Active Electrode Materials for High-Performance Lithium-Ion Battery

Yihan Deng*

Dulwich International High School Programme, Suzhou, 215021, China

*Corresponding author: hanna.deng26@stu.dulwich.org

Abstract. The global demand for energy storage solutions has surged in response to rapid technological and economic growth. Lithium-ion batteries (LIBs) have become essential because of their superior energy density, power density, long lifespan, and relatively lower environmental impact. This review examines the structure and key components of LIBs, including recent technological advancements, focusing on the materials for LIBs. It not only highlights the critical role of electrode materials in enhancing the performance of LIBs but also reviews the challenges associated with current materials and the opportunities for improvement. Significant emphasis is placed on the development of advanced cathode and anode materials to address issues in stability, strength, cycle life, and electrochemical performance. Additionally, the review explores emerging strategies to overcome these challenges, providing a comprehensive overview of future research directions that could lead to the next-generation LIBs. Finally, this review is crucial for advancing the design and efficiency of LIBs, paving the way for more sustainable energy storage systems.

Keywords: Lithium-ion battery; electrode material; energy storage.

1. Introduction

Achieving carbon neutrality is crucial for the sustainable advancement of human society. Renewable energy sources are pivotal in reducing carbon emissions and transforming the global energy system. As highlighted by the World Energy Council, Global electricity generation from wind turbines and photovoltaic modules by 2020 is approximately 474 gigawatts (GW) and 100 million GW, respectively [1]. Achieving national decarbonization goals will require substantial integration of renewable energy sources into the power grid. However, a major challenge with renewables like wind and solar is their intermittency. As a result, developing suitable energy storage technologies to complement the growth of renewable energy is essential. Lithium-ion batteries (LIBs) stand out as the most advanced and widely utilized. This is due to their notable advantages, including high energy and power density, extended lifespan, and low self-discharge rates even in extreme temperature conditions.

LIBs, initially developed in 1991 and first commercialized by Sony Corporation, have enabled the widespread use of portable electronics like smartphones and laptops, which have become essential in modern life [2]. In recent years, LIBs have garnered significant interest as a potential energy storage solution for both electric vehicles (EVs) and large-scale energy storage systems. As global efforts intensify to reduce CO_2 emissions, LIBs are expected to play an increasingly vital role in driving the green transformation of electricity distribution and transportation systems [3]. Despite years of development, lithium-ion batteries still face many challenges. This paper focuses on electrode active materials, summarizing the development history, classification, and application of cathode and anode active materials and anticipating future development trends.

2. Working Mechanism of LIBs

A LIB is an electrochemical cell that generates energy through electrochemical reactions. LIBs are composed of several key components: the anode, cathode, electrolyte, separator, and current collector (Fig. 1). The anode functions as the negative electrode, while the cathode serves as the positive electrode, with lithium ions transferring between them via the electrolyte. During charging, lithium

ions travel from the cathode to the anode, while during discharging, they move in the reverse direction, from the anode to the cathode [4]. The half-reactions taking place at the cathode and anode in LIBs can be expressed as follows:

$$LiCoO_2 \leftrightarrow Li_{1-x}CoO_2 + xLi^+ + xe^- \text{ (cathodic half)} \quad (1)$$

$$xLi^+ + xe^- + 6C \leftrightarrow Li_xC_6 \text{ (anodic half)} \quad (2)$$

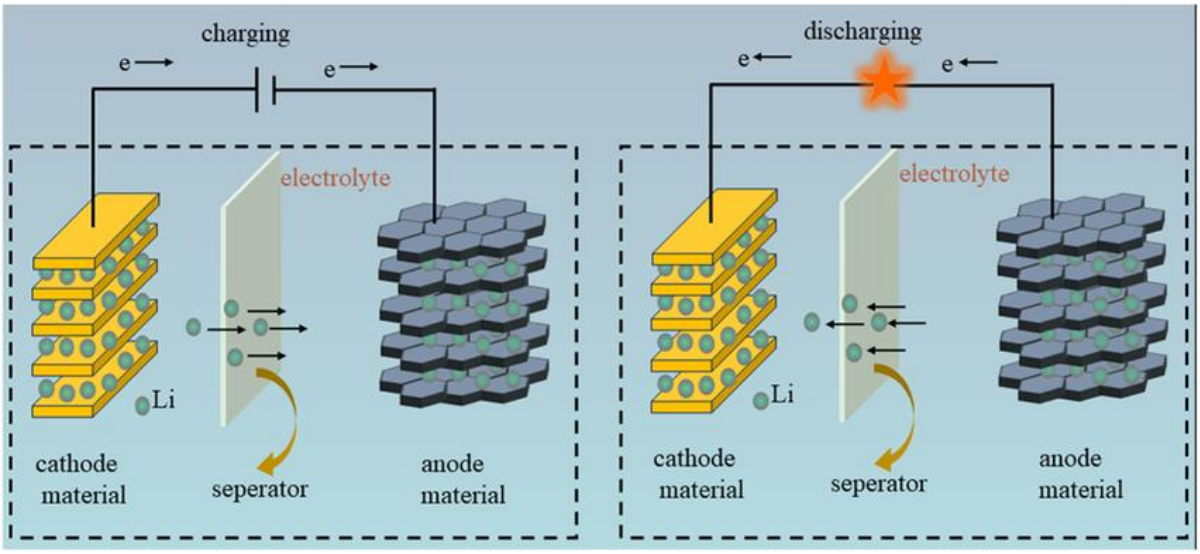

Fig. 1 Working mechanism demonstration of LIB [5].

3. Cathode Active Materials

The commercialized cathode active materials can be categorized based on the crystal structure into three main types: layered structure, spinel structure and olivine structure. The crystal structure determines the properties of a material. For example, the layer structure materials, such as lithium cobalt oxide ($LiCoO_2$), typically show high energy density making them more suitable for portable energy derives. The spinel structure, such as lithium manganese oxide ($LiMn_2O_4$), shows excellent rate performance and is applicable in high-power applications. On the other hand, the olivine structure materials, such as lithium iron phosphate ($LiFePO_4$), exhibit high thermal stability and are more often used in applications requiring safety. In this section, we will describe different materials in detail, discussing their respective structures and performance characteristics.

3.1. Layered Structure Materials

Layered materials are the first commercially available cathode-active materials for LIBs. They typically show high energy density and poor thermal stability. The most widely used layered structure materials are $LiCoO_2$ and $Li[Ni_xCo_yMn_z]O_2$.

3.1.1 $LiCoO_2$

$LiCoO_2$ was first developed in 1980, which made a significant advance in the history of LIBs. In 1991, Sony first commercialized $LiCoO_2$ as the positive electrode material, combining with the carbon anode to produce the first successful LIBs. From an electrochemical perspective, Li_xCoO_2 is a promising material due to its high theoretical capacity of 274 mAh/g and high energy density. However, oxygen loss occurs when the delithiation state exceeds 50% ($x>0.5$ in $Li_{1-x}CoO_2$), leading to safety risk in full cell (>4.2 V). To solve the problem, bulk doping and surface coating technologies have been developed to inhibit oxygen loss at a high delithiation state. Nowadays, the delithiation state of commercial $LiCoO_2$ can be over 80% ($x>0.8$ in $Li_{1-x}CoO_2$). $LiCoO_2$ shows the highest volumetric energy density among all cathode materials for LIBs. In the future, $LiCoO_2$ may be used in all-solid-state LIBs for EVs, offering enhanced performance and safety.

3.1.2 $Li[Ni_xCo_yMn_z]O_2$

The development of $Li[Ni_xCo_yMn_z]O_2$, also known as NCM, is based on their earlier materials like $LiCoO_2$ and $LiNiO_2$. Early work has investigated different Ni concentrations, with a focus on compositions like NCM523 (Ni:Co:Mn= 5:2:3), NCM622 (Ni:Co:Mn = 6:2:2), and 8:1:1 NCM811 (Ni:Co:Mn = 8:1:1) for applications requiring high density. Since Ni is the redox-active element in NCM, the higher the Ni content, the higher the energy density. However, because of the weaker Ni-O bonds, there is a drop in thermal stability and structural stability along with a decrease in cycling ability with this increase in Ni content. Furthermore, the reactivity of the surface layer with respect to chemical interactions is intensified because of its inherently more oxidative characteristics of the Ni^{3+}/Ni^{4+} redox potential.

In a LIB, the separator serves to physically isolate the anode from the cathode, preventing short circuits. This thin, porous membrane allows lithium ions to pass through during both the charging and discharging processes. Both thermal and structural stability have been improved to enhance capacity retention. In fact, the combination of Ni, Mn, and Co provides several good points. For instance, Ni offers energy density, Mn provides structural stability, and Co improves electronic conductivity.

Fig. 2 illustrates the relationship between the composition and performance of NCM oxides. It is evident that there is a trade-off between the cell's capacity and its thermal stability when choosing a cathode material. Furthermore, extra lithium is typically added during synthesis to make up for the lithium lost during sintering. The excess lithium in the final sample exists as Li_2O, which readily reacts with H_2O and CO_2 in the air, forming LiOH and Li_2CO_3 at room temperature. The remaining carbonate subsequently breaks down into CO_2 during the formation (charging) process, leading to gas expansion and raising additional safety concerns [6]. Among the different layered NCM oxides, $LiNi_{0.8}Mn0.1Co_{0.1}O_2$ has attracted significant attention due to its high discharge capacity, around 200 mAh/g at a 0.2 C current rate within 2.8–4.3 V.

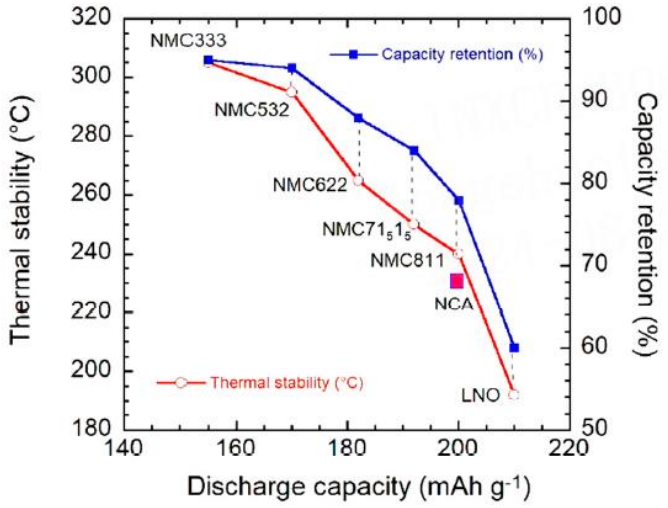

Fig. 2 The relationship between composition and performance in layered nickel-manganese-cobalt oxides plays a critical role. Selecting a suitable cathode material requires balancing the cell's capacity and its thermal stability [7].

3.2. Spinel Structure Materials

Materials made of spinel $LiMn_2O_4$ are becoming increasingly popular due to their cost-effectiveness, reversibility, fast intercalation and de-intercalation of Li ions [8]. The spinel structure of $LiMn_2O_4$ (space group: Fd3m) consists of a closely packed configuration of oxygen ions at the 32e position, with Mn ions positioned at the octahedral 16d site, and Li^+ occupying the tetrahedral 8a site. In $Li_xMn_2O_4$ ($0 < x \leq 2$), Mn_2O_4 forms a three-dimensional framework for Li^+.

Li ions occupy the 8a sites when $0 < x \leqslant 1$ at around 4 V. At 3 V, however, the inserted Li^+ ions move into the octahedral 16c sites, which share faces with the 8a tetrahedral sites. This migration of Li ions from the 8a to the vacant 16c sites triggers a first-order phase transition to $Li_2Mn_2O_4$. Furthermore, an increase in Mn^{3+} concentration induces Jahn-Teller distortion, lowering the crystal symmetry from cubic to tetragonal $Li_2Mn_2O_4$. As a result, it is generally believed that the electrochemical performance of spinel $LiMn_2O_4$ is better at 4 V than at 3 V. Despite this, $Li_2Mn_2O_4$ can still be detected on the surface of $LiMn_2O_4$ in a 4 V cell after the discharge process, as it forms as an over-discharge byproduct [9].

In summary, $LiMn_2O_4$ suffers from capacity fading, especially at temperatures around 55 °C, which causes Mn ion dissolution. A well-established approach to address these issues involves improving the electrode-electrolyte interface by applying a protective coating to the material's surface, minimizing direct contact with the electrolyte.

3.3. Olivine Structure Materials

$LiFePO_4$ provides outstanding cycling performance, is cost-effective, and benefits from the abundance of iron. Upon the insertion and extraction of Li^+, it has been noted that the two concurrent phases, namely $LiFePO_4$ and $FePO_4$ are discernible, both of which are characterized by the occupation of an identical space group. The insertion and extraction of Li^+ are related to the motion of the two-phase interface. A shrinking core model has been suggested, where Li ions pass through the phase barrier and migrate inward from the particle's surface. As lithiation progresses, the interface surface area decreases until it reaches a critical point, after which the rate of Li insertion can no longer support the applied current.

TEM analyses revealed that lithiation and de-lithiation in $LiFePO_4$ occur through two-phase reactions involving $LiFePO_4$ and $FePO_4$ [10]. This was observed through the migration of the step-shaped phase boundary along the b-axis or [010] direction, as depicted in Fig. 3. The study confirms the presence of a lattice mismatch at the phase boundary, leading to dislocations in the $FePO_4$ side, created by the transformation between the two phases. Additionally, due to the elastic deformation that accommodates the transition strain, the orientation of LiFePO4 slightly changes compared to $FePO_4$. During cycling, these dislocations build up and may result in additional flaws or cracks that impair the system.

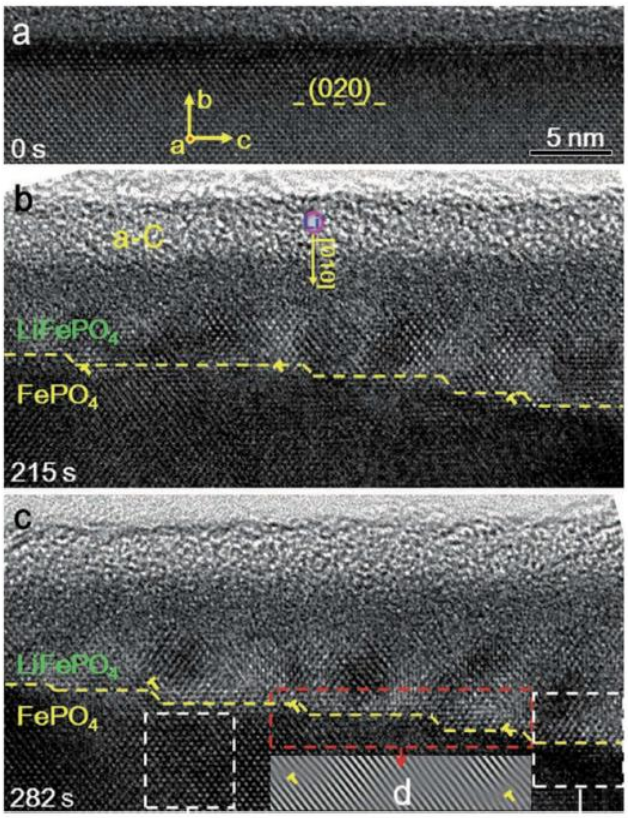

Fig. 3 Phase boundary between $FePO_4$ and $LiFePO_4$ and its migration along the [010] direction during lithiation [10].

4. Anode Materials

The anode is another core component of LIBs. Since the negative electrode material may store lithium ions during charging, it has a great contribution to the function and performance of the battery. Nowadays, several types of anode materials for LIBs have been studied, such as lithium, silicon, graphite, inter-metallic or lithium-alloying materials.

4.1. Intercalation Type Anode Materials

Carbon-based substances serve as the pioneering anode materials investigated and utilized in the fabrication of LIBs. LiC_6 is produced through the intercalation of lithium ions. LiC_6 manifests a discharge plateau beneath 0.2 V, relative to the Li^+/Li couple, and it boasts exceptional dynamic characteristics with respect to the intercalation of lithium [11]. Nevertheless, its resistance to overcharging is somewhat compromised owing to the modest insertion/ejection potential of lithium ions within the graphite structure. The high graphitization crystallinity and pronounced orientation of the lamellar structure further compound this.

Hard carbon promotes the diffusion of Li^+ ions, allowing for rapid charging and discharging thanks to its wide channels. Consequently, it delivers a high capacity and outstanding rate performance.

Lithium titanium oxide ($Li_4Ti_5O_{12}$) is a well-known intercalation anode material that provides high safety and outstanding cycling stability, making it a promising alternative to traditional graphite anodes. Fig. 4 illustrates the delithiation/lithiation process of $Li_4Ti_5O_{12}$ at voltage ranges of 3, 1-3, and 0.01-1 V, respectively [12]. Due to the minimal volume changes and highly stable structure of $Li_4Ti_5O_{12}$ during charge and discharge cycles, the issue of capacity loss from volume expansion is effectively prevented, resulting in an exceptionally long cycle life. Consequently, it has been extensively researched for applications in long-lasting lithium-ion batteries.

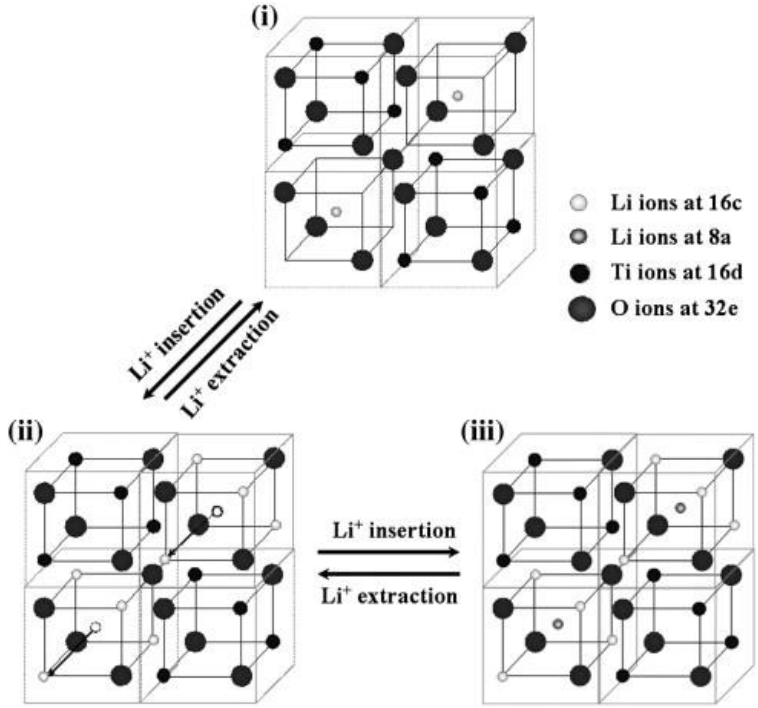

Fig. 4 Scheme of the Li^+ interaction and de-intercalation from the spinel $Li_4Ti_5O_{12}$ structure at (a) 3, (b) 1-3 and (c) 0.01-1 V [12].

4.2. Conversion Type Anode Materials (CTAM)

CTAMs have gained attention as promising anode materials for LIBs, thanks to their appealing properties and high theoretical specific capacity. One advantage is that they are relatively cheaper to produce compared to alloy anode materials, largely because many CTAMs are naturally occurring. Examples of such materials include magnetite (Fe_3O_4), pyrite (FeS_2), and pyrolusite (MnO_2). Additionally, due to their lower lithium intercalation potential, CTAMs, unlike graphite anodes, do not generate lithium dendrites, potentially offering improved operational safety for LIBs. However, CTAMs have significant drawbacks, including inherently poor electronic and ionic conductivity, as well as ongoing electrolyte decomposition.

4.3. Alloying Type Anode Materials

Alloy anode materials mainly come from groups IVA and VA. These materials store lithium through an alloying reaction, forming a LiwM alloy. For example, the alloying reaction for silicon (Si) is as follows [13]:

$$Si + 4.4Li+ + 4.4e- \leftrightarrow Li4.4Si \quad (3)$$

While lithium metal is an ideal candidate, its use is hindered by issues like dendrite formation and growth. Tin-based materials, offering higher volumetric capacity and lower operating voltage, have emerged as some of the most promising alternatives to graphite. Numerous Sn-based materials have been developed and studied to date. However, when considering factors such as volumetric capacity, operating voltage range, mass load, binder, and carbon content, some of these materials still fail to meet the requirements for high energy density.

5. Conclusion

In summary, LIBs are one of the most prevalent and widely utilized power sources today, primarily due to their high energy density, extended cycle life, and relatively low environmental footprint. This paper offers an in-depth review of LIBs, with a particular emphasis on the active materials used in their design and construction.

At present, various cathode materials, such as $LiCoO_2$, $LiMn_2O_4$, Li $(Ni_xMn_yCo_z)O_2$, and olivine ($LiFePO_4$), have been extensively studied. Each cathode material has its own set of challenges. For instance, layered structure oxides like $LiCoO_2$ show high energy density but suffer from insufficient cycling stability. The above issues can be addressed by strategies such as bulk doping and surface coating. Additionally, enhanced electrochemical performance can be achieved by blending layered oxide with more stable cathode such as LMO and LFP. Future research for cathode materials focuses on new materials that offer high capacity, high cyclic performance, low cost and long-lasting stability, especially with features to prevent thermal runaway.

Generally, anode materials used in LIBs include carbon, alloys, transition metal oxides, and silicon, among others. Many of these materials suffer from significant volume changes. This issue can be addressed by using nanocomposites, nanostructured silicon, nonporous structures, or nanowires. Another common problem is dendrite formation, which can be reduced by ensuring smooth and pure electrode surfaces. Anatase TiO_2-based anode electrodes face challenges with imperfect chemical diffusivity, necessitating appropriate porosity in the anode materials to mitigate this issue. There is still considerable research needed to develop an ideal anode material that overcomes these limitations and offers superior electrochemical performance.

Apart from cathode and anode materials, electrolytes used in LIBs are also of significant concern. Organic solvents have the potential to emit noxious fumes, which consequently entail the perils of unforeseen explosions and environmental contamination. Thus, further research on electrolytes is needed to prevent the generation of toxic gases. Efforts should focus on developing environmentally friendly battery materials while also enhancing operational performance.

References

[1] Yang Zhenguo, Zhang Jianlu, Kintner-Meyer Michael CW, et al. Electrochemical energy storage for green grid. Chemical Reviews, 2011, 111(5): 3577-3613.

[2] Liang Yeru, Zhao Chen-Zi, Yuan Hong, et al. A review of rechargeable batteries for portable electronic devices. InfoMat, 2019, 1(1): 6-32.

[3] Das Himadry Shekhar, Rahman Mohammad Mominur, Li Shuhui, et al. Electric vehicles standards, charging infrastructure, and impact on grid integration: a technological review. Renewable and Sustainable Energy Reviews, 2020, 120: 109618.

[4] Roy Poulomi and Srivastava Suneel Kumar. Nanostructured anode materials for lithium ion batteries, Journal of Materials Chemistry A, 2015, 3(6): 2454-2484.

[5] He Geping, Mi Yuanmei, Wang Di, et al. Synthesis methods and applications of semiconductor material ZnWO4 with multifunctions and multiconstructions. Energy Technology, 2021, 9(12): 2100733.

[6] Jo Chang-Heum, Cho Dae-Hyun, Noh Hyung-Joo, et al. An effective method to reduce residual lithium compounds on Ni-rich Li[Ni0.6Co0.2Mn0.2]O2 active material using a phosphoric acid derived Li3PO4 nanolayer. Nano Research, 2015, 8: 1464-1479.

[7] Julien Christian and Maurer Alain. NCA, NCM811, and the Route to Ni-Richer Lithium-Ion Batteries. Energies, 2020, 13(23), 6363.

[8] Yang Chunxiang, Deng Yuanfu, Gao Man, et al. High-rate and long-life performance of a truncated spinel cathode material with off-stoichiometric composition at elevated temperature, Electrochim Acta, 2017, 225: 198-206.

[9] Thackeray Michael M., Yang Shao-Horn, Kahaian Arthur J., et al. Structural fatigue in spinel electrodes in high voltage (4 V) Li/LixMn2O4 cells, Electrochemical and Solid-State Letters, 1998, 1(1): 7.

[10] Zhu Yujie, Wang Jiangwei, Liu Yang, et al. In situ atomic-scale imaging of phase b1oundary migration in FePO4 microparticles during electrochemical lithiation, Advanced Materials, 2013, 25(38): 5461-5466.

[11] Son Dong-Kyu, Kim Jisu, Raj Michael Ruby, et al. Elucidating the structural redox behaviors of nanostructured expanded graphite anodes toward fast charging and high-performance lithium-ion batteries. Carbon, 2021, 175: 187-201.

[12] Hsieh Chien-Te, Chen I-Ling, Jiang Yun-Ru, et al. Synthesis of spinel lithium titanate anodes incorporated with rutile titania nanocrystallites by spray drying followed by calcination. Solid State Ionics, 2011, 201(1): 60-67.

[13] Kummer Malin, Badillo J.P., Schmitz A., et al. Silicon/polyaniline nanocomposites as anode material for lithium ion batteries. Journal of The Electrochem Society, 2013, 161(1): A40.