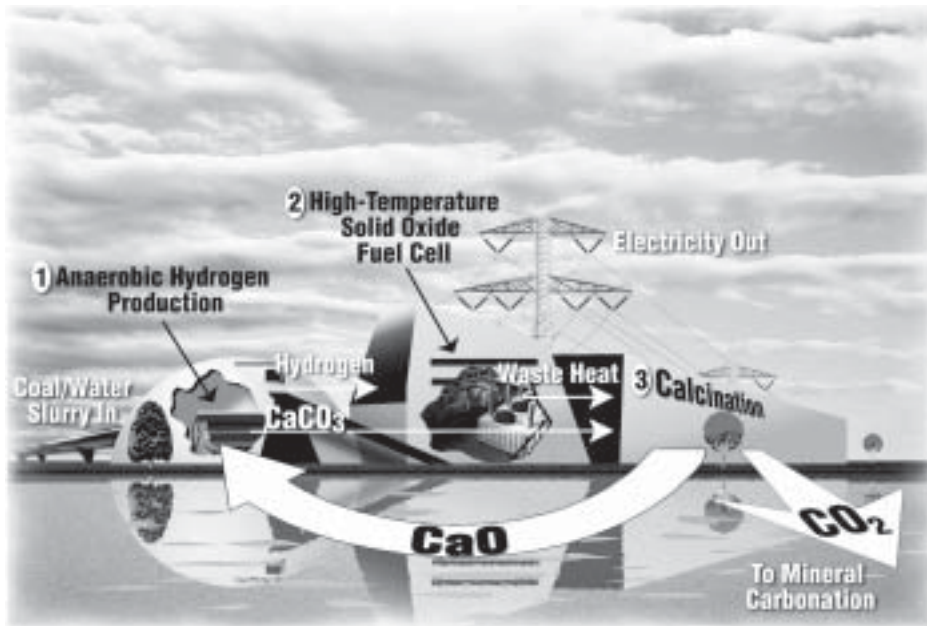




Energeia



Hydrogen Storage on Carbon Nanotubes

Bradley Bockrath
National Energy Technology Laboratory

Single-walled carbon nanotubes are remarkable forms of elemental carbon. Their unique properties have stimulated the imaginations of many scientists and engineers to propose a wide range of applications. At NETL, the Advanced Materials Research Team has looked at one of the proposed applications which is relevant to fuels for the future, and that is hydrogen storage.

Carbon nanotubes struck the fancy of chemists immediately on the first report of their existence by Iijima. It is interesting to look back on some of the connections that go along with this story. First, the discovery of nanotubes came out of an investigation of the soot left behind during the production of fullerenes by the arc discharge process. Even if fullerenes had no other practical value, we have the intense interest they generated to thank for the advent of the era of carbon nanotubes. Fullerenes were first identified by mass spectroscopy. This follows in the decades old tradition of chemists that is the use of spectroscopic evidence as a prime tool to determine the structure of new molecules. The structure of nanotubes was obtained by a different approach: direct physical observation using transmission electron microscopy (TEM). Perhaps the full recognition and appreciation of this new form of elemental carbon had to await the development of powerful tools for visualization of objects on the nanoscale.

Nanotubes do have a dramatic visual impact. If beauty rests on symmetry, nanotubes have inherent beauty.

Zero Emission Coal — Competitive, Highly Efficient Electricity Production from even High Sulfur Coals

Alan A. Johnson
ZECA Corporation

Until recently, it was conventional wisdom that 'clean coal' meant abandoning high sulfur coal resources, reducing plant efficiencies and increasing costs. ZECA Corporation is developing a new 'Zero Emission' technology that was invented at Los Alamos National Laboratory. It may stand this preconceived notion on its head. The ZECA Technology has the potential to readily accept high sulfur coal, double plant efficiencies and produce power at essentially the same cost as a modern utility designed to meet existing and proposed environmental regulations.

This novel coal gasification and power generation concept includes the capture and sequestration of CO₂, and

the elimination of all other emissions to the air. The power generation process is a combustion-free chemical process that converts coal and water to hydrogen that is in turn used to fuel a solid oxide fuel cell. The CO₂ separation is an integral part of the process and raises power generation efficiency. The estimated busbar efficiency is about 70 percent. The CO₂ is permanently sequestered in a second process as an inert solid mineral carbonate.

This article is an update that follows a presentation that the author (then President of the Coal Association of Canada) made on behalf of the Zero Emission Coal Alliance to the Coal Prep 2001 conference in Lexington Kentucky. The 'ZEC Alliance' has now been reorganized as ZECA. Technical advisors to the ZEC Alliance included the U.S. Department of Energy, the

Zero Emission Coal, (cont.)

Electric Power Research Institute, the Gas Technology Institute, Columbia University and the National Mining Association.

The ZECAAlliance engaged Nexant, Inc., a Bechtel technology and consulting company, to use the LANL's 'Zero Emission Coal' concept to design a conceptual process to achieve the goal of zero air emissions for a power plant. Figure 1 from that report, shows two aspects of the ZECA Technology. The top portion illustrates an anaerobic gasification and power generation concept, which produces hydrogen for use in solid oxide fuel cells. The bottom of the diagram shows the process for reaction of the CO₂ gas with common magnesium silicate rock and the production of an inert mineral carbonate solid for permanent CO₂ sequestration.

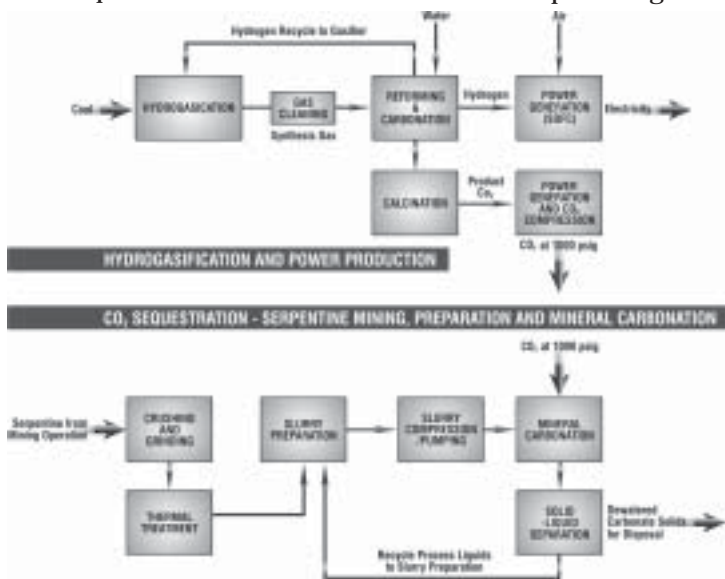
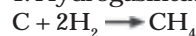


Figure 1.

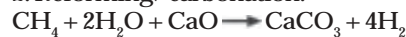
Gasification of coal, or other feedstocks, is accomplished through hydrogasification: a combustion-free process requiring no oxygen or additional energy inputs (Equation 1). The gasification is followed by operations to convert (reform) the synthesis gas from a mixed gas stream of mainly methane with some carbon monoxide and other constituents to a gas stream composed mainly of hydrogen (Equation 2). The lime, or CaO, is then recovered by heating (Calcining) the limestone or calcium carbonate (CaCO₃) that forms in step 2. The calcining also produces a relatively 'pure' stream of CO₂ that is at high pressure and ready to be sequestered (Equation 3).

The main chemical reactions involved in the process are:

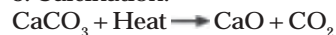
1. Hydrogasification:



2. Reforming/ carbonation:



3. Calcination:



A little over half of the produced hydrogen is sent to a (yet to be designated) sulfur-tolerant, Coal Compatible Solid Oxide Fuel Cell (CCFC). This hydrogen is electrochemically consumed to produce electricity and 'waste' heat. This heat, in fact, is not wasted but sent back to drive the calciner. The remainder of the hydrogen is recycled back to the gasifier to keep the process going. While the thermal energy from the CCFC is returned to the process, providing the energy needed to

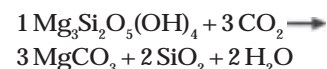
convert the calcium carbonate back to lime for recycling as the CO₂ capture medium, the thermal energy carried with the CO₂ stream is converted in a heat recovery steam generator to steam, which is in turn used to power compressors that raise the CO₂ pressure to 1000 psi for transport or further processing. In the basic 'ZECA' concept, the nearly pure stream of compressed CO₂ is sent to a mineral carbonation process

for permanent sequestration of the CO₂ as a carbonate solid. This process is a highly accelerated version of the same reaction used by nature to remove CO₂ from the air over geological time-scale. A broad survey of magnesium silicate resources shows that quantities of the mineral are sufficient to sequester all the existing carbon resources.

In the mineral carbonation process, large quantities of the mineral Serpentine are mined, finely ground and heat pretreated to form the reactive feedstock to carbonate with the CO₂. An aqueous slurry is prepared

from the Serpentine. The carbonation reaction of the CO₂ with the slurry is performed at high pressure, and results in finely precipitated solids, which are separated from the liquid. The liquid is returned to the process and the solids are sent to a final disposal area. Work is ongoing at a number of DOE and associated laboratories to modify the process to avoid heat pretreatment and improve the product ease of handling. The main chemical reaction in the carbonation process is:

Serpentine to Magnesite



In addition to Serpentine, experimental work has been done with Olivine, a similar mineral that does not need heat pretreatment.

It is important to note that mineral sequestration is not the only way to safely secure CO₂. It is included in the basic ZECA design only as a 'fail safe' process to make certain that there is an ultimate solution for carbon management. The conceptual design and cost estimating work indicate that the gasification – power generation process has the potential for high efficiency, even including the separation and pressurization of a concentrated stream of CO₂ for sequestration. Nexant estimated that the busbar, higher heating value basis efficiency would be about 70 percent. Cost and economic estimates for the gasification and power generation process show values potentially competitive with other power generation technologies such as natural gas combined cycles and integrated gasification combined cycle (IGCC) with CO₂ capture. The

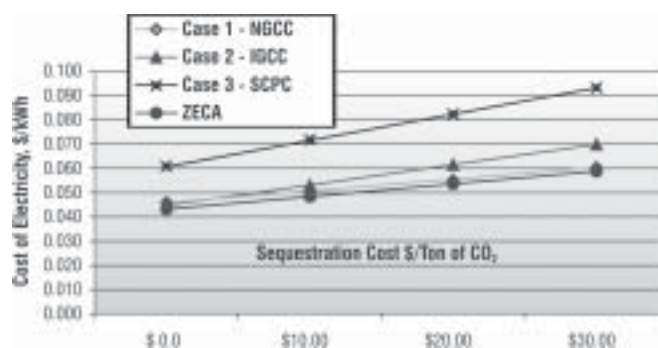


Figure 2. Natural gas at \$2.70/Million Btus.

study indicates that construction costs for the gasification and power generation facility would be on the order of

Zero Emission Coal, (cont.)

\$1,600 per kW. The competitive advantage is most strongly in favor of the technology when CO₂ sequestration is included, as illustrated in Figure 2.

Case 1 (on about the same line as ZECA) represents a natural gas turbine combined cycle; Case 2 is an IGCC plant and Case 3 is a super-critical pulverized coal plant. All the plants included CO₂ capture. The cost for natural gas used here is \$2.70 per million Btus, which may be conservative given future projections for gas prices. The type of sequestration is not specified, but costs are varied from \$0 to \$30 per ton of CO₂ to show the impact of CO₂ generation and sequestration on the total cost of electricity for the different technologies. (Natural gas at double the amount used here or about \$5 adds just over 2¢ per kW-hr to the price of electricity assuming a 40% conversion efficiency of fuel to electric energy.)

Electricity is the plant's main product. Under some market conditions, the plant could be designed to produce hydrogen for sale or use along with electric power. Also, in the initial implementations of this concept it is expected that less efficient hydrogen turbines will be used in place of the fuel cell, reducing the overall efficiency to a still excellent 55 percent but that the cost of electricity would still be competitive.

Costs and economics for the mineral carbonation and sequestration operation are more difficult to quantify at this point in the program. Laboratory work is in progress sponsored by an ongoing U.S. Department of Energy program. ZECA's mineral carbonate assessments are focused on highlighting the issues to be resolved and improvements needed to make mineral carbonate sequestration attractive to industry and localities where the process plants might be located.

We recognize the relative immaturity of the ZECA technology and that several components require further development. However, the potential for high efficiency, economic production of hydrogen and electric power from coal and other fuels (petroleum coke and bitumen) with CO₂ separation, provides strong incentives for future investment and work.

The high efficiency reduces fuel consumption and related environmental issues at the front end and post combustion. By eliminating all air emissions, the plant avoids any need for incremental retrofits that often result from ever increasing environmental requirements. In certain scenarios, compared to PM 2.5 control costs for existing plants, the elimination of PM 2.5 issues by the ZECA process could largely compensate for the cost of mineral carbonate sequestration. More importantly, because the ZECA Technology employs a completely closed system, removal of sulfur can be accomplished by using sacrificial CaO beds or other standard means on each cycle. The removal process need not be absolute as the remainder is continuously recycled in the system. This factor alone could reclassify huge high sulfur coal resources as acceptable fuel for clean energy production.

The ZECA concept may also be one of the technologies that aid in the pursuit of a hydrogen based economy. Depending on the plant design and economic scenarios, hydrogen could be the primary product. Alternatively, if the ZECA concept is employed in conjunction with petroleum refining operations, the hydrogen could be used to produce clean liquid fuels for bridging infrastructure gaps until low cost hydrogen, distribution systems and competitive fuel cell technologies become available.

The business and technical plan optimistically call for a pilot plant for tests and operations in about 5 years. We are working with equipment, materials and process suppliers to better determine the availability of components, and will be performing additional process design and optimization tasks.

Highly efficient, competitive and pollution-free utilities that can generate electricity or produce hydrogen using any coal without air emissions — that's the 'ZECA' concept — an ideal solution to the world's growing energy demands.

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Hans-Joachim Zioc (Los Alamos National Laboratory) and John Ruby, (Nexant Inc., A Bechtel Company) also contributed to this article.

Hydrogen Storage, (cont.)

Further, their cylindrical structures led to suggestions that they would be ideal gas storage materials. The appearance of these potential storage materials conveniently coincided with the revivification of interest in the hydrogen economy. The potential for coupling carbon-based storage materials to supply pure hydrogen to automotive fuel cell power plants was quickly seen. Initial reports of experiments showing high levels of hydrogen storage were encouraging. Theoreticians were then quick to calculate the possible amounts of hydrogen that could be stored using arrays of tubes of various sizes and packing parameters. Since the appearance of the initial reports, the results have been varied and controversial. Some are higher, some lower; some imply physisorption, and some chemisorption. It is clear that storage is a complex issue, partly because the materials are far more complex than the visual comprehension of the single ideal nanotube would allow.

Single-walled carbon nanotubes do not come to the laboratory experimentalist as ideal structures. Rather than being the perfect and straight cylinders typically depicted in illustrations, they more often look like piles of cooked spaghetti. If made by laser ablation or arc discharge, several forms of carbon besides nanotubes are typically present. Carbon clutter composed of amorphous carbon, fullerenes, "bucky onions," and graphitic debris may be present to a greater or lesser degree. Depending on their post-synthesis treatment there are variable numbers of defects in the structures. Not every sidewall may be perfect. There are holes here and there. Functional groups are attached to the edges of the holes and at the uncapped ends of the graphene walls. The metals used as catalysts in the synthesis are encapsulated in graphitic sheets, entwined in nanotube bundles, and resistant to efforts to separate them. Various methods have been developed to remove the metals, but none is perfectly selective. Further, the tubes can be damaged when the metals are removed during the purification process.

Experimentalists engaged in hydrogen storage research are learning to deal with carbon nanotubes and their far from fully understood characteristics. Together with my colleagues at NETL, Drs. Edward Bittner and Milton Smith, an investigation of hydrogen adsorp-

Hydrogen Storage, (cont.)

tion was begun that has developed two main aspects. One aspect is analytical. Other than visual inspection by TEM, how does one learn about the complexity of the particular sample of nanotubes in question? Temperature programmed oxidation is one way to characterize samples of tubes based on chemical reactivity. An example is shown in Figure 1. During thermal gravimetric analysis (TGA) using air, it is seen that the rate of weight loss varies as the temperature is increased. The differential of this weight loss curve can be fit by a series of peaks, thus indicating that oxidation proceeds in defined stages. If different parts of the sample required different temperatures for oxidation, it seemed logical that peaks in the differential of the TGA could be manipulated by choice of the gas stream used in the analysis. In fact, each peak shifts to a lower temperature when pure oxygen is substituted for air and to higher temperatures when carbon dioxide is used. Significantly, some peaks were well-separated under carbon dioxide, suggesting that part of the sample could be selectively removed by limiting the oxidation temperature at a value between the low and high temperature regions. In fact, this idea worked quite well when it was transposed from an analytical to a larger scale using samples on the order of a fraction of a gram. That result led in turn to a pleasing discovery about hydrogen storage capacity.

A brief description of our measurement of hydrogen storage capacity is necessary before discussing the results. In general, determinations of gas uptake have been made based on either pressure change or gravimetric methods. Each method has advantages and disadvantages. We chose to use a recently developed instrument, a tapered-element pulse mass analyzer, to determine isotherms. This instrument's attractive features include a flow-through design that promotes good contact of the gas stream with the sample in the packed bed and good time resolution with the measurement of small mass changes. This allows both the amount of gas that is adsorbed and the rate of its adsorption to be probed. The latter is an important consideration in discerning physisorption from chemisorption. We have found that in progressing through a programmed pressure experiment, the weight of the sample bed reaches equilibrium within seconds after each pressure jump. This

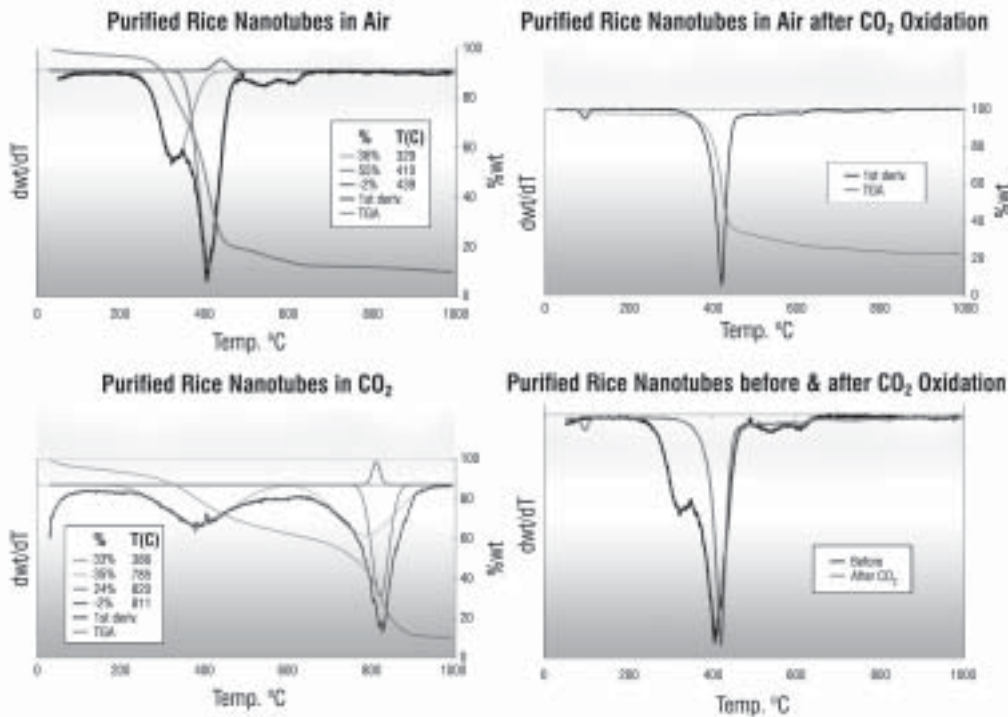


Figure 1. Investigation of single-walled carbon nanotubes by TGA. Carbon dioxide provides better resolution and can be used to selectively remove the most reactive components of a purified nanotube sample.

is consistent with a purely physisorption process. Five examples of isotherms obtained with this instrument are given in Figure 2. The first is for a sample of single-walled nanotubes made by the laser ablation method. They were purchased in the "raw" and the purified forms. The nitric acid treatment used in the purification reduces the metals content and removes extraneous carbon material. For both the raw and purified tubes, the storage capacity is lower than that of an activated carbon when measured at 25 °C and 700 psia, the upper pressure limit of our instrument. Still it is evident that higher pressures would lead to greater storage. The adsorption capacity increased significantly after partial oxidation under temperature controlled conditions with carbon dioxide. A further increase was found after the oxidized samples were heated to 700 °C in helium, which drove off a large fraction of the oxygenated functional groups. This combination of CO₂ oxidation and mild pyrolysis increased the hydrogen capacity of the original sample by a factor of nearly three. Thus, nanotubes are amenable to activation. Many techniques have been developed to activate conventional carbons over the years. Perhaps a similar array of methods can be employed to tailor the adsorption properties of nanotubes as well.

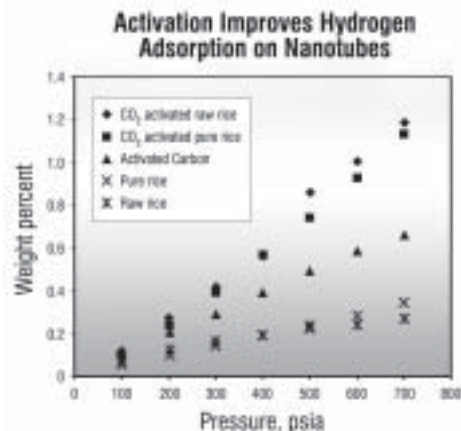


Figure 2. Activation of carbon nanotubes using CO₂ improves their hydrogen storage capacity.

This work has a theoretical as well as experimental dimension. Prof. Karl Johnson of the University of Pittsburgh has been simulating the physisorption of hydrogen and other gases on nanotubes for several years. The more refined models take into account complex arrays of nanotubes and the introduction of functional groups. The Monte Carlo simulation for an array of tubes of similar dimensions as the purified sample that was used at NETL agrees with the experimental results. The next step is to identify the physical and chemical features of a nanotube array that would lead to the result obtained with

The Scientist versus the Journalist Meeting a Communication Chasm Head-On

Marybeth McAlister
Editor, *Energiea*

Who? What? Where? Why? When? How? Asking these questions is the first thing the student learns in journalism school. The goal of training journalism students is to produce writers who can obtain any piece of information required to write a clear, objective newspaper article. These stories are traditionally aimed at an eighth-grade reading level. This works fairly well when the story is about a fire, a murder, or some other gruesome event.

It doesn't work as well for in-depth coverage of complex scientific issues.

Part of my job as public relations coordinator at the CAER is to find the appropriate scientist* to interview when a reporter calls about a particular issue. Initially, I was surprised by the researchers' moans and groans on these requests. What was so bad about talking to a member of the media? What was wrong with being represented in the popular press as experts on a subject? The answer? According to one scientist, "They always get it wrong. If they don't get it completely wrong, they get it partially wrong, which is sometimes worse, because then they think they are experts." One scientist here says that he has been misquoted or misinterpreted so many times he refuses to participate in interviews.

How do we bridge this gap? On the one hand there is the scientist, who sees his innumerable data as exciting enough to translate into a front-page story (complete with graphs and tables) or the lead-off on the nightly news. On the other hand stands the ever-skeptical journalist who thinks he can walk into a research institution that was unknown to him the previous day, and come out with a clear, interesting, factual story. (Journalists are people who generally did not do so well in college chemistry, if they took it. Their course requirements rarely ventured into the realm of physical or life sciences).

It has become a rarity that reporters (especially television) have the luxury of time to research topics with any kind of depth. At most they may be allowed one week to explore and digest the subject at hand. Next week's topic could be, and probably will be, completely unrelated to



today's. Editors must allow their reporters enough time to do a thorough job. Also, the media corporations need to develop their own in-house experts on particular subjects. Keep the same reporters on their "beats" as long as possible (e.g., medical, business, energy, agricultural) so that their sources have enough time to develop a relationship with them and trust them. This can only take place through time and several interviews.

While most reporters that I know like to think they represent TRUTH, JUSTICE and THE AMERICAN WAY, the truth is that they work for companies in a capitalist society that want to make as much money as possible. They have shareholders to answer to. The trend I'm seeing is for shorter stories, more advertising, and flashy headlines, rather than earnest, thoughtful discussions of complex problems. As long as the trend of the 30-second sound bite continues, I don't see much of an improvement.

It is the scientist's responsibility to speak consistently and concisely in an

interview. Remember that the person doing the interview only has a temporary and slight interest in the topic at hand: don't try to demonstrate how smart you are. They know you have a PhD and are an expert in the field. That is why they are interviewing you. Scientists should also remember that if small points from the discussion were misunderstood and are incorrect in the report, it doesn't really matter. Remember the audience. The small town housewife, who just got her kids off to school and has a minute to read the morning paper, will notice a story that says the university is performing research on energy. Scientists are trying to make coal burn cleaner and more efficiently. This is good news for her and her family. That is all that matters to her. If the exact parts per million of emissions is incorrect in the article, it is irrelevant.

For those details, we depend on our trade and scientific journals. We are lucky in the energy industry that we have so many good ones. That is really the place to focus on details. Those publications are written and read by peers. Those popular trade journals, along with refereed publications, are where the real news of trends, research, and breakthroughs occur.

It seems that every 10 to 15 years, energy re-emerges in the news. It is currently one of the popular topics for investigation. Many local and national stories will be written and broadcast on a range of topics within the industry. Many will be irksome and provoking in their biases, wrong information, and just plain stupidity. However, remember that it keeps people thinking about energy. One of the most dangerous things that can happen is for our population to become complacent about it. That is when the problems begin.

Remember, you can always write a letter to the editor.

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**Scientist here refers to both scientists and engineers. I understand that lumping these two professions together could provoke an entirely separate future editorial.*

Hydrogen Storage, (cont.)

the carbon dioxide activated materials. This coordinated approach leads to the design of better experiments both in the laboratory and on the computer.

Where does this leave us and what are the prospects? A storage capacity of 1 wt % hydrogen is considerably short of the stated DoE target of 6 wt%. Going to higher pressures with this sample would bring us closer, but probably not to the target level. Nonetheless, avenues for improving storage capacity remain open. Methods for chemical activation are a long way from being exhausted. The reasons for the improved performance we have seen are not yet clear, but further experiments can tell us more. Much attention has been devoted to single-walled nanotubes, but multi-walled tubes may offer potential as well. One thing may already be evident. The best material for gas storage may not be the ideal nanotube structures and arrays frequently assembled in theoretical studies, but a chemically

and physically disordered array engineered to provide molecular nooks and crannies better able to trap and retain hydrogen. Build a better hydrogen trap and the world will drive to your house in a fuel cell powered car.

Having spent a good bit of time working in a national laboratory that has devoted considerable attention to coal, the whole new field of nanotube research brings special associations to mind. The inherent problems in characterizing both materials are in many ways strangely similar. Both are black, insoluble materials. Both contain an inorganic component that originated in the formative process; the intimately mixed mineral matter in coal and the encapsulated catalytic metals in nanotubes. Both have intriguing pore structures that have sparked controversy. The "blind" pores of coal have their answer in capped carbon nanotubes. Oxygenated functional groups play a big role for

both. Pyrolysis has been used to release these groups in both cases. The potential for making derivatives at carboxylic and phenolic sites has been well explored for coal and is now beginning to be exploited for tubes. Both are held together strongly by intermolecular forces and associative bonds that are not totally understood. Both swell and take in solvents to various degrees. Techniques that have been developed over the last few decades to investigate the structure of coal would undoubtedly be helpful. Some valuable insights have been recently reported that resulted from using techniques reminiscent of those used in coal characterization and one anticipates far greater progress in the near future.

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