Next Generation Li-ion Batteries

Name = Mr. Avinash Pandey

Affiliations = Madan Mohan Malviya University of Technology, Chemical Engineering Department, Gorakhpur, Uttar Pradesh, India.

ORCID=0000-0003-0844-1532

Abstract

Lithium-ion batteries have been the nucleus of the digital modernization, especially when acknowledging the exponential rise in the digital-dependency of human beings on devices such as mobile phones, laptops etc. As they play such a vital role in various electronic equipment, over the years various efforts have been made to increase their capacity, cyclability and battery life with higher safety measures. At present, $LiCoO_2$ batteries with carbonaceous anode and $LiPF_6$ dissolved in organic solvent as electrolyte are the most used batteries. However, the toxic nature of Co, low cyclability of carbon anodes and the inflammable nature of organic electrolyte requires an alternate form of Li-ion battery to take its place in the commercial markets. To meet the high demand of the society it is vital to develop next generation lithium-ion batteries with enhanced performance, capacity, cyclability and safety measures which can be developed at nanoscale using $LiFePO_4$ and silicon nanowires as the two electrodes with an inorganic electrolyte such as fluid SO_2 that is incombustible in nature. The following content briefly explains the challenges faced by the current generation of lithium-ion batteries and the recent progress made in those areas to tackle the said problems.

Introduction

Lithium-ion batteries have been around for almost 3 decades now and were first commercialized in 1991 by Sony. Since then they have replaced other forms of electrochemical batteries in various electronic devices and equipment, and are now used exclusively in mobiles and laptops at present [1]. Its usage has also been expanded to electric vehicles as they have high efficiency of 80 to 90 % with great power storage capacity, fast charging, long battery life and great safety measures [2][3] . Lithium metal batteries, however have been observed to have even higher theoretical specific energy and energy density as compared to lithium ion batteries but they can't yet be commercialized as their ability to recharge is very low and there misuse can lead to fire and explosion. Li-ion batteries can also be designed in various shapes and sizes and hence are very space efficient in the device they are deployed in.

They don't have the problem of memory effect which is seemingly a major issue in all Nickel based batteries. The potential per gram of the electrode material that these batteries can generate is approximately 3 times than that of a Nickel based battery, hence they require much smaller number of cells to supply a constant voltage than any Nickel based battery. The self-discharge rate of a lithium-ion battery is also nearly 4 to 6 times lesser than Nickel based battery and have higher cyclability when compared to any Ni battery.

Basic Operation

A battery is a network of many electrochemical cells connected in series to amplify voltage or connected in parallel to amplify current or the mixture of the two to supply the required output. In a typical Li-ion cell there are two electrodes, an electrolyte that serves as a connecting medium for the two electrodes and a separator which is usually a microporous boundary that stops the flow of electrons between the electrodes but allows the movement of Li-ions through it. The two electrodes differ in potential and the material they are made up of. The positively charged electrode is called cathode and is made of an intercalated Lithium compound with a transition metal as the central metal atom. Example- $LiCoO_2$, $LiFePO_4$ etc. The negatively charged electrode is called anode and is made out of a conductor material with large gaps between the consecutive inter molecular layers or higher range order inside which the Li-ions reside during the charging of the battery.

For a common $LiCoO_2$ – Graphite battery, the electrochemical reactions that occur inside the cell are- Half reaction on cathode :

$$CoO_2 + Li^+ + e^- \longleftrightarrow LiCoO_2$$

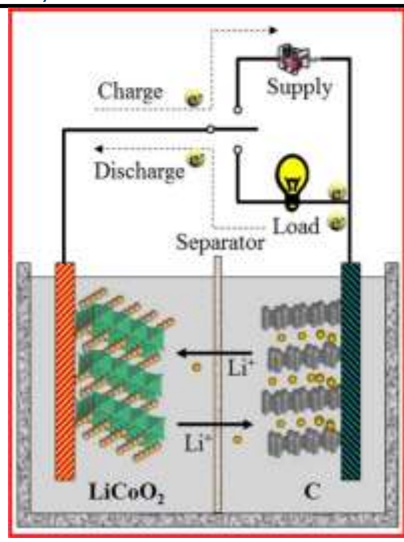


Fig 1- An illustration of various components and charging/discharging process of a $LiCoO_2$/Graphite Li-ion battery.[1]

Half reaction on anode:

$$LiC_6 \longleftrightarrow Li^+ + C_6 + e^-$$

Therefore the full reaction inside the cell looks like :

$$LiC_6 + CoO_2 \longleftrightarrow LiCoO_2 + C_6$$

When the Li-ions migrate from cathode to anode the charging process of the battery takes place and when they migrate from anode to cathode the discharging process of the battery takes place. The central metal atom of the intercalated salt gets oxidized and reduced during the charging and discharging process respectively. During deep- discharging of a battery a permanent reaction takes place between the electrodes which can cause severe harm to the electrode material, increase the internal resistance of the battery and decrease the effective battery life.

$$Li^+ + e^- + LiCoO_2 \longrightarrow LiO + CoO$$

Cathode Material

Many compounds have been used as a cathode material for the Li-ion batteries over the years to supply various voltage outputs as per required. Some of these materials include TiS_2, MnO_2, $LiCoO_2$. $LiMnPO_4$, $Li_2M_xMn_4XO_8$ (M=Fe,Co) etc in various form of layered structures. In the present age the most used cathode materials are $LiCoO_2$ and $LiFePO_4$, having a better life cycle

than any of the other cathode materials. $LiCoO_2$, because of its stable nature on exposure to atmosphere is much safer to use, as it does not explode or catch fire when exposed to atmosphere. However, the problem with a $LiCoO_2$ cathode is the toxicity of cobalt and high market price of the material

The $LiFePO_4$ cathodes has been preferred over $LiCoO_2$ over the past few years because of there comparatively lower cost and lower environmental damage. They also excel at stability, work cycle and temperature tolerance(20-70^{0}C).

However, these cathodes have low electronic and ionic conductance of 10^{-10}S/cm and 10^8cm^2/s. Also the 1D channel present in this material for Li^+ diffusion gets easily clogged by impurities and crystal defect in the iron lattice. To overcome this, nano-scale cathodes are used, as it was observed that rate of diffusion is higher on nano-scale. To mend the poor conductivity of $LiFePO_4$ the material is either doped with a different material or coated with carbon. The metals used for doping usually are Mg, Ti, Zr or Nb[8][9].These enhance the material conductivity by 10^8 times the original value. Also they have low polymerization even at high specific current supplies. There have been cases of better performance and retention capacity of $LiFePO_4$ batteries when the cathode is doped with different metals such as Ni, Co etc in a stoichiometric ratio of 9:1 or the $LiFePO_4$ used is off-stoichiometry.

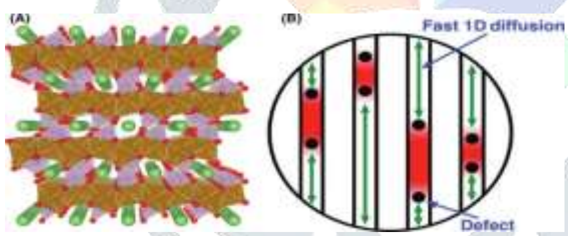


Fig 2- (A). Crystal structure of $LiFePO_4$ with Li-ion movement along 1-D channel (B). 1-D channel of $LiFePO_4$ with fast diffusion of Li^+ ion and defect in the channels causing restriction in diffusion.[22]

Anode Material

Anode materials have an even wider array of potential composites for anode formation, when compared to cathode. Carbon containing compounds have been extensively used for making anodes over the past few decades and are still the most commonly used anodes for Li-ion batteries. These carbon-composite anodes contain electrodes made out of Graphite, Carbon compounds formed by reaction with other metals such as Tin, Cobalt etc and Disordered Carbon obtained from there precursors using heat treatment processes such as carbon obtained from Polyparaphenylene (PPP) which is a very commonly used anode material[14][15].The major problem faced by a carbon-composite anode battery is poor cyclability and battery life because of the gradual permanent distortion of there crystal lattice with every charge/discharge cycle. Also the specific capacity of carbon is very low when compared to the present requirements. To overcome the problems of Carbon composite anodes, a nano-scale solution was derived by using a Carbon nanotube-TiO_2 nanoparticle composite which provides higher specific capacity as well as lesser pulverization [7]. These anodes follow the insertion/extraction cycling process whereas some other anode material such as SnO_2 or Sn-Si/C follow the Li-alloy reaction mechanism. The use of the composite helps with the cyclability of Sn and the higher specific capacity of Carbon.

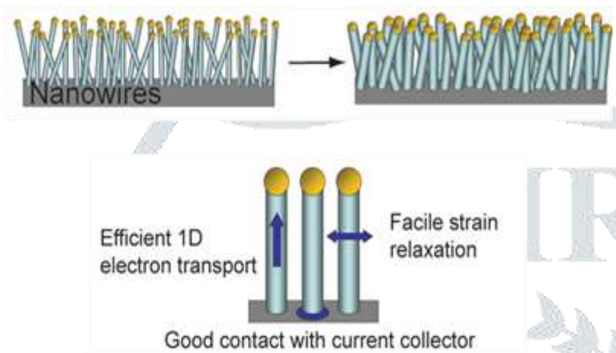


Fig 3- Excellent stability of Silicon nanowires after repeated Lithiation/Delithiation and schematic depicting the advantages of Si NW over Si film and particle anodes. [21]

Silicon composites are the emerging solution for low specific capacity carbon anodes as they have much higher specific capacity[4]. Silicon composite nanowires have high resistance to pulverization phenomena. These nanowires are formed by the Super-critical Fluid-Liquid-Solid technique which is a bottom-up Chemical Vapor Deposition (CVD) method for nanofabrication[5]. A drawback of these anodes is the high cost and very low tapped density which means they need to cover large volume in order to provide required energy which makes it an impractical choice for batteries in portable devices.

Electrolyte and Separator

Electrolyte is an integral part of any battery and has a great impact on the battery performance and safety of the battery. The choice of an electrolyte depends on many factors including but not limited to, the electrodes chosen and the temperature of the surrounding at which the battery is being operated. An electrolyte is made up of a single or mixture of Li salts($LiPF_6$)dissolved in mixture of organic solvents(EMC). The concentration of the electrolyte is very crucial to energy density, efficiency, and cyclability of the battery as a high viscosity electrolyte shows less interaction with the electrodes, hinders ionic movement at low temperature and is more expensive whereas low viscosity electrolyte causes low cyclability at high temperature and can form Solid- Electrolyte Interface causing increase in internal resistance of the battery resulting in compromised battery life. The use of organic solvents has always been a question for these electrolyte as they are highly flammable compromising safety and form SEI with the carbon anodes. A solution to this was introduction of gelatinous electrolyte containing Li salts and and solvents in a high-density polymer network which solves the spillage issue of a liquid electrolyte and enhances the safety [18].

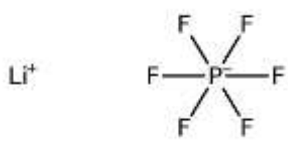
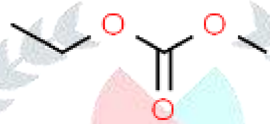
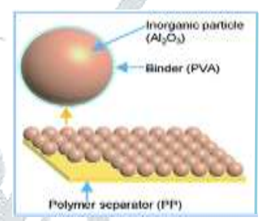
(A). 
(B). 
(C). 

Fig 4 : (A) Chemical structure of $LiPF_6$. **(B)** Chemical Structure of EMC (Ethyl Methyl Carbonate). **(C)** Ceramic coated polyolefin Separator with PVA as Binder. [18]

Separator is also an essential part of the cell separating the two halves of the cell and allow only the migration of the Li-ions through it, restricting the movement of electrons through the electrolyte. They also prevent the two electrodes from coming into direct contact and causing the cell to short circuit. The Li-ion separator must be permeable, and the pore size ranges from 30 to 100nm. The qualities of a good separator involve stable nature towards the other components of the cell, able to absorb the mechanical shocks, economically cheap and allow easy movement of Li-ions through it. Polyolefin obtained by polymerization of olefin ethylene is the most used separator with a membrane thickness of 25μm and a pore-size of 10nm.

Conclusion

Li-ion batteries have undergone various development phases from the time of their first commercialization and intensive research still continues in order to develop the next generation batteries with higher energy density, better performance and safety measures. According to me, $LiFePO_4$ at nano-scale shows great capacity as a cathode material as it exhibits high diffusion rate, better cyclability and stability than any other cathode material. As for the anode, intensive

research is required to develop a cheaper technique for producing silicon nanowires with higher tapped density as silicon nanowires, despite of being expensive have very high energy density and resistance to pulverization making it a better anode material that can be used in next generation

Li-ion batteries. It also doesn't form Solid-Electrolyte Interface (SEI) with the organic solvents.

The field of electrolyte also requires an inorganic alternative such as fluid SO_2 in order to enhance the safety measures of the battery as organic solvents are highly inflammable and often catch fire when exposed to high temperatures. Polyolefin is a great separator with excellent mechanical properties and can still be easily deployed in the next generation batteries. Intensive research is being conducted in these field in order to obtain the next generation Li-ion batteries with higher capacity, cyclability, battery life and safety measures at an effectively cheaper price and hopefully the next generation Lithium ion batteries will be commercialized in the upcoming decade.

References

1. Deng, D., M. G. Kim, J. Y. Lee, and J. Cho. 2009. Green energy storage materials: Nanostructured TiO2 and Sn-based anodes for lithium-ion batteries. Energ. Environ. Sci. 2:818–837.

2. Yoshino, A. 2012. The Birth of the Lithium-Ion Battery. Angew. Chem. Int. Edit. 51:5798– 5800.

3. Joan Lowy 2013. NTSB: Boeing 787 battery shows short-circuiting. The Associated Press.Basu, S., C.Zeller, P. J. Flanders, C. D. Fuerst, W. D. Johnson, and J. E. Fischer. 1979. Synthesis and properties of lithium- graphite intercalation compounds. Mat. Sci. Eng. 38:275–283.

4. Chan, C. K., H. Peng, G. Liu, K. McIlwrath, X. F. Zhang, R. A. Huggins, et al. 2008.

5. High-performance lithium battery anodes using silicon nanowires. Nat. Nanotechnol. 3:31–35.

6. Li, H., X. J. Huang, L. Q. Chen, Z. G. Wu, and Y. Liang. 1999. A high capacity nano-Si composite anode material for lithium rechargeable batteries. Electrochem. Solid State Lett. 2:547–549.

7. Wilson, A. M., G. Zank, K. Eguchi, W. Xing, and J. R. Dahn. 1997. Pyrolysed silicon- containing polymers as high capacity anodes for lithium-ion batteries. J. Power Sources 68:195–200.

8. Poizot, P., S. Laruelle, S. Grugeon, L. Dupont, and J. M. Tarascon. 2000. Nano-sized transition-metaloxides as negative-electrode materials for lithium-ion batteries. Nature 407:496–499.

9. Yi, T. F., X. Y. Li, H. P. Liu, J. Shu, Y. R. Zhu, and R. S. Zhu. 2012. Recent developments in the doping and surface modification of LiFePO4 as cathode material for power lithium ion battery. Ionics 18:529–539.

10. Du, N., H. Zhang, and D. R. Yang. 2012. One-dimensional hybrid nanostructures: synthesis via layer-by-layer assembly and applications. Nanoscale 4:5517–5526.

11. Zaghib, K., J. B. Goodenough, A. Mauger, and C. Julien. 2009. Unsupported claims of ultrafast charging of LiFePO4 Li-ion batteries. J. Power Sources 194:1021–1023.

12. Wu, X.-L., L.-Y. Jiang, F.-F. Cao, Y.-G. Guo, and L.-J. Wan. 2009. LiFePO4 Nanoparticles Embedded in a Nanoporous Carbon Matrix: Superior Cathode Material for Electrochemical Energy-Storage Devices. Adv. Mater. 21:2710–2714.

13. Kumar, T. P., R. Ramesh, Y. Y. Lin, and G. T. K. Fey. 2004. Tin-filled carbon nanotubes as insertion anode materials for lithium-ion batteries. Electrochem. Commun. 6:520–525.

14. Bogart, T. D., D. Oka, X. Lu, M. Gu, C. Wang, and B. A. Korgel. 2013. Lithium Ion Battery Peformance of Silicon Nanowires with Carbon Skin. ACS Nano 8:915–922.

15. Bonino, F., S. Brutti, P. Reale, B. Scrosati, L. Gherghel, J. Wu, et al. 2005. A disordered carbon as a novel anode material in lithium-ion cells. Adv. Mater. 17:743–746.

16. Zheng, T., J. S. Xue, and J. R. Dahn. 1996. Lithium insertion in hydrogen-containing carbonaceous materials. Chem. Mater. 8:389–393.

17. Lou, X. W., C. L. Yuan, and L. A. Archer. 2007. Double-walled SnO2 nano-cocoons with movable magnetic cores. Adv. Mater. 19:3328–3332.

18. Xu, K. 2004. Nonaqueous Liquid Electrolytes for Lithium-Based Rechargeable Batteries. Chem. Rev. 104:4303–4418.

19. Meyer, W. H. 1998. Polymer Electrolytes for Lithium-Ion Batteries. Adv. Mater. 10:439–448.

20. Wang, X., Z. Wen, Y. Liu, and X. Wu. 2009. A novel composite containing nanosized silicon and tin as anode material for lithium ion batteries. Electrochim. Acta 54:4662–4667.

21. Chan, C. K., H. Peng, G. Liu, K. McIlwrath, X. F. Zhang, R. A. Huggins, et al. 2008. High-performance lithium battery anodes using silicon nanowires. Nat. Nanotechnol. 3:31–35.

22. Malik, R., D. Burch, M. Bazant, and G. Ceder. 2010. Particle Size Dependence of the Ionic Diffusivity. Nano Lett. 10:4123–4127.