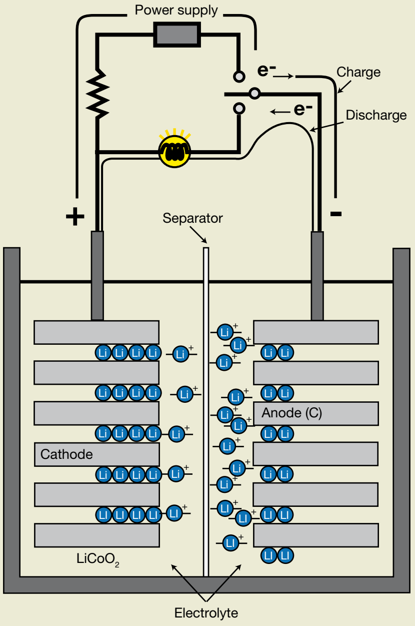
Power player

Claudia Flavell-While speaks with Yoshio Nishi, the Sony engineer who led the development of the ubiquitous lithium ion battery

Figure 1: Principle of lithium ion secondary batteries



Lithium ions carry the current by moving from the cathode to the anode during discharge. The process is reversed by applying an external charge of same polarity. The graphite anode allows lithium ions to embed themselves safely in the material, while the $LiCoO_2$ cathode binds and releases lithium via electrochemical reduction and oxidation. During charge and discharge, lithium ions simply shuttle back and forth between the cathode and anode and thus Sony named this system the "lithium ion battery".

Our world today is one of gadgets, of electronics, of mobile everything – communication, computing, entertainment.

Big devices, securely resting on a desk, with leads snaking a trail to the plug in the wall are *so* 1980s. Laptops have turned planes, trains and sofas into offices, smartphones replace the TV and stereo (as well as your Filofax, map and spirit-level, to name but a few), and handheld spectrometers give you instant results without two days of lab time.

None of this would be possible without a crucial innovation that powers practically all of this on-the-go gadgetry: the lithium ion battery, or LIB.

So far, so obvious, you might think. But how many people would have known that the driving force behind the development and commercialisation of the LIB is a chemist and chemical engineer?

no household name

Yoshio Nishi may be a corporate senior vice president of Sony, but he is not a household name. Google the term "lithium ion battery" and you will probably come across the American physicist John Goodenough, who identified the cathode materials for the LIB and, according to his Wikipedia entry, "is widely credited for the identification and development of the lithium-ion rechargeable battery". You may also read that Li-ion batteries were commercially launched in 1991 by Sony. But it's unlikely you'll find the name of Nishi, the Sony research engineer who headed the team tasked with turning Goodenough's theory into a practical reality.

early days

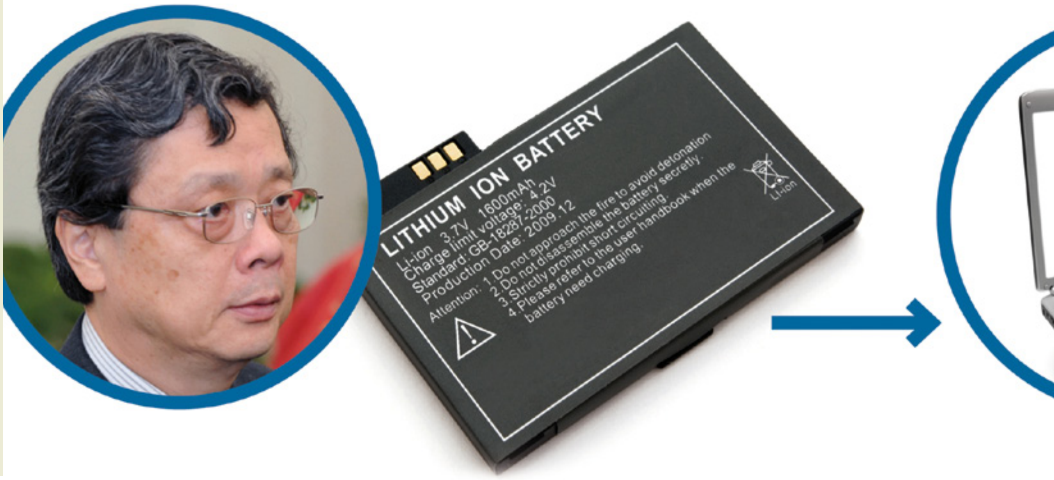
Yoshio Nishi, born in Nagoya, Japan, in 1941, studied solid physical chemistry in the engineering department at Keio University in Tokyo and graduated in 1966. "I joined Sony just after my graduation because I wanted to research semiconductor materials," Nishi tells ***tce***. Sony was researching materials for a lot of interesting novel devices ranging from semiconductors to photovoltaic devices and from electro-acoustic transducers to recording media, many of which used sophisticated materials including semiconductors.

Ironically, Nishi never got to work on semiconductors. He spent his first eight years in fuel cells R&D, followed by 12 years on electro-acoustic materials, and then 20 years developing and refining LIBs, starting as general manager of the LIB development team during the crucial early development phase.

Sony was keen to develop lithium-based rechargeable batteries as an alternative to nickel-cadmium batteries, mainly because they promised a much greater energy density and attract fewer environmental concerns.

"At first, we assumed that important applications of LIB were to audio and visual equipment such as cassette players, mini-disc players, home video cameras and others," Nishi says. "Two or three years after the first introduction of LIB we proposed LIB to PC makers and it brought about big changes to LIB market. And soon, cellular phones manufacturers became another important customer."

Even so, in the early stages of the development, people in the sales division protested against the development. "Even



many battery companies said that lithium ion batteries were premature and that the rechargeable battery for the next generation would be a nickel-metal hydride cell," Nishi says.

electrode choices

Unlike Goodenough, who used metallic lithium as an anode, Nishi and his team wanted to investigate the use of carbonaceous anodes. Metallic lithium is liable to catch fire and to suffer from poor cyclic performance. To overcome these drawbacks, Nishi and his team tried making anodes from materials which could store lithium, thus giving him the crucial lithium at the anode while keeping the risks to a manageable level, and achieving excellent cyclability. Graphite was a prime candidate – its layered structure allows atoms of another element to be inserted between the layers, a process known as intercalation. The intercalated anodes worked well, but turned out to be impractical for mass production.

The third option was to use a pure carbon anode and replace a different component of the battery with a lithium compound (after all, the battery needed source of lithium ions). The team investigated lithium electrolytes but dismissed the idea because the battery could not practically hold enough electrolyte solution to store sufficient lithium ions. The cathode remained as the last practical solution. Indeed it turned out that a lithium cobalt oxide ($LiCoO_2$) cathode would permit lithium ions to be inserted and extracted via simple electrochemical reduction and oxidation (see Figure 1).

not so easy

If this sounds easy, then nothing could be further from the truth, Nishi says. "We continually experienced one difficulty soon after another," he wrote in a 2001 paper on his work.

The first problem was the size of the $LiCoO_2$ particles. The established production process, of calcinating a mixture of tricobalt tetraoxide (Co_3O_4) and lithium carbonate (Li_2CO_3) at 950°C produced a very fine powder which, thanks to its large surface area, was highly reactive. An external short circuit or crushing force could cause all the particles in one area to react simultaneously which, in the worst case scenario, could set the battery on fire.

By using granular pellets of Co_3O_4 and Li_2CO_3, adding an aqueous solution of polyvinyl alcohol resin and a slight surplus of Li_2CO_3, Nishi and his colleagues managed to obtain coarser particles needed to make the battery safe.

The anode proved to be even more troublesome. Graphite was a useful material for intercalating lithium, but turned out to be incompatible with the then-prevalent propylene carbonate electrolyte solutions. Ethylene carbonate would have been a suitable alternative, if only it wasn't solid at room temperature, and no addition of solvents would sufficiently lower its melting point. The team suggested soft carbon such as coke as a useful alternative to graphite, but it turned out insertion of lithium ions causes the soft carbon to expand which in turn negatively affects performance. Hard carbon (Figure 2) does not suffer from that drawback, and under the right circumstances can trap even more Li ions than graphite.

However, the team suffered a massive setback just as Sony was about to start up the large-scale production of hard carbon. In early experiments, the researchers had produced hard carbon by carbonising the raw material, heat treating it at 1100-1200°C before grinding it down to the required particle size. However, hard carbon is, as the name suggests, extremely hard. To make the grinding process less onerous, the team decided to first grind and then heat-treat the carbon in the full scale process.

Alas hard carbon produced this way was much less active than the old process and, and would barely adhere to the poly(vinylidene fluoride) (PFDF) binder. Unfortunately, this was not discovered until

Figure 2: The morphologies of graphite, soft carbon and hard carbon

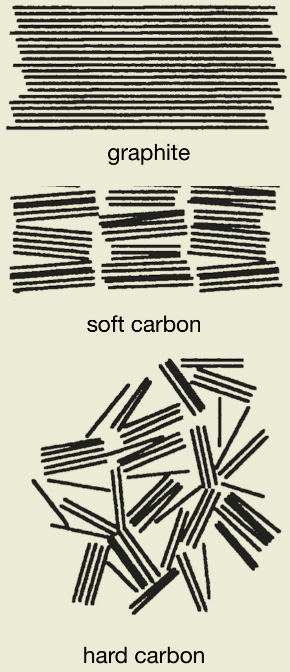
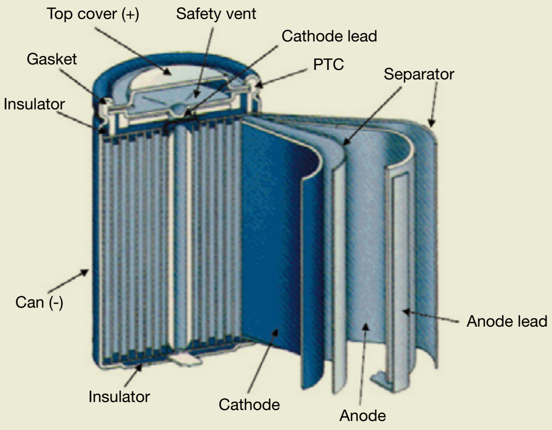


Figure 3: A typical LIP

The anode consists of copper foil covered in graphite powder and PFDF. The cathode is formed of aluminium foil covered in $LiCO_2$ powder and binder, separated with microporous polyethylene film, wound together in a tight spiral and filled with electrolyte solution.



> “new applications including electric vehicles, hybrid electric vehicles, and stationary power sources will create a huge market for LIBs”

the very day the new full-scale production line, which was based on the new process, was due to be opened with a formal ceremony. Nishi decided to abstain from the opening and instead locked himself away in the lab searching for a solution, which was eventually found in the form of an improved binder.

safety first

Before Sony could commercially launch the LIB in 1991, the other issue to address was safety. The solvents and the lithiated carbon present in the batteries are flammable, and the engineers had to develop safety mechanisms to prevent batteries from overheating and potentially catching fire as a result of abuse. Several mechanisms were implemented (some shown in Figure 3), including vents to prevent overpressure, the porous membrane separating anode and cathode was designed to soften so the pores would close in the event of a temperature spike, elements with a positive temperature coefficient were added to prevent thermal runaway, and a mechanical link that would disconnect the cathode lead if pressure built up inside the battery.

Even so, over the years there have been numerous incidents of batteries causing phones and laptops to spontaneously combust or explode, and millions of batteries worldwide were recalled. What had happened?

Nishi acknowledges that fierce price competition has caused sales departments to put a lot of pressure on engineers and production staff to switch to less expensive materials or shorten the tact time, while in other cases device designers have ignored the battery manufacturer’s usage specifications. “Engineers have to clarify how such cost cuts will affect the battery performance, especially safety, and they should not easily compromise on what they believe is important,” he said in a 2009 interview with the technology news portal Tech-On. He says that in the early days of LIBs, battery engineers always accompanied the sales staff on customer visits to explain to device designers exactly what they could and could not do – a practice Nishi thinks could do with reviving.

looking ahead

Since their launch, a succession of improvements has tripled the energy density of LIBs from 200 Wh/l to 600 Wh/l. Future developments, such as the replacement of graphite with silicon or tin, will increase the energy density even further. Companies such as Nexeon, which has developed LIBs with silicon anodes, predict a 40% rise, to over 800 Wh/l. Improvements to the cathode, while still a little further off, could eventually see energy density triple to 1200 Wh/l.

LIBs will power electric vehicles and hybrid electric vehicles, which will lead to a huge rise in demand. While LIBs will no doubt eventually be superseded by something even better, Nishi expects that it would take at least another 20 years to develop a credible alternative.

Nishi says: “There is a modern Japanese proverb, ‘A cellular phone without battery is a mere empty box’. With mobile devices everywhere, all of which rely on LIBs, the important of these batteries will increase more and more.

Furthermore, new applications of LIBs including electric vehicles, hybrid electric vehicles, stationary power sources and others will create a huge market for LIBs. “The most important thing, however, which we must always keep in mind is ‘safety and quality first’,” he says. “Remember that, and a brilliant future lies before LIBs.”

“I now work for about 15 companies related to LIB industries as an adviser or consultant and would like to contribute further improvement of LIBs." **tce**

Next month: Nicholas Leblanc, who in the midst of the French Revolution developed the industrial soda process

The results are in!

We asked you to vote for which chemical engineer featured last year changed the world the most, and you responded. The results were exciting to watch – Bessemer (steel), streets ahead for most of the voting period, was pipped to the post in the closing stages by Haber and Bosch (fertilisers) by just one vote, with Kane & McKeen (penicillin) just behind. We also promised that we would give away a Kindle e-book reader among the entrants. Step forward Wallace Barnett - your prize is on its way.

Which chemical engineer(s) had the greatest impact on the world today?