

“Nanocarbons for Energy Conversion: Supramolecular Approaches”

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Introduction

Carbon in its oxide and hydrocarbon forms is the cause of the energy and transport sectors’ biggest headache: climate change, so it is fitting that allotropes of this most versatile element look so promising to play a part in the modernisation of energy conversion. Naotoshi Nakashima (Kyushu University, Japan) brings together a collection of chapters showcasing some impressively creative nanoscience, predominantly from Japan, as part of Springer’s Nanostructure Science and Technology series. On reading, one is left with the impression that these fascinating materials will surely play some part in the coming decarbonisation of the economy.

Nanocarbons, as the name implies, are the allotropes of carbon that take the form of molecules of nanometre dimensions. The archetypal nanocarbon is graphene – a single layer of sp^2 hybridised atoms arranged in a two-dimensional hexagonal lattice. Nanotubes are essentially rolled up sheets of graphene, while fullerenes are essentially graphene sheets curled up into spheroids. Other nanoscale carbons, such as nanoporous carbon, carbon black and carbon foams are also discussed.

Nanocarbons for Fuel Cells

A large portion of the book is dedicated to the role of nanocarbons in fuel cells (FCs), so it is worth giving a brief overview of FCs and the associated functions of nanocarbons. FCs share features with both internal combustion engines and batteries. Like an internal combustion engine fuel is oxidised, producing exhaust gas, and like a battery chemical energy is converted to electrical energy. In the case of the popular proton exchange membrane fuel cells (PEMFCs) the fuel is commonly hydrogen, which is split into protons and electrons at the anode. Electrons are forced to flow through an external circuit because the electrodes are separated by an electrically insulating proton conducting polymer membrane such as Nafion™. Protons move through the membrane to the cathode where they react with oxygen and electrons that have travelled through the external circuit to form water. The overall reaction is the oxidation of H_2 to H_2O .

FC performance is largely determined by materials performance. Looking in more detail, at the anode side H_2 diffuses through the gas diffusion layer (GDL) to reach the catalyst. The GDL is often composed of carbon fibres which allow electrons to flow from the catalyst to the current collector and H_2 to diffuse between them to the catalyst. Platinum nanoparticles catalyse the splitting of H_2 into protons which are transported across the proton exchange membrane to the cathode and electrons which are transported along carbon fibres to the current collector.

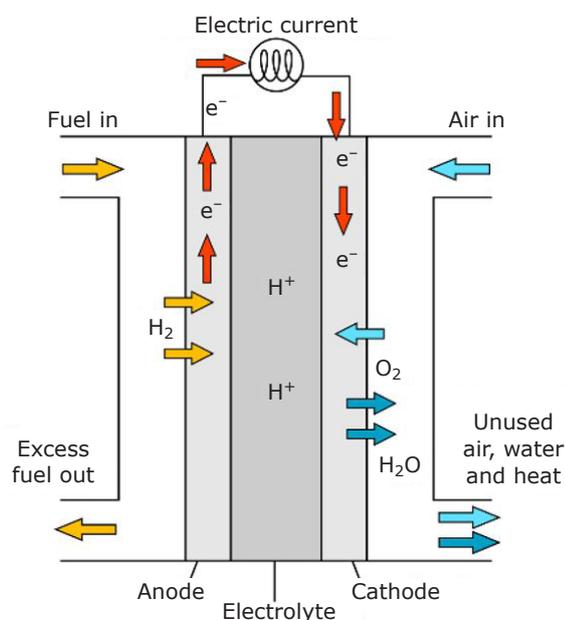


Fig. 1. The operation of a PEMFC. Creative Commons Zero 1.0 (CC0)

Carbons are crucial to the performance and cost effectiveness of FCs, especially as catalyst supports where their high specific surface area enables a low Pt loading for a given power density and their conductivity provides a pathway for electrons to move between the Pt catalyst and the conducting fibres. FC performance can be greatly enhanced by improving the surface properties of nanocarbons for better gas accessibility and distribution of Pt nanoparticles. Their conductivity has a significant effect on power density and their chemical and thermal stability has a large influence on FC durability.

Carbon Nanotubes

On the topic of FCs, some particularly interesting work on multiwalled carbon nanotubes (MWCNTs) as catalyst supports for H_2 PEMFCs by Naotoshi Nakashima and Tsuyohiko Fujigaya of Kyushu University, Japan, can be found in Chapter 1. The authors first address the difficulty of dispersing Pt nanoparticles onto nanotubes due to the lack of binding sites for deposition. Oxidation of the nanotubes is one method of introducing hydrophilic groups for binding, however this reduces the nanotubes' electrochemical stability. To get around this problem the authors present a protocol for wrapping MWCNTs with conjugated polymers which bind to the nanotube surface through π - π interactions and on top of which the Pt catalyst can

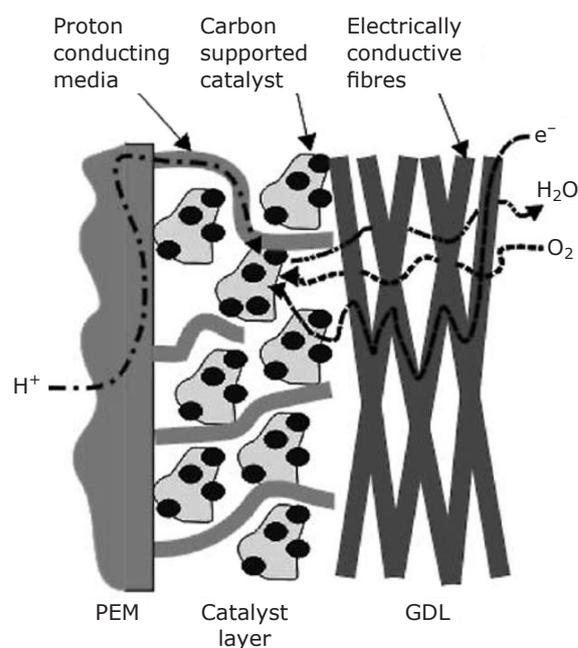


Fig. 2. The transport of gases, electrons and protons in a PEMFC. (1) Creative Commons Attribution-Share Alike 3.0 (CC-BY-SA)

be more easily deposited. Chapter 1 also features durability tests of membrane electrode assemblies (MEAs) using polymer wrapped nanotubes as compared to polymer wrapped carbon black. Nanotube MEAs are found to maintain a significantly higher activity after several thousand cycles of durability tests compared to carbon blacks due to the inherent structural stability of the polymer wrapped pristine nanotubes.

Chapter 2, which is also written by Nakashima, follows on nicely from the first, exploring polymer wrapped nanotubes as catalyst supports for direct methanol FCs. A significant problem for direct methanol PEMFCs is methanol crossover where methanol diffuses through the NafionTM membrane to the cathode where it reacts with O_2 , poisoning the Pt catalyst. While alternative transition metal cathode catalysts are more methanol resistant because they suppress its oxidation this is counterbalanced by lower oxygen reduction reaction (ORR) activities than Pt. Nakashima presents a solution to this problem by coating the polymer wrapped Pt decorated nanotubes with an outer layer of poly(vinylphosphonic acid) (PVPA) polymer, which increases methanol tolerance by the proposed mechanism of preferentially blocking diffusion of the larger molecule while only slightly reducing O_2 accessibility. The PVPA is also found to reduce carbon corrosion of nanotube and carbon black catalyst supports.

Another highlight on the topic of FCs is the review by Matsuhiko Nishizawa of Tohoku University, Japan, of carbon nanotube (CNT) based enzymatic biofuel cells in Chapter 15. Enzymatic biofuel cells are FCs in which an enzyme takes the place of Pt nanoparticles as the electrocatalyst. At the anode, the enzyme oxidises fuels such as fructose or glucose and generates electrons that are carried to the current collector by a conducting carbon support. At the cathode O_2 is reduced to H_2O by another enzyme. An advantage of biofuel cells is that the incredibly high selectivity of the enzyme means impure fuel feeds can be used and there is no need for a separator, making the overall design simply a pair of enzyme functionalised electrodes exposed to solutions containing fuel and O_2 . The simplicity of the design makes them suitable for miniaturisation for use in implantable electronic devices. CNTs are presented as promising enzyme support materials due to their biocompatibility and high specific surface area. Previous attempts to immobilise enzymes onto nanotube electrode structures have created nanostructure films before enzyme modification. However, Nishizawa reports a method by which enzyme modification precedes film production so that the nanotubes pack ideally around the enzymes. This is achieved by adding an enzyme solution to a CNT forest which shrinks to a near hexagonal close packed structure on drying, entrapping the enzymes between the nanotubes and resulting in superior activity compared to previous production methods.

Materials Characterisation

A fantastic piece of FC material characterisation work is presented in Chapter 5 by Somaye Rasouli and Paulo J. Ferreira working at the University of Texas at Austin, USA. They describe the technique of identical location transmission electron microscopy (TEM) as a way to understand the mechanism of Pt nanoparticle growth on CNTs in PEMFCs. One of the main causes of performance decline of PEMFCs is the instability and coarsening of Pt nanoparticles on carbon supports, which reduces the total surface area of active catalyst. The authors proposed four possible mechanisms of coarsening: Ostwald ripening, particle migration on the carbon support and coalescence, particle detachment and particle dissolution and reprecipitation. While the ideal way to investigate the mechanism would be to do *in situ* TEM and concurrent voltage cycling on a MEA, the release of moisture into the vacuum chamber precludes this. Furthermore, accelerated

stress tests on MEAs make it difficult to tease apart the contribution to performance decline from different components. In order to study specifically Pt nanoparticle instability Arenz *et al.* first deposited the nanotube supported catalyst onto a gold TEM grid, initially observed the foil to define an area of interest, cycled the grid in a three-electrode electrochemical cell and then re-characterised the identical area of interest by TEM. It was found that carbon corrosion of nanotubes in voltage cycling in which carbon is lost as carbon dioxide, converting the hexagonal lattice to heptagon and pentagon rings, causes the Pt nanoparticles to move across the nanotube surface, possibly to reduce interfacial energy. As the nanoparticles move on the nanotubes they make contact with each other before coalescing to form larger particles.

Nanocarbons in Hydrogen Production

Aptly, the complementary theme of the role of nanocarbons in H_2 production is explored in Chapters 9 and 19. In Chapter 9 Yutaka Takaguchi and Tomoyuki Tajima of Okayama University, Japan and Hideaki Miyake of Yamaguchi University, Japan, describe a new category of H_2 evolving photocatalysts based on semiconducting single walled carbon nanotubes (s-SWCNTs). Nanotubes can be metallic or semiconducting, i.e. have or not have a band gap, depending on the rolling angle between the axis of the tube and the crystallographic directions of the rolled graphene sheet. The productivity of H_2 from photocatalysts can be improved by expanding the range of active wavelengths from ultraviolet to near infrared (IR). The new category of nanotube based photocatalyst reported promisingly shows H_2 evolution under near IR radiation. However, s-SWCNTs are seldom used for this application due to the high exciton (electron-hole pair) dissociation energy, the fact that nanotubes form bundles that allow excitons to be transferred between tubes and also because they are difficult to disperse in H_2O . These problems are addressed rather ingeniously through the fabrication of a coaxial cable composed of an s-SWCNT covered with a layer of C_{60} fullerenes, which are themselves functionalised with a hydrophilic dendron moiety which readily complexes with Pt, the cocatalyst for H_2 evolution. The cable is made simply by sonicating the nanotubes in a H_2O solution of the amphiphilic fullerodendron, which self assembles around the nanotubes due to π - π interactions. This hydrophilic dendron moiety makes the nanotubes more easily dispersible in H_2O , while

the nanotube-C₆₀ heterojunction formed improves exciton dissociation. Furthermore, the problem of bundle formation is resolved by the isolation of the nanotubes from each other.

Lithium-Ion Batteries and Solar Cells

The FC's biggest competitor in the race to decarbonise transport – the lithium-ion battery – may also benefit from the use of nanocarbons in future. Of particular interest is the review of nanocarbons as alternatives to graphite in anode materials written by Seok-Kyu Cho and Sang-Young Lee of Ulsan National Institute of Science and Technology (UNIST), South Korea and JongTae Yoo of Korea Institute of S&T Evaluation and Planning (KISTEP, South Korea in Chapter 18. The main advantage of these materials is that they could potentially have significantly higher Li capacities than graphite. For example, the capacity of C₆₀ fullerenes was shown by Armand *et al.* to be 12 Li atoms per fullerene. However, this was only realised once the problem of reduced C₆₀ dissolving in liquid electrolyte was worked around by substituting for a polyethylene oxide-based gel polymer electrolyte. Theoretical calculations of the Li storage potential of nanotubes show them to have capacities much greater than graphite, however these have yet to be realised experimentally. The authors conclude that the gap between theory and experiment motivates more work to better understand the lithiation mechanism of nanotubes.

The book covers the potential roles of nanocarbons in several aspects of the future decarbonised economy, covering power generation from H₂ and production of H₂. Chapter 20 covers the applications of nanotubes in grid energy generation from solar cells with an emphasis on CNT-silicon solar cells and CNT based perovskite solar cells. Feijiu Wang and

Kazunari Matsuda of Kyoto University, Japan and Nagoya University, Japan provide a clear overview of the general principles of solar cells, which nicely sets the context for the chapter. Perhaps most intriguing is the ability of semiconducting SWCNTs to generate multiple excitons from one photon, meaning they may be able to surpass the Shockley-Queisser limit on the maximum efficiency of single junction solar cells, which assumes one exciton per photon. While there are many applications for nanotubes, from hole transport layers to transparent conducting electrodes, the authors point to a significant barrier to commercialisation: the presence of metallic nanotubes in the mixtures used for studies, which increase contact resistance due to their difference in work function and band gap.

Conclusions

This book covers a very broad range of applications for nanocarbons and while much of the underlying chemistry and materials science transfers between chapters, it is unlikely that any single reader would be familiar with all the concepts covered. The reviewer would recommend this book for any researchers working with carbon nanomaterials, particularly nanotubes, as well as researchers working with PEMFCs. Overall, an interesting read that reminds the reader of the impressive versatility and seemingly endless applications of carbon nanomaterials.

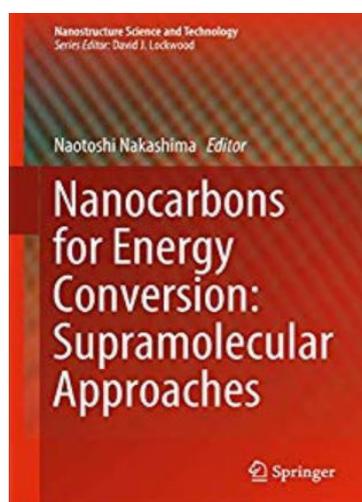
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The Reviewer



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