



FOCUS ISSUE OF SELECTED PAPERS FROM IMLB 2016 WITH INVITED PAPERS CELEBRATING 25 YEARS OF LITHIUM ION BATTERIES

The Development and Future of Lithium Ion Batteries

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This year, the battery industry celebrates the 25th anniversary of the introduction of the lithium ion rechargeable battery by Sony Corporation. The discovery of the system dates back to earlier work by Asahi Kasei in Japan, which used a combination of lower temperature carbons for the negative electrode to prevent solvent degradation and lithium cobalt dioxide modified somewhat from Goodenough's earlier work. The development by Sony was carried out within a few years by bringing together technology in film coating from their magnetic tape division and electrochemical technology from their battery division. The past 25 years has shown rapid growth in the sales and in the benefits of lithium ion in comparison to all the earlier rechargeable battery systems. Recent work on new materials shows that there is a good likelihood that the lithium ion battery will continue to improve in cost, energy, safety and power capability and will be a formidable competitor for some years to come.

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Just 25 years ago (1991), Sony Corporation announced a new product called a lithium ion battery. This announcement followed on the heels of a product recall of phones using Moli Energy lithium/MoS₂ batteries because of a vent with flame causing injury to the user.¹ Sony (as well as a number of other companies) had been trying to develop a lithium metal battery with a manganese dioxide positive electrode, but had safety problems with this system as well. The author is familiar with these safety incidents because of his work at the same time at Energizer Research Laboratory with the Li/MnO₂ systems. Cells under test would show indications of dendritic lithium shorting (observed as negative voltage spikes during charge) followed by occasional and unpredictable cell explosions. The interest in lithium metal technology was due to the high specific energy and energy density of these cells. The improvement over previous aqueous systems was due to the high cell potential and low atomic weight of lithium compared to all other negative electrode materials that had been investigated. Other lithium batteries had been investigated – notably, the Li/TiS₂ system by the Exxon group, and the Li/NbSe₃ system by the Bell Laboratory group.² The Exxon system was plagued by safety problems and it was established that not only the lithium negative electrode was unsafe, but also the electrolyte, which was composed of LiClO₄ salt dissolved in an ether solvent (primarily dioxolane) was shock sensitive and liable to explode under sufficiently strong shock conditions. The cycle life was also very limited because of the poor recycling efficiency of the lithium electrode. Most studies utilized an excess of lithium metal in the cell to give an apparent improved efficiency, but when the excess lithium was used up, the capacity dropped rapidly with each cycle. This work with lithium, although unsuccessful, led to considerable learning about the process and material requirements. Secondary cells were found to be much more sensitive to impurities such as water in the electrolyte and the electrode materials. Also, the processing methods were found to be different from those of primary batteries. This work was helpful in developing the lithium ion battery to the excellent state of the present systems. This paper reviews the work in lithium metal batteries that led to the invention and development of the lithium ion system. The battery as first developed and as it exists today and finally discusses the shortcomings of the present system and likely improvements that will determine the future capabilities of the lithium ion battery. The development of entirely new systems such as other metal anodes, other insertion systems such as sodium ion batteries, gaseous or liquid cathode systems will not be considered here, but the reader must be aware that a different rechargeable battery concept has the potential to displace at least some of the lithium ion

battery applications due to higher energy, power, better safety or lower cost.

Early Lithium Ion Batteries

While Sony was clearly the first to manufacture and sell lithium ion batteries, a number of previous studies were prelude to the 1991 product. The idea of a battery in which the lithium ion moved reversibly between the positive and negative electrodes was first formulated by Armand in the late 1970s, using intercalation materials of different potentials for the two electrodes, and is often called a rocking chair battery because of the flow of lithium ions back and forward between the two electrodes.³ The idea was quickly taken up by Lazzari and Scrosati and implemented with a lithiated tungsten dioxide electrode and a titanium disulfide electrode.⁴ The potential range was only 0.8 to 2.1 volts and the electrodes both featured high molecular weights, but the important principle was established as the cell cycled for over 60 cycles although the charge voltage was limited to about 2.2 V and discharge to about 1.6 V.

A seminal discovery by the Goodenough laboratory⁵ was the ability of the family of lithiated transition metal oxides of the NaFeO₂ structure to reversibly deintercalate and reintercalate lithium ions at relatively high potentials (but voltage was limited to prevent electrolyte oxidation). Nickel and cobalt as well as mixtures of these with Mn, Al, Fe, etc. were all found to have this ability and the later adoption of this patented material (LiCoO₂) formed the active positive material of Sony's lithium ion battery. Slightly later, J. C. Hunter of the Eveready Laboratories⁶ discovered a new form of MnO₂, designated as the λ form, with a spinel structure, and prepared from LiMn₂O₄ (also a spinel form), that could be reversibly reduced and oxidized in a nonaqueous electrolyte at a high potential similar to that of LiCoO₂ with a similar capacity. This material was also later selected for a number of higher rate batteries for commercial applications.

The discovery of suitable negative electrode materials was somewhat more complicated than the positive electrode materials. Early work on graphite and carbonaceous materials had shown that lithium ions can be intercalated, the process was complicated by the co-intercalation of solvent molecules, during which solvent reduction and disruption of the carbon structure occurred.⁷ Early work on graphite electrodes, such as the early patent by Basu of Bell Laboratories,⁸ or Yazami of University of Grenoble,⁹ did not take this factor into account and would have been unsuccessful in practical batteries. An important finding by Fong, Von Sacken and Dahn, showed that petroleum coke was much better than graphite for resistance to solvent co-intercalation and reduction, while addition of ethylene carbonate to PC greatly improved the resistance on both graphite and petroleum coke.¹⁰ However,

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Yoshino and coworkers, from Asahi Kasei (a Japanese battery supplier of separators and electrolytes) had already described the benefits of lower temperature carbons such as petroleum coke in a seminal patent¹¹ that has resulted in identifying Yoshino as the true inventor of the lithium ion battery. In this patent the combination of lower temperature cokes (calcination temperature preferably between 800 and 1600°C and a formula involving the L_c and ρ X-ray parameters) and a LiCoO_2 material slightly modified from that suggested by Goodenough. The commercial cokes used by the Dahn group were heat treated at approximately 1300°C, and therefore were comparable to those used by Yoshino et al., and the reversible capacities of the cokes cycled at low rates were only half that of the graphite (x in Li_xC_6 was 0.5 for coke and 1.0 for graphite). Because Yoshino et al. used pure starting materials, rather than petroleum in most instances, the purity of the coke was much higher than those used by Dahn's group. A further difference in the two studies was the salt used in the electrolytes. Dahn's group used LiAsF_6 , which had been found by numerous workers to be one of the best electrolyte salts for secondary lithium metal batteries, but Yoshino et al. used LiClO_4 , LiBF_4 , and LiPF_6 , which were in common usage in Japan for primary lithium metal batteries in Japan. Yoshino et al. also studied various binders including polymethylmethacrylate, polyvinylidene fluoride, and various elastomers, while the Dahn group used only ethylene propylene diene monomer (EPDM) which had been used extensively for secondary lithium metal batteries. The Dahn group tested the carbonaceous positive electrode against lithium instead of a metal oxide. Therefore, they did not observe the severe corrosion of an aluminum positive electrode carrier with the LiAsF_6 electrolyte. The author observed such corrosion in full cell experiments with (Cu-C/ LiCoO_2 -Al) cells in later experiments that would have obviated the use of that salt in full cells.¹² Finally, the separators used by the Dahn group were all of microporous polypropylene, while Yoshino et al. recommended a microporous polyolefin separator and frequently employed polyethylene rather than polypropylene. Asahi Kasei has published an internet profile of Dr. Yoshino and his work on lithium ion batteries which includes much of this early work.¹³ Asahi Kasei later formed a joint venture to create A&T Battery Corp. to make lithium ion batteries. A&T now operates as a subsidiary company within Toshiba.

While the main elements of a lithium ion battery were laid out by Yoshino et al., there were many studies required to make a truly commercial battery with superior properties compared to nickel cadmium and the newly discovered nickel metal hydride batteries. The need was great, because of the deficiencies of these earlier batteries, particularly the memory effect, low specific energy, poor charge retention and environmental problems with the cadmium system.¹⁴ Also, the electronics industry was rapidly developing, particularly in the so-called 3Cs of computations, communication and cameras. Sony was a leading company in consumer electronics and had shown a willingness to bring out inventive new products that had no previous market. Sony was a relative newcomer to the battery business, learning the alkaline primary cell technology and business via a joint venture with Union Carbide Battery Products Division, but severed the arrangement in 1986 and began work in earnest on rechargeable batteries.¹⁵ Some of the main elements of the Sony development have been discussed by Yoshio Nishi^{16,17} (an expert in electrolytes and carbon materials in batteries) and Kazunori Ozawa¹⁸ (a coating expert brought in from the magnetic tape division to oversee the electrode development).

The initial development utilized a low temperature coke (1200°C heat-treatment temperature) for the negative electrode because of the good stability with electrolytes, even though the specific capacity was low.¹⁷ For a second generation negative electrode, a hard carbon (initially prepared from polyfurfuryl alcohol) with higher specific capacity was substituted for the coke.^{17,19} Hard carbon negative has a sloping discharge curve, but has higher specific energy than coke, good safety and better rate capability than many cokes.^{17,20} A still later development was the now commonly used mesophase carbon microbeads (MCMB). This type of carbon is prepared by heat treating a precursor material commonly used to make artificial graphite (such as petroleum pitch) to a moderate temperature such as 400°C, causing

a mesophase of spherical particles to form, quenching to a lower temperature to stabilize the mesophase particles and extracting the isotropic material surrounding the spheres. The collection of particles is then reheated at a higher temperature to improve graphitization. MCMBs have proven to have excellent properties for many lithium ion batteries (especially those heat treated at high temperature - 2600°C - with near spherical shape, and thus low surface area compared to particle size, and high degree of graphitization) which gave a still higher specific capacity and a flat discharge profile.¹⁹ The positive electrode material, LiCoO_2 , was carefully designed to have coarser particle size and good crystallinity. Work with smaller particle size led to safety concerns. The process involved granulating PVA, Co_3O_4 , and excess Li_2CO_3 and calcining in air with a fixed CO_2 content.¹⁷ While a commercial polyvinylidene fluoride (PVDF) was used initially, a lack of adherence of the positive electrode material was discovered shortly before introduction of the product. A crash project with Kureha Chemical Ind. Co. developed an improved material by grafting carboxylic acid anhydride onto the PVDF giving greatly improved adhesion to the Al carrier foil.¹⁷ Ozawa¹⁸ mentions the capability of Sony in producing magnetic tape as helpful in manufacturing the coated electrodes. There is no doubt that part of this experience involved the use of excellent production coating machinery, but, as confirmed by Toru Nagaura,²¹ one of the key engineers on the project, the particular kind of high energy mixing of the coating slurry was also of great importance. Ozawa also mentions that nickel coated iron cans were critical to the success of the project because stainless cans originally selected because of the presence of trace amounts of HF, was found to have too high resistance for the applications envisioned. The separator selected was a biaxially stretched microporous polyethylene material.¹⁶ The cell size selected was 18650 (following the adopted nomenclature for cylindrical lithium primary cells, the first two numbers represent the diameter in mm and the remaining numbers represent the height of the cell in tenths of mm - thus the common 2016 coin cell is 20 mm diameter and 16 tenths of mm in height). This choice is close to the volume of subC rechargeable nickel based batteries, the most popular size at the time for small electronic devices, (17.9 cm³ for subC and 16.5 cm³ for 18650 size) and unique to lithium ion so that a 1.2 V NiCd or NIMH cell could not replace the lithium ion cell nor *visa versa*. The electrolyte chosen was ethylene carbonate with a linear dialkyl carbonate, much like the presently used dimethyl carbonate and diethyl carbonate and the salt was LiPF_6 of high purity and state of dryness.¹⁸ This all carbonate solvent had the important property of oxidation resistance up to about 4.5 V. Subsequent improvements in electrolyte have mostly involved the use of additives to improve the passivating film on the negative material, improve the oxidation stability of electrolyte to the positive active material and in some cases reduce the flammability of the electrolyte.

The original Sony product with coke negative had energy density of 200 Wh/l and specific energy of 80 Wh/kg with a charge limitation of 4.1 V. The cell with hard carbon negative had 295 Wh/l and 120 Wh/kg with a 4.2 V charge limitation. With the later use of MCMB negative material the energies were 400 Wh/l and 155 Wh/kg.¹⁷ While Sony remained the industry leader for some time, competition from many other producers²² finally led to a planned withdrawal of Sony from the battery market with the intended transfer of the battery business to Murata group.²³

Present Day Lithium Ion Batteries

The present day market for lithium ion batteries is far more complicated than the original small electronic devices for the 3C market mentioned above. Many additional markets have been opened for small devices such as toys, lighting (LCD and fluorescent lights), e-cigarettes and vaporizers, medical devices, and many others. The discovery^{24,25} that lithium ion battery packs using 18650, 26700 and 26650 sizes can be designed to operate at much higher power than originally suspected has opened markets for portable electric tools, garden tools, e-bikes and many other products. While high energy 18650 cells now have as much as 3.4 Ah, the high power cells have

Table I. Properties of various cathode materials used in commercial lithium ion batteries at the present time and the advantages, disadvantages and applications in full cells. LCO is LiCoO_2 , LMO is LiMn_2O_4 , NCA is $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{O}_2$, NMC is $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$, and LFP is LiFePO_4 .

Cathode Material	Midpoint voltage vs. Li (C/20)	Specific Capacity (Ah/kg)	Advantages	Disadvantages	Applications
LCO	3.9	155	In common use, good cycle life, good energy	Moderate charged state thermal stability,	Mainly smaller portable electronics (3C)
LMO	4.0	100–120	Very good thermal stability, inexpensive, very good power capability	Moderate cycle life, lower energy	Higher power applications such as power tools and electric motive power
NCA	3.7	180	Very good energy, good power capability, good cycle life	Moderate charged state thermal stability, sensitive to moisture even in discharged state	Excellent for motive power and premium electronic applications
NMC	3.8	160	Very good combination of properties (energy, power, cycle life and thermal stability)	Patent issues	Both portable and high power applications including power tools and electric vehicles
LFP	3.4	160	Very good thermal stability and cycle life, good power capability	Lower energy, special preparation conditions	Mainly used in high power such as power tools and energy storage applications, patent issues

sacrificed some capacity to obtain 20A or higher continuous discharge capability in the 18650 cell size. While some cells claim as high as 2.5 Ah capacity, it is difficult to sustain such a high capacity during cycling. Modeling studies by Reimers²⁶ and Spotnitz and coworkers²⁷ show clearly the important effect of multiple tabs and tab placement. Other important design variables are the electrode thickness, the carbon content of the positive electrode, the porosities of the electrodes and the type of carbon used in the negative electrode.

In addition, the development of ceramic coatings to the separator or the positive electrode has had a beneficial effect on preventing internal short circuiting during cycling due to adventitious presence of metal particles on the surface of electrodes. These particles are small and generally airborne and frequently result from mechanical slitting of the electrodes. The separator is only of the order of 12 to 25 μm thick so the concept that very small conductive particles can penetrate the separator and cause a short has been acknowledged as a major failure mechanism of lithium ion batteries. Such separator coatings may be on one or both sides of the polyolefin separator and may be as thin as 2 μm thick. Additional advantages of coating the separator are a much reduced shrinkage of the separator at shutdown temperatures (shutdown of current due to separator melting may not be successful if the separator shrinks to the extent that direct contact between anode and cathode is permitted), better cycling in the case that a weak short circuit degrades capacity during cycling without causing a safety incident, and improved electrolyte wetting because of the easily wet inorganic oxide ceramic phase.^{28,29} Even more complex coatings are becoming common as for example, the Sumitomo separator used by Panasonic and Tesla Motors involves a coating with ceramic particles as well as an aromatic polyamide (aramid polymer) to increase the penetration strength of the coating.³⁰

While it is difficult to get confirmation from the battery industry, it seems clear that silicon in small amounts is now added to the graphite based negative electrode.³¹ The extremely high specific capacity of lithium silicon alloy anodes (over 3000 mAh/g compared to the maximum of 372 mAh/g for graphite) means that even a small amount of silicon incorporated into graphite particles has a marked effect on the specific capacity of the negative electrode.³² There are many ways already investigated to include a small amount of silicon micro or nano particles onto the surface of graphite particles and each graphite supplier uses their own proprietary process. For example, 400 to 500 mAh/g materials are commonly available now and are no doubt used in the premium lithium ion batteries providing over 3 Ah capacity in 18650 cells. These cells have high cycle life as well as high capac-

ity and are only slightly more expensive than conventional graphite cells.

Present cathode materials in common use include the original LiCoO_2 (abbreviated as LCO) and LiMn_2O_4 (abbreviated as LMO). An excellent and still developing material is $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$ (generally called NMC and of the same R3-m structure in the original Goodenough patent⁵ except for some ordering in the transition metal layer). The subscripts are usually called by their atomic ratios as 532, 442 or 811 (except for the initially investigated $x = y = 1/3$ which is called 333 or 111). The most commonly used materials are 111 and 532. In addition, a highly competitive material is $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}$ (NCA), also a layered R3-m structure. A more recent material developed competitively by several groups is LiFePO_4 (LFP) with a 1D tunnel structure. Each of these materials has certain advantages and disadvantages and has been applied to different applications. Table I gives a summary of the key properties, advantages and disadvantages and the main applications at the present time.

A snapshot of the battery industry in early 2015 may be obtained from the work of Pillot,²² now available on the internet. Pillot has a reputation for providing accurate data on present production as well as a conservative approach to extrapolated values for future production. Reference to Pillot²² shows that the battery use of LCO is still the largest at 45 kilotons (KT) of material, but definitely leveling off. The use of NMC is next at 35 KT and growing, LMO is next at 18 KT and growing somewhat, LFP at 10 KT seems to be leveling off, and NCA at about 9 KT is growing strongly. The expense and supply concerns have limited the upside potential of LCO and there continue to be safety incidents, especially with lower volume cell producers. Two of the newer applications, electronic cigarettes and so-called hoverboards (2 wheeled self-balancing boards) have had numerous safety incidents reported in which the lithium ion batteries have sparked and flamed causing injuries and property damage. A U. S. Fire Administration document reported in 2014 on at least 25 fires related to lithium ion batteries in electronic cigarettes,³³ and many more have been reported in various media since. CNet reported that as a result of over 60 fires, over 501,000 hoverboards have been recalled by the US Consumer Product Safety Commission.³⁴ It is certainly in the interest of the battery industry to strongly react to prevent such occurrences as rapidly as possible. Part of the investigation of such incidents should be to identify the components of cells, particularly the cathode, the separator and the electrolyte. The rapid rise of NMC is partly due to the flexibility of the material for both high energy and high power applications. Thus, many power tool batteries that originally had LMO

Table II. Batteries for Present Battery Electric Vehicles sold in US.

Manufacturer	Model	Battery size (kWh)	Battery Chemistry	Battery Supplier	Vehicle range (mi)	Vehicle range (km)
Tesla	S	60–100	C/NCA	Panasonic/Tesla	208–315	334–508
Tesla	X	60–100	C/NCA	Panasonic/Tesla	208–315	334–508
BMW	i3	22,33	C/NMC	Samsung/Bosch	80,114	129,183
Nissan	Leaf	24,30	C/LMO (C/NMC)	AESC and LG Chem [†]	84,107	135,172
Volkswagen	e-Golf	24,35.8	C/NMC	Panasonic (Sanyo Div.)	83,124	135,200
Chevrolet	Spark	19	C/LFP	A123	82	132
Fiat	500e	24	C/NMC	Samsung/Bosch	87	140
Kia	Soul EV	27	C/NMC	SK Innovation	90	145
Smart	Fortwo EV	17.6	C/NMC	LG Chem	68	109
Ford	Focus EV	35.5	C/NMC	LG Chem	100	160
Mercedes	B-Class Electric	28	C/NCA, (C/NMC)	Panasonic/Tesla and SK Innovation [†]	85	137
Mitsubishi	I	16	LTO/LMO	Toshiba	62	100
Honda*	Fit EV	20	LTO/LMO	Toshiba	82	132
Toyota*	RAV4 EV	41.8	C/NCA?	Panasonic/Tesla	113	182

*Discontinued Models.

[†]In process of changing suppliers.Note: NCA = $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}$; NMC = $\text{LiNi}_{1-x-y}\text{Mn}_x\text{Co}_y$; LMO = LiMn_2O_4 ; C = graphite; LTO = $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

as the cathode material, now have NMC. Also, consumer electronics applications frequently use NMC because of easier manufacturing processes than NCA and the various cell geometries possible with this material (cylindrical, pouch, and rectangular cells). The disadvantage listed in Table I is the patent issue. This is a complicated legal issue, but two patent holders, BASF-Argonne National Laboratory and 3M have competing patents in the US related to similar materials with excess lithium and manganese, which have introduced difficulties in batteries sold in the US. NCA is used by a few major producers such as SAFT and Panasonic to make high energy and in some cases, high power cells. These are generally premium cells and have the highest cost as a result. LFP has lower energy density because of its lower voltage and generally lower tap density, but, because of its good power and good thermal stability, has been used in more rugged applications such as e-bikes to good effect. The reader is referred to Reference 35 for structural details and other property measurements of these materials.

Deficiencies of Present Lithium Ion Batteries and Likely Improvements

There are several deficiencies of present day lithium ion batteries that, if remedied with suitable ease and cost parameters, would enable superior lithium ion batteries that could open new applications and expand the market for present ones. This section will discuss deficiencies of the lithium ion battery and possible approaches to improve the technology. First it is important to consider certain market factors that will have important ramifications on cost, material availability, and needed technology improvements to enable mass production of different cell types and sizes.

Market pull is strongly acting on lithium ion battery manufacturers as application companies and governments around the world are asking for increased capacity and energy with lower cost to fulfill the needs of greenhouse gas reductions through implementation of electric vehicles of all types to replace petroleum and energy storage so that intermittent renewable energy sources such as wind and solar can replace coal and natural gas fuels for energy production. The cost element is particularly important, for example, for motive power applications, especially for plug-in hybrid vehicles (PHEV) and battery electric vehicles (BEV). Recent estimates place the cost of producing lithium ion cells is as low as \$145 per kWh and the cost of a battery pack as low as \$190 per kWh.³⁶ The goal of most auto manufacturers and the US Department of Energy is \$125 per kWh for a battery pack.³⁷ While the Tesla Motors Model S BEV has a 60 to 100 kWh battery, the new Chevrolet Bolt BEV will have a 60 kWh battery and the Tesla Model 3 will have a “less than” 60 kWh battery pack when available. The latter models are the first mass market BEVs that will

have in excess of 200 miles (320 km) range which is believed to be a requirement for general public acceptance. Tables II and III give the data on many BEVs and PHEVs in current production including battery sizes and US Environmental Protection Agency (EPA) estimated ranges, ranked by present sales in the US.

Notice that only the very expensive Tesla models have 200 or more miles in range in Table II. The Chevrolet Bolt and Tesla Model 3 were not included because they are not yet in production and precise battery size and range are not yet available. The values in Table III for PHEV vehicles have a wide variation in battery size from about 6 to 18 kWh and all electric range from about 14 to 50 miles (22 to 80 km). Clearly, there is no consensus among vehicle manufacturers which range is acceptable to consumers given that more range means higher battery cost. This may be the reason that EV sales in 2015 were higher worldwide than PHEV sales.²² Only a few years ago, the PHEV was a widely viewed intermediate step to electrification of vehicles, but it appears that consumers who are interested in electrification would rather go directly to EVs than settle for a PHEV at least at this time. This consumer acceptance will have a profound effect on the volume of lithium ion batteries produced in total kWh and increases the pressure on battery manufacturers to reduce the cost and increase the specific energy of their product.

A second area of major production possibility is that of energy storage in connection with stabilization and storage for the electric grid. This area is driven as much by the requirements of government regulations and incentives to enable renewable energy sources such as solar and wind generation, which are inherently intermittent, to fit the demands of electrical utility producers and users.³⁸ Many government and private demonstration projects are proceeding around the world and a great many energy storage schemes including alternative storage devices such as pumped hydro, compressed air, flywheels, etc. as well as many battery types such as flow batteries (mainly aqueous based at this point), lead acid, high temperature and others in addition to lithium ion. While the other methods do not concern this work, it is a fact that many of the demonstrations involve lithium ion because of the long cycle life and calendar life possible with conservative charging and discharging regimes. In addition, cost is a very important driver for use of lithium ion, but some applications such as frequency stabilization are not as cost sensitive. If lithium ion batteries are adopted for these applications, great demands will be placed on the availability of materials, especially lithium carbonate. It is likely that a very conservative approach will be used for lithium ion batteries, while inherently safer systems such as aqueous flow batteries will continue to see more innovation in order to achieve low cost objectives.

To consider the likelihood of specific energy improvements in lithium ion batteries we need to consider the limitations that exist

Table III. Batteries for Present Plug-in Hybrid Electric Vehicles sold in US.

Manufacturer	Model	Battery Size (kWh)	Electric Range (mi)	Battery Chemistry	Battery Supplier	Electric Range (km)
Chevrolet	Volt	18.4	53	C/NMC	LG Chem	85
Ford	Fusion Energi	7.6	21	C/NMC	Panasonic	32
Ford	C-Max Energi	7.6	21	C/NMC	Panasonic	32
BMW	X5	9.2	14	C/NMC	Samsung/Bosch	22
Hyundai	Sonata Plug In	9.8	27	C/NMC	LG Chem	43
Audi	A3 Plug In	8.8	16	C/NMC	Panasonic (Sanyo Div.)	26
Volvo	XC90 Plug In	9.2	25	C/NMC	LG Chem	40
BMW	i8	7.1	23	C/NMC	Samsung/Bosch	37
Porsche	Cayenne SE-Hybrid	10.8	14	C/NMC	Samsung/Bosch	22
BMW	3 Series Plug-in	7.6	14	C/NMC	Samsung/Bosch	22
Mercedes	S550 Plug In	6.4	20	C/NMC	Panasonic (Sanyo Div.)	32
Mercedes	GLE 550E Hybrid	8.8	19	C/NCA and C/NMC	Tesla and SK Innovation [†]	30
Porsche	Panamera SE-Hybrid	9.4	22	C/NMC	Samsung/Bosch	35
Cadillac	ELR	17.1	39	C/NMC	LG Chem	60

[†]Changing suppliersNote: NCA = $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}$; NMC = $\text{LiNi}_{1-x-y}\text{Mn}_x\text{Co}_y$; C = graphite.

now. Table IV gives a picture of the main deficiencies and possible remedies as the author perceives them.

As mentioned earlier, alloy anodes have been investigated for lithium ion batteries for many years because of the potential for much higher capacity density and specific capacity than the carbonaceous anodes, even in comparison to C_6Li compound. The large volume change for most alloys causes a disruption of the protective layer on the anode particles that limit the amount of corrosion in the non-aqueous electrolyte. Composites of the alloying metal with carbons of many types and treatment temperatures and various other conductors such as nitrides have led to improved coulombic efficiency such that a number of companies now seem to be using a combination of graphite and modified silicon or tin in the negative electrode. It is anticipated that this work will continue and anode capacity density will continue to improve and other properties will remain good.³⁹

Present commercial lithium ion battery electrolytes limit the charging potential to about 4.2 V (except for the lower voltage LFP), which in turn limits the amount of charge that present cathode materials can accept. Because of the instability of LiCoO_2 at higher voltages due to a loss of oxygen,³⁵ the industry has developed great caution in applying higher charging voltages and in fact the charging method for most

producers is to use a constant current charge (usually at the C/2 or C rate) up to around 4.2 V and a constant voltage charge until the current drops to a value of about 10% of the initial value. This allows a full state of charge to be obtained with a minimum time on the charger while avoiding sudden oxygen loss and a safety incident. Other materials such as NMC and NCA do not suffer oxygen loss and safety concerns at higher voltage, but a slower oxidative degradation of the electrolyte occurs, which limits cycle life of the system. These losses are a result of the sensitivity of the electrolyte solution to oxidation at higher potentials. Many researchers have tried coating the particles of NMC or NCA as an example and had some hopeful results, but as yet no manufacturer has adopted this strategy.⁴⁰ It is well known that most electrolytes contain additives to improve cycle life, but again the use of additives for improvement of cycle life for NMC or NCA at higher voltage charging has not yet been implemented by manufacturers (see for example,⁴¹ and references therein). Both of these approaches are promising and a combination of the two approaches may be required to give sufficient stability in both cycle life and calendar life to a system using a relatively stable cathode like NMC or NCA at perhaps as much as 4.6 V charging potential and specific capacity as high as 230 Ah/kg (an improvement on a cell basis of as much as 30%). Recent

Table IV. Deficiencies of present lithium ion batteries and possible remedies.

Location of Deficiency	Deficiency	Possible remedy
Carbonaceous anode (negative electrode)	Low capacity density (Ah/l)	Replace carbon with improved alloy anode that allows high coulombic efficiency, good power capability, low irreversible capacity, and low cost with little or no loss of specific capacity or cell voltage
Negative electrode-electrolyte interface	Low coulombic efficiency with alloy anodes caused by solid electrolyte interphase (SEI) growth on first cycle and continuing with cycling	Improved coatings, functional binders and/or electrolyte additives to protect the interface during large volume changes
Positive electrode (lithiated transition metal oxide or phosphate)	Low specific capacity (Ah/kg) and charging voltage limited	Replace with new cathode material that allows high coulombic efficiency, good power capability, low irreversible capacity, and lower cost with little or no loss of capacity density or cell voltage
Positive electrode-electrolyte interface	Low coulombic efficiency at higher voltage limiting specific capacity and cycle life and causing increased cell impedance with cycling	Improve coating of cathode material, binders and/or electrolyte additives that can prevent impedance increase with cycling, dissolution of transition metal ions
Separator	Penetration with conductive particles or lithium dendrites	Improved coatings of separators that do not impede ion flux, salt diffusion or fluid flow, but can improve penetration strength or combine chemically with lithium dendrites
Metal collectors	Solid metal foils add to cost and take away from energy as they are inert in the system, yet must be thick enough to provide adequate electrical and thermal conductance	Perforated or expanded metal collectors are in common use for primary lithium batteries and secondary aqueous batteries, but have not been engineered for lithium ion

studies of aging through time (calendar life aging)⁴² and through cycling by study of coulometric changes with cycle life, impedance and other methods,⁴³ have verified the primary effect of corrosion at the negative electrode at all potentials and state of charge (SOC) which is accompanied by SEI growth and a parabolic rate of degradation.⁴⁴ Also verified is a degradation at the positive electrode, which increases with SOC and has a concomitant effect on the negative electrode as oxidized species migrate from positive to negative electrodes. There is a secondary effect, which can be quite important (as with LMO positive electrodes), where manganous ions (+2 valent) dissolve from the positive electrode at low SOC and are reduced further at the negative electrode to form metallic Mn. This Mn is composed of nanosized crystals which can act as catalysts to remarkably increase the rate of corrosion at the negative. These reactions are all reduced by judicious selection of electrolyte additives. Smaller amounts of other transition metal ions such as Co^{+3} , Ni^{+2} or Fe^{+3} ions from LCO, NMC, or LFP cathodes can dissolve and migrate to the negative to exacerbate corrosion of the negative, particularly at high temperatures of operation or storage. There is no doubt that study of electrolyte additives will continue to contribute to improving lithium ion batteries. Other studies involve the use of new solvent components which eliminate the use of ethylene carbonate (a component in all commercial lithium ion cells to date).⁴⁵

Many studies have been carried out on new cathode active materials. The discovery that layered materials with excess lithium and manganese can provide well over 200 Ah/kg specific capacity was made independently by two groups. The Thackeray group at Argonne National Laboratory described the materials⁴⁶ as composite materials with a formulation: $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$, where the dot implies a combination of two domains of the LiMO_2 and the $\text{Li}_2\text{M}'\text{O}_3$ components exist side by side.⁴⁷ The Dahn group at Dalhousie University described material of the same composition, but written as $\text{Li}[\text{Ni}_x\text{Li}_{(1/3+2x/3)}\text{Mn}_{(2/3-x/3)}]\text{O}_2$, where the three components: Ni, Li, and Mn within the brackets and on the transition metal layer, are a solid solution.⁴⁸ Later work explored the addition of Co and other elements to the formulation. The exciting aspect of the materials is the high capacity when up to 4.5 V is used as a charging limit, as much as 250 Ah/kg. There are several disadvantages which continue to merit study. The first charge has a high irreversible capacity and subsequent charges have a different profile which implies that structural changes in the material have occurred. The material has a relatively low power capability. Also, the cycle life is not great unless careful coating of the particles is carried out and the profile continues to change at a slow rate, with a declining average voltage, so the power capability of the system continues to deteriorate. These matters and some of the structural complexities are described in recent reviews.⁴⁹⁻⁵³ It is clear from these papers that many problems remain with these materials, but the incentive to continue to try to improve them is strong. A recent paper by Qui et al.⁵⁴ presents evidence that surface treatment of the pristine material by carbon dioxide results in removal of oxide ions (and lithium ions) to form lithium carbonate which can be removed by water washing. The oxygen deficient surface is much more stable to cycling and to 55], power capability (cycling is stable at 1C cycling) and the capacity is found to be about 280 to 300 Ah/kg. Also, the presence of oxygen vacancies was found to lessen the oxygen loss from the samples compared to pristine materials. The loss of voltage was not much changed, however, indicating that more work is needed.

Work by the Tarascon group at College de France has gone back a step from the above work to study the simpler series of compounds Li_2MO_3 , where M is Mn^{+4} , or a mixture of cations with average valence of 4 such as $\text{Ru}_x\text{Mn}_{1-x}$,⁵⁵ $\text{Ni}_{0.5}\text{Te}_{0.5}$,⁵⁶ $\text{Ru}_y\text{Sn}_{1-y}$,⁵⁷ and $\text{Ru}_y\text{Ti}_{1-y}$.⁵⁸ These materials are capable of high capacity, but evidence varying degrees of voltage fade which the authors relate to the stability of peroxo complexes in the oxide lattice associated with the type of coordination of lithium and higher valent ions to oxide ion. This proposal is analogous to other, more stable, dichalcogenides such as FeS_2 (pyrites) which has disulfide dianions throughout the structure. The use of ruthenium is a problem for the cost of cathode materials, but the insights into structural effects on the charged and discharged ma-

terials shed light upon the behavior of many of these high capacity materials. A theoretical analysis of such materials as well as new materials by the Berkeley group under Ceder has confirmed that the surroundings of the oxygen ion is very important to the likelihood of the formation of either a hole on a given oxygen (representing an oxidized anion) or a peroxo ion (similar to that proposed by Tarascon et al.) and further developed the theory to predict high capacity for certain disordered oxides containing second d-block transition metal ions such as Nb and Mo.⁵⁹ This work also explains results from specific compounds in a rock salt structure that have been shown to have high capacity and high diffusion coefficients for lithium ion (good rate capability). The compounds are $\text{Li}_{1.25}\text{Mn}_{0.5}\text{Nb}_{0.25}\text{O}_2$ ⁶⁰ ($\approx \text{Li}_{1.3}\text{Mn}_{0.4}\text{Nb}_{0.3}\text{O}_2$) and $\text{Li}_{1.2}\text{Ni}_{1/3}\text{Ti}_{1/3}\text{Mo}_{2/15}\text{O}_2$ and by inference two additional materials $\text{Li}_{1.25}\text{Nb}_{0.25}\text{Mn}_{0.5}\text{O}_2$,⁶¹ and $\text{Li}_{1.211}\text{Mo}_{0.467}\text{Cr}_{0.3}\text{O}_2$.⁶² This work is exciting as it points the way to high capacity with available materials. However, much of the work is carried out at 50°C or higher, indicating a rate capability problem.

The role of the binder is mentioned above and in Table IV with respect to the interface of both negative and positive electrodes. Recent progress for negative electrode binders is discussed in a recent review from Guyomard's group at Nantes University.⁶³ The improvement in capacity and cycling stability for silicon alloy electrodes is striking and gives optimism for the future of high capacity negative electrodes in the future. An example of the work under way with the so-called PEDOT:PSS (poly(3,4-ethylenedioxythiophene): polystyrene sulfonate) functional binder for positive electrodes (LFP in this case) is given in Ref. 64 This material is highly conductive and forms a polyelectrolyte suspension which also acts as a binder with good rheological characteristics. The work with additives is beyond the scope of this paper, but it is clear that they perform an important role in all lithium ion batteries and must be considered in combination with binder studies to complete the work on interfacial reactions.

As mentioned in Table IV, investigations on the separator continue to be important. As the safety aspects were discussed above, only one reference to new work on nanofibrous separators is included as being typical of present investigations.⁶⁵

Finally, it should be mentioned that several investigators are studying the possibility of 3D architecture of lithium ion battery structures including porous or expanded metal collectors. This would help to increase battery density and spatial utilization if production friendly concepts are developed. A typical anode study is referenced below.⁶⁶

The result of these advances discussed above if realized could yield lithium ion batteries with specific energies of 400 Wh/kg with at least moderate power density. This would represent an increase of about 60% compared to the best of today's 18650 cells with 3400 mAh capacity and could come about within the next several years. This prospect confirms the author's belief that the future for lithium ion batteries continues to be bright, especially if manufacturers are careful to maintain safe practices in manufacturing processes and new designs.

Conclusions

Twenty five years ago, the lithium ion battery made its debut into the market place as a result of innovative work by Asahi Kasei and development and marketing by the Sony Corporation. The realization of lithium ion batteries came about rapidly and has continued to display remarkable progress in capacity, energy, power and cost reduction. Safety remains a strong concern for the industry, but developments in separator technology have improved the outlook for safer batteries. With recent progress in new materials, the author projects that the lithium ion battery will continue to improve in all of its properties with successful implementation of new battery concepts in active materials, inert materials and cell designs.

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