

Out of Kyoto: Warming Up to Materials

By any measure, the Kyoto protocol worked out after days of intense negotiations during the recent United Nations Conference on Global Warming is path-breaking. For the first time, all nations of the world have volunteered to cut back their countries' emission of heat-trapping gases. The promised reductions vary from country to country. The industrially developed countries have pledged to cut their greenhouse gas emissions by 2010 to a few percent below their 1990 levels. Countries of the European Union will cut their gas emissions by 8%, the United States by 7%, and Japan by 6%. The developing nations, notably China and India, were given no targets but have also agreed to explore ways of minimizing their industrial emissions. This will be crucial since energy demands in developing countries are growing rapidly. China, for instance, will need about 83 quadrillion BTU by 2015, an increase over 130% of its current demand.

Some areas of protocol sounded controversial. The "rich" countries, for instance, could buy credits from lower polluting countries, the so-called "carbon trading," or claim emission credits for implementing clean energy systems in other countries. The amount of warming predicted by scientists was itself challenged (it is 2.38

degrees, or less, or even more) along with the usefulness of the recommended cutbacks in preventing global warming. There were also concerns that the rewards for the cutback would come only in the distant future, or not at all. The cutback would also involve changes in behavior by billions of people. Will it ever be possible to achieve this? There is a major gap between the Kyoto protocol and current policies.

Technologies and policies are going to be the tools that industries and governments will have to use to implement the Kyoto goals. While governments may introduce new legislations and tax breaks to control emission levels, encourage energy efficient alternatives, and to increase the use of renewable energy options, the major response will have to come from cost-competitive and environmentally friendly technologies. In these areas, the technology wish list can be grand, ranging from radical innovations that will make

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solar panels or fuel cells the cheapest generators of electricity, to more mundane alternatives like reengineering the existing turbines to operate more efficiently and with less pollution. In all these, materials hold the key. Materials have to be tailored to operate at the highest thermodynamic efficiency and they should be affordable. Such developments are already happening in a few areas. Solar cells are once again coveted. It is estimated that the needs of a typical home in the United States, for instance, can be met by a mere 30 square ft. solar panel! A modest increase of 1 mile per gallon in fuel efficiency of internal combustion engines would save 5% in the overall fuel consumption of the United States. Such promises are now driving the development of new materials and systems. Wind turbine blades fabricated from composite materials have made wind power competitive. Proton membrane fuel cells are becoming possible because of an innovative processing technology for depositing the platinum. New materials enable fly wheels to operate safely and more efficiently. The impact of new materials and processing technologies in these areas is, by any standards, impressive and more is on the anvil.

In the following pages, we present a montage of recent happenings in this area. The scope of the following articles are as different as the material issues they discuss: from solar cells to a national initiative to make gas turbines that are less polluting and more efficient. But all these articles share a common vision: to make the aspirations of Kyoto come true.

V.S. ARUNACHALAM

Photovoltaics: Heading for the Suburbs

Martin A. Green

1997 was a key year for photovoltaics. After more than a decade of steady growth at 15–20% per annum to reach \$1 billion in sales in 1996,¹ the industry expanded worldwide by a massive 38% during 1997.² Driving this accelerated growth was a change in application. Solar cell applications started to shift from small scale, remote area use and the cells headed for the suburbs.

The trend began with the "1,000 roof" program in Germany in 1993, which saw 2,250 private residential rooftops equipped with government-subsidized, grid-connected photovoltaic systems. These approximately 30-m² systems sup-
See Photovoltaics on page 5.

Material Challenges in Rechargeable Lithium-Ion Batteries and Direct Methanol Fuel Cells

Prashant N. Kumta

The discovery of intercalation and the ability to intercalate alkali metal ions such as lithium into the transition metal oxide and sulfide crystal framework in 1970 has led to a major renaissance in the area of rechargeable batteries. Sony, in 1991, transformed the concept into reality by introducing the rechargeable lithium-ion battery in the market, and is, in fact, currently poised to invest \$90 million to double its production of lithium-ion rechargeable batteries by March 1998.^{1,2} The field has therefore emerged as one of the major markets in consumable power sources. Recent trends indicate that by 2002, Li-ion
See Batteries and Fuel Cells on page 5.

Materials Needs for High-Efficiency, Low-Emission Gas Turbines Being Developed for the 21st-Century Electric Power Generation

Patricia A. Hoffman

Energy is perhaps the most intractable part of the planet's environmental problems. On one hand, the energy systems themselves are the cause of the most troublesome environmental problems at every geographical scale from local to global. On the other hand, the energy-system characteristics that cause these problems are often costly and time consuming to change. At the global level, heat-trapping gases from fossil fuel combustion is the largest contributor to the "greenhouse effect."

Natural gas provides important energy
See Gas Turbines on page 6.

Photovoltaics *Continued from page 4.* ply power to the grid during the daytime, but draw power from it at night. The initiative then moved to Japan, which has targeted 80,000 rooftop installations by the year 2000. Over the current financial year alone, straining present industry production capacity to its limits, 10,000 roofs are due to be equipped with photovoltaics, with one-third subsidy from the Japanese government. Not to be outdone, in June 1997, President Clinton announced the U.S. "one million roof" program, targeting this number of roofs by 2010. In November 1997, the European Commission formally adopted a White Paper on renewables which calls for 500,000 solar roofs by 2010 as well as an export initiative of 500,000 solar systems for the developing world.

Manufacturers have embraced these initiatives, announcing a spate of planned production facilities which are expected to triple total world cell production capacity by the end of the year 2000. A recent survey identified 260 MW of such planned new capacity,³ with an astonishingly wide range of cell materials and technologies to be used.

Most of these new facilities will use the monocrystalline Czochralski silicon wafer technology which has been the workhorse of the industry in the past. By using "off-specification" material from microelectronics, the photovoltaics industry has been able to benefit additionally from the economies of scale of the former. The major change in this area has been a shift from the traditional "screen-printing" approach to cell fabrication to the "laser grooved, buried contact" approach developed by the author's group.⁴ Recently, BP Solar announced it would be converting its entire European production to this new technology, which would account for 8% of present world production by the end of 1998.⁵

Another large market segment would

continue to be based on multicrystalline silicon from "cast" or directionally solidified ingots. This is a higher throughput ingot production process than the Czochralski process, which is also able to use poorer source material. Other planned plants are based on ribbon silicon prepared by the edge-defined, film-fed-growth (EFG) method where the silicon ribbon is grown from a miniscus along the top of a carbon die.

After supplying the consumer product industry for nearly two decades, thin film amorphous silicon (a-Si:H) cells are now available in large, outdoor power modules with new production capacity for these modules also planned. To overcome stability issues and to increase cell performance, these new facilities will produce doubly- or triply-stacked tandem cells, with the lowermost cells alloyed with germanium to reduce the material bandgap, allowing response to red light filtered through the overlying cell or cells.⁴ Present modules give about 50% the power output per unit area compared to the standard crystalline silicon product.

Other thin film cell materials scheduled to make an appearance in production are both cadmium telluride (CdTe) and copper indium diselenide (CIS), including the latter's alloys with gallium (CIGS) and sulfur (CIGSS). Cadmium telluride has proved particularly robust in terms of material deposition approaches, but its commercialization has been slowed by concerns arising from its toxicity. CIS technology was close to commercialization in the late 1980s, but has been put on hold for a decade while problems with manufacturability were addressed. The performance of these technologies in production is expected to be intermediate between that of amorphous and crystalline silicon product.

The final thin film technology due to make an appearance is that based on

polycrystalline silicon. Although silicon is not as strong an absorber as other semiconductors due to its indirect bandgap, "light trapping schemes" which randomize the direction of light, once in the cell, can increase its apparent optical thickness by up to 50 times. Most randomized light is totally internally reflected, due to the small escape cone arising from silicon's high refractive index.⁴ Some of the planned production will be based on relatively thick silicon films deposited onto ceramic substrates, while another will be based on films less than 5- μ m thick, deposited onto glass.

The increased production capacities are expected to lead to steadily reduced cell costs. Two recent studies^{6,7} which included most of the previously mentioned technologies concluded that all were capable of cell production costs at or below \$1/W peak generating capability, compared to the present large volume market prices of \$4/W and small volume retail prices of \$6/W.

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Batteries and Fuel Cells

Continued from page 4.

will account for 51% of the worldwide battery pack unit market.³ The prime advantage of these cells in the bulk is the use of lithium ions rather than elemental lithium, thus enhancing the safety of the battery. In line with the advances in rechargeable lithium batteries, the direct methanol fuel cell (DMFC) technology is also gaining momentum. It is projected by research analysts at Jet Propulsion Laboratory (JPL) that the market for fuel cells will be \$8 billion a year by 2002 and the systems operating from the fuel cell in turn would

become a \$50-billion-a-year industry. This technology is particularly unique because of its ability to provide continuous power with the use of methanol. It is an attractive alternative to the hydrogen fuel cell in view of its higher energy density (≈ 5 kWh/l) in comparison to hydrogen (2.6 kWh/l). Furthermore, it is a convenient fuel because of the low cost, ease of handling and storage, and capability for distribution. At present, the performance is approximately 34% or 1.4 kWh/l of methanol and efforts are directed at maximizing its utilization.⁴

Initial experiments on LiCoO₂ eventual-

ly qualified its use in the commercial Sony battery.⁵ Since then a number of materials studied such as LiNiO₂, LiMn₂O₄, and several doped transition metal oxides have emerged into the forefront as candidate materials.⁶ The most well-studied system in the category of mixed oxides, and also geared for commercialization in the next generation lithium-ion batteries, is LiNi_xCo_{1-x}O₂ ($x > 0.75$). The materials in this system are known for their improved stability in comparison to LiNiO₂ while retaining discharge capacities in excess of 150 mAh/g. In the area of negative electrodes, graphite and coke have been the

two materials that have received the most attention although other forms of poorly crystalline carbon have also been studied. The theoretical capacity of carbon (1 Li/C₆) is 372 mAh/g; however, commercial systems are using carbons with significantly lower reversible capacities.⁷ Recently, Fuji has claimed via several patents a high reversible capacity that is potentially achievable (\approx 600 mAh/g) in the amorphous-tin-oxide system containing elements of group III, IV, or V.^{8,9} Idota et al.^{8,9} claim tin oxide to be the preferred anode material for the next-generation Li-ion batteries wherein capacities equivalent or greater than 2Li/Sn can be achieved without the formation of metallic lithium (dendrites) on the electrode surface as seen in carbon.

A major challenge in this rapidly evolving battery technology lies in the identification of methods to stabilize the cathode structures and techniques to control the electrochemical processes so that the batteries can provide stable power over a large number of cycles. Some of the most formidable problems arise due to unstable irreversible crystallographic transformations, presence of cationic defects due to nonstoichiometry, and polarization losses due to compositional inhomogeneities and presence of secondary inactive phases. All the materials identified so far, however, including those with new dopants, are based on the intercalation reaction of one mole of lithium into the transition metal oxide framework.

Identification of new materials with significantly higher capacities over a larger voltage range will be dictated by the ability to process materials or compounds containing more than one lithium ion that could participate in the charge and discharge processes. It is unlikely though that intercalation would be the only preferred mechanism responsible for the stable performance of such materials. In the area of anodes, the identification of amorphous-tin-oxide-based materials is certainly a step in this direction. A characteristic problem in this system is the irreversible loss in capacity during the first discharge related to the dissociation of the glass matrix.

Processes or approaches to eliminate or minimize such problems would be critical in its application in the future. All these improvements are based on the existing technology using liquid electrolytes, and any increments in the operating voltage would necessitate the identification of stable solvent systems. Finally, and most importantly, the challenge is always to develop new and innovative processes to synthesize materials with the desired and improved materials chemistry, structure, and microstructure for optimum performance. Although solid state techniques are the widely accepted methods of fabrication, it is essential to capitalize on the advantages of wet chemical processes and develop methodologies and designs to initiate the transition from laboratory to industry. Such activities are already being explored at Carnegie Mellon University (CMU) for the identification and development of protocols for the synthesis of existing and new electrode materials. These concepts and approaches are also being extended for thin film batteries wherein the challenge lies in identifying stable solid electrolytes with good ionic conductivity.

Current state-of-the-art methanol fuel cell is based on the use of noble metal catalysts (Pt-Ru) facilitating the oxidation of methanol and a proton exchange membrane (Nafion) promoting the transfer of protons.¹⁰ The catalytic activity drives the electrochemical reactions to form water via efficient proton transport through the membrane. One of the major materials-related challenges rests on the ability to completely utilize the catalytic activity of the noble metals without poisoning. Another task is to enhance the mass transport of protons through the membrane and accelerate the oxidation kinetics without promoting methanol cross-over. Commercially available catalysts are usually synthesized using standard reduction of halide precursors. Although the catalytic efficiency is good, the key to improved utilization will be the generation of fine nanoscale particles of moderate to high surface area with uniform chemical composition so that enhanced catalytic activity can be attained. Commercialization of

these fuel cells will largely depend on reduction in the cost of fabrication and loading of these expensive noble metal catalysts. Efforts are therefore focused on identifying new processes utilizing different precursors that will help to synthesize high performance catalysts and lower the catalyst loading. At the same time, the search for alternative catalyst materials not involving expensive noble metals still continues. Another challenge in generating stacked fuel cells with high power is the ability to identify electrically conducting and electrochemically robust porous materials to replace carbon as the backing medium. Efforts at CMU and JPL are concentrated on development of catalyst and backing structures while focusing on improving the stack design to demonstrate the feasibility of the fuel cell for high power applications.

Several materials-related issues are important for advancing the lithium-ion and direct methanol fuel cell technologies. Advances in materials processing and increased understanding of the materials chemistry and electrochemical reactions will play a pivotal role in dictating the future of these two prominent power source technologies.

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Gas Turbines *Continued from page 4.*

efficiency gain. For example, natural gas combined-cycle electricity generation is the cleanest, lowest cost, and highest efficiency fossil fuel system currently available in the United States. Plants with efficiencies of 52–55% are currently in operation. Further advances require significant new technology development and will lead not only to

improved natural gas power generation systems but to the improvement of coal, biomass, and waste systems as well.

Electricity generation from both natural gas and coal is projected to increase significantly in the United States through the year 2015 to meet the increased demand and to offset the decline in electricity generation from nuclear power. With the low cost of

natural gas, and the relatively low capital requirements for gas-fired capacity compared to coal-fired capacity, natural gas is expected to triple its share of electricity generation. Consequently, the relatively low capital cost of gas turbines will enable them to capture a large portion of the growing electric power market: The Energy Information Agency estimates that

gas turbines will satisfy up to 81% of new electric demands.

To meet this technology challenge the Advanced Turbine Systems (ATS) program was initiated in 1992 as a cooperative effort of the U.S. Department of Energy (DOE), gas turbine manufacturers, universities, natural gas companies, and electric power producers. The prime goals of the ATS program are to meet or exceed 60% combined cycle efficiencies in the utility market and to increase the efficiencies of industrial turbines by 15%; superior environmental compliance (NO_x levels less than 8 ppm and less than 20 ppm CO without the use of post-combustion systems); and reduction in the cost of electricity by 10%. A single percentage point increase in fuel efficiency can reduce life cycle operating costs of a typical 400–500 MW combined cycle plant by \$15–20 million.

Projects in the ATS program are organized under two major activities: major system development and technology base development. The major system development in the industrial turbine sector is being performed by Solar Turbines and Allison Engine Company and in the utility turbine sector by General Electric Company and Westinghouse Electric Corporation. The technology base development contains a sub-element on materials/manufacturing technology directed by DOE—Oak Ridge Operations and Oak Ridge National Laboratory, with work performed at national laboratories, universities, and industry.

The achievement of such high efficiencies will require operation at higher temperature and pressures. Turbine manufacturers have stated a need for turbine rotor

inlet temperatures (RITs) of greater than 1427°C (2600°F), compared to the current RIT for utility systems 1294°C (2350°F) to meet the ATS goals. Novel materials and components will be needed to withstand these conditions as well as the oxidation/corrosion environment of the working fluids, steam, and product gases. The initial approach selected was to transfer technology already in use in aircraft engine gas turbines. In addition to the higher RIT for ATS machines, service life requirements are significantly longer (4,000 h for aircraft engines compared to 50,000 h maintenance goal for ATS). The key to achieving these higher operating temperatures and extended times will be new materials and manufacturing technologies.

The initial ATS Materials and Manufacturing Program Plan, published in 1994, outlined seven categories of needs identified by the gas turbine industry: (1) coatings and process development; (2) single-crystal airfoil manufacturing technology; (3) materials characterization; (4) technology information exchange; (5) turbine airfoil development; (6) ceramics development; and (7) catalytic combustor materials. Work is now in progress in the first four of these categories. The development and demonstration of self-reliant thermal barrier coating (TBC) is being performed in programs at Westinghouse Power Generation and Pratt and Whitney. Development of manufacturing technology for single-crystal turbine airfoils is being performed in programs at Howmet and PCC Airfoils. National laboratories, universities, and industry are involved in materials characterization. Technology information exchange involves annual meetings, work-

shops, and participation in national and international conferences.

The transition of aircraft single-crystal technology to land-based gas turbines has been a major challenge. The large blade sizes require longer casting times at high temperature. Cores and molds used in aircraft engine castings have not been adequate and new molds and cores are being developed. The larger blades are also more prone to casting defects. Since yield has a direct bearing on cost, additional improvements will be required to meet ATS cost goals. Alloy melting procedures have been developed and transitioned into production that significantly reduce the sulfur content in the turbine airfoil alloys. Sulfur has been shown to significantly reduce oxidation resistance and influence spallation of TBC. New TBCs have been identified with improved environmental resistance and longer life as determined in laboratory and bench tests. Engine testing is planned in the future for selected candidates.

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