

Present status and future potential of Lithium Ion Batteries

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Abstract

Lithium ion battery (LIB) is the most efficient energy storage device presently used in day to day activities. It consists of cathode, anode and electrolyte. A polymer separator is placed between the electrodes to avoid short circuit. The electrode materials must possess electronic as well as ionic conductivity whereas electrolyte is a purely ionic conductor. Electrode materials are being developed with the aim to increase the energy density, power density, cycling stability and safety of the cell. Among several cathodes $\text{Li}(\text{Ni}_x\text{Mn}_y\text{Co}_z)\text{O}_2$, $\text{Li}(\text{Ni}_x\text{Al}_y\text{Co}_z)\text{O}_2$, LiFePO_4 and among anodes carbon are being used in present day batteries.

Keywords: Lithium ion batteries, NMC333, LCO, LiFePO_4 (LFP), Graphitization of carbon

Introduction

Lithium ion batteries (LIB) are ubiquitous in most modern electronics ranging from electric-shavers to laptops. Lithium with its highest oxidation potential, low mass and high mobility, confers LIBs with high specific energy and power density. They also offer high cycle life, charge-discharge efficiency, as well as low capacity-fade. These factors combined with the relative earth abundance of LIB component elements, make it far superior to other battery chemistries like lead-acid and Nickel Metal Hydride (NiMH). Moreover, LIBs do not suffer from memory effect problem like Ni-Cd batteries and offer voltages nearly three times that of latter (Fig. 1). The self-discharge rate is also very low for LIBs (< 5% per month) as compared to Ni-Cd or Ni-MH batteries (~20-30% per month). Moreover, the global reserves of Li (~ 18 ppm of earth's crust) stand at ~ 43.6 Mt[1], sufficient for building ~12-14 billion electric vehicles (EVs), i.e. 10 times the current global number of automobiles. They have thus, become the focus of research from both industry and academia to meet the growing energy and power density requirements.

LIB Construction and working

A LIB is composed of a cathode (positive electrode) and an anode (negative

electrode), separated by an ion-conducting but electron blocking separator dipped in an electrolyte. The anode and cathode consist of electro-active material coated on metallic (Cu and Al respectively) current collector sheets that provide mechanical strength as well as a pathway for electron conduction to external circuit.

The first commercially successful LIB, introduced by Sony in 1991, (Fig. 2), utilized LiCoO_2 and carbon as cathode and anode, respectively. During charging cycle, electrons flow out of the Al current collector through external circuit towards anode. Meanwhile, Li^+ ions flow out into the electrolyte, traverse the ion permeable separator and intercalate between the graphene layers of carbon anode, where they are neutralized by the electrons entering from external circuit forming LiC_6 . The reverse process occurs during discharging process. It is this reversible to and fro shuttling of electrons and Li ions in the external and internal circuit respectively, that allows for storage/usage of electrical energy in a LIB.

Since Li is the most electropositive element (-3.04 V with respect to Standard Hydrogen Electrode), utilizing Li metal as anode would yield the highest cell voltage. Early attempts at this were foiled due to growth of lithium dendrites (tiny metallic

whiskers), upon deposition of Li^+ on anode during charging. These sharp dendrites eventually punctured the separator film and electrically shorted the cathode and anode, leading to a fire. This dendrite formation leading to battery fires was the major reason behind recall of Li/MoS_2 based batteries introduced in 1980s[2]. To overcome this issue, Li metal was replaced by carbon. In this case, the Li^+ ions are intercalated between the graphene layers of carbon.

Choice of electrode materials

a) Cathode Materials

For a material to be used as cathode in a LIB, it should have (i) low cost and be environment friendly (ii) high specific energy and power densities (iii) high Li^+ and electronic conductivity (iv) low structural and volume changes during charge/discharge cycles (v) chemical inertness towards electrolyte used in LIB (vi) electrode host structure tolerant to wide range of stoichiometry with respect to Li (vii) highly reversible lithiation/delithiation process in host structure (viii) high thermal stability. Moreover, the chemical potential of both cathode and anode must be well matched to the potential window (HOMO and LUMO) of electrolyte to allow large reversible capacity.

The cathodes for LIBs may be broadly classified as intercalation or conversion type depending on the basis how Li^+ are stored in them. In the former, Li^+ intercalates between inter-layer spacings in the host structure during discharging. Layered oxides (LiCoO_2), olivine (LiFePO_4), tavorite (LiFeSO_4F) and spinel (LiMn_2O_4) structures belong to this type, and they have a typical specific capacity in the range 100-200 mAh/g and typical voltage in the range 3 to 5V vs Li metal as anode. On the

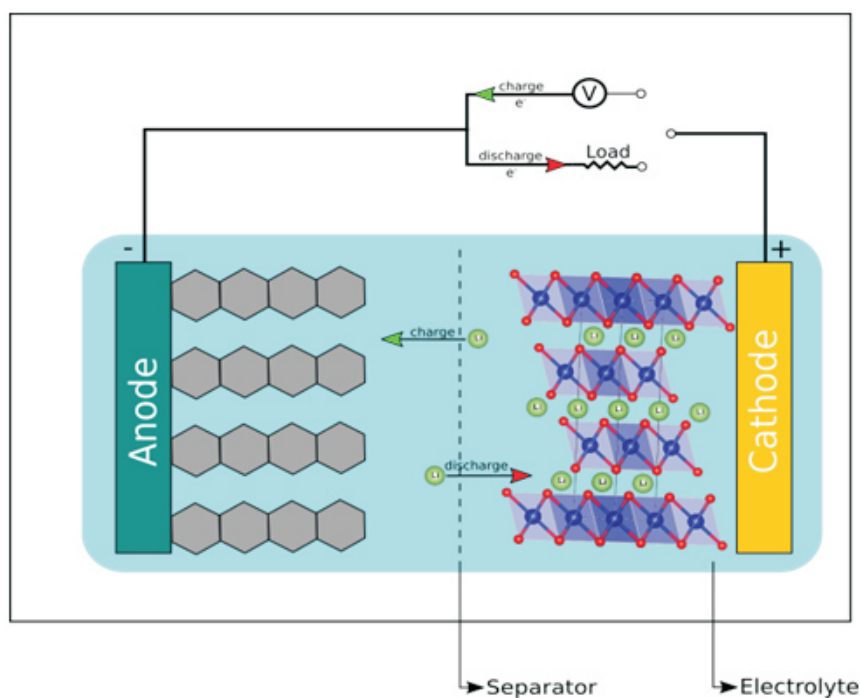


Fig. 1: Schematic of working of a typical intercalation type LIB

other hand, in conversion type, Li^+ ions displace the cation in the host cathode structure, leading to the formation of nano-precipitate of metallic cation during discharge.

The very first cathode that was developed for rechargeable LIBs was of the intercalation type, relying upon Li ion intercalation between layers of metal dichalcogenides (like TiS_2 and TaS_2). It was not commercially successful due to safety issues from Li metal anode but it paved the way for other layered materials.

The first commercially successful cathode material is LiCoO_2 [3](Fig. 3). It offers a higher voltage (3.5 – 4 V vs Li/Li^+) compared to the ~2V offered by LiTiS_2 and could be made in lithiated state enabling use of safer graphite anode. It possessed a high theoretical capacity (274 mAh/g), though only about half of it could be practically extracted in a reversible manner without structural changes. Its low thermal stability and specific capacity prompted research to replace Co with other transition metal ions. It was observed that certain metals provided certain desirable traits such as (i) increased thermal, cycling stability, lower cost (ii) prevention of cation migration to Li site (iii) increased capacity.

So, there was a move towards making binary/ternary oxides to get synergistic

effects. Among these materials, the most successful have been ternary (Ni/Mn/Co and Ni/Co/Al) oxides commonly referred as NMC and NCA, respectively. These oxides not only have similar/higher specific capacity compared to LCO but also achieve it at a lower cost due to reduced use of expensive Co. At the same time use Ni compensating for any capacity loss due to electro-chemically inactive Al/Mn ions.

b) $\text{Li}(\text{Ni}_x\text{Mn}_y\text{Co}_z)\text{O}_2$ ($x+y+z=1$)

Of the NMC oxide compositions developed, one of the first commercialized composition was NMC333: $\text{Li}(\text{Ni}_{0.3}\text{Mn}_{0.3}\text{Co}_{0.3})\text{O}_2$. Although NMC333 provides a reasonably high capacity (~150 mAh/g), it has a lower rate performance when compared to LCO.

It was observed that as the Ni content is increased in NMC, the specific capacity increases at the cost of thermal stability as well as rate performance due to Ni^{2+} ion's propensity for cation mixing. It even became the basis for categorization, with material containing >50% Ni classified as Ni-rich NMC. These Ni-rich materials suffer from low thermal stability as well as increased cation mixing leading to lower rate performance and high cell impedance[4]. The increased amount of Ni ions also correlates with increased amount of Ni^{4+} , with a low LUMO, which easily

oxidizes electrolyte speeding up cell degradation. To counter this issue, one strategy is to have core-shell particles, with a Ni-rich core contributing high specific capacity, and a Ni-poor shell that is more stable and does not oxidize electrolyte[5]. This approach was found to reduce electrolyte degradation but the difference in composition of core and shell led to differential volume changes during cycling.

c) $\text{Li}(\text{Ni}_x\text{Co}_y\text{Al}_z)\text{O}_2$ ($x+y+z=1$)

As discussed previously, Al can be used instead of Mn to provide enhanced thermal stability. The use of Al instead of heavier Mn yields higher specific capacity but slightly lower voltage vs Li metal. In contrast to NMC, only limited amount of Al(0.05-0.10) can be incorporated into NCA before the material begins to suffer from poor Li ion conductivity. Therefore, all practical compositions of NCA tend to Ni-rich and suffer from similar problems as Ni-rich NMC such as cation mixing, electrolyte oxidation etc. The most successful composition in NCA that is used in Tesla's EVs is $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}$.

d) LiFePO_4

One of the major safety concerns related to LIBs based on LCO and NMC is related to evolution of O_2 from the cathode with rising temperature. This evolved O_2 , then oxidizes electrolyte and other components in an exothermic fashion, and hence raise the temperature and even result in feedback loop that ends in a fire[6]. To mitigate this mechanism of catastrophic failure, it was proposed to use bulkier polyanions (XO_4)³⁻ ($\text{X}=\text{P/S/As/Sb}$) instead of O^{2-} in case of LCO. The rationale was that the stronger X-O bond would prevent the oxygen release failure mode seen in LCO. LiFePO_4 (LFP) was found to be the most promising with complete reversible exchange of Li ions in the 1-D channels of its olivine structure (see Fig. 3) as well as reasonable voltage of 3.5 V. LFP offers higher thermal stability, stable discharge potential as well as lower costs. The issue with LFP is its lower electronic and ionic conductivity compared to LCO and NMC. The poor conductivity is generally mitigated by synthesizing smaller nano-particles, applying a conductive carbon coating[7] as well as by cation doping. With these improvements, in spite of its lower energy density, it has found application in electric buses where safety and cost concerns outweigh volume/mass of cells.

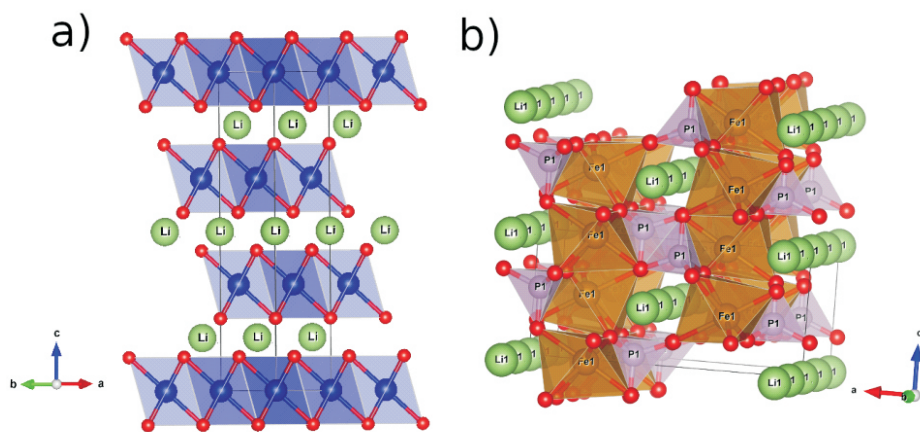


Fig. 2: (a) Layered structure of LiCoO_2 and (b) Li^+ channels of LiFePO_4

Anode Materials

To address the safety concerns posed by use of lithium metal as anode for lithium ion batteries, several alternate materials have been proposed. The alloying materials like Si-Li, Sn-Li suffered from low cycle life due to their large volume changes while Li-Al although stable under cycling exhibited very low rate capability as well as specific capacity.

i) Carbon

Due to the above mentioned drawbacks of alloying anodes, carbon has been considered and that quickly emerged as the most promising candidate due to its low lithiation/delithiation potential ($\sim 0.1 \text{ V}$ vs Li metal), good reversibility, high Li ion and electronic conductivity, low volume change during charging/discharging ($\sim 10\text{-}20\%$ strain), low cost and high availability. Li^+ ions are stored between two graphene planes, since one Li^+ can be stored per 6 carbon atoms, it has a theoretical capacity of 372 mAh/g . During the early days, when it was attempted to intercalate lithium into graphite, the propylene carbonate (PC) based electrolyte underwent decomposition. This decomposition layer was christened “Solid Electrolyte Interphase, SEI” and that separated the solid graphite electrode from the liquid electrolyte[9]. Moreover, PC molecules also intercalated between graphene layers leading to poor reversibility as well as loss of capacity as it exfoliates layers of graphene.

The Li^+ ion storage capacity was found to increase with increasing graphitization of carbon but it also decreased the stability of SEI. In more graphitic carbon, PC would

intercalate more and cause greater exfoliation. These findings in fact, prompted Yoshino et al [10] to choose coke-carbon, a less graphitic carbon that gave a moderately high capacity of $\sim 200 \text{ mAh/g}$ but with good reversibility and cycle stability for their patent of first secondary LIB. The co-intercalation of PC with Li^+ was subsequently solved by Fong et al. [11] using a mixture of PC along with ethylene carbonate (EC)[11]. They showed that electrolyte decomposition and SEI layer formation only occurs during the first few charging cycles and that the formed SEI layer persists during subsequent cycles with no capacity loss. Combinedly, these factors laid the foundation for graphite to become the most used anode material in commercial LIBs.

ii) $\text{Li}_4\text{Ti}_5\text{O}_{12}$

LTO possesses much better thermal stability, long cycle life and high rate capability due to its extremely efficient “zero-strain” ($\sim 0.2\%$ volume change) lithium insertion/extraction mechanism. It's higher lithiation/delithiation potential also prevents electrolyte decomposition at anode and eliminates loss of Li towards formation of a SEI layer (as opposed to carbon). Moreover, this high potential disfavors Li dendrite growth, even at high charge/discharge rates. This lack of SEI accords the high rate performance to this material and makes it a good choice for batteries requiring high power and large cycle-life but moderate energy capacity[13]. It was due to the above advantages that LTO was successfully commercialized despite its higher cost, higher lithiation/delithiation voltage $\sim 1.5 \text{ V}$ vs Li/Li^+ and lower capacity (175 mAh/g theoretical capacity).

Future Potential

a) Lithium-Sulphur and Lithium-Air

Lithium-Sulphur batteries are expected to succeed the current generation of lithium ion batteries due to several advantages of S such as (i) low cost and high availability (3% of earth's crust) (ii) it is environmentally benign (iii) it has high specific capacity (theoretical cap.: 1675 mAh/g) (iv) it has a lower operating voltage ($\sim 2 \text{ V}$) of Li-S compared to $\sim 3.7 \text{ V}$ for intercalation cathodes and can enhance cycle life due to reduction in possibility of electrolyte oxidation.

The theoretical capacity of Li-S batteries is expected to be five times of the current LIBs based on intercalation cathodes. The challenges that are being tackled towards practical utilization of these batteries are:

- Low electronic conductivity (10^{-31} S/cm) and large volume change ($\sim 80\%$) on cycling: This is being addressed by formulation of nanocomposites with enhanced conductivity and large void space.
- Low cycle life due to solubility of intermediate polysulphides (Li_2S_x) in the electrolyte leading to net loss of S content in electrode: electrolyte additives are being explored.

Lithium-air batteries mark another step forward in terms of specific capacity, with a theoretical capacity of 3840 mAh/g , i.e. 10 times more compared to current LIBs. They operate by reducing oxygen (from air) at cathode and oxidizing lithium at anode. This heterogeneous electrochemical coupling of gaseous O_2 and metallic Li in a safe, reversible and efficient manner is being pursued by researchers all over the world.

Conclusions

LIBs continue to be the dominant storage technology for high energy and power density applications. Advances towards practical implementation and Li-S and Li-air batteries are expected to keep up with growing demands for electric mobility applications. Safe, efficient and environmentally sustainable LIBs are expected to help reduce our carbon footprint and reduce dependence on polluting fossil fuels.

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References

- [1] C. Grosjean, P. H. Miranda, M. Perrin, and P. Poggi, "Assessment of world lithium resources and consequences of their geographic distribution on the expected development of the electric vehicle industry," *Renew. Sustain. Energy Rev.*, 16, (2012) **1735–1744**.
- [2] K. Brandt, "Historical development of secondary lithium batteries," *Solid State Ion.*, 69, (1994) **173–183**.
- [3] K. Mizushima, P. C. Jones, P. J. Wiseman, and J. B. Goodenough, " Li_xCoO_2 (0," *Mater. Res. Bull.*, 15, (1980) **783–789**.
- [4] J. Oh et al., "High-rate cycling performance and surface analysis of $\text{LiNi}_{1-x}\text{Co}_{x/2}\text{Mn}_{x/2}\text{O}_2$ ($x=2/3, 0.4, 0.2$) cathode materials," *Mater. Chem. Phys.*, 222, (2019) **1–10**.
- [5] Z. Chen, Y. Qin, K. Amine, and Y.-K. Sun, "Role of surface coating on cathode materials for lithium-ion batteries," *J. Mater. Chem.*, 20, (2010) **7606–7612**.
- [6] K. Liu, Y. Liu, D. Lin, A. Pei, and Y. Cui, "Materials for lithium-ion battery safety," *Sci. Adv.*, 4, (2018) **9820**.
- [7] Z.-X. Chi, W. Zhang, F.-Q. Cheng, J.-T. Chen, A.-M. Cao, and L.-J. Wan, "Optimizing the carbon coating on LiFePO_4 for improved battery performance," *RSC Adv.*, 4, (2014) **7795–7798**.
- [8] A. N. Dey, "Electrochemical Alloying of Lithium in Organic Electrolytes," *J. Electrochem. Soc.*, 118, (1971). **10**.
- [9] E. Peled, "The Electrochemical Behavior of Alkali and Alkaline Earth Metals in Non aqueous Battery Systems—The Solid Electrolyte Interphase Model," *J. Electrochem. Soc.*, 126,(1979), **2047**.
- [10] A. Yoshino, K. Sanekika, and T. Nakajima, "Secondary battery," **US4668595A**, May 26, 1987.
- [11] R. Fong, U. von Sacken, and J. R. Dahn, "Studies of Lithium Intercalation into Carbons Using Non aqueous Electrochemical Cells," *J. Electrochem. Soc.*, 137, (1990) **2009**.
- [12] T. Ohzuku, A. Ueda, and N. Yamamoto, "Zero Strain Insertion Material of $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ for Rechargeable Lithium Cells," *J. Electrochem. Soc.*, 142,(1995) **1431**.
- [13] K. Zaghbi et al., "Safe and fast-charging Li-ion battery with long shelf life for power applications," *J. Power Sources*, 196, (2011) **3949–3954**.