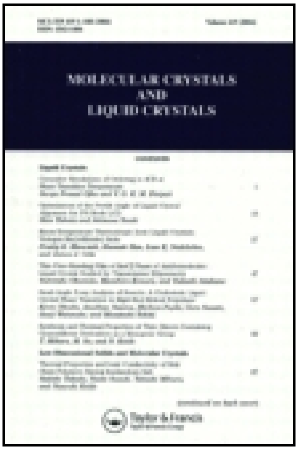

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Fifty years of carbon research and future prospects

Peter A. Thrower [a]

[a] Professor Emeritus of Materials Science, The Pennsylvania State University, Editor-in-Chief, CARBON Journal

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FIFTY YEARS OF CARBON RESEARCH AND FUTURE PROSPECTS

Peter A. Thrower
Professor Emeritus of Materials Science, The Pennsylvania State University, Editor-in-Chief, CARBON Journal

The history of carbon research for the last fifty years is reviewed together with an analysis of some of the topics that have been 'hot' during this period. Electrical contacts, irradiation damage, intercalation, adsorption and fullerenes are some of the topics highlighted. Future possible uses of carbon in electronics, fuel cells and medicine are considered, together with carbon structures, which may eventually be formed.

Keywords: carbon history; research prospects

INTRODUCTION

This meeting comes at a milestone in carbon research. The Carbon Society of Japan is publishing the 200th issues of TANSO and the CARBON journal is entering its 40th volume. At the same time I can look back on twenty years of association with the journal, something impossible to imagine back in 1982. It is therefore appropriate to spend some time reviewing these last few decades, using data from the CARBON journal, and to look into the crystal ball for what may lie ahead.

THE FIRST ISSUES

The first issue of TANSO was published over 50 years ago in 1949 by 'The Society of Carbon Research'. This was only four years after the end of WWII and four years before that first small meeting in Buffalo, NY which was to become known as the First Biennial Conference on Carbon. It contained two review articles and three original research papers, two of which were

I am grateful to all my colleagues at the former AERE Harwell, The Pennsylvania State University and throughout the world for their interest and support during the last 40 years, and to the ISNC 2001, Nagano organisers for their invitation to present this paper.

concerned with sliding electrical contacts, brushes, and submitted from Institutes concerned with railroad electrification. A search of the first 39 volumes of CARBON has revealed only two papers on carbon brushes, illustrating how dramatically the focus of our research has changed. Throughout the first year of TANSO the emphasis remained on electric carbons, electrodes and crucibles.

When the first issue of CARBON appeared in October 1963 the emphasis had already changed. That first issue contained 13 research papers, including three each concerned with pyrocarbon and with magnetic properties. However, it is obvious from the first volume that the major driving force for carbon research at that time was the use of synthetic graphites in nuclear reactors. Over 25% of the papers published in that first volume were concerned with the effects of neutron radiation on the properties of such graphites. It was also at that time that some of the pioneering work on oxidation was carried out. The names of the authors almost read like a "Who's Who"of carbon research – Dresselhaus, Inagaki, Tsuzuku, Walker, Deitz, Pacault, *et al.*

Radiation damage has since become a rare topic for CARBON as illustrated in Figure 1. From taking up nearly 25% of the journal in its first volume it has shrunk to zero in 2001.

It is fair to say that the lack of publications concerned with carbon brushes and radiation damage does not indicate that we know everything we need to know about these topics. Some consulting work I did many years ago on electrical brushes soon revealed that the appliance manufacturers were simply interested in making them last longer than the warranty period, but not in radically improving the product. As many of the world's graphite-moderated power reactors reach projected lifetimes and

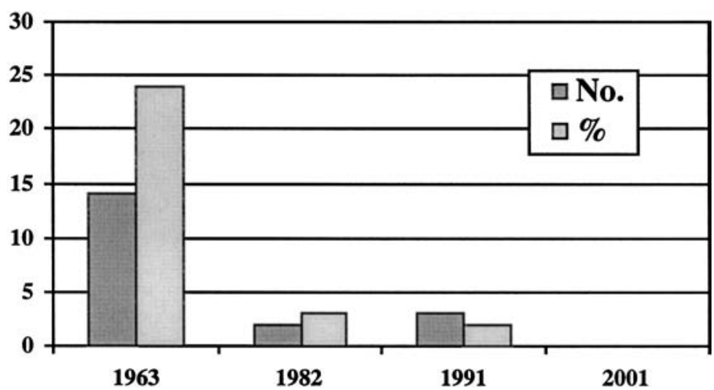

FIGURE 1 Number and % of papers on radiation damage published in CARBON.

anticipate further usage, there is need for more data on dimensional and property changes. Burchell [1] provides curves showing almost runaway growth of the material above 30 displacements per atom, but there are no data points in this region. Does the material break apart? Is an equilibrium state eventually reached? These questions need answers if reactor lives are to be extended.

MORE RECENT HOT TOPICS

Over the last twenty years there have been other topics that were in vogue on occasions. There are four, intercalation, adsorption, fibers and fullerenes that come to mind, and an examination of their relative appearance in the journal is interesting. Figure 2 shows the number of papers (analysed using their titles) on these topics during four different years of publication.

Twenty years ago the topic of the moment was intercalation. It was somewhat of a ‘dream’ topic for both physicists and chemists. What chemical entities could be intercalated? What stages of intercalation did they demonstrate? To have two-dimensional compounds in which one could change the intercalated atom from e.g. chlorine to bromine to iodine chloride, provided theoretical physicists with tremendous scope for property evaluations, and there was even the promise of electrical conductors better than copper.

While the subject appears to have cooled recently, the number of intercalation publications has been maintained by the tremendous world-wide interest in the lithium ion battery. A steady stream of around

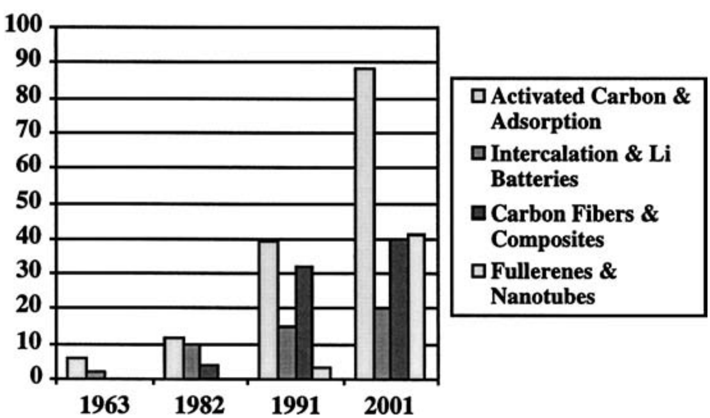

FIGURE 2 Numbers of manuscripts published in CARBON during four different years whose titles reflect the four topic areas shown.

ten papers per year has been supplemented to as many as twenty in the last five years because of this battery interest and many more have been published in other journals.

Adsorption has always been a topic of interest in CARBON, buts it has emerged as the forerunner in popularity in recent years. A survey of papers presented at Carbon '01 this past July indicates that over 30% were somehow related to activated carbon and adsorption. Recent submissions to CARBON have been concerned with the production of activated carbons (AC) from around 30 different precursors ranging from (alphabetically) almond shells to sawdust. They have even added two new words to my vocabulary, 'chitosan' and 'rockrose' (neither recognized by my computer spell-checker).

It seems that there are two driving forces for this new emphasis on activated carbons. One is the wish to find something useful to do with organic waste material such as corn cobs and apple pulp, and the other is the pressing need to deal with environmental contamination. The uses of activated carbons continue to increase both in applications and quantity used.

Carbon fibers and composites are relatively new carbon materials. During the late 1960's they were handled with considerable secrecy at AERE Harwell, where I then worked. They were expensive and there was still much to learn about their production and properties. We knew they were lightweight strong and stiff materials, but we could not perhaps imagine that they would become a component in affordable sports equipment such as we see today. The development of the mesophase pitch based fibers was a major step forward.

The use of carbon/carbon composites in aircraft brakes continues to be a subject of interest, especially the investigation of innovative ways of producing the matrix carbon using CVD techniques. Recent results from China on a 'rapid directional diffused CVI' process are of interest here [2].

During the last decade the undoubted topic of novelty has been the fullerenes and nanotubes. In 1991 there were only three papers published on this topic in CARBON, a figure which had grown to over 40 in 2001. When one of my former colleagues produced a model of a proposed C_{60} molecule in 1970 it was instantly dismissed as impossible. That its discovery was recognised by the award of a Nobel Prize in 1996 is a lesson for us all. Never say 'never'!

THE FUTURE?

One thing we learn from the past is the impossibility of predicting the future, but at this juncture one gets out the 'crystal ball' and tries to do just that. In the future there will undoubtedly be innovative applications for existing materials, or those that have seen incremental improvements in their properties, and there will almost certainly be new materials affording completely new possibilities. Some of these are already indicated in current research.

Space Exploration

Because of their light weight carbon/carbon composites have already seen much use in space applications, but the future will almost certainly see carbon films or fibers used as tethering devices (ropes) for spacecraft and solar sails. It is projected that by using solar sails to harness starlight it would be possible to get to Alpha Centauri in around 40 years. A recent science fiction novel by William Gibson (famous for the "Neuromancer" book) made many references to a material called 'polycarbon' used for these purposes. Perhaps the final section of this manuscript will point the way to what this material might be. [A company having this name and now part of SGL has existed in California for many years.]

Superconductors

The expansion of the fullerene lattice by doping with alkali metals (A_3C_{60}) is known to result in an increase in the critical temperature (T_c) for superconductivity [3,4]. Recent studies on doping with $CHCl_3$ and $CHBr_3$ have also produced a lattice expansion, with a T_c value of 117 K for $CHBr_3$ [5]. The value of T_c increases linearly with lattice parameter. The authors conclude that "if the lattice parameter can be further increased by $\sim$1% T_c is expected to exceed 150 K." The challenge is how to expand the lattice without losing its cohesion. What happens if one does the same with CHI_3? Here is an obviously exciting research result which one hopes will point to true high temperature superconductivity.

Electronics

The discovery of carbon nanotubes has led another 'dream world' for theoretical physicists. To have nanosized structures of pure carbon that can be either conductors or semiconductors, depending on their diameter and chirality, would have been in the realm of unimagined science fiction only a few years ago. Not only is this now a reality, one can also control the semiconductor band gap by controlling the tube diameter. A recent paper to CARBON explores the possibility of a T-junction nanotube providing a semiconductor-metal junction [6]. The development of carbon nanocircuits must be something we can expect to occur in the future. Their small size and light weight will open a totally new world of electronics.

The major challenge facing us is to produce these different structures in a controlled manner, or at least discover a systematic way of sorting them from the mixture resulting from current production techniques. There is much still to be done in this area.

Since I started to write this paper a report has appeared in NATURE of the development of a transistor made using semiconducting carbon nanotubes perpendicularly oriented between two thin layers of gold [7]. The nanotube layer is less than 2.5 nm thick, far thinner then the equivalent structure in current silicon transistors. A smaller size means faster switching. The revolution is already under way!

Fuel Cells and Hydrogen Storage

While there is no doubting the ability of carbon materials to store hydrogen relatively safely, there is still a big question concerning the amount. The 60 wt% values claimed by Chambers *et al.* [8] remain elusive despite many attempts by others to achieve similar results. Is the secret of this high value in the structure of the tubular herringbone nanofibers? Can such materials be produced economically in sufficient quantities to satisfy the demands of a fuel cell driven automobile industry?

Medical Applications

The medical applications of carbon go back to ancient Egypt and Greece where charcoal (AC) was used for detoxification. In recent years the thromboresistance of carbon has been well recognised and the carbon heart valve has been in extensive use since around 1970. While over two million of these devices, of around 20 different designs, have been implanted, the carbon was alloyed with silicon to provide the necessary toughness. However, silicon is a potentially thrombogenic substance. In 1998 the first pure carbon (On-X®) heart valve was introduced by MCRI. The ultrafine grain structure of this material provides better surface finish, a 48% higher fracture toughness and much lower thrombogenicity.

With this in mind, the world of medicine seems open to carbon. Appleyard *et al.* [9] have produced highly oriented mesophase graphite, which can be made as a tape and as a spring. Shibagaki and Motojima [10] have produced carbon microcoils. Surely one of these can be developed into an endovascular stent! Over half a million of these devices are used each year in the USA alone, and there are prospects for the use of similar devices in e.g. the bile duct. Current problems with restenosis might be reduced if such developments take place.

Extracorporeal uses for carbon., taking advantage of their adsorptive properties are also likely in the future. The capacity of activated carbons to remove middle molecular weight toxins is known to far exceed that of conventional dialysis, but for this to happen new high-purity materials, almost certainly using polymer precursors, need to be developed.

New Materials

At this point we enter the world of pure speculation. We have already mentioned the relatively recent discovery of the fullerenes, and their crystallization into fullerites with a hardness exceeding diamond has already been demonstrated [11]. A recent publication reports the synthesis of a linear [2+2] addition polymer of C_{60} [12]. Although the authors state that they would like to think it could have a useful application, their work suggests that it will not be found as a nanowire. Stabilization with small cations might be possible.

The spherical nature of C_{60} makes one wonder whether a two dimensional polymer could be formed. Perhaps such a two dimensional entity could be stacked in layers? Is it possible that we could make a kind of 'graphite' with buckyballs replacing carbon atoms?

A further recent submission to CARBON [13] reports the formation of 'ozopolymers' of C_{60} and C_{70} by the prolonged ozonation of these fullernes. The C_{60} polymers are reported to have an electrical conductivity three orders of magnitude lower than pure C_{60}.

Conclusion

Obviously there is no conclusion to carbon research! The exciting developments of the last fifty years will surely be matched by what will happen in the next fifty. We can only imagine.

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