Forty years of research on solid metallic lithium batteries: an interview with Liquan Chen

By Hong Li

Li-ion batteries were first commercialized by Sony in 1991 and have been used widely in portable electronic devices, electric vehicles and grid applications. Although Li-ion batteries have achieved a phenomenon commercial success and become so pervasive and indispensable in our modern life, their development has been sluggish and fallen way behind the rapid advancement of electronic technologies. Batteries with a higher energy density than Li-ion batteries are highly desired for many emerging applications. It is widely recognized that solid metallic lithium batteries (SMLBs) are one of the most promising candidate technologies. The first research on SMLBs was reported by Michel Armand in 1978. At almost the same time, Liquan Chen studied lithium-ion conductors in Germany with Werner Weppner in 1977. When he came back to China in 1978, he initiated and pioneered the research on SMLBs and related fundamental studies of solid-state ionics in China for the first time. In this interview, Prof. Chen reviews his work of the past 40 years in solid lithium batteries and lithium-ion batteries, and the renaissance and future prospects of SMLBs.

LI$_3$N: THE FIRST ATTENTION

NSR: How did you start your research on battery technology? 
Chen: At the end of 1976, when the scientific community in China re-connected with the outside of the world, I went to the Max-Planck-Institute for Solid State Research in Stuttgart, West Germany then, as a short-time exchange scholar. As I was engaged in crystal growth research at the Institute of Physics of CAS, my mentor, Professor A. Rabenau, accepted me to work on crystal growth in his laboratory. At that time they were growing lithium nitride (LI$_3$N) single crystals, which were being studied almost throughout the entire institute. This material is a super-ionic conductor and could be used to make solid lithium batteries. Its energy density should be much larger than that of the lead-acid battery, and it may be used for electric vehicles. I immediately realized that it is an important material, and that it was very important to develop better understanding of this field. So I wrote right away to the leadership of the Institute of Physics to ask to change my research direction. The leaders agreed with me quickly. I proposed to Professor Rabenau that I should study the super-ionic conductor, and he immediately agreed, but on condition that I first finished the crystal growth task he had assigned to me. I took five months, rather than a year, to complete that task, and then began to learn solid-state electrochemistry and to research the super-ionic conductor. This was also the beginning of the study of solid lithium batteries. After returning to China in 1978, I continued to study solid-state ions, which are highly relevant for solid-state lithium batteries and their applications. Two years later, the laboratory of solid-state ions was established at the Institute of Physics CAS. It was the first laboratory in this field in China.

NSR: What was your favorite topic in solid batteries? What were the problems and challenges in the field then?
Chen: The solid-state lithium battery was a new generation of battery, and attracted great attention from all over the world at that time. A fast ion conductor for lithium is the key material for manufacturing this kind of battery. The lithium-ion conductivity of the LI$_3$N crystal in the a-b plane is very high (1.2 × 10$^{-3}$ S/cm at room temperature), but its decomposition voltage is very low. Therefore it was realized that it is actually not possible to use this material as an electrolyte in a solid lithium battery. At that time, the ionic conductivity of other lithium-ion conductors was very low, so it was urgent to explore new lithium-ion conductors. The study of fast ion conductors and solid-state lithium batteries were the key issues in the sixth and seventh five-year plans (1980–1990) of CAS. The first ‘863’ program of the Ministry of Science and Technology also included solid-state lithium batteries as a major research theme.

We have done the following work in my laboratory.

Solid solution ionic conductor

We first studied LI$_{14}$Zn(GeO$_4$)$_4$, known as LISICON, which did not appear to be a good room-temperature lithium-ion conductor. But we found that this material is a solid solution formed by simply adding Zn$_2$GeO$_4$ to Li$_4$GeO$_4$. As a result, the high temperature phase of Li$_4$GeO$_4$ is stabilized at room temperature, which explains the high ionic conductivity of LI$_{14}$Zn(GeO$_4$)$_4$. We extended this idea to other systems, as a new way to explore fast lithium-ion conductors.

We also investigated the LI$_3$VO$_4$–LI$_4$SiO$_4$ system, and found that LI$_{13.3}$V$_{0.7}$Si$_{0.3}$O$_4$ has an ionic conductivity of...
1.8 × 10⁻⁵ S/cm at room temperature. It does not react with lithium at high temperatures, and can be used as a solid electrolyte for lithium batteries. At the same time we found that the solid solution Li₃₋₅V₀.₄Ge₀.₆O₄ in Li₄GeO₄–Li₃VO₄ has anionic conductivity as high as 4 × 10⁻⁵ S/cm at room temperature.

Amorphous fast ionic conductor

We soon discovered that the ionic conductivity of the crystalline material is much lower than that of the amorphous counterparty with the same composition. So we studied the ionic conductivity of amorphous oxides such as LiB₂O₄. We soon realized that the ionic conductivity of the amorphous material is increased anomalously during the pre-crystallization stage. This high ionic conductivity can be preserved at room temperature by retaining the amorphous state through quenching. We learned that if the oxygen in an oxide was replaced by a more easily polarized sulfur atom, the ionic conductivity could be readily increased. For example, the room-temperature ionic conductivity of the amorphous Bi₂S₃–Li₂S–LiI is up to 1.1 × 10⁻⁴ S/cm.

Addition compound ionic conductor

An addition compound in the LiI–CH₃OH system was first synthesized by Professor Weppner. We studied it concurrently. Its melting point is 46°C, and at 20°C it has a lithium-ion conductivity as high as 2.2 × 10⁻⁴ S/cm. However, this material is not stable with lithium because it contains an -OH group. So we explored other additive compounds with better stability.

Polymer ionic conductors

Polymer ionic conductors are polymers doped with metal salts. They have high ionic conductivity, good plasticity and are easy to make as thin films with large area. Therefore these polymer materials are good solid electrolytes for solid lithium batteries. We studied some factors that affect their lithium ionic conductivity, and found that the polar side group helped to dissolve a lithium salt, but was not conductive to lithium-ion migration. It was found later that the ionic conductivity could be greatly enhanced by copolymerization as the intramolecular conduction is far more effective. The ionic conductivity of the copolymer PECH–PEO–LiClO₄ at room temperature is up to 1.24 × 10⁻⁵ S/cm. This is an effective way to improve the ionic conductivity of polymer.

Composite ion conductor

We studied the properties of ionic conductors containing second-phase particles (DSPP). It was widely recognized that the ionic conductivity at room temperature of a composite ion conductor is greatly increased relative to the pure material. The ⁷Li NMR spectrum of such a composite ion conductor consists...
of a wide peak with a narrow peak superimposed. The narrow peak is caused by fast motion of the Li$^+$ ion, which moves to the interface between the mother phase and the second-phase particles. The more obvious the small peak, the greater the increase in ionic conductivity. Therefore, the increase of the ionic conductivity is directly related to the structure of the interfacial layer and to the size of the second-phase particles.

LI-ION BATTERIES: OUR CONTRIBUTION

NSR: When did research on Li-ion batteries using liquid electrolytes start? What were the contributions to this technology from Chinese researchers?

Chen: In 1990, Sony in Japan announced the successful development of a lithium-ion battery: the ‘rocking chair’ battery proposed by Armand in 1978. Although at that time the Ministry of Science and Technology in China strongly supported the commercialization of nickel–hydrogen batteries, almost all of those working on solid lithium batteries both inside and outside CAS started at this time to pursue nonaqueous Li-ion batteries.

In my laboratory, research on Li-ion batteries can be divided into two periods. Before 2000, it was focused on Li-ion battery materials and battery technology, as well as the engineering issues involved in their commercialization. After 2000, the focus has shifted to nano-ionics, combining theoretical study with experimental research.

In the first stage, we studied preparation methods, basic properties and improvement of materials related to Li-ion batteries. We prepared LiCoO$_2$ and LiMn$_2$O$_4$ by microwave assisted synthesis, and looked at the formation mechanism and microstructural evolution of the products. We prepared nanoscale graphite-based anodes by pyrolysis of phenolic and furfural resins. We investigated the bonding properties of Polytetrafluoroethylene (PTFE), Polyvinylidene Fluoride (PVDF) and Polyacrylonitrile (PAN), as well as their reactivity with Li$^+$, and found that PVDF and PAN were the best available binders.

After achieving significant progress, in 1994 with the help of entrepreneurs we built a laboratory-scale production line to study the technology for a 18650 cylindrical Li-ion battery. In January 1996, our technology was granted CAS identification. In December 1998, by relying mainly on home-made equipment, domestic raw materials and our own technologies, we completed the first 18650 cylindrical Li-ion battery test production line, with an annual production capacity of 200,000 cells. Beijing Xingheng Battery Co. Ltd. was established in 1999, meaning that Li-ion battery commercialization had finally been realized in China.

These are some of the creative results in the second phase of our study of materials for Li-ion batteries.

Surface modification of LiCoO$_2$, Li (NMC)O$_2$ and LiMn$_2$O$_4$

Our theoretical calculations elucidated the reason for poor stability for LiCoO$_2$ and other layered cathode materials under high charging voltage. We found that surface coating is a simple way to improve the stability. The calculations and experiments showed that γ-Al$_2$O$_3$ is a good coating material. After coating treatment, the cathode materials can be charged to 4.5 V or higher. In the same way, by surface coating with γ-Al$_2$O$_3$, a surface solid solution LiMn$_{2-x}$Al$_x$O$_4$ is formed on LiMn$_2$O$_4$, and the cyclability and performance are improved.

Na-doping at the Fe site in LiFePO$_4$

By first-principles calculations, we predicted that the energy band structure of LiFePO$_4$ can be changed by doping with Cr. Our experimental results show that the addition of 1–3% Cr to LiFePO$_4$ leads to an electronic conductivity increase by a factor of $10^7$–$10^8$ at room temperature. However, the electrochemical performance becomes poor. First-principles molecular dynamics simulations show that the transport of the Li$^+$ ion in LiFePO$_4$ is one-dimensional. Cr doping blocks these 1D transport channels. We proposed to avoid this by Na-doping at the Fe site. The experimental results show that the electronic conductivity of the material can be improved by 8 orders of magnitude with just 1% Na-doping at the Fe site. The charge/discharge rate is also improved. This important result shows the value of combining theory and experiment.

Nano-Si anode materials

We were the first to propose using nanostructured silicon as a high-capacity anode material in 1997. It is now internationally recognized that nano-silicon will be the anode material for the third generation of lithium-ion batteries. During the past 19 years, the mechanism of lithium storage in nano-silicon has been studied. The material with a reversible capacity of 380–2000 mAh/g are now being produced in a pilot production line,
and start testing in some full cells. Nano-silicon seems the only electrode material for Li-ion batteries that has been proposed and developed in China.

Size effect for lithium storage in nano materials

For the first time we found experimentally that a stable fluoride nanocomposite could store lithium ions, thanks to a new mechanism of interfacial storage. This is the only one of eight reversible lithium storage mechanisms that has been discovered and confirmed in China.

Start-up theoretical calculations in Li-ion batteries

In 2001 we began to recruit graduate students in theoretical physics, so that we could be better placed to combine theoretical and experimental research. The surface modification of LiCoO$_2$ and the electronic conduction modification of LiFePO$_4$ mentioned above are both results of combining such theoretical studies with experiment.

We calculated the theoretical energy density of 1172 electrochemical energy-storage systems to find and eliminate candidate materials. Based on these results, we proposed a roadmap for the development of rechargeable batteries. It is clear that the lithium/air battery will be the ultimate rechargeable battery for electric vehicles in view of gravimetric energy density.

NSR: What lessons can we learn when research shifted from solid to liquid lithium-ion batteries during the 1990s?

Chen: The studies on fast ion conductors and solid-state batteries supported by CAS and Ministry of Science and Technology (MOST) provided the knowledge, technology, equipment and talent, a concrete foundation for Li-ion battery research and production. In the 1990 s, not only did we carry out the research on solid-lithium-battery related materials, but also began to explore and investigate battery manufacturing technology and equipment, as well as develop the equipment for charging and discharging of batteries. During the interim inspection of the 863 plan, a radio and recorder powered by a solid-state lithium battery was demonstrated. The achievement exhibition of the first 863 project was show-cased some solid-state batteries made by using manual coating winding machines and other manual equipment.

China’s early Li-ion battery commercialization greatly benefited from the experience accumulated during the 1990 s, and because of the wide use of manual equipment in production, Li-ion battery prices could be quickly reduced. These efforts promoted China’s lithium-ion battery industry quickly to the top three players worldwide.

SOLID LITHIUM BATTERIES: A RENAISSANCE STAGE

NSR: Research on solid-state lithium batteries seems to be speeding up again. Is this right?

Chen: Solid-state lithium batteries are still recognized as central to the future of rechargeable battery technology. Who gains the first opportunity will gain the initiative. Previously we have been largely following foreign developments. But if we start research early on solid lithium batteries, we could be ahead of the field.

Although lithium-ion batteries will continue to be useful, increasing the energy density to more than 300 Wh/kg demands that we consider solid-state lithium batteries. What’s more, Li-ion batteries with organic carbonate electrolytes might catch fire, but solid-state lithium batteries have no such risk. Lithium metal has a capacity of about 3700 mAh/g, which is 10 times that of graphite. Because lithium metal itself is the lithium source, materials without lithium can be used as cathode. Therefore it is relatively easy to select a cathode material.

The key issue for solid-state lithium batteries is to develop a suitable solid electrolyte material. It must meet two criteria: first, it should have higher conductivity for lithium ions at room temperature (in the order of $10^{-3}$ S/cm or higher), and second, there should be a good interface between the electrolyte and the electrodes, anode and cathode. There are two families of solid electrolyte materials: inorganic solid electrolytes and polymer electrolytes. At present, there are four or five kinds of mature inorganic solid electrolyte and polymer electrolyte, but none of them can completely meet all the requirements. Through the development of polymer/ceramic composite materials, however, it should be possible to develop solid electrolytes satisfying all the demanding requirements. And the existing lithium-ion battery equipment may partially be used to manufacture solid-state lithium batteries, which means that there need to be no increase in cost to achieve industrial upgrading and transformation. In this way it is possible to make China a strong competitor and a leading player globally in the field of lithium battery research and manufacturing.
**NSR:** When might solid-state lithium batteries be commercialized?

**Chen:** Electric vehicles are urgently needed here. China has become the leader in production and sale of electric vehicles, but the battery is the key. We need to think about the layout of China’s lithium industry, and how lithium batteries can meet China’s demand for electric cars.

By using a nanostructured silicon/carbon composite with a capacity of $\sim 500 \text{ mAh/g}$ as the anode material and a high-capacity nickel-based layered oxide or a manganese-based lithium-rich material as cathode, the energy density of lithium-ion batteries could be expected to reach the goal of 300–350 Wh/kg. In order to make the energy density still higher, perhaps as much as 500 Wh/kg, we need research on solid lithium batteries.

To accelerate this process by identifying new candidate materials, we need a 'materials genome initiative', involving high-throughput, multi-scale computation and screening, and data-mining technology and methods. The formation of big data with experimental and calculated data and the use of materials informatics will contribute to our understanding of the basic scientific problems of ion diffusion, lithium storage capacity, charge transfer, structure evolution and so on. Even more important is that we must attract and nurture the bright young minds in China to this exciting field of sustainable clean energy. We must strive to achieve solid-state lithium battery commercialization in five years. Our goal must be achieved, and our goal can be achieved!

—Liquan Chen

Hong Li is a Professor of the Institute of Physics, Chinese Academy of Sciences.

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