

Before Li Ion Batteries

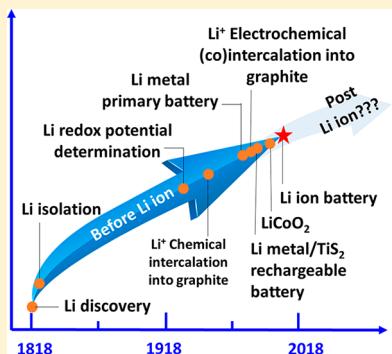
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ABSTRACT: This Review covers a sequence of key discoveries and technical achievements that eventually led to the birth of the lithium-ion battery. In doing so, it not only sheds light on the history with the advantage of contemporary hindsight but also provides insight and inspiration to aid in the ongoing quest for better batteries of the future. A detailed retrospective on ingenious designs, accidental discoveries, intentional breakthroughs, and deceiving misconceptions is given: from the discovery of the element lithium to its electrochemical synthesis; from intercalation host material development to the concept of dual-intercalation electrodes; and from the misunderstanding of intercalation behavior into graphite to the comprehension of interphases. The onerous demands of bringing all critical components (anode, cathode, electrolyte, solid-electrolyte interphases), each of which possess unique chemistries, into a sophisticated electrochemical device reveal that the challenge of interfacing these originally incongruent components often outweighs the individual merits and limits in their own properties. These important lessons are likely to remain true for the more aggressive battery chemistries of future generations, ranging from a revisited Li-metal anode, to conversion-reaction type chemistries such as Li/sulfur, Li/oxygen, and metal fluorides, and to bivalent cation intercalations.



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consisting of multiple components. In order for such a system to function, it is critical for all components therein to be electrochemically synchronized. The lengthy history of LIB development witnessed such synchronization, which proceeded simultaneously with the development of intercalation science and materials.

This Review aims to recount the history between the discovery of the Li element in 1817 to the commercialization of LIBs in the 1990s. As taught by Winston Churchill, "The farther back you can look, the farther forward you are likely to see"; such a historical retrospective brings us inspiration and insight into the future. Scrutinizing the historical literature with contemporary hindsight allows us to examine from an advantageous angle how ingenious designs, accidental discoveries, intentional breakthroughs, and deceiving misconceptions interplayed to generate the unique chemistries and materials for such a sophisticated electrochemical device. Such knowledge should help guide us in the quest for future batteries.

In recounting the history, we understood and interpreted the related historical documents from a modern perspective, which might differ from those of the original authors at the time. We have been informed by personal communication about many findings that have not been published. However, in this Review, we mainly relied on open literature, including journal publications, patent disclosures, and news pieces.

1. INTRODUCTION AND SCOPE

As one of the most prominent technologies in human history, Li-ion batteries (LIBs) have significantly reshaped our lives since their initial commercialization in the early 1990s, while continuous improvements in materials and chemistries of their derivative descendants might dictate our energy future.

Unlike many scientific discoveries, LIB was not born at a single "eureka" moment. A battery (or any electrochemical device such as a fuel cell or double layer capacitor) is a system

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2. PRELUDE

It all started with this element: the first metal on the periodic table, lithium (Li). Among all metals, Li has the lowest atomic number (and hence the smallest atomic weight, 6.95) and the lowest density (0.534 g/cm³). Located in the alkali group, Li is also one of the most reactive metals. Although its existence was first identified in 1817 by Johan August Arfwedson in a mineral ore called Petalite and it was reported in January 1818 by Jöns Jakob Berzelius in a letter entitled “Ein neues mineralisches Alkali und ein neues Metall (a new mineral alkaline and a new metal)” (Figure 1) addressed to the editor of *Journal fuer Chemie und Physik*

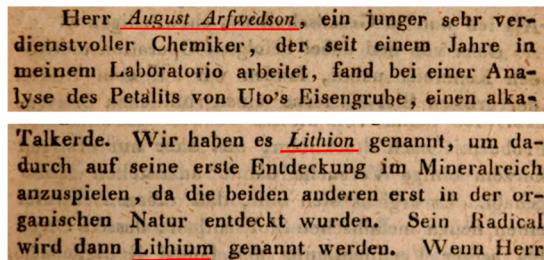


Figure 1. Excerpt from a letter by Jöns Jakob Berzelius dated January 27, 1818, to the editor of *Journal fuer Chemie und Physik*, in which he reported the discovery of a new alkali by Johan August Arfwedson. Because this species was first found in a mineral ore known as Petalite ($\text{LiAlSi}_4\text{O}_{10}$), Berzelius named it “Lithion” after the Greek word “lithos (stone)”, and the corresponding element lithium. This is believed to be the very first time that the word “lithium” was made known to the public. Image reproduced from *Journal fuer Chemie und Physik* (ref 1).

Physikalische Chemie,¹ the isolation of its elemental form proved to be especially difficult because of its reactivity. Among the numerous attempts,^{2–6} Sir Humphry Davy seemed to succeed when he applied a voltaic pile to fused lithium carbonate and caught transient glimpses of “bright scintillations” on a platinum electrode.^{2,3} However, it was William Thomas Brande who is generally credited for successful isolation of elemental Li; he obviously obtained a sufficient amount of the metal, as he described in 1821 the observation of “a shining, white, combustible metal” when a voltaic pile was applied to molten lithium oxide.⁷ Thus, from its very first days, Li was associated with electrochemistry. It took much longer for its electrochemical power to be truly recognized. More than 50 years after the discovery of Li (and more than 60 years after the isolation of Na and K by Sir Humphry Davy),⁸ French science fiction novelist Jules Verne gave Captain Nemo the most advanced battery chemistry known at the time to power his “Masterpiece containing Masterpieces”, the submarine *Nautilus*. Thus, he wrote in *20,000 Leagues Under the Sea*:⁹

“Sodium?”

“Yes sir...sodium must be regarded as the most electromotive element of all...”

It was not until 1913 that Lewis and Keyes realized that Li is more electromotive than any other metal.¹⁰ In that seminal work, they prepared a Li amalgam (Li/Hg intermetallic) and painstakingly measured the relative potentials between Li, its amalgam, and a calomel (Hg_2Cl_2) electrode in a propylamine solution of LiI , from which they accurately derived the Li potential as 3.3042 V vs calomel, or 3.0564 V when translated into the standard hydrogen electrode scale. They declared Li as the electrode material with the “highest electrode potential”. This statement still holds true today, and it sets the foundation

for Li to be the ultimate anode material for all potential batteries.

The energy (E_{cell}) of a battery cell is proportional to both cell voltage (V_{cell}) and capacity (C_{cell}):¹¹ $E = C_{\text{cell}} \times V_{\text{cell}}$ (or $E = \int_a^b V_{\text{cell}} dC_{\text{cell}}$), where V_{cell} is the difference between cathode (positive electrode) and anode (negative electrode) potentials and C_{cell} is matched by both anode (C_a) and cathode (C_c) capacities according to the following relation:

$$\frac{1}{C_{\text{cell}}} = \frac{1}{C_a} + \frac{1}{C_c}$$

The fortuitous combination of a small atomic weight, extremely low reduction potential, and monovalent charge renders Li with such unique qualities that are nearly impossible for other elements or compounds to rival.¹² The oxidation of a unit weight of Li (or reduction of Li^+) must be accompanied by a large number of coulombs, which translates to a high gravimetric capacity (3 860 mAh/g) in battery terminology. However, its volumetric capacity (2 061 Ah/L) is less attractive due to its low density. In comparison, the gravimetric capacity of Li (Figure 2A) is second only to that of Be (5 950 mAh/g), while the volumetric capacity (Figure 2B) is lower than those of Be, Al, Zn, and Mg (10 800, 8 080, 5 550, and 3 600 Ah/L, respectively). Indeed, the multivalent character of those elements offers a significant advantage in terms of capacities, but a corresponding penalty also comes from the multivalence nature: the double or triple charges located on these cations (Be^{2+} , Al^{3+} , Zn^{2+} , and Mg^{2+}) of roughly the same size as Li^+ induce enormous difficulty for them to move in an environment that likes to interact with them. Such interactions of ions with their environment, often known as “solvation”, is ubiquitous in liquid/solid electrolytes or the interstitial channels within electrode lattices or across the heterogeneous interfaces and interphases, and the especially high difficulty in moving multivalent ions is still encountered today in the developments of Al-, Mg-, Ca-, or Zn-batteries.^{13–16}

When applying electrode potential, the advantages of most multivalent cations rapidly vanish, as revealed by the energy densities projected for single metal electrodes if an imaginary 4 V cathode is coupled with these metals (Figure 2C). Beryllium still stands out as the only exception, beating Li in both gravimetric and volumetric energy densities, but its high toxicity, low abundance, and potential radioactivity make it virtually impossible to appear in any devices usable in daily life. For these reasons, Li attains its supremacy in high energy density batteries.

With this supremacy, Li has essentially dominated the efforts to seek higher energy density batteries in the last five decades. Even when Li metal itself was no longer considered as a viable anode for rechargeable batteries, the shadow of its supremacy could still be felt in chemistries based on Li-containing materials, whether in the form of Li intermetallic (Li-alloy) compounds or when Li^+ is used as an intercalant in a host. Among these efforts, the most prominent fruition is undoubtedly the lithium-ion battery (LIB), a battery that has significantly changed our lives in the 21st century.

The quest that led to LIBs has been lengthy and onerous, with accumulated contributions from numerous dedicated researchers. With this Review, we try to commemorate these pioneers and their efforts while drawing important lessons that will continue to help shape development of materials and chemistries for future batteries.

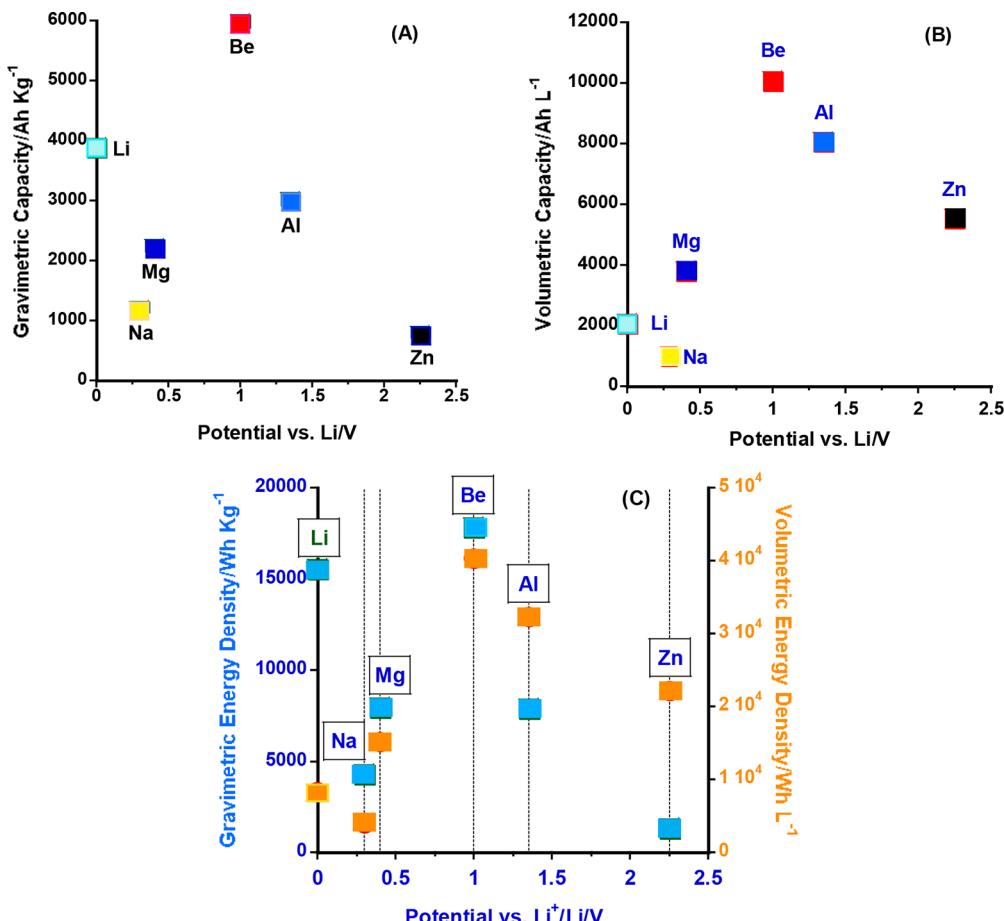


Figure 2. Supremacy of Li as negative electrode (anode). The gravimetric (A) and volumetric (B) capacities of several metal anodes vs their electrode potential (relative to Li/Li⁺), and (C) the projected gravimetric and volumetric energy densities provided by these metal anodes when coupled with an imaginary 4 V cathode.

3. WHY A BATTERY IS COMPLICATED

The sluggish progress in battery chemistries/materials has been often contrasted against the exponential advances in semiconductors and electronics. The latter, blessed by the so-called “Moore’s Law”,¹⁷ have accelerated the rapid miniaturization of consumer electronics since the 1960s, during which the clumsy batteries therein often took the blame for slowing things down. The gap between the two worlds can be best exemplified by the following comical extrapolations (Figure 3a): If we take the first rechargeable lead-acid battery developed by French inventor Gaston Planté in 1860 as the starting point and assume the evolution of its energy density (~1 Wh/kg or 3 600 J/kg) is governed by Moore’s Law, then by 1928 the energy stored in a 1 kg battery would equal the detonation yield of the first atomic bomb (~10¹¹ Wh or ~10¹⁴ J); by 1950, this energy would equal to what could be converted from the battery mass following Einstein’s mass-energy equation $E = MC^2$ (~10¹³ Wh or ~10¹⁶ J). If the trend continues, within a century this number will become truly “astronomical”, as a battery pack used in Tesla semitruck (~3 000 kg) would contain the energy comparable to that released from the explosion of a Type IA Supernova (~10⁴¹ Wh/kg or ~10⁴⁴ J)! In reality, the highest energy density achieved today (2018) remains below 400 Wh/kg or ~10⁶ J/kg, with an average growth rate of merely ~5% per year since 1970 (Figure 3b).

What separates the worlds of battery and electronics is the different mobile species they try to move. While electronics concerns itself with moving only electrons, which are weightless and volumeless and could act like a wave in certain scenarios (therefore, quantum characteristics such as tunneling could be invoked), an electrochemical process is chemical in nature, requiring the movement of comparatively clumsy ionic species with significant mass. Because even the lightest ion (proton) is more massive than an electron by at least 3 orders of magnitude, the motion of all ions is characterized by slower chemical diffusion, without any quantum benefits that electron transport usually enjoys. To further complicate the storage kinetics of batteries, the movement of each ion requires the corresponding movement of its counterion in the electrolyte in order to maintain global charge neutrality. This Coulombic drag does not exist for electron movement. According to analysis by Rolison and Nazar,¹⁸ if the annual performance improvement can be expressed as 1/2ⁿ, where *n* is the number of transport functions, electron movement in an integrated circuit only involves an *n* of 1, representing the doubling of computing performances every 2 years; meanwhile, for the coupled diffusions of electrons, ions, and molecules in a battery, *n* is at least 3, which predicts roughly a 10% improvement per year. In actuality, this number could be $\gg 3$ considering that concerted movements of anions, cations, and solvating molecules are often required.

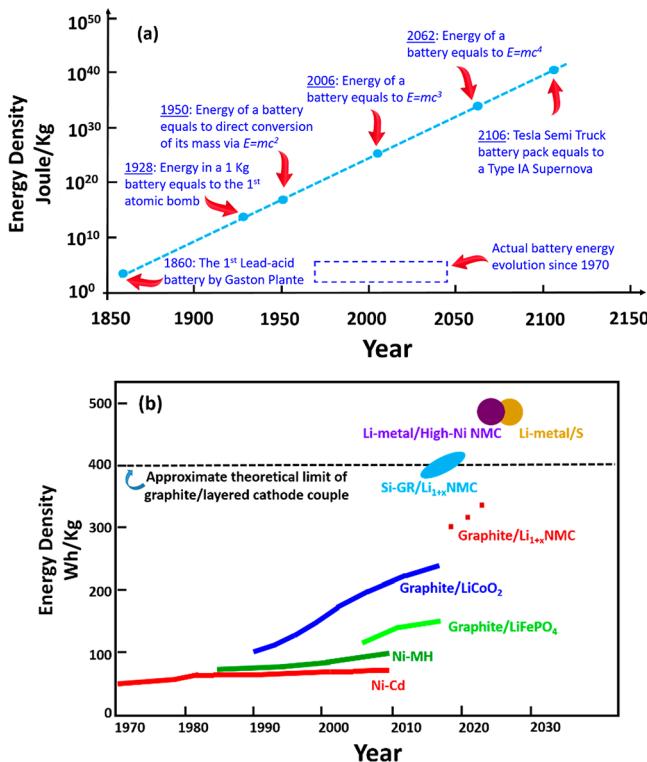


Figure 3. Battery against Moore’s Law: (a) Prediction if energy stored in a battery was governed by Moore’s Law, and (b) the actual evolution of gravimetric energy densities for various battery chemistries. Note that the rectangular shape outlined by blue-dashed line at the bottom of (a) corresponds to (b). The figure is reconstructed based on communications with Dr. Christopher McCoy.

These fundamental differences place battery materials development on a much less glamorous and definitely much more challenging track. Like all electrochemical devices, batteries consist of only four active components: a positive electrode (*cathode*), a negative electrode (*anode*), and an *electrolyte* connecting the electrodes ionically. Such a configuration is deceptively simple, but in reality, the multiple interactions and reactions among these three components, direct or indirect, make the invention of new battery chemistry incredibly difficult and highly fortuitous. A thorough balance has to be executed among these three components, with several key performance metrics (energy and power densities, cycle and calendar lives, efficiency, safety, and cost) being optimized simultaneously through careful design, selection, and integration of them.¹⁹ The presence of “inert” components (separators and electrode substrates and additives) complicates things further, as they are not really inert both chemically and electrochemically. This complexity is best legendized by an aphorism well-circulated within the battery community that “Given the best anode, cathode, separator and electrolyte, one could produce the worst battery by simply putting them together”. After all, less than only two dozen battery systems, primary and rechargeable altogether, have been successfully commercialized since Alessandro Volta put together the very first battery (Volta Pile) more than two centuries ago.

LIB presents no exception. All active and inert components in it, i.e., graphite as anode intercalation host, transition metal oxide or phosphate of various lattice structures as cathode intercalation host, the nonaqueous aprotic electrolytes based

on organic carbonate solvents and Li salts of highly fluorinated anions, and the polyolefin separators rich in high pore volume to accommodate electrolytes, along with the two interfaces between electrolytes and electrodes (solid-electrolyte interphase (SEI) at anode^{20,21} and cathode-electrolyte interphase (CEI) at cathode²²) and their corresponding substrates as current collectors, were the products of numerous achievements in fundamental understanding, materials design and development, and accidental and serendipitous discoveries. In particular, the integration of these individual achievements was the result of long and arduous efforts, which gradually crystallized into a single novel electrochemical device, where these components are interfaced to work with each other, as precisely as in a timepiece.

4. QUEST FOR THE “HOLY GRAIL”

Based on the determination of Li electrode potential by Lewis and Keyes,¹⁰ rechargeable batteries employing a Li metal anode became the Holy Grail. The quest for this “superbattery”²³ experienced numerous upheavals and downfalls and is still ongoing today.

The extreme electrode potential of Li metal suggests extremely high chemical and electrochemical reactivities. In fact, almost nothing could remain thermodynamically inert upon contact with Li metal. Therefore, finding an electrolyte that can work with a Li metal anode or any Li-containing materials with similar electrode potential, such as graphite, silicon, or tin fully loaded with Li⁺, presents the most severe challenge to the efforts of developing a rechargeable Li-based battery. In this consideration, the efforts of seeking a workable anode actually consist of two closely entangled parts: the development of anode materials that operate at potentials similar to Li, and the development of electrolyte materials that can support such anode chemistries with reasonable stability. In retrospect, the stabilization of the graphite anode in carbonate-based electrolytes acted as a bottleneck in the success of LIBs.

While pure Li metal was first obtained by electrolyzing molten Li₂O,⁷ the earliest room-temperature Li-plating was achieved by Laszczyński and Gorski in 1897 using a nonaqueous electrolyte based on LiCl solution in pyridine.²⁴ Due to poor salt solubility and ionic conductivity (10⁻⁶ to 10⁻⁵ S/cm),^{25–27} an astonishingly high cell voltage (from 10 to 100 V) often had to be applied in order to force Li⁺ transport and reduction, and Li deposition occurred in poor quality at very low Coulombic efficiencies (CE%), typically in the range of 20–40%. While such low efficiencies might be acceptable in devices for electrochemical synthesis or electroplating reactions, they are not acceptable for a rechargeable battery to be sustainable because a battery is a closed system, where active materials consumed by parasitic reactions cannot be replenished. Typical Coulombic efficiencies acceptable for batteries must be >99% in order to be meaningful. According to Albertus et al., a 99.98% efficiency is required for a commercially viable Li metal electrode that must experience 1000 cycles.²⁸

Among the early Li-electrodeposition literature, the thesis by Harris published 60 years ago (under the supervision of Tobias) should be regarded as a milestone,²⁹ in which the author comprehensively evaluated nonaqueous electrolytes based on cyclic carbonate esters as solvents, including ethylene carbonate (EC), the so far indispensable solvent used in modern LIBs. He was also the first to realize the different

solvation behaviors between aqueous and nonaqueous electrolytes and predicted that in the latter the cations would be more preferentially solvated than the anion. This difference led to a series of critical properties whose impacts were only understood much later, from bulk (liquid structure, phase diagram), ion transport (ion conductivity, transference number), to interfacial and interphasial properties (interphase formation, charge transfer at interfaces).^{19,30} Although these early efforts were intended for Li metal preparation and isolation rather than using it as electrode material reversibly under electrochemical conditions (hence, CE% therein does not have to be $\gg 99\%$ as required in rechargeable batteries),³¹ they built up a solid knowledge foundation for Li metal/electrolyte compatibility beneficial for the later battery-research efforts. It was during this era that researchers realized that, for better Li-deposition quality (or better stability between Li metal and electrolytes), the nonaqueous solvents and the resulting electrolytes must be not only anhydrous (moisture-free) but also aprotic, which would exclude, for instance, organic amines and alcohols that had been frequently used as nonaqueous solvents. The choice of those aprotic solvents was thus gradually narrowed down to two major classes: alkyl ethers and carbonic/carboxylic esters. Other polar solvents could be sporadically selected from inorganic acid esters, nitriles, sulfones, sulfoxides, etc. However, even today, the majority of nonaqueous electrolytes are still based on these two solvent classes.³⁰ Another less apparent but nonetheless influential fruit from these works is the structure of the salt anion. The low solubility of LiF and LiCl in nonaqueous solvents and the consequently poor ionic conductivities induced high polarization and poor efficiencies and has forced researchers to look for ways of promoting solubility for these electron-rich anions. One effective solution was to add a strong Lewis acid (such as AlCl₃), which forms a complex anion with the halides ([AlCl₃X]⁻, X = Cl, Br, or I).^{29,31} Such complex anions, with much better delocalized charge, offer much higher solubility and electrochemical stability against oxidation and can be viewed as the direct ancestors of tetrafluoroborate (BF₄⁻) or hexafluorophosphate (PF₆⁻). These two anions eventually prevailed as popular choices for soluble and stable lithium salts, with PF₆⁻ being used at the industrial scale in modern LIBs.

The early 1960s witnessed the first wave of enthusiasm in Li-based batteries, mainly driven by governmental and military interest in high energy density storage chemistries; hence, most literature in this era exists in the form of technical reports submitted to government agencies,^{32–36} which all aimed at using a Li metal anode coupled with a transition metal halide as cathode in nonaqueous electrolytes. Needless to say, the performance of these battery systems cannot be anywhere close to being satisfactory, because problems exist all over the cell in each and every component: the morphological instability of Li metal during repeated cycling, the structural irreversibility of the conversion-reaction-type materials MX_n (M = Ag, Cu, Fe, Co, etc.; X = F, Cl), and the reactivity between Li metal and nonaqueous electrolytes, which were mostly based on various lithium halides dissolved in esters. The majority of these works used propylene carbonate (PC) instead of EC as solvent, although both of them have been characterized by Harris.²⁹ This preference of PC over EC apparently comes from the low melting temperature of PC (-48.8°C) as compared with 36.4°C of EC, which hints at an especially narrow liquid range. A hidden assumption underneath this preference, however, is actually the general belief

that PC and EC should be “essentially the same”²⁹ in their electrochemical behaviors given the minute structural difference of a single methyl group. During the several decades after Harris’s work, EC was only occasionally used as cosolvent with PC, apparently helping to decrease viscosity and increase conductivity.³⁴ It only turned out much later that we might have paid a heavy price for this choice of convenience, which could have significantly delayed our understanding about the lithiation chemistry of graphitic materials and the importance of interphases.

Strong evidence supporting the above suspicion can be found in a report submitted by Rao and Hill in 1967, where the authors described their efforts of depositing Li metal from PC solution of LiAlCl₄ on various substrates.³⁷ Among the used different materials was graphite, on which, according to the authors, “no visible deposit of lithium was observed”. Examination of the data reveals that the graphite electrode never reached the Li-deposition potential (-2.80 V vs Ag , or 0 V vs Li); instead, it stays at a plateau of $\sim 0.50\text{ V vs Li}$, followed by essentially zero stripping capacity (Figure 4). This work

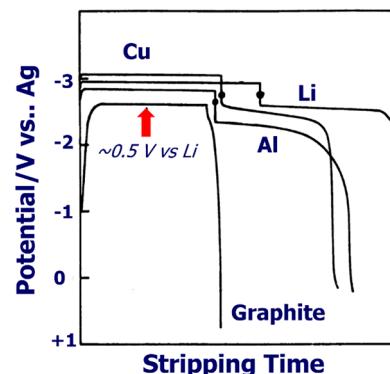


Figure 4. First unconsciously documented graphite exfoliation by PC-based electrolyte, while the researchers attempted to plate and strip Li metal on various substrates using LiAlCl₄ dissolved in PC. Note that the typical exfoliation potential should be $\sim 0.7\text{--}1\text{ V vs Li/Li}^{+}$. The lower potential value demonstrated here might be the consequence of the extra high current (equivalent to C-rates of 10–20) applied on the cell. (Graph adapted from ref 37. Source: 1967 U.S. Army TR no. 2.)

actually represents the very first documented solvent cointercalation and subsequent graphite exfoliation caused by gassing of PC, although the authors were unaware of the chemistry and reaction mechanism underlying their observations. Had an EC-based electrolyte been used instead of PC in this work, the electrochemical Li⁺ intercalation into graphite could have been accomplished at least 20 years earlier!^{38,39} Today, enabled by EC, lithiated graphite (LiC₆) is electrochemically synthesized in each charging cycle of every LIB, which has been recognized as one of the key developments in the history of LIBs, although why the minute structural difference of a single methyl group incurred such significantly distinct interphasial chemistries between EC and PC is still not well understood.^{40–44}

One important concept developed during this period, the solid-electrolyte interphase (SEI), will have long-lasting influence that goes beyond Li metal to virtually any advanced battery systems, as long as their electrodes operate at potentials away from the thermodynamic stability limits of electrolytes. Almost as soon as Li metal was found to be stable in nonaqueous electrolytes, people suspected that a passivation

process was responsible,^{45–49} because the reduction potentials of almost any nonaqueous solvent are far above the potential of Li^0/Li^+ . Dey even proposed that Li_2CO_3 is the composition of such film and that Li^+ will possess a transference number of 1.0 across this film.⁴⁷ It was Peled who formally named it SEI²⁰ and established the basic laws governing SEI properties for Li that nowadays universally hold true far beyond Li metal: (1) it consists of solid products from the reaction between Li metal and electrolytes; (2) it conducts Li^+ ; and (3) it does not in first approximation conduct electrons. It should be noted that most anode materials in aqueous and nonaqueous batteries rely on, at least partially, a protective surface film that allows for the electrochemical reactions but prevents the reactivity versus the electrolyte. The formation mechanisms of and electron/ion transport functions in these films, however, may vary considerably; therefore, the use of the term SEI is not always fully appropriate.²¹

The direct accomplishment from those studies on Li metal behavior in nonaqueous electrolytes is the commercialization of primary (nonrechargeable) Li batteries in the 1970s,^{50–54} some of which are still on the market today for special applications, but the efforts to make Li metal rechargeable was deemed to be herculean: The reactivity of Li metal with liquid electrolytes makes its reuse extremely unsafe, as represented by the sustained loss of Li during each plating/stripping cycle, either in the form of reaction products with electrolytes (SEI) or as “dead Li” that no longer participates in cell reactions but possesses high surface area, hence being extremely reactive chemically. Even for the portion of Li metal that can be recovered, its crystallization often adopts a preferential growth manner due to the uneven nucleation on the Li surface, leading to nanowires known by the name “dendrites”. Tremendous efforts were made to seek the right electrolyte that can prevent dead Li and dendrites.⁵⁵ Ether-based electrolytes, especially those utilizing cyclic derivatives of furans, were considered favorites due to their much more stable nature against reduction,^{56–59} but the poor resistance of ethers against oxidation often sets limitations on their application in cells with high-voltage (>4.0 V) cathode materials, not to mention that dendrites were still inevitable under high rates.⁵⁹

Despite the potential risks associated with the Li metal anode, numerous companies endeavored to commercialize such high-energy systems. Notable among such companies is a Canadian establishment (Moli Energy). Its rechargeable Li metal batteries based on MoS_2 cathode were the first of their kind. Focusing on AA cells, Moli developed a first-generation technology in 1985 and significantly improved its capacity later on. By 1988, they marketed an AA cell with >2 Wh under the brand name Molicel, but these products soon failed following a number of fire incidents in cell phones^{60,61} and a mandated recall of cell phones employing these batteries in Japan. These events marked an end of mainstream efforts at the Holy Grail. The only exception was an effort that continued through the 1980s and eventually led to the commercialization of polymer electrolyte batteries employing Li metal anode and V_2O_5 cathode as backup power systems for telephone exchanges in a small niche market for the stationary storage sector.⁶¹ By using solid polymer electrolytes at elevated operation temperatures ($>60^\circ\text{C}$), where the modulus of Li metal is lower than that of the electrolyte while practically usable ionic conductivities could be enabled, developers managed to control the formation of dendrite to a certain extent.⁶² Nevertheless, safety hazards still happened occasionally.⁶²

Part of this technology survived and continued to operate in a number of electric cars in North America and Europe.^{62–64}

Looking forward by 20 years, 2010 would see the renaissance of the interest in Li metal rechargeable batteries. By that time, LIB technology would have become mature and have been gradually approaching the energy density ceiling allowed by insertion/intercalation/host chemistries. Armed with knowledge of materials design at a nanoscale and tools of atomic resolution and *in situ*/operando capability, researchers restored the quest for the Holy Grail.^{65–69}

5. INTERCALATION BYPASS

Long before the Moli Energy fallout, intercalation hosts had been proposed as electrodes for new concept rechargeable batteries, either as one of the electrodes (mainly the cathode, as in Figure 5a) or as both anode and cathode, which could accommodate either cation or anion (Figure 5b and c). Figure 5b (dual-interaction) represents the fundamental configuration adopted by modern LIBs. Before the name “lithium-ion battery” was officially given to the specific cell design using a carbonaceous anode host,⁷⁰ the general configuration was once

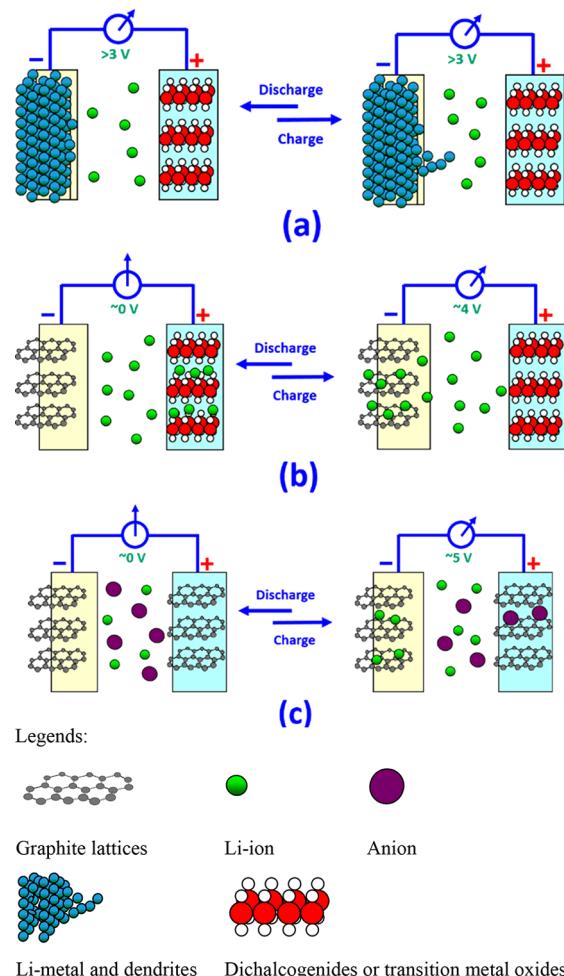


Figure 5. Schematic drawing of a few representative battery configurations: (a) a half intercalation cell where the cathode is an intercalation host for Li^+ but the anode is still Li metal; (b) the basic configuration of modern LIB cells consisting of two intercalation hosts that accommodate Li^+ at different potentials; and (c) a “dual-ion intercalation” battery based on simultaneous cation (Li^+) and anion intercalations into graphite as reported by Read et al.⁷³

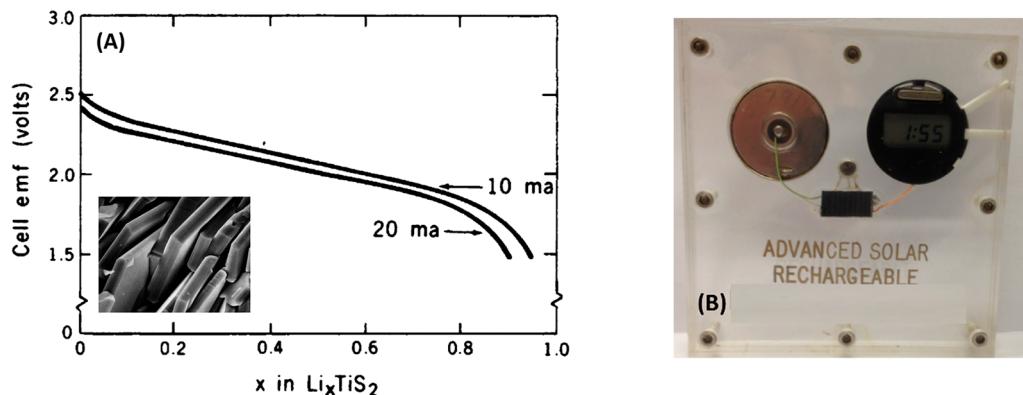


Figure 6. (A) Discharge voltage profiles of cells with LiTiS_2 at different current densities; (inset) scanning electron microscopy (SEM) micrographs of the layer-structured LiTiS_2 . Reproduced with permission from ref 92. Copyright 1976 AAAS. (B) Prototype Li-battery cell based on LiTiS_2 as intercalation cathode powered by a solar cell. Because it still used Li metal anode, the Li dendrite issue inevitably still exists. However, its cycling stability still outperforms the Li–Al/ TiS_2 cell, as in this case the alloy volume change does much more serious damage to the cell-cycling stability than Li dendrite. Reproduced with permission from ref 96. Copyright 2015 Elsevier.

known under different names (ion transfer cells, shuttle-cock batteries, rocking chair batteries, etc.) with various insertion/intercalation hosts.^{71,72} The insertion/intercalation concept eventually transformed both cathode and anode designs from the original conversion-reaction type, but it took a much lengthier and more difficult pathway for the anode than the cathode, because of the reactivity issues between anode and electrolyte, sensitive nature of graphitic anode host to solvent cointercalation and the related interphasial chemistry.

Historically, the intercalation concept stemmed from the host–guest chemistry, which studies supramolecular structures enabled by noncovalent bonding between host and guest species. Such host–guest complexes usually demonstrate new properties differing from the parental species, and the noncovalent nature of their bonding often makes their formation reversible.⁷⁴ The electrochemical extension of the intercalation concept would lead to a cell design in which the host (either anode or cathode) accepts or surrenders a guest (an ion, either positively or negatively charged) upon electrochemical oxidation or reduction (Figure 5b and 5c). The electrode potential is determined by the nature of the interaction between the charged host lattice and the guest ions.⁷⁵ During the entire intercalation or de-intercalation process, the basic lattice structure of the hosts experiences little change (“topotactic”), as opposed to the conversion-reaction-type materials, such as Li metal itself, the metal halide, and sulfur-based cathode materials, that see severe phase and lattice changes in each cycle of charging and discharging accompanied by destruction and reformation of chemical bonding. Whittingham was the first to draw a clear demarcation between the intercalation-reaction and conversion-reaction materials and directly associated the cell reversibility to the minimum structural changes occurring in the host lattice.⁷⁶

Early studies of intercalation focused on highly covalent oxides or sulfides (W, Mo, V, Nb, and Ti), whose corner or edge sharing creates channels for facile mass transport and ion conduction.^{77–84} Treating it as a variant of a symmetrical concentration cell using two identical hosts as described by Hever in 1968,⁸⁵ Armand established an early mathematical model based on intercalation cells with two different hosts,⁷⁵ although at the time it remained unclear which materials serve as ideal hosts. The first actual unsymmetrical intercalation cell that shuttled Li^+ back and forth was demonstrated by Lazzari

and Scrosati.⁸⁶ While confirming the feasibility of the intercalation concept, the high electrode potentials of the anode materials used therein (LiWO_2 , $\text{Li}_6\text{Fe}_2\text{O}_3$) led to low cell voltage and energy density when coupled with transition metal oxides or dichalcogenide cathode materials (TiS_2 , WO_3 , NbS_2 , CrO_x , MoO_3 , and V_2O_5).^{86–88} Thus, the advantage of an intercalation cell is as apparent as its disadvantage: *excellent reversibility* (due to minimum structure change) at the expense of *compromised energy density* (due to the inert mass and volume of host lattice). In the time when the use of a Li metal electrode was still hopeful, such electrode designs were deemed to be unattractive.

The petroleum crisis in the early 1970s promoted enthusiastic activities in seeking new energy-storage technologies, among which the rechargeable battery was recognized as indispensable whether used in conjunction with solar, wind, ocean-wave, or other energy-harvesting systems. With significant interest and investment from petroleum corporations, a series of intercalation materials of layered structures were developed around this time,^{76–84,89–95} with the seminal work of Whittingham standing out. He demonstrated, to the surprise of the community at the time, that transition metal dichalcogenides (TiS_2) can accommodate Li^+ with excellent reversibility at astonishing speed for ionic movement within solids, which is sufficient to support cell reactions of reasonable rates (Figure 6A). In 1977 a team at Exxon adopted aluminum (Al) metal as an anode, which was known to form an alloy with Li at very low potential (0.3–0.4 V vs Li^+/Li , depending on Li uptake in the Al host), and coupled it with Whittingham’s cathode. The resultant Li–Al/ TiS_2 cell could be classified as a Li-ion battery by definition, because there was no pure Li metal in this cell,⁹⁵ although its anode is an alloy host instead of a topotactic host for Li^+ . Like all alloy-type electrodes, an Al-host experiences dramatic volume changes upon accommodating and releasing Li^+ , an issue that still has not been well resolved as of today; hence, we know that such cells would not present impressive cycle life. On the other hand, the half-intercalation cell with LiTiS_2 cathode and Li metal anode showed much better cycling stability, and in 1980 Exxon demonstrated such cells as part of a solar-rechargeable power system (Figure 6B).^{89,90,92} The unusual stability of this rechargeable Li-metal cell is best manifested by the fact that,

after 35-year storage, the cell still worked with more than 50% of its original capacity retained!⁹⁶

Although the electrode potentials of chalcogenides are intrinsically low (~ 2.0 V vs Li/Li⁺), these results inspired numerous efforts pursuing various sulfide-based cathode materials. Meanwhile, Canadian researchers believed that the isostructural MoS₂ should be a superior electrode choice to TiS₂, given that the former is naturally occurring while the synthesis of the latter was sophisticated.^{97–108} With backing from a key player in the molybdenum mining industry, Moli Energy, mentioned earlier, was established to commercialize this technology.

Nevertheless, the eventually successful LIB cathode material came from Goodenough and co-workers,^{109–111} who correctly predicted that transition metal oxides rather than sulfides would not only remain stable at high oxidation states (Sⁿ⁻ in chalcogenides have a tendency to be oxidized to S⁰ or to react with moisture to generate H₂S) but also provide higher potentials (>4.0 V vs Li/Li⁺) and hence higher cell voltage and energy density. A series of layered structure materials based on LMO₂ ($M = V, Cr, Co, Ni$) were synthesized and explored, and LiCoO₂ (LCO) was identified as the winner, whose Li content could be removed down to 0.067 while charging up to 4.70 V. At that time the electrolyte (LiBF₄ in PC) could support the reversible operation of LCO for only a limited number of cycles with obvious capacity fading. When adopted in commercial LIB cells much later, energy density had to be traded for reversibility by limiting the amount of Li removed to ≤ 0.50 .

The work by Goodenough et al. inspired a wave of efforts exploring diversified materials of varying chemistries and structures. This enthusiasm lasted for decades, and the materials subsequently developed include spinel-type Mn oxides pioneered by Thackeray, Goodenough, and co-workers;^{112–115} olivine-type iron phosphates by Padhi, Nanjundaswamy, and Goodenough,^{116,117} followed by numerous attempts of Chen and Dahn,¹¹⁸ Chiang and co-workers,¹¹⁹ and Ceder and co-workers^{120,121} to improve their intrinsic low conductivity; various solid solutions of Ni, Mn, and Co oxides by Ohzuku and co-workers,^{122–124} Dahn and co-workers,^{118,125,126} and Amine and co-workers;¹²⁷ various structural variation of conventional spinel with excess Li in transition metal layers by Thackeray, Johnson, and co-workers;^{128–132} and different “5 V class” high-voltage materials by Amine et al.,^{133,134} Thackeray and co-workers,¹³⁵ Kawai et al.,¹³⁶ and Sun et al.^{137,138} Some of these materials became topics of intensive research, while a few even made it into commercial LIBs manufactured today. With balanced merits between energy density and reversibility, LCO remained one of the most reliable cathodes and, as of today, is still being used as the flagship cathode material in billions of LIBs on the market, mostly for electronic consumer products. Among those numerous intercalation hosts constructed upon transition metal oxides, Mn-based materials (spinel and solid solutions consisting of Ni–Mn–Co at varying ratios) were always favored as a strong competitor for LCO in terms of rate, cost, and safety, but the issues associated with Mn dissolution in acidic electrolytes, which constantly incurs active materials loss, and the unique disproportionation tendency of Mn in those solid solutions (Jahn–Teller distortion¹¹⁴) still present challenges.

Nevertheless, the first fruition of the intercalation concept happened at the cathode side. However, to make a full battery,

the intercalation cathode materials still need a successful intercalation anode, which proved to be much more difficult.

6. ANODE CHALLENGE

Equally important for an intercalation LIB cell, an anode host encountered far more difficulties than its cathode counterpart did. The challenges mainly arise from its interfacing with electrolytes, and the complications can be classified into two sources:

(1) Mismatch between Electrolyte Stability and Anode Operating Potential: The ideal anode potentials, which should be close to that of Li, are often situated beyond the reduction limits of almost all electrolyte solvents. A few ether-based solvents might constitute the only exceptions that are capable of remaining almost stable near the Li potential, but their stability against oxidation is rather poor. Meanwhile, most cathode materials known today could be comfortably enveloped within the oxidation stability limits of ester-based electrolytes (Figure 7), unless the high-voltage (>4.5 V)

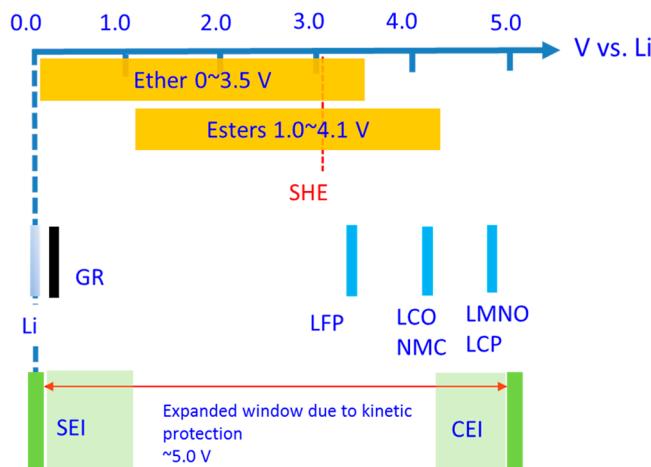


Figure 7. Schematic potential diagram showing the mismatch between the electrochemical stabilities of electrolyte and the redox potentials of most anode and cathode materials used in modern LIBs. GR, LFP, LCO, NMC, LMNO, and LCP stand for graphite, lithium iron phosphate, lithium cobalt oxide, lithium nickel manganese cobalt oxide, lithium manganese nickel oxide, and lithium cobalt phosphate, respectively.

cathodes are used. Nevertheless, there has never been a single solvent electrolyte that can provide a thermodynamic stability window wider than 4 V. The efforts of formulating electrolytes have always been a game of compromise. When ester-based electrolytes were eventually selected to support the cathode chemistries above 4.0 V, their stability with the anode at low potential requires kinetic protection from an interphase. With knowledge about interphasial chemistry absent at the time, tremendous trial-and-error efforts were conducted, many of which were in unsuccessful directions.

(2) Sensitivity of the Graphitic Anode to Solvent Cointercalation: The ideal anode hosts, used in state-of-the-art LIBs, are graphitic carbon materials that consist of graphene layers held together by weak van-der-Waals forces.^{139,140} The graphite layered structure can intercalate Li⁺ at a potential close to Li⁰ (~ 0.10 V vs Li/Li⁺) but is also susceptible to a collection of simultaneous and competitive reactions, among which the most prominent are the cointercalation of both Li⁺ and solvent molecules into the graphite structure and the

subsequent decomposition of such solvent molecules, leading to possible gassing inside graphite and destruction of the graphite structure (“exfoliation”).⁴⁰ Such complications prevented the early researchers from harnessing this very promising anode material for decades, until sufficient knowledge about the interphasial chemistries was accumulated. In comparison, although solvent-*co*-intercalation could also occur with certain layered cathode structures,¹⁴² the effect is far less destructive due to the much stronger forces (both Coulombic and covalent in nature) between the transition metal and the oxygen slabs; therefore, solvent cointercalation at the cathode side never evolved from a mere inconvenience into a disastrous phenomenon.

The early intercalation materials were almost exclusively developed as Li-free cathode hosts; therefore, in their initial implementation in batteries, they were still coupled with a Li metal anode serving as a Li source (Figure 5a), and consequently the cells inherited all the stability and safety issues of Li metal. When Li metal was still a hopeful approach, the adoption of an anode intercalation host did not look that attractive. What worsened the case further is that the anode hosts known at the time were also transition metal oxides, whose high potential incurred unacceptable energy penalties.

Among the sporadic efforts in the 1980s at the dual-intercalation concept, there was one particularly worth mentioning. Using Goodenough’s cathode (LiCoO_2) and Scrosati’s anode (MoO_2 and WO_2), Auborn and Barberio assembled a series of 2.0 V class dual-intercalation cells,¹⁴³ but what distinguished their work from the previous attempts was the initial discharged state of these cells, which consisted of lithiated cathodes and delithiated anodes. In other words, the cells were assembled with all the needed Li^+ stored at the cathode instead of the anode side. A similar strategy of a lithiated cathode was demonstrated to be feasible by Whittingham earlier using lithium dichalcogenide cathode and a metal substrate without anode active species;¹⁴⁴ nonetheless, the dual-intercalation configuration adopted by Auborn and Barberio bears closer resemblance to modern LIBs.

In fact, a number of aqueous batteries (Ni/Cd, Ni/MH, and lead-acid) were well-known to be assembled in the discharged state already, but for Li-based chemistries that require nonaqueous media to operate, this unusual practice brought unexpected advantages in both better processing convenience and higher safety. The former, apparently deriving from the “air stability” of the discharged electrodes, significantly relaxed the stringent moisture-exclusion requirements during handling and assembly of the cell parts before electrolyte injection; while the latter reduced the possibility of catastrophic failures such as fire or overheating upon the injection of electrolytes, a risk that might occur when a “dry” cell without electrolyte already has an internal physical short-circuit post assembly operations.

In retrospect, however, the real value of this work lies in the inspiration it provided to the later LIB cell developers. The initially discharged cell configuration cleverly circumvents a very aggravated and potentially dangerous procedure: the direct handling of the anode material in its lithiated form (LiC_6), which is extremely reactive not only with respect to ambient moisture but also with electrolyte solvents.^{139,140} The formation of the SEI between lithiated carbon LiC_6 and electrolytes is exothermic and would proceed uncontrollably if allowed to happen instantaneously, resulting in not only a poor

quality (protectiveness) of the SEI but also sudden heat release that could trigger a safety hazard, depending on the carbon surface area. Instead, the assembly of full LIB cells in the “discharged state” avoids all these troubles. For millions of pristine LIB cells manufactured today, their very first charging process in the factory realizes a gradual *in situ* electrochemical synthesis of LiC_6 , accompanied by a gradual (and possibly stepwise) formation of SEI, all of which is conducted in a safe and reliable manner, within a closed cell where the atmosphere is well controlled.

One additional benefit brought by this discharged-state approach is less apparent but equally important: gradual formation allows the interphases to be more deliberately tailored and manipulated with electrolyte additives, because most of these additive molecules were designed to reduce (or oxidize) at a potential where bulk electrolyte components (solvents and salt anions) are still stable.^{145,146} Such manipulation would be impossible or at least less effective if the interphase formation occurs instantaneously, where all electrolyte components might be involved with little discrimination. The majority of LIBs manufactured nowadays employ one or more additives in their electrolytes, which has become a billion-dollar industry. Exploration of new battery chemistries beyond LIBs only makes the search for new electrolyte components more important than ever.

The recall of Moli Energy cells in 1989 abruptly changed researchers’ perception about dual-intercalation batteries. At the time, Moli was not the only company attempting to develop Li metal rechargeable batteries; hence, the incident captured intense attention from a worldwide audience, among which were Japanese electronics giants Sony, Sanyo, Hitachi, and Matsushita. These companies were seeking an answer to the demand for improved batteries with higher energy densities to support the rapid development of portable electronics. Sooner or later, they terminated their rechargeable Li metal ventures and focused on the search for a proper anode intercalation host. It is clear that, at the time of the Moli recall, major efforts were already well underway in Japan to commercialize technology that subsequently became known as LIBs.

Among all the candidate anodes, carbonaceous hosts were the favorite, not only because of their low potential when fully intercalated by Li^+ and their high capacity of accommodating Li^+ but also because of their high abundance in nature and the multiple ways to tailor their structure and morphology from natural precursors. The capacity of 372 mAh/g or 756 mAh/mL (for C_6) and 339 mAh/g or 719 mAh/mL (for LiC_6), once considered mediocre in comparison with Li metal (3856 mAh/g or 2062 mAh/mL), now became acceptable as soon as more desired advantages such as better safety, reversibility, and efficiency could be materialized.^{139,140,145–149}

Long before any serious efforts in Li-based batteries, and even long before the formation of the “host–guest” chemistry concept, graphite was known to accommodate in its interlayer structure a variety of guest species, which could be cations (Li^+ , K^+ , Cs^+ , etc.), anions (halide-based complexes, etc.), or neutral (NH_3) species. Such intercalation processes could be either chemical or electrochemical in nature. In fact, as early as 1938, Rüdorff and Hoffmann demonstrated an “ion-transfer cell”, in which hydrogen sulfate anions (HSO_4^-) were electrochemically shuttled reversibly between a pair of symmetrical graphite electrodes (Figure 8).¹⁵⁰ Distinct stages (I and II) of hydrogen sulfate–graphite compounds could be identified from the

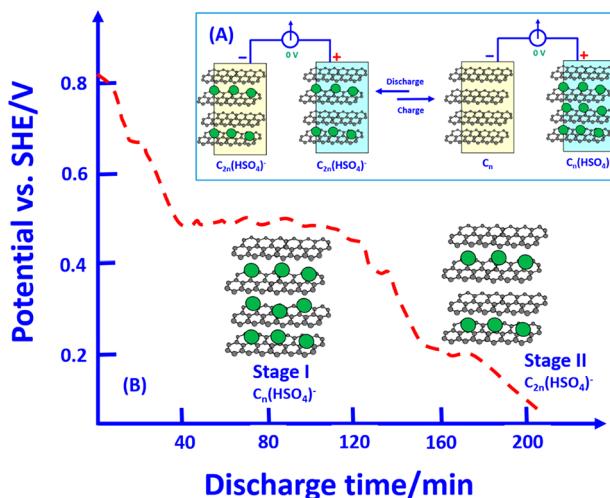


Figure 8. (A, upper inset) Dual-intercalation hydrogen sulfate ion cell of Rüdorff and Hoffmann, who coupled a graphite electrode fully loaded with hydrogen sulfate ions (stage I) with another pristine graphite electrode and shuttled hydrogen sulfate ions reversibly between two electrodes. (B, lower center) Potential profile of such a graphite electrode displaying two distinct sections corresponding to the transition from stage I to stage II as hydrogen sulfate ions deintercalate from one graphite electrode and intercalate into another. The figure was reconstructed from ref 150. Copyright 1938 ZAAC.

potential profile of the graphite electrode versus normal hydrogen electrode. This cell should be regarded as the antique ancestor of modern LIBs.

The intercalation of alkali metal cations into graphite was discovered much earlier,^{151,152} but all these intercalations were conducted via chemical means, i.e., by directly reacting graphite with molten metal or its vapor, during which the alkali metal (Li, K, Rb, and Cs) transferred its electron to the conductive band of the sp²-hybridized carbon in the graphene sheet and entered the interlayer structure of the latter. Hence, in such graphite-intercalation compounds (GICs), these alkali species are believed to exist in ionic states to different extents, which has been supported by overwhelming experimental and spectra evidence.¹⁵³ However, charge transfer does occur, especially at high guest populations such as C₆Li, where Li⁺ should be only partially ionic.^{147,148,153} Due to the high reactivity of Li metal, Hérod found that the intercalation by Li⁺ had to be carried out at moderate temperatures or via vapor; otherwise, a competitive reaction of a conversion-reaction nature would occur, leading to the full reduction of carbon by Li, destroying the graphite structure and generating lithium carbide.^{154,155}

Differing from all its alkali cousins, Li⁺ can be packed at a much higher density at stage I (LiC₆), while K⁺, Rb⁺, and Cs⁺ can only form MC₈. Na, on the other hand, stood out alone because its GIC is thermodynamically disfavored, with the exception of extremely diluted GICs,¹⁵³ or when Na⁺ is assisted by solvent molecules, whose cointercalation occurs at astonishingly high reversibility and rate.¹⁵⁶ Beside packing

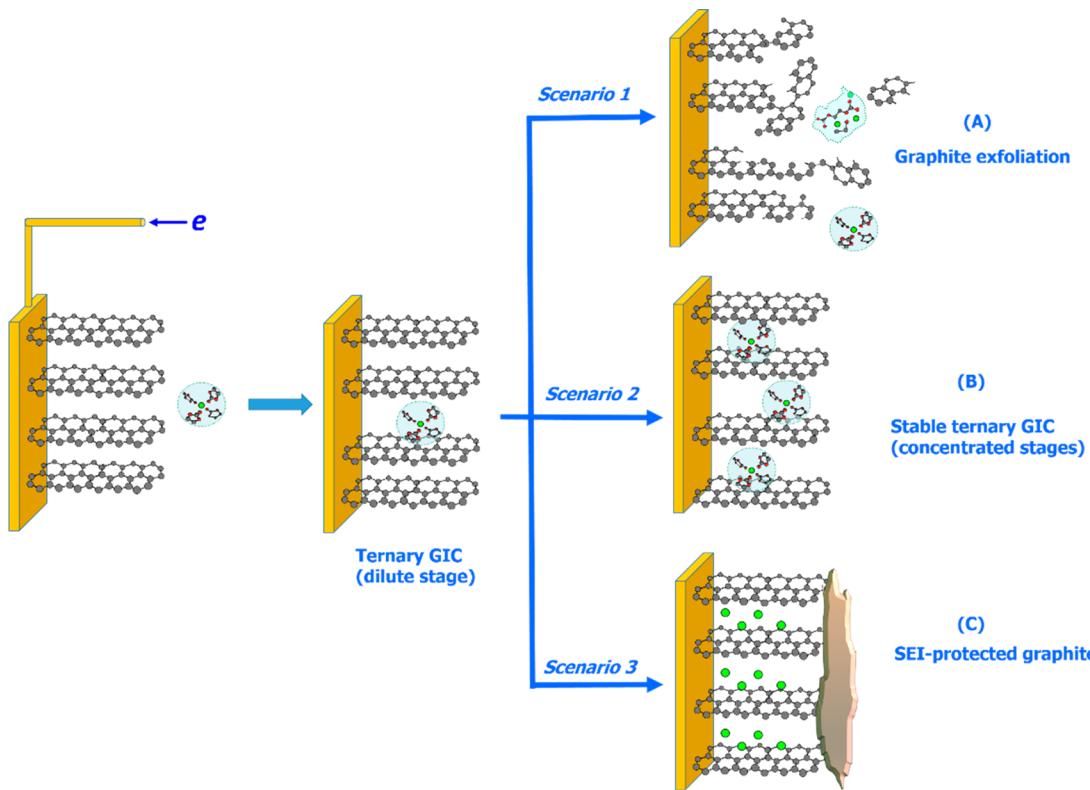


Figure 9. Formation of a ternary GIC and its three different fates depending on the solvents. (A) Extensive graphitic exfoliation induced by the reductive decomposition of unstable solvent molecules residing within the graphitic structure. (b) Formation of cointercalation GIC due to the high stability of solvent molecules toward reduction. (c) Reductive decomposition of electrolyte components (mainly solvent molecules), which produces compounds that deposit in a compact manner on the graphite surface, leading to the formation of a protective solid-electrolyte interphase (SEI). It is the SEI that ensures the reversible Li⁺ intercalation in graphite.

density (capacity), the Li^+ -intercalation potential also occurs at the lowest value (~ 0.10 V vs Li) compared with other alkali metals.^{139,155} The combination of these two factors, apparently a legacy of the Holy Grail character of the element Li itself, makes Li-GIC an ideal material as an anode intercalation host.

However, to use Li-GIC as anode in a rechargeable battery, the lithiated form has to be electrochemically synthesized, and this has to be done in a near perfectly reversible manner. That is where the problems arise.

Early efforts of intercalating Li^+ into graphite electrochemically never succeeded because of the side reactions caused by solvent cointercalation with Li^+ and the subsequent gassing and exfoliation of graphitic materials by these solvent molecules that could not form a protective SEI.^{148,149} Dey and Sullivan identified the major reactions on graphite, when the nonaqueous electrolytes were based on PC, as the quantitative decomposition of PC on graphite;¹⁵⁷ this was observed earlier by Rao and Hill,³⁷ but at the time the electrochemistry was not understood (Figure 4). Besenhard and colleagues, on the other hand, recognized that almost any electrochemical process on graphite involves the unique structure of graphite: multiple graphene layers held together by weak van de Waals force, which is hence susceptible to the invasion by guest species. They proposed that, in a wide variety of electrolytes, when graphite was cathodically polarized (i.e., when an electron is injected into graphite), what actually happened before a major reduction reaction was cointercalation,^{157–159} because the structure of solvated Li^+ residing between graphene layers would be thermodynamically favored. Such a GIC with three components (graphite, Li^+ , and solvent) was named “ternary GIC” (Figure 9), whose fate is determined by the electrochemical stability of the solvents, with two different scenarios:

(1) The solvent is unstable against reduction, whose existence can only be detected by fast scan and whose decomposition induces eventual exfoliation. PC is the representative molecule of this class. In 2005 Wagner et al. were able to observe the *in situ* formation of such a ternary GIC, providing the most direct evidence for such a cointercalation mechanism.⁴¹

(2) The solvent is stable against electrochemical reduction (in the time scale of the experiment), and therefore a stable and even reversible ternary GIC could be formed. This happens when the solvents are ethers (dimethoxyethane (DME), as the most frequent example) or dimethyl sulfoxide.^{159–162} More recently, it was found that Na^+ , which cannot intercalate into graphite at sensible concentrations, could form very stable and reversible ternary GIC as long as ethers were used as solvents.^{156,163–165}

A third scenario, the most important of all but unknown at the time, occurs when the solvent is *unstable* against reduction as well, but its decomposition results in compounds that deposit on the graphite surface as an effectively stable solid protective layer and stop further electrolyte decomposition.

In the absence of interphase knowledge, and still using PC or ethers of varying lengths as dominant electrolyte solvents, researchers in the 1950s through 1980s were unable to realize the third scenario and electrochemically synthesize lithiated carbon (LiC_x , where $x > 6$). In 1980, Basu claimed a rechargeable battery using stage I Li-GIC (LiC_6) as the anode,¹⁶⁶ but the lithiated graphite used therein had to be prepared by directly reacting graphite with molten Li metal,^{167,168} and the electrolyte itself had to be a molten salt

consisting of alkali metal chlorides, which, even at eutectic composition, required the cell to operate at temperatures above 300 °C. Japanese researchers at Sanyo claimed the first room-temperature cell with LiC_6 as the anode¹⁶⁹ in electrolyte consisting of a mixture of PC and DME, which was followed by Basu¹⁷⁰ using an electrolyte based on 1,3-dioxolane. We know today that neither of these cells could possibly deliver decent cycle life, simply because these electrolytes induce either scenario 1 or scenario 2, or both simultaneously, which excludes the possibility that C_6Li can be reversibly synthesized electrochemically therein. Beside the electrolytes, the chemically synthesized anode, LiC_6 , is already in the charged state, which is highly reactive and neither practical nor safe to handle.

One well-known work that must be emphasized in the history of carbonaceous anode materials was conducted by Yazami and Touzain, who in 1983 described a seemingly successful electrochemical synthesis of Li-GIC.¹⁷¹ A solid polymer electrolyte consisting of LiClO_4 dissolved in poly(ethylene oxide) (PEO) was used to avoid cointercalation, but the low ion conductivity of such an electrolyte (10^{-8} to 10^{-5} S/cm at room temperature) makes the Li^+ transport extremely sluggish, especially at the electrolyte/electrode interface. To force Li^+ into graphite, electrochemical titration techniques rather than simple galvanostatic means were used, generating a few distinct stages according to the graphite potential vs Li/Li^+ as displayed in Figure 10. Examining the potential profile from

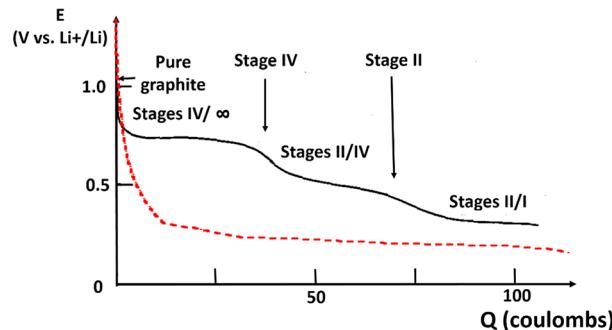


Figure 10. Attempt to electrochemically intercalate Li^+ into graphite from a polymeric electrolyte, where the cell potential profile observed (the solid black line) is plotted against the electric quantity infused into graphite. Figure reconstructed with permission from ref 171. Copyright 1983 Elsevier. The red-dashed line represents the potential profile of naked Li^+ intercalation into graphite structure, which was realized much later in carbonate-based electrolytes.

a modern perspective revealed that the equilibrium potentials for each stage seemed to situate at much higher values than they should in typical nonaqueous liquid electrolytes containing EC that were developed later, thus raising legitimate question about whether small ether molecules existed in the polymer and caused cointercalation, as evidenced by the plateaus at 600–700 and 300–400 mV, respectively. Nevertheless, this work served as an inspiration for later LIB developers because it demonstrated that electrochemical synthesis of Li-GIC in a cell could be possible.^{172,173}

In fact, because the authentic electrochemical lithiation of graphite in nonaqueous electrolytes was never realized until the early 1990s, nobody exactly knew at what potential each stage of the Li^+ -GICs will be formed. A rather interesting example is the work reported by Takasu et al. in 1984, who claimed that

LiC_5 , a highly lithiated state that does not actually exist, was formed at ~ 0.70 V vs Li.¹⁷⁴ The article was later disputed by Dey, who suggested that the observed process was merely the graphite exfoliation caused by PC in the electrolyte used.¹⁷⁵ It is well accepted nowadays that the highest stoichiometry that Li^+ can achieve in a graphitic structure is LiC_6 . Forcing any additional Li^+ into graphite will lead to the creation of Li–Li covalent bonds,¹⁷⁶ which borders on metallic Li deposition and hence might cause the resurgence of Li dendrite issues. Nevertheless, due to the absence of an accurate understanding about the electrochemically synthesized Li^+ -GICs, similar controversies over the formation of Li^+ -GIC in electrochemical cells still puzzled researchers from time to time.^{159,177,178}

The complexity arising between electrolyte solvent and the graphitic structure forced researchers to seek carbon materials with more disordered (or less graphitic) structures, which are not as sensitive to solvent cointercalation because a large portion of amorphous carbon regions therein serve as covalent joints that strongly keep the graphitic portions together (Figure 11a and b). Extensive efforts were made in searching

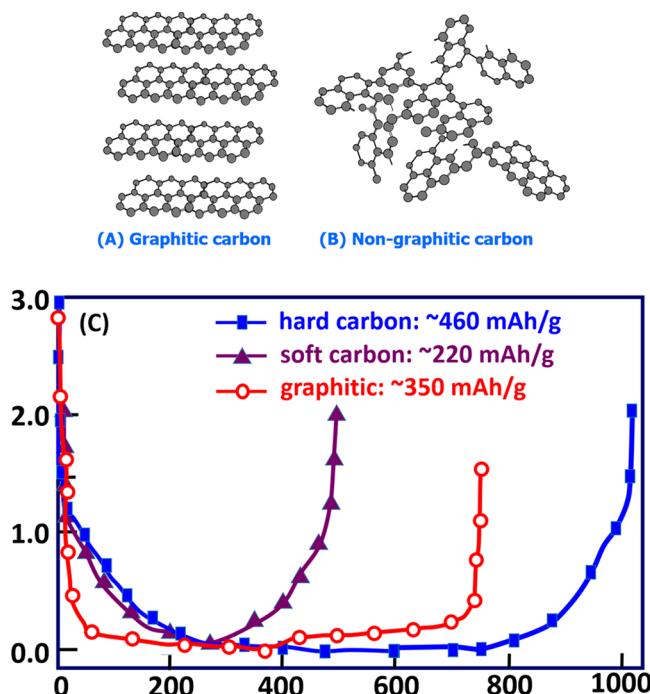


Figure 11. Schematic drawings of (A) graphitic carbon lattice and (B) nongraphitic (both soft and hard) carbon consisting of randomly oriented graphitic islands conjoined by amorphous carbon regions. (C) Typical potential profiles for the electrochemical lithiation and delithiation of soft, hard, and typical graphitic carbons in the first cycle. The reversible discharge capacities (which are utilizable) are indicated in the legends. Note that hard carbon (blue square) displays the highest capacity (450 mAh/g); however, its volumetric capacity is lower than that of graphite, besides its higher cost, the sloping voltage profile, and the lower Coulombic efficiency in the first lithiation/delithiation cycle.¹⁸⁸

for such an ideal carbon material, as represented by the large host of papers/patents published in this period, most of which were from Japanese companies, with the scope of materials ranging from conventional carbonaceous allotropes of diversified structures to highly conjugated polymers, which can be viewed as carbon-like without experiencing sufficient

pyrolytic processes.^{179–188} Such efforts were driven by the hidden consensus that graphite exfoliation induced by electrolyte solvent cointercalation could not be resolved from the electrolyte side; therefore, it was necessary to disrupt a perfect graphitic structure by introducing disorders so that Li^+ intercalation in carbonaceous hosts could be made reversible.

These less-graphitic carbon materials fall into two distinct groups: *soft* and *hard* carbons, where the adjectives (“soft” or “hard”) indicate how difficult it is to crystallize their amorphous structure into ordered (graphitic) structure at temperatures above 2500 °C.^{139,140} However, they do share two electrochemical characteristics: (1) both are stable against exfoliation by PC-containing electrolytes, and (2) their electrochemical lithiation is represented by a rather slanted potential profile in the range between 1.0 and 0.0 V vs Li (Figure 11c). When compared with the typical lithiation profile of a graphitic host that is characterized by an almost perfect plateau at ~ 0.1 V vs Li corresponding to the formation of LiC_6 (Figure 11c), substantial energy penalties apparently were induced for both soft and hard carbons. Soft carbon (as represented by petroleum coke) in the worst cases can achieve only half the capacity of a fully lithiated graphite with the formation of $\text{Li}_{0.5}\text{C}_6$, while hard carbon could approach the capacity of LiC_6 and even more but still suffers from the slanted voltage profile as well as higher irreversible loss in the first cycle (Coulombic efficiency only $\sim 76\%$). The capacitive-like behavior observed in both soft and hard carbons is the result of their amorphous carbon structure, whose lithiation compounds are much less well-defined in both ordering and stoichiometry. Despite the above drawbacks, these carbonaceous materials did electrochemically intercalate/deintercalate Li^+ with decent reversibility. They are not ideal anode hosts from an energetics perspective, but they worked.

7. INTEGRATION

By the mid-1980s, almost everything was ready for LIBs to be born. At the time, each component (lithiated transition metal oxides as Li^+ -intercalation cathode host, nongraphitic carbonaceous materials as Li^+ -intercalation anode host, nonaqueous electrolyte solvents, and lithium salts with complexed anions) had been under investigation for decades. The accumulated knowledge provided a sufficient technology reserve for the engineers attempting to integrate these components into a single working device.

The timing was also right. Although the shadow of the oil crisis was long lifted, the rapid advances in semiconductors and microelectronics during the years have been driving explosive growth of portable consumer electronics, whose list included cassette players, video cameras, cellular phones, and laptop computers. These new gadgets created a tremendous demand for improved portable power sources that require more energy than AA-size batteries could supply. Meanwhile, in light of the pollution and landfill issues caused by mercury-containing nonrechargeable alkaline batteries, the wakening public awareness of environmental issues exerted strong pressures on the manufacturers to look for a more sustainable solution. A rechargeable battery of high energy density never looked so tempting.

It was not surprising that Japanese electronics giants (Sony, Matsushita, and Sanyo) became the major driving force behind the commercialization of LIBs, but the first group that successfully assembled a dual-intercalation cell that resembles the modern LIB did not belong to any of these companies. The

honor went to a development team around Kuribayashi and Yoshino at the petrochemical giant Asahi Chemical.^{172,189,190}

Starting in the early 1980s, the Asahi team had been considering a nonaqueous rechargeable battery design that could operate above 3.0 V and provide much higher energy density than the 1.2–2 V aqueous battery chemistries either on the market or under development. At the time the only rechargeable battery technology available for portable applications was based on nickel/cadmium (Ni/Cd) chemistry, which provided mediocre energy densities with serious environmental issues. Efforts were once initiated to miniaturize lead-acid chemistry as a low-cost alternative to the toxic Ni/Cd, but these efforts ultimately proved unsuccessful, as people soon found out that small lead-acid cells with mediocre cycle lives proved to be more likely discarded by consumers, causing additional environmental pollutions. A cleaner nickel-based chemistry, nickel/metal hydride (Ni/MH), was under development during the 1980s and was eventually commercialized in 1990 by Matsushita (Panasonic). Although it is a viable power source for portable applications, its energy density remained moderate due to its aqueous nature. On the other hand, a few rechargeable systems with higher energy densities were indeed already available at the time, such as sodium/sulfur or sodium/nickel chloride batteries using solid ceramic electrolyte,¹⁹¹ but these chemistries can only operate at high temperatures (200–400 °C), which raised issues not only with inconvenience if used in portable applications but more importantly with safety; thus, their opportunity to power portable electronics was essentially precluded. Despite major investments in these various rechargeable battery systems for years, none of these chemistries was deemed to provide realistic solutions for portable applications.

The Asahi team selected LiCoO₂ developed by Goodenough and co-workers as cathode,^{109–111} and, inspired by the reported electrochemical lithiation of graphite by Yazami and Touzain,¹⁷¹ attempted to couple it with a carbonaceous host that can reversibly accommodate Li⁺ at relatively low potentials. Initially, polyacetylene was used as such an anode host,^{189,192,193} but its low density as well as poor air stability forced researchers to look elsewhere, including to vapor-deposited carbon fiber and eventually and petroleum coke. The latter, a soft carbon in nature, was available in large quantities and at low cost from the petrochemical industry as a distillation residue. During these efforts, the Asahi researchers were apparently influenced by the then-mainstream belief that carbonaceous materials of perfect graphitic structure cannot support reversible Li⁺-intercalation chemistry. Meanwhile, they also realized that the crystallinity in those carbonaceous materials dictates how much Li⁺ could be reversibly stored. Therefore, an optimum balance existing between the carbon's crystallinity and its resistance against exfoliation by PC was sought after. In fact, in the claim section of their important patents on LIBs,^{188,189,194} the crystallinity degree of carbonaceous materials was even strictly quantified based on X-ray diffraction data, so that certain irregular structure could be maintained for better performance. From today's view, this restriction would rule out the majority of the modern LIBs operating on graphitic carbon anodes, although according to Kuribayashi,¹⁸⁹ this was deliberately done to distinguish from the earlier proprietary work.^{166,169,170}

Nevertheless, in early 1986, the LIB configuration designed by the Asahi team already bore rather close resemblance to modern LIBs:¹⁷¹ a transition metal (LiCoO₂) cathode, a

nongraphitic carbonaceous (petroleum coke or vapor grown carbon fiber (VGCF)) anode, and a porous polyolefin separator soaked with nonaqueous electrolyte consisting of lithium perchlorate (LiClO₄) dissolved in PC. The strategy of assembling a full cell at discharged state, first demonstrated by Whittingham¹⁴⁴ for Li-metal cells and then by Auborn and Barberio¹⁴³ for dual-intercalation cells, was also adopted, which significantly simplified the process control thanks to the much lower moisture- and air-sensitivity of a lithiated cathode and a delithiated anode.

As the idiom predicts, "The devil always hides in the details". Most of the integration efforts were dedicated to engineering the components so that their disadvantages could be minimized and to interfacing the different components, either active or inactive, so that they could work with each other. For example, considering that the ionic conductivity of nonaqueous electrolytes is lower than their aqueous counterparts by orders of magnitude, for sufficient current to be drawn, the cathode and anode sheets were tightly wound in relatively (at the time) thin electrodes as spiral rolls so that the contact area between the two electrodes could be maximized. Such design significantly differs from the majority of the batteries known at the time, whether aqueous rechargeable (Ni/Cd, lead-acid, etc.) or nonaqueous primary (lithium thionyl chloride (Li/SOCl₂), lithium sulfur dioxide (Li/SO₂), etc.), but is rather similar to those high power density devices such as double layer or dielectric capacitors. The current collectors, on which the active materials are coated, also presented a challenge in light of the extreme potentials (~0 V for anode and >4 V for cathode) involved. Aluminum (Al) foil was found to be an ideal current collector for the cathode, because of its ability to self-stabilize in the electrolytes at high potentials (>4 V), a process known as passivation, which exonerates the use of any noble metal.¹⁸³ On the other side, copper (Cu) foil was found to be the ideal current collector for the carbonaceous anode, because it does not form an alloy with Li at low potential and is hence able to maintain its mechanical integrity during repeated cycling. To ensure optimum adhesion of active materials to these metal surfaces, poly(vinylidene difluoride) (PVdF) and carboxymethyl cellulose or styrene–butadiene latex materials were identified as effective binders for cathode and anode materials, respectively. Deviating from this optimum design by, for example, mistakenly switching Al and Cu would result in disastrous cell failure, as Cu cannot withstand high voltage, where it will oxidize into Cu⁺ and Cu²⁺ at ~3.0 V and then dissolve into electrolyte as a parasitic shuttle, while Al forms alloys with Li at low potential, whose drastic volume change upon each lithiation/delithiation cycling causes eventual disintegration of the current collector.¹⁹⁵ Similar synchronization efforts were also conducted for other inert components, such as the separator (its stability against both anode and cathode materials in the charged state, pore structure, tortuosity, and uptake of nonaqueous electrolyte) and nickel-coated steel cell packaging material (its inertness against chemical and electrochemical corrosion by the electrolyte).

In the summer of 1986, the Asahi team brought their optimized battery materials and components to a small company, Battery Engineering, in the Hyde Park suburb of Boston, MA, U.S.A., and used the manual winding machines there to assemble the first 200 prototype cells. At least part of the reason for them to do so, instead of hiring a Japanese battery company, was the concern of keeping secret the fact that a 4 V rechargeable battery was about to be born. The "C-

sized” cells underwent a series of safety tests conducted by an independent service provider, NTS, whose results convinced the U.S. Department of Transportation (DOT) to certify these cells, still nameless at the time, as “non-lithium metal battery” that can be shipped in the same manner as dry battery cells. It must be mentioned that, at that time, DOT had already enacted quite stringent limits for the shipment of batteries containing even small amounts (0.5 g) of Li metal. These limits originated from numerous safety incidents caused by primary lithium batteries such as Li/SOCl₂ and Li/SO₂ chemistries. Indeed, the argument that such cells did not contain any Li metal was so strong that it later contributed to the name “lithium-ion battery”.

Later on, after LiClO₄ was pointed out as a strong oxidizer that has the potential to react violently with organic solvents at high temperature or under impact, the Asahi team changed the electrolyte to lithium tetrafluoroborate (LiBF₄) dissolved in a mixture of PC, gamma-butyrolactone (γ BL), and EC. The fluorinated salt anion is less reactive with carbonate molecules and more effective in passivating the Al current collector. During the course of the scale-up development, the electrolyte composition experienced further evolution. Eventually lithium hexafluorophosphate (LiPF₆) dissolved in PC was adopted before the commercialization of the first LIB. In all these cases, the highly polar PC remained as the main solvent of the electrolyte responsible for dissolving lithium salts, which was allowed by the nongraphitic carbon anodes used therein.

In general, the Asahi team was very successful with the initial prototyping cells. It should be mentioned that, around the same time this “nameless” battery was assembled, a competing technology, the nickel/metal hydride (Ni/MH) chemistry, also neared the edge of commercialization after decades of research and material refinement.^{196–198}

Unfortunately, the initial success with the prototype cells did not make Asahi known as the company for the commercialization of LIBs. In January 1987, Asahi Chemical signed a nondisclosure agreement with Sony and demonstrated their achievements to the latter, which became the main driving force to commercialize this new rechargeable battery chemistry of 4 V.¹⁸⁹

As a leading manufacturer of portable electronics, Sony had a clear vision for high energy density batteries. Fully aware of the rapid developments in semiconductor and microelectronics following Moore’s Law, they accurately foresaw the emerging market for portable digital devices and the accompanying demand for improved portable power sources to support these devices. Therefore, back in 1975 Sony had already established a joint venture (Sony-Eveready) with the chemical giant Union Carbide, aiming to enhance their battery product line as well as to develop a new rechargeable battery chemistry. On December 3, 1984, the worst industry disaster ever recorded in human history happened in Bhopal, India, in which leaked toxic gas killed thousands and affected over half a million people. This tragedy apparently caused Union Carbide to divest itself from many R&D efforts and placed an abrupt end to the joint venture. Forced to continue the pursuit on its own, Sony started the research on a Li-based battery in 1985, which Union Carbide had been reluctant to do due to safety concerns in their previous joint venture. An independent company, Sony Energytec was established in March 1986, with Keizabura Tozawa as its head. After their interaction with Asahi Chemical, Sony accelerated its own R&D efforts in this 4 V rechargeable battery.^{169,199–205} At one point in the frenzy of

the activity, six parallel projects were conducted at the same time in Sony Energytec to prepare and test a large number of materials. Such an ambitious gamble succeeded, and a breakthrough was made. Tozawa named it the “lithium-ion battery” to highlight the absence of any Li metal in the cell,⁷⁰ which was later supported by diversified experimental data that indeed most Li retains an ionic nature while intercalated within the graphitic structure.^{139,188}

On February 14, 1990, Sony announced to the world that a new 4 V rechargeable battery delivering nearly three times of energy of Ni–Cd chemistry was being manufactured (4.1 V, 80 Wh/kg, 200 Wh/L). Meanwhile, Sony described this new battery in multiple industry presentations and began to reveal its development to a small number of target users. On March 6 of the same year, during a 20 min presentation at the Third International Battery Seminar in Deerfield Beach, Florida, Nagaura from Sony described this new battery.²⁰² More detailed information was provided in the following publications,^{203,204} which revealed that the basic cell configuration appeared rather similar to the prototype cells assembled in Asahi team’s initial efforts in 1986, i.e., LiCoO₂ and petroleum coke coated on Al and Cu current collectors, respectively, with minor changes such as PVdF being used as binders for both electrodes and an electrolyte consisting of LiPF₆ dissolved in PC. However, tremendous engineering efforts were again dedicated to tame the devil in the details. For example, LiCoO₂ fine particles (1–3 μ m) produced via conventional calcination process at 950 °C would induce a potential safety hazard in the case of abuse due to their high surface area; therefore, special preparation protocols had to be developed to make coarse granules of LiCoO₂ in the range of ~20 μ m. An optimum heat-treatment temperature had to be found for petroleum coke, so that it could best perform in PC-based electrolytes, and the salt anion (LiPF₆) containing a more labile fluorine bond than LiBF₄ was identified to passivate the Al current collector more effectively, forming AlF₃ on the surface and further stabilizing the cell at voltages > 4.0 V. Sony’s rich expertise in ceramic processing and precise surface coating, accumulated in its long history of manufacturing magnetic memory media, played a key role in the successful design and production of the first generation of LIBs.

As mentioned above, all these early LIBs used carbonaceous materials with a certain amount of structural disorder as an anode, so that exfoliation would not be induced by PC-based electrolytes. An interesting fact worth noting is that, similar to Asahi team’s patent that tried to distance its carbonaceous material from the graphite,¹⁹⁴ the early Sony publications called their anode materials at charged state “lithium carbon intercalation compounds” (Li-CICs) to reflect the fact that graphitic carbons cannot support electrochemical intercalation of Li⁺.^{200,204,205} In fact, the researchers at the time believed that the most ideal carbon materials should have an average interlayer distance (d_{002}) of ~0.37 nm, which is much wider than that of graphite (0.335 nm), so that the entrance/exodus of Li⁺ would occur with little resistance.^{199,200} To achieve this ideal interlayer distance, starting from the second-generation LIB, Sony switched from petroleum coke (which is soft carbon) to hard carbon that was synthesized from polyfurfuryl alcohol resin.^{188,201} Hard carbon does provide a reversible capacity close to (or even higher than) the theoretical fully lithiated carbon (LiC₆), but this change also triggered a chain of new issues,²⁰⁰ from the need for a new optimum heat-treatment temperature, to modifications in processing and

coating, to unexpected interaction with polymeric binders, etc. The energy densities of the second-generation LIBs increased to 120 Wh/kg and 295 Wh/L, respectively, thanks to the higher cell voltage (4.2 V) and higher capacity brought about by adoption of hard carbon.

Almost immediately, this new battery chemistry outperformed the existing Ni/Cd and the emerging Ni/MH (Figure 12). Nevertheless, a five-year period in the 1990s was

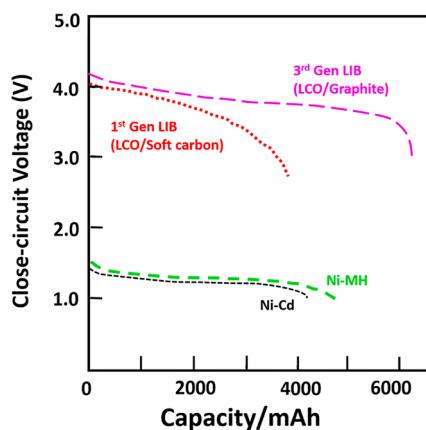


Figure 12. Performance comparison between the first-generation (using petroleum coke) and third-generation (using graphite) LIBs against Ni/Cd and Ni/MH batteries.

still captivated by the competition between Ni-MH and LIB. This debate existed only due to the high volumetric energy density of Ni-MH and its relatively low cost. From today's viewpoint, the winner is quite clear, as LIBs progressively expand year after year into broader applications such as vehicle electrifications, power tools, various unmanned aero-/ground/underwater vehicles, mega-watt-hour class grid-storage units, and electric flights.

The very first LIBs produced in 1991 were only utilized in a few models of cell phones including HP-211 by adopting the cylindrical form factors of 14500 and 20500 (by convention of battery industry, the first two digits represent the diameter in mm and the following two digits represent the height/length in mm),²⁰² respectively; however, it was the form factor of cylindrical 18650 that became the industry standard. Initially 18650 cells were designed for Sony CCD-TR1 8 mm camcorder; hence, this form factor bore the geometric signature of its parent device: the length of 65 mm is defined by the width of the camcorder so that it can be held by a single adult palm, while the diameter of 18 mm is the maximum size allowed by a safety calculation, which predicted that thermal runaway would not occur at such a diameter for a cell capacity of 1000–1300 mAh.¹⁸⁹ Despite the drastically improved single-cell capacities and the diversified applications LIBs were adapted to, this unique form factor survived various changes in portable products over the next few decades and remains a major product even today. An extreme example would be Tesla electric cars, most of which, as of 2018, are still running on battery packs consisting of nearly seven to nine thousand 18650 cylindrical cells.

8. THE THIRD SCENARIO

It was after the commercialization of the first-generation LIBs that the third scenario became known. As described in section 6, this scenario refers to an electrolyte solvent that is unstable

and undergoes reduction on graphite, but its decomposition results in stable compounds that densely deposit on the graphite surface as a protective layer, thus stopping further electrolyte decomposition. This protective layer stays as a permanent subcomponent on graphite during the lifetime of the LIB and allows graphite, instead of nongraphitic carbons, to be used as the most optimum anode material.

Compared with the painstaking efforts of stabilizing carbonaceous anode materials in nonaqueous electrolytes by altering carbon structure and rendering it less graphitic, this scenario provides a much more ideal solution from the electrolyte side, which resolves these undesired interactions between the graphite structure and the electrolyte (i.e., intercalation and exfoliation) without sacrificing too much Li⁺-storage capacity nor its intercalation potential, both of which were encountered in both soft carbon and hard carbon. It not only opens an avenue to the much cheaper graphite materials but also reclaims the energy loss due to the slanted voltage profiles of both soft and hard carbon materials, which is enabled by its almost perfectly flat voltage profile (Figure 11c). This latter characteristic of graphite anode rewards the LIBs using graphite anodes the advantage of higher energy density when a fixed upper limit of charging potential is set, as is often the case with portable electronics.¹⁸⁸

This scenario was made possible by the combination of graphite and EC, to be more precise, the combination of a highly graphitic carbon and an electrolyte that contains EC but not PC or ether-based solvents. The latter two solvents had been frequently used as the main solvents ever since the dawn of nonaqueous electrolytes but would represent scenarios 1 and 2, respectively. Any electrolyte formulations containing either of these suffer from either scenario 1 or 2, preventing the full lithiation of graphite to LiC₆.

Although as early as 1958 EC was already evaluated as an electrolyte solvent,²⁹ its use in battery research has been rather rare, mainly because of its high melting point and the hidden assumption that EC and PC are "essentially the same". Naturally, out of convenience, PC was chosen over EC in most cases. During the years before the birth of LIBs, EC was occasionally reported for sporadic advantages in various aspects, such as its high dielectric constant to raise salt solubility, its lower viscosity to improve ion transport, or its lower polarization on cathode,^{206–211} but these advantages never created sufficient uniqueness that distinguishes EC from PC.

Japanese researchers seemed to be the first to realize that the electrochemical lithiation of graphite can be supported by EC-based electrolytes, although, due to the intentional ambiguity of patent disclosures, it is rather difficult to determine whether the specific combination of an EC-based electrolyte and a graphitic carbon anode had been adopted in the cell. For example, a family of patents filed by Sanyo between 1981 and 1991 claimed a series of graphitic anode materials and a series of nonaqueous electrolytes that include EC.^{38,169,212,213} From the perspective of patent rights, it should have covered scenario 3, but the absence of a specific example as well as supporting data made it uncertain whether these inventors really achieved the electrochemical synthesis of LiC₆ in nonaqueous electrolytes, especially when the electrolyte claims in these patents often include PC and 1,2-dimethoxyethane (DME, a commonly used ether solvent). Similar claims were made by a 1984 patent filed by Bridgestone, with similar ambiguities.²¹⁴ A more recent patent in 1990 claimed

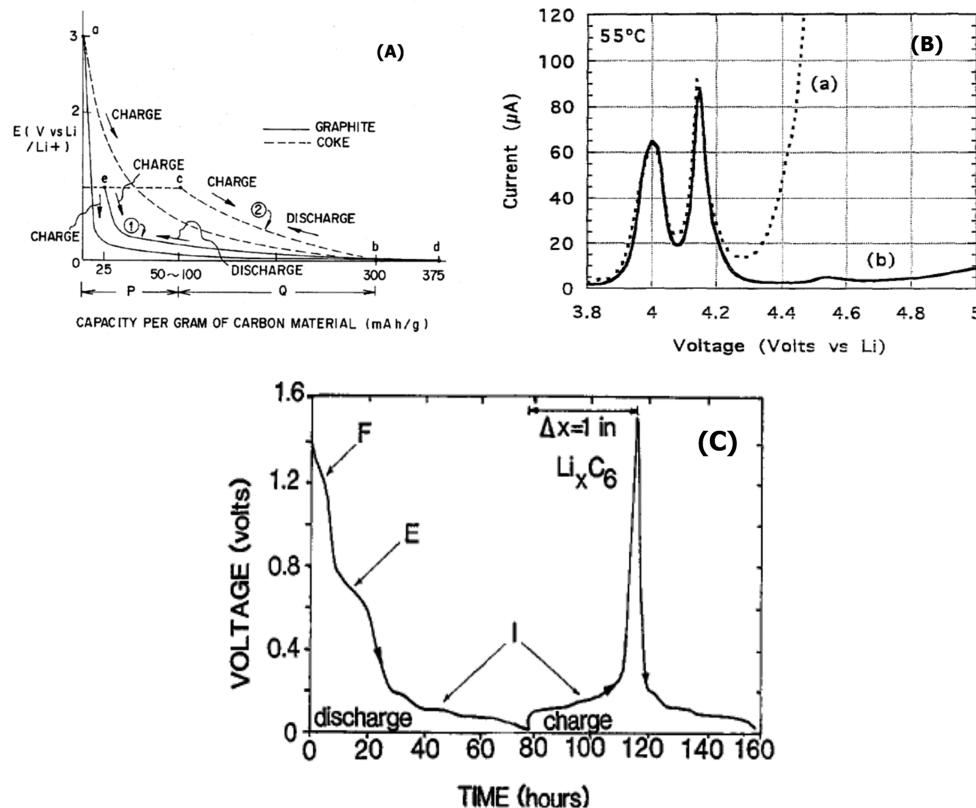


Figure 13. Third scenario realized when EC encounters graphite. (A) First documented electrochemical synthesis of LiC_6 in “EC-based, PC- and ether-free electrolyte”. (Adapted from ref 217. Source: 1991 United States Patent and Trademark Office, www.uspto.gov.) (B) Anodic stability of such an electrolyte on a cathode ($\text{Li}_2\text{Mn}_2\text{O}_4$) surface at elevated temperature. Reproduced with permission from ref 220. Copyright 1993 Electrochemical Society. Plot (A) represents an electrolyte based on a mixture of carbonate and ether and (B) represents an electrolyte based on a mixture of a cyclic and a linear carbonate. (C) First published correlation between EC and the protective SEI on graphite surface. Reproduced with permission from ref 39. Copyright 1990 Electrochemical Society. The electrolyte is a mixture of EC and PC.

electrolytes that consisted of lithium hexafluorophosphate (LiPF_6) dissolved in the mixture of EC with a linear carbonate selected from the group of dimethyl carbonate (DMC), ethylmethyl carbonate (EMC), or diethyl carbonate (DEC).²¹⁵ This electrolyte formulation essentially represents the skeletal composition of electrolytes used in modern LIBs; however, the anode material used therein was only broadly described as “carbonaceous”. Hence, one still cannot be sure whether the electrochemical synthesis of LiC_6 indeed occurred in this invention. The specific patent filed by Takahashi et al., with the priority date of December 12, 1990, not only described the skeletal electrolyte composition based on mixed solvents of EC and other acyclic carbonates (DMC, DEC, etc.) but also specifically claimed its use with a graphite anode.²¹⁶ At this point it seemed the successful electrochemical synthesis of LiC_6 should have been achieved. In the following patent filed by the same company (Sanyo) in 1991, numerous examples of the reversible Li^+ intercalation into various graphitic carbon materials (natural and synthetic graphite, etc.) were clearly demonstrated (Figure 13a).²¹⁷ This seems to be the first explicitly documented electrochemical lithiation of graphite in PC-free nonaqueous electrolytes.

Around 1993, the merits of such an EC-containing, PC-free, and ether-free electrolyte composition were suddenly made known to the world.^{218–221} In addition to the benefits on the graphitic anode, Guyomard and Tarascon also demonstrated that these electrolytes are stable against oxidation up to high potentials, which enables the application of most transition

metal oxide intercalation materials (Figure 13b).^{220,221} In no time “EC-containing, PC-free, and ether-free” became the core principle of basic electrolyte compositions adopted for the LIB using graphitic carbon anode. The third-generation LIBs went on the market in 1993–1994, while this class of EC-based electrolytes have become the mainstream electrolyte baseline used by the majority of battery researchers to this today. Of course, specific electrolyte composition always changes with battery chemistry or LIB manufacturer, but the skeletal structure of EC mixed with one or more acyclic carbonate (DMC, DEC, EMC, etc.) almost never changed. While the understanding of SEI deepens and more tools to manipulate SEI chemistry such as additives are becoming available, the restriction on PC has been somehow relaxed, so that its presence could alleviate the high melting point of EC. But EC has become an indispensable component, a constant among numerous variables within electrolyte composition. Only recently was its use questioned in terms of its potential negative effect on the cathode surface.²²²

Thus, the encounter of EC and graphite finally begot the mainstream configuration of modern LIBs. From an academic point of view, the paper published by Dahn and co-workers in July 1990 undoubtedly stood out as it set an important milestone that will affect electrolyte or LIB studies for many years to come.³⁹ Although still using an electrolyte that contains PC, i.e., lithium hexafluoroarsenate (LiAsF_6) dissolved in a mixture of EC and PC, they successfully achieved the very first documented electrochemical synthesis of LiC_6 despite the

low first-cycle coulombic efficiency incurred by PC-presence, which corresponds to a capacity close to the theoretical value of 372 mAh/g, at a potential of ~0.10 V vs Li (Figure 13c).

More important than this achievement was the fundamental understanding that enlightened the electrochemistry community. They established a clear correlation between the reversibility of Li^+ -intercalation chemistry in graphitic carbon and the presence of EC in the electrolyte. By comparing the potential profiles between the first and the following cycles, they correctly inferred that a passivation process must have happened during the very first lithiation, which would prevent further irreversible reactions in the following cycles while supporting the reversible Li^+ intercalation/deintercalation. Because such a protective layer is similar to what is deposited on the Li metal surface when it contacts with nonaqueous electrolytes, they transplanted the term “solid-electrolyte interphase (SEI)” that Peled had created for Li metal²⁰ and attributed the irreversible capacity observed in the first cycle, which is proportional to the surface area of the graphitic carbon electrode, to the formation of such an SEI on graphitic carbon.

These basic principles still hold true today, and since then SEI became a topic that has attracted intense studies. Thanks to the contribution from Aurbach and co-workers, the basic chemical composition of the SEI has been identified as lithium salts of alkylcarbonates generated via a single-electron reduction pathway from carbonate molecules.^{223–226} This key chemical identity continues to receive more support in recent studies from modern characterization tools,^{227–234} while new but minor species were also added to the repertoire of SEI ingredient.¹⁹

On the other hand, the formation process of SEI, which only occurred in the initial cycles of every LIB, should be preceded by a transient cointercalation process according to Besenhard, Winter, and co-workers.^{141,158,159} The formed ternary GIC would serve as a transient precursor for an SEI chemical ingredient (Figure 9).^{227,228} Needless to say, such a formation process must be heavily influenced by the solvation sheath structure of Li^+ .^{228,229} In typical LIB electrolytes (i.e., salt dissolved in mixed solvents at moderate concentration), preferential solvation of Li^+ ^{230,231} and consequently preferential reduction of certain solvent molecules usually occur.²²⁸ Cyclic carbonate molecules (EC or PC), because of their stronger binding with Li^+ , are normally preferred over their acyclic cousins (DMC, EMC, etc.) when solvating Li^+ . That is exactly why the interfacial and interphasial processes, no matter the formation of an interphase by EC or the exfoliation of graphitic by PC, are dictated by these cyclic rather than acyclic carbonate molecules.^{232,233}

When salt concentration deviates from the moderate value (~1.0 M) and wanders into the so-called “super-concentration” regime, the above principle still holds true, but more and more the salt anions instead of solvent molecules become the source of SEI chemistry, leading to a series of “unusual” electrochemical properties that have become an area of new interest.^{235–237} At its extreme, even water could be stabilized over a wide electrochemical stability window,²³⁸ allowing for lithiated graphite (C_6Li) and transition metal oxide (LiCoO_2 or LiMnO_2) cathodes to couple into a high-voltage (4.0 V) aqueous LIB²³⁹ that potentially offers a comparable energy density but extremely safe alternative to the nonaqueous LIBs.

Drawing a lesson from the historical misunderstanding and misconceptions that once occurred in the history of LIB

development, today’s researchers fully recognize the importance of basic science in the interphasial chemistry and processes, the interactions and inter-reactions among cell materials, which doubtlessly will constitute the key to the next-generation, more-energetic battery chemistries, be it conversion-reaction, anionic-redox, Li metal, or something presently still unknown.

9. EPILOGUE

Nearly 30 years after its commercialization, LIB has become beyond any doubt one of the landmark technologies that has profoundly changed our lives. In fact, it was the commercialization of LIBs that hatched a new era, which not only sees the increasing quality of various portable applications including smartphones and tablets but also marks the beginning of a revolutionary movement that significantly impacted the vehicle electrification and grid storage for stationary applications.²⁴⁰ Tremendous interests were generated, and an astronomical amount of funding has been invested by both governments and private sectors around the globe. The two thematic issues of *Chemical Reviews* published in 2004 and 2014^{241,242} comprehensively covered these advances.

When evaluated in terms of market size and sectors of industry impacted, LIB is listed as the no. 1 among the top 50 most disruptive technologies that altered the course of human history.²⁴³ It directly powered the rapid growth of portable electronics that provide us with communication and entertainment with both digital quality and mobile convenience. Carrying the momentum, it also penetrated the markets of higher strategic significances to the energy and environmental future of this planet: transportation and grid storage.²⁴³

The quest for a better battery continues. It was speculated that the maximum energy density expected from intercalation chemistry rests around 400 Wh/kg or 1000 Wh/L.²⁴⁴ To break such a limit and approach a new milestone of >500 Wh/kg, electrode materials of certain conversion-reaction nature have to be adopted. We have seen such efforts on both anode and cathode sides: increasing amount of Si used in mixture with graphite host, exploration of Li-metal, bivalent cation chemistries, metal fluoride conversion-reaction cathodes, etc. These aggressive chemistries promise higher energy densities but also come with higher challenges in terms of safety and reversibility. An interphase that stabilizes these chemistries with electrolyte becomes a critical know-how.

Now armed with the knowledge in interphasial chemistry, the capabilities in tailoring materials at nano- or even molecular lengths, the advanced *in situ/operando* characterization tools, and the unprecedented power to compute,^{68,69,245–251} researchers are revisiting the Holy Grail Li metal anode;^{65,252–255} harnessing unconventional redox processes in transition metal oxide lattices so that more than one Li^+ per formula might be accommodated;^{256–258} making the conversion-reaction-type chemistry reversible at a nanoscale;²⁵⁹ seeking ways to move multivalent cations (Mg^{2+} in particular) across heterogeneous interphases and solid lattices;²⁶⁰ or attempting to expand the electrochemical stability window of water so that aqueous batteries might deliver comparable energy/power densities with LIBs but with unprecedented safety.^{237,239,261,262}

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Notes

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Brian Barnett has been active in the battery industry for more than 35 years. His research has focused on the development of new battery materials and technology, assessment of new technologies, and development of battery safety technology. As Vice President at TIAX/CAMX Power since 2002, his major focus has been on battery materials, cell designs, and battery safety technologies, and he has spoken on extensive subjects related to battery technologies. His research at Arthur D. Little prior to TIAX brought him into contact with early efforts internationally to develop lithium-ion technology, and he has helped edit first-person accounts of such projects. He has recently established a new company, Battery Perspectives, and can be reached at brian@batteryperspectives.com.

Kang Xu has been in the electrolyte area for 30 years. He focused his research interest in synthesis and characterization of electrolyte materials and fundamental understanding of chemistries, dynamics, and kinetics of electrode/electrolyte interphases. He is currently a Lab Fellow and Team Leader at U.S. Army Research Laboratory and an Adjunct Professor at University of Maryland. He cofounded the Center of Research on Extreme Batteries (CREB) and serves in its Steering Committee. He has been recognized by more than 20 awards, including the 2015 Invention of the Year of University of Maryland, 2017 International Battery Association Technology Award, and 2018 Electrochemical Society Battery Research Award. Among the limited number of his hobbies is the passion for history, which in part drove the formation of this Review, as his tribute to the pioneers in the community of electrochemistry and battery science. He can be reached at conrad.k.xu.civ@mail.mil or kang_xu@hotmail.com.

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