

# 30 Years of Lithium-Ion Batteries

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Over the past 30 years, significant commercial and academic progress has been made on Li-based battery technologies. From the early Li-metal anode iterations to the current commercial Li-ion batteries (LIBs), the story of the Li-based battery is full of breakthroughs and back tracing steps. This review will discuss the main roles of material science in the development of LIBs. As LIB research progresses and the materials of interest change, different emphases on the different subdisciplines of material science are placed. Early works on LIBs focus more on solid state physics whereas near the end of the 20th century, researchers began to focus more on the morphological aspects (surface coating, porosity, size, and shape) of electrode materials. While it is easy to point out which specific cathode and anode materials are currently good candidates for the next-generation of batteries, it is difficult to explain exactly why those are chosen. In this review, for the reader a complete developmental story of LIB should be clearly drawn, along with an explanation of the reasons responsible for the various technological shifts. The review will end with a statement of caution for the current modern battery research along with a brief discussion on beyond lithium-ion battery chemistries.

and climbed sharply in popularity. It could be argued that it was the creation of the transistor at a small enough scale that fueled the research for better rechargeable batteries.<sup>[1]</sup> Or, it could have been just out of pure scientific curiosity that such research was undertaken.<sup>[2]</sup> Regardless of the initial cause(s), about 30 years ago Sony Co. commercialized the world's first lithium-ion battery (LIB). LIB's revolutionization of portable electronics led to an explosive increase in research interest throughout the following years. Adding to this interest, governments around the world became more conscious of the role of greenhouse gases in climate change and launched numerous initiatives on green energy technologies (solar, wind, etc.) and electric vehicles with energy storage systems at the core of these solutions. Consequently, **Figure 1** reveals that research into batteries had drastically increased from 2010, far exceeding the percentage rate of

## 1. Introduction

Demand for high-performance rechargeable batteries had become so tangible and ubiquitous in the recent years that its numerous requirements and functions had nearly risen to the status of common knowledge. Like most scientific-engineering fields, such a strong desire for advanced light-weight batteries was not always the case. Research into batteries began modestly

increase of overall publication across all research field. In the span of 7 years, researchers around the globe have added at least 119 188 new publications on batteries from 2010 to 2017 representing a 260% growth in total literature volume based on the search query "batteries" (on the Web of Science online database). This represents about a 4.5 times the % rate of increase in general published literature.

While the growth of battery research was impressive, the goals of research have not changed over the years: to decrease the weight and size of the battery, increase the cycle durability, maintaining safety while minimizing cost have always been the mandate of all battery scientists. Recent reviews on LIBs have provided a good overview of the historical and technical challenges of LIBs.<sup>[3–5]</sup> However, in accordance with the 30th anniversary of Advanced Materials (Wiley-VCH), this review will aim to provide a comprehensive story of the development and advancement of the lithium-ion battery systems with emphasis on the electrode materials over the past 30 years. From the lab setting to commercialization and current cutting-edge research, this review will discuss the main roles of material science in the development of LIBs. As LIB research progressed and the materials of interest changed, different emphasis on the different subdisciplines of material science were placed. Early works on LIBs focused more on solid state physics whereas near the end of the 20th century with nanotechnology on the rise, researchers began to focus more on the morphological aspects (surface coating, porosity, size, and shape) of electrode materials. We hope to clearly draw for the readers a complete story of the driving forces responsible for the various technological

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shifts in LIBs and research themes. This review concludes with perspective of the future of LIBs in terms of application and material science.

## 2. Commercialization of the Lithium-Ion Battery

The market for the generic battery started with the invention of portable electrical systems such as portable electronic calculators, implantable electronics or even simple flashlights. There have been many battery technologies prior to the inception of LIBs. It could have been the oil crisis in the 1970s<sup>[6]</sup> that motivated researchers to search for a superior battery system to replace petroleum.<sup>[7,8]</sup> It could also have been the invention of the transistor with its yearly size reduction<sup>[9]</sup> that urged consumers and companies to demand a new energy storage device. Irrespective of its origin, the desire for a system such as LIBs can be ultimately traced to the performance deficiencies of its predecessors. The secondary battery technologies that existed years prior to LIB (such as the Ni metal hydride and lead-acid system) possessed low energy densities with limited future potential. The search for a higher energy density system had drawn researchers to the wide voltage window of organic electrolytes, lithium's highly reducing nature ( $-3.04$  V vs standard hydrogen electrode) and low atomic mass.<sup>[7]</sup> Furthermore, the small atomic radius of Li-ions offered a high diffusion coefficient when used as the charge carrier and theoretically, appeared to be a very promising system for the high energy density and high-power demands of portable energy storage systems.

Historically, the ancestor of the current rechargeable LIBs can be traced back to the rechargeable Li metal battery (LMB). The first account of a cell that resembled a secondary LMB was published by Lewis and Keyes in 1913.<sup>[10]</sup> It was not until 1965 that the more familiar lithium metal anode in propylene carbonate based electrolyte was attempted by Selim et al.<sup>[11]</sup> at NASA, where practicality concerns were expressed about the low stripping/redeposition efficiency of  $\approx 50$ – $70\%$ . The following years yielded numerous research articles on the problems and potential solutions for rechargeable Li metal anodes, but with little success.<sup>[12–14]</sup> In the mid-1970s, work by Vissers et al. and Gay et al. at Argonne National Laboratory (ANL) explored high temperature ( $450$  °C) Li and Li-Al alloy/ $\text{FeS}_2$  system.<sup>[15]</sup> While this battery design did possess high energy density, it was intended for off-peak grid energy storage and electric vehicles which had little applicability for portable electronics.

### 2.1. The Search for a Cathode

The earliest iterations of a cathode that resembled the current cathode materials were designed by Whittingham.<sup>[16]</sup> The layered crystal structure of near metallic metal dichalcogenides such as  $\text{TiS}_2$  and  $\text{TaS}_2$  were used to store Li-ions. Whittingham called the Li-ion storage reaction, “the intercalation mechanisms” which was highly reversibly due to minimal changes in the crystal structures. He explained that this phenomenon stemmed from  $\text{TiS}_2$ 's ordered layered structure with alternating Ti and S sheets. The ordered structure did not have disordered Ti cations distributed randomly throughout the crystal



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lattice which was beneficial for Li-ion transfer.<sup>[2]</sup>  $\text{TiS}_2$  was later paired with a Li or Li-Al alloy metal anode, forming the Li/ $\text{TiS}_2$  system and commercialized by Exxon in the late 1970s at  $280$  Wh  $\text{L}^{-1}$  ( $130$  Wh  $\text{kg}^{-1}$ ).<sup>[2]</sup> This product was sadly restricted to the coin cell level and was only applied in watch batteries.<sup>[17]</sup> The main problems of Exxon's commercial Li/ $\text{TiS}_2$  system can be categorically divided into the cathode, electrolyte and the anode. Although the  $\text{TiS}_2$  cathode possessed a high Li-ion intercalation capacity ( $\approx 240$  mAh  $\text{g}^{-1}$ ) and high cycle durability, the

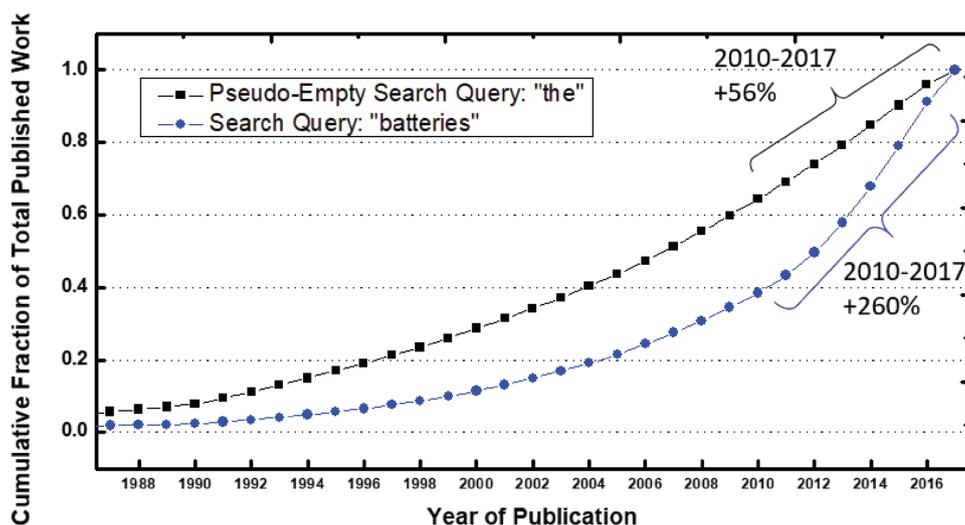
voltage was relatively low ( $\approx 2$  V vs Li/Li<sup>+</sup>) and was usually made in the “charged” (delithiated) state which meant it required a Li source in the anode. Furthermore, TiS<sub>2</sub> was problematic to handle in ambient conditions due to its spontaneous release of toxic H<sub>2</sub>S gas upon contact with moisture. The electrolyte was very dangerous due to the shock sensitive LiClO<sub>4</sub> salt while the safety and stability of a Li metal-based anode were still of great concern. This dangerous nature of a Li-metal anode was later experienced firsthand by Moli Energy Ltd in Vancouver, Canada in their Li/MoS<sub>2</sub> (MOLICEL) batteries in the late 1980s.<sup>[18]</sup> Moli Energy issued a total recall of all of their Li/MoS<sub>2</sub> batteries used in cell phones due to reports of battery fires. This discouraged the commercial use of metallic Li-anode for the near future, making the Li/TiS<sub>2</sub> and Li/MoS<sub>2</sub> two of the few LMBs that ever made it to the market. Such severe problems with Li-metal based battery technologies although unfortunate, presented themselves as the design criteria for the next generation of battery technologies. A cathode that was stable in ambient condition (ease of manufacturing) which also possessed a high energy density and an anode that was stable to cycle with limited safety concerns soon became the key benefits of the next generation of batteries.

A few years post “commercialization” of Li/TiS<sub>2</sub>, the first appearance of the modern layered metal oxide was made in February of 1980 where Godshall et al. at Stanford University published an article regarding the use of a high voltage metal oxide cathode material namely LiCoO<sub>2</sub> (LCO).<sup>[19]</sup> While LCO of Godshall et al. was operated at elevated temperatures of 400–450 °C, a few months later, Mizushima et al. reported a room temperature LCO cathode using organic electrolytes.<sup>[17]</sup> LCO had a very similar layered crystal structure (Figure 2a) to TiS<sub>2</sub> but offered many crucial advantages such as its stability in ambient conditions (moisture), a significantly higher Li-ion insertion voltage (3.5–4 V vs Li/Li<sup>+</sup> in propylene carbonate as shown in Figure 2b). If one mole of Li was extracted from one mole of LCO, the calculated theoretical capacity was 274 mAh g<sup>-1</sup>. Unfortunately, it required a very high voltage (5 V vs Li/Li<sup>+</sup>) to completely delithiated LCO. Such a high

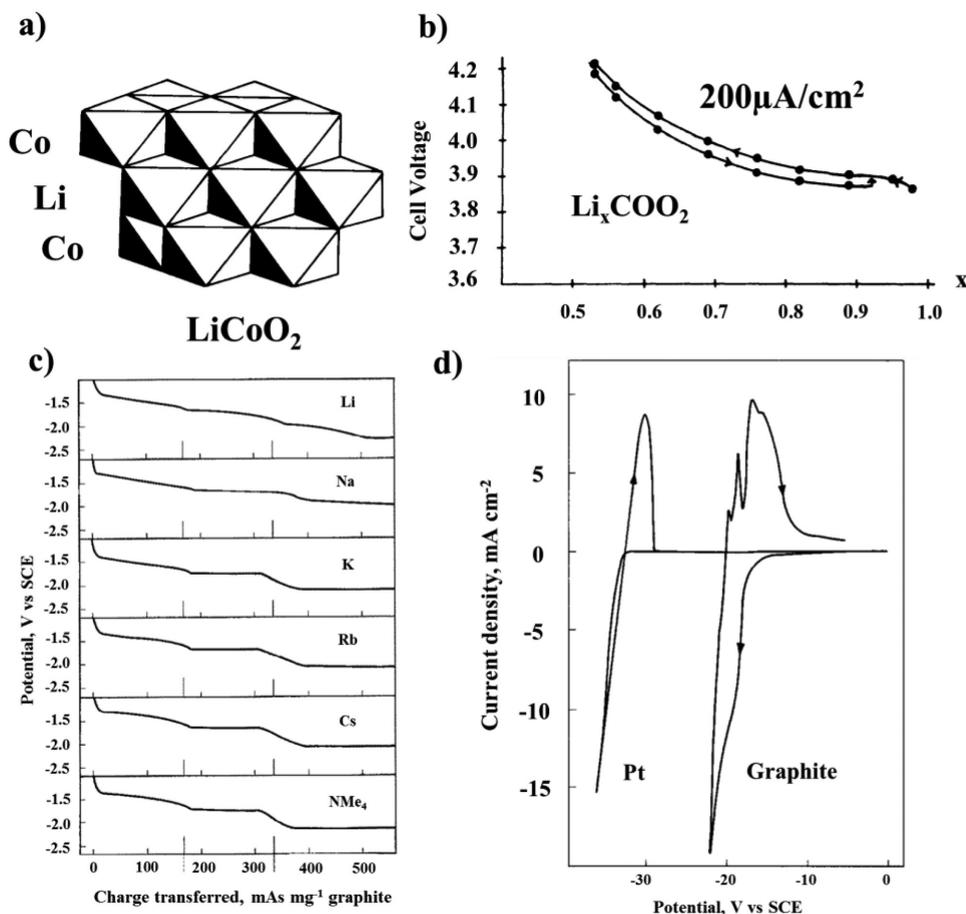
voltage would cause the oxidation of the organic electrolyte and instability of the cathode material. Accordingly, a complete delithiation was found to result in a severe 5% irreversible capacity loss at each cycle as reported by Amatucci et al.<sup>[20]</sup> which was quite prohibitive for practical application. The “practical capacity,” or the capacity of Li-ions which can be reversibly extracted and inserted into LCO was around half of the theoretical which was more than enough at that time. Another advantage, that indeed was the key to LCO’s success, was the fact that LCO was manufactured in its lithiated state which provided more freedom for the choice of anode material.

## 2.2. The Search for an Anode

The search for an anode that was safer and more stable than pure Li metal had already undergone great progress almost in parallel to the search for a cathode. While primary batteries with a Li anode had been long available to the consumer, the secondary LMB to this day have never reached widespread commercialization due to concerns regarding energy efficiency and safety. The challenges of finding a suitable anode were more problematic than the cathode and led to many abandoned concepts that never made it to market.<sup>[21]</sup> Concepts such as the Si–Li and Sn–Li alloying anodes were discouraged by the large volume change upon lithiation and the subsequent disintegration of electrodes.<sup>[14]</sup> The LiAl alloy anode was rather promising compared to the other alloy candidate and provided >90% Coulombic efficiency<sup>[13,22]</sup> but only when it was limited to an impractically low capacity of 5 C cm<sup>-2</sup> ( $\approx 1.4$  mAh cm<sup>-2</sup>) at a low current density of 1 mA cm<sup>-2</sup>.<sup>[23,24]</sup> In 1980, Lazzari and Scrosati published work on an insertion based tungsten dioxide anode and paired it with TiS<sub>2</sub>.<sup>[25]</sup> Though Li-ion insertion and extraction reactions from WO<sub>2</sub> were highly reversible, it was required to be first lithiated (externally by Li metal) to Li<sub>x</sub>WO<sub>2</sub> in order to introduce Li-ion into the TiS<sub>2</sub>/WO<sub>2</sub> full cell. Other problems with this design were the anode’s high voltage (0.75 V vs Li/Li<sup>+</sup>) and low capacity (125 mAh g<sup>-1</sup>).<sup>[26]</sup>



**Figure 1.** Comparison of literature growth from 1987 to 2017 between search query “batteries” (blue circles) and pseudo-empty search query “the” (black squares) in the field of search “topic,” utilizing the website Web of Science accessed through: <https://webofknowledge.com/> on October 25 2017.



**Figure 2.** a) The crystal structure of LCO and b) the discharge/charge voltage profile of LCO. Reproduced with permission.<sup>[17]</sup> Copyright 1980, Elsevier. c) Discharge voltage profile of intercalation of various alkali metals into graphite in  $\text{LiClO}_4$ ,  $\text{NaBF}_6$ ,  $\text{KPF}_6$ ,  $\text{RbI}$ ,  $\text{CsI}$ ,  $\text{NMe}_4\text{Cl}/\text{DMSO}$ . d) Cyclic voltammetry of Li-ion intercalation into graphite in 1 M  $\text{LiClO}_4/\text{DMSO}$  electrolyte. Reproduced with permission.<sup>[24]</sup> Copyright 1976, Elsevier.

Of all the directions of anode research, the carbon-based anode was deemed the most promising. This mainly because the lithiation/delithiation reactions of carbon materials were quite reversible, carbon had a high capacity ( $372 \text{ mAh g}^{-1}$ ), and the lithiation potential was low. The first reported use of an intercalation based graphite anode was by Besenhard in the mid-1970s,<sup>[23,24]</sup> where various alkali-ions such as Li, K, Na, Rb, and Cs were intercalated into graphite. Figure 2a shows Besenhard's first reported lithiation (along with insertion of the other alkali-ion) voltage profiles of a graphite anode with its cyclic voltammetry shown in Figure 2b. Quick to follow were the numerous reports of organic electrolyte decomposition on the surface of graphite upon lithiation<sup>[23,27]</sup> which was identified to have an electrode blocking effect to promote Li-plating.<sup>[27,28]</sup> First coined by Peled in 1979, this decomposition layer that separated the graphite from the bulk liquid electrolyte will be forever known as the solid electrolyte interphase (SEI).<sup>[29]</sup>

Later in 1981, Basu at Bell Labs patented a high temperature ( $375\text{--}500 \text{ }^\circ\text{C}$ ) molten salt cell which was implemented with a  $\text{LiC}_6$  graphite anode and metal sulfide cathode.<sup>[30]</sup> Without an organic electrolyte, the graphite anode was stable with no SEI. Two years later in 1983, Basu filed another patent on an ambient temperature secondary battery that used a  $\text{LiC}_6$  anode and  $\text{NbSe}_3$  cathode in a 1,3-dioxolane (DOL) solvent with  $\text{LiAsF}_6$

salt electrolyte.<sup>[31]</sup> In the same year, Yazami and Touzain published work on a  $60 \text{ }^\circ\text{C}$  operating temperature graphite anode cell with a solid electrolyte and demonstrated its reversibility through cyclic voltammetry.<sup>[32]</sup>

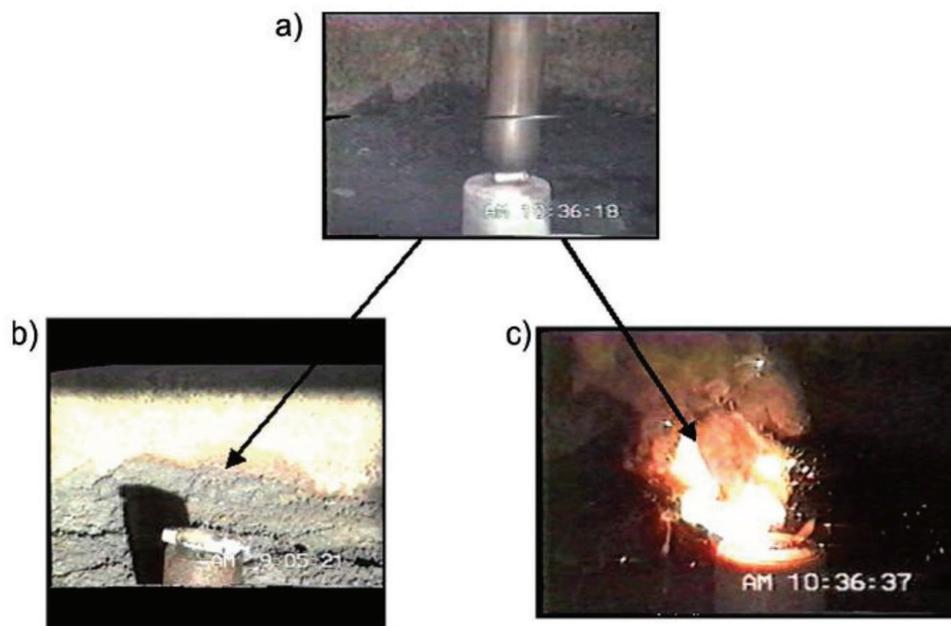
High-temperature molten salt designs of Basu were obviously prohibitive for consumer electronics while the solid electrolyte design by Yazami possessed impractically high internal cell resistance. Among these works, the most feasible anode for application in consumer electronics was Basu's room temperature ether based organic electrolyte system. While DOL and other ethers were known to form very stable passivation layers over graphite,<sup>[33]</sup> they were anodically unstable against a high voltage cathode such as LCO.<sup>[34]</sup> Accordingly, during this period, the more anodically stable PC was by far the most reported/common solvent in organic electrolytes for secondary lithium-ion based batteries.<sup>[35]</sup> During the same period, A. Yoshino of Asahi Kasei Corporation was working on a secondary  $\text{LiCoO}_2/\text{polyacetylene}$  full cell<sup>[36]</sup> but had also moved on in favor of the higher energy density graphite-based anodes. He expressed concerns over the poor energy efficiency caused by the high cell impedance of the large SEI layer and looked for another carbonaceous anode to substitute graphite.<sup>[36]</sup> There was a proportional relationship between the degree of graphitization and capacity. However, it was also found that the more graphitic the

structure carbon was, the more unstable the SEI formation. PC would intercalate into the graphite structure, causing exfoliation of the graphite layers.<sup>[37]</sup> It was later discovered in 1990 by Dahn, that in general if the graphitic structure was disordered such as those of soft carbons (less graphitized carbon), the higher the cyclability. He explained that the stability was probably increased due to the many lattice defects which pinned graphite layers together making them harder to be exfoliated.<sup>[38]</sup> Nishi later added that since the spacing between the graphite layers ( $d_{002}$ ) were too small, the graphite would contract and expand significantly during cycling. In contrast the larger intrinsic spacing of hard/soft carbon limited this effect.<sup>[39]</sup> In 1987, Yoshino et al. settled on coke-carbon, a type of soft carbon that demonstrated a reversible capacity of  $\approx 200 \text{ mAh g}^{-1}$  (out of a theoretical of  $372 \text{ mAh g}^{-1}$ ) with excellent capacity retention.<sup>[40]</sup> He paired it with the LCO cathode discovered by Goodenough in a PC mixed with diethyl carbonate-based electrolyte and patented what we now call the LIB.<sup>[40]</sup> While there had been many notable milestones reached on both the cathode and anode, it was this final work on the anode and cell integration by Yoshino that laid the last layer of foundation for modern LIBs and made him the commonly accepted inventor of LIBs. However, prior to mass production, the safety of this secondary battery had to be validated. Borrowing a battery safety testing facility, Yoshino subjected his new cells to a standard safety validation test which consisted of impacting an “iron lump” on the LIB. The testing apparatus is shown in **Figure 3a**. **Figure 3c** shows an exploding LMB after experiencing the impact. Whereas in **Figure 3b**, the deformed LIB cell did not explode nor catch fire. Where so many have failed, Yoshino’s new LIB did not. He described this result as, “the moment when the lithium-ion battery was born,<sup>[36]</sup>” since this was the last barrier before this technology can be granted commercial relevancy. Shortly after, Sony Co. in 1991 and A&T Battery Co.

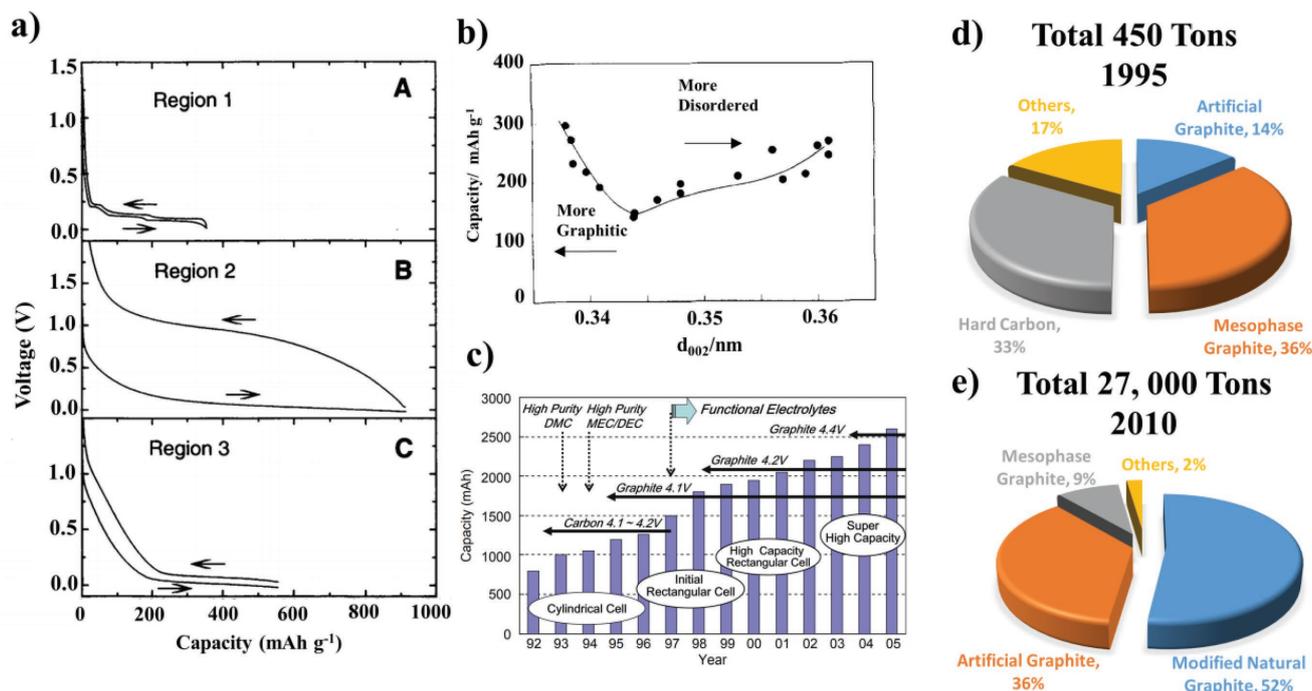
(a partnership between Asahi Kasei Co. and Toshiba) in 1992 commercialized the LIB for consumer electronics at  $200 \text{ Wh L}^{-1}$  and  $80 \text{ Wh kg}^{-1}$  which were charged to  $4.1 \text{ V}$ .<sup>[41]</sup> The commercialization of LIB was quickly received by companies as it filled a much-loathed gap in the market. Finally, a battery was simultaneously small, light, and durable while being reasonably priced for electronics such as camcorders and cell phones.

### 2.3. Post Commercialization Enhancements

The creation of the LIB revolutionized the way portable electronics were designed and enabled the many hand-held electronics that defined many aspects of modern human life. Post commercialization, LIBs underwent notable performance increases. With the cathode mostly left unchanged (initially), modifications to the anode and electrolyte were made to reach higher energy densities, higher discharge/charge rates, and longer cycle life. Investigations into carbonaceous anode led to the definition of three distinct classes of materials: graphite, hydrogen-containing carbon, and hard carbon by Dahn in 1995. The various generic voltage charge/discharge profiles of these materials are shown in **Figure 4a**.<sup>[42]</sup> In contrast to graphite and hard carbon, the capacity of the hydrogen-containing carbon material was large, but the overpotential during delithiation was far too severe for any practical application and was abandoned.<sup>[43]</sup> Somewhat complementing the work by Dahn, A. Satoh of the Toshiba Corporation recognized in 1995<sup>[44]</sup> that the capacity and charging stability of the carbon depended on its  $d_{002}$  spacing. Shown in **Figure 4b**, at  $d_{002} = \approx 0.344 \text{ nm}$  the capacity was at a minimal. By decreasing the spacing (becoming more graphitic) or increasing (becoming hard carbon) the capacity could be raised. Like graphite, hard carbon possessed a higher capacity than soft carbon but did not suffer



**Figure 3.** Photos of the safety validation tests performed for Yoshino: a) image after the cells was impacted with the iron lump, b) Yoshino’s LIB after impact, and c) the flaming aftermath of the LMB cell. Reproduced with permission.<sup>[36]</sup> Copyright 2012, Wiley-VCH.



**Figure 4.** a) Charge/discharge profile for graphitic, hydrogen containing, and hard carbon. Reproduced with permission.<sup>[42]</sup> Copyright 1995, The American Association for the Advancement of Science. b) Relationship between carbon type and capacity. Reproduced with permission.<sup>[44]</sup> Copyright 1995, Elsevier. c) Absolute capacity in mAh of LIBs from 1992 to 2005 with corresponding technological trends. Adapted with permission.<sup>[51]</sup> Copyright 2009, Springer Nature. Approximate market share of various anode materials in d) 1995 and e) 2010, with data estimated from ref. [54].

from the same exfoliation problems as graphite and enjoyed enhanced stability. Furthermore, in contrast to the small  $d_{002}$  of soft carbon (0.344 nm), the larger  $d_{002}$  spacing (>0.372 nm) did not experience much volume change (1% change vs 10% for graphite<sup>[45]</sup>) upon lithiation and provided excellent reversibility even at a higher charging voltage (4.2 V full cell, delithiation for LCO and lithiation for hard carbon).<sup>[39]</sup> As such, the second generations of LIB did not use soft carbon (coke) but instead hard carbons<sup>[40]</sup> produced from carbonized highly crosslinked polymers such as phenolic resins.<sup>[46]</sup> Hard carbon endowed the anode with superior stability<sup>[47]</sup> and the 2nd generation of the LIBs were rated at 220 Wh L<sup>-1</sup> and 85 Wh kg<sup>-1</sup> and charged to 4.2 V.<sup>[41]</sup> This was about a  $\approx 10\%$  increase in volumetric energy density over its first generation and was improved up to 295 Wh L<sup>-1</sup> and 129 Wh kg<sup>-1</sup>.<sup>[39]</sup> Unfortunately, in addition to its lower mass density (larger spacing between graphite layers), hard carbon possessed an unusually large irreversible first cycle capacity. This consumed significant amounts of Li-ions from the cathode on the first charge and ultimately required extra cathode capacity to compensate, lowering the overall energy density.<sup>[43]</sup> Moreover, the lithiation/delithiation plateaus of hard carbon (and even soft carbons) were sloped whereas graphite's voltage plateaus were exceptionally flat. A graphite anode was once again sought after. The use of graphite was initially prohibitive due to the unstable SEI formed by PC.<sup>[34]</sup> An initial adjustment to the electrolyte was the substitution of the propylene carbonate electrolyte solvent with ethylene carbonate (EC). EC was known in the 1980s to offer a more stable SEI layer compared to PC but had a high melting point of  $\approx 39$  °C. It was mandatory for EC to be mixed with other solvents to

remain in a liquid state at room temperature with a reasonable viscosity.<sup>[48]</sup> In 1990 Fong et al. proposed to use EC and PC in a 50:50 mixture and demonstrated that the incorporation of EC prevented the intercalation of PC into the graphite structure and ultimately mitigated the detrimental exfoliation of graphite.<sup>[49]</sup> This restricted the irreversible SEI formation to mostly occur on the first discharge cycle and remained stable for the subsequent cycles. The use of EC mixed with PC and other carbonates in the electrolyte was one of the main reasons that allowed for the reintroduction of graphite in commercial LIBs in around 1995–1997.<sup>[50–52]</sup> The high capacity of graphite still came at a cost of cyclability which meant hard carbon was not fully abandoned. Graphite and hard carbon each had their own benefits and disadvantages with some even blending them together.<sup>[53]</sup> However, by the mid-1990s, most LIBs have already shifted toward a graphite anode (Figure 4c) which already represented over half of the total anode market by 1995 with the remaining mostly occupied by hard carbon (Figure 4d).<sup>[54]</sup> By 2010 (Figure 4e), the market share of hard carbon effectively disappeared and was completely dominated by graphite-based materials. The presence of hard carbon in the LIB anode market never recovered ( $\approx 7\%$  in 2016),<sup>[55]</sup> but research is still recently being conducted on this material for LIB.<sup>[56]</sup> If hard carbon's large initial irreversible capacity can be avoided then it could still be revived commercially.

In addition to the innovations made on the electrolyte, this movement away from hard carbon was due to the innovations made on graphite materials. Within the class of graphite anodes, there were the synthetic and natural graphite types. Produced by Kawasaki Steel Co., a type of synthetic graphite

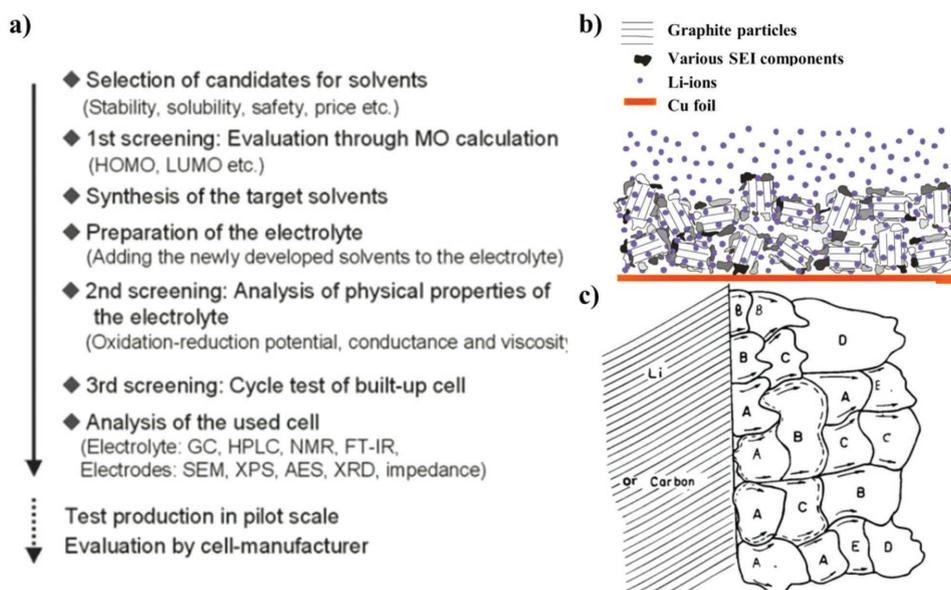
known as mesophase carbon microbeads (MCMB), offered high electrode packing density and low surface area which decreased the amount of SEI formation (more stable).<sup>[45,57]</sup> MCMB was very popular initially but was expensive due to the high temperature (2800 °C) nature of its production.<sup>[58]</sup> The demand for MCMB drastically decreased from 1995 to 2010 as the massive artificial graphite (MAG, manufactured by companies such as Hitachi Ltd.<sup>[59]</sup>) became a very popular anode material occupying ≈40% of the LIB anode market share by 2006.<sup>[59,60]</sup> MAG were aggregated graphite particles of 20–30 μm in diameter. They possessed a larger surface area of about 320 m<sup>2</sup> g<sup>-1</sup> which resulted in 30 Ah kg<sup>-1</sup> of irreversible capacity on first lithiation compared to the MCMB's 20 Ah kg<sup>-1</sup> at 150 m<sup>2</sup> g<sup>-1</sup>.<sup>[61]</sup> However, this was justified by the far superior rate capability of MAG owing to the enhanced accessibility of the graphitic layers. Also, the packing density of MAG was superior due to its large particle size. By 2010, the presence of MAG in the market was significantly higher than MCMB. The artificial graphite class of materials was undoubtedly exceptional materials as anodes for LIBs. Their downfall was the high cost of manufacturing stemming from high production temperatures.

Natural unmodified graphites were much cheaper but unstable due to the intercalation of PC and the subsequent exfoliation of its graphitic layers. Therefore, without the use of significant amounts of EC in the electrolyte, natural graphite cannot be used unless some clever modifications were made. Moving away from the mostly solid-state physics based work on LIB thus far, work on the graphite anode now took a more contemporary material science approach. Natural graphite found commercial success by introducing a thin carbon coating over the surface,<sup>[62]</sup> surface functionalized,<sup>[63]</sup> and also coated with Zr<sup>[64]</sup> to limit direct contact with the electrolyte. It should also be noted that many other technologies such as the alloy, conversion and intercalation based anode have been pursued simultaneously during this time period. Si and Sn alloys were heavily studied<sup>[65]</sup> but did not make a widespread commercial appearance. The problems associated with the enormous volume change is still a challenge to this day. Whereas the conversion based chemistries also poses the same volumetric problems but also introduces prohibitively high charging overpotential.<sup>[66]</sup> Of the many attempted anode technologies, lithium titanate or specifically the Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> has been the only other widely successful anode technology out in the market. Its incredibly reversible intercalation coupled with its relatively high lithiation potential made it a very robust material.<sup>[67]</sup>

Ever since the graphite anodes were made feasible in 1995–1997, the volumetric capacity has undergone significant enhancements (from ≈350 Wh L<sup>-1</sup> in 1997 to ≈625 Wh L<sup>-1</sup> in 2011).<sup>[54]</sup> In parallel to anode research, electrolyte research led to the realization that the stability of the SEI dictated the lifespan of the LIB.<sup>[68]</sup> If the SEI was not sufficiently passivating/stable, it was possible for the continuous formation of SEI layers on the surface of the anode. The SEI was found to grow slowly but noticeably at each cycle, resulting in the continuous consumption of electrolyte. As the electrolyte became more and more depleted after each cycle, the cells eventually failed from either an excessive overpotential due to an abnormally large amount of SEI material covering the anode or by simply drying out.<sup>[51,69]</sup> Without a proper control of the SEI, improvements in cycle

life could not be achieved (with or without EC) and sparked an immense amount of research. Initially this led to very early development of high purity electrolytes (removal of water)<sup>[70]</sup> and the mass production of high purity electrolyte solvent in 1992 by Ube Industries Ltd.<sup>[51]</sup> Later, the industry focused on a new concept and began searching for a “functional” electrolyte additives that did not replace the PC solvent but complimented PC and decoupled the many confounding requirements of the electrolyte.<sup>[50]</sup> The movement away from hard carbon to the higher capacity graphite occurred from 1995 to 1997 and was also partially driven by progress made in functional electrolyte additives. The search for high-performance electrolyte additives by Ube Industries Ltd. entailed a rigorous screening process as shown in **Figure 5a** as described by Yoshitake.<sup>[51]</sup> To search for a superior electrolyte additive, the design criteria must first be understood. As summarized concisely by Goodenough and Kim,<sup>[71]</sup> the stability of the electrolyte is related to the electrolyte's lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) levels. If the electrochemical potential of the anode was higher than the LUMO of the electrolyte then the electrolyte would be reduced on the anode. If the electrochemical potential of the cathode was lower than the electrolyte's HOMO, the electrolyte would be oxidized on the cathode. The oxidizing potential of the electrolyte often dictated the maximum charging voltage of the cell. The criteria for the reduction of electrolyte on the anode was often fulfilled for LIBs due to the low potential of lithiated carbon. First the solvents would be screened based on its HOMO and LUMO levels. The idea was to identify a high voltage electrolyte additive (i.e., low HOMO) possessing a LUMO which was more easily reduced by the anode than that of the electrolyte solvent (i.e., LUMO<sub>additive</sub> < LUMO<sub>solvent</sub>). This was key in decoupling the physical requirements of electrolyte solvent (i.e., viscosity of EC) with the SEI formation requirements. After the identification of such an electrolyte additive, it was synthesized and the calculated LUMO and HOMO levels potentials were confirmed by measuring the oxidation and reduction potential. Finally, the last step was to fabricate and evaluate various cell performance indices.

The fruits of such work were the commercialization of high purity, functional electrolyte in 1996 by Ube Industries Ltd. under the name Purelyte.<sup>[51]</sup> While exact chemicals were rarely explicitly published and considered as key trade secrets, potential additives such as vinyl acetate, divinyl adipate, and allyl methyl carbonate were added at compositions that were specific to the anode technologies used by the customers (battery manufacturer). These additives allowed for a stable graphite anode in PC even without EC which boosted the low-temperature performance of the cell. Other major changes to the electrolyte included the addition of vinylene carbonate (VC) and fluoroethylene carbonate (FEC) which polymerized over the lithiated graphite (SEI stabilizer),<sup>[74]</sup> flame retardants,<sup>[75]</sup> separator wetting agents,<sup>[76]</sup> and overcharge protection.<sup>[77]</sup> Arguably, the electrolyte additive is the most impactful parameter to achieve enhancements in cell performance. Above all the benefits of these additive, the formation of the SEI can be specifically considered as the single most important chemical phenomenon that has allowed for the use of such reductive anodes. It prevents the direct contact between the anode and the electrolyte



**Figure 5.** a) New electrolyte identification methodology from Ube Industries Ltd. Reprinted/adapted with permission.<sup>[51]</sup> Copyright 2009, Springer Nature. b) Schematic of SEI in relation to the anode. Reproduced with permission.<sup>[72]</sup> Copyright 2010, Elsevier. c) Schematic of SEI composition where A = Li<sub>2</sub>O, B = LiF, C = Li<sub>2</sub>CO<sub>3</sub>, D = polyolefins, and E = semicarbonates. Reproduced with permission.<sup>[73]</sup> Copyright 1997, Electrochemical Society, Inc.

(Figure 5b), while allowing for Li-ion transfer. This selective electron passivation offered by the SEI significantly enhanced the stability of LIBs. The composition of the SEI has been considered as complex blend of LiF, Li<sub>2</sub>O, Li<sub>2</sub>CO<sub>3</sub>, and polyolephines as shown in Figure 5c.<sup>[73]</sup> One important function of the salts is to facilitate Li-ion conduction through the SEI layer, if the Li-ion transfer is too slow, the subsequent overpotential can promote Li-plating.<sup>[74]</sup> Such a film was formed by the reduction of organic electrolytes solvents to form polymeric films over the surface. The polymeric layers provides an elastic characteristic that is important to prevent SEI breakage during graphite's volume expansion.<sup>[79]</sup> FEC has the capability of transforming into VC (also a crucial additive) which serves to form very stable films over the surface of the anode and has become one of the most important electrolyte additive for current cutting edge Si anode systems.<sup>[80]</sup> Unfortunately, this review cannot properly cover the vast research area of electrolytes and its indispensable role in the development of LIBs. Very informative reviews on electrolyte solvents<sup>[50]</sup> and additives<sup>[51,81]</sup> can offer more information to the readers on the historical development of the electrolytes for LIB.

As for the cathode, a 40% increase in energy density can be achieved by simply charging LCO cathode to a higher voltage (4.5 V instead of 4.2 V) as the number of Li-ions that are extracted from the LCO are increased.<sup>[82]</sup> However, high voltage charging (>4.2) can be detrimental to the cycle stability and safety of the cell. The highly delithiated state of LCO was problematic. Its unstable nature promoted the physical cracking of LCO particles,<sup>[83]</sup> oxygen evolution,<sup>[84]</sup> cobalt dissolution and deposition on the anode,<sup>[82]</sup> and electrolyte decomposition.<sup>[85]</sup> Surface coatings of inert materials such as Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and ZrO<sub>2</sub> have been investigated to prevent direct contact between the electrolyte and LCO in attempt to enable > 4.2 V LCO cathodes.<sup>[86]</sup>

Near the end of the 20th century, the LIBs for consumer electronics began to move away from liquid electrolyte cells with metal housing and began manufacturing cells made from plastic casings. Such batteries had many names but were generally called the Li-polymer battery (LPB).<sup>[87]</sup> At the heart of the LPB technology was the nature of the electrolyte. Ideally, a LPB should have a solid-state electrolyte composed of a polymer membrane (polyethylene oxide and polyacrylate among others) blended with a Li salt which later became primarily propylene oxide/ethylene oxide copolymers.<sup>[88]</sup> However, the liquid free LPB were only operable at >60 °C due to high impedance from the solid-state electrolyte. By swelling the polymer membrane with the electrolyte solution, a type of gel was formed which can be considered as a compromise between solid state and liquid electrolyte. The initial polymers used for gelling were high molecular weight polyethylene oxide, polyacrylonitrile, and polyvinylidene difluoride. Bellcore Lab used polyvinylidene difluoride/hexafluoropropylene copolymer and attracted much attention from the industry but was recalled because the liquid started separating from the polymer.<sup>[88]</sup> Depending on the interaction between the electrolyte and the polymer, a gel electrolyte can be very efficient at eliminating any free electrolyte liquid in the cell. Sony Inc. was the first company to properly mix the polymer with the electrolyte solution to obtain a gel electrolyte that did not leak any liquid and commercialized it in their 3<sup>rd</sup> generation LIBs.<sup>[52]</sup> By reducing the volume of free liquid inside the cell, the need for robust/bulky/heavy packaging such as metal casings were eliminated. This increased the gravimetric energy of LIB solely due to the decrease in packing weight. There was also a significant cost reduction as manufacturing LPB was more stream-lined than the traditional methods. Finally, the last benefit of LPB was the safety it introduced. In addition to the obvious benefits of employing less electrolyte (highly flammable), the polymer electrolyte

was found to be especially good at limiting dendritic lithium formation.

### 3. The Electric Vehicle's Demands for a New Battery

Beyond its early and modern dominance in the consumer electronics market, LIBs were also implemented in the power tool and uninterrupted power supply where some of the new LIB cathode technologies such as the spinel  $\text{LiMn}_2\text{O}_4$  and olivine  $\text{LiFePO}_4$  were applied.<sup>[89]</sup> The lightweight and compact nature of LCO based LIB appeared to be very attractive compared to other battery technologies. However, the ultimate and most exciting market that was ambitious even for the LIB, was the electric vehicle (EV) market.

The electrification of transportation has been identified as a crucial component to reduce mankind's greenhouse gas emission.<sup>[90]</sup> Acting both as a green revolution to the internal combustion engine and a potential load leveler for the energy grid,<sup>[91]</sup> EVs have become the main focus of many discussions of mankind's future energy economy.<sup>[92]</sup> Today, almost all major car manufacturing companies have at least either one type of hybrid vehicle or a full EV (xEV, x = pure and hybrid) on their product line. The battery is one of the most defining features of a xEV, almost all the disadvantages (driving range, charging time, cost and safety) of an xEV can be traced to a limitation or problem of its battery technology. While there were other markets for LIBs such as power tools and consumer electronics, 43% of all manufactured LIBs in 2016 are represented by demand in the electric vehicle sector (xEV including electric busses) and forecasted to be  $\approx 50\%$  in 2025.<sup>[55]</sup> With such a large percentage of the current day LIB market occupied by xEVs, the historical development of LIB was clearly intertwined and driven by the design requirements of xEVs.

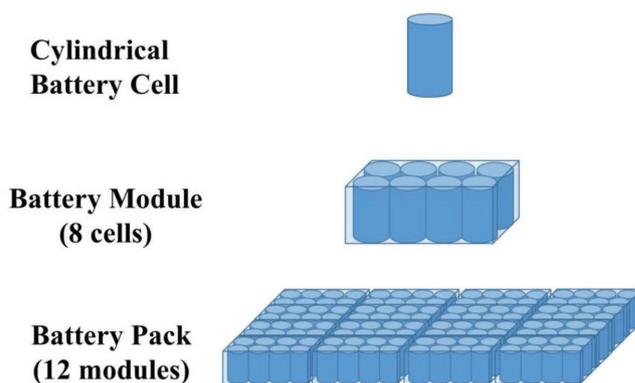
#### 3.1. History of Electric Vehicles

The beginning of the electric vehicle could be found as far back as 1873 (earlier than the first gasoline vehicle in 1885) by R. Davidson who built the first practically useable EV in Britain.<sup>[8]</sup> Later in 1897, the Electric Carriage & Wagon Company later acquired by the Electric Vehicle Company, was the first to bring forward EVs as a commercial possibility to the United States. The original intention of this technology was to replace or compete with horse-drawn taxi cabs. Although some success was initially enjoyed in North America and Europe with over 2000 vehicles delivered, the company declared bankruptcy in 1902. This was caused by the combining effect of a lower than specified delivered performance, expensive lawsuits based on the Selden patent<sup>[93]</sup> and fierce competition from the gas powered and steam-powered vehicles.<sup>[94]</sup> Sadly after this brief period of commercial success, the electric vehicle would be considered nothing more than a niche novelty item for the better part of the century to come. The next major spark that induced interest into xEVs was the energy crisis in the 1970s. In 1976, USA implemented its Electric and Hybrid Vehicle Research Development and Demonstration Act (Public Law 94-413).<sup>[8]</sup> With

emphasis on demonstration, this was mainly to see how feasible it was to develop xEVs that were comparable in performance to modern internal combustion engines.<sup>[95]</sup> Electric vehicles that commercially surfaced in the 1990s did not perform well as products. Examples such as the lead-acid based General Motors EV1, high-temperature Na-S based Ford Ecostar and the Ni-Cd hydride battery based Chrysler TEVan, all suffered from either a prohibitively low range ( $<150$  miles) or high cost of purchase and long recharge time.<sup>[96]</sup> Only a meager 4017 total electric vehicles were leased/sold from 1996 to 2000 in the USA across all companies<sup>[97]</sup> and were often speculated to be leased/sold at a monetary loss to the manufacturer.<sup>[98]</sup> The viability of fully electric vehicle was limited by the high cost of manufacturing and low driving range per charge. By finding and exploiting the middle ground between the range and recharging problem, Toyota introduced the world's first mass-production hybrid electric vehicle, the Toyota Prius in the late 1990s with Honda following closely after with the Honda Insight.<sup>[99]</sup> As hybrids vehicles can rely on its internal combustion engines to extend the range, both the Toyota Prius and Honda Insight did not require the use of high energy density batteries but instead implemented the Ni-Cd hydride battery and found commercial success. The gas efficiency and greenhouse gas emissions of hybrids were superior to pure internal combustion engines, but this was nevertheless a compromise on pure EVs. The high energy density LIB was a great answer to the range problems of EVs but proved to be difficult to replicate its success in consumer electronics market. The first example of a LIB based EV was the Nissan Altra introduced in 1997. The Altra was able to offer up to 192 km in range with a 350 kg LCO cathode based on 12 modules battery pack with each modules containing eight 100 Ah cells (schematic shown in **Figure 6**).<sup>[100]</sup> At the time, the Altra had the lowest battery weight to range ratio among the available EVs (comparison table shown in **Table 1**).<sup>[97]</sup> However, the cost of the Nissan Altra was high ( $\approx 51\,000$  US\$) for a low range of 192 km. Ultimately, Nissan only ever leased/sold an underwhelming 110 units of the Altra model.<sup>[98]</sup>

#### 3.2. Cost and Safety, the Two Factors for EVs

The contribution of cost to the commercial failure of the Altra could be explained by a study of L. Gaines at ANL in 2000



**Figure 6.** Schematic of the battery cell-module-pack design of the Nissan Altra.

**Table 1.** Comparison between the first LIB EV with other EVs in 2002.<sup>[97]</sup>

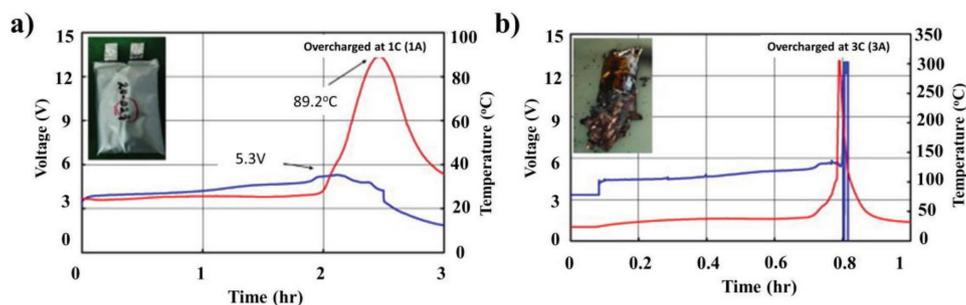
EV model	Battery type	Battery weight [kg]	Driving range [km]	Price [sale US\$/rent US\$]
GM EV-1	Pb-Acid	553	88–152	33 959 424
	NiMH	410	120–208	43 995 499
GM S-10	Pb-Acid	612	64–88	32 995 N/A
	NiMH	N/A	104–128	42 995 N/A
Ford Ranger EV	Pb-Acid	N/A	80	32 795 349
	NiMH	N/A	104–136	42 795 450
Toyota RAV4	NiMH	450	202	45 000 N/A
Honda EV Plus	NiMH	450	200–220	44 999 454
Nissan Altra	Li-ion	350	192	50 999 599
Chrysler EPIC	NiMH	N/A	128–144	N/A 450

where she estimated that 150 US\$ kWh<sup>-1</sup> was the threshold for EV to have competitive pricing compared to internal combustion engines.<sup>[100]</sup> Assuming the price of Co was 10 US\$ lb<sup>-1</sup>, it was estimated that the material cost alone would be 300 US\$ kWh<sup>-1</sup> for the Altra, which was already double of the targeted 150 US\$ kWh<sup>-1</sup>.<sup>[100]</sup> With even more stringent cost targets made by the US Joint Center for Energy Storage Research (100 US\$ kWh<sup>-1</sup>),<sup>[101]</sup> it was clear that next generation LIBs must include a significant cost reduction. Patents pertaining to cheaper technologies such as the layered LiNiO<sub>2</sub> cathode (which was not safe) were already granted to researchers as early as 1998,<sup>[102]</sup> but achieving a cheaper alternative while maintaining safety was significantly more difficult. Recent trending news of xEVs' battery succumbing to fire/explosion<sup>[103,104]</sup> and cell phone batteries<sup>[105]</sup> and are quite reminiscent of Moli Energy's LMB fire in the late 1980s.<sup>[18]</sup> While the cost is important, the safety of LIBs was paramount.

Catastrophic failures of the LIBs were typically the manifestation of phenomena such as the formation of dendritic lithium at high charge rates.<sup>[106]</sup> This occurred because the overpotential generated at higher current densities lowered the experienced potential of the anode to that of favoring Li-ion reduction (i.e., Li-plating). A method to reduce to the chance of Li-plating was to increase the absolute capacity ratios between the anode and cathode (colloquially known as the N/P ratio).<sup>[107]</sup> By having an excessive amount of Li-ion storage sites the potential of the anode can be kept higher which thermodynamically reduces the chance of Li-plating even when presented with a

polarization. Beyond this methodology, researchers began looking into higher lithiation potential anodes (which would not reach the Li-plating potential) such as lithium titanate oxide (LTO) in 1995,<sup>[108]</sup> the Li<sub>3-x</sub>M<sub>x</sub>N (M = Co, Ni or Cu, x = 0.1–0.6) anode systems in 1996<sup>[109]</sup> and conversion reaction anodes (amorphous tin oxide) in 1997.<sup>[110]</sup> Among these anode technologies, only LTO had been successfully commercialized into EVs such as the Honda Fit.<sup>[111]</sup> While the other anodes had problems with cycle stability, LTO was known for its highly reversible “zero-strain” lithium insertion and extraction mechanism. Furthermore, LTO's high lithiation potential did not thermodynamically favor the decomposition of electrolyte which made it extremely stable and robust but sacrifice the cell voltage and capacity (i.e., lower energy density).<sup>[110]</sup> Another strategy was the use of a ceramic modified separator due to its insignificant effect on energy density which have drawn both academic<sup>[112]</sup> and commercial interest.<sup>[113]</sup> Panasonic cells made for Tesla Inc. are known to implement a separator coated by a thin layer of ceramic.<sup>[3]</sup> The modified separators are manufactured and supplied by Sumitomo Chemical Co. and are used to increase the puncture strength of the separator, and thereby reduce the chance of internal short-circuiting.<sup>[114]</sup> Changes in the electrolyte composition to increase the Li transference number could also help by reducing the polarization which in turns reduces the favorability of Li-reduction on the anode.<sup>[50,115]</sup>

A complementing phenomenon to Li-plating was the problem of overcharging the cells. The high energy density demands from the industry can be partially met by increasing the charging voltage of the cell. If the charging voltage was higher, then more energy can be extracted from the cell. However, when LiCoO<sub>2</sub> is overcharged/over-delithiated to Li<sub>x→0</sub>CoO<sub>2</sub>, the formation of Co<sub>3</sub>O<sub>4</sub> and O<sub>2</sub> begins to occur which leads to the highly exothermic combustion of electrolyte, Li and carbonaceous materials.<sup>[116]</sup> This process was drastically amplified if the charging rate was increased, which was most likely due to the higher occurrence of Li-plating. At 1C (Figure 7a) the voltage dropped due to a partial internal short circuit while the temperature increases to ≈90 °C and the cell expanded in volume. When the current was increased to 3C (Figure 7b) the cell underwent a complete internal short (voltage dropped to 0) and the temperature increased sharply to ≈300 °C. If the heat removal system design for the battery cannot transfer the thermal energy quickly enough to quench the reaction, then there is a very serious risk of a thermal runaway reaction resulting in flaming battery cells (cell burned



**Figure 7.** The relationship between temperature and charging voltage during an overcharge test of a LiCoO<sub>2</sub> cell at a) 1C and b) 3C. Reproduced with permission.<sup>[116]</sup> Copyright 2008, Elsevier.

from catastrophic failure Figure 7b).<sup>[104,117]</sup> A more thorough understanding of LIB safety can be found through the following review.<sup>[118]</sup>

Amid the problematic safety concerns of overcharging and the cost concerns of using LCO, LIB still remained the most promising battery technology for EVs due to its unequivocally high energy densities. The next design parameters: safety and cost were aimed simultaneously by researchers. Interestingly, the issue of LCO's expensive raw material cost was well known in the battery fields and it was always envisioned that alternatives must be found before commercialization can be successful. Obviously, this was not how events unfolded, as the LCO based LIBs did find its first commercially successful application in the expensive but popular consumer electronics such as the cell phone and camcorder markets. However, this early notion of cost awareness among many researchers drove research on cheaper alternatives such as Mn, Fe, Ni, and Al based cathodes years prior to Sony Co.'s commercialization.

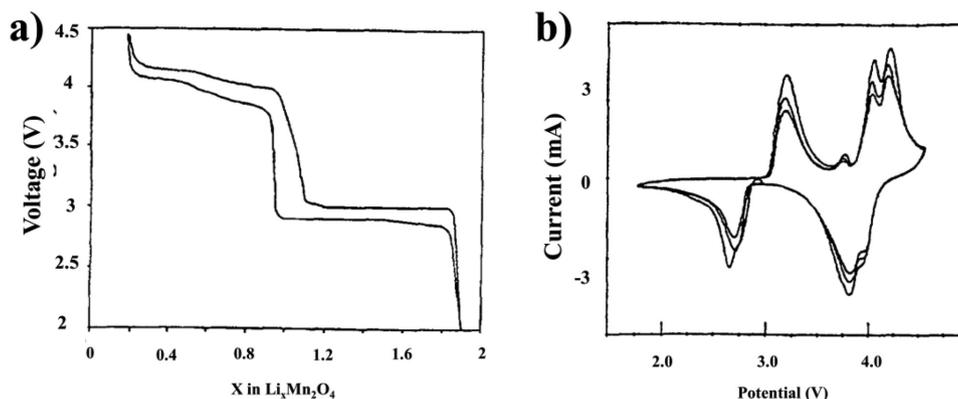
### 3.3. The Search for a 2nd Generation Cathodes

#### 3.3.1. Lithium Manganese Oxide

MnO<sub>2</sub> was a very common cathode material for primary batteries such as the Zn/MnO<sub>2</sub> aqueous Leclanché cells (patented in 1867), where protons would be inserted into the structure of MnO<sub>2</sub>.<sup>[120]</sup> MnO<sub>2</sub> was investigated as a cathode in a Li based rechargeable battery years (1974) before LCO,<sup>[121]</sup> and could store about 308 mAh g<sup>-1</sup> at 5 V versus Li/Li<sup>+</sup> which was much higher than the commercial LCO. Furthermore, Mn offered a substantial cost advantage over LCO due to the cheap price of Mn. However, it suffered from severe structural changes when lithiated from MnO<sub>2</sub> to the rock salt structure of LiMnO<sub>2</sub> rendering it practically useless as a rechargeable cathode material.<sup>[122]</sup> In 1981, Hunter published an article about the lithium diffusion in spinel LiMn<sub>2</sub>O<sub>4</sub><sup>[123]</sup> but it was not until 1983 that Thackeray demonstrated the 3D spinel structured LiMn<sub>2</sub>O<sub>4</sub> (hausmannite, LMO) with a dual discharge plateau at 3 and 4 V versus Li/Li<sup>+</sup> as an alternative to LCO,<sup>[121,124]</sup> shown in the charge/discharge voltage profile (Figure 8a) and cyclic voltammetry plot (Figure 8b). Similar to LiMnO<sub>2</sub>, LMO was significantly cheaper than LCO, less toxic, possessed greater thermal

stability at charged state and higher power density due to its 3D framework structure.<sup>[125]</sup> But unlike LiMnO<sub>2</sub>, the spinel crystal structure endowed it with better cycle stability, making it promising for EVs. Based on work by Thackeray, Tarascon et al. at Bellcore was the first to pair the LMO cathode with a carbon anode (analogous to the Sony's LCO cells) and reported relatively stable performance at room temperatures.<sup>[126]</sup> However, the benefits of LMO were met by several challenges at lower discharge voltages such as the Jahn–Teller distortion,<sup>[127]</sup> volume expansion due to phase transformations and the dissolution of manganese from the cathode via disproportionation reaction ( $2\text{Mn}^{3+} \rightarrow \text{Mn}^{2+} + \text{Mn}^{4+}$ ) induced by the HF acid produced from the reaction between LiPF<sub>6</sub> (electrolyte salt) and trace water impurities in the electrolyte. The generated Mn cations migrates to the graphite anode and increased the charge-transfer resistance of the anode.<sup>[128]</sup> These phenomena resulted in severe cycle life degradation and was further amplified by increased cycling temperatures ( $\approx 50\text{--}70\text{ }^{\circ}\text{C}$ ).<sup>[129]</sup> It was found that the intrinsic reason for the instability of LiMn<sub>2</sub>O<sub>4</sub> was the oxygen deficient nature of its crystal structure.<sup>[130]</sup> Work by Yoshio and co-workers have demonstrated a strong relationship between the cycle stability and the oxygen content in the Mn spinel structure.<sup>[131]</sup> If the oxygen was stoichiometric, the addition of metal substituents such as Al and Mg into the spinel structure was found to limit the Mn dissolution and enhanced its cycle stability at higher temperatures (50 °C).<sup>[132]</sup> However, a study at ANL demonstrated that even with a minimum amount of Mn ions in the electrolyte (such as Li<sub>1.06</sub>Mn<sub>1.95</sub>Al<sub>0.05</sub>O<sub>4</sub>), the reduction/deposition of Mn on the surface of graphite was still observed.<sup>[133]</sup>

LMO was not an ideal candidate to replaced LCO in LIBs for xEVs. Although, LMO was cheap and could be reasonably stabilized by comprising capacity (theoretically, LMO possessed 148 mAh g<sup>-1</sup>), the practical capacity was limited to 110 mAh g<sup>-1</sup> to ensure stable cycling.<sup>[134]</sup> This had limited the commercial use of LMO to only about 10% in 2005 which were mostly in cell phones by NEC Co. where LCO dominated the market<sup>[135]</sup> and decreased to 8% (absolute usage still increased)<sup>[55]</sup> as of 2016. Today, most of its applications are in power tools and EVs such as the Nissan Leaf where it is mixed with other more expensive, less safe but higher energy density Co based layered materials to reduce the overall cost and enhance the safety.<sup>[136]</sup>



**Figure 8.** a) Thackeray's voltage profile and b) the cyclic voltammetry profile of LMO. Reproduced with permission.<sup>[119]</sup> Copyright 1997, Elsevier.

### 3.3.2. Lithium Iron Phosphate

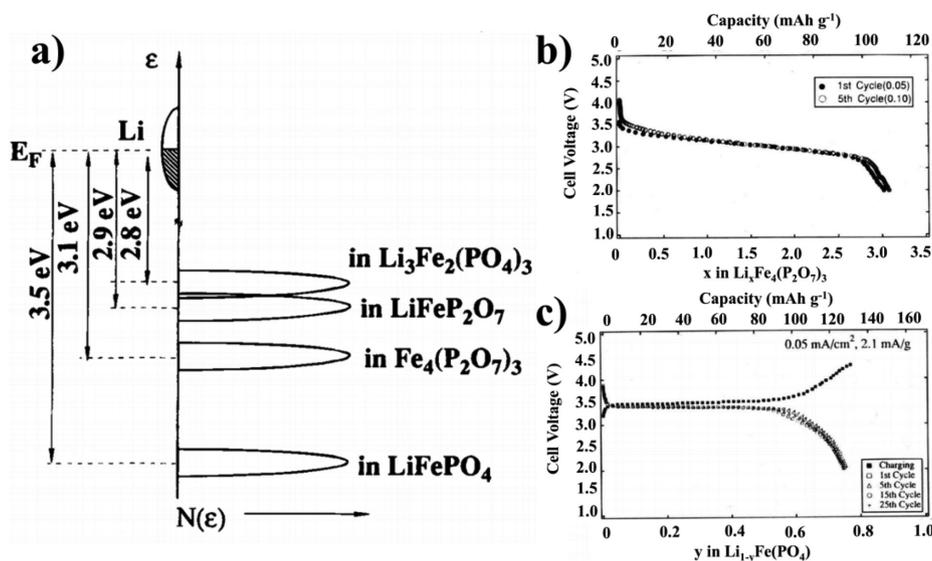
Another class of cathode materials were the olivine structured  $\text{LiFePO}_4$ . Initially, the cheap  $\text{LiFeO}_2$  was investigated by Sakurai et al. in 1996 but the capacity was low ( $\approx 100 \text{ mAh g}^{-1}$ ) and the lithiation profile was severely sloped.<sup>[138]</sup> Later the polyanions ( $\text{Fe}_2\text{SiO}_4$ ) with a NASICON framework, was investigated by Manthiram and Goodenough in 1989 and was found to possess a flat voltage plateau.<sup>[139]</sup> In 1997, another metal polyanions ( $\text{PO}_4$ ) in the form of 1-D ordered olivine structured  $\text{LiFePO}_4$  (LFP),  $\text{LiMnPO}_4$ ,  $\text{LiCoPO}_4$ , and  $\text{LiNiPO}_4$  were investigated by Padhi et al. now at University of Texas-Austin.<sup>[140]</sup> At the time, Padhi discovered that out of all the metal phosphates tested, LFP was the only one that could reversibly extract and insert Li-ions. LFP was significantly cheaper than the Co based cathode and possessed similar capacity making a promising candidate for EVs. Historically, various forms of iron phosphates were also investigated.  $\text{LiFeP}_2\text{O}_7$ ,  $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ ,  $\text{Fe}_4(\text{P}_2\text{O}_7)_3$  and  $\text{LiFePO}_4$  all demonstrated ability to reversibly insert and extract Li-ions. It was found that  $\text{Fe}^{3+}/\text{Fe}^{2+}$  couple of  $\text{LiFePO}_4$  possessed the largest gap from the Fermi level of Li and lithiated at 3.5 V versus  $\text{Li}/\text{Li}^+$ <sup>[137,141]</sup> as shown in Figure 9a. The differences in the charge/discharge voltage profile between  $\text{Fe}_4(\text{P}_2\text{O}_7)_3$  and LFP are shown in Figure 9b,c respectively. LFP has a higher lithiation voltage of  $\approx 3.5 \text{ V}$  whereas  $\text{Fe}_4(\text{P}_2\text{O}_7)_3$  begins with  $\approx 3.5 \text{ V}$  but slopes downward to  $< 3.0 \text{ V}$ . Additionally, LFP was inherently safer than the layered metal oxides. Due to the strong P–O bond, the oxygen release seen in LCO that led to catastrophic failure was not possible from the LFP structure. Thermal decomposition experiments indicated that LFP only released a small amount of heat ( $147 \text{ J g}^{-1}$ ) at  $> 250 \text{ }^\circ\text{C}$ .<sup>[142]</sup> The  $\text{LiFePO}_4$  possessed a two-phase lithiation process at  $\approx 3.5 \text{ V}$  versus  $\text{Li}/\text{Li}^+$  which offered an extremely stable voltage plateau in contrast to the single-phase intercalation process of layered oxide materials with a sloped lithiation voltage profile. However, in contrast to the spinel Mn or the layered dichalcogenides

of  $\text{TiS}_2$  and  $\text{CoO}_2$  cathode materials, LFP was not electrically conductive and does not become any more conductive at any state of lithiation. This prevented the use of bulk LFP particles in the cathode which severely hindered its initial commercialization. Strategies included incorporating a conductive carbon coating over the particles,<sup>[143]</sup> conductive networks<sup>[144]</sup> and reduction in particle size.<sup>[142]</sup> The use of material science to control features at the nanoscale achieved carbon-coated nanosized LFP and was commercialized in the early 2000s by A123 Systems Inc.<sup>[54,145]</sup> In contrast to LCO and LMO, the commercialization of LFP was quite dramatic with a multi-front patent battle between University of Texas for Goodenough, Nippon Telegraph & Telephone, and A123 from MIT.

The smaller particles and conductive coating endowed good electrical percolation to the insulating LFP particles. However, the nanosized LFP suffered from a low tap density. The low tap density caused a low volumetric capacity. Along with its low lithiation potential of 3.5 V, LFP has been widely recognized as a cheap, low energy density cathode. LFP does however possess a higher stability, higher rate capability and superior good abuse tolerance compared to the layered oxide cathodes.<sup>[136]</sup> In 2016, LFP occupied about 36% market share of all LIB cathode materials with most of its application in electric busses and power tools where the energy density is not as stringent of a design requirement.<sup>[55]</sup> The low energy density of LFP has limited its adoption into the EV market. Two of the few occurrences of LFP in EVs were in the Coda Automotive EV in 2010,<sup>[146]</sup> and the Chevrolet Spark.<sup>[3]</sup>

### 3.3.3. Ni-Based Cathodes

The two 2nd generation LIB technologies discussed thus far (LMO and LFP) did not and still do not have much of a presence in the modern EVs. Perhaps the most impactful and fruitful cathode materials for xEV applications were the layered Ni–Mn–Co oxide (NMC) and Ni–Co–Al (NCA) oxides. The origin of these two materials can be traced back to the layered  $\text{LiNiO}_2$  (LNO). LNO was first synthesized and isolated by L. D. Dyer in 1954,<sup>[147]</sup> but the first electrochemical testing of  $\text{LiNiO}_2$  was in 1985 by Thomas et al. where a single voltage profile was shown.<sup>[148]</sup> LNO was a material that possessed a similar layered structure material compared to LCO<sup>[149]</sup> but with a higher capacity ( $220 \text{ mAh g}^{-1}$ ) and energy density ( $800 \text{ Wh kg}^{-1}$ ).<sup>[150]</sup> LNO was originally investigated as a cheaper alternative to LCO due to the lower cost of Ni and slightly lower voltage versus  $\text{Li}/\text{Li}^+$  compared to LCO which mitigated anodic electrolyte decomposition.<sup>[151]</sup> Unfortunately, LNO suffered from many problems such



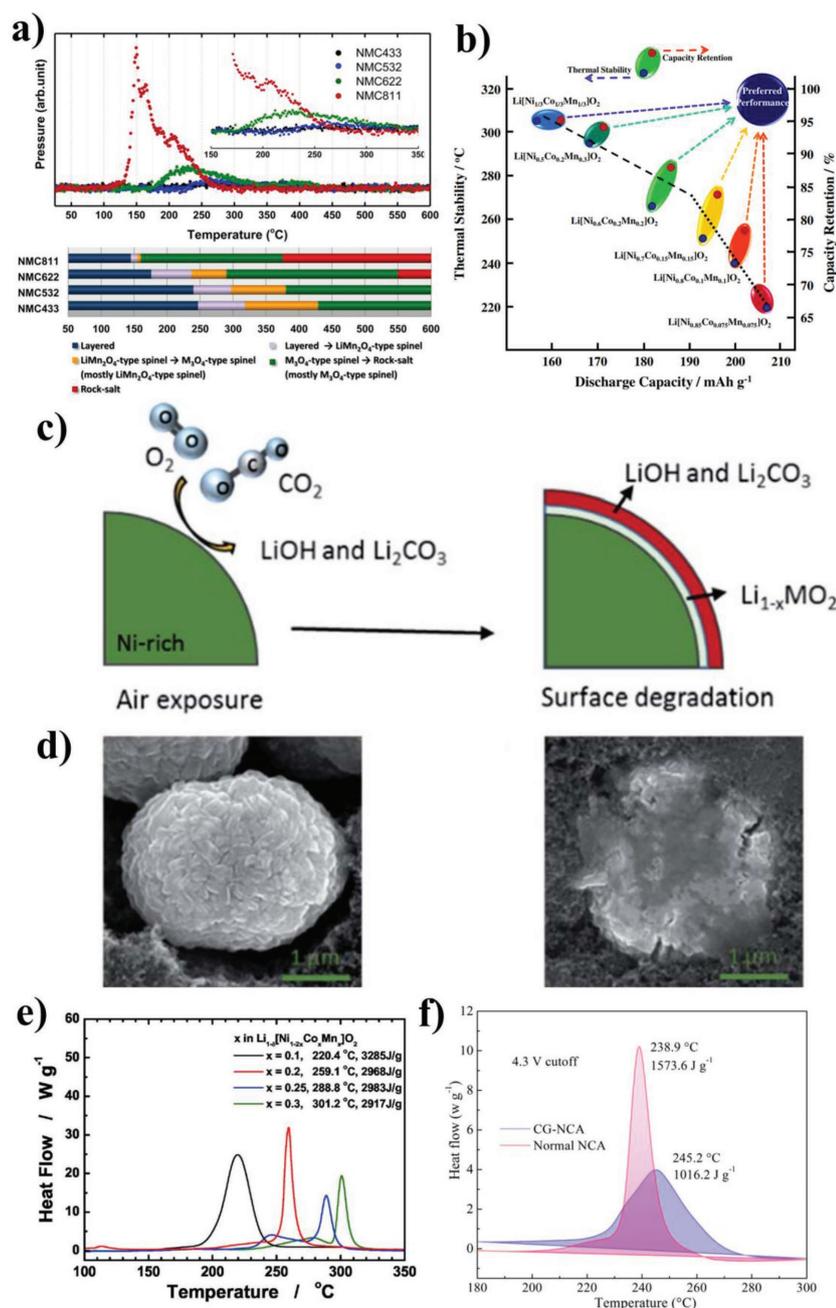
**Figure 9.** a) The Fermi level of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  in various structures. Charge/discharge voltage profile of b)  $\text{Li}_3\text{Fe}_2(\text{P}_2\text{O}_7)_3$  and c)  $\text{LiFePO}_4$ .<sup>[137]</sup> Reproduced with permission.<sup>[137]</sup> Copyright 1997, Electrochemical Society, Inc.

as: low 1st charge/discharge Coulombic efficiency and inability to sustain deep charge cycles due to severe changes in crystal structure where  $\text{Ni}^{2+}$  tended to relocate irreversibly to  $\text{Li}^+$  sites due to its similar atomic size (cation mixing).<sup>[4]</sup> The cation mixing effect severely deteriorated the rate performance of LNO. Moreover, the thermal stability of LNO was extremely poor and worse than LCO.<sup>[152]</sup> These problems effectively rendered it unusable for the industry.<sup>[41,153]</sup> Based on these problems, researchers abandoned the single metal LNO system and moved onto dual metal systems. Researchers discovered that if  $\text{Co}$ ,<sup>[154,155]</sup>  $\text{Al}$ ,<sup>[156]</sup> or  $\text{Mn}$ <sup>[155,157,158]</sup> was partially substituted for Ni in LNO, the cation mixing between  $\text{Ni}^{2+}$  and  $\text{Li}^+$  was reduced and the irreversible crystal structure transitions experienced at deep charges was prevented, resulting in enhanced cyclability and capacity. In terms of safety, a standard safety test for next-gen metal oxide based cathode had become dynamic scanning calorimetry, where the thermal stability was quantified by its decomposition temperatures. Researchers found that the onset temperature of thermal decomposition of LNO mixed with any of the three metals was delayed compared to LNO and LCO.<sup>[159]</sup> It was recognized that the incorporations of any singular selection of these three metals with Ni clearly offered substantial but distinct benefits. For example, the incorporation of Mn indeed enhanced thermal stability and cycle stability,<sup>[160]</sup> but the practical reversible capacity was low<sup>[161]</sup> and the synthesis of  $\text{LiNi}_{1-x}\text{Mn}_x\text{O}_2$  ( $0 < x < 1$ ) was rather difficult to achieve.<sup>[162]</sup> Similarly, though improvements on thermal stability from adding Al was apparent, it was not as beneficial as the other metals in preventing the migration of  $\text{Ni}^{2+}$  to vacated  $\text{Li}^+$  sites resulting in a large initial irreversible capacity and poor rate performances.<sup>[163]</sup> Finally, the mixing of Co with Ni undeniably prevented the migration of  $\text{Ni}^{2+}$  but still possessed a strong exothermic reaction peak upon heating to higher temperatures and did not satisfy thermal stability concerns.<sup>[159,164]</sup> It was clear that the mixing of only a singular selection of metal was insufficient, thus researchers began to simultaneously substitute two different metals for Ni forming a ternary layered metal oxide and found synergistic effects.<sup>[165]</sup> One of the most common mix of metals of commercial relevance was the ternary NMC system. First invented and patent filed at 2001 (2004 granted) by researchers at Argonne National Laboratories,<sup>[166]</sup> the NMC system is the most widely used lithium-ion battery in EVs. The main benefits of NMC were its increased capacity, high decomposition temperature, use of lower toxicity material and the reduced cost due to the substitution of both Co and Ni with cheap Mn. Initially, the cycle stability and electronic conductivity was lower than LCO and posed concerns for the commercial application of ternary metal oxides. However, drastic changes in performance were found when tuning the ratio between the three metals and led to intensive research into finding the best mix between the metals. Each metal had a different role in NMC, Ni was responsible for providing capacity as it was oxidized from  $\text{Ni}^{2+} \rightarrow \text{Ni}^{3+} \rightarrow \text{Ni}^{4+}$ ,<sup>[167]</sup> while  $\text{Mn}^{4+}$  was not electrochemically active but maintained the structural stability and lowered the cost.<sup>[168]</sup> Co was oxidized from  $\text{Co}^{2+} \rightarrow \text{Co}^{3+}$  after the oxidation of  $\text{Ni}^{2+}$  and prevented the Ni from migrating in the Li sites. Research on NMC cathode began with low Ni ratios. In 2001 Ohzuku and Makimura synthesized and tested  $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ <sup>[169]</sup> while in the same

year, Dahn and co-workers<sup>[170]</sup> investigated  $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$  ( $x = 0.25$  and  $0.375$ ), the work from both of these groups introduced the NMC class of material to the battery field. All ratios demonstrated reasonably high capacities ( $>150 \text{ mAh g}^{-1}$ ), good cycle stability (depending on the charge cut off voltage<sup>[150]</sup>) and enhanced thermal stability.<sup>[171]</sup> NMC with  $x = 1/3$  has exhibited inferior rate performances due to the lower Li-ion diffusion compared to LCO and was often blended with the safer, higher rate performance and cheaper LMO. This blend of NMC–LMO has become a very popular cathode material among researchers and industry as the LMO provided extra safety to the system, in addition to lowering the cost and increasing the power density.<sup>[136,172]</sup> In 2011, Z. Li and Whittingham<sup>[173]</sup> sought to find an optimal NMC ratio, testing NMC 333, 442, and 992. Compared to NMC 333, NMC 442 possessed a higher capacity at low currents and comparable capacities at higher currents while reducing cost (lowered Co content from 33% to 20%). NMC 992 was found to possess significantly poorer capacity at high discharge rates and was less stable. In general, it was realized that the higher the Ni content in the cell, the higher the intrinsic specific capacity but at a cost of poorer stability and rate performance.<sup>[174]</sup> Specifically, NMC materials with Ni content  $>50\%$  (known as Ni-rich compounds) were particularly problematic.

Ni-rich cathodes can almost be considered as another class of layered cathode material. While Ni-rich compounds were theoretically denser in energy and cheaper (lower Co content), they were usually problematic to implement due to safety and cycle stability concerns. The relationship of Ni content on thermal stability and oxygen gas generation is shown in **Figure 10a**. Following the convention: NMC 433 (4-Ni:3-Mn:3-Co molar ratio), the ratio with the least amount of Ni exhibited the least amount of gas generation and at a higher decomposition initiation temperature. Every subsequent increase in Ni content noticeably decreased the onset temperature for phase change from the original layered to spinel structure and rock salt which sped up the overall degradation phase transformation process.<sup>[174,175]</sup> Additionally, the higher Ni content and reduced Co content promoted the irreversible migration of  $\text{Ni}^{2+}$  to  $\text{Li}^+$  sites<sup>[176]</sup> which severely hindered  $\text{Li}^+$  transfer throughout the structure of the NMC particle and increased the overall cell impedance.<sup>[177]</sup> Though the exact mechanism that caused these detrimental effects were not fully understood, it was clear that the combining effect of phase transition and impedance increase resulted in poorer cycle performance at higher Ni contents. A comprehensive relationship between Ni content, specific capacity, cycle stability and thermal stability is shown in **Figure 10b**. Very recently, based on density functional theory, researchers concluded that more  $\text{Ni}^{4+}$  are present in Ni-rich materials which readily oxidizes the electrolyte and oxygen ions due to its relatively low LUMO which promoted oxygen generation and electrolyte decomposition.<sup>[178]</sup>

Strategies to achieve viable Ni-rich NMC materials typically revolved around preventing the transformation of the NMC layered phase. Yang and Xia have demonstrated that doping with  $\text{Li}_2\text{MnO}_3$  can suppress the phase transition.<sup>[183]</sup> Adopting a more morphological themed approach, researchers at ANL developed the now popular strategy coating of less reactive (lower Ni content) NMC or other cathode materials over a Ni-rich particle (core-shell structure) which required specific



**Figure 10.** a) The dependence of thermal stability in gas evolution on Ni content in NMC. Reproduced with permission.<sup>[175]</sup> Copyright 2014 American Chemical Society. b) The dependence of Ni content on discharge capacity and capacity retention and thermal stability in NMC. Reproduced with permission.<sup>[179]</sup> Copyright 2013, Elsevier. c) Schematic of storage side reactions of Ni-rich cathode materials and d) the corresponding SEM image before (left) and after (right) storage. Reproduced with permission.<sup>[180]</sup> Copyright 2016, Royal Society of Chemistry. e) Thermal stability in W g<sup>-1</sup> of various Ni compositions in NMC. Reproduced with permission.<sup>[181]</sup> Copyright 2007, Electrochemical Society, Inc. f) Thermal stability of regular NCA and modified NCA (Ni:Co:Al = 0.8:0.15:0.05). Reproduced with permission.<sup>[182]</sup> Copyright 2017, American Chemical Society. All thermal stabilities measurements were conducted after charging to 4.3 V.

expertise for precisely controlling the coverage.<sup>[184–186]</sup> This strategy mitigates the surface exposure of high Ni-content NMC to the electrolyte which is the main interface where undesired reactions occurs. However, the key disadvantage of this strategy

is the mismatch in volume change between the core and shell material cutting off charge transfer pathways.<sup>[185]</sup> This phenomenon is the main reason for the cycle degradation of core shell Ni-rich structures. Building upon this work, in 2009 ANL has created what is called a concentration gradient shell (CGS).<sup>[187]</sup> CGS uses a shell that consisted of a Ni concentration gradient with the Ni-content highest near the center and lowest at the surface covering a Ni-rich core. This material was synthesized by simply precipitating NMC with progressively lower Ni content onto a Ni-rich core (substrate). Such a strategy has been shown to completely eliminate the structural mismatched generated in the core-shell strategy but tended to degrade due to migration of Ni content toward the surface.<sup>[188]</sup> Further advancement in this technology created what is known as the full concentration gradient (FCG)<sup>[189]</sup> where the Ni and Mn concentrations varied all the way from the core to the surface which further led to the two-sloped full concentration gradient (TSFCG)<sup>[190]</sup> where a smooth concentration profile of Ni, Co and Mn was created from the core to near the surface with an abrupt concentration change near the surface. Both FCG and TSFCG offered substantially higher performance benefits over the CGS materials, with the TSFCG material demonstrating excellent stability over 500 cycles in a full cell configuration (Si-based anode) delivering 350 Wh kg<sup>-1</sup> on the first cycle.<sup>[190]</sup> Initially, the lower Ni- content NMC have found significant application in the industry, representing ≈26% by mass of all battery cathodes<sup>[55]</sup> sold in 2016 and has become by far the most popular cathode material for EVs. Currently, NMC 333 and 532 represents a large portion of the NMC market with NMC 622 and 811 still at minority,<sup>[55]</sup> but higher Ni content cathodes are expected to be more and more prevalent in the near future.<sup>[191]</sup>

In addition to Ni-rich NMC, another Ni-rich ternary metal cathode material was the NCA system. NCA was slightly better than Ni-rich NMC in terms of energy density but had a slightly lower discharge voltage due to slightly different active redox pairs.<sup>[192]</sup> The first appearance of the NCA system was in 2001 by Lee and co-workers<sup>[193]</sup> and has become a very popular cathode material with Panasonic implementing it in the Tesla vehicles.<sup>[111,194]</sup> The most popular mix was: LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub> and has been known colloquially among industry and researchers as NCA.<sup>[195]</sup> One should note that NCA incorporates relatively low level of its third metal (Al at 5–10%), much lower than the Mn in NMC (10–40%). This was because the use of higher levels

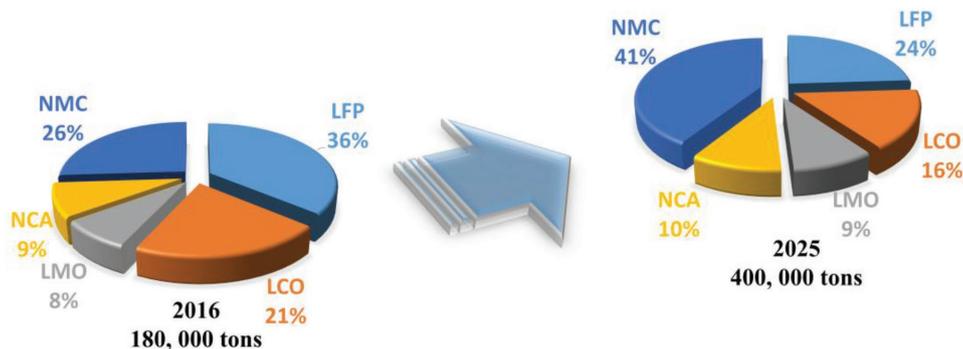
of Al (>10%) resulted in severe capacity decay and poor Li<sup>+</sup> ion diffusion throughout its structure.<sup>[159,165]</sup> Because NCA can only operate acceptably at low Al content, all metal ratios of NCA are usually considered Ni-rich and also suffers from the corresponding disadvantages. A common problem between all Ni-rich is the chemical sensitivity of Ni<sup>3+</sup> which along with residual excess Li (from its lithiation manufacturing steps) promotes adsorption of moisture and CO<sub>2</sub> forming LiOH and Li<sub>2</sub>CO<sub>3</sub> (schematically shown in Figure 10c and experimentally in Figure 10d) which has been shown to limit cycle life. During storage in ambient air, the surface Ni-ions reacts with CO<sub>2</sub> and moisture forming insulating layers on its surface.<sup>[180]</sup> Furthermore, similar to the Ni-rich NMC cathode, the Ni cation in NCA is known to dissolve into the electrolyte due to the HF created by the reaction between LiPF<sub>6</sub> (electrolyte salt) with trace amounts of water.<sup>[150]</sup> This phenomenon decayed the cathode and had very recently led material scientists to apply more resistive coatings composed of ZnO,<sup>[195]</sup> FePO<sub>4</sub>,<sup>[196]</sup> Li<sub>3</sub>PO<sub>4</sub>,<sup>[197]</sup> AlPO<sub>4</sub>,<sup>[198]</sup> LiMnPO<sub>4</sub><sup>[199]</sup> among many other similar concepts from work done on surface coatings for NMC. Al offered good thermal stability compared to LCO and LNO but still underwent severe exothermic reactions at higher temperatures (200–250 °C) when NCA was at its delithiated state.<sup>[182,200]</sup> The thermal stability of NCA was inferior to NMC 333<sup>[192]</sup> due to the higher Ni content which rendered it problematic for commercial use. However, when compared to NMC 811, the thermal stability of NCA was far superior. As shown in Figure 10e, thermal decomposition of NMC 811 began to occur at ≈190 °C and peaked at ≈220 °C releasing 3285 J g<sup>-1</sup>. For NCA, the thermal decomposition began to increase at ≈200 °C peaking at ≈239 °C and only released 1573 J g<sup>-1</sup> (Figure 10f). Besides Panasonic/Tesla Inc., no other EV company uses a pure NCA cathode, but Automotive Energy Supply Corporation (AESC) does supply NCA mixed with LMO cathodes for the Nissan Leaf EV.<sup>[136]</sup> In 2016, NCA only occupied ≈9% (16 200 tons) of all battery cathode materials sold (180 000 tons) and is forecasted to reach about 40 000 tons (10%) in 2025 if Tesla Inc. continues to incorporate NCA into their cathodes.<sup>[55]</sup>

### 3.3. The Current Status of Electric Vehicles and Lithium-Ion Batteries

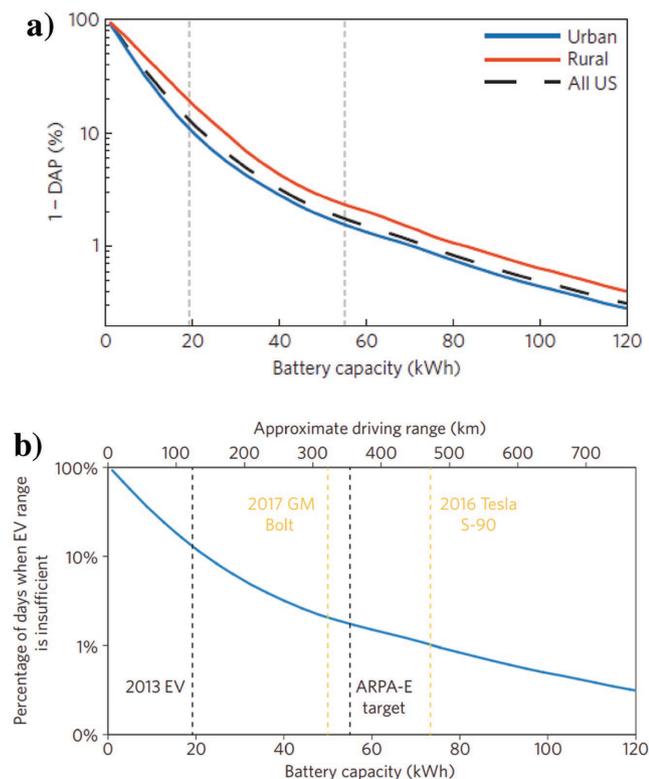
It is typically recognized that materials with <60% Ni content have been fully commercialized while >80% is still under

develop.<sup>[201]</sup> Overall, the commercialization of Ni-based layered oxide cathode materials (NMC and NCA) has been quite successful, representing a total of 35% of the battery market in 2016 (Figure 11) and instrumental in improving the range and cost of EVs. From its early stage at the Electric Vehicle Company (2000 units sold), to the current increase in interest by almost all automotive companies, the incorporation of these new cathodes had undoubtedly made an impact on the commercialization of xEVs. The market penetration of xEVs increased drastically over the recent years. Just in the year of 2014, the total sales of xEVs have reached 320 000 vehicles with over half being pure EVs (182 400 vehicles). Although this only represented 0.3% of all passenger vehicles sold during this time span, it was orders of magnitude higher than the EVs sold in the past decades.<sup>[202]</sup> Companies such as Toyota, Honda, GM, Tesla Inc. have heavily invested in a xEV based future. Volvo Cars have even recently announced that they will be looking to completely electrify (either EV or hybrid) its passenger vehicles line by 2019.<sup>[203]</sup> Several European countries have set goals to eliminate the internal combustion engine by 2040.<sup>[204]</sup> With a global market size of >\$2.4 billion in 2011, >\$8.9 billion in 2015, and a forecasted >\$14 billion by 2020,<sup>[205]</sup> it is now hard to imagine a future society without EVs. However, there is still much room for improvement.

The energy density requirements of EVs have always been a topic of much discussion. While it played a crucial role in the development of LIBs it appears that the current driving range for even pure EVs are approaching satisfactory levels for the consumer. The energy density targets (volume and mass basis) have nearly been reached by current LIBs. Cell-level volumetric energy density was targeted at 750 Wh L<sup>-1</sup><sup>[206]</sup> and the state-of-the-art high tension cylindrical 18650 cells for Tesla Inc. are already at 600–650 Wh L<sup>-1</sup> (20% less for pouch and prismatic cell configurations).<sup>[207]</sup> Cell-level gravimetric energy density of current LIBs (248 Wh kg<sup>-1</sup> in Tesla Model S 2014<sup>[136]</sup>) are reasonably close to the targeted 350 Wh kg<sup>-1</sup>.<sup>[206]</sup> A study was conducted by Needell et al. on the impact of higher range EVs where they proposed the metric: daily vehicle adsorption potential (DAP) as shown in Figure 12a.<sup>[208]</sup> The DAP is defined as the % of days that a pure-EV would not be able to make the driver's daily trips on a single charge. Inversely, 1-DAP represents the % of days that drivers of EVs will be required to recharge within the day. Shown in Figure 12b, in 2013, the 1-DAP of the Nissan Leaf (88 Wh kg<sup>-1</sup>) was about 10%. This means that in 2013,



**Figure 11.** Mass percent of all LIBs market shares of the leading materials in 2016 and forecasted to 2025.<sup>[55]</sup>

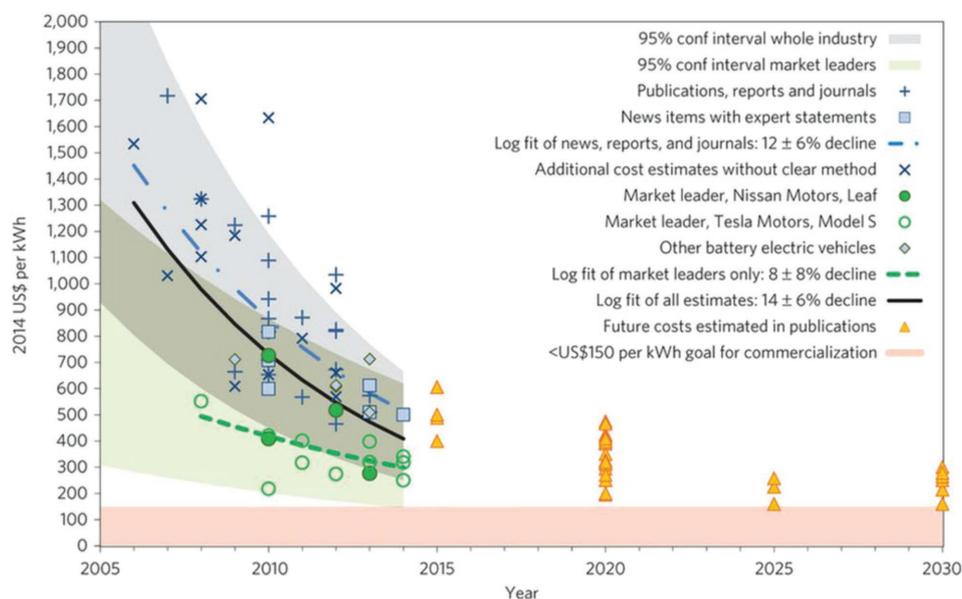


**Figure 12.** a) Impact of the type of driving (urban, rural) in the US on the 1-DAP value. Reproduced with permission.<sup>[208]</sup> Copyright 2016, Springer Nature. b) Relationship between the % of days when the EV range is insufficient (1-DAP) versus the battery capacity and the range with 2013 EV (Nissan Leaf @ 88 Wh kg<sup>-1</sup>) and 2016 Tesla Model S-90 labeled on graph. Reproduced with permission.<sup>[211]</sup> Copyright 2016, Springer Nature.

around 10% of the time the drivers will not be able to return home without requiring a recharge. The 2016 Tesla Model S-90 has a 1-DAP of only about 1–2%. It was argued that such a low percentage of 1-DAP is already sufficient for the widespread adoption of EVs into the markets for that specific geographical location of study. While the exact implications on the EV market penetration of a 1-DAP value of 1% are subjective without any concrete input from the consumers, it is still quite surprising that future solutions to the very popular problem of energy density will most likely experience diminishing returns. This suggests that the most important challenge for the electrification of transportation is probably not its energy density (albeit still important for other LIB applications), but instead the cost of LIBs. However, it should be noted that the cost and energy density are intrinsically related. This is because higher energy density electrode requires less active material and therefore, lowering the cost of manufacturing. Nevertheless, the cost targets of <150 US\$ kWh<sup>-1</sup> for battery packs<sup>[206,209,210]</sup> have yet to be met by any of the battery manufacturing companies.

The cumulative cost benefits thus far of these new cathode and anode materials can perhaps be summarized in the modeled cost of productions by the US Department of Energy (DOE), Vehicle Technologies Office. Over a 7-year span, the modeled cost has decreased ≈70% to ≈268 US\$ kWh<sup>-1</sup> (2015).<sup>[212]</sup> While there are still a large volume of estimates from literature that ranges from 1700 to 1000 US\$ (YR:2014) as summarized by Nykvist in Figure 13a, there were a number of corroborating optimistic estimates claiming ≈220–400 US\$ (YR:2014) kWh<sup>-1</sup> (Figure 13b)<sup>[209]</sup> and 250 US\$ kWh<sup>-1</sup> in 2015.<sup>[55]</sup>

Reported in 2014 by Advanced Automotive Batteries (data presented in Table 2), the main battery technologies used in EVs were NCA, NMC, and LMO usually blended with NCA or NMC due to LMO's low specific capacity.<sup>[111]</sup> LFP is currently



**Figure 13.** Estimated cost of battery packs in 214 US\$ kWh<sup>-1</sup> from 2005 to 2014 and forecasts to 2030. Reproduced with permission.<sup>[209]</sup> Copyright 2015, Springer Nature.

**Table 2.** List of battery company, their vehicle of application, and battery material.<sup>[111]</sup>

Battery company	Vehicle of application [company/model]	Battery material [anode  cathode]
AESC	Nissan/Leaf	Graphite  LMO-NCA
LG Chem	Renault/Zoe	Graphite  NMC-LMO
Li-Tec	Daimler/Smart	Graphite  NMC
Li Energy Japan	Mitsubishi/i-MiEV	Graphite  LMO-NMC
Samsung	Fiat/500	Graphite  NMC-LMO
Lishen Tianjin	Coda/EV	Graphite  LFP
Toshiba	Honda/Fit	LTO  NMC
Panasonic	Tesla/Model S	Graphite  NCA

a very popular cathode material for BYD Auto, a major EV producer in China.<sup>[191]</sup> In contrast to the wide selection of cathode technologies, the anode of choice for passenger xEVs remains to be carbon based with only Toshiba among the shown companies utilizing LTO as the anode. LTO has found more application in the electric bus market with companies such as Microvast demonstrating significant interest in the safety aspect of this technology.<sup>[213]</sup> Interestingly, there are no reported use of LCO in any of the EVs, possibly suggesting that the cost benefits of adding the allegedly cheaper low-Co cathodes should have already been reflected in the price of EVs. This implies that most recent cost reduction were achieved solely through process optimization such as the current movement away from the 18 650 cylindrical cells to the 21 700 format.<sup>[214]</sup> Estimates from industry, when maintaining the use of NMC cathode material, there was still a substantial drop in the cost of cathode from  $\approx 64$  to  $\approx 40$  US\$ kWh<sup>-1</sup> in the time frame of 2010–2015 which was due to the increased NMC production efficiency.<sup>[55]</sup> Cost reductions were also experienced in the separator, electrolyte, anode technologies, and from economies of scale (recycling, overhead, utilities) even though the same base materials were used. However, without another major change in materials, these cost reductions were ultimately limited as reflected in the asymptotic approach to 150 US\$ kWh<sup>-1</sup> of forecasted cost curves (Figure 13b,d). Furthermore, since the costs of nickel and cobalt are quite volatile (Co increased from  $\approx 15$  US\$ lb<sup>-1</sup> in 2005 to 52 US\$ lb<sup>-1</sup> in 2007 and recent increases from  $\approx 10$  US\$ lb<sup>-1</sup> in 2015 to  $\approx 27$  US\$ lb<sup>-1</sup> in 2017)<sup>[210]</sup> the marginally acceptable forecasted prices could be easily invalidated. In addition to the simple cost of raw material, the safety concerns could also have severe monetary penalties for battery manufacturers. In 2006, Sony's recall of its LIB in laptops have resulted in a 40% loss that year in their battery business.<sup>[55]</sup> After lacking a sufficient recovery, Sony has recently sold its battery business to Murata in 2016 which could be an indication of the financial severity of a recall.<sup>[215]</sup>

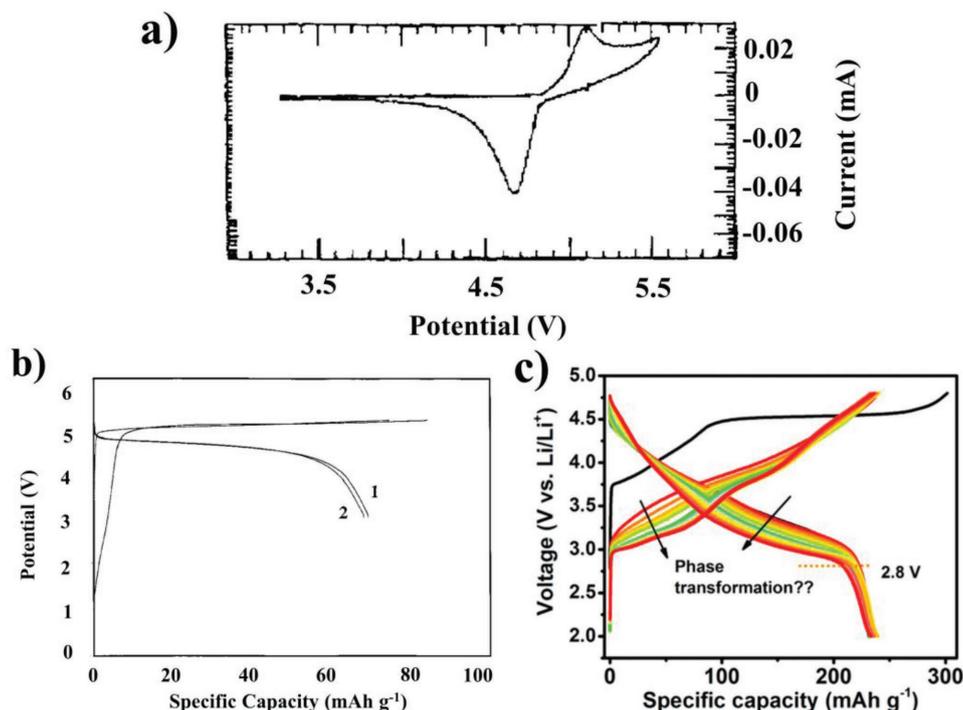
#### 4. Next-Generation Li-Ion Battery Research

Next generation Li-ion battery technologies with potentially huge cost and performance benefits could be the answer to

reaching the cost and energy density targets. Systems such as Li- and Mn-rich cathodes, 5 V cathodes, and silicon anode have been extensively researched.

5 V cathode materials were considered as a potential candidate for “next-generation” LIBs. This class of material includes the spinel LiMn<sub>1.5</sub>Ni<sub>0.5</sub>O<sub>4</sub> (published by Dahn in 1997<sup>[216]</sup> and patent filed in 1997 by Amine et al.<sup>[217]</sup>), inverse spinel LiNiVO<sub>4</sub> (Dahn and co-workers in 1994)<sup>[218]</sup> and the olivine LiCoPO<sub>4</sub> (by Amine in 2000)<sup>[219]</sup> among others which all possessed an extremely high discharge voltage profile of  $>4.5$  V versus Li/Li<sup>+</sup> as shown in the cyclic voltammetry (Figure 14a) and charge/discharge voltage profiles (Figure 14b). As the energy density is a product of capacity and discharge voltage, this class of material is envisioned to achieve energy densities well above 400 Wh kg<sup>-1</sup>. One of the main problems associated such high voltage cathode is the oxidation of the electrolyte. Traditional carbonate-based electrolytes cannot withstand potentials higher than 4.3 V vs Li/Li<sup>+</sup> and will be oxidized if used with 5 V cathodes. Accordingly, researchers have employed more anodically stable electrolytes such as ionic liquids, sulfones, nitrile, carbonates derivatives, and carbonates with additives.<sup>[220]</sup> Additional problems with 5 V cathodes were unique to the type of the material but similar to its parental archetype. For example, similar to the spinel LiMn<sub>2</sub>O<sub>4</sub>, Mn<sup>2+</sup> dissolution is a concern for the spinel LiMn<sub>1.5</sub>Ni<sub>0.5</sub>O<sub>4</sub> cathode especially at high temperatures<sup>[221]</sup> while the LiCoPO<sub>4</sub> olivine cathode also suffers from poor electronic conductivity much like the olivine LFP.<sup>[222]</sup> Although the nature of the problems and solutions were similar to its parental archetype,<sup>[223]</sup> the 5 V cathode materials have yet make it to market.

Another class of material that also employs high voltages is the Li- and Mn-rich (LMR) cathode or sometimes known as layer-layered/layered-spinel material. Pioneered at ANL, the concept was to substitute entire crystal units rather than just cations.<sup>[225]</sup> Versions of this material composed of a layered *R-3m* structured LiMO<sub>2</sub> (where typically M = Ni) stabilized by a *C2/m* structured monoclinic Li<sub>2</sub>MnO<sub>3</sub>. Together, this combination was often written as  $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$  where  $0 < x < 1$ .<sup>[134,226]</sup> The first patent on LMR was filed by Thackeray and Amine in 2001<sup>[166]</sup> and later published by Lu and Dahn in 2001,<sup>[157]</sup> which demonstrated a reversible capacity of  $\approx 200$  mAh g<sup>-1</sup> for 50 cycles at 55 °C from 4.6 to 2.0 V versus Li/Li<sup>+</sup>. In addition to a high theoretical specific energy ( $\approx 900$  Wh kg<sup>-1</sup>), the cost benefits of completely removing Co makes this material quite attractive. Unfortunately, this material is still far from commercialization. The initial promises of LMR were met with severe performance challenges. These performance hurdles were due to the LMR's high voltage (up to 4.6–4.8 V vs Li/Li<sup>+</sup>) charging requirements in order to “activate” the Li<sub>2</sub>MnO<sub>3</sub> component and realize its high capacity.<sup>[227]</sup> There were many ensuing issues that are involved in this process: 1) This voltage range is beyond the stability window of the typically used electrolyte. 2) The transformation of the crystal structure on the surface of LMR particles<sup>[228]</sup> forms what is known as the surface reconstruction layer which limited Li-ion diffusion. This layer was formed during the activation process of Li<sub>2</sub>MnO<sub>3</sub>, where oxygen atoms are irreversibly removed.<sup>[229]</sup> Without oxygen atoms, the destabilized Ni-ions irreversibly migrates to vacant Li-ion sites.<sup>[230]</sup> The result was a spinel-like layer situated



**Figure 14.** a) Cyclic voltammety and b) charge discharge profile (1st and 2nd cycle) of the 5 V cathode. Reproduced with permission.<sup>[219]</sup> Copyright 2000, Electrochemical Society, Inc. c) Charge/discharge profiles of LMR, demonstrating its characteristic voltage fade problem. Reproduced with permission.<sup>[224]</sup> Copyright 2015, American Chemical Society.

between a rock-salt-like outer layer and the original LMR layered structure in the bulk.<sup>[134]</sup> 3) The removed oxygen tends to react continuously with the electrolyte forming an evergrowing SEI layer over LMR. The combination of the surface reconstruction layer and the continuous SEI formation ultimately leads to severe voltage decay. This lead to the interesting situation where the capacity might exhibit relatively high stability but both the charge and discharge voltage profile drops significantly as presented by Zheng et al.<sup>[224]</sup> as shown in Figure 14c. The first cycle Coulombic efficiency was found to be very low which was associated with the high charging voltage activation process. The activation process for LMR contains a large portions of irreversible capacity which made it problematic for pairing electrodes in a full-cell.<sup>[231]</sup> The final problem of LMR cathode stems from its relatively poor conductivity which results in rate performances inferior to that of commercial cathodes (NMC, NCA, etc.).<sup>[232]</sup>

Proposed mitigation strategies for the problems of the 5 V cathode and LMR were both very similar to the methodologies taken in Ni-rich field of research. By applying a surface coating of various materials,<sup>[134,224,233]</sup> the direct contact between LMR and the electrolyte is limited and so for the degree of SEI formation on the cathode. Techniques based more on solid state physics are also very popular. Lattice substitution for Al,<sup>[234]</sup> Mg,<sup>[235]</sup> Ti<sup>[236]</sup> among other elements can help to prevent the phase changes, limiting voltage decay or improve the conductivity.<sup>[237]</sup> Though scientifically insightful, most of the reported lab scale tests cannot be scaled to the commercial level. Accordingly, the 5 V spinel and LMR class of cathodes have yet to find commercial application. Researchers have even

combined the  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_2$  with the LMR system, known as the integrated layered-spinel structure.<sup>[238]</sup> First proposed by Park and Thackeray in 2006,<sup>[238a]</sup> this combines the benefit of the high capacity of LMR with the fast lithium diffusion of the spinel structure.

Alloy based anodes<sup>[239]</sup> such as Ge,<sup>[240]</sup> Sn,<sup>[241]</sup> and especially Si has recently drawn much renewed attention most likely due to the onset of research into nanotechnology. Early on (prior to 1976), these alloy-based anodes have already been researched as a potential replacement to the unstable and dangerous pure Li anode.<sup>[242]</sup> The problem with alloy based anodes is the enormous volume expansion upon lithiation (>300% for Si) which cause severe electronic disconnections and promote continuous SEI formation. Strategies adopting nanowire structures<sup>[243]</sup> and nanoparticles<sup>[244]</sup> demonstrated enhanced utilization and stability of Si anode. To follow was an explosive research interest into the Si anode technology with focus surrounding the use of breathable conductive networks,<sup>[245]</sup> porous breathable Si morphologies,<sup>[246]</sup> Si dimensional control among other techniques.<sup>[247]</sup> It is also not necessary to fabricate an anode solely with Si as the active material, it is possible to blend Si with graphite or hard carbon to achieve a high capacity ( $700 \text{ mAh g}^{-1}$ ) without the severe cycle degradation for pure Si.<sup>[60]</sup> Often neglected in literature, the volume expansion will affect the volumetric capacity at the cell level.<sup>[248]</sup> With rumors describing Tesla Inc.'s incorporation of small amounts of Si (in the form of  $\text{SiO}_x$ ) into their anodes to boost energy density,<sup>[249]</sup> Si based anodes are arguably the most important next-gen anodes material,<sup>[206]</sup> but probably only certain configurations of Si anodes will be commercially viable. The commonly used

nanoparticles in literature will most likely pose severe challenges in achieving appropriate volumetric energy densities.

## 5. Future Perspectives

Throughout the years, the focus of research has switched from different lithium-based battery chemistries, involving many of the various sub disciplines of material science and electrochemistry. From our documentation of the historical development of LIB, it appears that many of the commercially successful materials (LCO, NMC) were mostly developed with strategies revolving around a more solid-state physic themed. Techniques such as changing the crystal structure or the substitution of one transition metal for another: Li-MnO<sub>2</sub> to LMO, LNO to NMC, and NCA enabled the commercialization of almost all the current LIB electrode technologies. After optimization of the crystal structure, a more morphological approach was taken in hopes of achieving greater performance. Some of these benefits were commercially realized in the case of reducing the size of LFP particles and the morphology of synthetic graphite (MCMB and MAG). Arguably, such precise control in material morphologies were made possible due to the numerous advancements in nanoscience. Researchers such as Besenhard in 1997 used these techniques to revisit concepts such as Li-alloy anodes (Sn) and provided encouraging results based on nanoparticles.<sup>[189]</sup> From the implementation of novel synthesis techniques to the application of advanced microscopy techniques for morphological and mechanistic confirmation, more and more nanotechnology terminologies such as core-shell,<sup>[184]</sup> surface coatings,<sup>[250]</sup> nanostructures, nanosized and nanoscale effect,<sup>[251]</sup> began to appear in cutting edge battery research literature. Previously abandoned chemistries such as conversion reaction based materials, lithium-sulfur battery, Si anode, lithium metal battery among others have once again resurfaced both academically and commercially (for Si) with a pronounced emphasis on nanotechnology.

From the groundbreaking research of nanowires for reducing the mechanical stress of Si anodes<sup>[252]</sup> to the polysulfide trapping capabilities of porous carbon with nanosized pores for S cathode,<sup>[253]</sup> it appears that the spark for many of these initially abandoned chemistries began specifically with nanotechnology. It seems that nanomaterials will play an instrumental role in battery science both practically and academically.<sup>[254]</sup> Interestingly, the improvement of the commercial Li-based batteries has not been as spectacular when compared to the volume of literature published regarding nanomaterials and LIBs. This is most likely due to two major pitfalls of modern battery research: nanomaterials and proper testing conditions. These two pitfalls have most likely led some researchers to overstate the importance of their work which resulted in a situation where the growth in the volume of literature for Li-based batteries is not necessarily reflected in the performances of commercial batteries. Much of recent papers on Li based battery research are composed of some form of materials engineering with testing conditions that are questionable for commercialization. Commonly overlooked factors such as electrolyte amount, electrode thickness, while not penalizing for publications, cannot be practically transferred to the more stringent commercial scale.

In the future, researchers must be quick to point out these factors such as those in the field of lithium sulfur battery. Though nanomaterial can offer valuable insight into the underlying natural phenomenon occurring, its role must be clearly understood by scientists. The low volumetric energy density,<sup>[255]</sup> and poor film forming abilities of nanoparticle<sup>[256]</sup> will undoubtedly complicate if not restrict its commercial scale-up. Fortunately, there are strategies that can be used to mitigate the disadvantages of nanomaterials. A common strategy implemented in Li-S battery entails the agglomeration of the nanosized sulfur host into micron sized secondary particles. This method will reduce the exposed surface area leading to ease of electrode fabrication while also increasing the packing density of the electrode.<sup>[256,257]</sup> Although some success has been found utilizing nanotechnologies, there is still much work to be done to bridge the gap between lab-scale and commercialization to enable next-gen performing Li-based batteries.

While there were many markets for LIBs after consumer electronics such as E-bikes and power tools, the next major challenge that dictated the research of LIBs was the xEV market. The simultaneous goals of high energy/power density, safety and lower cost have proved to be a challenging task for LIB battery scientists around the globe. In 2018, nearly 30 years after its initial commercialization, xEVs still only represent a fraction of the passenger market. Current technologies such as NMC, NCA, LMO, and LFP will continue to serve their respective roles in the xEV and asymptotically approach the cost and energy density targets if the support systems remain stagnant (cost of raw materials and government incentive programs). LIBs have enabled next-gen consumer electronics and currently, the status of LIBs could be described as: in progress of enabling xEVs.

xEVs are often considered green, but in reality it is only as green as its electricity source. If the electricity was generated from a coal plant, the use of xEV might contribute similar if not more CO<sub>2</sub> than an internal combustion engine. Therefore, grid-level energy storage systems (GESS) can be considered as another potential LIB application that is even more intimate to the energy problem than xEVs. The most detrimental problem with renewable energy source such as wind, hydro and solar are their intermittent nature which can be solved by GESS through buffering this intermittency. Smart grid is a proposed decentralized grid design that allows for the optimized scheduling (deployment, storage and demand response) of numerous different energy generation source (fossil fuel or renewables).<sup>[258]</sup> Such a grid design will facilitate the adaptation of renewable resource into the energy market and is crucial in combating against climate change.<sup>[259]</sup> This application of GEES has similar requirements to EVs such as energy efficiency, power density, low cost, high cyclability but less emphases are placed on safety and energy density.<sup>[260]</sup> While the development of LIB for EV is nearing 27 years (~1991 to present), its application in GESS will most likely take less time. LIBs based GESS such as the Tesla Powerwall have already been commercialized into what is known as a micro-grid (a decentralized energy storage concept) where relatively small size battery packs are installed directly into individual homes. As part of the bigger smart grid concept,<sup>[258]</sup> these small energy storage systems can be leveraged to buffer the

intermittent nature of household/government/corporate solar panels and wind turbines with technologies. Recently, a large-scale (100 mW powering over 30 000 homes) LIB based grid energy storage system was also delivered by Tesla Inc. to South Australia to act as the intermittency buffer of wind energy.<sup>[261]</sup> LIBs are quite competitive among other off-peak energy storage systems in terms of lifespan and power/energy densities. Of all its evaluation indices, the high cost of LIB have presented itself as the main problem against its widespread use in grid storage.<sup>[262]</sup> As one might notice, cost is also one of the underlying factors that is preventing the widespread commercialization of xEV. The implementation of LIBs for GESS will most likely follow shortly after, if not in-sync with the widespread adoption of xEV if the supply of raw materials can keep up with the large kWh demand required to have a presence in the GESS market.

There is currently a large concern on whether the estimated supply of Li is enough to support the inevitable demand for LIBs. LIB recycling has also become a popular field of research as it can at least partially alleviated the demand of LIB raw materials. Furthermore, though LIBs are considered a green energy technology, its main constituents are not. Co and Ni are toxic to the environment/humans<sup>[263]</sup> and the commonly used LiPF<sub>6</sub> salt in electrolytes are known to form HF when exposed to air.<sup>[264]</sup> The environment implications of LIBs waste will no doubt play a large regulatory role in the future of the LIBs industry. Fortunately, recent studies on LIBs recycling have already began looking into recycling the heavy metals in the cathode through chemical, bioleaching and physical methods.<sup>[265]</sup> These methods usually produces Co, Ni in its various compounds such as Ni(OH)<sub>2</sub> and even LiCoO<sub>2</sub> which could stand as a significant economic benefit for the manufacturers and made the entire LIB industry's material supply more manageable.<sup>[266]</sup> Alternatively, in anticipation for potential Li supply crisis, researchers have also begun to focus on non-Li based battery electrochemistries such as Na, K, Mg, Ca, and Al. Particularly, recent progress in Na-ion batteries could pose as a serious contender for grid level storage.<sup>[267]</sup>

The role that Li-based batteries played in revolutionizing consumer electronics and electric vehicles has been clearly indispensable and will probably continue to be so for the foreseeable future. The first commercialized LIB by Sony Co. in 1991 had its energy density as the main design criteria. Since consumer electronics were inherently somewhat of a luxury item, the cost was less important. Modern improvements into the consumer electronics LIB still holds to this theme while research into LIB for xEVs mandates cheaper cells. We hope this review have presented to the next generation of battery scientists and even veteran battery scientists with a comprehensive developmental history of Li-ion batteries. From its early lithium metal battery iterations to the current thriving LIB industry and now back to lithium metal-based batteries, the evolution of LIB has presented itself as a very interesting story driven by commercial demand. Indices such as energy density, cycle life, cost, and safety have very much dictated its evolutionary pathway. To ensure the longevity of the xEV market, significant progress must be made in the intrinsic battery chemistries of the electrodes.

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## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

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