continue the trend of replacing platinum with palladium as a cost-reduction strategy. Toward this end, researchers at General Motors have developed a platinum-free perovskite catalyst that rivals the performance of a platinum-based catalyst at reducing NO_x levels under lean-burn conditions (Kim et al., 2010).

DISCUSSION

In response to a question about the role of theory in his work on electrocatalysts, Bullock said that theory and computational models were very helpful in providing insights into how these reactions work and increasing confidence that postulated intermediates in proposed mechanisms really existed. Theory has not yet reached a point where it can predict which molecules to make from the ground up, but theory has been very helpful in understanding energy potentials, reaction intermediates, and step-by-step mechanisms.

With regard to the synthetic complexity and cost of the ligands used with cheap metal catalysts, Bullock acknowledged that these are important issues. He added, though, that the ligands developed at PNNL, despite their apparent complexity, are easy to make in a two-step synthesis from simple starting materials.

He also noted that the cheap metal catalysts developed so far for organic synthesis have not yet achieved turnover rates comparable to palladium-based catalysts. He hoped that industry would now step in and take the catalysts developed in academia and make the improvements needed to create commercially viable catalysts based on cheap, abundant metals.

Finally, Bullock pointed to the importance of being open to unusual and unexpected results. Past examples of such advances should be kept in mind so that novel and important results are not ignored because they are so different from past findings.

Lambert was asked about the high-sulfur marine diesel used in many parts of the world, and she noted that vanadium-based catalysts are highly tolerant of sulfur, but currently they lack the necessary temperature stability. Improving that stability could be a fruitful avenue of research, and in fact a number of catalysts have been developed. She added that there is little commercial pressure for such a catalyst because regions of the world that use high-sulfur diesel fuel do not have stringent standards for particulate matter.

In response to a question about what happens when a vehicle runs out of urea, Lambert replied that the vehicles are designed to run at slower speeds, which frustrates drivers and provides an incentive to refill the urea containers on the vehicles.

Lambert pointed to an increase in research on batteries and electric vehicles at Ford and elsewhere. But she also said that "the internal combustion engine is not dead." Fundamental research still needs to be done on exhaust gas emissions even as electric vehicle technologies advance.

5

Optoelectronics and Photovoltaics

Beyond their use as catalysts, critical materials have widespread applications in other technologies, including technologies that could undergo rapid expansion in the future. Many critical elements are used in the display and solid-state lighting (SSL) industries. They also are components in many photovoltaic technologies, which are expected to undergo continued rapid growth. Several speakers noted that research to reduce the quantities of these materials needed in new technologies is important, but so is the development of new supplies and improved refining and recycling capabilities.

CRITICAL MATERIALS IN OPTOELECTRONICS

Rare earth elements are used widely in the field of optoelectronics. Europium is a key element in red phosphors, mostly in the form of europium-doped yttrium oxide. Erbium-doped fiber amplifiers are critical components in fiber optics, and erbium, neodymium, and holmium are important dopants in yttrium aluminum garnet (YAG) lasers. White light-emitting diodes (LEDs) will soon be the predominant user of indium in terms of volume, though ITO will continue to find use in the photovoltaic, display, and SSL industries. Chelated heavy metal and rare earth metals, such as palladium, platinum, iridium, and europium, also are used in the display and SSL industries.

Some Lesser Known Facts About Critical Materials

Though it was noted earlier in the workshop that the rare earth elements are not all that rare, what is not widely appreciated, said Joseph Shinar, is that there is only a rough correlation between abundance and price. If the correlation was strong, iridium would be two orders of magnitude more expensive than gold, while in fact it is hardly more expensive at all.

As was shown in Figure 2-5, the rare earth elements are reasonably abundant; they lie between the 25th and 75th percentile in terms of natural abundance, with cerium being the most abundant rare earth and lutetium the least. Quoting Gschneidner (2011), Shinar noted that rare earth elements are found all over the globe, not just in China, which holds about 31 percent of the known reserves. In fact, the United States has one of the historically highest-grade deposits in the world, located at Mountain Pass, California.

In 1970, China possessed 75 percent of the known rare earth reserves, referring to yttrium plus the lanthanides. At that point, China demonstrated a strong presence in the rare earth market. However, in the 40 years since then, China's share of the world reserves of these elements fell to about 30 percent as new deposits were discovered even though China grew its reserves through discovery by some 290 percent (Gschneidner, 2011).

Recently, said Shinar, China changed its policies, introducing production quotas, export quotas, and export taxes; enforcing environmental legislation; and refusing to grant new rare earth mining licenses. In addition, China announced it will no longer export rare earths because of rapid growth of internal markets and limited reserves, especially the heavy rare earth elements gadolinium through lutetium. As a result, the price for rare earth materials and products containing rare earth has risen to the level at which mining companies and producers outside of China can make a profit. In 2009, estimated non-Chinese production of rare earth oxides was 4 kilotons (Gschneidner, 2011). Also, the smuggling of rare earth elements from China appears to be an important source of these metals, Shinar said.

Another unappreciated fact about the rare earth elements is only about 57 percent of the cerium produced today is used. The reason for this is that cerium must first be removed from rare earth flow streams before the other elements can be isolated via a countercurrent liquid-liquid extraction process. As a result, cerium is overproduced by about 50,000 tons per year and must be stored at a real cost (Gschneidner, 2011). As expected, the rare earth industry would welcome new large cerium applications, but so, too, would all other users of rare earth elements because a balanced cerium market would significantly reduce the prices of the other rare earth elements.

Shinar observed that rare earths can be separated into three categories—surplus, balanced, and tight. Only neodymium, terbium, and dysprosium fall into the tight-supply category. Other than cerium and holmium, which is actually one of the rarest of rare earth metals, supplies and demands for the other rare earths are well balanced. It is also important, he added, to remember that the proven reserves of rare earths are growing rapidly.

The solution to the expectation that supplies will become tight as a result of China's new policies is to increase mining, Shinar stated. That, in fact, is happening because MolyCorp is investing in reopening and expanding its operations at Mountain Pass. Workforce training also will be important.

One lesser-known fact about the critical elements is that the supply of ITO, the quintessential transparent conducting material, is totally dependent on zinc production, and the demand for zinc is not expected to grow much in the future because of macroeconomic factors in China, Canada, Korea, and Japan. Annual production of indium is approximately 900 tons, with primary production of 600 tons and recycling and stockpiles providing the rest. Recycling occurs primarily through removing the thin ITO layer coated on glass used in LCD monitors, flat-screen televisions, and other display devices.

Demand for ITO, which accounts for 85 percent of all indium demand, is expected to grow by 15 percent per year over the next 3 years. Emerging uses are in copper-indium-gallium-selenium solar cells, electrode-less lamps, mercury alloy replacements, and nuclear reactor control rods. Though indium prices are much the same as they were 5 years ago, the price has spiked thanks to China's recent crackdown on small lead and zinc refiners amid environmental concerns.

Critical Metals

Shifting his focus from the general to the specific, Shinar spoke next about europium red phosphors, particularly europium-doped yttrium oxide, or yttria. Europium accounts for about 0.3 percent of mined rare earth metals, and the demand of about 400 tons of oxide per year is balanced by supply. Yttrium represents 6 percent of mined rare earths, and its supply and demand are balanced as well, at about 8.5 kilotons of oxide per year.

"The main use of red phosphors is as the R in RGB," said Shinar. He explained that ytrium doped with 4 to 6.5 percent europium produces an intense red phosphorescence at 611 nanometers (nm) (Sylvania, 2010). "Even though RGB monitors and televisions are soon going to be found only in museums, red phosphors are still used extensively in compact fluorescent lamps (CFLs). And hot on the heels of CFLs are white LEDs for solid-state lighting." But even though the demand for europium and yttrium will continue to grow, proven reserves of these metals are outpacing expected increases in demand.

Erbium accounts for about 0.5 percent of mined rare earths, and the demand of 700 tons of oxide per year is balanced with supply. Erbium is used as a colorant and as a stabilizer for zirconium in jewelry, but its most critical use is in the repeaters used in optical fiber networks that operate with a carrier wavelength of 1.5 microns. These repeaters, which are optically pumped lasers, are incorporated into fiber networks every few kilometers to boost the optical signal. Shinar noted the demand for these lasers may slowly wane as wireless communications steadily grow.

A niche application for rare earths is in neodymium, erbium, and holmium-doped YAG lasers. YAG lasers, which are very robust, efficient solid-state lasers, are staples in optical electronic labs and are used extensively in spectroscopy and ultrafast spectroscopy. Holmium-doped YAG lasers also are used extensively by urologists in laser lithotripsy. Though these are niche applications, they are critical ones nonetheless. Of the three rare earths used in these lasers, only neodymium is in tight supply. Though it represents 16 percent of mined rare earth oxides, it is used extensively in the neodymium-iron-boron magnets incorporated in wind turbines. Of the 23 kilotons of neodymium oxides mined, 2.8 kilotons go into wind turbines alone. Holmium represents about 0.1 percent of mined rare earth oxides, and its supply of 100 tons of oxide per year exceeds demand.

Indium demand is expected to grow rapidly with the development of what are called indium group II-V devices for use in the street lighting market. These devices, which are based on new technology for growing high-quality indium-doped gallium nitride, are superior replacements for fluorescent and high-pressure sodium lamps in overhanging street lights. The City of Anchorage, Alaska, estimates that replacing 25 percent of its streetlights with these new lamps will reduce energy costs by 50 percent and save the city some $360,000 per year. In addition, maintenance costs should drop given that these bulbs have an expected lifetime of 100,000 hours—over 11 years—compared with 5,000 hours for fluorescent and high-pressure sodium lamps. Perhaps more importantly, the new lamps improve visibility dramatically because of superior color rendering.

Indium is also used in ITO photovoltaic devices, displays, and SSL industries. Shinar focused his remarks on organic LEDs (OLEDs), which first appeared in a commercial product in 1998 and is now making major inroads in display devices. In 2007, Sony introduced an 11-inch OLED television, but at a cost of $2,500 it was not a big selling item. Since then, at least one company announced it was introducing a much bigger OLED television, but it has yet to appear on the market. OLED displays can have contrast ratios of 1,000,000:1, but LED technology has not been standing still, and experts continue to argue about which technology produces better displays.

One application of OLED with great potential in the market is the use of white OLED (WOLED) in lighting panels. Potentially, these devices can be more efficient than fluorescent lights and produce more accurate color rendering. In addition, WOLED devices can be flexible and can even become mirrors when turned off. Today's state-of-the-art devices produce 87 lumens/watt (lumens/W) at 1,000 candelas/m^2. The goal is to produce devices that generate 300 lumens/W.

ITO is essential to all of this work because it is the preferred transparent conducting electrode in thin-film photovoltaics, and it is the only transparent conducting electrode in all LCDs and OLEDs. Researchers are making advances in developing transparent zinc oxide and aluminum oxide electrodes, but those efforts are not yet close to producing a commercially viable product.

One of the most promising alternatives is poly(3,4-ethylenedioxythiophene): poly(styrenesulfanate) (PEDOT:PSS). Though this material has been studied for over 10 years, the recent development of a fabrication process that creates multilayered PEDOT:PSS devices has produced a breakthrough in organic photovoltaic and OLED performance (Kim et al., 2011). The new process involves blending these polymers with polyethylene glycol (PEG), immersing the blend in PEG, and then annealing. Even though transmission goes down with each additional layer, sheet resistance also goes down, and that, said Shinar, is important. These PEDOT:PSS sheets are smoother than ITO, which is good for OLEDs, and their refractive index is lower, which reduces internal reflection and increases light output.

In fact, said Shinar, multilayer PEDOT:PSS OLEDs are up to twice as efficient as a standard ITO OLED. And in more recent work, which his group has not yet published, a two-layer PEDOT:PSS OLED produced a maximal luminous power efficiency of 100 lumens/W without coupling enhancement tricks. "With microlens arrays, which typically can double the out-coupling enhancement, these devices would be beyond 200 lumens/W," said Shinar.

It is important to remember, though, that ITO devices are a moving target with continually improving performance. Recently, for example, chlorinated ITO-based OLEDs showed impressive efficiencies (Helander et al., 2011). The power efficiency reported for these devices exceeded 200 lumens/W, which is approaching the Department of Energy's goal of 300 lumens/W. Not too long ago, this was considered a pipe dream, said Shinar. The external quantum efficiency for chlorinated ITO is "an amazing 53 percent," he added. "For every two electrons you inject into the OLED you get one photon out, and not just out, but in the direction you want."

Heavy Metals

Shinar noted that heavy and rare earth metal atom chelates, using palladium, platinum, iridium, and europium, are going to continue to be important in the display and SSL industries because they produce the best phosphorescent emitters. As he explained, "In all OLEDs, injection into the emitting layer results in 25 percent singlet excitons and 75 percent triplet excitons, and in fluorescence only the singlet excitons are radiative." As a result, the maximum internal quantum efficiency is only 25 percent. Heavy metal chelate-based phosphors, however, are radiative with triplet excitons, so their use is critical to achieve high internal quantum efficiency for any OLED device.

In fact, when researchers from the Universal Display Corporation successfully fabricated phosphorescent OLEDs using heavy metal chelates, they boosted internal quantum efficiencies into the 90 to 100 percent range. This success, said Shinar, explains why this company is now worth between $500 million and $1 billion.

Shinar noted that iridium, because of its use in these phosphors, should be considered a critical metal. It is the least abundant of the platinum-group elements, yet today it is priced lower than gold. Major commercial sources of iridium are found in South Africa, Russia, and Canada. Iridium is difficult to refine and is produced in small quantities, but supplies have increased in response to a four-fold increase in demand to 334,000 ounces in 2010, largely a result of the inclusion of iridium crucibles in backlit LED televisions and the increased demand for iridium-tipped automobile sparkplugs. "The sharp increase in demand and the small, relatively illiquid market for iridium had a significant impact on price," said Shinar. In August 2011, iridium was priced at $1,050 per ounce (eBullionGuide.com, 2011).

Efforts to develop room-temperature phosphors free of heavy metals have begun, but the best results so far still fall short of the mark. Shinar wondered if more research in this direction should be initiated. One possibility would be to exploit triplet-triplet annihilation to produce singlet excitons that could increase the internal quantum efficiency well beyond 25 percent.

In closing, Shinar noted that "for optoelectronics, the critical in critical resources is questionable. There is no single silver bullet because the situation has improved, and instead there are many potential silver bullets for different problems."

KEY MINERALS IN PHOTOVOLTAICS

One reason that PV technology is such an exciting area today, said Ken Zweibel, is that solar energy is such an abundant resource (Figure 5-1). The sheer size of the solar energy "reserve" dwarfs all other potential sources of renewable energy and is more than an order of magnitude larger than all coal, uranium, petroleum, and natural gas reserves combined.

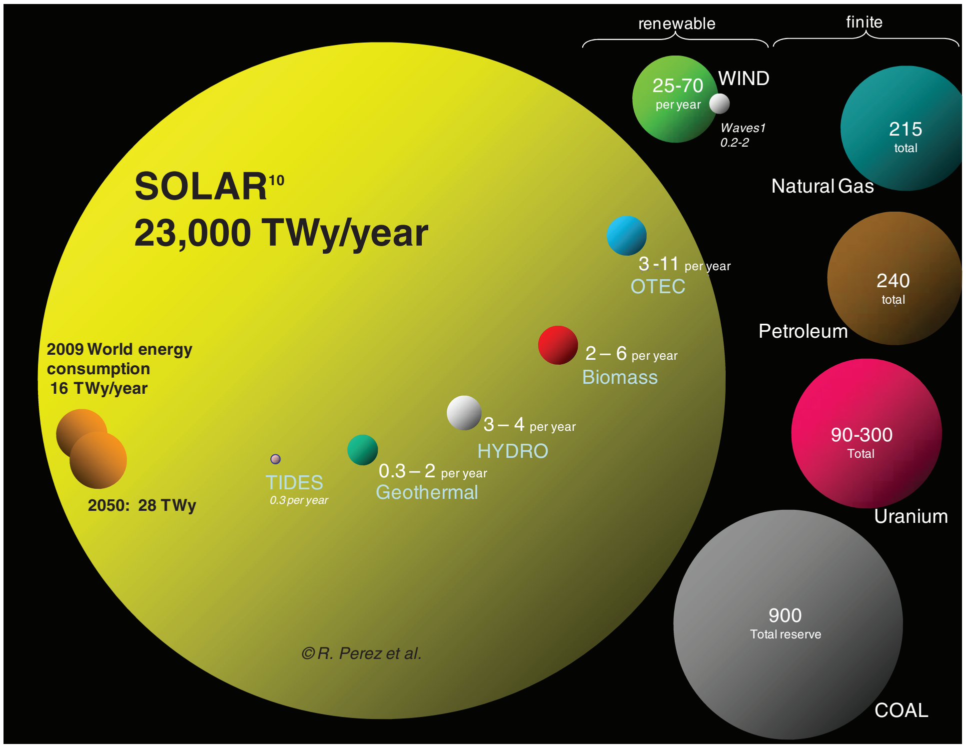


FIGURE 5-1 Solar energy dwarfs all other sources of renewable and finite energy sources.
SOURCE: Perez (2009); Perez et al. (2011).

Furthermore, an important characteristic of solar energy has been its historical reduction in price, Zweibel explained.

A plot of the price of the global average solar energy power module in constant dollars versus cumulative sales shows a consistent relationship from 1976 to 2009 (Figure 5-2).

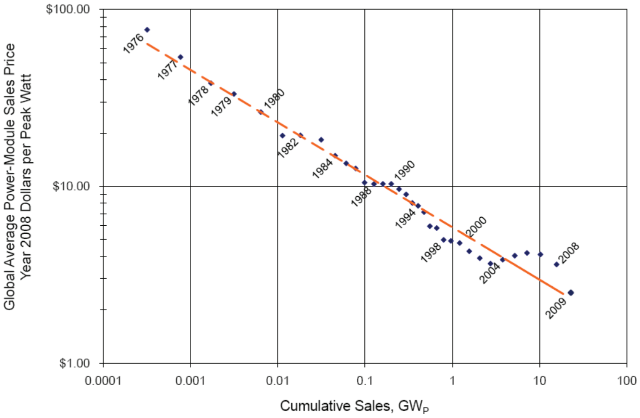


FIGURE 5-2 Between 1976 and 2009, the price of solar energy power modules has declined as cumulative sales increased as a result of aggressive pricing for market share.
SOURCE: Paula Mints, Principal Analyst, Navigant Solar Services Program, March 8, 2010.

Over 35 years, each doubling in sales volume has produced a 20 percent drop in price. Today, said Zweibel, “prices are dropping like a stone, with the cost now down to $1.30 or $1.40 per watt for the modules, whereas only a few years ago, it was closer to $3 per watt.”

At the same time, worldwide photovoltaic module production has risen exponentially over the past decade, with China’s entry into the market providing a huge boost in world output. In large part because of increased production from China, output nearly doubled in 2010. China first entered the market in 2006 and now accounts for over half of the world’s production of PV modules. Chinese production has grown so quickly that prices worldwide have plummeted. As a result, margins are now very thin, and many PV module manufacturers, including those in China, are facing financial difficulties.

The beneficiaries of the plummeting cost of PV modules are those who install PV systems, and as production has increased so has the number of PV installations (Figure 5-3). In 2010 alone, the total peak megawatts installed more than doubled, with Germany leading this dramatic uptake in PV use. In 2011, growth in the amount of PV installed returned to more normal levels, which accounts for the glut in supplies.

In terms of cumulative installations, PV now produces about 40 gigawatts (GW) of power worldwide. Growth in output is similar to that seen decades earlier when natural gas

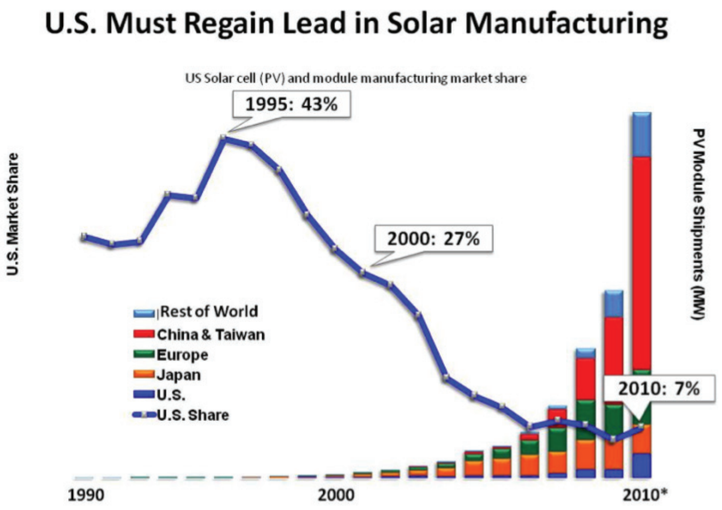


FIGURE 5-3 Production of photovoltaics has exploded over the past decade. (Consider U.S. solar cell (PV) and module manufacturing market share.)
SOURCE: PV News and Navigating Consulting, http://energy.gov/articles/competition-worth-winning [accessed December 22, 2011].

and nuclear power started becoming significant components of the energy infrastructure.

Germany, said Zweibel, is a special case and is far ahead of every other country in the world in terms of PV uptake. PV now supplies about 10 percent of peak energy use in the middle of the day, or about 3 percent of the country's total energy usage. Using comparable measures, wind provides about twice the total amount of power as solar does in Germany.

Photovoltaics are semiconductors operating at about 10 percent efficiency. It takes 10 km^2 of PV to produce 1 GW of power. For thinner PV modules, that translates into 10 cubic meters of crystalline silicon per gigawatt of power.

The Department of Energy's Solar Vision calls for PV to account for 10 percent of U.S. electricity output by 2030, which would be approximately 600 GW, compared to today's output of around 20 GW. The International Energy Agency predicts that solar will generate 50 percent of the world's electricity by 2050, though Zweibel found this figure hard to accept.

Meeting Future Demand

Zweibel listed a number of key technologies that will play a major role in the future growth of PV as an electricity source. Crystalline silicon currently holds about 90 percent of the market, with cadmium telluride accounting for the remaining 10 percent. Emerging and promising materials include copper indium selenide alloys with gallium and sulfur, and type III-V multi-junction semiconductors for concentrator-containing solar cells. Commercially viable but less competitive are amorphous and thin-film silicon on glass. Emerging technologies that are less assured of success include organic dye-based "Graetzel" cells and plastic cells.

The most important materials that are needed to produce solar power today include silicon, silver, tellurium, and cadmium, with steel, aluminum, and copper being used in the contacts and housings and other bulk components. Emerging technologies could require significant quantities of indium, selenium, molybdenum, gallium, germanium, arsenic, and ruthenium. Many other metals, such as nickel, zinc, and tin, are used in minor amounts.

There are a number of bottlenecks. For example, the risk and timing of investment, including the unpredictability and rapid alteration in demand, have led to silicon shortages. "Because of the capital cost for making purified silicon, there was a time when the silicon purification industry was out of sync with the demand from solar," said Zweibel. The demand for silicon by the solar industry is now larger than the demand from all the other semiconductors in the world. "That transition was hard for traditional silicon purification companies to grasp."

Other bottlenecks involve extraction of the elements needed to meet growing demands from the solar industry. If there is not enough of a particular element available to meet the immediate or short-term future demand, it may not be economically feasible to increase extraction in a timely manner. Similarly, there may not be refining capability to meet increased demand, or it may not be economical to refine ores with low concentrations of the needed element. Finally, supplies may exist, but they may not be accessible for purchase because of market or political forces.

Specific materials have unique issues. The availability of coated glass substrates has been a problem for short periods of time. Materials such as tellurium used in cadmium telluride, indium used in copper indium selenide alloys, and gallium could have price and supply issues at mid- and long-term time frames. Of these, indium is also used in significant amounts in liquid crystal displays.

Today, materials such as tellurium, indium, gallium, molybdenum, and selenium add between \$0.002/W to \$0.03/W to PV costs, with silver adding \$0.09/W, numbers that Zweibel characterized as being small. However, the costs of each of these materials can rise dramatically in response to even small changes in supply and demand. Given that \$0.10/W to \$0.20/W separates the best PV modules from the least competitive modules, changes as small as \$0.03/W can be significant. "Something that goes from 3 cents to 15 cents per watt could be prohibitive," said Zweibel.

Using Less Material

There are various strategies for reducing the amount of material needed to produce electricity. One approach is to use thinner layers of material, though that reduces the amount of light absorbed. That problem can be solved by adding backside mirrors, which can enable the thickness of the semiconductor layer to be reduced in some cases by a factor of 10.

Boosting device efficiency reduces the amount of material needed. Doubling the efficiency of a device means using half of the material to generate the same amount of electricity. Recycling, both internally in terms of manufacturing waste and externally as far as recovering materials from old modules, can have a significant impact on supplies.

Already, such strategies have played a role in reducing material demands from PV manufacturing. For example, the cadmium telluride layer has been decreased from 3 microns to 0.67 microns with little difficulty in light absorption. Thinner copper indium selenide alloys—0.75 microns compared to 2.0 microns—have reduced demand for indium, selenide, and gallium. Silver replacements are now being tested, and Zweibel predicted that silver will be replaced eventually in PV modules.

By 2030, such efforts could reduce the per-watt demand for rare metals. Zweibel predicted that tellurium use could drop from 100 to 16 metric tons/GW. Indium usage could drop from 30 to 9.4 metric tons/GW. Gallium usage could fall from 8 to 2.3 metric tons/GW.

Although such reductions are important, demand will nonetheless soar if the world truly meets the goal of getting 10 percent of its electricity from PV. Reaching this goal implies 600 GW/year annual production, which would require 10,000 metric tons of telluium per year, compared to 120 metric tons used today. The total availability of tellurium is about 2,000 metric tons per year today. Indium use would reach 6,000 metric tons per year, gallium 1,500 metric tons per year, molybdenum 18,000 metric tons per year, and selenium 9,600 tons per year.

Research may yield solutions to these impending supply problems, Zweibel said. If not, the most important recent commercial PV technology—the development of cadmium telluride—will have an uncertain future because of tellurium availability. In addition, the most important emerging commercial technology—copper indium gallium selenide—will have an uncertain future because of indium, selenium, and gallium availability. It is essential, he said, to find new supplies and develop new refining capabilities for tellurium and indium. Otherwise, all scenarios to meet demand for PV will be highly challenging. "The lack of U.S. commitment to extraction and refining inside our borders is a concern for U.S. PV competitiveness," Zweibel concluded.

DISCUSSION

In response to a question about the role of chemistry in developing new materials, Shinar said that chemistry lies at the heart of developing WOLEDs and OLEDs, since each of these devices depends on complex organic chemistry and polymer chemistry. As an example, he said that chemists have been studying polyanilines as transparent conducting organics and are trying to solve stability issues. The problem is not that chemists do not want to work on developing these materials but that there is not much funding available to do so. In terms of inorganic materials, research is proceeding slowly, and these materials are hard to develop.

In response to a question about potential environmental issues associated with the widespread use of cadmium, Zweibel said that, because the manufacturers take the modules back at the end of their lifespan and recycle all of the cadmium telluride, the system is actually a closed loop. Also, cadmium telluride is much less dangerous than cadmium. For those reasons, there has been no backlash against the use of very thin, very stable layers of cadmium telluride in PV.

Zweibel replied to a question about the impact of the dramatically lower price for silicon cells on the technology development by noting that copper indium selenide technology is already suffering a good deal of push-back because it has to make price goals that have moved down so quickly. He added that, although he once thought that thin films would dominate the future of PV, "I no longer think that, and I would say that it is going to be a horserace for the next 20 years."

In response to a question about mining bismuth telluride as a significant source of tellurium, Zweibel noted that there are places in the world where this mineral is accessible and where the tellurium is highly concentrated, as high as 17 percent in at least one instance. These deposits are likely to change the supply issue dramatically when the current production sources—copper, zinc, lead, and gold mining—start proving inadequate. He noted, too, that tellurium is the most abundant metal in the universe with an atomic weight over 40 Daltons, even though it is depleted in the Earth's crust (Cohen, 1984). There are large deposits in undersea ridges, and some companies are starting to show interest in undersea mining at these ridges, which are rich in many other materials as well (Hein et al., 2001).

In response to a question about the role of chemistry in developing new materials, Zweibel said that chemists play a critical role in two areas. In the development of mainstream PVs, the most effective researchers in this area are chemists. It is chemists who develop the understanding of how materials behave during processing and about the fundamental behavior of the materials themselves. The second area where chemistry is important is in manufacturing, which is really a chemical engineering problem and relies heavily on the knowledge of chemical engineers.

When asked about installation costs, Zweibel said that large-scale installations are largely mechanized and that the cost per watt can be as low as $0.20/W out of a total cost of $2.50/W to $3.50/W, with the module's cost running at $1.00/W to $1.50/W. For residential applications, installation costs are higher. The Germans have worked out the most efficient installation methods, and their costs run about $1.00/W to $1.25/W with total system costs at $3.50/W. Residential installation costs also run higher because of the soft costs involved, such as marketing and sales. He noted that the United States can learn much from the German experience.

Finally, when he was asked about the role of chemists in the development of photovoltaics, Zweibel said that they are at the center of that process, despite the substantial involvement of electrical engineers, physicists, and others. It is "important to understand how that chemistry happens both in terms of the processing and in terms of the nature of the material itself." Chemists also are needed in the large-scale manufacturing of photovoltaics, which is very dependent on chemical engineering. "Chemists are really the heart and soul, to a great degree, of this technology and of photovoltaics."

6

Critical Materials in Large-Scale Battery Applications

The amount of energy that can be stored by a battery depends on the specific battery technology being used and on the amount of material in the battery. For large-scale battery applications, therefore, such as storage of energy for grid-scale applications, the availability of battery materials is critical. However, other factors are also important, such as processing costs, battery assembly, and the cost of secondary components.

The integration of batteries into the energy supply system on a large scale is ultimately a systems problem that involves processing, structure, properties, and performance of materials with considerations of cost, policy, and environmental impacts. Furthermore, the system is so large that it will take at least a decade or two for a new technology to mature and have a significant impact.

CRITICAL MATERIALS FOR BULK ENERGY STORAGE

"Grid-scale energy storage is considered to be the holy grail for electricity storage," said David Bradwell. "Whether it's supporting conventional resources such as nuclear, solar, or wind, there is a great demand to have storage on the grid in order to balance electricity supply and demand."

The current electrical grid supplies power in real time in response to demand. When demand increases, output must increase. As demand changes throughout the day, generators ramp up and down to meet that demand. When supply and demand become decoupled, the result can be catastrophic failure, as was the case with the 2003 blackout that affected millions of people in the northeastern United States. When a few generators went down, there was no buffer in the system to account for the sudden decrease in supply.

Energy storage can act as a buffer on the grid. It can smooth out the power from intermittent renewables, such as solar and wind, and it can match the supply from generators on the grid powered by nuclear energy, natural gas, and coal.

Power, Energy, and Material Constraints

There are two important considerations for energy storage: power and energy. Power, Bradwell explained, is a surface area effect. To produce more power from solar cells requires a larger surface area of photovoltaics to capture more light. There are other ways to capture more light without changing surface area, such as with concentrating mirrors or changing the thickness of the semiconductor layers, and those approaches to optimizing the use of a given amount of surface area can have a significant impact on the amount of active material required to produce a given amount of power. New materials, such as cadmium telluride, also play a role in the amount of material required to produce a given amount of power.

Energy is a function of volume. Battery storage capacity is directly related to the amount of active material used. "If you want to store a lot of energy in a battery, you need a lot of active material," said Bradwell. "There is no way to get around it. There is no opportunity for optimizing the amount of material used with battery storage."

As a result of this basic limitation, it is important when thinking about battery storage on the scale needed for energy grid applications to consider the various constraints regarding battery materials. A major constraint is the abundance of a given material on Earth, as described in previous talks. For example, iridium might prove to be a great battery material, but its low abundance rules it out as a real candidate for large-scale battery applications. The same holds true for tellurium, for which some phenomenal battery chemistries exist. On the other hand, lithium's crustal abundance is quite high, as is that of magnesium and antimony, two materials that also hold promise in battery technology.

The scale of production, the reserve base, and the cost also can be limitations. Focusing on three specific chemistries—sodium sulfur, lead oxide or lead acid, and lithium iron phosphate—Bradwell explained that it is important to look not just at raw material costs, but at total battery costs. The elemental cost of sodium sulfur is tiny, less than $0.10/kilowatt-hour (kWh), whereas that for lead acid is much higher, between $10 and $30/kWh, and lithium iron phosphate costs come in around $1/kWh. Looking at the total cost of the battery paints a different picture. Sodium sulfur batteries cost $300 to $500/kWh, while a lead acid battery costs between $100 and $300 kWh and a lithium iron phosphate battery costs between $300 and $1,000/kWh (Wadia et al., 2011). The Advanced Research Projects Agency-Energy goal is $100/kWh (Figure 6-1).

Electrode material costs are not the only driver of battery cost. Processing costs to produce high-purity starting materials, battery assembly, and the expense of secondary components such as the electrolyte, current collector, current lead, housing, and safety features can be important cost factors. High-purity sodium and lithium iron phosphate are expensive to produce. In contrast, if the cost of lithium were to increase by a factor of 10, it would have little effect on the price of a lithium battery, said Bradwell.

Supply issues can be a concern. The United States has substantial reserves of lithium brines, and China, Canada, Brazil, and Australia have reserves of lithium carbonate. Bolivia has the largest resources of lithium brines, but their profitability is uncertain. There are strategic concerns about lithium supplies, but lithium ranks at the low end of supply risk in terms of minable reserves.

"Cost and natural abundance alone do not appear to be major limitations for lithium," said Bradwell. "There are opportunities for better understanding the system and the processing costs and materials. In the academic world, people get very excited about making something that works and works well, but for these broad-scale applications, we should be thinking about assembly, processing, manufacturability of the system, and scalability." He added that there is an opportunity for possible collaboration between those who are inventing the chemistries and batteries and the experts who could ultimately help build and deploy these systems.

New approaches to making batteries can use lower-cost processes and assembly methods. In addition, it may be possible to develop batteries that use lower-purity, and therefore lower-cost, materials. There may also be ways of improving lithium extraction processes to enable the use of lower-quality ores or brines.

Grid-Scale Storage

While the conventional metrics for battery storage are energy density and power density, the key metrics for grid-based storage are cost, lifespan, and energy efficiency, said Bradwell. Looking at energy density, lithium and sodium sulfur batteries score well, while pumped hydroelectric power compares poorly. However, for grid storage, pumped hydro dominates (Figure 6-2) because of its low cost to deploy, long lifespan, and its greater than 70 percent efficiency. Bradwell noted that there is a nice relationship between the cost of a technology and its deployed capacity. At a cost of between $100 and $200/kWh, adoption takes off.

Other promising battery technologies include flow batteries, magnesium batteries, and zinc manganese oxide batteries. Lead acid batteries, a technology that has been around for a long time, also have the potential to contribute to grid-based storage.

Challenges must be solved for all of these new battery chemistries. Dendrite formation, a particular problem with zinc batteries, occurs when metal is deposited on a battery electrode, extends across the electrode, and eventually shorts the battery. Electrode cracking and deterioration is still a challenge that arises when material intercalates within the structure of the electrode. This is a major mechanism for electrode failure in batteries. Nanostructured materials may solve this problem, but these materials are more expensive to use.

Interfacial film growth caused by the slow reaction with electrolytes is another major challenge. The electrolyte in a

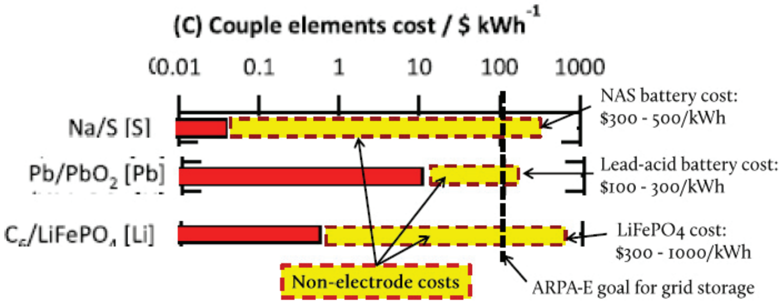


FIGURE 6-1 Costs of raw electrode material affect final battery costs.
SOURCE: Adapted from Wadia et al. (2011, p. 1596, in Bradwell 2011a).

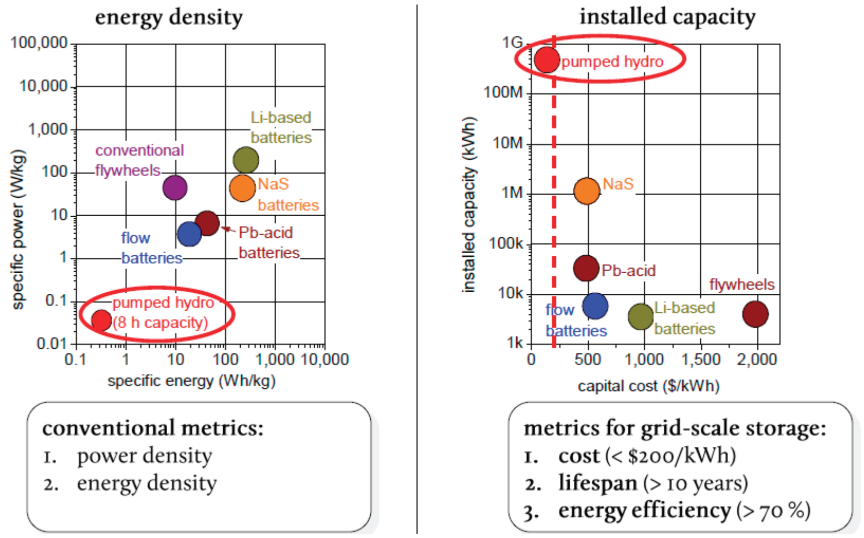


FIGURE 6-2 Grid-based energy storage technologies have different energy densities and installed capacities.
SOURCES: ESA (2010); Bradwell (2011b).

lithium battery is actually unstable. It reacts with the electrode and forms a layer on the surface of the electrode that grows slowly. The layer is necessary for battery performance, but it should be stable. As the layer grows, it increases the battery's impedance and lowers performance.

Flow batteries are an interesting technology in which energy is stored in an electrolyte that is pumped across a membrane surface. Fuel cells are getting increasing attention, but efficiency is the big challenge there. Lithium battery efficiencies reach 90 to 95 percent, while the round-trip efficiency on a fuel cell is typically closer to 50 percent. What is encouraging, said Bradwell, is that most of the new approaches that researchers are pursuing use Earth-abundant materials such as zinc, magnesium, lithium, manganese, sodium, and lead. Very few of the new chemistries use resource-constrained materials.

In his work, Bradwell took inspiration from the metals industry's experience that prices drop as production increases and that prices drop more when materials are processed as liquids. "Both iron and aluminum are produced as liquid metals [that are] handled and processed in a continuous manner, which also keeps the costs low," said Bradwell. "In particular, the aluminum smelter was the inspiration for the liquid metal battery project."

An aluminum smelter is a huge electrolysis machine that works as follows: aluminum oxide is poured into a layer of molten cryolite, which at 960°C is so corrosive that it dissolves aluminum oxide and dissociates it into aluminum ions and oxygen ions. A 700-milliampere/cm^2, 4-volt (V) current is passed from cathode to anode, which oxidizes aluminum ions to liquid aluminum. This pools underneath the electrolyte and reduces oxygen to carbon dioxide, which is vented to the atmosphere. Though a simple reaction in theory, it proved to be difficult to carry out in practice. Before this process was developed, aluminum was more expensive than gold.

In essence, Bradwell explained, an aluminum smelter is half of a battery that cannot be recharged because it generates a gaseous product that cannot be reclaimed. The solution was to replace this gaseous component with another liquid metal. In the liquid metal battery, an electropositive liquid metal is separated from an electronegative metal by a liquid electrolyte. The three liquids self-segregate based on contiguous immiscibility between the metal and electrolyte layers. The battery operates at high temperature, though less than that of an aluminum smelter, and uses low cost materials. The aluminum industry's experience suggests that the electrodes will have a 5- to 10-year lifespan before they need refurbishing.

The first generation battery he and his collaborators built used liquid magnesium and antimony as the two electrodes. At low current densities, this battery was 74 percent efficient, with a coulombic efficiency—a measure of self-discharge—of 99.7 percent per cycle. The voltage of this initial battery was low, only 0.5 V compared to 3.5 V for a lithium-ion battery. Fundamental research and chemical development efforts have raised the output to 0.9 V, which is still low but sufficiently high to continue work on this system, and coulombic efficiency has increased to greater than 99.9 percent. Projected costs for such a battery would be less than $100/kWh. Bradwell acknowledged that a significant amount of work needs to be done on failure mechanisms, chemistry optimization, scale-up, and systems engineering.

Semiconductor Recycling

During the course of developing the liquid metal battery, Bradwell and his collaborators came up with a new method for recycling or reprocessing intermetallic compounds such as tellurium. While running electrochemical experiments on molten zinc chloride, the researchers noted that, under an applied potential, zinc would start depositing on one of the electrodes, with the corresponding release of chlorine gas. This is standard electrochemistry and not a surprise, but when they added zinc telluride to the system, experimental data showed that tellurium was dissolving as an anion, a totally unexpected finding because metals usually dissolve as cations.

This finding prompted Bradwell and his colleagues to develop a system for producing zinc and tellurium from zinc telluride, which while interesting is not relevant to anything practical because zinc telluride is not widely used. Cadmium telluride is, however, so the researchers created a method for taking cadmium telluride manufacturing scrap and converting it into high-purity cadmium and tellurium. This is not a technology relevant to batteries, he said in closing, but it could play a role in addressing concerns about tellurium supplies.

ALTERNATIVE MATERIALS FOR ENERGY SYSTEMS

Energy policy, said Jay Whitacre, can be represented as a polyhedron that connects characteristics subject to research and development such as structure, processing, properties, and performance with considerations of cost, policy, and environmental impact (Figure 6-3). If the field does not address issues of cost, policy, and environmental impact as part of its research on characteristics, the impacts of new energy technologies will be small.

When considering whether a new technology has market potential, Whitacre makes two assumptions specific to materials-intensive energy technologies. The first assumption is that cost is everything. To have an impact, projects must be huge, particularly given that the goal is to alter the way that the world consumes or distributes power and energy. This is a tremendous materials challenge, and not just with the cost of the materials. Other costs include the capital to manufacture these new technologies, the cost of production throughput, operational expenditures, transportation costs, and the expense of integrating new supply. Developers of these technologies also need to make a profit and return on their investments, which adds to a technology's costs. "We're not just doing this as a philanthropic exercise," said Whitacre. "You can't change the world with technology unless those technologies are profit-bearing."

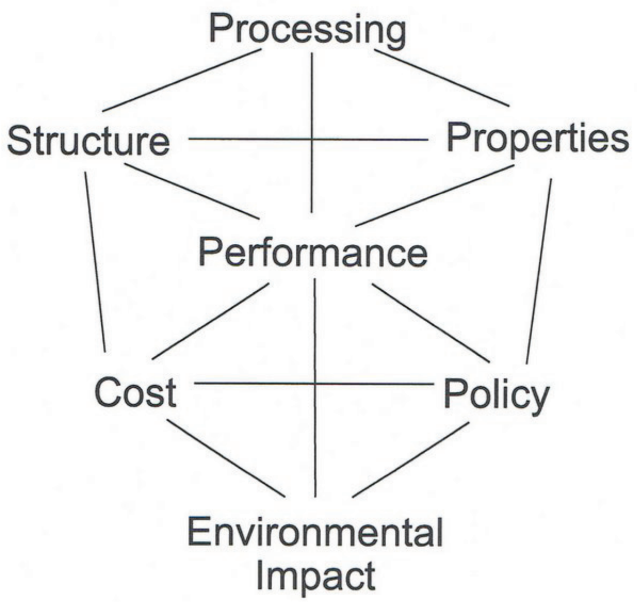


FIGURE 6-3 Factors in energy technology engineering can be envisioned as occupying the corners of a polyhedron.
SOURCE: Whitacre (2011).

The second assumption is that a systems-level perspective is the only one that matters for energy technologies. "The economy and policy makers only care about the macro implications of energy technologies," said Whitacre. "At the end of the day, they have to decide what to fund and what to give emphasis to if they are making policies that will affect the implementation of some technologies over others." As a result, black-boxing is critical—think of a technology in terms of a box that either produces electrons or stores and releases them. Then, determine how that box will fit in the existing system, how it will function in the system's environment, how it can improve the system in which the box sits, and how the box affects the cost, performance, and lifetime of the system.

Whitacre added that the movement of materials through the supply chain and value chain also should be examined this way—an analysis should determine what materials move into the box and what materials move out of the box. It is necessary, he said, to determine how this material flow affects the manufacturing cycle and disposal cycle. The conclusion from this assumption is that trade issues are crucial and should inform even fundamental research on technologies. It is important, too, to keep a 10- to 20-year timeframe in mind because that is how long it will take a technology being developed today to make a significant impact on the system.

Lithium-Ion Batteries

There is plenty of lithium in the world. According to the U.S. Geological Survey, there are some 32.5 million metric tons of lithium reserves worldwide, enough to make 32.5 billion vehicles equipped with today's lithium-ion batteries. Today, developed reserves are dominated by Chile and China, and the market is currently flooded with supply. Battery-quality lithium carbonate costs less than $5/kg, and the other materials in a lithium-ion battery—cobalt oxide, manganese oxide, copper, and aluminum, among others—are also relatively inexpensive and plentiful.

What is expensive is the system that all of these materials fit into to make a battery (Figure 6-4). The system includes current collectors, separators, and the electrodes themselves, which are active materials and quite thin at less than 100 microns per anode or cathode for high-powered devices. In addition, ancillary support such thin electrodes, and in fact the thinner the electrode, the more ancillary material is needed to support it.

There are trade-offs involving costs. Power costs more per unit of active material, but power is also worth more in many applications. More complex batteries may perform better and command a better price, but more complexity can create yield problems if cell-to-cell consistency is critical for performance.

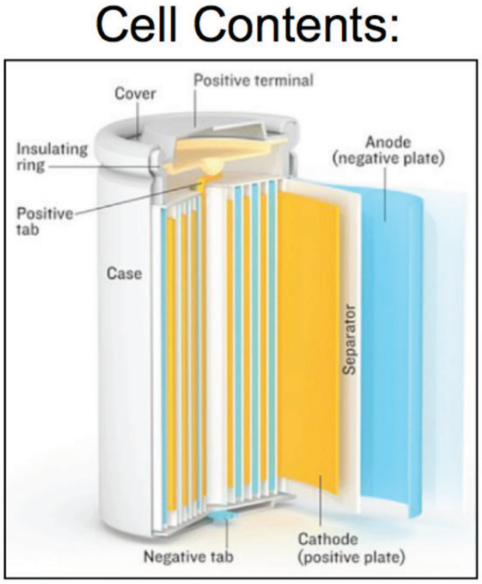
An examination of the bill of materials for a generic plug-in hybrid vehicle lithium-ion battery reveals that, of the $300 to $400/kWh cost of this battery, all of the materials cost about $100/kWh. Even if the lithium cathode cost went to $0, the next-generation automobile lithium-ion battery would still cost over $400/kWh. An assessment by the Boston Consulting Group (BCG, 2010) came to a similar conclusion, finding that materials represent about 12 percent of the cost of a lithium-ion battery supplied to an automobile manufacturer. Depreciation, research and development, and parts each accounted for a larger percentage of the cost of the battery.

The most expensive part of a lithium-ion battery is actually the electrolyte. Manufacturing costs associated with the organic solvent electrolyte are high, and its ionic conductivity is relatively low compared to aqueous electrolytes. Lower ionic conductivity means that the electrodes must be thinner, which in turn boosts the costs of the ancillary materials needed to support thin electrodes. A quick sensitivity study shows that batteries become cheaper as electrodes get thicker, but this demands a higher-conductivity electrolyte and clever electrode structural engineering. In addition, the rate capability goes down.

The bottom line is that adoption of lithium-ion battery technology is not constrained by materials. Rather it is constrained by the way the materials function and the complexity of the device itself.

Bulk Stationary Storage

The development of bulk stationary storage devices is critical to the next-generation grid and large-scale use of renewable energy sources. A handful of companies are making progress not through the use of innovative chemistry but through clever engineering and by filling specific niches where higher prices are justified. A technology developed by Xtreme, for example, is being installed on Maui, which has a major problem with frequency regulation because of all the wind power being generated there. Power developer AES Corporation is installing A123 Systems's batteries at what Whitacre called extreme pain points—places where



Pack Contents:

- Battery Cells
- Battery Management System (BMS)
- Power Electronics
- Inductors
- Switching Units
- Power Bus
- Thermal Control Unit
- Electronic Control Unit
- Sensors (thermal, accelerometer, current, potential)
- Frame/enclosure/safety shield

FIGURE 6-4 A lithiumlithium-ion cell has multiple components.
SOURCE: HowStuffWorks, circa 2006, Bryan Christie Design.

transmission problems are severe enough to justify the high cost of these systems.

Pumped hydro, a well-established technology, is not universally cheap, Whitacre noted. It requires a vertical gradient and plenty of cheap water, and it is not very energy dense. The real competitors for bulk storage are small natural gas turbines used for peak-hour demands and renewable leveling. They cost about $750/kW installed, and they can run for between 1 and 6 hours at times of peak demand.

Whitacre said he has been told by a major utility provider that at $1/W and a greater than 10-year lifetime, utilities will buy all the storage a company can produce. That means the cost of production must actually be less than that if the storage device manufacturer hopes to turn a profit. "That is a hefty goal and not an easy one," he said, "and if you can do this, you will change the world."

Using a simplified economic analysis, Whitacre derived a maximum cost of $5/kg, or under $50 watt-hours (Wh)/kg, for the entire cost of an economically feasible bulk storage device. This calculation took into account the number of cycles required of a relevant device, the amount of kilowatt-hours delivered per cycle, the cost of goods sold, the cost of materials, and the cost of assembling those materials into a device that would be sold in the market. The calculation also assumed that any device would have to cost approximately $100/kWh delivered over the device's lifetime.

These results, while based on an admittedly simplified analysis, suggest that there is a steep hill for any technology to climb. Lithium-ion batteries, for example, cost in the multiple hundreds of dollars of watt-hours per kilogram, and their total cost of goods is much higher, in the multiple hundreds of dollars per kilowatt-hour.

Moving to higher-energy-density materials could be a solution, but these are typically not as stable. "This is not a law," said Whitacre, "and I'm hoping somebody finds things that have 1,000 watt-hours per kilogram and can last 10,000 cycles. But in general the more energy you get out of a battery material per cycle, the more transition it has to go through in each one of those cycles, and the less stable it will be over thousands of those cycles."

Another solution would be to find a battery system that has a low energy density but extremely low cost, less than $5/kg. If this device could cycle rapidly or be more efficient and have a very long lifetime, it could prove economically feasible.

Whitacre is working on an aqueous electrolyte battery that might fit the latter scenario of low cost, low energy densities, and long lifetime. Aqueous electrolyte batteries are based on an old technology. Aqueous electrolytes have an order-of-magnitude-higher conductivity than organic electrolytes so they can be used with thick electrodes that can be much cheaper to manufacture and assemble into a final device.

Lead acid, nickel metal hydride, and alkaline systems are all examples of batteries that use an aqueous electrolyte. Whitacre and his colleagues are developing an aqueous lithium-ion system based on intercalation technologies (Manjunatha et al., 2011; Shivashankaraiah et al., 2011). The electrolyte is typically a neutral pH salt—either lithium nitrate or lithium sulfate—in water. Devices built so far have energy densities in the range of 55 kWh/kg, but most are stable for only hundreds of cycles and their voltage is at the low end.

One device that has displayed stability over thousands of cycles uses a high-surface-area activated carbon anode and an intercalating and de-intercalating lithium manganese oxide cathode (Wang and Xia, 2006). Whitacre explained that he took notice of this system when asked if sodium could replace lithium, since sodium is a much cheaper material. There had been some research on aqueous sodium batteries, but the results were not promising (Sauvage et al., 2007; Zhuo et al., 2006).

Whitacre, however, found that sodium manganate with an orthorhombic structure had very interesting cathode properties. This material, $Na_{0.44}MnO_2$, can be made in a variety of ways from baking soda and manganese dioxide, both of which are very inexpensive. The simplest way to make it is to mix the two starting materials and heat them in a furnace, though they can also be made by sol-gel and hydrothermal processes. The material has a needle-like morphology, is very anisotropic, and can have nanodimensional cross sections. With care, solid-state synthesis can produce high-purity material, contaminated with a small amount of manganese trioxide, that displays suitable properties for a cathode material.

For an anode, activated carbon is the material of choice, but activated carbon is actually a very expensive material, and the cost proposition for using it in a bulk storage device is impossible. To solve that problem, Whitacre has been using molasses as a source of carbon via pyrolysis and then activating it using potassium hydroxide, another relatively inexpensive material. Using a process that preheats the material and then completes the pyrolysis at 800°C in the presence of potassium hydroxide, Whitacre and collaborators generate a material with a surface area of nearly 3,000 m^2/g. Electrically, this material has properties that "put it above the laugh test." He said that if he can make this material for $3 to $4/kg, it would be a viable candidate.

When an anode made from this material is combined with a sodium manganate cathode and aqueous sodium sulfate as the electrolyte, the resulting cell was stable to 1.8 V and could be cycled between 0.4 and 1.8 V for thousands of cycles with negligible loss of capacity and 100 percent coulombic efficiency. The one area in which this cell fell short was in energy density, which was on the order of 15 to 20 Wh/kg versus the 30 to 40 Wh/kg that would make a battery made of these materials cost competitive. However, switching to a cubic spinel manganese dioxide cathode produced a cell that had an energy density of around 30 Wh/kg using very thick electrodes that are extremely stable and easy to manufacture. Moreover, cells made from this material can cycle far more than lead acid batteries.

Aquion, the company Whitacre founded, is now manufacturing batteries using this technology. The cells are encased in industry-proven polypropylene casings using industry-proven sealing technologies. The batteries have a modular product form factor that allows them to be strung together into eight-battery, 15-V modules that can then be stacked and connected in series or parallel as needed. Hundred-volt strings are now in use and 1000-V strings are being tested. The batteries have performed well when tested under conditions that simulate wind power generation over a period of days.

DISCUSSION

In response to a question about the power versus energy demands on a battery intended for use on the grid, Bradwell said that the real issue is the ratio of rated power to rated energy. Batteries for frequency regulation need to discharge for 15 to 45 minutes. A battery can have high power but not much energy and discharge repeatedly throughout the day. To support wind and solar, however, a battery needs to be able to discharge over a much longer period of time. Such batteries would need large energy storage capacity but, at lower power output, would create relatively low-stress demands on a battery. “You still need big batteries, but in terms of how fast you get the energy in and out of the system, it’s not as restrictive,” said Bradwell.

Responding to a question about the energy needed to heat a liquid metal battery, Bradwell noted that, once these batteries reach a certain size, they maintain temperature as a result of the heat generated as the battery cycles. He also noted that these batteries can be cycled at 90 percent efficiency, though at lower current densities.

When asked about the potential for metal-air batteries, Bradwell explained that the main problems with those batteries have to do with the kinetic difficulties in oxidizing oxygen, resulting in inefficient batteries. Metal-air batteries also have limited life cycles based on the experience with zinc-air batteries.

Bradwell was asked about the potential for lithium batteries in cars to serve as load leveling devices for the grid. He replied that in his opinion the negative impact that this would have on the lifetime of the battery would far outweigh the benefits. The battery in a Chevy Volt, for example, costs about $16,000, and load leveling would generate about $1/day in revenue.

In response to a question about what fundamental research needs to be done in the battery field, Bradwell responded that he would like to see modeling work done on the thermodynamics of liquid alloys. He noted that quantum-mechanical analyses have been applied successfully to crystalline systems, and he would like to see similar work done for liquid alloys.

In response to a question about whether this battery is actually a capacitor, Whitacre said that it is officially known as an asymmetric energy storage device or a “capattery” since it behaves as a hybrid of a battery and a capacitor.

Responding to a comment about how storage devices would be incorporated into the grid, Whitacre noted that a New York utility company recently put out a call for proposals for a peaking gas turbine to supply 1,600 GWh of power, and one of the responses was not for a power plant but for batteries that would be housed in several warehouses distributed across Long Island. The proposal has received high marks despite being slightly more expensive because residents in the Hamptons liked the idea of a warehouse-based solution with no emissions compared to a large gas turbine. The project is moving forward.

Whitacre was critical, in responding to a question about intellectual property protection, of the U.S. Patent Office. He said that patents covering new chemistries are worth very little. What are valuable are patents that control specific ways of using batteries and control algorithms for specific chemistries. Aquion’s patents actually cover the high-voltage strings that the company can make from its batteries. He explained that it is impossible to make such high-voltage strings without using batteries with the performance characteristics of the company’s batteries.

When asked about other promising technologies, Whitacre said that there is some very interesting work being done with lithium sulfur chemistry, which uses simple and inexpensive materials.

In response to a question about what fundamental research needs to be done in the battery field, Whitacre said that he would like to know more about the fundamental nature of pseudocapacitance in different types of electrolytes. He also cited the areas of dendrite formation and dendrite blocking as needing good fundamental research.

7

General Observations

Throughout the workshop, speakers made general observations about the issues associated with critical materials and the role of the chemical sciences in addressing those issues. These observations are gathered in this final chapter to capture the broad themes emerging from the workshop. These themes should not be seen as consensus conclusions of the workshop and are associated here with the speaker who made that observation.

- The level of criticality for a material depends on many factors, including physical availability, cost, importance in use, supply risk, concentration within a country, coproduction, potential for substitution, and environment and social concerns. (Eggert)
- The level of criticality for a material can change over time as the factors affecting criticality change. (Eggert)
- The importance of these factors differs from one material or element to another. (Eggert)
- Different groups have different definitions of critical materials depending on their needs and circumstances. (Eggert)
- Markets respond to both supply and demand signals but with time lags. (Eggert)
- Government has an essential role to play in pushing for undistorted international trade, streamlining regulation, facilitating the collection and dissemination of information, and facilitating research and development. (Eggert)
- The chemical sciences have an important influence on critical materials through research and development involving substitution, improvements in extraction and recovery, and improvements in manufacturing and recycling. (Eggert)
- Governmental policies also have a major influence on criticality, including policies on domestic production and processing, stockpiling, education, and diplomacy. (Bauer)
- Even if the price of a critical material is a small fraction of a catalyst, supply constraints can interfere with that application of the material. (Stevens)
- Research can reduce or eliminate the use of a critical material in a catalyst and thereby reduce or eliminate the effects of price or supply disruptions. (Chen)
- Replacing expensive metals with inexpensive metals in catalysts can produce significant savings and be more environmentally benign. (Bullock)
- Even in long-established applications like automotive catalytic converters, continued research can reduce the demand for precious metals, even where complete replacement of those metals is not yet feasible. (Lambert)
- Proven reserves of rare earths are growing rapidly, and one solution to tight supplies is to increase mining. (Shinar)
- Demand for some critical materials will soar if the world acquires a significant fraction of its energy from photovoltaics. (Zweibel)
- Resources constraints could be a critical factor in the development of grid-scale energy storage technologies. (Bradwell)
- Issues that need to be considered in establishing critical materials policies include trade restrictions, the extended times needed to develop new technologies, costs, and environmental impacts. (Whitacre)

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Appendixes

A

Workshop Agenda

THE ROLE OF CHEMICAL SCIENCES IN FINDING ALTERNATIVES TO CRITICAL RESOURCES:
A Workshop

Organized by:
Roderick Eggert, Colorado School of Mines; Pat Thiel, Ames Laboratory and Iowa State University; and Levi Thompson,
University of Michigan, on behalf of the Chemical Sciences Roundtable

September 29-30, 2011
The National Academies
500 Fifth Street, NW, Room 100
Washington, DC 20001

DAY ONE, September 29, 2011

8:00 a.m. Breakfast (Guest Speakers and CSR members only)

8:30 a.m. Welcome & Introduction to Workshop
Pat Thiel, Ames Laboratory and Iowa State University

PLENARY SESSION – INTRODUCTION & HISTORY
Chair, Mark Barteau, University of Delaware

8:40 a.m. **Roderick Eggert,** Colorado School of Mines *live webcast*
Minerals, Critical Minerals, and the U.S. Economy

9:20 a.m. **Diana Bauer,** U.S. Department of Energy *live webcast*
U.S. DOE Critical Materials Strategy

10:00 a.m. Break

CRITICAL MATERIALS AND CATALYSIS
Chair, Levi Thompson, University of Michigan

10:15 a.m. **James Stevens,** Dow Chemical *live webcast*
Finding Alternatives to Critical Materials in Catalysis

10:55 a.m. **Jingguang Chen,** University of Delaware
Alternative Materials to Replace Platinum in Catalytic and Electrocatalytic Applications

11:35 a.m. Open Discussion

12:35 p.m. Lunch (Keck Cafeteria)

1:35 p.m. **Morris Bullock,** Pacific Northwest National Laboratory
Design and Development of Molecular Electrocatalysts for Energy Conversions Using Abundant Metals

2:15 p.m. **Christine Lambert,** Ford Motor Company
Critical Materials in Catalysis: Novel Metals vs. Base Metals in Automotive Catalyst Systems

2:45 p.m. Open Discussion

3:45 p.m. Break

CRITICAL MATERIALS IN ELECTRONIC AND OPTICAL APPLICATIONS
Chair, Pat Thiel, Ames Laboratory and Iowa State University

OPTICS AND PHOTOVOLTAICS; ALTERNATIVES TO RARE EARTHS AND HEAVY METALS

4:00 p.m. **Joseph Shinar,** Ames Laboratory and Iowa State University
Critical Materials in Optoelectronics

4:40 p.m. **Ken Zweibel,** George Washington University
Key Minerals in Photovoltaics

5:20 p.m. Open Discussion

6:20 p.m. Adjourn, dinner on your own

DAY TWO, September 30, 2011

8:00 a.m. Breakfast (Guest Speakers and CSR members only)

8:30 a.m. Day Two Opening Remarks
Levi Thompson, University of Michigan

CRITICAL MATERIALS IN ELECTRONIC AND OPTICAL APPLICATIONS
Chair, William Carroll, Occidental Chemical Corporation

BATTERIES: ALTERNATIVES TO LITHIUM

8:40 a.m. **David Bradwell,** Liquid Metal Battery Corporation

9:20 a.m. **Jay Whitacre,** Carnegie Mellon University

10:00 a.m. Break

10:15 a.m. Open Discussion

11:15 a.m. Closing Remarks

11:45 a.m. Adjourn

12:00 p.m. (CSR Member Business Meeting begins, Room 105)

B

Organizing Committee Biographies

Roderick G. Eggert is professor and director of the Division of Economics and Business at the Colorado School of Mines, where he has taught since 1986. He was editor of *Resources Policy*, an international journal of mineral economics and policy, from 1989 to 2006. Previously he taught at The Pennsylvania State University and held research appointments at Resources for the Future (Washington, DC) and the International Institute for Applied Systems Analysis (Austria). He has a B.A. in earth sciences from Dartmouth College, an M.S. in geochemistry and mineralogy from The Pennsylvania State University, and a Ph.D. in mineral economics from Penn State. His research and teaching have focused on various aspects of mineral economics and public policy, including the economics of mineral exploration, mineral demand, mining and the environment, microeconomics of mineral markets, and most recently mining and sustainable development. He served for two terms on the Committee on Earth Resources of the National Research Council (NRC). He served as chair of the NRC Committee on Critical Mineral Impacts on the U.S. Economy, which authored the 2008 report *Minerals, Critical Minerals, and the U.S. Economy*.

Patricia A. Thiel is the Division Director for Science and Technology at Ames Laboratory and a Distinguished Professor of Chemistry at Iowa State University (ISU), where she is active in research, teaching, and administration. In research, she is known for her work in three main areas: nanostructure evolution on surfaces, surface properties and structures of quasicrystals (a complex type of metallic alloy), and the chemistry of water adsorbed on metal surfaces. Thiel is an enthusiastic teacher of physical chemistry. She has held several administrative posts at ISU, including chair of her department. Thiel received her B.A. in chemistry at Macalester College, and her Ph.D. in chemistry at the California Institute of Technology in 1981. After postdoctoral work at the University of Munich as a von Humboldt Fellow, she joined the technical staff at Sandia National Laboratories, Livermore, then moved to ISU in 1983. In her early academic career there, Thiel was recognized with awards from the Camille and Henry Dreyfus Foundation and the Alfred P. Sloan Foundation, and by a National Science Foundation Presidential Young Investigator Award. Later, she was elected a Fellow of the American Vacuum Society, the American Physical Society, and the Institute of Physics.

Levi T. Thompson is the Richard Balzhiser Professor of Chemical Engineering at the University of Michigan. Other honors and awards include the National Science Foundation Presidential Young Investigator Award, the Union Carbide Innovation Recognition Award, the Dow Chemical Good Teaching Award, the College of Engineering Service Excellence Award, and the Harold Johnson Diversity Award. He is co-founder, with his wife Maria, of T/J Technologies, a developer of nanomaterials for advanced batteries and fuel cells. He is also Consulting Editor for the *AIChE Journal*, and a member of the External Advisory Committee for the Center of Advanced Materials for Purification of Water with Systems (NSF Science and Technology Center at the University of Illinois) and AIChE Chemical Engineering Technology Operating Council. Professor Thompson earned his B.ChE. from the University of Delaware, and M.S.E. degrees in chemical engineering and nuclear engineering, and a Ph.D. in chemical engineering from the University of Michigan. Research in Professor Thompson's group focuses primarily on defining relationships between the structure, composition, and function of nanostructured catalytic and electrochemical materials. In addition, he has distinguished himself in the use of micromachining and self-assembly methods to fabricate microreactor, hydrogen production, and micro-fuel cell systems. Professor Thompson leads a large multidisciplinary team developing compact devices to convert gasoline and natural resources into hydrogen. Recently, he was appointed founding Director of the Hydrogen Energy Technology Laboratory.

C

Guest Speaker Biographies

Diana Bauer, Ph.D.
Diana Bauer is Director of the Office of Economic Analysis within the U.S. Department of Energy's Office of Policy and International Affairs. In this position, she oversees economic and technology systems analysis. Last year, she led the drafting of DOE's Critical Materials Strategy. Before joining DOE, she led the extramural sustainability research program at the U.S. Environmental Protection Agency (EPA), focusing on topics such as green manufacturing, green building, transportation, and land use planning. She is one of the principal authors of EPA's research strategy for sustainability. Previously, she led the Center for Climate Change and Environmental Forecasting at the U.S. Department of Transportation. She has a Ph.D. in mechanical engineering from UC Berkeley.

David Bradwell, Ph.D.
David Bradwell is currently a Visiting Scientist at the Sadoway Group, as well as Chief Technical Officer at Liquid Metal Battery Corporation, which is working to commercialize grid-level energy storage. Dr. Bradwell received his B.Sci. in engineering physics from Queen's University (2005); his M. Eng. in materials sciences and engineering from the Massachusetts Institute of Technology (2006); and his Ph.D. in materials sciences and engineering from the Massachusetts Institute of Technology (2010). Dr. Bradwell's research projects include high-amperage rechargeable batteries for stationary energy storage applications.

Morris Bullock, Ph.D.
Morris Bullock is a Laboratory Fellow and the Director of the Center for Molecular Electrocatalysis (efrc.pnnl.gov) at Pacific Northwest National Laboratory (PNNL), an Energy Frontier Research Center (EFRC) funded by the Department of Energy. He received a B.S. from the University of North Carolina at Chapel Hill, where he did undergraduate research with Tom Meyer. He obtained his Ph.D. working for Chuck Casey at the University of Wisconsin. He was a postdoc with Jack Norton at Colorado State University from 1984 to 1985. From 1985 to 2006, he was at Brookhaven National Laboratory (Long Island, New York), where his research focused on organometallic chemistry, involving synthetic, mechanistic, and kinetics studies of transition-metal hydride complexes. Bullock and his co-workers developed catalytic ionic hydrogenations, in which ketones are hydrogenated by proton transfers and hydride transfers from transition-metal hydrides. These catalytic reactions use abundant, inexpensive metals (molybdenum and tungsten) rather than traditional precious metals such as ruthenium. In 2006 he moved to PNNL. The research of the EFRC he directs there focuses on understanding and controlling proton movement in multiproton, multielectron reactions of critical importance to energy transformation reactions needed for a secure energy future. Electrocatalysts are needed for interconversion between electrical energy and chemical energy (fuels). Molecular electrocatalysts based on nickel or iron are being developed for the oxidation of hydrogen and for the production of hydrogen, as alternatives to the use of the precious metal platinum in fuel cells. He recently edited a book, *Catalysis Without Precious Metals* (Wiley-VCH, 2010).

Jingguang G. Chen, Ph.D.
Jingguang Chen is the Claire D. LeClaire Professor of chemical engineering and co-director of Energy Frontier Research Center at the University of Delaware. He started his career at the Exxon Corporate Research Laboratories in 1989 and moved to the University of Delaware in 1998. He served as the Director of the Center for Catalytic Science and Technology during 2000-2007 and the Interim Director of the University of Delaware Energy Institute during 2008-2010.

He has over 240 journal publications and 16 U.S. patents. He is active in serving the catalysis and energy communities, including responsibilities as the Chair of the Gordon Research Conference on Catalysis in 2002, the Chair of the Philadelphia Catalysis Club in 2004, the Catalysis Secretariat of the American Chemical Society in 2007, and the Board of Directors of the North American Catalysis Society.

Roderick Eggert, Ph.D.

Roderick Eggert received his B.A. in earth sciences from Dartmouth College (1978); his M.S. in geochemistry and mineralogy from The Pennsylvania State University (1980); and his Ph.D. in mineral economics from The Pennsylvania State University (1983). Dr. Eggert is currently the Director of the Division of Economics and Business at the Colorado School of Mines. He is also a professor within the Division of Economics and Business. Dr. Eggert is a member of the Advisory Committee of the Mineral Economics Research Program at Catholic University of Chile. He serves as an editor for *Resources Policy*, an international journal of mineral economics and policy published by Elsevier Science (Oxford, UK). Dr. Eggert is also President of the Mineral Economics and Management Society. Dr. Eggert's full CV can be found at http://econbus.mines.edu/Rod-Eggert-Professor.

Christine K. Lambert, Ph.D.

Christine Lambert is currently the Technical Leader at Ford Research and Advanced Engineering. Dr. Lambert received her B.S. in chemical engineering from Lamar University in Beaumont, Texas and her Ph.D. in chemical engineering from Tulane University in New Orleans, Louisiana. Dr. Lambert's current responsibilities at Ford Research and Advanced Engineering consist of diesel aftertreatment catalyst development, including diesel oxidation catalysts, lean NO_x catalysts, and diesel soot filters, as well as gasoline particulate filtration. Prior to this assignment, Dr. Lambert led a 5-year DOE-funded project to develop selective catalytic reduction (SCR) of NO_x with aqueous urea to demonstrate 2007 federal emission standards with a 6,000-lbs light-duty diesel truck. In particular, she worked with suppliers to develop highly active and durable SCR catalyst formulations. Her team's work led to the development of the 2011MY Ford Super Duty Diesel catalyst system. Dr. Lambert was recognized in 2009 as a "Young Leader" by the Automotive Hall of Fame in Dearborn, Michigan, and was also recognized in 2005 by Tulane University with a Harold A. Levey Award, which is presented annually to recognize an alumna/us of the Tulane School of Engineering for professional achievement during the 5- to 10-year period after graduation. Dr. Lambert holds eight U.S. patents and is co-author of 65 technical publications and presentations in the areas of supported metal catalysts and emission control systems for diesel vehicles.

Joseph Shinar, Ph.D.

Joseph Shinar is currently a Senior Physicist of the Ames Laboratory, USDOE, Professor and Chair of the Department of Physics and Astronomy, and Professor of Electrical and Computer Engineering at Iowa State University (ISU), Ames, Iowa. He has co-authored over 250 publications, co-edited 3 volumes, co-invented 5 patents, and delivered over 150 invited talks at national and international conferences, research centers, and universities. In 2004 he was awarded the ISU Foundation Outstanding Achievement in Research Award and elected Fellow of the American Physical Society.

James C. Stevens, Ph.D.

Dr. James C. Stevens is a Corporate Fellow in the Core Research and Development Department of The Dow Chemical Company, where he has worked for 32 years. Jim's primary field of research is in the area of new catalysts, particularly in the area of polyethylene, polypropylene, ethylene/styrene copolymers, and the high-throughput discovery of organometallic single-site catalysts. He has been involved with the discovery and commercial implementation of Dow's INSITE™ technology and constrained-geometry catalysts, which are used in the production of over 2 billion pounds of polyolefins and elastomers per year. Dr. Stevens is now working to develop solar energy products and is involved in the development of Dow's POWERHOUSE Solar Shingle, which is the first building-integrated photovoltaic product that can be installed by regular roofing contractors. Dr. Stevens is an inventor on 92 issued U.S. patents, over 1,100 global patents, 18 publications, and 2 books. Jim has won a Dow "Inventor of the Year" award five times, and was presented the Dow Central Research "Excellence in Science" Award. In 1994, Jim was a co-recipient of the U.S. "National Inventor of the Year" Award, presented in the U.S. Congress. In 2002, The Dow Chemical Company was awarded the National Medal of Technology by President George Bush, based in part on the work of Dr. Stevens in the area of olefin polymerization catalysis. Jim is the 2004 recipient of the ACS Delaware Section "Carothers Award," honoring scientific innovators who have made outstanding advances and contributions to industrial chemistry. Jim was awarded the American Chemical Society "ACS Award in Industrial Chemistry" in 2006. Dr. Stevens also received the Herbert H. Dow Medal, the highest honor Dow awards to the company's scientists and researchers. Jim was awarded the 100th presentation of the Perkin Medal in 2007, widely considered to be the highest honor in American industrial chemistry. Jim was the 2007 recipient of the University of Chicago Bloch Medal and the 2011 North American Catalysis Society "Houdry Award," the highest honor of this society. Texas A&M University has recently honored Dr. Stevens with an Honorary Doctor of Letters Degree for "innovative research which has expanded the boundaries of catalysis, polymer chemistry and underlying disciplines, and resulted in large-scale commercial processes." He is a member of the National Academy of Engineering and a Fellow of the AAAS. Jim has invented or contributed significantly to the commercialization of a large number of products, including AFFINITY™ polyolefin plastomers, ENGAGE™ polyolefin elastomers, ELITE™ enhanced polyethylene resins, NORDEL™-MG EPDM rubber, NORDEL™-IP elastomers, Dow XLA-fibers, INDEX™ ethylene/styrene copolymers, VERSIFY™ propylene copolymers, INFUSE™ Olefin Block Copolymers, and the Dow POWERHOUSE Solar Shingle. There is hardly a car produced in the world or a grocery store anywhere that does not contain a polymer that was invented by Dr. Stevens' group. Jim received a B.A. in chemistry from The College of Wooster in 1975. He obtained a Ph.D. in inorganic chemistry from The Ohio State University in 1979. Jim is an advisor to the National Science Foundation Center for Chemical Innovation, Solar Fuels based at Caltech.

Jay Whitacre, Ph.D.

Jay Whitacre received a PhD. from the University of Michigan in 1999. He held various positions at Caltech and the Jet Propulsion Lab before taking his current professorship at Carnegie Mellon University (CMU) in 2007. There he develops functional materials systems and performs economic/environmental impact assessment for energy technologies. His early work at CMU resulted in the conception of a novel scalable energy storage device. In 2008 he founded Aquion Energy, a company that has grown to over 60 employees. He is currently on leave from CMU to serve as full-time CTO for Aquion as it scales a pilot manufacturing plant in Pittsburgh, Pennsylvania. Professor Whitacre has over 50 peer-reviewed papers and patents.

Ken Zweibel, Ph.D.

Ken Zweibel has almost 30 years experience in solar photovoltaics. He was at the National Renewable Energy Laboratory (Golden, Colorado) much of that time and was the program leader for the Thin Film PV Partnership Program until 2006. The Thin Film Partnership worked with most U.S. participants in thin-film photovoltaics (PV) (companies, universities, scientists) and is often credited with being important to the success of thin-film PV in the United States. Corporate participants in the Partnership included First Solar, UniSolar, Global Solar, Shell Solar, BP Solar, and numerous others. Zweibel subsequently co-founded and became President of a thin-film CdTe PV startup, PrimeStar Solar, a majority share of which was purchased by General Electric. Zweibel became the founding Director of The George Washington University Solar Institute at its formation in 2008. Zweibel is frequently published and known worldwide in solar energy. He has written two books on PV and co-authored a *Scientific American* article (January 2008) on solar energy as a solution to climate change and energy problems.

D

Origin of and Information on the Chemical Sciences Roundtable

In April 1994 the American Chemical Society (ACS) held an Interactive Presidential Colloquium entitled "Shaping the Future: The Chemical Research Environment in the Next Century."[1] The report from this colloquium identified several objectives, including the need to ensure communication on key issues among government, industry, and university representatives. The rapidly changing environment in the United States for science and technology has created a number of stresses on the chemical enterprise. The stresses are particularly important with regard to the chemical industry, which is a major segment of U.S. industry, in terms of trade and employment opportunities for a technical workforce. A neutral and credible forum for communication among all segments of the enterprise could enhance the future well-being of chemical science and technology.

After the report was issued, a formal request for such a roundtable activity was transmitted to Dr. Bruce M. Alberts, chairman of the National Research Council (NRC), by the Federal Interagency Chemistry Representatives, an informal organization of representatives from the various federal agencies that support chemical research. As part of the NRC, the Board on Chemical Sciences and Technology (BCST) can provide an intellectual focus on issues and fundamentals of science and technology across the broad fields of chemistry and chemical engineering. In the winter of 1996 Dr. Alberts asked BCST to establish the Chemical Sciences Roundtable to provide a mechanism for initiating and maintaining the dialogue envisioned in the ACS report.

The mission of the Chemical Sciences Roundtable is to provide a science-oriented, apolitical forum to enhance understanding of the critical issues in chemical science and technology affecting the government, industrial, and academic sectors. To support this mission the Chemical Sciences Roundtable will do the following:

- Identify topics of importance to the chemical science and technology community by holding periodic discussions and presentations, and gathering input from the broadest possible set of constituencies involved in chemical science and technology.
- Organize workshops and symposiums and publish reports on topics important to the continuing health and advancement of chemical science and technology.
- Disseminate information and knowledge gained in the workshops and reports to the chemical science and technology community through discussions with, presentations to, and engagement of other forums and organizations.
- Bring topics deserving further in-depth study to the attention of the NRC's Board on Chemical Sciences and Technology. The roundtable itself will not attempt to resolve the issues and problems that it identifies—it will make no recommendations or provide any specific guidance. Rather, the goal of the roundtable is to ensure a full and meaningful discussion of the identified topics so that the participants in the workshops and the community as a whole can determine the best courses of action.

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[1] American Chemical Society. 1994. *Shaping the Future: The Chemical Research Environment in the Next Century.* Report from the Interactive Presidential Colloquium, April 7-9,Washington, D.C.