Improving Energy Density in Lithium-Ion Batteries Using Nanomaterials

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Abstract. Lithium-ion batteries are pivotal in modern energy storage, powering everything from consumer electronics to electric vehicles. Despite their advantages, current materials limit their energy density, particularly for electric vehicles. This paper explores the potential of nanomaterials to enhance lithium-ion battery performance, focusing on anodes, cathodes, and electrolytes. The study discusses the limitations of traditional graphite anodes and highlights nanostructured silicon and metal oxides as alternatives to significantly increase capacity and reduce volume expansion. For cathodes, it examines how nanomaterials like S-TiO_2 yolk-shell structures and high-voltage cathode materials can improve energy density and stability. The role of nanostructured solid electrolytes in enhancing ionic conductivity and overall battery performance is also analyzed. The paper addresses the challenges of using nanomaterials, such as higher costs and the need for scalable production methods. It suggests future research directions, including optimizing nanostructures and developing cost-effective manufacturing processes. The findings underscore the potential of nanotechnology to overcome current limitations and significantly boost the energy density of lithium-ion batteries.

Keywords: Lithium-ion batteries, nanomaterials, nanotechnology.

1. Introduction

Lithium-ion batteries have revolutionized the field of energy storage, becoming an essential component in a wide range of applications, from consumer electronics to electric vehicles and renewable energy systems [1, 2]. Lithium-ion batteries have high energy density, and long cycle life and are environmentally friendly, making them the preferred choice for powering devices like smartphones, laptops, and electric vehicles (EVs) [3]. Especially in the field of EVs, lithium-ion batteries help EVs offer an alternative to fossil fuels and contribute to the reduction of greenhouse gas emissions in the future [2]. However, with the development of EVs, the energy density of traditional lithium-ion batteries is not enough to support the better performance of the EVs [4]. For example, Batteries are limited by their size within the EVs, and the upper energy density limit (250-693 Wh/L) of existing materials in batteries is insufficient to help the EVs achieve a long-range [4]. The traditional materials of Lithium-ion batteries, the battery consisted by traditional material is shown in Figure 1, are limiting the energy density increasing [5]. Therefore, finding emerging materials to improve the battery energy density limitations is an extremely urgent issue.

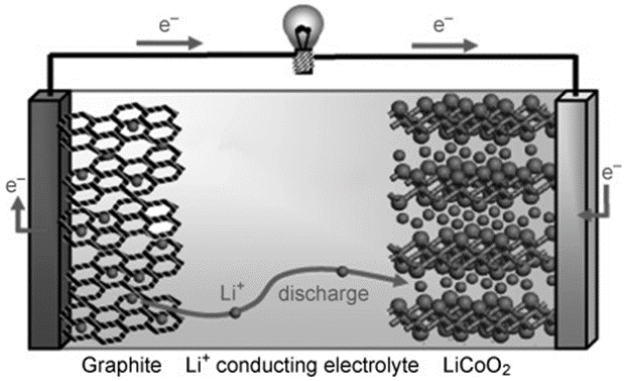


Figure 1. The scheme of the first-generation lithium battery [5]

The nanomaterial is a good choice for improving the energy density limitations of Lithium-ion batteries since it has a high surface area, porosity and high mechanical strength, which make it possible to push the limits of energy density [6, 7]. The nanosized particles in the anode, cathode, and electrolyte can provide short distances in diffusion to enhance the dynamic properties of ions. Therefore, charging and discharging speed can be increased by changing the size from micrometer to nano size [6]. The high mechanical strength can make the material have a large fracture size of particles. The battery doesn't have to rely on graphene's low volume expansion rate and uses materials with higher energy density [5]. This paper explains and analyses the feasibility of nanomaterials for batteries in three directions, lithium battery anodes, cathode and electrolytes.

2. Nanomaterials in Anode Design

The traditional anode material in lithium-ion battery normally uses graphite. The graphite has advantage of low expansion volume, low cost and compatibility with electrolytes. However, since graphite only has 372 mAh g^{-1} specific capacity, it is relatively lower now compared with metal and other elements such as silicon (4200 mAh g^{-1}) [8, 9]. This property of graphite anode limits the energy density and capacity of the lithium-ion battery. Therefore, the nanomaterial will likely replace graphite as the new anode.

2.1. Nanostructured Silicon

Silicon has long been the subject of research by scientists as a potential anode material [5]. Silicon has a low delithiation potential of approximately 0.4 V relative to Li/Li^+ and a high specific capacity [10]. Therefore, silicon has been considered as a possible material to increase the energy density of batteries. People use silicon and Lithium alloys to try as the anode in batteries, the anode of silicon and lithium alloy suffers from the volume expansion of silicon and Lithium alloys. It normally has a 420% volume expansion compared with the original one [11, 12]. It results in the degradation of the anode which breaks the battery rapidly [13]. Although silicon and Lithium alloys have those weaknesses, it does not mean silicon is useless in Lithium-ion batteries. The nanowire can solve most problems of the silicon and Lithium alloys. Since the mediums which are porosity are provided by the nanowire of silicon, it makes silicon and Lithium alloys anode can resist more mechanical stress between particles [10]. In this way, it reduces the degradation of the silicon anode. As shown in Figure 2. It has space between each one. When the nanowire of silicon expands, it intersects each other and each silicon nanowire has enough space to resist the stress of expansion [14].

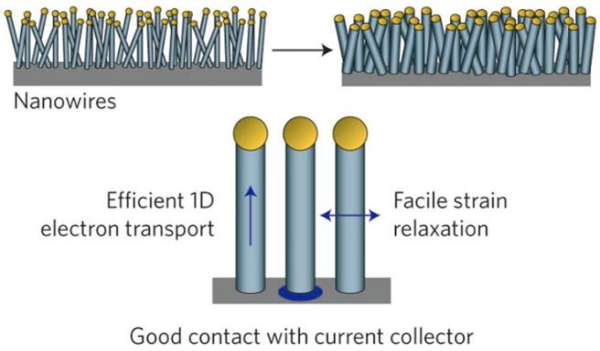


Figure 2. The nanowire before and after the volume expansion [14]

Meanwhile, silicon nanowires can be directly grown on the current collector, obviating the need for adhesive substances to bind the particles to the collector. Adhesive substances often pose challenges due to the stresses induced by volumetric expansion and contraction during charge and discharge cycles. If these connections fail, it can lead to anode fracture and subsequent battery failure. While amorphous silicon has been used as an inorganic adhesive to address this issue, directly growing silicon nanowires on the collector eliminates the need for such adhesives, thereby enhancing the structural integrity and performance of the anode.

2.2. Metal Oxides and Hybrids

The silicon nanowire contains high theoretical capacity about 4200 mAh g^{-1} and silicon nanoparticles mitigate the issues related to volumetric expansion (up to 420%) during lithium intercalation. The small size of the particles allows them to fit the expansion and contraction cycles, reducing the risk of cracking that larger particles normally faced problems [8, 9]. In cycle life perspective, the nanoscale dimensions can shorten lithium diffusion paths (the crystal solid diffusion will be reduced by using nanoscale dimensions), which enhances the kinetics of lithium insertion/extraction and helps in maintaining structural integrity over many charge/discharge cycles [6]. Therefore, the silicon nanowire can improve the battery overall energy density by high theoretical capacity and small size particles with low expansion.

2.3. Advanced Carbon Materials

Not only silicon nanowires but also nanostructured metal oxide materials have the potential to help enhance the performance of lithium-ion batteries. The traditional material in anode, graphite, normally has problems related to the formation of lithium dendrites during charging and discharging due to low voltage, which can pass through the diaphragm and lead to internal short circuits, cell damage and heating up until fire [15]. The formation of Lithium dendrites on the surface of the graphite anode is due to the low operating potential of about 0.1V [16]. Therefore, searching the high operating potential material using in anode is essential problem. Based on Figure 3, the region of the material between capacity and potential is shown. The high operating potential will reduce the lithium dendrite stacking in Lithiation/Delithiation processing. Therefore, the Titanium oxides are good choice in anode, which can reduce the lithium dendrite stacking. In this way, TiO_2 (B) has been found by scientists to be a promising anode carrier, and due to the unique crystal structure, the total Li^+ occupancy of the ten possible sites in TiO_2 (B) can lead to a theoretical capacity of up to 420 mAh g^{-1} [17]. However, In the course of their research, scientists have discovered serious drawbacks to titanium oxide, with poor electronic conductivity (~10-12 S cm^{-1}) due to its large band gap (3.09-3.22 eV) preventing titanium oxide from becoming a replacement for graphite at the anode [18].

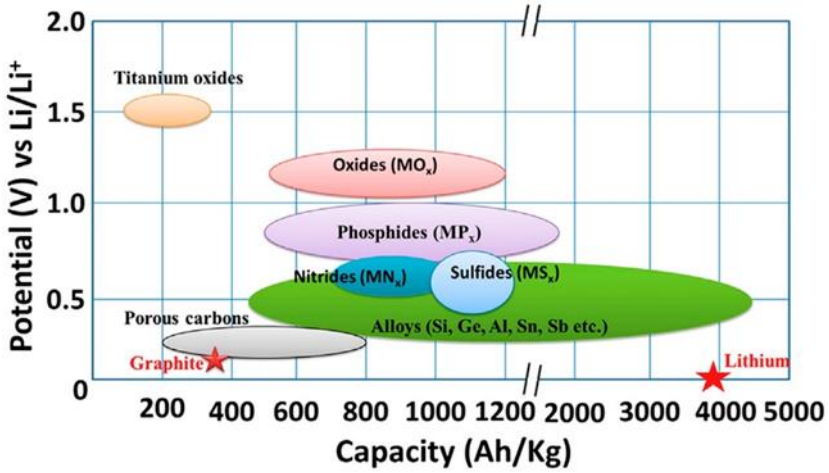


Figure 3. Specific capacity and average potential of most common anode materials for LIBs [19]

Similar to silicon, TiO_2 (B) has been extensively studied by scientists who employ morphology engineering to enhance its electrical properties. Various nanostructures of TiO_2 (B) have been investigated, including nanotubes, nanowires, nanorods, nanoribbons, nanofibers, nanosheets, and nanoparticles. Due to its low volume expansion rate, TiO_2 (B) nanostructures can significantly increase energy density by expanding the particle surface area and reducing diffusion distances. This morphological optimization helps improve the overall performance and stability of lithium-ion batteries.

3. Nanomaterials in cathode Design

3.1. Nanostructured Cathode Materials

The cathode material also has the potential to improve in energy density of the lithium-ion battery. Sulfur can become the cathode material since Sulfur has a low cost and high specific capacity [14]. In the lithium-ion battery, the Sulfur had 80% volume expansion compared with the original one and converted to Li_2S [14]. The lithiation of sulphur is more serious than that of other compounds in that the expansion of the electrode allows soluble compounds to escape [14]. This results in a significant reduction in the capacity of the battery. It significantly prevents the development of an energy density limit for lithium-ion batteries. Therefore, nanomaterials have the potential to help improve the energy density limit of the cathode as a way to increase battery capacity. Based on the study of S-TiO_2 yolk-shell nanostructures and polymer-coated hollow sulphur nanorods, scientists believe that the cathode can be protected by resisting expansion through the internal voids of hollow sulphur nanorods [20, 21]. The structure of S-TiO_2 yolk-shell is shown in Figure 4.

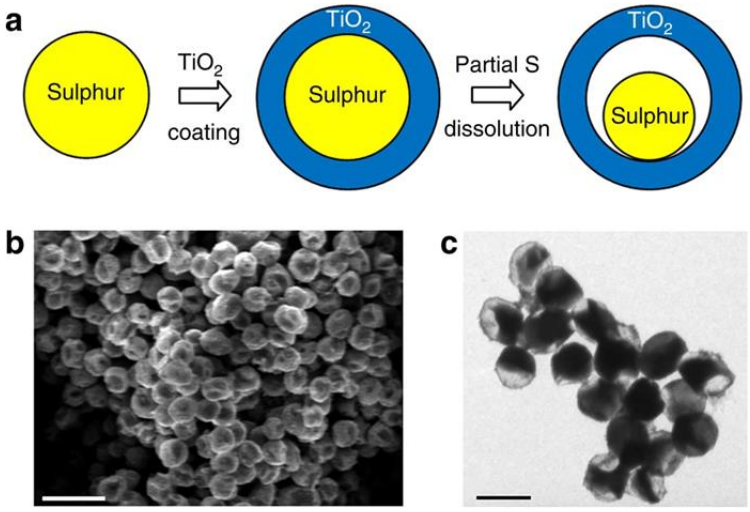


Figure 4. The S-TiO_2 yolk-shell nanostructure [21]

3.2. High-Voltage Cathode Nanomaterials

The combination of high-voltage positive electrodes with metal or graphite anode electrodes offers a viable route to future high-energy batteries. For example, lithium cobalt oxide (LCO), lithium iron phosphate, manganese-based cathode, etc. are all high-pressure materials in the cathode that have the potential to increase volumetric energy density. Especially with the vigorous development of electronic goods and EVs, the demand for high volumetric energy density has increased dramatically. The volumetric energy density of the cathode is seen as a crucial part of the commercialisation of lithium batteries [22]. With the research and development of cathode materials for lithium batteries, nickel-cobalt-manganese ternary (NCM) and LCO have become the cathode materials applicable to two different fields [22].

Firstly, Lithium cobaltate receives favour in lithium-ion batteries for small electronic products such as iPhones. Due to the relatively high compaction density, LCO has a better volumetric energy density compared to NCM. Since the volumetric energy density of pure LCO is not ideal, scientists have applied doping to improve the volumetric energy density for the battery. For example, Mg doping for NCM has a better electronic conductivity, especially when Co has been replaced by Mg which is found by Mladenov M [23]. Therefore, LCOs are widely used in computers, communications, and consumer electronics markets.

Secondly, NCM is widely used as cathode material for EV batteries due to its relatively low cost and good thermal stability compared with $LiCoO_2$. For the NCM, the focus of scientists' research is mainly on the composition of the atomic components. Different ratios of atomic components will affect the capacity and thermal stability [24]. Generally speaking, the higher the Ni content in the

NCM, the higher the reversible capacity. However, high Ni content also leads to reduced structural and thermal stability when the NCM anode is deeply charged [25]. For example, Ni, Co and Mn atomic ratios are close to 50:20:30 and 40:30:30, which is two NCM material in business with good electrical conductivity and energy density [26].

Therefore, the two cathode materials is used in different applications. There have potential for research to improve the volumetric energy density of these materials.

4. Nanotechnology in Electrolytes

Electrolytes in lithium-ion batteries is usually divided into the liquid electrolyte and solid electrolyte. People in the beginning usually used liquid electrolytes in lithium-ion batteries, due to the excellent ion conductivity of the liquid electrolyte [17]. However, due to the lack of thermal stability of the liquid electrolyte, the liquid electrolyte easy to result in serious problems. For example, the short cycle lifetime and unsafety always affect the development of the liquid electrolyte [17]. Lithium metal is prone to form dendrites during the charging process, and liquid electrolytes are unable to inhibit the formation of dendrites leading to fires [18]. And then when batteries are damaged by expansion or impact, liquid electrolytes are very easy to leak and then fire, which is intolerable and a major limiting factor in the development of liquid electrolytes.

4.1. Solid-State Electrolytes

Solid electrolytes are nowadays considered to be more promising and utilised. For example, Instead of liquid electrolytes, people use solid electrolyte diaphragms to accomplish ion transport [27]. Although solid electrolytes are relatively safer and have a long cycle life, they have the potential to improve ionic conductivity. In solid electrolyte transport is by diffusion through crystal defects such as Schottky and Frenkel point defects [27]. Nanomaterials can effectively shorten the diffusion distance, which means that the rate of ion conductivity is enhanced to improve battery performance. For example, Ceramic electrolyte nanowires have also been added to polymer matrices to create thermally stable solid electrolytes to prevent fires caused by dendrite build-up [28]. Xue Wang used of vertically aligned ceramic nanoparticles in polymer matrices effectively improved ionic conductivity to 1.67 × 10-4 S cm-1at 25°C [28]. However, the difficulty with the ion conductivity in lithium-ion batteries also from the ionic conductivity between different crystalline phases which also affects the final solid electrolyte conductivity, e.g. cross-interfacial jumps and diffusion along the interface [28]. Since nanocomposites can take advantage of the rapid diffusion of ions at the interface and the large volume ratio at the interface between the nanoparticles, they can significantly improve the ion conductivity in lithium-ion batteries [29]. Therefore, nanotechnology is very helpful in increasing the ion conductivity and improving the energy density of lithium-ion batteries.

5. Current Challenges and Future Directions

Nanomaterials have great potential to be the material that changes the energy density of lithium-ion batteries. Based on the information mentioned above, there are already research directions for nanotechnology to improve lithium-ion batteries. However, nanomaterials used in lithium-ion batteries also face some challenges. Nanomaterials can be more costly for factories due to their small size compared to micron-sized materials [30]. A larger surface area improves lithium-ion batteries while consuming more electrolytes and lithium ions, resulting in lower capacity and energy density. People need to find an equilibrium between a stable solid electrolyte and a high surface area. As materials for lithium-ion batteries, nanomaterials can already be used in batteries to improve energy capicaity. However, for commercial applications, more low-cost and high-yield preparation methods have not been well researched [30].

In the future, people could increase the energy density of batteries by investigating more nanostructures to help improve the problem of too high surface area. People also improve energy

density by researching solid electrolytes to help reduce electrolyte losses. The micron-sized secondary particles are a good direction to solve those problems [30]. The most important is that for mass production of nanoscale materials is the path that commercialisation must go through. For various industries, mass-produced nanomaterials can only be well used in the battery field. Therefore, for the future low-cost poduction is an important direction.

6. Conclusion

In conclusion, this paper highlights the transformative potential of nanomaterials in enhancing the energy density and overall performance of lithium-ion batteries. Traditional materials, such as graphite anodes, have limitations in capacity and energy density, which hinder the advancement of applications, particularly in electric vehicles. The introduction of nanostructured materials, including silicon and metal oxide anodes, has demonstrated significant improvements in capacity and stability by mitigating issues related to volumetric expansion and enhancing lithium diffusion kinetics. For cathodes, nanomaterials such as S-TiO_2 yolk-shell structures and high-voltage materials like lithium nickel manganese cobalt oxides (NMC) show promise in increasing volumetric energy density and maintaining stability under high energy conditions. These advancements are crucial for meeting the growing demand for high-performance batteries in consumer electronics and electric vehicles. In the realm of electrolytes, the shift from liquid to solid-state electrolytes facilitated by nanotechnology presents a safer and more efficient alternative. Nanostructured solid electrolytes enhance ionic conductivity and prevent dendrite formation, addressing key safety and performance challenges in lithium-ion batteries. Despite the clear advantages, the commercialization of nanomaterials in lithium-ion batteries faces challenges, particularly in terms of cost and scalable production methods. Future research should focus on developing cost-effective, high-yield preparation techniques and optimizing nanostructures to balance high surface area with stable performance. Overall, the integration of nanomaterials in lithium-ion batteries represents a promising direction for future advancements in energy storage technology, with the potential to significantly improve the energy density, safety, and longevity of these crucial devices..

References

[1] Masias A, Marcicki J, Paxton WA. Opportunities and challenges of lithium-ion batteries in automotive applications. ACS energy letters. 2021; 6 (2): 621-30.

[2] Chen X, Shen W, Vo TT, Cao Z, Kapoor A. An overview of lithium-ion batteries for electric vehicles. In2012 10th International Power & Energy Conference (IPEC) 2012; 230-235. IEEE.

[3] Lu L, Han X, Li J, Hua J, Ouyang M. A review on the key issues for lithium-ion battery management in electric vehicles. Journal of power sources. 2013, 226: 272-88.

[4] Deng J, Bae C, Denlinger A, Miller T. Electric vehicles batteries: requirements and challenges. Joule. 2020; 4 (3): 511-5.

[5] Bruce PG, Scrosati B, Tarascon JM. Nanomaterials for rechargeable lithium batteries. Angewandte Chemie International Edition. 2008; 47 (16): 2930-46.

[6] Lee KT, Cho J. Roles of nanosize in lithium reactive nanomaterials for lithium ion batteries. Nano today. 2011; 6 (1): 28-41.

[7] Jiang C, Hosono E, Zhou H. Nanomaterials for lithium ion batteries. Nano today. 2006; 1 (4): 28-33.

[8] Li M, Lu J, Chen Z, Amine K. 30 years of lithium-ion batteries. Advanced Materials. 2018; 30 (33): 1800561.

[9] Cao W, Zhang J, Li H. Batteries with high theoretical energy densities. Energy Storage Materials. 2020; 26: 46-55.

[10] Zamfir MR, Nguyen HT, Moyen E, Lee YH, Pribat D. Silicon nanowires for Li-based battery anodes: a review. Journal of Materials Chemistry A. 2013; 1 (34): 9566-86.

[11] L. Y. Beaulieu, K. W. Eberman, R. L. Turner, L. J. Krause and J. R. Dahn, Electrochem. Solid-State Lett., 2001, 4, A137—A140.

[12] L. Y. Beaulieu, T. D. Hatchard, A. Bonakdarpour, M. D. Fleischauer and J. R. Dahn, J. Electrochem. Soc., 2003, 150, A1457—A1465.

[13] J. O. Besenhard, J. Yang and M. Winter, J. Power Sources, 1997, 68, 87—905.

[14] Sun Y, Liu N, Cui Y. Promises and challenges of nanomaterials for lithium-based rechargeable batteries. Nature Energy. 2016; 1 (7): 1-2.

[15] Seh ZW, Li W, Cha JJ, Zheng G, Yang Y, McDowell MT, Hsu PC, Cui Y. Sulphur-TiO2 yolk-shell nanoarchitecture with internal void space for long-cycle lithium-sulphur batteries. Nature communications. 2013; 4: 1331.

[16] Zhou, W. D., Yu, Y. C., Chen, H., DiSalvo, F. J. & Abruña, H. D. Yolk–shell structure of polyaniline-coated sulfur for lithium–sulfur batteries. J. Am. Chem. Soc. 2013,135, 16736–16743

[17] Manthiram A, Yu X, Wang S. Lithium battery chemistries enabled by solid-state electrolytes. Nature Reviews Materials. 2017; 2 (4): 1-6.

[18] Nano-silicon/carbon composite anode materials towards practical application for next generation Li-ion batteries. Journal of The Electrochemical Society. 2015; 162 (14): A2509.

[19] Mehrer, H. Diffusion in Solids: Fundamentals, Methods, Materials, Diffusion-Controlled Luo F, Liu B, Zheng J, Chu G, Zhong K, Li H, Huang X, Chen L.

[20] Wang X, Zhai H, Qie B, Cheng Q, Li A, Borovilas J, Xu B, Shi C, Jin T, Liao X, Li Y. Rechargeable solid-state lithium metal batteries with vertically aligned ceramic nanoparticle/polymer composite electrolyte. Nano Energy. 2019; 60: 205-12.

[21] Wang S, Chen L. Interfacial transport in lithium-ion conductors. Chinese Physics B. 2015; 25 (1): 018202.

[22] Maier J. Defect chemistry: composition, transport, and reactions in the solid state; part I: thermodynamics. Angewandte Chemie International Edition in English. 1993; 32 (3): 313-35.

[23] Liu N, Lu Z, Zhao J, McDowell MT, Lee HW, Zhao W, Cui Y. A pomegranate-inspired nanoscale design for large-volume-change lithium battery anodes. Nature nanotechnology. 2014; 9 (3): 187-92.

[24] Bandhauer, T.M.; Garimella, S.; Fuller, T.F. A critical review of thermal issues in lithium-ion batteries. J. Electrochem. Soc. 2011, 158, R1–R25.

[25] Goriparti S, Miele E, De Angelis F, Di Fabrizio E, Zaccaria RP, Capiglia C. Review on recent progress of nanostructured anode materials for Li-ion batteries. Journal of power sources. 2014; 257: 421-43.

[26] Opra DP, Gnedenkov SV, Sinebryukhov SL. Recent efforts in design of TiO_2 (B) anodes for high-rate lithium-ion batteries: A review. Journal of Power Sources. 2019; 442: 227225.

[27] Wang X, Wang X, Lu Y. Realizing high voltage lithium cobalt oxide in lithium-ion batteries. Industrial & Engineering Chemistry Research. 2019; 58 (24): 10119-39.

[28] Mladenov M, Stoyanova R, Zhecheva E, Vassilev S. Effect of Mg doping and MgO-sur0face modification on the cycling stability of LiCoO2 electrodes. Electrochemistry Communications. 2001; 3 (8): 410-6.

[29] Liu S, Xiong L, He C. Long cycle life lithium ion battery with lithium nickel cobalt manganese oxide (NCM) cathode. Journal of Power Sources. 2014; 261: 285-91.

[30] Lee KS, Myung ST, Amine K, Yashiro H, Sun YK. Structural and Electrochemical Properties of Layered Li [Ni1− 2x Co x Mn x] O2 (x=0.1–0.3) Positive Electrode Materials for Li-Ion Batteries. Journal of The Electrochemical Society. 2007; 154 (10): A971.