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Creation and Destruction of C₆₀
and Other Fullerene Solids

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Final Report

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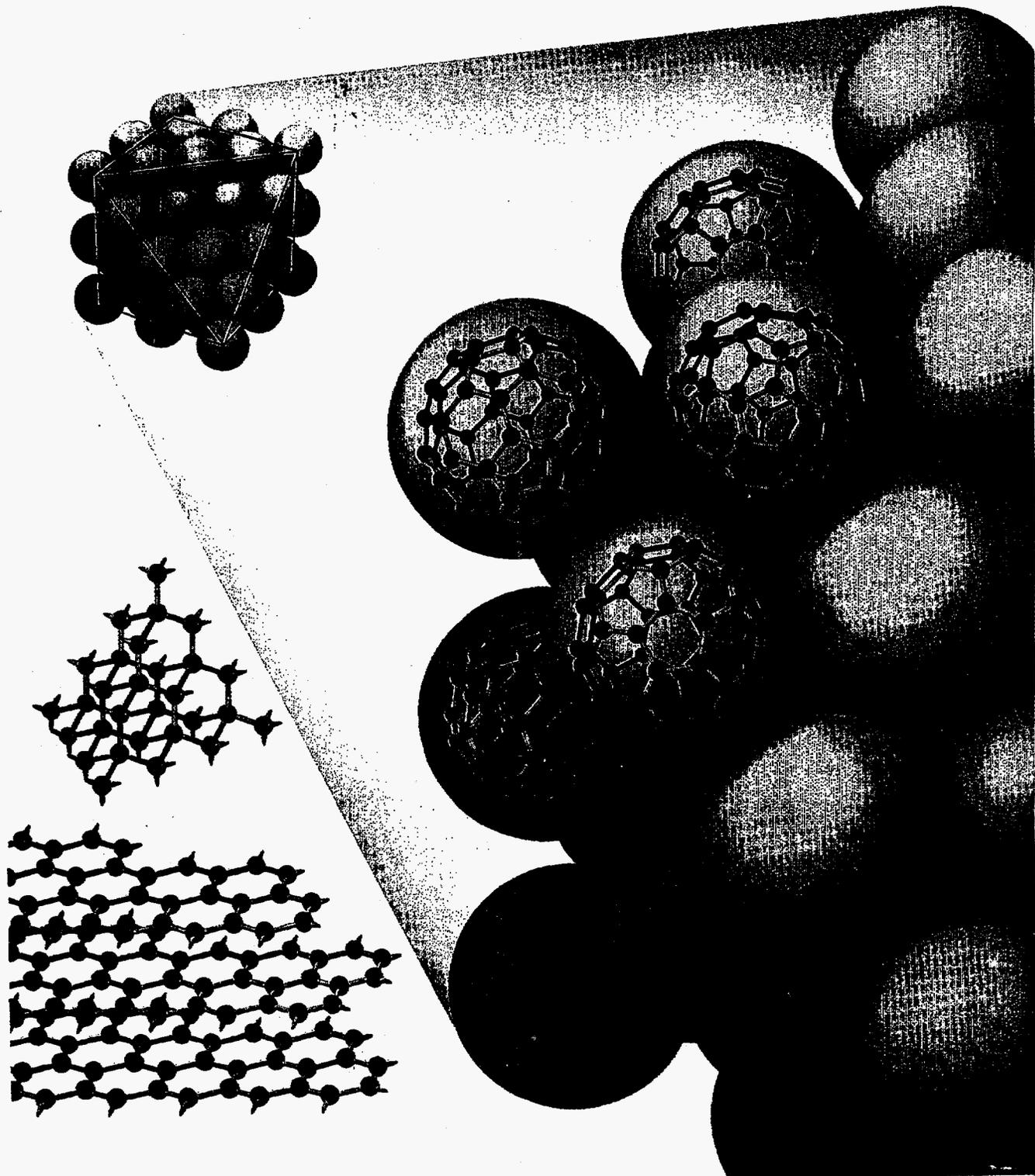
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The three forms of solid carbon. The corner cut from the C_{60} crystal cube reveals a (111) crystal plane where molecules stack in hexagonal arrays. The structures of diamond and graphite are shown at the middle and bottom left. (Drawing © 1991, Henry Hill, Jr.)

1 Overview

The 1990 announcement of the Huffman-Krättschmer fullerene-production technique [1] set off a world-wide explosion of research into the properties and potential applications of C_{60} and C_{70} . In the last five years, 4,000+ fullerene articles have appeared in the scientific literature dealing with these fascinating molecules and their condensed phases. They possess a complex chemistry reminiscent of the alkenes, and this has led to the syntheses of numerous new compounds and fullerene-based materials, with suggested applications ranging from medicine to photo-conducting polymers to rocket fuel. The work summarized in this report focused on the creation and destruction of fullerene-based materials, for the purpose of producing new materials of interest. This three year project was supported by a grant from the Advanced Energy Projects Division, Office of Basic Energy Sciences, U. S. Department of Energy (DE-FG03-93ER12133). Following are outlines of the work completed in each of the three years, a section devoted to the professional and educational development of those involved, a brief section on the outlook for fullerene-based materials, and an appendix listing the publications resulting from this project.

2 First Year

During the first year, the work focused on the construction of two new fullerene-production chambers (led by Huffman), and on early studies of carbon nanotubes (led by Seraphin).

Fullerene Production

Our fullerene-production research required the construction of two new fullerene generators. One chamber, built principally by graduate student Frank A. Tinker, was used over the course of this project for a systematic study of fullerene production conditions, with the objective of better understanding the mechanism of fullerene formation. This apparatus ultimately incorporated full computer-control of the electrode motion, and continuous computer monitoring of the current and voltage. For example, the data plotted in Figure 2 show the ability of the system to maintain a particular current flow throughout a burn. Tinker's chamber was used during the first year to make multi-walled carbon nanotubes, single-walled bucky tubes, as well as to carry out a number of preliminary soot-production studies. Ultimately, the results from this project formed the subject of a Ph. D. dissertation [2]. The second chamber, built by graduate student Michael C. Zumwalt, was specifically designed for a study of fullerene production in "mixed" atmospheres (i. e., mixtures of helium and other gases). Both chambers were built entirely within vented hoods so that this research was carried out as cleanly and safely as possible.

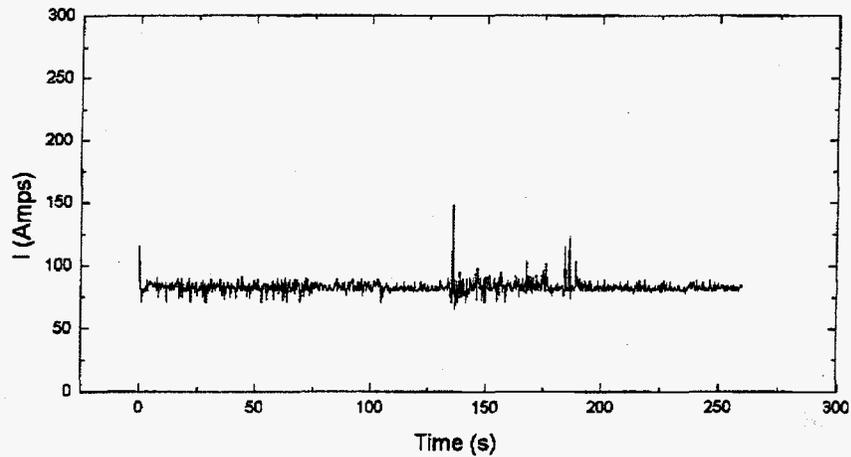


Figure 2: Current as a function of time during a 100 mm burn showing the apparatus' ability to maintain a constant feedback value.

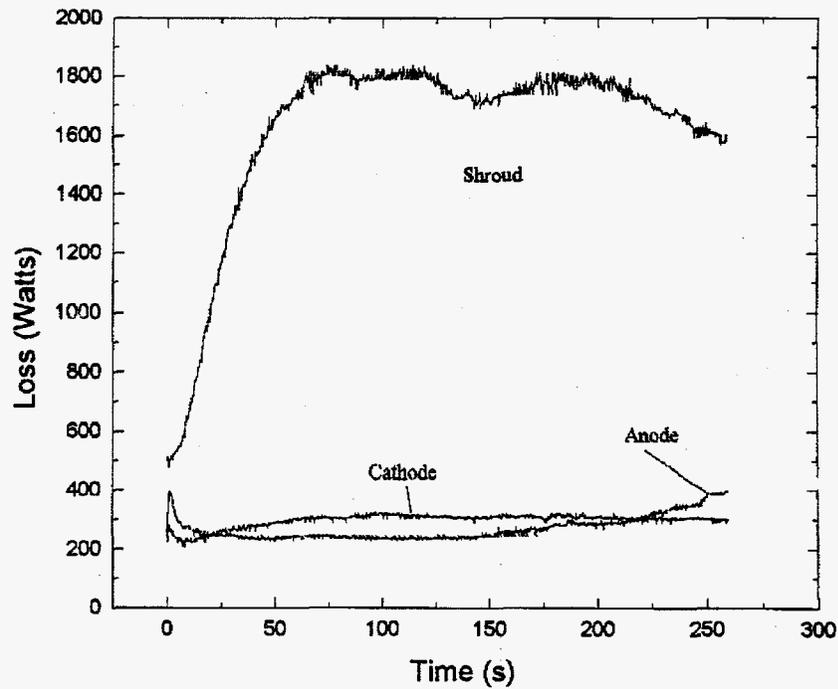


Figure 3: Power (heat) loss from anode, cathode, and shroud during a 100 mm burn. This is an example of the "test-bed" chamber data monitoring activities.

Nanotubes and Nanoparticles

In collaboration with workers from Materials and Electrochemical Research, Inc. (Tucson), Seraphin's group published a major paper in *Carbon* on the effects of varying the nanotube production conditions [3], and reported in *Nature* on the first production and characterization of carbon nanotubes containing yttrium carbide nanocrystals [4].

Other Work

In collaboration with Mark M. Ross's group at the Naval Research Laboratory, Lamb and Huffman published an article in *Science* on the production of the first *odd*-numbered fullerenes C_{119} , C_{129} , and C_{139} [5]. These clusters are formed catalytically by reaction with ozone, and are the products of the coalescence of two C_{60} s, a C_{60} and a C_{70} , and two C_{70} s, respectively, less one carbon atom. Besides the production of large, odd-numbered clusters, these results suggest a new route to the functionalization and derivitization of the fullerenes through controlled ozone-catalyzed cage-opening reactions. These remarkable new structures are also an excellent example of the synthesis of new materials (in this case C_{119} , C_{129} , and C_{139}) by the "destruction" of the fullerenes C_{60} and C_{70} . In collaboration with the group of Prof. Peter R. Bernath of the University of Waterloo, during the first year Huffman's group prepared samples of pure C_{60} and C_{70} , and measured the gas-phase infrared emission spectra of these molecules as a function of temperature [6]. Besides providing accurate measurements for future theoretical work, the results of this effort will be of use in searches for the fullerenes in astronomical objects.

3 Second Year

During the second year, systematic explorations of fullerene production conditions were carried out, and the nanotube/nanoparticle work was extended to include a study of the effects of using metal-doped electrodes on the production of carbon nano-structures. Described below are some of the highlights of the second year's work.

Fullerene Production

A core project in this work concerned the formation process of fullerene molecules. There are at least five theoretical models that detail separate pathways leading to fullerene formation. With no consensus in the scientific community for any one pathway, it is clear that more experimental work is needed. In this laboratory, work centered on elucidating the formation mechanism by attempting to trap their intermediates. The first steps of fullerene growth involve the combinations of atomic and small carbon molecules, hence the intermediate steps may include molecules containing the pentagons and hexagons, of which the fullerenes are

also made. Eventually, the combination and closure of these intermediate molecules should form fullerene molecules.

The attempt to trap the intermediates was carried out in a specially designed carbon-arc vacuum chamber. This chamber produces fullerenes by the vaporization of graphite rods in a controlled helium/hydrogen atmosphere. In the presence of pure helium, only carbon-carbon reactions take place. However, in the presence of a gas which is highly reactive with carbon, namely hydrogen, intermediate molecules may be frozen-out and kept off the pathway leading to fullerenes. Intermediates consisting of pentagons and hexagons tied-off around the edges by hydrogens are known as polycyclic aromatic hydrocarbons (PAH's).

Sample results from this project are shown in Figure 4, which displays mass spectra of four samples made with increasing levels of hydrogen. Two basic conclusions can be drawn. First, both the infrared (not shown) and mass spectra of the 0% and 3% H₂ samples are quite similar. While the mass spectra show C₆₀, toluene (M/Z = 92), and some contaminants as the primary constituents, the infrared spectra show all of the above, including C₇₀. It is somewhat surprising that the C₆₀ yield is only slightly affected, as reports in the literature suggest that fullerene yield is drastically affected at percentages below 3% H₂ [7]. One may conclude that fullerene yield is highly chamber dependent. Second, a trend in PAH production becomes apparent when the 15% and 50% H₂ sample spectra are examined. Though C₆₀ can still be seen in the 15% H₂ sample, quite a few other peaks are now present, and are interpreted as evidence of the formation of PAH molecules. Looking now at the mass spectrum of the 50% H₂ sample, we see that not only does the number of PAH's increase with hydrogen, but the centroid of the corresponding mass distribution increases as well, i. e., as hydrogen is added, larger and larger PAH's are produced. The results from the project were ultimately published in a scholarly volume on fullerenes [8], and formed the subject of a Ph. D. dissertation [9].

Nanotubes and Nanoparticles

The work begun during the first year on determining the effects of arc-discharge processing conditions on the production of carbon nanotubes and nanoparticles was extended during the second year. The effects of variation in pressure, voltage, electrode gap, and electrode geometry were characterized, with TEM studies forming the core of the analyses. Some qualitative dependencies of the morphology, density, and location of the nanotubes in the reaction chamber were observed, which ultimately may contribute to controlling the fabrication of these novel carbon structures.

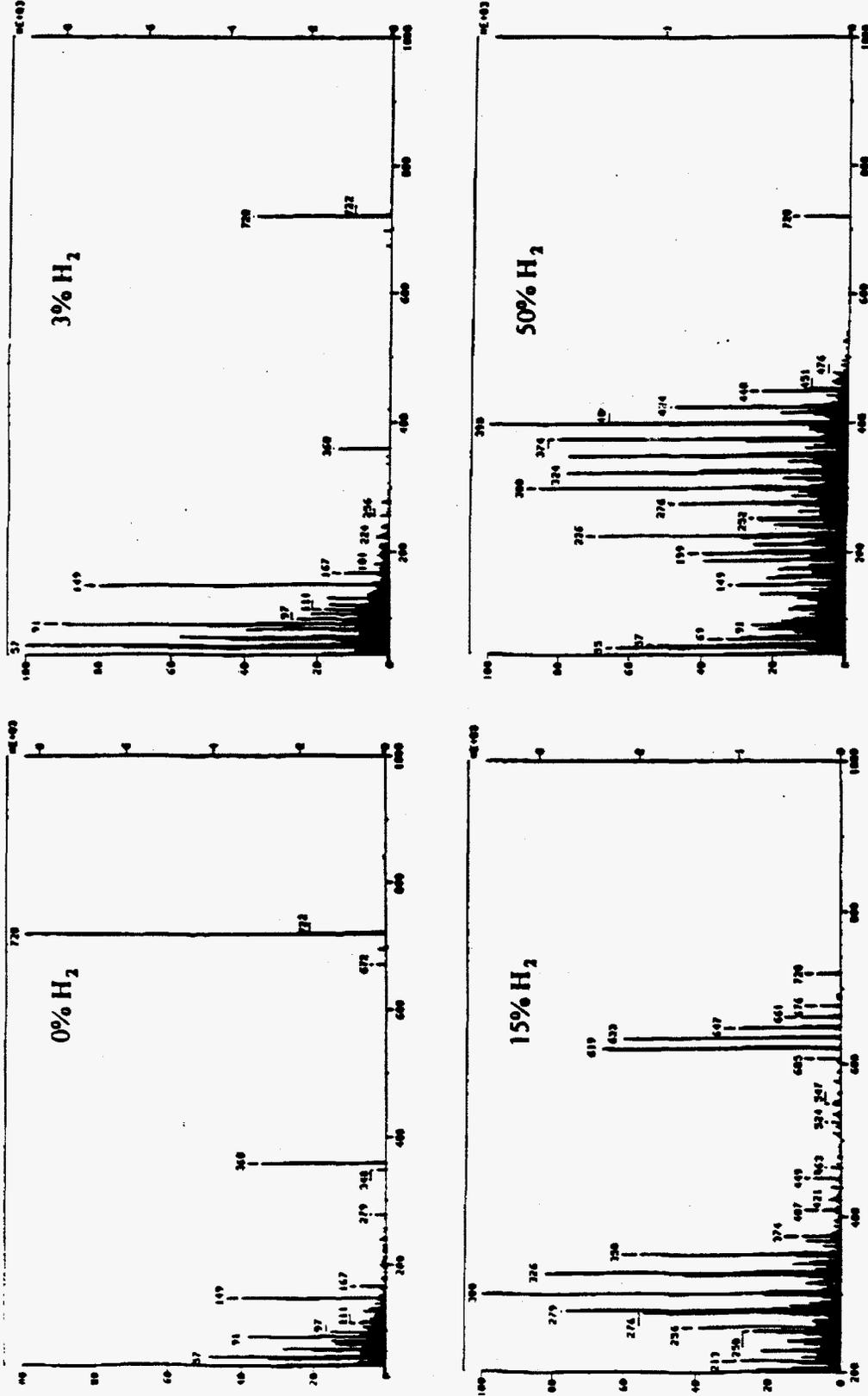


Figure 4: Electron-impact mass spectra of selected samples, showing the effects of hydrogen poisoning.

During the second year, our understanding of nanotube preparation improved in two ways; both relating to the addition of metals and metal compounds to the anode. First, the catalytic presence of transition metals and their carbides was used to stimulate the formation of single-walled nanotubes in high yield. Novel growth phenomena, such as strings of spherical, multi-walled "beads" were also observed in these studies [10]. Second, the efficient production of carbon-encapsulated nanocrystals of metals and metal compounds was explored. It is interesting to note that some metals and their compounds were readily encapsulated, others stayed outside the carbon cages, and some even inhibited the formation of cages altogether. Systematic studies involving a large variety of catalytic materials and a wide range of processing conditions were begun.

Other Work – Production of Larger Fullerenes

It is now well known that fullerene soot contains appreciable quantities of *hundreds* of larger, soluble, all-carbon clusters besides C_{60} and C_{70} . Fullerenes as large as C_{500} have been detected with mass spectrometry in solvent extracts [11], and it appears that in these mixtures of larger fullerenes every even-numbered carbon cluster beyond C_{82} is present in some concentration. Of this extensive family of molecules, only C_{76} , C_{78} , and C_{84} have been isolated in "reasonable" (tens of milligrams) quantities. An important part of our effort to prepare novel fullerene materials was our program devoted to synthesizing, isolating, and characterizing the giant fullerenes. To meet the need for starting material, during the second year we built a high-volume fullerene-soot generator. This system is rugged, easy to operate, and capable of producing ≈ 1 kilogram of fullerene soot per day. Given the typical yield of $\approx 0.3\%$ of mixed larger fullerenes, 1 kilogram of soot yields ≈ 3 grams of mixed, larger fullerenes in the extraction step.

4 Third Year

During the third year of the project, our work included the production of the higher fullerenes, mass spectrometry, and the production and characterization of nanometer-sized, carbon-coated ferromagnetic particles.

Fullerene Production

The fullerene community has invested considerable effort into HPLC separation of a few of the higher fullerenes, with "success" being measured in micrograms or perhaps a few milligrams. As it seemed clear that this approach will not provide commercial quantities of the higher fullerenes any time soon, we concentrated on "low-tech" approaches. It is worth pointing out that modest methods sometimes succeed where sophisticated attempts fail –

indeed, the Krätschmer-Huffman technique for fullerene production [1] is the epitome of "low technology" when compared to the molecular-beam approaches that preceded it. For our separations work, we have concentrated on developing large-scale, "low-tech" column-chromatography systems and systems that exploit differences in solubility among the various fullerenes. Since materials cost will be a central consideration in any future application of the higher fullerenes, we are primarily interested in systems involving low-cost materials (e. g., bulk chromatography packings (alumina, activated charcoal, etc.) and low-cost, relatively safe solvents (toluene, hexane, etc.). Figure 5 shows some preliminary mass-spectral results from an experiment where differences in solubility were used to prepare cuts rich in the higher fullerenes. Although the enrichment per pass of this approach is modest, the losses are negligible, hence multiple passes should give greatly improved enrichment with acceptable final yields. Where appropriate, this method is especially suitable for large-scale processing.

Throughout this work, mass-spectrometric studies constituted one of the core areas of our analytical effort. As part of this project, we purchased and installed a new time-of-flight mass spectrometer (TOF/MS). This rugged, easy-to-operate instrument has a resolution of ≈ 4000 in the reflectron mode/lower-mass range (< 7000 amu), and resolution of ≈ 300 in the linear mode/upper-mass range ($< 150,000$ amu). The reflectron mode is useful for characterization of most "small" molecules, including, of course, fullerene-based species, and the linear mode will be suitable for study of large biomolecules such as proteins. No other such instrument was located on campus, and the capabilities offered by the TOF/MS more than met the crucial needs of our fullerene program. As a bonus, this facility also has been of great utility to the University life-sciences community. Figure 5, which shows data obtained using this instrument, nicely illustrates the power of TOF/MS.

Nanotubes and Nanoparticles

During the third year of the project, the nano-phase materials portion of the work focused on the encapsulation of metals and their carbides into the hollow cores of carbon nanoclusters. A total of twenty elements were co-deposited with carbon in an arc discharge, typically by the evaporation of metal/carbon composite electrodes. The deposits, found in the soot at the reactor walls or as slag on the cathode, were characterized using scanning and transmission electron microscopy, electron-energy-loss spectroscopy, and x-ray diffraction. The products fell into four categories: (1) Those containing elements that can be encapsulated as carbides (B, V, Cr, Mn, Y, Zr, Nb, Mo); (2) Those containing elements that cannot be encapsulated, yet tolerate the formation of graphitic carbon cages (Cu, Zn, Pd, Ag, Pt); (3) Those containing elements that form stable carbides while competing with/pre-empting the formation of carbon cages (Al, Si, Ti, W); and (4) Those containing the metals Fe, Co, and Ni. The presence of members of the last group in the arc discharge stimulates, under various conditions, the formation of single-walled buckytubes, of strings of nanobeads, and of nanometer-sized, carbon-coated ferromagnetic particles. This last class of structures typi-

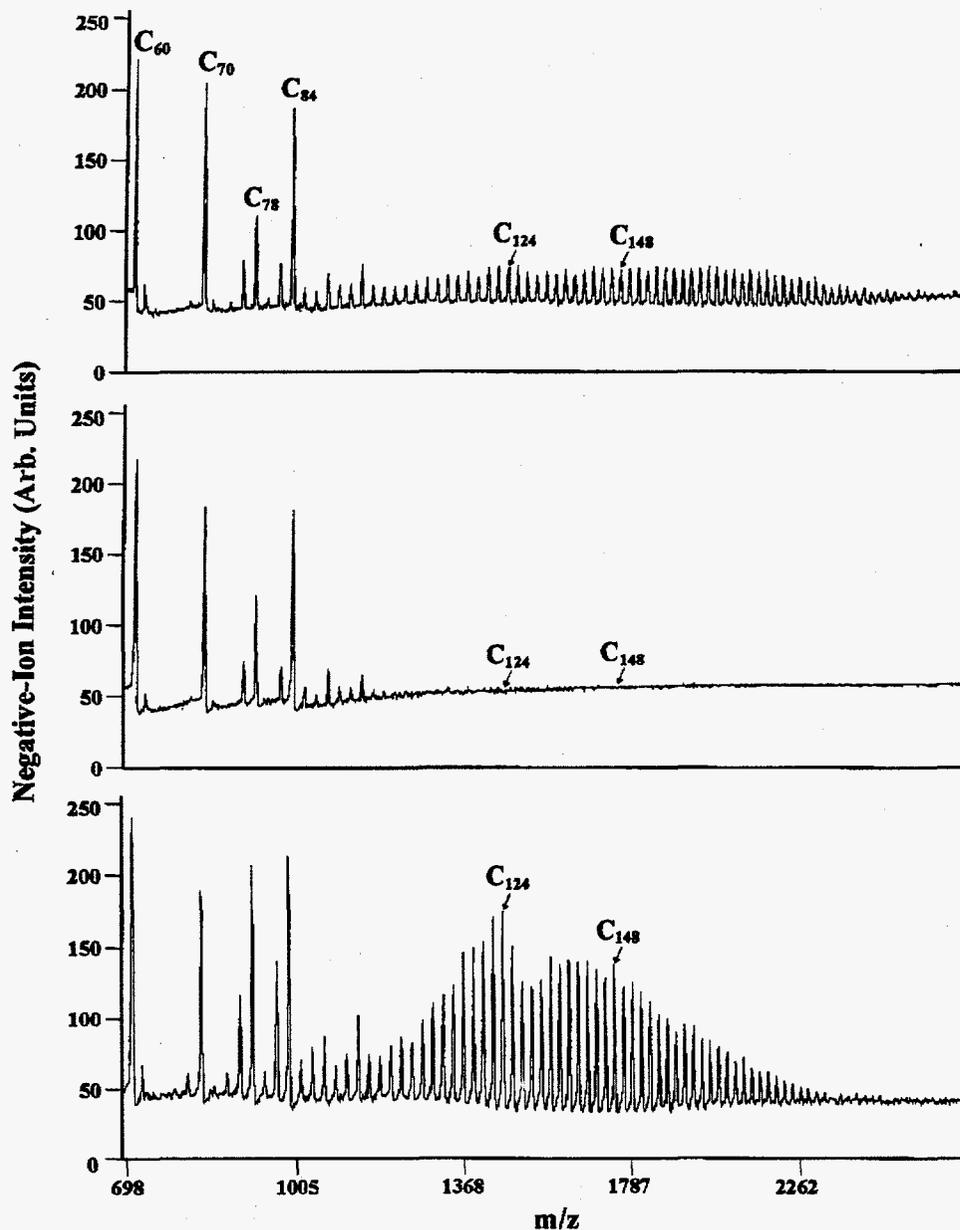
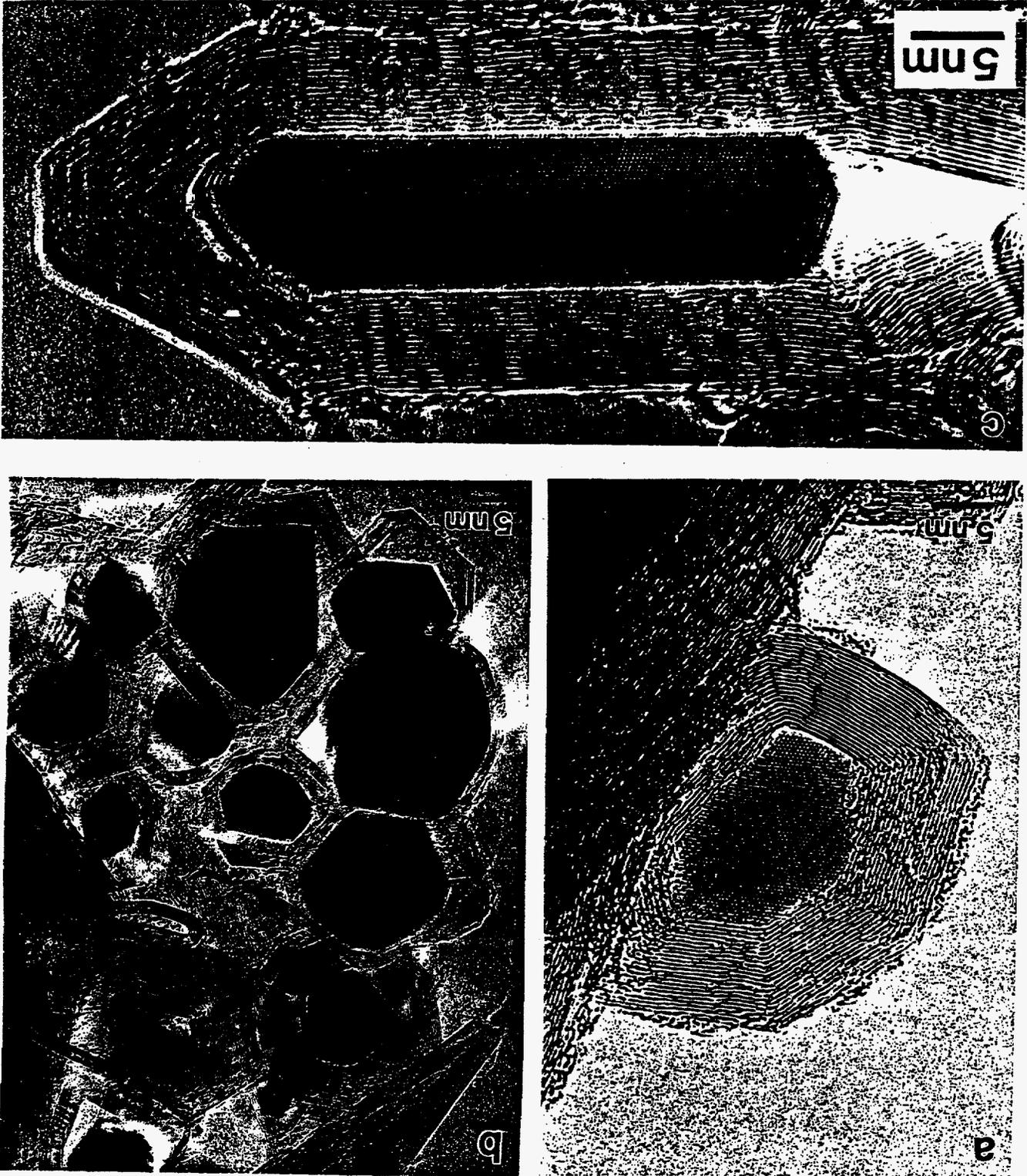


Figure 5: Fractionation of a mixed-fullerene sample via exploitation of differences in solubility. The top panel shows a mass spectrum of the starting mixture, while the middle and bottom panels show spectra of two markedly different fractions obtained by this process. Two representative giant fullerenes, C₁₂₄ and C₁₄₈, are marked for emphasis.

cally consists of particles with diameters in the 15-80 nm range. The cores of these particles are metal crystals, not carbides, and the carbon coatings are 1-2 graphitic layers for the Co and Ni, and an amorphous carbon coating for the Fe particles. When such samples are treated either by annealing or immersion in nitric acid, those particles with complete carbon shells remain intact, and further graphitization of the carbon coating by either of the two treatments is observed. Particles that are only partially coated are not protected, and are sintered by annealing or dissolved by the acid bath. Figure 6 shows TEM images of nanoparticles filled with YC_2 , MoC, and NbC nano-crystals, and Figure 7 shows SEM images of carbon-coated ferromagnetic particles, all produced as part of this work.

Figure 6: TEM images of nanoparticles filled with (a) Y_2O_3 , (b) MoC, and (c) NbC nano-crystals.



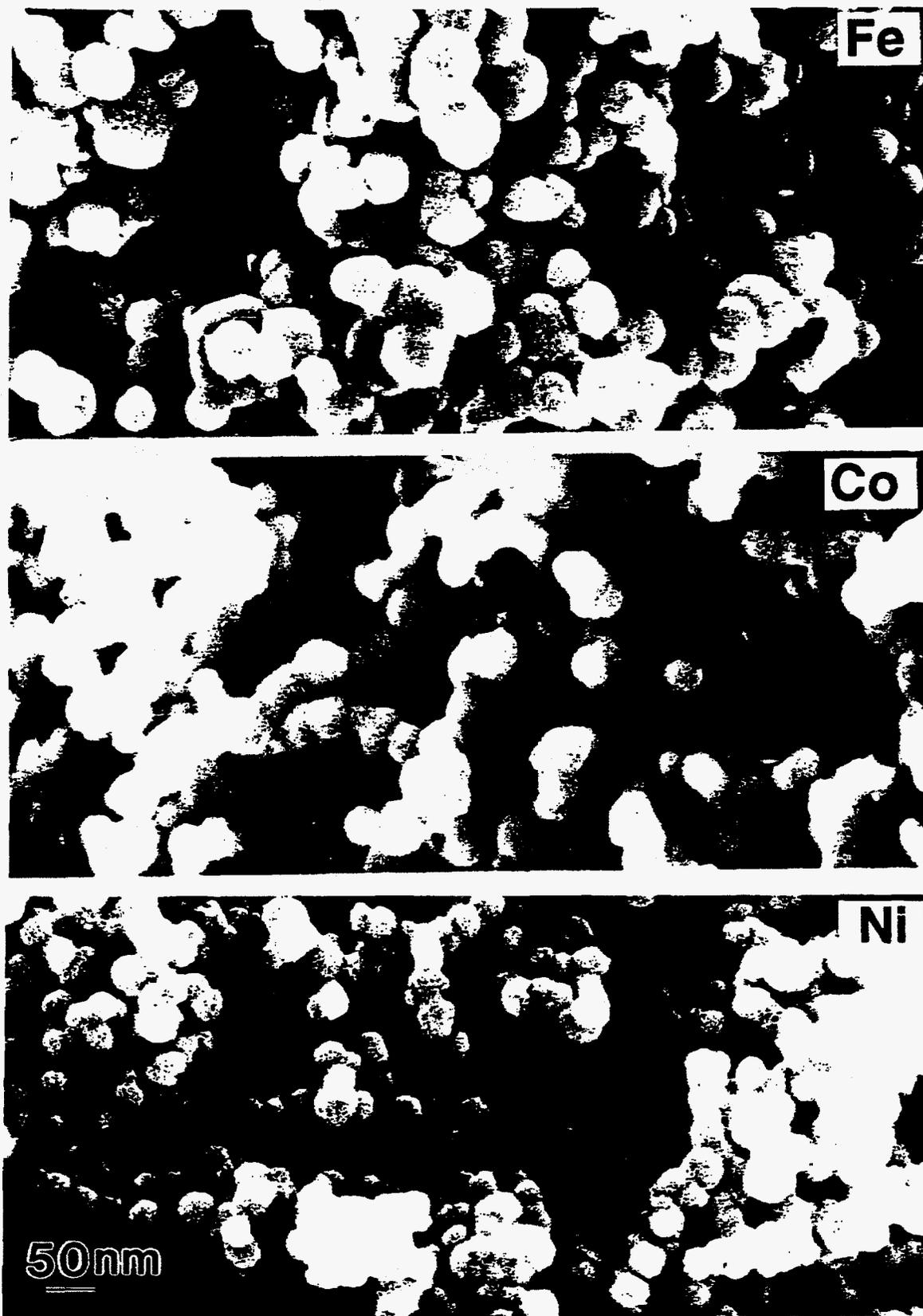


Figure 7: SEM images of ferromagnetic, carbon-coated nanoparticles, produced by the co-evaporation of carbon and Fe, Co, and Ni.

5 Professional and Educational Milestones

Over the course of this project, members of our group received a number of honors, and important educational milestones were reached. Highlights include:

- Huffman shared the 1993 Materials Research Society Medal;
- Huffman gave invited talks at the 1993 Boston and 1994 San Francisco Materials Research Society meetings, at the 1993 International Workshop on Fullerenes and Atomic Clusters in St. Petersburg, Russia, and at the Budapest Academy of Sciences;
- Seraphin was elected Sloan Fellow in 1993;
- Jun Jiao received a Master's degree in Materials Science and Engineering in December, 1993;
- Jun Jiao received the Presidential Award, Microscopy Society of America, August 1993, and the Best Student Paper Award from the Arizona Society for Electron Microscopy and Microbeam Analysis, 1993;
- Dan Zhou received the Presidential Award, Microscopy Society of America, August 1994, and the Best Student Paper Award from the Arizona Society for Electron Microscopy and Microbeam Analysis, 1994;
- Seraphin has been invited to serve as a Senior Editor in Materials Science for *Microscopy Research and Techniques*;
- Huffman shared the 1994 Hewlett-Packard Europhysics Prize, and received the 1994 Outstanding Alumni Award from the University of California, Riverside;
- Seraphin has established and is directing microscopy laboratories that serve K-12 science education and other outreach programs, including engineering summer camps, the Honors Center LEAP Program, and the Minority Students Program;
- Huffman gave invited talks at The Chemical Physics of Fullerenes 10 (and 5) Years Later Nato Advanced Research Workshop (Varenna, Italy, June 12-16, 1995), and at the 1995 International Workshop on Fullerenes and Atomic Clusters in St. Petersburg, Russia;
- Dan Zhou received a Ph. D. in Materials Science and Engineering in September, 1995;
- Huffman received an honorary Doctor of Laws degree from Pepperdine University in December, 1995;

- Frank Tinker received a Ph. D. in Physics in May, 1995;
- Michael Zumwalt received a Ph. D. in Physics in October, 1995;
- Molly Minke received a Master's degree in Materials Science and Engineering in May, 1996;
- Seraphin was promoted to Associate Professor of Materials Science and Engineering in April, 1996.

6 Prospects for the Future

Although the initial wave of "fullerene fever" is abating, the long-term prospects for these materials remains quite bright. The field has left its infancy, and we are now covering the hard, middle ground between the initial round of discoveries and the point at which we can begin to make decisions about potential applications. While some of the early speculations now look doubtful (e. g., C_{80} has not proven to be a superior lubricant), there is real reason for optimism on other fronts. Following are short discussions of two specific applications that may mature in the near future (5-10 years?), and some brief comments on the long-term future of the field, namely materials based on the fullerenes beyond C_{60} and C_{70} .

Rocket Propulsion

One of the most intriguing potential applications of the fullerenes would utilize them as a component in rocket fuel. This work has been in progress since 1993, and is being carried out by a group located at the United States Army Missile Command (MICOM) in Huntsville, Alabama [12].

There is a class of small, tactical rockets whose solid fuel is 25-40% carbon black, depending upon the recipe. The carbon black contributes energy upon burning, and also has favorable mechanical properties. The propellant in these rocket motors is not a powder, but rather is formed into a solid shape. These motors have two chambers: In the primary chamber, which contains the fuel, combustion is begun, producing a stream of hot, particle-laden gas; In the secondary chamber, combustion is completed, thus producing thrust. An obvious design requirement is that all of the fuel burn inside the motor - fuel that burns outside the rocket produces no thrust. Because the combustion of the carbon particles is rate-limited by the chemistry on the surface of the particles, there is a minimum residency time for the particles, which leads to a minimum size for the secondary chamber. Clearly, any improvement which allows one to reduce the size of the secondary chamber while increasing the size of the fuel-containing primary chamber will result in increased range. Enter the fullerenes

- the Army group has reported measurements showing that the fullerenes yield the same energy-per-gram upon combustion as does carbon black, while burning much more quickly [12], which implies a possible reduction in the size of the secondary combustion chamber. Consequently, they estimate that replacing the carbon black with fullerenes could result in a 10-20% increase in range.

Energy Storage

This last example of potential utility of the fullerenes, namely energy storage, is one that our group at the University of Arizona has become involved with over the last year. Our project, which is just under way, centers on the production and characterization of novel hybrid materials that combine fullerenes and carbon-bearing aerogels, with the specific goal of engineering superior materials for energy storage.

Porous carbon materials have important commercial uses ranging from catalysis to filtration to energy storage, and their continuing development is a very active field in materials science. Among porous carbons, carbon aerogels and carbon-bearing aerogels hold exceptional promise for energy-storage applications [13]. These extremely fine-scale, ultra-low density, open-pore structures can be made with point-to-point resistances as low as one Ohm, surface areas as high as 800 m²/gm, and can serve as "host" matrices for a wide variety of nanophase materials. They are stable at high temperatures, and can be formulated to tolerate aqueous electrolytes. Because of the method of preparation (sol-gel processing followed by supercritical-solvent extraction), they can be cast in a wide variety of shapes, including thin-film coatings. Discussions of these and other properties may be found in articles listed in Reference [14].

Among many other novel and potentially useful properties, fullerenes have great theoretical potential for energy storage (certain C₆₀ derivatives can be reversibly charged to -6 in solution [15], and many hydrogens can be reversibly added to a single C₆₀ [16]). The practical challenges in constructing fullerene-based energy storage devices have been those of getting the charge on and off the ball, and of making a large effective surface area of fullerenes. Although potentially useful reactions work in solution, one cannot readily transport charges within fullerene solids, which are insulators. The marriage of aerogels and fullerenes, which results in a class of materials with a very large surface of exposed fullerenes per cm³, may provide a synergistic solution to these problems. The fullerenes should also provide an easily controllable way to increase the active surface area of carbon aerogels, while the aerogel should provide an excellent mechanical support and electrical connection for the fullerene molecules. In cases where charge transport may not be important (e. g., hydrogen storage), one should be able to combine fullerenes with non-conducting aerogels. The materials properties of fullerenes make them excellent candidates for incorporation into aerogels. They sublime at low temperatures (≈ 500 °C for C₆₀), are stable at high-temperatures, and are soluble in a variety of organic solvents.

The evaluation of fullerenes in solid polymer electrolytes, which have potential application in rechargeable batteries, has been reported [17]-[20]. Electrochemical intercalation of alkali metals in fullerenes, which could serve as a battery electrode, has also been observed [18], [20], [21]. A recent study [22] suggests that the electrochemical oxidation of fullerenes is difficult, and they are relatively resistant to chemical oxidation in perchloric acid [23]. These observations suggest that fullerenes may be sufficiently stable in aqueous electrolytes for use in double-layer ultracapacitors. In our work, we plan on synthesizing a variety of fullerene/aerogel hybrid materials to be tested for utility in rechargeable batteries and electrochemical capacitors. These structures offer the possibility of serving as a superior host for the efficient storage of electrochemically active species, e. g., hydrogen or lithium, which are used in the negative electrodes of rechargeable batteries designed for electric vehicles. The use of carbon compounds for these applications would reduce the need for the toxic, heavy-metal compounds (e. g., lead, cadmium, and mercury) currently used or contemplated for use in rechargeable batteries. In addition to battery applications, the charge-storage capacity in the double layer of fullerenes may provide improved electrochemical capacitors useful for energy management in electric vehicles. In conjunction with a colleagues at Lawrence Berkeley National Laboratory, we have submitted a proposal to the Department of Energy to support this work [25].

Giant Fullerenes, Endohedral Fullerenes, & Buckytubes

Between 1985 and 1989 the marvelous new carbon molecules C_{60} and C_{70} existed only as events recorded by mass spectrometers. By the end of 1990, scientists all over the world were experimenting with bulk quantities and single crystals of the pure materials. One of the major findings that followed the initial breakthrough was the discovery of a wide variety of other fullerenes and related structures - hundreds of larger fullerenes (C_{76} , C_{78} , C_{84} , etc.), endohedral fullerenes, clustered fullerenes, single- and multi-walled nanotubes, onion-like structures, etc. As rich and varied as this class of materials is, however, it is sobering to realize that beyond C_{60} and C_{70} , very few of these fullerene materials actually exist in pure form - In fact, most of these materials are now known only by mass spectrometry or electron microscopy.

What we have learned from those higher fullerenes that have been isolated (principally C_{76} , C_{78} , and C_{84}) clearly indicates that, in terms of chemical behavior, the giant fullerenes should not be thought of as simply bigger versions of C_{60} and C_{70} . The structural details vary greatly from fullerene to fullerene - for instance, C_{60} has icosahedral (I_h) symmetry, the highest symmetry possible, while C_{76} possesses chiral (D_2) symmetry, one of the lowest. On the basis of electrochemical data, it has been suggested that the chemistry of the fullerene family will exhibit a rich diversity, with the properties of C_{60} and C_{70} making up only a fraction of the picture [26]. Calculations of the HOMO-LUMO gaps for the fullerenes C_{60} - C_{100} result in a range of values from 0 to almost 2 eV [27], which also strongly indicates a

wide range in chemical behavior.

In terms of potential solid-state applications, the importance of obtaining and characterizing these materials is perhaps even more clear. Once isolated, the condensed phase of each fullerene will represent a separate crystalline allotrope of carbon with unique scientific and commercial possibilities. The fact that alkali-doped C_{60} superconducts, while alkali-doped C_{70} does not, is one obvious example of diversity within this family of materials. Applications that exploit the diffusion of gases into fullerene solids (gas separation, gas storage, etc.) suggest themselves naturally as ones that would benefit from a choice of molecular sizes.

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