Brief History and Future of the Lithium-Ion Battery

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1 DEVELOPMENTAL PATHWAY OF THE LIB

1.1. What is the LIB?

The lithium-ion battery (LIB) is a rechargeable battery used for a variety of electronic devices that are essential for our everyday life. Since the first commercial LIB was manufactured and sold in Japan in 1991, the LIB market has continued to grow rapidly for nearly 30 years, playing an important role in the development of portable electronic products such as video cameras, mobile phones, and laptop computers. Furthermore, the market of LIBs in electric vehicles is expanding extremely fast, as is that in applications for large-scale energy storage systems. The LIB can also facilitate the practical use of a higher proportion of renewable energy sources in smart grid systems by providing storage to balance out differences in power generation and consumption over time. With these developments, it is anticipated that the LIB market will reach the scale of US$20 billion in 2020.

Before starting my story of the development of the LIB, let me explain how the battery works and how it differs from other batteries. As shown in Table 1, batteries can be classified by two basic aspects; whether they disposable (primary) or rechargeable (secondary), and by the type of electrolyte employed, either aqueous or nonaqueous. Aqueous electrolyte is

	Aqueous electrolyte battery	**Nonaqueous electrolyte battery (high voltage/high capacity)**
Primary battery (disposable)	Manganese dry cell, Alkaline cell	Metallic lithium battery
Secondary battery (rechargeable)	Lead-acid battery, Nickel-cadmium battery, Nickel-metal hydride battery	Lithium-ion battery

Table 1. Classification of batteries.

water that contains ions, whereas nonaqueous electrolyte is an organic solvent that contains ions.

Manganese dry cells and alkaline cells are most commonly used for small electrical goods such as flashlights and clocks. They are disposable and contain aqueous electrolyte. Lead-acid batteries, nickel-cadmium batteries, and nickel-metal hydride batteries also contain aqueous electrolyte, but they are rechargeable. Lead-acid batteries are commonly used for car batteries. These widely used aqueous batteries are easily manufactured.

Generally, battery performance is evaluated in terms of electromotive force and capacity. Electromotive force refers to the voltage generated by a battery. This determines the energy density of the battery, which is the available energy of the battery in a given size. The higher the electromotive force, the smaller the battery can be to run a certain device. Battery capacity represents the maximum amount of energy that can be extracted from the battery under certain specified conditions, and this is determined by the amount of active material contained in the battery. Larger capacity is better, of course, but the capacity of an individual battery can change depending on its age and, if it is rechargeable, the number of times and conditions under which it has been charged and discharged.

Aqueous batteries have a disadvantage in the available electromotive force. In principle, it is limited to around 1.5 V, the voltage at which water of the electrolyte begins to dissociate by electrolysis. Therefore, aqueous batteries need to become larger as they become more powerful. Batteries that use aqueous electrolyte thus face a natural limit in terms of energy density, which therefore restricts the scope for reduction of size and weight for a given capacity.

On the other hand, nonaqueous electrolyte batteries can obtain an electromotive force of 3 V or more per cell, offering much greater possibilities in terms of increasing energy density. An important example is the metallic lithium battery, a primary battery which had already been commercialized when I started my research on the LIB in 1981. It uses nonaqueous electrolyte and metallic lithium as a negative electrode material.

Reviewing these batteries, it is clear that a nonaqueous secondary battery was highly desirable, and the market started to seek one in the late 1970s. Professor M. Stanley Whittingham proposed the application of electrochemical intercalation using compounds such as TiS2 as the battery cathode, and research was actively conducted.1 Demand for the new battery was, however, truly heightened by the revolutionary advancement of information technology which occurred in the early 1980s, bringing portable electronics into fashion. This led a growing need for small and lightweight rechargeable batteries, and the obvious first step was to convert the metallic lithium primary battery into a secondary battery. Unfortunately, even the best efforts could not succeed for two main reasons: 1) under charging, lithium tends to precipitate on the negative electrode in the form of dendrites, which easily cause short-circuiting, and 2) the high chemical reactivity of metallic lithium resulted in poor battery characteristics, including inadequate cycle durability due to side reactions, and moreover posed an insurmountable problem in terms of safety due to the inherent risk of a thermal runaway reaction. Please look at Figure 1. These photographs were taken at an experiment to assess the safety of the metallic lithium battery in 1986. Just 20 seconds after a battery cell was smashed by a steel weight, it started to burn intensely. This experiment strongly indicated the necessity to seek new electrode materials other than metallic lithium to ensure the safety of the battery.

Current commercial LIBs do not contain metallic lithium. They are defined as nonaqueous secondary batteries using carbonaceous material as the negative electrode, and transition metal oxides containing lithium ions (most often $LiCoO_2$) as the positive electrode. Carbonaceous material is basically charcoal, and $LiCoO_2$ is a metallic oxide, a kind of ceramic. In the completely discharged state, lithium atoms are only contained as part of the cathode. Under charg-

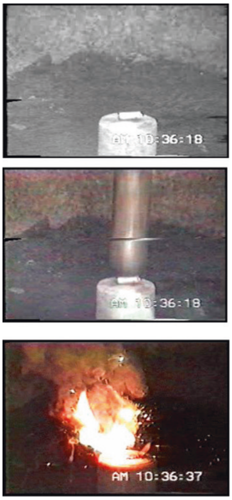

Figure 1. Safety test of primary battery using metallic lithium as anode.

ing, lithium ions are released from the cathode and migrate through the electrolyte into the carbonaceous material of the anode. The reverse reaction occurs during discharging, and electric energy is stored or released by repeating these reactions reversibly. Cell reaction without chemical transformation provides stable battery characteristics over a long service life, including excellent cycle durability with little degradation by side reactions, and excellent storage characteristics. The operating principle of the LIB is illustrated in Figure 2.

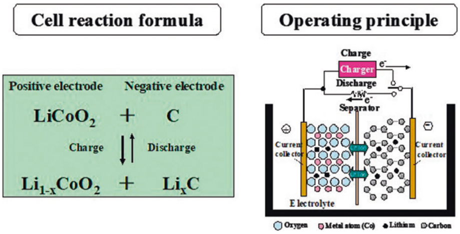

Figure 2. Electrochemical cell reaction formula and operating principle of LIB.

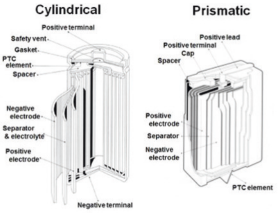

Figure 3. Cell structure of LIB.

Figure 3 shows the structure of the LIB cell. One on the left is the cylindrical type, which is commonly used for laptop computers, while the prismatic type on the right is for mobile phones. With such a structure the LIB achieves high cell voltage and high energy density, which is the key for small size and light weight. Without the invention of the LIB, we would not have been able to enjoy the information technology revolution led by the widespread use of mobile phones and portable computers. Next, I would like to describe the path I took to develop the world's first LIB.

1.2 The beginning

What happened in 1981?

My journey for the discovery of the LIB started in 1981. Technological development achieved this year was also very significant. The US space shuttle Columbia succeeded in its first flight. Also, IBM launched the world's first PC which ran a version of MS-DOS, the operating system released by Microsoft in the same year.

Among all the astonishing events that happened in that year, the most significant for me was Japan's first receipt of the Nobel Prize in Chemistry. Dr. Kenichi Fukui was awarded the prize for establishing the frontier molecular orbital theory. In simple terms, this theory claims that we are able to obtain a good approximation for chemical reactions or properties of a particular material by calculating the movement of electrons contained in the material. This implies the ability to predict chemical reactions without performing actual experiments, and therefore scientists are able to identify what they are looking for much more quickly. Recently, computer simulation based on this theory is being used to identify the effects and side effects of medicine, which is a great contribution to society.

Polyacetylene: The plastic that conducts electricity

The frontier molecular orbital theory triggered a huge advance for the creation of new materials for the LIB electrodes. In order to see how it worked, we need to consider how pi electrons behave in the case of alternating single and double bonds, which is called a conjugated system.

Importantly, the conjugated system allows the pi electrons to move across all the adjacent aligned orbitals. Here, the pi electrons do not belong to a single atom or bond but spread consistently across the whole group of atoms. Imagine that there is a material formed by carbon atoms joined together with infinite chains of conjugated double bonds. What kind of property would this material have? The pi electrons in such a material would work similarly to free electrons in metallic solids, which allow the substance to conduct an electric current. This means it is possible to create a plastic material that conducts electricity.

A number of scientists reached the conclusion that, in theory, it is possible to prepare the simplest material with structure shown in Figure 4 called polyacetylene (PA). PA is prepared by polymerizing acetylene gas, which has carbon-carbon triple bonds. Unfortunately, most attempts by scientists to synthesize PA with electric conductivity simply failed. It turned out to be rather difficult to form the infinite chains of conjugated double bonds, and so the pi electron could not move around the entire mass. Consequently, such materials did not exhibit electric conductivity.

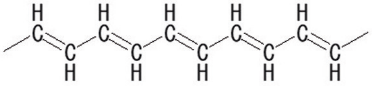

Figure 4. Chemical structure of polyacetylene.

The first successful preparation of highly conductive PA was reported by Professor Hideki Shirakawa in the 1970s. He used a method called thin-film polymerization to produce the material with metallic luster and silvery texture, which was highly conductive. Professors Shirakawa, Alan Heeger, and Alan MacDiarmid were awarded the Nobel Prize in Chemistry in 2000 for this astonishing discovery.

Batteries made of plastic

The PA discovered by Professor Shirakawa held amazing properties as a plastic. In addition to being a conductor, the material could also act as a semiconductor, meaning it could be used to make transistors, and moreover it could be used to make solar cells. These unique properties sound rather magical considering the great similarity between PA and polyethylene (PE). Shown in Figure 5, PE is a non-conductive material and the most common plastic around us.

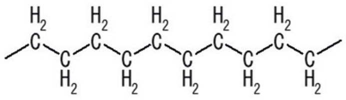

Figure 5. Chemical structure of polyethylene.

Let's look at Figure 4 again and compare the structure of PA with that of PE in Figure 5. They share the same basic structure except that the carbon atoms in PA connect to each other with alternating single and double bonds. The pi electrons in the double bonds enable the material to have these fascinating characteristics.

The property of PA that attracted me the most was its capacity to transfer electrons as an electrochemical reaction when an external voltage is applied. This characteristic is exactly what is required for the material of the battery electrodes. By applying voltage, we can eliminate negatively charged pi electrons from the bond to create positively charged PA. The removed electrons can be returned just as easily. This means that a battery with a PA electrode can charge and discharge. This positively charged PA is called p-doped PA and was expected to be cathode material. On the contrary, we can add extra electrons to the double bond structure to create negatively charged PA. This is called n-doped PA, which was thought to be suited to anode material. As you can see, PA with its pi bond structure shows extremely unique properties that allow it to be either the anode or cathode. Most researchers working at the time focused on p-doped PA because of its stability when contacting air and water, and its high electromotive force that reaches 4 V or more. I, however, decided to develop the anode with n-doped PA. As I mentioned, unstable metallic lithium anode material was preventing the commercialization of non-aqueous secondary batteries in the 1980s, so finding an alternative anode material would be a significant advancement of battery technology. I also found that n-doped PA could be highly stable as long as its contact with water is totally avoided. Being inspired by the achievements of Fukui and Shirakawa, my research to develop a new secondary battery started in 1981.

1.3 Encounter with perfect cathode material

Development of n-doped PA anode started off with enhancing the functionality of the material by improving the catalyst methods and properties of the electrolyte, etc. Usually, the quality of electrodes is first assessed separately for the anode and cathode, and then overall assessment is performed in the assembled state. As research progressed, the quality of PA anode got significantly better, and my confidence in this material was heightened. However, when I finally decided to assess the anode in the battery, I realized a serious problem. There was no suitable cathode material. Here is a list of the major cathode materials available for nonaqueous secondary batteries in the early 1980s: TiS_2, VSe_2, V_2S_5, $Fe_{0.25}V_{0.75}S_2$, $Cr_{0.75}V_{0.25}S_2$, $NiPS_3$, $FePS_3$, $CuCo_2S_4$, CuS, $NbSe_3$, MoS_3, Cr_3O_4, V_6O_{13}, V_2O_5, MoO_3. They all turned out to be unusable with our PA anode because of the lack of lithium in them. These materials were designed to be paired with metallic lithium anode, so they didn't have to contain lithium. Formula (1) shows the chemical reaction that occurs in a battery using metallic lithium as an anode and TiS2 (titanium disulfide) as a cathode.

$$Li + TiS_2 \rightarrow LiTiS_2 \qquad (1)$$

During discharging, lithium ions in the anode are transferred to the TiS_2 cathode, which forms $LiTiS_2$, and these ions go back to the anode during charging. Obviously, this ion transference does not occur once metallic lithium anode is replaced with PA. It was such a disappointment, since our PA had quite superior quality as anode.

Months passed without being able to find any suitable cathode material, but at the end of 1982 the situation suddenly changed for the better. It was the last working day of 1982, and I was clearing up my office for the New Year. I managed to dig out some research papers that I intended to read but hadn't gotten around to. Since I had some time to kill in the afternoon, I decided to read them. This was when I encountered the 1980 paper published by a research team led by Professor John B. Goodenough, who was at Oxford University at the time.[2] It was my "eureka" moment. The research reported the discovery of the new compound $LiCoO_2$, which was described as a good cathode material for secondary batteries.

This compound has a crystalline structure comprised of alternating layers of Li cations and cobalt oxide anions. This allows not only the release of Li ions from the outer layer of the crystal but also from inside the structure, making a large number of ions available for transfer. Furthermore, $LiCoO_2$ enabled the achievement of cell voltage of 4 V or more, providing high battery capacity. Importantly, the report stated that the authors hadn't found a suitable anode material to form a secondary battery. I instantly drew a formula of the chemical reaction between PA and $LiCoO_2$, which looked like Formula (2).

$$PA + LiCoO_2 \rightarrow PA\text{–}\ xLi^+{}_x + Li_{(1-x)}CoO_2 \qquad (2)$$

This promising-looking formula worked for real inside a test tube battery which we urgently made to try out the electrode combination at the beginning of 1983. This was such an emotional moment that marked the birth of the first LIB using a PA anode. Not only achieving superior safety than existing secondary batteries with a metallic lithium anode, the first LIB was considerably lighter than any other competitors at the time. In the same year, I successfully filed a patent for the new principle of the first LIB using PA for the anode and $LiCoO_2$ for the cathode. This is the official public acknowledgement of the first LIB.

This innovation wouldn't have happened if any of the following three events didn't occur: the formation of the frontier molecule orbital theory by Kenichi Fukui, synthesis of highly conductive PA by Hideki Shirakawa, and formulation of $LiCoO_2$ by Professor John B. Goodenough. To me, it was a miracle that these events coincidentally happened at roughly the same time, when I was exactly in the right environment to utilize them for the first LIB.

1.4 Development of anode material

After completing the principle of the first LIB using PA anode and $LiCoO_2$ cathode in 1983, we continued trying to improve battery performance in order to achieve commercialization. As the research progressed, however, I began to find several shortcomings associated with PA. One is its low chemical stability when exposed to oxygen and heat. Exposure to oxygen could be prevented by sealing the battery completely, but the deterioration that occurs under heat was much harder to avoid. Another major limitation of PA stemmed from its low real density, 1.2 g/cm^3, which results in low battery capacity for a given volume. Since the real density of lead is 13.6 g/cm3, the new battery with PA was much lighter than a lead-acid battery, but the volume did not differ greatly when their capacity was matched. This almost certainly meant that it would be impossible for us to make a small battery with PA even if the heat stability problem could be solved.

Although we hadn't totally given up on PA, we started to look for alternative materials with the conjugated molecular structure. The most favorable candidate was carbonaceous material, which has relatively high real density of above 2 g/cm3. As represented in Figure 6 below, carbonaceous material has a molecular structure with carbon atoms connected by alternating single and double bonds.

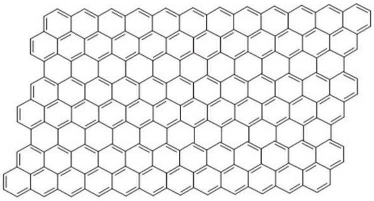

Figure 6. Chemical structure of carbonaceous material.

We gathered various carbonaceous materials from manufacturers and tested their functionality as an anode. With huge disappointment, we could not find a workable sample at all. The year was 1984, and I was very frustrated not only with our inability to find a solution for PA but also with the difficulty of obtaining a suitable carbonaceous material. Our research progress came to a halt.

Fortunately, this negative situation didn't last long. Good news was actually brought by a different business division of our company. The company has diversified business fields, and one of them is fiber production. There was a fiber research center in the south of Japan, and in the 1980s they were developing a new type of carbon fiber. Their product was called VGCF (vapor-phase grown carbon fiber), prepared by a unique method that vaporizes hydrocarbon gas in a furnace at 1 000 °C, in which carbon fiber grows. The gas used for the procedure was aromatic compounds such as benzene and toluene. Once it goes through the furnace, thin carbon fiber of several microns diameter is left on the wall, and this starts to grow just like hair. This fiber is very similar to carbon nanotubes that have a cylindrical nanostructure, but VGCF's filament diameter is 1 000 times thicker. It was later found that VGCF actually has a carbon nanotube in its core, but carbon nanotubes were not discovered until 1991. At the time, we didn't even look for such a thing; we were simply overjoyed with the superior performance of VGCF when used as an anode material for the LIB. Normally, the crystallinity of the material increases with higher carbonization temperature, and 1 000 °C is considered too low to form a highly crystalline structure. However, the VGCF has relatively high crystallinity for a material carbonized at that temperature, and this unique property provided just the right degree of crystallinity to effectively intercalate and release the lithium ions when used as a negative electrode.

With this VGCF, the carbon/$LiCoO_2$ battery configuration was completed. This LIB is the first of its kind to achieve the small size and light weight that matched what was needed in the market. In 1985, I filed a patent covering the basic configuration of the new battery,[3] and other related technologies were also filed as separate patents. From this point our research started to accelerate toward commercialization.

1.5 Safety test

About the time when we discovered the VGCF anode material, our new battery had to face another challenge; proving it was safe enough to be sold on the market. As I mentioned, the nonaqueous secondary batteries previously under development had all failed to reach the market because of their lack of safety. The reason was the hazardous metallic lithium being used for the negative electrode. Therefore, theoretically speaking, replacing the metallic lithium with carbonaceous material should remove the problem. The degree of improvement was, however, the most important aspect we had to demonstrate. The safety level required for a battery to be used by the general public is extremely high, and we had no idea if our new battery would meet the target.

The method of testing was another issue as well. No guideline or regulation on testing procedures for this kind of battery existed. Referring to safety tests for similar products, we decided to apply over 10 different assessments to prove that the new LIB was safe to be sold. Without delay another problem arose. We had no idea where to perform such a potentially dangerous experiment. The outcome of the test was unpredictable, and the situation could be hazardous. The first idea was to do it on the riverbank near the research center, but it turned out that we needed to get permission from the local authority. Since we had little hope of getting permission for this, we gave up on that idea. Changing tactics, we started to look for another business division in our company that was developing something dangerous, just to see how they had dealt with a similar situation. Our company has a diversified business portfolio, and there were lots of research and development projects going on. We finally found what we were looking for: the explosives business. Our company was dealing in explosives, so it owned an explosives testing site in the mountains of southern Japan. The personnel in the explosives business did us an enormous favor, allowing us to use their site to test the safety of our battery.

The results were astonishing. The images in Figure 7 show the first battery destruction test on an LIB, in which a steel weight was dropped on the battery.[4] To be used by the general public, the chemical reaction that occurs in the battery after the massive impact should not pose any danger to people.

The result was in stark contrast to the same test performed on the metallic lithium battery described above and shown in Figure 1, which started to burn 20 seconds after the impact due to its highly reac-

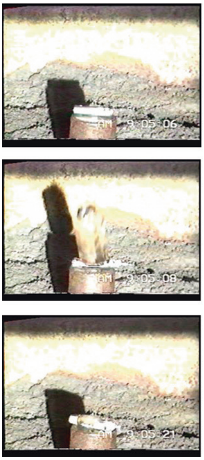

Figure 7. Safety test of LIB.

tive anode. The new carbon/$LiCoO_2$ battery, on the other hand, showed no sign of danger even one hour after being smashed. This result guaranteed that we could continue our research, and ultimately it was a very positive step toward the commercialization of our LIB.

2. COMMERCIALIZATION OF THE LIB

The LIB was thus commercialized in the early 1990s as a small and lightweight rechargeable battery, making a major contribution to our current society of mobile IT. As the LIB market in mobile IT (consumer electronics) has grown for over 25 years, battery performance and reliability have increased while the cost has come down. The LIB is now entering another period of transformation in automotive (electric vehicle) applications.

I will briefly review the current LIB technology and market. Based on its characteristics of small size and light weight, LIBs have become very widely used in small consumer electronics products for mobile IT. Some 4 billion LIB cells are currently manufactured for this application in a year. The largest share of these is for mobile phones including smartphones. Looking at the history of mobile phones, I will describe the key role LIBs played in their widespread adoption. The origin of mobile phones can be traced to the "shoulder phones" which came on the market in the mid-1980s. As the name indicates, it wasn't a handheld device, but one requiring a shoulder strap to carry. Weighing around 3 kg, it was essentially a car phone redesigned to be carried around like a shoulder bag.

It was in the early 1990s that the handheld devices known as mobile phones went on sale. The first generation, called 1G, mostly used nickel-metal hydride (NiMH) batteries, though a few models did adopt the then newly developed LIB. The 1G system was analog, and the ICs operated at 5.5 V. Therefore, using NiMH which produced 1.2 V per cell, 5 cells in series were needed, while the LIB produced 4.2 V per cell, so 2 cells in series were needed. For a few years, the mobile phone market was shared by NiMH and LIB. The advent of second-generation, or 2G, mobile phones was a major turning point. The system was changed from analog to digital, and the IC voltage was reduced from 5.5 V to 3 V. The lower voltage meant that while 3 NiMH cells would still be required, the device could operate with only a single LIB cell. This was a critical difference, as it enabled the design to be greatly simplified. The mobile phone soon completely switched to LIB, and the phones themselves became much small and lighter, in turn driving their more widespread adoption. This ushered in the IT revolution from around 1995, followed by 3G and now smartphones. As such, the LIB, being a small and lightweight battery with an output of 4.2 V, undoubtedly played a key role in enabling today's IT society.

Now the LIB is at another turning point. Electric vehicles are emerging as a major LIB application. Figure 8 shows the annual LIB market by capacity of batteries delivered in GWh for mobile IT and automotive applications. While the automotive application began around 2010, its growth remained moderate for a few years as sales of electric vehicles fell short of expectations due to high cost and short driving range. This began to change in 2015, when electric vehicle market growth accelerated as an effect of China's strict environmental regulations taking effect in 2018. When China adopted a national policy of promoting electric vehicles to deal with air pollution problems such as PM2.5, European automobile manufacturers, which had been somewhat passive about electric vehicles, swiftly changed course. In 2017 the LIB market scale for automotive applications slightly exceeded that for mobile IT, and rapid growth in the automotive sector has continued ever since. By 2025, the automotive market is forecasted to be 7–8 times larger than the mobile IT market for LIBs.

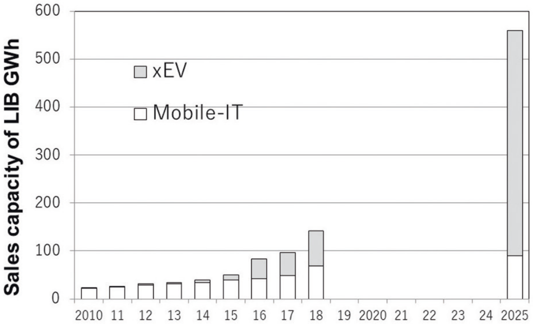

Figure 8. Capacity-based LIB market scale by category. Source: B3 Corporation Report.

3. ACHIEVING A SUSTAINABLE SOCIETY FOR THE FUTURE

Despite various discussions all around the world, we still don't have a clear solution to environmental problems. I see a trilemma between the environment, the economy, and convenience. Sustainability cannot be achieved in society if any one of these three is prioritized at the expense of the other two. How can this trilemma be overcome? I think two recent buzzwords offer a clue. We hear of CASE (connected, autonomous, shared, and electric vehicles) and MaaS (mobility as a service). Very soon, I believe these concepts will not only revolutionize transportation, but also transform our society into a truly sustainable one.

In combination with fast-evolving technologies such as AI (artificial intelligence), IoT (the internet of things), and 5G (fifth generation telecommunications networks), LIBs will play a central role. Autonomous electric vehicles with artificial intelligence will become widespread throughout society. They will be provided as a service that people subscribe to for a monthly fee. This service will not only be available in big cities, but also in rural areas. Since the vehicles will be shared by many people rather than owed individually, the cost per person will be reduced to one-seventh.

Spread throughout society, in addition to eliminating traffic accidents and congestion, such vehicles will act as a reservoir of stored energy. The electricity they store would last for ten hours if fifty power plants shut down. The vehicles charge up their batteries at fully automated charging and discharging stations when there is an ample supply of power. Conversely, they automatically discharge themselves at these same stations to supplement grid power when necessary. This facilitates greater adoption of renewable energy sources such as wind and solar whose power generation tends to be intermittent.

Such a transformation will impact every aspect of society, not just transportation. People will be able to live in comfort, with a robust economy, and minimal environmental burden. This is my vision of how the trilemma can be overcome and society can become sustainable very soon.

Current LIB performance is already approaching the level that would be required. Energy density and cost are both nearing the point where the social transformation I described would be possible. However, durability would need to improve significantly in this scenario, since the batteries would be required to undergo frequent cycles of charging and discharging. I consider that batteries would need to cycle 5,000 times, enabling vehicles to travel a total of 600,000 km, in order to enable this scenario. Technological developments to improve cycle life will thus be critical.

LIBs will play a central role in enabling a sustainable society to be achieved very soon. Battery technology linked with AI, IoT, and 5G will drive innovation throughout society. CASE and MaaS will enable an automobile-dependent society to be sustainable. The trilemma between the environment, the economy, and convenience will be overcome. This is my vision, and I will continue to devote my efforts to helping bring it about.

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