

Invent or Discover

the art of useful science

[Sample Chapter 4: Lithium ion battery]

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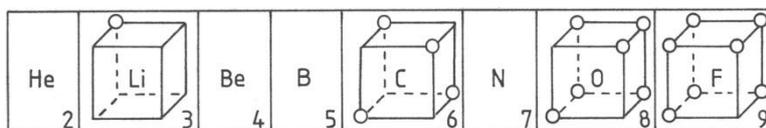
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‘ . . . we shall be able to invent new instruments which shall a thousandfold surpass in energy those which we at present possess?’

(Michael Faraday)

Ferdinand Porsche started work with the Béla Egger Electrical Company in the Vienna of 1893. He adapted electric motors to operate directly on the road wheels of horseless carriages, as they were then known. Next, he worked for Jakob Lohner & Co., makers of luxury carriages. By 1898 the company offered for sale a carriage with a massive pack of lead—acid batteries powering electric motors fitted directly to the hubs of the front wheels. The motors each resembled a massive cake, with the lines of the wheel spokes seeming to divide the cake in slices. The batteries delivered a surge of power for a burst of speed along the flat but their weight on hill climbs was a tombstone.

To Porsche’s fertile mind the solution was obvious. Combine one of the internal combustion engines, recently brought to market by Karl Benz, with a dynamo to charge a battery big enough to power to electric motors. This original hybrid auto, the Lohner-Porsche Electromobile, was a magnificent machine. Porsche also designed a people’s motor, a Volks Wagen, the humbler but much loved Beetle. His son designed the Porsche 356, that classic of fast motoring. Porsche’s Electromobile however, was no people’s motor. The company could only sell several hundred of these costly vehicles despite their enticing speed and comfort. The new Daimler-Benz manufacturer offered Porsche a job as designer of autos powered entirely by internal combustion engines.

On the streets of cities from Chicago to Berlin, around 1900, there were equal numbers of horse drawn carriages, and two horseless types, one with an electric motor, the other with an internal combustion engine. Electric motors were almost ideal for automobiles: simple, few moving parts, high torque available throughout the operating range, no gearbox, smoothly silent and capable of great speed. Sheer power was as seductively exhilarating then as it remains today, but only for as long as there was energy left in the battery.

The internal combustion engines in some of these horseless carriages were from various lines of invention. George B. Selden of Rochester, New York State, miniaturized the original static engines used in factories for use in a horseless

carriage and applied for a patent in 1879. Meanwhile, from Mannheim, Germany, Karl Benz patented his Motorwagen in 1885. It was powered by a four stroke engine designed by Nicolaus Otto. In America the strictly commercial concept of an automobile costing no more than six month's wages by the average worker was about to be realized by Henry Ford's crucial invention: the assembly line for the Model T. The last hurdle in the rush to the era of the automobile was the problem of getting the stubborn things started. The driver engaged the motor with a hand-crank and with all force swung it to rotate the cylinders against their internal pressure. Once the engine fired that crank could sometimes spin out of control against the driver's hand.

Electric autos avoided such macho display followed by humiliation. Salesmen had been selectively marketing them for women to drive, with the promise of freedom about town in convenient elegance. But by 1912 Charles Kettering was able to patent an effective electric self-starter. Self-starters not only created excellent, although ironic, business for makers of lead—acid batteries, they buried the remains of the original electric auto as a business model.

Thus it was that these complicated, clattering, booming, belching, infernal internal combustion engines – technically inferior in all but one respect to electric motors – won the market. The engine was supplied with a reliable, portable and densely energetic fuel: gasoline distilled from newly discovered reserves of petroleum oil. There lurked a dire problem.

Electricity from chemicals

The electrical storage battery was invented by Alessandro G.A. Volta, a professor of physics at the University of Pavia in the Italy of the 1790s. He sought an instrument to test a recent proposition of Luigi A. Galvani at the University of Bologna – a medical researcher who proposed that all animal muscles generated their own electricity. Volta had connected the fact that Galvani's tests on muscle included instruments of brass and iron, with his own observation of the tingling effect of a pair of different metals held against his tongue. Could the electricity emanate from the paired metals? He imitating his observation with a neat pile of alternating small discs of silver and zinc separated by discs of cardboard soaked in dilute acid. The taller the pile, or the more piles that were connected by wires to form a battery, the greater the electrical energy available.

Volta experimented with different combinations of metals and solutions in his battery. He measured the result with the standard instrument of those days – a gold-leaf electroscope, which has a close pair of thin gold foils that repel away from each other when electrically energized. On analyzing his records Volta gained a glimmer of insight into what he called an electromotive force. He drew up a list of relative reactivities, or electrochemical tensions. Paired zinc and copper discs gave a modest force; zinc with silver a slightly stronger force; whilst copper with silver just a feeble force. Zinc is separated widely from silver in this series of reactivities.

Volta's invention was instantly popular and spread as a powerful research tool and source of industrial energy. Electrical storage batteries played a key role during the early industrial revolution – new elements such as sodium and potassium could be discovered by assembling a large voltaic battery and feeding its electric current through a crucible full of the molten chemical salt. Hunting for new elements became popular, especially ones so spectacularly reactive as potassium. But the energy latent in the contrasting metal discs, or electrodes, was eventually consumed by internal chemical reactions. The batteries were not rechargeable.

In 1859 Gaston Planté presented the first rechargeable battery to a market eager for a battery both portable and packing a punch of energy. One of them nestles beside the engine of every standard automobile but most of us never give them a second thought. Until they fail one cold damp morning. Then, with a freshly charged battery installed, a turn of the ignition key produces a brief whizzing from the starter motor and the main engine springs to life. Compare the size of the battery with that of the engine and its large lumps of cold heavy pistons to be forced against the cylinder pressures and viscous oil just to rotate that engine enough to fire it. Or try hand cranking an antique automobile. The energy of the battery is astonishing in its dense concentration, silently waiting for you in its grimy box of acids and metals.

That battery is the same one as Planté's – albeit with the benefit of a century and more of accumulative improvements. His battery originally used two sheets of lead, separated by linen cloth or rubber sheet, rolled into a spiral, and all immersed in dilute sulfuric acid contained in a tall glass pot. This arrangement of two identical lead sheets by itself could not spontaneously produce electricity; there was no chemical difference between the metal plates to create an electrical potential.

Planté's stroke of inventive genius was to connect a freshly assembled lead—acid battery to a source of electricity. Electric current in the wire connected to one of the lead plates energized it to form lead dioxide on the surface of the plate. The other electric wire, of opposite charge, connected to the other lead plate, changed the surface of the plate into a spongy form of lead. Now there was an electrochemical difference between the plates and when the charging wires were connected instead to a load, then electricity would flow spontaneously in the opposite direction and perform work. To light a lamp or turn a motor. A lot of work if each of these cells were connected in series to form a battery with boosted voltage.

When exhausted from their labors, the batteries could be recharged from the electricity available from a recent invention, the mechanically powered dynamo. The dynamo was the generator of electricity with current of constant polarity, direct current, and invented as a replacement for those messy batteries. As it turned out dynamos became intertwined partners of batteries in a long and fruitful relationship and lead—acid batteries can be found from marine navigation buoys to electric fences.



One hundred years of invention and innovation produced two main types of battery that remain commonly used today. For heavy duties the lead—acid rechargeable battery, and for use in torches and toys the sealed alkaline non-rechargeable battery. All done without any adequate knowledge or understanding of the chemical mechanisms of what the molecules and ions were doing, or the physical mechanisms of what the atoms and electrons were doing. Thus the invention and practical development of early batteries owed far more to empirical observation and trial and error experimentation than to understanding the fundamental workings of batteries. Demand for batteries as practical devices became a whirlwind of pressures. As long as something could be cobbled together that worked better than its predecessor then understanding of what was happening between these pungent solutions and electrodes, in their leaking boxes and jars, would have to wait a while, as long as electrical energy could be tapped from the conducting wires.

So this simple, old, invention, this accumulator of electricity, is the continuing baseline for any hopes for a second and predominant uptake of electric cars. To power an automobile engine, who can invent a better rechargeable battery?



The invention of the electric telegraph met a huge demand of people to be able to send messages to each other across the widening spread of industrialized countries. However, there was a block across the highway to expansion of telegraphy and other electrical industry. Chemical electricity from the early batteries was an expensive and troublesome business, mainly because of the rate at which the electrodes were consumed. Obviously, Planté's invention of the lead—acid rechargeable battery was not by itself a full answer, for an independent source of electricity was needed, some way of generating the stuff other than clever mixes of chemicals.

Michael Faraday, working initially as assistant at the Royal Institution in London, provided the first answer in 1831. He built a demonstration generator powered by hand-cranking a metal disc to spin between the arms of looped magnet. Current was drawn off through a metal brush applied to the rim of the disc. The mysterious energy of magnets was coaxed down a path to controllable electricity: electromagnetism could now be manipulated.

Nevertheless, there was no electrical generator in the 1830s in a practical sense. The simplest of these generating devices produce an alternating current, going one way then the other through the conducting wires because the essential magnet has, by its basic nature, a field at one end that spreads out in the opposite direction to a field at the other end. Direct current is necessary to recharge a battery, thus it was not until an innovation to split very rapidly the flow of current that the design of a suitable generator was completed. This problem engaged many experimenters over the next several decades. Metal brushes picked up the current from the different sections of wound wires that were rotated fast within a cylindrical magnet. This

commutator, as they called it, eventually enabled the announcement on the same day in 1867 of the ‘Dynamo-electric Machine’ as Werner Siemens in Berlin called it. The generator of Charles Wheatstone announced in London produced the same results, but with different circuitry. Now the power of these generators was increased far beyond the laboratory experimenter’s models by replacing the permanent magnets with electromagnets. The high power delivered as direct current jump-started the second industrial revolution: power to recharge batteries, power for electrolysis and electroplating, power for arc furnaces.

Several competing inventors had already demonstrated the electric motor, in principle at least. What enabled electric motors with the power to replace horses or steam engines was the thinking behind these improved dynamos. The claims to fame by inventors of the first practical electric motor are numerous, but Thomas Davenport who earned his living as a village blacksmith in America did take out the first patent for what he called ‘. . . an Application of Magnetism and Electro-Magnetism to Propelling Machinery.’ That United States patent was numbered 132, in 1837. Invention was galvanized by the new law to protect intellectual property that had recently been passed in America.

This account is in danger of reading like an application to patent a perpetual motion machine. Let’s start from the beginning. The energy released by fusion of nuclei in our Sun comes to us on Earth as electromagnetic radiation, that in turn heats the seas and air to form clouds, thence rainwater falling on high ground. That water, from its state of high potential energy, will very readily flow, under the influence of the field of gravity from the mass of Earth, back toward the sea. The water can be diverted into a water wheel, which turns a dynamo-electric machine, producing electrical current to recharge a battery. The battery in turn can be fitted in the back of a carriage that has an electric motor connected to its wheels. The horse connected to the front of the carriage can then be retired to pasture to power itself by eating lots of grass. Growth of the grass is, of course, also powered by solar radiation. It still reads like perpetual motion . . .

Lithium in batteries

In 1896 the US Patent Office granted an application for an electric battery, proposing use of an electrode made of the metal lithium. An alarming choice: lithium is in the group of metals with sodium and potassium that react with water; the alkali metals. These soft grey shiny lumps are made of atoms with their outer electrons so loosely bound to their small nuclei that the electrons will readily escape to rip into molecules of water with enough force to split them into the hydrogen and hydroxyl ions. The spare electron combines with hydrogen ions to form hydrogen atoms, as gas; a highly combustible situation. The reaction of lithium is actually the most energetic of these metals with water in terms of the amount of heat released, but it is slower thus not self-igniting. Nonetheless, sulfuric acid in lead—acid batteries is troublesome enough, but exploding batteries – you must be joking! No, the inventor, Johan W.Th. Olan of New York, was entirely serious. He shunned zinc and favored metals of more intense chemical reactivity.

The reactive power with water would be controlled by the formation of oxides of these metals within the battery and by matching these positive electrodes with strongly negative electrodes. Olan was not the only inventor at that time intrigued by the rich possibilities of these highly reactive materials. The question for us is where did these inventors get these ideas about the energetic potential of lithium for batteries?

John Dalton, a teacher of mathematics and natural philosophy working in his laboratory in the Manchester had proposed a theory of atoms in 1803. Despite wide opposition to this crazy idea, he remained fascinated by the ability of his atoms to combine in fixed proportions and as a function of their weights relative to each other. But Dalton's idea of fixed proportions could not cope with simple but variable mixtures like metal alloys. As if that was not problem enough, skeptics refused to accept this idea of invisible atoms until somebody could demonstrate their existence somehow. It was up to others to enliven the idea of Dalton's atoms with positive and negative electrical charges.

At the College of Medicine in Stockholm, was Jöns Berzelius, a medical doctor with responsibilities for pharmacy and a rapidly deepening interest in fundamental chemistry. Inspired like many others by Volta and his battery, Berzelius developed a theory of chemical combination, based on the proposition that atoms could be viewed as having a positive or negative charge and would combine as opposites: positive potassium to negative oxygen. After 10 years of intense analysis of elements and their compounds, using crude apparatus and impure materials, he had examined two thousand combinations which enabled him to place the forty or so known elements in a table ordered by their chemical equivalent weight, relative to oxygen at the top of the table. This was the support that Dalton's atomic theory needed, for chemists at least, although skeptics abounded for many more years. Berzelius's way of thinking about how atoms combine was often known as the dualism theory of the chemical bond and remained in use for another century. Despite not providing deep understanding, this theory worked in an admirably practical way.



Michael Faraday made intensive studies of the volume and weight of oxygen and hydrogen given off from water when it was electrolyzed with the help of a small amount of dissolved conducting salt. Other most informative materials were chlorides of tin and of lead. These he prepared as the dry salts to be melted around an electrode of platinum and an opposite electrode of platinum was dipped into the molten mass. They were good conductors of electricity in their own right, without being dissolved in water. The tin alloyed to the first electrode and the resulting mass was weighed and compared to the amount of electrical current that had been used. Again and again, Faraday performed such experiments until he could ask whether he and his peers might: ' . . . invent new instruments which shall a thousandfold surpass in energy those which we at present possess?'

Faraday was a stickler for terminology. He set out to redefine core descriptors used in electrochemistry and invent new ones for the things he, and others, had found but not yet defined. For us the most important is his name for substances that are either electro-negative, or electro-positive in relation to the relevant electrode. He coined the simple and general term *ion* for these substances. In his main paper of 1834, he provided a table of the ions he knew about. There is some familiarity with modern chemistry, with a big group of one polarity starting with oxygen, followed by chlorine, iodine and so on. The group of the opposite polarity starts with hydrogen, followed by potassium, sodium, lithium . . . The familiarity disappears at the end of that group with complex organic materials such as quinine and morphine mistakenly listed as ions. Every ion on this list is accompanied by a number, its electrochemical equivalent weight, relative to hydrogen at 1. This list was substantially the same as that ground out so laboriously by Berzelius, but Faraday had obtained, incidentally, his data by a method more simple and accurate. One gram of hydrogen will combine with 35.5 grams of chlorine to give hydrogen chloride, thus the equivalent of chlorine relative to hydrogen is 35.5, and so on through as many elements as were amenable to such laboratory manipulations.

Ionic theory

Despite all the work of the early electrochemists there remained toward the end of the 1800s some extraordinarily simple questions to be asked. What happens to table salt, sodium chloride, when it is added to water? It disappears, it becomes invisible, and although 10 grams of salt added to 100 grams of water in a plastic pot of 10 grams will total 120 grams, those amounts of salt and water as exact volumes, instead of mass, do not add up. The total volume actually decreases slightly because a crystal of dry salt occupies more space as a crystal than when it is dissolved in water.

To explain why requires a knowledge of the state of sodium chloride dissolved in water. What did this simple everyday word *dissolve* actually mean? Of course everybody knew what it meant – except for certain curious chemists. What chemists knew then was that dry crystalline salt is not a conductor of electricity, nor is pure water, but salty water conducts electricity readily; as any modern yachtsman at sea in a boat full of electronic equipment will confirm. Obviously the silvery metallic sodium, highly reactive with water, and the green toxic gas chlorine, become very different things when combined as crystals of table salt. How, precisely, do they differ yet again when dissolved in water? Who might be brave enough to ask such silly questions?

Svante A. Arrhenius was a doctoral student, registered at the University of Uppsala but preferring to work at the Physical Institute of the Swedish Academy of Sciences in Stockholm. He chose a topic forbidden by one of his supervisors. He tackled the estimation of molecular weights of substances by measuring their electrical conductivity in solution. His initial results were confusing because his method was inappropriate. He wondered if the effect of the concentration of the dissolved substance on the conduction of electricity was a more significant

problem. Struggling in a lonesome borderland between physics and chemistry, he nearly failed his doctoral examination in 1884. His examiners misunderstood the message. Despite all, Arrhenius remained confident his results were a signpost to something new. They indicated that when a good electrolyte such as table salt, is in a dilute solution in water, then all of the molecules of the original salt dissociate into separate charged particles independently of any electric current that may be applied later. These charged particles have separate properties that are constant and can be nothing other than the ions of Faraday. But they were a very different thing from what Faraday had conceived of. Clearly the proposition of a single molecule of sodium chloride as something equivalent to a single molecule of, say water or carbon dioxide, was no longer tenable. The sodium and chlorine can only combine as a huge mass of the two elements held together in a dry crystal, or in a balance of vast numbers of the two ions in watery solution. The question remained, however, of why these two widely dissimilar elements had such an affinity for each other? Such simple questions – so deeply penetrating.

Arrhenius ended his intellectual isolation by interesting a group of others with his results. The group became known as the Ionists. Their studies on the energetic relationships between components of chemical reactions enabled them to test the ideas of mathematicians on the concept of free energy. This is the capacity of a defined and confined system, such as a chemical reaction, to release energy. The important point is that energy is able to do useful work by flowing from high potential to lower potential. After the flow and the work done, the energy remains because it cannot be either destroyed or created. But it becomes disordered. In other words, the closed system increases in entropy. Energy in an ordered form inevitably tends toward a disordered form; thus the entropy of the system increases spontaneously, without any help from any outside agency. All that is needed is the presence of ordered energy at one place.

Useful work, of course, is precisely what we seek with this story. By a significant convergence, the experiment to consolidate understanding of this elusive concept used a battery. Across the terminals of a battery there is a ready and powerful ability to do useful work. The energy is derived from precisely defined chemical reactions and measurable to small fractions a volt. The free energy available to do work from a single electrochemical cell is directly proportional to the voltage measured across the terminals. The force is able to flow because one electrode is paired with another that differs on the reactivity scale of Volta, once the electrodes are connected with a conducting wire.

Voltage is sometimes called potential difference and can be likened to the head of water in a wide pipe leading from a high reservoir to a turbine wheel far below. Potential energy is stored in the reservoir; energy is the capacity of a body for doing work. When the spigot is opened the water flows, under the influence of the field of the Earth's gravity. As the water flows the energy flows as kinetic energy and is delivered to the turbine for useful work. Thermodynamics arose as a science in the context of the first industrial revolution, with its steam engines powered by burning coal. How to transfer the energy of heat into work without too much

waste? To apply that robust, almost tangible, style of reasoning to the silent and invisible workings of a battery was a bold leap of imagination.

By the mid 1800s the efforts of many chemists had grouped around certain ideas of the chemical bond. August Kekulé epitomized the thinking. He proposed that each element has a fixed number of units of affinity or bonding, and these are usually known as valences. It is not as simple as that, but a useful example is the combination of hydrogen with valence 1 and oxygen with valence 2 to form H_2O ; two hydrogen atoms will readily combine with one oxygen atom to form water. Or take methane, the four valences of carbon and the single valence of hydrogen allow the combination CH_4 . Much of the evidence for these combinations came from the synthesis work on the laboratory bench and factory floor that chemists were so busy with. The imperative to arrange this new information in tables and charts and rankings of electronegativity became irresistible. How could the increasing number of newly discovered elements be arranged to make useful predictions?

The table of elements that is now definitive saw an early formulation based on a musical analogy: octaves with a period of eight. The Periodic Table, as it became known, was independently developed then announced within the same year by Dmitri Ivanovich Mendeleev working in Russia, then Julius L. Meyer in Germany. The independent origin of Meyer's table was a welcome confirmation in this field of so many competing but half-baked proposals. The patterns Mendeleev discerned as he sorted, arranged and rearranged the scraps of empirical data then available gave him the courage to leave gaps to allow for insufficient information. Gaps that should have been filled by an element. He had only sixty three known elements to work with at that time. He did not know the others, but he knew that he did not know.

He ventured even further out into the unknown because his table enabled him to predict key characteristics of these elements – clues for parties of element-hunters. Atomic weight was the basis of the ordering of the elements in Mendeleev's first table, but when other characters of elements did not fit he was prepared to ignore atomic weight. What he and nobody else knew was that an ordering according to the structure of the atoms of the various elements was the real basis of these patterns.

The table is wide and in blocks of elements of related chemical character. Hydrogen is king, sitting on a lonesome throne at top left. Along toward the far right top is oxygen and carbon. Down from hydrogen, in a column vertically below comes lithium, then sodium, potassium and so on. Another column to the right of the one headed by oxygen is fluorine, beneath which is chlorine, bromine and others. Hydrogen at top left, oxygen over at the right; sodium far left and chlorine far right. As any early electrochemist could have predicted, once they had sight of Mendeleev's table.

So how might electronegativity and valence be explained in the light of the wider understanding given by these tables? What was the bond between these elements?

To say it was electrical, the attraction of opposites, of negative toward positive, was a common tentative step along a path that might lead to an answer.

Electrical? What was this stuff called electricity? Since the 1830s some chemists had been prepared to tackle this, at a time when many scientists refused to believe in this nonsense about matter being made of invisible particles. If you cannot see it, weight it, record its charge, then just think about it. Do some thought experiments whilst ignoring the derision of empiricists. Richard Laming was one such thinker; a surgeon, philosopher, inventor and industrial chemist, working in Britain and France. Somehow he found time to develop a mental model of the structure of the atom that proved, eventually, much like the real thing. He was not, however, encumbered any experimental work of his own on the subject.

If there is a unit of charge, could not this unit be represented as a particle? Something like an atom, but presumably smaller so that one atom could have more than one of these units associated with it? Nobody believed Laming – he provided neither data nor equations. So he took up work inventing processes for the coal-gas industry. The story of the discovery of electrons, and understanding their deepest of meanings is complex and continues today at the furthest frontiers of quantum physics. A little of that story is told in Chapters 5 and 6.



It is timely to re-introduce lithium to our story. This element has just three electrons, arranged around the central nucleus in two distant layers called shells. The innermost shell can only accommodate two electrons and is full. The next outer second shell can accommodate eight electrons but has just one electron in lithium. Contrasting strongly with lithium is another simple element found by moving rightwards across the first irregular row at the top of the periodic table. It is fluorine, a noxious gas. Fluorine has its outermost shell occupied by seven electrons. This element has an overwhelming need to complete its outer shell to eight electrons. It will ferociously scavenge that extra electron from almost anywhere. In taking up this one electron, an atom of fluorine itself becomes what is known as reduced. It thereby goes into an energetically more favorable condition as an ion, gaining a negative charge from the extra negative electron.

An atom of lithium has one electron to spare, and if it can get rid of it then the lithium itself becomes what is known as oxidized. It also goes into an atomic arrangement that is energetically more favorable, as a positively charged ion. For every reduction there has to be an oxidation; this essential combined action is known as a redox reaction. Thus lithium fluoride is a chemical compound held tight by the bond between the negative and the positive ion. Similar in some ways to table salt, lithium fluoride is also useful in making glass highly transparent to ultra-violet light for optical instruments.

Fluorine is the most electronegative element. Conversely lithium is belongs to the group of metals of lowest electronegativity that includes sodium and potassium. The property of electronegativity, when seen tabulated on a scale finalized in 1932

by Linus Pauling, at the California Institute of Technology, does not fit exactly into an ordering by atomic weight or the atomic number order of the periodic table. However, the important general rule for extracting power from batteries is that the more the contrasting ions are apart from each other on that scale the greater the stored energy that can be delivered as electricity. The stark problem for a battery technologist is that closer they are to the ends of this scale, the more reactive they are.

Gilbert N. Lewis, a physical chemist then working at the Massachusetts Institute of Technology, developed a simple graphical representation of electron shells into a theory of how atoms bond together. The fluorine and lithium share one electron between them to become that white powder. The electron is not fussy who it associates with. Electrons are fundamentally independent, hence their readiness to move along a metal wire or fly through the vacuum of a cathode ray tube.

Despite its continuing simple usefulness, Lewis's scheme did not survive the deeper understanding of atomic structure and bonding relationships that became known as quantum dynamics. The most important development for this story is the contribution of Erwin Schrödinger. Most of the early researchers on quantum theory were lively characters, none more so than Schrödinger, and the stories of his extraordinary life, battles and loves have been told often. Schrödinger's struggles mostly concerned his determination to deal with these corpuscular electrons, these sub-atomic particles, as waves. Not as if they were waves, but the real thing, energy waves if you like, and certainly nothing like hard balls of planets orbiting round their sun.

For each electron around the nucleus of each element Schrödinger proposed a unique combination of characters called the wavefunction of the electron. It can be used to work out the chance of an electron being in a particular position. Of greatest importance for this story is how calculation of wavefunctions increases understanding of how atoms and molecules arrange themselves naturally into configurations that have the least energy, thus the most stable and the least likely to change into something else as energy is released from them. The Schrödinger equations became crucial in quantifying what happens when atoms and molecules interact. Not only did the theory prove useful to chemists; when Clinton Davisson and George Thomson simultaneously but independently demonstrated by experiment the wave nature of electrons, then Schrödinger's determination to invent purely mathematical ideas of electrons as waves was vindicated.

Further understanding by physicists of the structure of atoms with their protons and the existence of electrons, followed by the understanding of quantum levels of energy of electrons, permitted understanding of fields of energy in relation to discrete particles. The concept of a field of energy could be visualized as the lines of force between a positive charge of a proton or group of protons in an atomic nucleus, and a separate negative charge of an electron. The lines of force go outward from the positive particle and inwards toward the negative particle. This is fundamental and spontaneous, without any external energy or force applied. A battery producing a flow of electricity through the conducting wires connected to a

workload, the filament in a torch bulb, will have a field of energy around the wire. The energy is expressed as the spontaneous flow of electrons in the direction of an ordered state of energy to a less ordered state.

Starting from the negative electrode, made of a metal that has negative electrons easily available because they are not tightly held by the positive nucleus, then those electrons will flow toward a metal in the positive electrode that is in an ionic state because it is combined with other atoms. That ionic state is attractive to the electrons because its electrons are more tightly bound by the nucleus than in the metal of the negative electrode and it easy for the energetic electrons from the negative electrode to combine with those ions. This is the process of chemical reduction. It only works in a battery if there is a flow of positive ions that balances the flow of negative electrons, and that flow is almost instantaneous.

Electric automobiles

For this this story we now need to bypass the countless innovative improvements in existing battery types, and the invention of completely new ones. To reach the point where the long recognized potential of lithium for use in batteries was realized in working systems requires a leap over this maze. Not a leap into thin air however, let me use a slender account of how understanding the role of energy in human affairs changed during the early to mid 1900s to bridge the void. The stories of three researchers will suffice as examples.

With the formulation of the three laws of thermodynamics, followed by the concept of free energy, the intellectual tools became available to consider the wider implications of these laws for human society and industry. Frederick Soddy, the discoverer of isotopes, who we will meet again in Chapter 5, used his fame and fortune as a Nobel laureate to widen his interests as far as the social economics of energy. Soddy protested against the ultimate futility of trying to maintain continuous growth of tangible, real, wealth within the finite system of our Earth. Such growth is exponential, whilst energy, as the fundamental resource for all living things, comes almost entirely from the fixed influx of solar radiation.

A petroleum geologist working for the Shell company in Texas in the 1940s to 60s, then for the United States Geological Survey, came to the related conclusion that continuous growth of tangible wealth can be only a transient phase in human history. Either stability is achieved, following a logistic curve, or collapse ensues. He was M. King Hubbert, and like Soddy understood that the first industrial revolution was powered first by wood and charcoal. When they became too expensive the more energy-dense fossil sources of carbon were substituted because they were economically advantageous. As fossils, these latter fuels are obviously finite in amount. The date of such a peak will not be known until after the event, but before that happens the question for scientists and technologists is obvious: what can we provide in anticipation?

Charles D. Keeling worked in the astronomical observatory atop Mauna Loa, the massive volcano of Hawaii. He had been measuring the concentration of carbon dioxide in the atmosphere at several sites since 1958 using an instrument he had designed as a doctoral student at the California Institute of Technology. (Measurements taken on a volcano are adjusted for any outgassing from the volcano.) His work at the observatory started as a part of the International Geophysical Year, under the sponsorship of Roger R.D. Revelle, the Director of the Scripps Institute of Oceanography. Revelle had recently published a paper suggesting that the oceans had a more limited capacity to absorb additional carbon dioxide than previously thought. In 1958 Keeling found 310 parts per million of carbon dioxide; the records rose by four parts per million in the brief period of his initial study and continue rising at an increasing rate to this day. Keeling attributed the rise to our burning of fossil fuels.

Many chemists read and understood the writing on the wall about carbon dioxide and incoming solar radiation. Some of them were in a position to act. They dusted down their electrochemistry textbooks and files of old patents and asked: can we make ourselves useful whilst making some money out this interesting problem? Can we invent a better battery?



A while ago, the Ford Motor Company tested a small delivery vehicle, the EcoStar. It was powered by a battery both simple and alarming. The battery had a negative electrode of sodium and a positive electrode of sulfur. A potent combination, the more so when the battery was brought to its operating temperature of above 300°C. In preparing the battery for use, by the time the temperature was above 115°, both electrode elements melted, thus could potentially react together with awe inspiring vigor. To extract an electric current from this combination whilst preventing a minor catastrophe a combined electrolyte and separator was needed. Inertness was essential, without a trace of water, but the separator had to permit one or other of the ions of these electrodes to pass through, without the atomic forms interacting.

The separator material was one of the oxides of aluminum, beta-alumina. It was formed, as a ceramic, into a thin close-ended tube to contain the molten sodium and separate it from the molten sulfur. The special property of this oxide of aluminum is that it will allow ions of sodium to pass but not the full metallic form of sodium. This potential means of harnessing to the same vehicle two such wild horses of the periodic table was described in paper published by Yu Yao, an employee of the Ford company, in 1967. However, the electric vehicle did not appear on the test circuits until 1992 and despite the efforts of several other companies in America, Europe and Japan the sodium—sulfur battery was consigned to specialty uses such as back-up storage in electricity distribution systems.

Behind the decision of a major automobile manufacturer to develop a line of battery powered vehicles is a rationale full of contradictions. It is driven by fear of suffering the same fate as those manufacturers of mechanical cash registers and typewriters who failed to adapt to the electronics revolution. A major problem is

persuading customers to buy these new autos, with their high show-room price as the first in a series of disincentives. The manufacturers suffer from technological lock-in, or asset-inertia. The character of a manufacturer becomes dependent on the historical path it has followed as a result of many short-term and a few strategic decisions; path dependence in the jargon of social economists. Automobile manufacturers are in lock-step with their customers in a macabre dance, a loop endlessly repeating. Cheap autos running on plentiful cheap gas enable suburbs of desirable housing to spread further and further from the workplace, requiring more cheap autos running on cheap gas. How to break out of this squirrel cage to avoid commercial annihilation once gas becomes scarce?

During the early stages of their battery development, the Ford company asked a solid-state physicist to referee a project proposal for development of these batteries. John B. Goodenough thus became intrigued by the challenge posed by such electrical potential to be plucked from extreme chemistry. Goodenough did his early research first at the University of Chicago then at the Lincoln Laboratory of the Massachusetts Institute of Technology, financed by the US Army, Navy and Airforce, and later the Defense Advanced Projects Agency. He produced during the 1950s a steady flow of papers on mineral crystals: their molecular structure, magnetic properties and relations with ions. The crystal known as spinel is typical and is composed of magnesium aluminum oxide. Spinel of other types are often beautifully colored with translucent red, blue or green; some are highly valued gemstones. For a physicist, and possibly a defense agency, these were fascinating for their unexplored lattice structures, the role of valence electrons, ion interactions, and bonding energies, all in relation to determining their magnetic properties.

Meanwhile the lure of lithium had led to the first commercially available battery using lithium as an electrode. Nobuo Watanabe and Masataro Fukuda developed it whilst working for Matsushita Electrical Industries (now Panasonic Corporation) in Japan. The company first applied it to fishing baits and similar specialist applications. Not only did the inventors dare use metallic lithium for the negative electrode but the positive electrode contained fluorine. This frighteningly potent combination was only kept in check by having the fluorine in combination with a special form of carbon, and these two electrodes separated by what they described in the patent, with routine evasiveness, as simply a non-aqueous electrolyte. Clearly this electrolyte was the secret of their success. Patents are to make legally binding your claim on priority, not inform competitors how they can copy your secrets.

Non-aqueous electrolyte with a lithium electrode was a concept dating from 1913. Gilbert Lewis had published a pair of papers describing his experiments on potassium and lithium as electrodes. Using the organic solvent propylamine, he demonstrated the energetic potential of lithium as an electrode was higher than either potassium or sodium, despite expectation of the opposite from their relative positions on the scale of electronegativity. Lewis did not explain in any detail what was happening between his lithium and electrolyte and still by the time of Watanabe's battery there was insufficient understanding of exactly what chemical

reactions were occurring in these cells. Nevertheless, this new, non-rechargeable lithium battery for ordinary commercial sale was the fulfillment of many of the dreams of inventors stretching back 80 years. Flung open were the doors to a new age of commercial lithium batteries because they did what the customers wanted: small, neat as a button, much longer lasting than any competitor, they were and remain ideal for powering watches, calculators, and medical devices.

From the Matsushita patent can be traced back references to patents in the early 1890s proposing the use of metals of low electronegativity as electrodes, including lithium. By the 1950s, these inventions and their patents were gathering pace in specific attempts to serve the market for powering small transistorized electronic devices. Small powerful batteries were needed. Researchers proposed crystal lattices that would conduct electric current by migration of ions. Moreover, they could modify the conductivity of such a barrier between the electrodes by introduced defects in the lattice structure of the crystal. The positive electrode could be of oxygen, or even fluorine. It would need to be contained within an absorptive and electrically conductive material, the ideal being finely particulate carbon, or soot in other words. Chemists in the 1960s were proposing the use of non-aqueous electrolytes, that is, a variety of organic solvents. The negative electrode could be lithium and that should be a spongy mass with a large surface area achieved by forming it into spheres of a fraction of a millimeter in diameter. The positive electrode would be sulfur or a halogen such as iodine.

By the time Watanabe and Fukuda were applying for their patent in 1968, inventors in America were testing equally challenging combinations of lithium metal for the negative electrode. For the positive electrode there would be the acid hydrogen fluoride, to be restrained from its extreme corrosiveness by combination with a multivalent metal such as iron or manganese. To contain this alarming mixture the new super-inert plastic Teflon was proposed. Such invention and innovation continued and soon there was a wide variety of batteries of this type, supplying the massively expanding market for batteries of low current, long life and small size. They remain with us, but their limitations were stark: typically they are non-rechargeable and small. In an electric delivery van the driver's wristwatch may be powered by a lithium button cell invented in 1980, but the power to move the van could be a lead—acid battery, invented in 1859.

Remaining unmet was strong demand for a rechargeable battery that was compact enough for ordinary electronic devices or could be combined in a pack to power a road vehicle. Again, people's urge to speak to each other was the pull from customers along the path leading to the required battery. Communication satellites need battery power; their solar panels cannot provide electricity during the regular shading of the satellite by Earth. High reliability was essential but ordinary considerations for a consumer product did not apply. The original answer was the nickel—cadmium battery, invented back in 1899, but needed was something capable of very many cycles of discharge / recharge, and preferable a little more power.

Researchers had to invent an alternative, through an intensive program with substantial military funding. They designed the nickel—hydrogen battery specifically for use in space, with a positive electrode of nickel hydroxide and a negative electrode of hydrogen adsorbed onto platinum. The metal host for the hydrogen is formed into a black powder with a very high surface area for its weight. The electrolyte is potassium hydroxide in concentrated aqueous solution that allows hydrogen ions to move back and forth in the redox reactions of discharge under a workload and recharging from the solar panel electricity. The US Navy rocketed into orbit the first satellite to use this type of battery in 1977.

As that design concept emerged, researchers saw in it such potential that various groups started adapting it to batteries for ordinary customers. The newcomer was the nickel—metal hydride battery. The positive electrode was again nickel hydroxide and the negative electrode hydrogen. This time the hydrogen was inserted within the interstices of a complex mixture of metals known as an intermetal.

These metals were not in the form of a true alloy where the elements are thoroughly mixed into a homogenous solid of new properties. Instead, an intermetal consists of a mixture of metals that retain many of their own crystalline and surface characteristics together with a highly porous structure at a sub-microscopic level. The earliest intermetal used for this consisted of lanthanum and nickel. Now they are complex mixtures of additional metals in the lanthanoid group of the periodic table, typically with nickel and similar metals such as cobalt. Hydrogen forms a minutely thin layer on the inner surfaces of this intermetal to produce a new chemical combination called a metal hydride; the hydrogen is adsorbed onto the metal. The electrolyte is the same as in the nickel—hydrogen battery and the electrochemical reactions are basically the same. Hydrogen ions swing back and forth from discharge to recharge; tennis balls the size of protons whacked from one side of the court to the other.

Despite the success of that type of battery, something better was sought. A battery that did not lose a significant amount of its charge each day just by sitting there unused, a battery packing a denser concentration of electrical energy to send the automobile on its way for a worthwhile number of miles, just by itself. There is a dual connection between that route and the route to the lithium ion battery. There was the concept of one type of ion swinging or rocking back and forth between the electrodes. That had to be paired with the concept of restraining the destructive power of such ions within structures having highly specialized physical and chemical properties. A row of gates for horses and jockeys who waited at the starting line of a racing track for the marshal to complete the electrical circuit releasing the gates. These concepts were thick in the air by the 1970's, the inventive side of the imaginations of researchers became fired up by the lure of profits from better batteries pulling from the market, combined with the knowledge of impending energy crises pushing from the suppliers of new techniques.

A summer school was held in Italy in 1972 to discuss emerging understandings of batteries of the type known as solid-state. That is, those having an electrolyte that

was not watery and electrodes of special physical and chemical characteristics. Such characteristics would be favorable for the movement in the battery under conditions of discharge and recharge of ions that are described as fast. Hydrogen ion was the obvious example: small, fast and reactive. Sodium ion was another obvious one, and maybe even lithium ion could be included in the proceedings. The North Atlantic Treaty Organization sponsored the school; military demand for mobile electrical power will never be sated. One of the organizers was Brian C.H. Steele, from Imperial College, London. He also contributed a paper simply titled 'Chemical Diffusion'. He wrote about the constituent atoms or ions in a battery spending only a short time on any one crystal lattice site before being thermally agitated onto a neighboring site in a 'random walk'. What a casual phrase: wandering home through the park on the way home from a bar? Although the image of a drunk is often used in the huge literature on the random walk, it belies the enormity of the concept and the progress in understanding since the days of John Dalton and his life-long efforts to persuade his peers of the reality of atoms. The statistical treatment of what could happen to atoms randomly jiggling about was one of the origins of quantum theory. For thinking about better batteries, it was the potential of fast ions to move readily, but controllably, through containing molecular frameworks, or skeletons, which caught the attention of many at that conference.

At the Bell Telephone Laboratories, Murray Hill, New Jersey there was a team working on new materials for use as electrodes. These would act as a structure into which smaller things could be interleaved; like a college textbook of many well thumbed pages, full of stick-it notes, old lottery tickets. The students who put these items there, if they were studying chemistry or physics, might have called these placements intercalations. A biology student might describe them as interstitial. A chemical structure comprised of metals, salts and oxides of metals in molecular layers, may be described as an intercalation compound. It permits much smaller bodies such as hydrogen molecules or ions to slip into the interstices of the complex compound; into gaps and holes within the layered or crystalline structure. Carbon in the form of graphite is naturally layered; it readily admits various other bodies, as guests welcomed by a host.

At Bell Labs a team led by John Broadhead took out patents based on experiments to test the idea of intercalating the material for a positive electrode, or what they called the electrochemically active species, into a layered host material with the important additional characteristic of being conductive to electricity. The active material of the positive electrode would be iodine or sulfur and the negative electrode would be lithium. The electrolyte had to be non-aqueous. The host for the iodine or sulfur would be a material known generally as a dichalcogenide.

The group of elements over on the right side of the periodic table are chalcogens: going down the row of group 16 are oxygen, sulfur, selenium, tellurium. The first two are non-metals and do not conduct electricity, the latter two have some characteristics of metals and are semi-conductors. A dichalcogenide would be a combination such as niobium, a metal that forms beautiful golden crystals, and selenium in loose combination. Disappointingly, this material proved to be a

mediocre host for intercalation of the electrode material. In tests it formed a mixture of uncertain structure rather than the hoped-for layers; the stack of shelves in a well stocked larder that they needed to make a new battery more powerful than all those already on the market.

Such layered structures had been for some time a popular subject for studying superconductivity, or the ability of some substances when extremely cold to conduct electrical current without resistance. The commercial incentive was obvious, especially for any material that could be a superconductor at what the insiders called high temperatures, and an ordinary outsider would recognize as the sort of temperature used in liquid nitrogen tanks to medical samples.

At the Synvar Research Institute, Palo Alto, California was Fred Gamble, with a varied team, working on dichalcogenides that were layered and could accept organic molecules as hosts. These could possibly be superconductors and Synvar had been established to research and develop these and similar materials. They were crystalline in structure, with metal layers separated by the organic material; the thickness of both layers was less than one nanometer. (There are one million of these tiny measures in one small but easily visible millimeter). Gamble and his colleagues wanted to study the behavior of electrons that were constrained by such structures to move in the two dimensions between these layers. Tantalum disulfide for example, as the dichalcogenide host, and pyridine as the intercalated guest. Guest seems an incongruous word to use for pyridine, that utterly foul smelling reagent and hazard in many labs, but chemical terminology is complicated enough already. Such new properties were seen then as possibly including answers to the question of how could highly reactive electrode materials be constrained to work as conduits of energy in a battery rather than become engulfed in flame.

This was one of the many strands of research that would lead to what is now called nanotechnology. When chemicals are in physical forms best measured in nanometers they acquire characteristics unknown to the ordinary bench-top scale of traditional chemistry. An example we are all familiar with is revealed with oil, a light oil such as diesel will do. In a glass beaker it is transparent and nearly colorless. Spill a drop from the nozzle of a fuel pump onto a puddle of water on a sunny day and instantly a kaleidoscope of vivid colors appears. As the film of oil thins out into the nano-scale, partial reflections of the sunlight are formed; the film becomes iridescent. Quantum electrodynamics can, with difficulty, explain such a commonplace thing. Nothing else can.

Gamble continued his work at Stanford University, where there was strong team led by Robert A. Huggins on the chemistry of ion transport in various solid substances. They were joined in 1968 by M. Stanley Whittingham, fresh from undergraduate and doctoral studies at the University of Oxford where he had been exposed to the ideas of Peter G. Dickens on the use of complex metallic mixtures as potential new electrodes. A good start: Whittingham was soon at that summer school in Italy, to present a detailed paper on techniques to record experiments on solid state batteries.

A seminal experience for all involved, with a swirl of ideas in a confusion of hypotheses being pushed way beyond existing understanding and established theory. The nascent field had practical applications wider than batteries: fuel cells, sensors, timers, ion pumps, capacitors, memory devices, and so on. After a few years in this heady academic atmosphere Whittingham was in a position to get not only what academics call a proper job, but a job with wide vistas of practical opportunity. He went to Exxon Research and Engineering Company, in Linden, New Jersey, to start a program on alternative energy production and storage.

Titanium was another likely metal to use in a dichalcogenide host and Whittingham tried it with sulfur, as titanium disulfide. This has a crystalline structure that forms in layers, or a lattice of molecules. These can act as the host for lithium because the van der Waals forces between the layers are slight, even for this weak force. Lithium was supplied as the negative electrode in the form of the metal in a flat plate and as ions in a non-aqueous electrolyte of lithium perchlorate dissolved in an organic solvent. On discharge of electricity to a workload through the external circuit, lithium ions traversed the cell to the positive electrode of titanium disulfide, balancing the flow of electrons in the opposite direction. During discharge, lithium ions were inserted between the layers of the titanium disulfide whilst they were removed from the plate of lithium metal. This gave a powerful cell and soon large batteries of them were being demonstrated at commercial auto shows as a tentative way to power electric vehicles.

Thus Stanley Whittingham invented the first rechargeable lithium ion battery, patented in 1977 and assigned to Exxon. As a demonstration of the potential of the intercalation concept for taming this wild element lithium, it was a huge success. As a useful battery, it failed because of problems observed under an electron microscope. The titanium disulfide behaved itself ideally, with negligible deformation of its structure whilst acting as host to lithium ions. Then during recharging, to return the lithium from its interstitial hideaway between the layers of titanium disulfide back onto the plate of lithium metal, some of the lithium was deposited as feathery protrusions into the electrolyte. Since these electrodes in a real battery, in contrast to a textbook diagram, need to be intimately close to each other to reduce internal resistance through the electrolyte, short circuits occurred. That is severely harmful to any battery, and a danger to users for a battery containing flammable lithium. At the very least this problem reduced the number of discharge / recharge cycles for the battery.

Other firms were interested in electrochemical energy. Tellingly, oil companies were already interested in such energy by the 1970s and now many of them have investments in various alternatives to oil, including batteries. It is easy and popular to demonize oil companies as not just obvious polluters of the oceans but as deniers of anthropogenic global warming, as anti-competitive restrictors of electric automobiles, and so on. Some of this is true, the rest is conspiracy theory. Large and complex organizations like to cultivate an appearance of inscrutable order and calm, often concealing anarchistic factions each with their own conflicting objectives. What is well documented fact is that in 1972 a part of a major oil company paid for and physically supported successful research that rapidly pointed

out a plausible route to the lithium ion rechargeable battery of the type in your portable telephone and computer, and possibly in your automobile. Moreover, Whittingham and his team frequently published, at that time and as always, in the major academic journals of electrochemistry and solid-state physics.

The late 1970s saw John Goodenough taking up the post of head of the Department of Inorganic Chemistry in the University of Oxford; the department where Stanley Whittingham learnt his art with Peter Dickens. Researchers were spreading the lithium battery field over a broad and competitive front, from America to Japan by way of Europe. Their challenge was to turn the encouraging concept of the lithium ion battery with an intercalated negative electrode, such as the lithium—titanium disulfide battery, into a design that swerved round the flaws of that specific battery and could deliver more concentrated energy. Goodenough diagnosed the double problem of trying to replace the metallic lithium negative electrode in that type of battery with an intercalation host. Doing so, whilst retaining a sulfur containing positive electrode, lowered the voltage too far.

Goodenough suggested to a visiting worker at the Oxford lab, Koichi Mizushima, that an oxide of a metal rather than a sulfide should improve things. Funding was available from the United States Air Force and the European Energy Commission. Soon Mizushima and the team had both lithium cobalt oxide or lithium nickel oxide as new positive electrodes that would give a voltage that truly reflected the electrochemical potential of lithium: four volts from a single cell.

They promptly patented the idea and went looking for industrial partners, first in Europe and America but found it difficult to convince battery manufacturers of the feasibility of scaling up for sale. So Goodenough tried an electronics company. As cell phones became smaller with miniaturized electronics, they became hungrier for power as color screens and internet connectivity were added. What was missing was a battery of sufficient energy concentration that would fit in these devices. The Sony Corporation, Tokyo, appreciated the potential of a single cell that could deliver four volts, even if some of that had to be relinquished by incorporating the lithium at the negative electrode into an intercalation host. The question was, what kind of host to restrain the unruly guest of lithium at the negative electrode?

An answer was already in circulation amongst various researchers. As early as 1973 Michel B. Armand had travelled over the border from his lab in France to that summer school in Italy where he presented a paper on the use of graphite as an intercalation host for batteries of high energy concentration. He showed a simple diagram of the planes of graphite just 0.67 nanometers apart and intercalated between them were thinly stacked molecules of chromium oxide. Between those stacked molecules there could be squeezed, by chemical manipulations, a metal with high activity such as sodium or lithium. They could be electrochemically active there both at room temperature, rather than in a molten state, and be constrained in their ionic form.

At Bell Laboratories John Broadhead and team continued to develop the materials available as a host for lithium at the positive electrode. The combination of

niobium with selenium was encouraging and Donald Murphy patented a battery system using 90% of niobium triselenide as the intercalation host for the positive electrode, with lithium metal as the negative electrode. This was an improvement on the system using titanium sulfide as the host for the positive electrode, but the problems of naked lithium metal in a battery any bigger than a button cell remained. How to contain lithium was the insistent question to which some unconventional thinking, or at the very least a compromise with commercial reality, was needed. Why not have an intercalation host at both electrodes; would that still provide sufficiently high voltage from a single cell to be attractive to a battery manufacturer? The concept of a lithium ion battery using swinging ions, as in the nickel—metal hydride battery, was in the air in the late 1970s.

Try it and see was an obvious approach – heuristic research. By 1983, from the Bell Labs, Samar Basu patented a battery with the niobium selenide as positive electrode host and carbon as the negative electrode host. Both would accept lithium ions, and lithium ions were present as a salt of lithium dissolved in an organic solvent. The lithium ions would be drawn from the carbon negative electrode across to the niobium selenide positive electrode as soon as the external circuit of the battery was switched on and discharged to a load. Using external energy as electrons pumped back into the system on recharge would gather the lithium ions back into their carbon host as the negative electrode. It was the first lithium ion rechargeable battery with both electrodes of the intercalation host type and in which the lithium ions swung back and forth between these hosts on discharge and charge.

That was the theory and the laboratory demonstration, but the concept was reduced to commercial practice elsewhere. By 1991, the Sony Corporation were in position to launch into the market for cell phone batteries, a lithium ion battery with a positive electrode of lithium cobalt dioxide and a negative electrode of lithium carbon. Kazunori Ozawa and T. Nagaura described this system in the early 1990s.



The route to this battery was long, faltering, meandering through dismal sloughs and up dead-end tracks. The journey continues. Something less toxic and expensive than cobalt is sought for a lithium ion battery. Iron phosphate was a substitute already incorporating within commercially available lithium ion batteries in the first decade of the 2000s; cheaper, safer and likely to be just as effective, but that is a story in the making. Lithium itself will remain not only chemically difficult to control, but its supply could become embroiled in geopolitical problems resembling those around oil. The more so if a large proportion of the global reserve is destined for transmutation into other elements in fusion power reactors, as described in Chapter 6. Notwithstanding all this unfinished business, the second dawn of the battery electric automobile is looking a lot brighter than the first one a hundred years ago.

To battery chemistry came an entire new cohort of researchers from these diverse fields. The understanding was there at last, the commercial demand had been

obvious for a century, and was growing urgent with the changing economics and politics of energy resources. Within twenty five years of that first lithium battery for use in illuminated fishing floats came the battery pack of lithium ion cells powerful enough to send a fashionable, if expensive, brand of entirely electric sports car, the Tesla, whizzing along Californian highways.



Alessandro Volta invented, with almost no precedent, the battery as a tool to answer a specific question of pure science. Why it worked he misunderstood, as did all of the many chemists and physicists who within a few decades realized the extraordinary potential of this tool. Of equally great importance in the development of technology was the improvement, by means of trial and error, of Volta's original design, resulting in a range of battery types. These were adequate to the modest technical needs of the devices they powered, particularly in the case of telegraphs.

The response of technologist inventors was rapidly effective and soon a huge industry of battery manufacture was generated. The cash flowed in and successful innovative searching for the better battery kept it flowing. The fact that the chemistry of these batteries was a mystery was little impediment to pragmatic industry. Moreover, many applications of batteries did not require portability, and in the cases where high current or long operation was required the solution was simple: connect them series or in parallel as bigger packs.

The mystery of effectively operating batteries is astonishing seen looking backwards: the periodic table, electrons, atoms and free energy were unknown to early battery scientists and technologists alike. These batteries were the epitome of heuristic invention and innovation. Don't ask us why it works, we know enough to formulate laws of its behavior for practical industry. Just tinker and test, imagine and innovate; all the while keep the cash flowing by selling more of the improved results.

The scientists who started with the battery as the best experimental tool they had seen were rewarded with a cornucopia of discoveries. Steady reliable electric current enabled the invention of the dynamo and the electric motor. With the electric motor suddenly the demand for portability of both the battery and passengers could possibly be met. Even before the rechargeable battery was invented, business minded innovators were experimenting with non-rechargeable batteries to power vehicles. The lead—acid battery had a brief period of glory as a means of powering passenger automobiles and without the biological and geological happenstance of easily available petroleum oil it could have been the main link with today's vehicles, rather than a slender branch to a few urban delivery vehicles.

Even when commercial realization of the limits of oil for powering vehicles eventually dawned, the lead—acid battery remained the main option for powering experimental vehicles. Researchers came to know that there were higher densities of energy to be delivered from other electrodes than forms of lead, but no one knew

how to tame the more electrically active elements or use combinations of elements as electrodes with the power represented by a large span across the periodic table. Lithium was the jewel in the jaws of the dragon of the periodic table: how could it be snatched away safely?

Inventors tried lithium and tried again, for an entire generation. One of the earliest patents proposing use of lithium as electrode for a battery was granted in 1896. Not until 1970 was there a patent for a battery with a lithium electrode that resulted in it being sold to ordinary customers. Even that was not rechargeable – excellent for wristwatches but what about automobiles? What would it take to harness this enormous chemical potential? The answer was no flash of the light bulb in an inventor's imagination. The answer came in sideways, collaterally, and from many people. A large and diffuse body of knowledge and understanding of how matter is organized and behaves at the atomic and sub-atomic level was borrowed from and adapted to the problem of the lithium battery.

The answer to the problem of taming lithium came from solid-state physics, from crystallography, superconductivity, the fascination of studying gemstones. It came from quantum physics. Not just beautiful crystals from the outside: the deep inner beauty of crystal configurations with their intricate molecular frames and balances of atomic forces was of far greater power to fascinate. From that fascination came a whole new field of understanding of what can happen between atoms and molecules at the level of the space between one plane of a crystal and the next plane. This was a completely new field of science, unknown to ordinary chemistry or physics. The midwife science of small dimensions delivered the technology of the nanometer sized universe.

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[Svant Arrhenius. Often it is claimed he discovered how carbon dioxide traps heat within the atmosphere. Rather, Arrhenius expanded on the ideas of others, whilst fully acknowledging them. Amongst the best known discoverers were the Egyptologist and mathematician Joseph Fourier in France, mountaineering glaciologist and physicist John Tyndall in Britain, and aviation pioneer and physicist Samuel Langley in America. That story is not so simple either: Tyndall showed that the huge amount of water vapor naturally in the atmosphere is the major trap for this heat. Furthermore, Arrhenius came to his conclusions through later studies on ice ages. He postulated the increase in temperature of our atmosphere would prevent another ice-age. Since carbon dioxide is a scarce resource for plants, more of it would stimulate the increased growth of crops necessary to feed a rapidly expanding human population. As a resident of Stockholm, a watery seaside city, Arrhenius might have wished he had made a place in his calculations for water melting off Arctic glaciers.]

[‘Is there not, then, great reason to hope and believe that, by a closer experimental investigation of the principles which govern the development and action of this subtile agent, we shall be able to increase the power of our batteries, or invent new instruments which shall a thousandfold surpass in energy those which we at present possess?’ Faraday 1834, pg. 122.]

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