

Lithium Ion Rechargeable Batteries

Tracing the Origins of Research and Development

- Focus on the History of Negative-Electrode Material Development

Tokio Yamabe

*Professor Emeritus, Kyoto University/
Professor, Nagasaki Institute of Applied Science*

In the fall of 2015, Japan was again buzzing with media reports about the Nobel Prize awarded to Japanese scientists. Unfortunately, there was no Japanese win in the field of chemistry, but one area of this category where Japan is seen as a strong contender for the prize is in lithium ion rechargeable batteries, where Japanese researchers have made great contributions. The names of Japanese candidates featured prominently in newspapers and other media in the expectation that this might be the year when they would clinch it. But although the names of certain candidates may be put forward, taking a closer look, it is not always easy to work out who created the lithium ion rechargeable battery and through what sequence of processes. In particular, there are many uncertainties relating to the development of the negative-electrode material .

In this interview, we speak with Tokio Yamabe, Professor Emeritus at Kyoto University, who has been involved from the start in fundamental research into lithium ion capacitors and lithium ion rechargeable batteries. Since he is also familiar with the key figures in the development of rechargeable batteries, Professor Yamabe was able to fill us in on some of the 'unrevealed' facts.



Tokio Yamabe ●

- 1959: Graduated from Kyoto University Faculty of Engineering
- 1981: Professor, Kyoto University Faculty of Engineering
- 2000: Professor Emeritus, Kyoto University
- 2000: Director of Institute for Fundamental Chemistry
- 2001: President of Nagasaki Institute of Applied Science (NiAS)
- 2005: Director of Institute for Innovative Science and Technology, NiAS
- 2013: Professor of Institute for Innovative Science and Technology, NiAS

It all started with research on polyacetylene.

– Thinking about the origins of the lithium ion rechargeable battery, would you agree that it had its beginnings in fundamental research on conductive polymers (polyacetylenes)?

Yamabe: That certainly applies when it comes to negative-electrode development. In the fall of 1977, an international conference on molecular conducting materials was held in New York, at which Professor Hideki Shirakawa (Nobel Prize laureate in Chemistry 2000) presented his surprising discovery that a polyacetylene film close to a synthesized insulator displayed metallic conductivities when doped. It was the first demonstration of the highly conducting polyacetylene (CH)_x, for which he was awarded the Nobel Prize, and I still remember clearly that I became very excited because I realized immediately that this polyacetylene would be a great subject for the quantum chemistry of nano-materials.

After that, having the opportunity to undertake joint research with Professor Shirakawa, I made further progress, while focusing on (CH)_x, in the study of the electronic properties and material design of conductive polymers, through the use of quantum chemistry. As I recall now, there was already some talk at the time of applying polyacetylene to use in rechargeable batteries.

– That would have been around 1980?

Yamabe: Yes, the first people to mention it were A. MacDiarmid and A. Heeger (both Nobel Prize laureates in Chemistry 2000). In 1980, soon after the discovery of conductive polymers (1977), they presented its further application to rechargeable batteries using electrochemical doping at the International Conference on Science

and Technology of Synthetic Metals (held in August at Helsingör, Denmark). Their presentation, which suggested the possibility of a very lightweight storage battery, attracted much attention. For this, they used doped lithium using polyacetylene for positive- and negative-electrodes. All of this is explained in detail in the journal *Gosei Kinzoku* (synthetic metals), a special issue of the journal *Kagaku* (chemistry), *Kagaku Zokan* 87, edited by Hideki Shirakawa and Tokio Yamabe, Kagaku-Dojin Publishing Company, Inc., published in 1980)*¹, which I compiled together with you around 35 years ago.



– Is that so? I had completely forgotten (laughs).

Yamabe: Then, the next year, 1981, they obtained a patent under the title “Secondary batteries based on reversible electrochemical doping of conjugated polymers”. This patent was many pages long and was very thorough in its content and certainly demonstrated their enthusiasm. Without doubt, they were the first people to consider applying polyacetylene to use in rechargeable batteries. Of course, they didn’t just acquire the patent, they also wrote scientific papers)*².

Discovery of PAS with outstanding doping characteristics

Yamabe: The problem was that it gradually became clear that polyacetylene was unstable and unsuitable for use in an electrode. So, a worldwide quest began to research and design a new conductive polymer and unknown carbon material with its skeletal structure extending two-dimensionally to replace it. Among the materials we studied during the course of our research, there were the PAS (see framed article on next page) that we discovered and which were later used as a negative-electrode material in the lithium ion rechargeable battery.

– About when would that have been?

Yamabe: That was around the beginning of the 1980s. The main substances explored as negative-electrodes included a wide range of carbon materials, from conductive polymers to graphite. It was 1980 when I first started

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● How was the key material PAS discovered ! ●

— How was this key material PAS discovered ?

Yamabe: Actually there are a few interesting stories concerning that. It was in 1982 when we published the first research paper that pursued this polyacene-type carbonaceous material from a theoretical point of view. Although this material was predicted from material design based on the analysis of quantum chemistry, by fortunate coincidence, it was discovered at almost the same time by my research collaborator, Dr. Shizukuni Yata of Kanebo, Ltd., that it can be obtained through the pyrolysis of phenol-formaldehyde resins. At the time, Kanebo, Ltd. was also engaged in research and development of carbon materials. During experiments in the heat treatment of phenol-formaldehyde resins to obtain carbonaceous materials, they happened to take out materials at the temperature of 400~700°C, lower than planned, and found that they had unexpectedly obtained this black solid substance with a metallic sheen. This is what we now call polyacenic semiconductive material (PAS), which could be described as a kind of synthetic metal (Figure 1).

— Is that serendipity, too?

Yamabe: As it was coincidental, I suppose you could say so. Straight away, we began careful and thorough investigation of its fundamental properties as a semiconductive electronic material using magnetic measurement, solid-state NMR, electrochemistry and other techniques. Specifically, we investigated the structure, electrical transport properties, and p- and n-type doping properties. It was around 1982 that we finally established that it was a nano-sized non-crystalline semiconductor with excellent doping and undoping properties, and very high lithium ion capacity. Later, it was also used as the negative-electrode material in the lithium ion rechargeable battery.

— Could you explain the properties of PAS as a substance in a little more detail?

Yamabe: In general, the polyacene group is a collective term for the materials of the so-called nano-sized graphite group that includes polyphenantrenes, polyarylenes, etc. of which the structure is formed through condensation of the benzene ring, like that of polyacene. However, the materials obtained by the heat treatment of phenol-formaldehyde resins in an inert atmosphere are found not to have formed a regularly

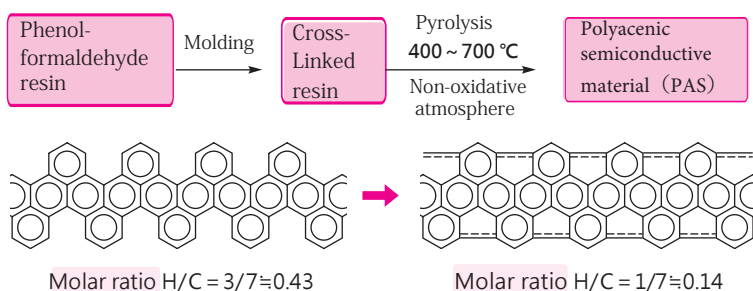


Fig. 1 Production method of polyacene-based semiconductive materials

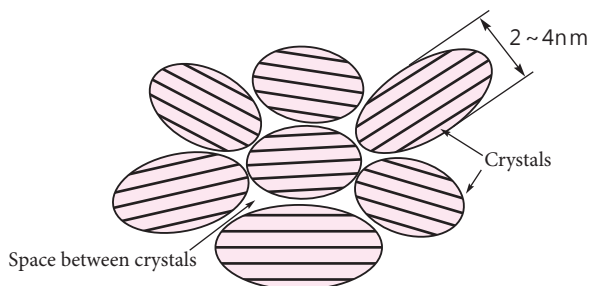


Fig. 2 Model structure of nano-graphene blocks

ordered polyacene skeletal structure according to the results from the X-ray diffraction analysis. It is a hard-graphitizable amorphous carbon mainly comprising the nano-sized polyacene structure, and so can be regarded as a form of amorphous carbon. In current terminology, I suppose they would be described as aggregates of “nano-graphene blocks” (Figure 2). This structure enables quite easy lithium ion transfer and the technique of pre-doping.

In the pyrolysis of phenol-formaldehyde resins, by controlling the temperature and time of the heat treatment, it is possible to obtain PAS materials with a wide range of H/C ratios, specific surface areas, interlayer distance, and conductivity rates. In Dr. Yata's 1984 patent, H/C ratio is set at between 0.05 and 0.5. In that sense, PAS are carbonaceous materials occupying a range from polyacenes ($\text{H/C} = 0.5$) to near to graphite ($\text{H/C} = 0$), and those generated by pyrolysis of phenol-formaldehyde resin can be seen as a promising prototype thereof.

— In that sense, you could say that those carbonaceous materials developed by various companies at the time converge on the PAS in question....

Yamabe: I think so. That is exactly where the basis lies for asserting the priority of PAS. There is also a scientific report which states this in academic terms (1997 *Chem. Rev.*[†]). For instance, it has been stated clearly that the carbonaceous material of the negative-electrode for the lithium ion rechargeable battery that was released on the market by Sony Corporation can be regarded as identical to PAS.

— So does that mean that PAS can be seen as the origin of research and development of negative-electrode material for the lithium ion rechargeable batteries today?

Yamabe: You can certainly think so. It is probably a corporate secret, but as one can imagine, a graphite structure that is fragmented to make it easy for lithium ions to move in and out but which is resistant to the formation of dendrites, that is precisely the structure of PAS.

[†] P. Novák, K. Müller, K. S. V. Santhanam, O. Haas, “Electrochemically Active Polymers for Rechargeable Batteries,” *Chem. Rev.*, **97**, 207 (1997) .

researching PAS with Dr. Shizukuni Yata et al., who at the time worked for Kanebo, Ltd. We presented our findings at a scientific conference in March 1982 (spring convention of the Physical Society of Japan) and in June of the same year, we published a scientific paper on PAS*³. At the same time, Dr. Yata applied for a patent*⁴ which described that we had succeeded for the first time in doping lithium ions into a negative-electrode made of PAS, and demonstrated the efficacy of this carbonaceous negative-electrode material and adapted it for use in a rechargeable battery.

At the time, it was generally not thought possible to perform stable electrochemical doping and undoping of lithium into carbon material using an organic electrolyte solution (in most cases propylene carbonate). In particular, experiments with graphite were challenging as it involved decomposition of the electrolyte solution. PAS, in contrast, was effective even with a propylene carbonate electrolyte solution, realizing a smoother lithium doping and undoping process.

— That is a very important point, but was lithium ion doping the key to adapting this substance for use in rechargeable batteries, as it had been with polyacetylene?

Yamabe: Yes, the essential point was whether lithium ions could be doped into the negative-electrode. In carbonaceous negative-electrodes, we had known for some time that graphite forms intercalational compounds with alkaline metals, and in 1975 it was reported that it forms intercalational compounds with lithium. The research of M. Armand et al. in 1977*⁵ was based on this finding, and in 1981 Hironosuke Ikeda of SANYO Electric Co., Ltd. filed a patent application for a graphite negative-electrode. Then in 1982, R. Yazami reported that electrochemical insertion and desorption of lithium ions was possible to and from a graphite (HOPG)*⁶ within solid electrolytes (polyethylene oxides), at over 60°C. These solid electrolytes differ from regular organic electrolyte solutions. Generally for lithium ion batteries, an organic electrolyte solution is applied because of its high ionic conductivity. But solid electrolyte at room temperature has no practical ionic conductivity. And regrettably, none of the above was sufficient for practical use.

As you know, there were two main trends in the research and development of negative-electrode materials for lithium ion rechargeable batteries. One was the approach from the field of electrochemistry centering on graphite intercalation compounds, and the other was the approach from the field of new nano- carbonaceous materials that had originated in polyacetylene. In the move toward practical application, I would say, in conclusion, it was the latter that played the leading role.

— I see. So at the time, were you mainly focused on exploring negative-electrode materials?

Yamabe: There was also the issue of the positive-electrode, of course, but the negative-electrode was more important in terms of storing electricity. As you know, the metallic lithium that had been used until then in the negative-electrode is highly active and there were safety issues*⁷. This is why battery researchers at the time were eagerly seeking a new material to replace metallic lithium.

That was precisely the situation from the late 1970s into the early 1980s. Looking back now, this period, which saw the concentration of scientific papers being published and patents being issued, was the dawning of the lithium ion rechargeable battery and lithium ion capacitor. In light of the findings of Professors Shirakawa and MacDiarmid, new developments had been under way, and it was just around then that the next set of achievements (patents and scientific papers) had started to appear.

— Amid all that activity, it's not easy to pinpoint which invention was first made by which scientist, is it?

Yamabe: Yes, you're exactly right. There are scientific papers, presentations at academic conferences, and patents, each of which has different aims and different procedures, so it really is difficult to decide who got there first. However, as far as the negative-electrode is concerned, I think that the first time when stable lithium doping and undoping — viewed as an absolute prerequisite for a lithium ion rechargeable battery — was demonstrated to be possible with a carbon-based material using a non-aqueous organic electrolyte was probably in our research with PAS. This was not just about the patent, but was also properly backed up by scientific papers.

Development of a PAS-based electric storage device

— These details are certainly not very well known. How did your joint research with Dr. Yata proceed in practice?

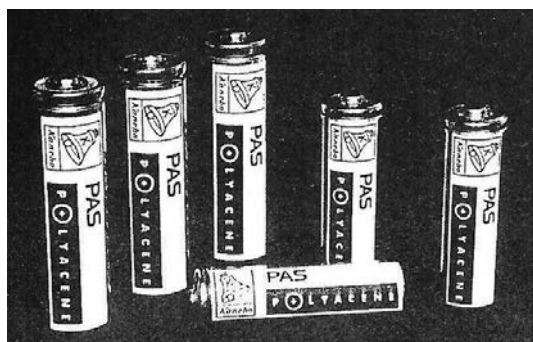
Yamabe: The research at Kanebo, Ltd. progressed with myself in charge of fundamental research and my collaborator Dr. Yata mainly in charge of applied research for product commercialization. I first met Dr. Yata in 1980 when he came to listen to my lecture on polyacetylenes. In this lecture, I touched briefly on the polyacenes that we mentioned just now as a promising substance that could be predicted based on quantum chemistry. This subject apparently captured Dr. Yata's interest, and we came up with the idea that something like a 'polyacene' could be produced by the heat treatment of polymer. That was why we decided to work together.



Dr. Shizukuni Yata

— Prior to this, did you have a theoretical prediction concerning polyacene?

Yamabe: Yes, that's right, that prediction was possible through analysis based on quantum chemistry. And, when Dr. Yata showed me the samples after the heat treatment of phenol-formaldehyde resin in his experiments, it looked like a shiny black thin chocolate bar, nothing like the thin film of polyacetylene with a metallic shine. We were determined to somehow or other make a success of the project and so we carried on with our joint research. Almost all of my scientific papers concerning PAS were co-authored with Dr. Yata and his group^{*8}. Sadly, however, he passed away in March 2012.



Photograph 1 PAS battery (left) and lithium ion capacitor (right)



Source: website of Taiyo Yuden Co., Ltd.

— When was commercialization actually realized?

Yamabe: Taking advantage of the outstanding characteristics of PAS, Kanebo, Ltd. commercialized two types of storage battery products. One was known as the "PAS battery", commercialized in 1989, which used PAS for the positive- and negative-electrodes (Photograph 1, left). Operated like a capacitor, it had compact dimensions and high capacity, and was highly reliable. It is still in widespread use today around the world as a backup power source for mobile telephones and other consumer appliances. This can be seen as the first product in which a conductive carbonaceous material was used for the electrode of an electric storage device.

The other type used PAS also in both electrodes, but the PAS used in the negative-electrode was subject to lithium ions doped in advance. Dr. Yata led the world in the development of this technology, which is known as the lithium ion pre-doping technique. Simply attaching a lithium sheet to PAS enabled the easy insertion of lithium ions. This allows the negative-electrode to operate in the same way as a lithium ion rechargeable battery. In other words, it is a highly unique device in which the positive-electrode operates as a capacitor and the negative-electrode as a rechargeable battery. This product was commercialized as a "lithium ion capacitor" (Photograph 1, right) in 1991, which was exactly the same year as the lithium ion rechargeable battery was released on the market. Today it is still used widely around the world in mobile telephones, IC memory cards, and other information and communication devices.

– By the way what is the difference between this capacitor and a rechargeable battery?

Yamabe: In the lithium ion capacitor, the positive- and negative-electrodes were each based on different principles, giving it a hybrid structure combining the oxidation-reduction reaction of a lithium ion rechargeable battery at the negative-electrode and the physical adsorption reaction of an electric double-layer capacitor at the positive-electrode. As for the negative-electrode, it is basically the same as a lithium ion rechargeable battery, but the difference is that one gives out the stored electricity quickly and the other does it slowly. It has outstanding characteristics including long-life, high capacity density, and higher safety than the lithium ion rechargeable battery. In the future, it has great growth potential in automotive use and as a supplementary device for renewable energy sources such as solar photovoltaics.

Where do the origins of the lithium ion rechargeable battery lie?

– The most standard lithium ion rechargeable battery currently on the market (see Table 1) uses lithium cobalt oxide (LiCoO_2) in the positive-electrode and not a literal graphite but a carbonaceous material in the negative-electrode, but there are a number of different opinions as to how this came about and some questionable data has certainly become mixed up in it. Particularly regarding the carbonaceous material for the negative-electrode, each company had its own strategic approach....

Yamabe: Each company has a position to defend, and it has to be admitted that the information has become confused. As with many industrial products, the lithium ion rechargeable battery was certainly not an exception in that it was not created by a single inventor, but was an achievement based on the findings of many different researchers. That's true particularly concerning the negative-electrode, where the story goes back quite a long way, with various efforts and cumulated research carried out by researchers, mainly in the fields of electrochemistry and materials science.

However, as I said earlier, at the beginning of the 1980s, it was generally thought not possible to perform stable electrochemical doping and undoping of lithium ions into graphite using an organic electrolyte solution. Nevertheless, we found that with our polyacene-based material (PAS), it was possible to do so both smoothly and stably.

Name	Structural formula	H/C ratio	Name	Structural formula	H/C ratio
Polyethylene (CH_2) _x		2	Carbon (C_{10}H) _x		0.1
Polyacetylene (CH) _x		1			
Polyacene (C_2H) _x		0.5			
Polyacenoacene (C_3H) _x		0.33	Graphite		0

Fig. 3 Structures of the polyacene family (those on color ground) and H/C ratio

H/C ratio represents the molar ratio of hydrogen (H) and carbon (C) comprising carbonaceous materials. First introduced by T. Yamabe et al., this index came to play a vital role for the evaluation of carbonaceous materials subsequently used for the negative-electrode.

– Around that time, carbonaceous materials close to graphite were being explored by many researchers. Was it your findings that provided the impetus?

Yamabe: Actually, the PAS patent filed in 1982 (see Table 2) was published in December 1983. I have the impression that various companies that saw it wanted to somehow avoid infringing the patent rights and therefore started to extend the scope of their research to include materials close to graphite with a low hydrogen to carbon ratio (Figure 3).

Then, in the mid-1980s, by combining such carbonaceous material for a negative-electrode and LiCoO_2 for a positive-electrode, the ancestor of the current lithium ion rechargeable battery that does not use metallic lithium for the negative-electrode was drawn up. The LiCoO_2 for a positive-electrode was of course developed in 1980 by J. B. Goodenough et al. through their research on transition-metal oxides. In its development, large contributions were made by Dr. Akira Yoshino of Asahi Kasei Corp. and Mr. Yoshio Nishi of Sony Corporation.

– These are of course names that are known, Dr. Yoshino as the inventor of the lithium ion rechargeable battery and Mr. Nishi as the engineer who was the first to commercialize it (see Table 1).

Yamabe: The fact that I am able to sit here today talking about this is thanks to the efforts and achievements of these two researchers and the many others who worked for practical realization and commercialization. At that time, the field was a hive of activity, and since Dr. Yoshino was a student in the same department of the faculty of Kyoto University as I, from the beginning of the 1980s he often visited my laboratory. It was after I told him about the existence of polyacetylene that he began polyacetylene research, and developed it to an electrode for the lithium ion rechargeable battery.

– It seems that you and Dr. Yoshino were researching in close proximity. If you don't mind me asking again, what ultimately was the origin of that research?

Yamabe: Looking at the major streams in research development that I have spoken of so far, you could perhaps say that the negative-electrode of today's lithium ion rechargeable battery has its origins in our PAS-derived lithium ion capacitor technology. If you seek the origin beyond this, the discovery of conductive polymers by Professor Shirakawa and his group, as I mentioned earlier, triggered the process, and it could also be seen as having started from the polyacetylene lithium ion battery developed by MacDiarmid and Heeger et al. Of course, the positive-electrode was Goodenough's achievement.

What determines the originality of the battery?

– What factor do you think determines the originality of this lithium ion rechargeable battery?

Yamabe: If only one person had single-handedly created the lithium ion rechargeable battery including both positive- and negative-electrodes, then there could be no objection to calling that person the inventor. But in the present case, each science behind the materials used in the positive- and negative-electrodes, in other words, the invention and creation of such materials should perhaps be considered separately. In this respect, I have already explained, and the remaining question is who first put them together. Actually, there is one opinion that it could easily have occurred to any battery researcher who had read Goodenough's papers to construct a lithium ion rechargeable battery using graphite for the negative-electrode.

– Do you mean that neither the development of the negative-electrode material, nor the ingenious combination of the positive- and negative-electrodes was totally irrelevant?

Yamabe: That opinion I cited just now was an extreme opinion. I think it is undeniable that the first combination of the positive-electrode (LiCoO_2) and negative-electrode (carbonaceous material) was what led to the creation of the lithium ion rechargeable battery. But, if you want to claim superiority for this combination, then you need to have both a correspondingly clear scientific basis and evidence.

– **Certainly we sometimes hear it said that a patent alone is insufficient as a scientific basis.**

Yamabe: In the sense of definite scientific evidence, the patent by itself will not do. It is essential to publish a properly researched scientific paper. In the world of science, the final judgment rests on the scientific paper. In the case of the development of the lithium ion rechargeable battery, there is one more important point that definitely ought to be mentioned. If the product is to be serviceable, then the question of how to establish safety is absolutely essential. Even today, the question of how to minimize the risk of ignition and explosion with the lithium ion rechargeable battery is an important issue. The reason why this product has survived is that there were engineers who tackled this issue head-on and resolved it in the early stage of development. This is something that deserves high praise. However superior the performance, a dangerous device will not survive as a widely adopted product. This safety question is an essential issue that cannot be ignored.

– **Thanks to your explanation, the uncertainty surrounding development of the lithium ion rechargeable battery has become a lot clearer. Could I ask you to give a final comment?**

Yamabe: Whoever the original inventor may have been, it remains true that the technology of the lithium ion rechargeable battery originated in Japan. This is a point I really want to stress. One more point is that looking back on the negative-electrode development process illustrates strongly the profundity of the discipline which we might call “carbon sciences” in Japan^{*9}. Japan definitely leads the world here, as demonstrated for example in the area of carbon fibers. It was because of such academic support and the highly mature environment that we were able to develop our unique and original technology while achieving breakthroughs. Still having an unknown nature, carbon is a very interesting material with the potential for greater development in the 21st century.

(Interview and text: Yuko Taira, Chief Editor, *Kagaku*)

Table 1 Superficially overviewed history of development of the lithium ion rechargeable battery

Year	Main events
1977	Hideki Shirakawa et al. discovered that chemical doping increases the conductivity of polyacetylene.
1980	J. B. Goodenough et al. at Oxford University announced the use of lithium cobalt oxide (LiCoO ₂) for the positive-electrode.
1981	Hironosuke Ikeda of SANYO Electric Co., Ltd. and his group filed a patent application for a rechargeable lithium battery using graphite for the negative-electrode.
1982	R. Yazami et al. at the French National Centre for Scientific Research reported that lithium ions can be electrochemically inserted to and desorbed from a graphite negative-electrode in solid electrolytes at high temperature.
1983	Akira Yoshino of Asahi Kasei Corp. and his group filed a patent application for a rechargeable battery using lithium cobalt oxide and polyacetylene for the positive- and negative-electrodes respectively.,
1985	Akira Yoshino et al. filed a patent application for a new rechargeable battery (prototype of the lithium ion rechargeable battery) using lithium cobalt oxide and carbon materials for the positive- and negative-electrodes respectively.
1991	Yoshio Nishi of Sony Corporation and his group commercialized a lithium ion battery.

Table 2 Main approved patents related to the lithium ion rechargeable battery

Application date	Main patents
1979 (April 5), EP	J. B. Goodenough et al.: Electrochemical cell and method of making ion conductors for said cell
1981 (February 28), EP	A. Heeger, A. MacDiarmid et al.: Secondary batteries based on reversible electrochemical doping of conjugated polymers
1981 (June 18), JP	Hironosuke Ikeda et al. of SANYO Electric Co.: Rechargeable lithium battery using graphite for the negative-electrode
1982 (May 31), JP	Shizukuni Yata et al. of Kanebo, Ltd.: Organic electrolyte battery, a rechargeable battery with a polyacene negative-electrode doped with lithium ion
1985 (April 30) (PD), JP	Kazuya Hiratsuka et al. of Toshiba Battery Co., Ltd.: Non-aqueous solvent rechargeable battery, consisting of the positive-electrode with metal chalcogenide compounds etc. and carbonaceous material with quasi-graphite structure
1985 (May 10) (PD), JP	Akira Yoshino et al. of Asahi Kasei Corp.: Non-aqueous rechargeable battery with lithium cobalt oxide and carbon materials for the positive- and negative-electrodes respectively
1990 (February 21), JP	Yoshio Nishi et al. of Sony Corporation: Carbonaceous material and its manufacturing method, and resulting non-aqueous electrolyte rechargeable battery

(PD): Priority date

- * 1. “The University of Pennsylvania group attracted attention after releasing its findings, i.e. application of polyacetylene to a rechargeable battery through the use of electrochemical doping. For example, when both electrodes each consisting of 0.1 mm-thick polyacetylene film are submerged in a THF solution containing lithium iodide and connected to a 9-volt DC power source, the lithium iodide is electrolyzed, the polyacetylene of the positive-electrode becomes doped with iodine, and the negative-electrode becomes doped with lithium. This doping in electrolyte is equivalent to the charging process. When an electric charge is connected to the two doped electrodes, the lithium ions and iodine ions react and electric power is generated”. (main text, p.171)
- * 2. P. J. Nigrey, D. MacInnes Jr., D. P. Nairns, A. G. MacDiarmid, A. J. Heeger. Lightweight Rechargeable Storage Batteries Using Polyacetylene (CH)_x as the Cathode-Active Material. *J. Electrochem. Soc.*, **128**, 1651 (1981).
- * 3. T. Yamabe, K. Tanaka, K. Ohzeki, S. Yata. Electronic Structure of Polyacenacene. A One-Dimensional Graphite. *Solid State Commun.*, **44**, 823 (1982).
- * 4. The title of the patent was “Liquid organic electrolyte battery”.
- * 5. In 1977, M. Armand et al. published the concept of a storage battery combining a graphite intercalational compound with metallic lithium foil, but no liquid suitable electrolyte solution was found. M. Armand, P. Touzain, *Mater. Sci. Eng.*, **31**, 319 (1977)
- * 6. Highly oriented pyrolytic graphite ; HOPG has excellent features like natural graphite, but is very expensive because of the complexity of the productive process and the necessity of high temperature heat treatment over 3000°C.
- * 7. At the time, a lithium non-rechargeable battery had already been commercialized that used manganese dioxide for the positive-electrode and metallic lithium for the negative-electrode. As an extension of this, development of the lithium rechargeable battery was also carried out. However, when metallic lithium was used for the negative-electrode, dendrite crystals of lithium grew on the electrodes after charging and discharging, causing a short-circuit with the risk of ignition, explosion, and other safety issues.
- * 8. There are approximately 60 PAS-related research papers. The representative papers are as follows:
 - 8-1) Electronic Structure of Polyacenacene. A One-Dimensional Graphite, T. Yamabe, K. Tanaka, K. Ohzeki, and S. Yata, *Solid State Commun.*, **44**, 823 (1982).
 - 8-2) Electric Conductivity of Polyacenic System Toward One-Dimensional Graphite, T. Yamabe, K. Tanaka, K. Ohzeki, and S. Yata, *Journal de Physique*, **44**, 645 (1983).

- 8-3) Electrical Transport in Pristine and Heavily Doped Polyacenic Materials, K. Tanaka, S. Yamanaka, T. Koike, T. Yamabe, K. Yoshino, G. Ishii, and S. Yata, *Phys. Rev. B*, **32**, 6675 (1985).
- 8-4) Electrical Conductivity and Thermoelectric Power in Polyacenic Materials, H. Ueno, G. Ishii, K. Yoshino, K. Tanaka, T. Yamabe, and S. Yata, *Syn. Met.*, **18**, 515 (1987).
- 8-5) Studies of Porous Polyacenic Semiconductors toward Application, S. Yata, Y. Hato, K. Sakurai, H. Satake, K. Mukai, K. Tanaka, and T. Yamabe, *Syn. Met.*, **38**, 169 -193(1990) .
- 8-6) Structure and Properties of Deeply N-Doped Polyacenic Semiconductor (PAS), S. Yata, H.Kinoshita, M.Komori, N.Ando,T.Kashiwamura,T.Harada,K.Tanaka,andT.Yamabe, *Proceedings of the Symposium on New Saled Rechageable batteries and Supercapacitors* 92-93, 502 (1993)
- 8-7) Polyacenic Semiconductor Materials (Application to Rechargeable Batteries), *Polymeric Materials Encyclopedia*, K. Tanaka, T. Yamabe, and S. Yata, CRC Press. Inc., 5308 (1996).

- * 9. An influential publication called “Tanso-gaku (carbon sciences)” (edited by Kazuyoshi Tanaka, Hidekazu Touhara, and Hisanori Shinohara, 2011) was issued by Kagaku-Dojin Publishing. This is a high-quality specialist book full of thought-provoking content that gives a systematic overview of the current state of carbon science, and carbon material research/application.

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Tokio Yamabe

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Tokio Yamabe, Nobuaki Murakami
Nagasaki Institute of Applied Science