Modern applications of new battery materials

Overview: New directions for battery materials

By C. A. Vlaic, S. D. Ivanov, A. Bund, Department of Electrochemistry and Electroplating, Ilmenau University of Technology, Ilmenau/Germany

Whether in terms of electric vehicles or portable digital devices, further advances are largely dependent on the development of batteries with improved performance. This includes increased charge capacity, higher rates of charging and longer lifetime but also increased user safety. As well as the conventional electrolytes, ionic liquids are also of interest and with them, novel anode and cathode materials. In respect of the former, tin oxide and titanium oxide appear to offer plentiful availability, environmental acceptability and a range of good electrochemical properties. Suitable cathode materials are metal oxides with lithium and one or two additional metals which, in most cases, can be modified to improve conductivity. Also of interest are compounds with spinel and olivine structures, both of which offer good electrochemical properties.

Neue Batteriewerkstoffe in der Anwendung – Ein Überblick

Vor allem die weiter voranschreitenden Entwicklungen im Bereich der Elektromobilität und der mobilen Datengeräte erfordern Batterien mit besseren Leistungen. Dies bedeutet höhere Ladekapazitäten, schnelle Ladezyklen oder längere Lebensdauer, aber auch höhere Sicherheit im Gebrauch. Neben den derzeitigen Elektrolyttypen kommen hierfür auch ionische Flüssigkeiten zum Einsatz und damit auch neue Verbindungen für Anode und Kathode. Als Anodenwerkstoff eignen sich vor allem Zinnoxid und Titanoxid, die eine gute Verfügbarkeit, gute Umweltverträglichkeit sowie vielversprechende elektrochemische Eigenschaften aufweisen. Als Kathode eignen sich Metalloxide mit Lithium und einem oder zwei weiteren Metallen, die in der Regel modifiziert werden, um deren Leitfähigkeit zu verbessern. Des Weiteren kommen Verbindungen des Typs Spinell und Olivin in Betracht, die beispielsweise auch ein gutes elektrochemisches Fenster besitzen.

Development of new electrode materials for lithium ion batteries (LIBs) with improved performance constitutes worldwide the focus of intense research. The new generation LIBs must be high power, high energy systems with a very long cycle life, excellent safety futures, low cost and environmentally benign. All these are critical demands for LIBs and constitute an important challenge for modern electrochemistry [1]. Future lithium ion batteries are expected to play a major role in the hybrid electric vehicles (HEVs) and full electric vehicles (EVs) as well as in the stationary storage of renewable energy. These domains are of major importance, considering the implications of diminishing natural resources and the necessity to reduce carbon dioxid (CO_2) emissions [2].

The conventional LIBs are rather light, have low self-discharge, no memory effect, a voltage of about 3.6 V and specific energy in the range of 100 Wh/kg to 150 Wh/kg. Generally, a lithium metal oxide/phosphate (140 mAh/g to 170 mAh/g specific capacity) is the main cathode component, while the anode is made of graphite (370 mAh/g specific capacity), both soaked in the electrolyte (a lithium salt dissolved in organic carbonates) and separated by a polypropylene membrane. The existing commercial LIBs power mobile devices such as laptops and cell phones having an energy density of 2 to 3 times larger than other rechargeable batteries [3]. In spite of this, commercial LIBs reach their limit regarding the energy density (per volume) and specific energy (per mass) [4]. For the future application of LIBs in EVs and clean energy storage the new electrode materials need an increase of at least one order of magnitude in their charge/discharge rate and energy density [3].

The battery safety constitutes a serious issue [2]. While heat dissipation is not a problem for low-rate applications, in the case of high rate batteries failure to accommodate/dissipate heat rapidly can lead to thermal runaway [5]. In order to prevent such catastrophic events, there are two possible strategies: first is to use current limiting devices and the second is to improve the electrolyte solution either by employing additives or by adjustment of electrolyte composition. Such safety additives are redox shuttles, shut down or flame retardant additives [6]. The principle behind the redox shuttle mechanism consists in reversible oxidation of redox species when the positive electrode reaches certain potential followed by diffusion to the other electrode where the redox species get reduced. However, in the case of high rate charging and discharging, the diffusion to the negative electrode is not fast enough [7]. In contrast to redox shuttles shut down additives can release gases that activate a current interrupter device or can undergo polymerization blocking in this way the transport of lithium ions in the electrolyte. For an improved composition of the electrolyte solutions, $LiPF_6$ could be replaced with less toxic lithium salts that are safer for the environment [2].

A special chapter regarding improved safety of LIB is the development of alternative electrolytes more reliable and stable than the present organic carbonates [8]. Particularly promising are solutions of lithium salts in ionic liquids. Ionic liquids (ILs) are room temperature molten salts formed by the combination of large organic cations and anions. ILs are characterized by many useful features such as: non flammability and very low vapour pressure, thermal stability up to 300 °C to 400 °C and wide electrochemical windows. On the down side, ILs are highly viscous, have low conductivity and considerable cost.

In the search for improved LIBs with higher power/energy densities the scientists look for new materials with improved performances as well as for improvements of the already tested materials.

Since the first battery commercialized by Sony in 1990, which was equipped with a $LiCoO_2$ cathode and a graphite anode, a large number of electrode materials have been proposed. The new cathodes studied so far can be divided into three different types: materials with layered structure, olivine group and spinel compounds [9]. Anode materials that could replace the commonly used carbon anode are alloys, intermetallic compounds, metal oxides and metal sulfides/nitrides.

Besides finding new electrode materials much effort is devoted to finding new and innovative improvements to the already established elements. All of these possible future generation materials have their own advantages and disadvantages. Consequently, finding original ways to enhance the positive features and diminish the negative ones is a promising approach which already delivered remarkable results. For example, there are numerous reports and comprehensive reviews [4, 10, 11] dealing with nanostructured anodes for LIBs and the significant enhancement of their performance obtained as a result.

1   Anode materials

Graphite, the anode of choice for today's LIBs, can intercalate just one lithium atom per graphene unit (LiC_6) [12]. There are other materials such as silicon that can accommodate more than four lithium atoms during the alloying processes and consequently $Li_{4.4}Si$ has a theoretical capacity of 4200 mAh/g which is more than 10 times higher compared to that of graphite. As was already pointed out efforts are made all over the world for replacing the currently used anodes with higher capacity materials. Some of these alternatives are presented below.

1.1   Metal alloys

Lithium undergoes alloying processes with a number of elements mainly in groups IV and V, such as silicon, tin, germanium, lead, phosphorous, arsenic, antimony, and bismuth, and also some other metal elements, such as aluminium, gold, indium, gallium, zinc, cadmium, silver, and magnesium [11]. For example, pure tin has a theoretical capacity of 994 mAh/g, which is three times higher than that of the graphite anode.

The alloyed anodes have high specific capacities, low operation potentials vs. lithium and satisfactory safety features. The main challenge in using them as anodes in LIB comes from the large volume change during lithium alloying/dealloying processes. The large volume variation causes cracking of the electrode material, resulting in significant irreversible capacity and severe capacity fading.

Several strategies have been tried in order to preserve the structural integrity of the alloys during their operation. The first approach involves nanostructuring of the anode material. Nanostructures of silicon can mitigate this problem because it becomes more flexible in accommodating large changes in volume, has shorter lithium diffusion lengths and can accelerate the charge transfer during alloying/dealloying processes [4, 13–15]. Various silicon nanostructures have been studied so far including silicon nanowires (SiNWs) [16, 17] nanoporous silicon [18], silicon pillars [19] nanorods [20] or nanotubes [21, 22]. The second approach is to use an additional component either in the form of nano-composites; (metal nanoparticles coated with carbon) or as a carbon matrix which acts as a buffer for the large volume change of the metallic nanoparticles. Sony announced the first commercialization of Nexelion battery, a commercial success that has an amorphous tin-based composite anode that contains cobalt and carbon [23].

1.2   Metal oxides

There are three different categories of metal oxides with distinct lithium storage mechanisms: tin dioxide (SnO_2), which undergoes alloying/dealloying processes during charge/discharge cycles; titanium dioxide (TiO_2), where the storing and release of Li+ proceeds through an insertion/deinsertion mechanism, and transition metal oxides (TMO) with M = Fe, Co or Cu, which react reversibly with Li+ through the so called conversion reactions [24].

The three reaction mechanisms are displayed in the following equations:

– Lithium-alloy reaction mechanism:
$$M_xO_y + 2yLi^+ + 2ye^- \rightarrow xM + yLi_2O \qquad <1>$$
$$M + zLi^+ + ze^- \leftrightarrow 4Li_zM \qquad <2>$$
– Insertion reaction mechanism:
$$MO_x + yLi^+ + ye^- \leftrightarrow 4\ Li_yMO_x \qquad <3>$$
– Conversion reaction mechanism:
$$M_xO_y + 2yLi^+ + 2ye^- \leftrightarrow 4\ xM + yLi_2O \qquad <4>$$
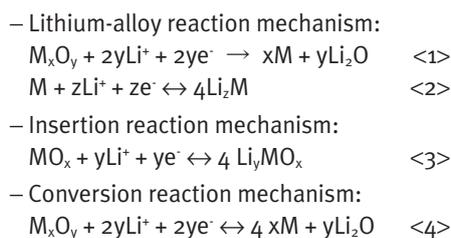
Due to its high theoretical specific capacity of ~790 mAh/g SnO_2 is considered a next generation anode material. There are two aspects that limit this possibility: first the large irreversible capacity during the first cycle (eq. <1>) when irreversible reduction of tin dioxid (SnO_2) to metallic tin occurs together with the solid electrolyte interphase (SEI) formation and the second is the large volume change of the metallic tin particles during reversible alloying and dealloying with lithium. There are many strategies towards dealing with these limitations such as designing unique nanostructures like 1D nano-rods, nanowires, or nanotubes; 2D nanosheets and 3D hollow or porous nanostructures. Another strategy is to combine tin dioxid with carbonaceous materials that buffer the volume change and provide enhanced conductivity [25]. In a recent study [26] a novel composite material of tin dioxid and ordered mesoporous carbon (SnO_2/OMC) could deliver a reversible capacity as high as 396 mAh/g up to 50 cycles of discharge/charge and also a good rate capability.

Since it has low toxicity, is environmentally benign and abundant, titanium dioxide (TiO_2) has become one of the most extensively investigated metal oxides [24]. Titanium dioxid has several polymorphs and some of them have been studied as electrode materials for LIBs including anatase, rutile and TiO_2-B. The latter material has about 350 mAh/g capacity, because it can accommodate double the amount of lithium [3]. The defect spinel $Li_4Ti_5O_{12}$ (LTO) is also an intercalation host for lithium and prototype lithium batteries using nanoparticulate LTO have already been constructed. Even though titanium dioxid has a rather low capacity (170 mAh/g for anatase) and inserts Li+ at a higher potential of about +1.7 V vs. Li+/Li it has the advantages of being easy to tailor structurally, has low volume expansion upon lithiation, a good stability, lack of lithium plating and SEI formation. Other aspects related to the use of titanium dioxid as anode for LIB are its low electronic and ionic conductivities, while nanostructure engineering is believed to be effective in overcoming these disadvantages.

A recently performed work [27], investigated amorphous and anatase titanium dioxid nanotube layers synthesized by means of titanium foil anodic oxidation as anodes for LIB in 1 M $LiPF_6$ ethylene carbonate/dimethyl carbonate (EC:DMC) standard electrolyte and in ionic liquid based electrolyte 1-butyl-1-methyl pyrrolidinium (trifluoromethyl) sulfonylimide ([BMP][TFSI]) containing 1 M Li[TFSI]. It was found that the type of electrolyte does not influence the voltammetric

behavior of amorphous titanium dioxid nanotube layers, whereas in case of anatase there is a slight inhibition of lithium ion intercalation in the IL based electrolyte due to the high viscosity difference between the two electrolytes. Titanium dioxid nanotube structures displayed a stable galvanostatic cycling, reaching the theoretical capacity of titanium dioxid. The long term cycling showed almost 100 % capacity retention for amorphous titanium dioxid nanotube layer, while anatase displayed a definite loss of capacity reaching 70 % retention after 200 cycles. The latter phenomenon was attributed to structural defects inherited during thermal treatment of the material.

Transition-metal oxides represent another category of metal oxide anodes which are based on conversion reactions [11]. Through the conversion reaction mechanism (eq. <4>) these oxides are converted to a metallic state along with lithium oxid (Li_2O) during the first lithiation and are reversibly returned to their initial state after delithiation. They have been intensively studied, but in spite of their high specific capacity, conversion compounds usually suffer from large voltage hysteresis between charge and discharge, which severely affects the overall efficiency of the electrode.

1.3   Metal sulphides/nitrides

A variety of transition metal-containing sulfides MS_2 (M = Fe, Ti, Co, Ni and Cu) have been studied as cathode materials. On the other hand, many other layered metal sulfides MS_2 (M = Mo, W, Ga, Nb and Ta) can be used as anode materials because they act as host lattices for Li+ guest ions yielding intercalation compounds [11]. Molybdenum disulfide (MoS_2) nanostructures with different morphologies were tested as anode materials in LIBs with ionic liquid-based electrolytes [28]. Comparing their performance with that of thin-film samples obtained by sputtering, the flat samples showed a reversible capacity of 525 mAh/g, whereas for the nanostructured samples a maximum capacity 225 mAh/g was found. The study demonstrated the compatibility of these anode materials with the ionic liquid based electrolyte which brings improved safety features to the battery.

2   Cathode materials

The cathodes used or studied for being applied in LIBs can be categorized as follows: lithium metal oxides which are lamellar compounds, spinels and olivine-type lithium transition-metal phosphates.

2.1   Layered lithium metal oxides

Lithiated cobalt oxide ($LiCoO_2$) is among the most studied electrode materials for LIBs [5, 9]. It is nowadays used in LIBs considering its advantages: a high working potential, is easy to synthesize and has an excellent cycling at room temperature. However, $LiCoO_2$ cannot be used for applications that require more power due to safety reasons. Besides this, it is expensive and highly toxic. By cycling $LiCoO_2$ at voltages above 4.2 V, a rapid drop of the capacity takes place due to structural changes and dissolution of cobalt in the electrolyte. Among the solutions investigated to address these challenges are attempts to enhance its stability by doping and coating with aluminium oxide (Al_2O_3) or zirconium oxide (ZrO_2) and approaches to nanostructure the material for enhancing the slow diffusion kinetics. Regarding the high toxicity alternative transition metal oxide cathodes such as lithium nickel oxide ($LiNiO_2$) and lithium manganese oxide ($LiMnO_2$) were investigated as well.

In this category of lamellar or layered lithium metal oxide compounds, to which $LiCoO_2$ belongs, new cathodes obtained by substitution of cobalt ions were investigated. Such materials are $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (LNMC) [29]. They were first reported by Ohzuku's group in 2001. The role of manganese in these electrode materials is to order the lithium ions, while nickel is the electrochemically active element. Cobalt is still needed in order to avoid the antisite defects, since they can damage the electrochemical properties even for very small defect concentrations.

2.2   Olivine group

Goodenough and co-workers conducted the initial studies on $LiFePO_4$ (LFP) which is of great interest as cathode material for LIBs [30, 31]. It has high energy density, high theoretical capacity (170 mAh/g), thermal stability, environmental friendliness, low cost, good cycling stability and long cycle life owing to small volume changes. The main problem is constituted by the fact that $LiFePO_4$ is an insulating material with poor electronic conductivity and low Li+ diffusion coefficient which seriously limits its low temperature electrochemical performance. Rate capabilities of all the $LiMPO_4$ materials are highly restricted by the sluggish kinetics of electrons and lithium ions transport and for this reason high electrochemical efficiency can be achieved only at low charge and discharge rates. The attempts to solve the conductivity limitations include doping, nanostructuring and carbon coating. Nevertheless, LFP is commercial material for high power batteries in spite of its low conductivity.

Other members of the $LiMPO_4$ family (with M being any mixture of Mn, Ni, Fe, Co) are still not yet competitive with $LiFePO_4$ [9]. The M^{2+}/M^{3+} redox potential vs. Li^+/Li increases with the atomic number to 3.4; 4.1; 4.8 and 5.1 V for M = Fe, Mn, Co, Ni. The last two voltages exceed the stability window of the organic carbonates. $LiMnPO_4$ (LMP) has an intrinsic electronic conductivity even smaller than LFP. For this reason it is necessary to decrease the size of the particles to the nano-scale and/or to coat the particles with conductive carbon or to change the electrolyte.

2.3   Spinel compounds

In the attempt to reduce the cost and improve safety, spinel material $LiMn_2O_4$ is regarded as the most promising cathode [32]. It has the advantages of being low cost, with acceptable environmental impact, high voltage, good safety and good rate capability. However, it shows poor cycling stability, suffers from dissolution of manganese into the electrolytes at high temperatures, has reduced cycling life at high charge/discharge rates, and a large polarization effect due to slow diffusion process and long diffusion paths. It has been demonstrated that the nanostructured spinel $LiMn_2O_4$ has improved rate capabilities, power densities and cycle performances due to better accommodation of volume changes and shorter diffusion lengths. The downside of this approach is the fact that nanostructured morphologies such as nanoparticles, nanowires or nanorods have high specific surface which brings higher surface reactivity and this accelerates the rapid dissolution of manganese into the electrolytes. Solutions to these problems are doping by the heterogeneous substitution of manganese ions with foreign ions such as lithium, boron, magnesium, aluminium, cobalt, zinc, chromium, or iron and surface coating with oxides and acid resistant materials such as ceramics (ZnO, Al_2O_3, Co_3O_4) which prevent dissolution of manganese by forming insulating passivating layers and induce structural integrity.

$LiMn_{1.5}Ni_{0.5}O_4$ (LMN) is the most studied system among the substituted lithium manganese spinels [9]. It provides access to Ni(IV)–Ni(II) formal valences at about 4.7 V vs. Li^+/Li. The challenge for this system is brought by the cathode/electrolyte surface reactions which lead to decreased performance.

3 Conclusions

This short overview of the challenges in achieving high energy, high power new generation LIBs underlines the stringent necessity to propose and study new electrode materials with enhanced electrochemical properties as well as to improve those already in use. Other aspects regarding the future generation LIBs are related to the need of enhanced safety features, longer cycle life and decreased costs. The intense research carried out presently on an impressive scale offers constantly solutions to many of these problems and hopefully a breakthrough in this field will come to light in the next period.

References

[1] V. Etacheri, R. Marom, R. Elazari, G. Salitra, D. Aurbach: Challenges in the development of advanced Li-ion batteries: a review; Energy Environmental Science, 4 (2011), p. 3243–3262

[2] B. Scrosati, J. Garche: Lithium batteries: Status, prospects and future; Journal of Power Sources, 195 (2010), p. 2419–2430

[3] P. G. Bruce, B. Scrosati, J.-M. Tarascon: Nanomaterials for rechargeable lithium batteries; Angewandte Chemie (International Ed. in English), 47 (2008), p. 2930–2946

[4] H. Wu, Y. Cui: Designing nanostructured Si anodes for high energy lithium ion batteries; Nano Today, 7 (2012), p. 414–429

[5] A. K. Shukla, T. Prem Kumar: Materials for next-generation lithium batteries; Current Science, 94 (2008), p. 314–331

[6] B. Wua, F. Peib, Y. Wub, R. Maob, X. Aia, H. Yanga, Y. Cao: An electrochemically compatible and flame-retardant electrolyte additive for safe lithium ion batteries; Journal of Power Sources, 227 (2013), p. 106–110

[7] N. Iwayasu, H. Honbou, T. Horiba: Overcharge protection effect and reaction mechanism of cyclohexylbenzene for lithium ion batteries; Journal of Power Sources, 196 (2011), p. 3881–3886

[8] V. Borgel, E. Markevich, D. Aurbach, G. Semrau, M. Schmidt: On the application of ionic liquids for rechargeable Li batteries: High voltage systems; Journal of Power Sources, 189 (2009), p. 331–336

[9] K. Zaghib, A. Mauger, H. Groult, J. Goodenough, C. Julien: Advanced Electrodes for High Power Li-ion Batteries; Materials, 6 (2013), p. 1028–1049

[10] J. R. Szczech, S. Jin: Nanostructured silicon for high capacity lithium battery anodes; Energy & Environmental Science, 4 (2011), p. 56–72

[11] L. Ji, Z. Lin, M. Alcoutlabi, X. Zhang: Recent developments in nanostructured anode materials for rechargeable lithium-ion batteries; Energy & Environmental Science, 4 (2011), p. 2682–2699

[12] M. M. Thackeray, C. Wolverton, E. D. Isaacs: Electrical energy storage for transportation—approaching the limits of, and going beyond, lithium-ion batteries; Energy & Environmental Science, 5 (2012), p. 7854–7863

[13] R. Huang, J. Zhu: Silicon nanowire array films as advanced anode materials for lithium-ion batteries; Materials Chemistry and Physics, 121 (2010), p. 519–522

[14] H. T. Nguyen, F. Yao, M. R. Zamfir, C. Biswas, K. P. So, Y. H. Lee et al.: Highly Interconnected Si Nanowires for Improved Stability Li-Ion Battery Anodes; Advanced Energy Materials, 1 (2011), p. 1154–1161

[15] K. Peng, J. Jie, W. Zhang, S.-T. Lee: Silicon nanowires for rechargeable lithium-ion battery anodes; Applied Physics Letters, 93 (2008), p. 033105–3

[16] C. Chan, H. Peng, G. Liu, K. McIlwrath, X. Fengzhang, R. A. Huggins, Y. Cui: High-performance lithium battery anodes using silicon nanowires; Nature, 3 (2007), p. 31–35

[17] E. Quiroga-González, E. Ossei-Wusu, J. Carstensen, H. Föll: How to Make Optimized Arrays of Si Wires Suitable as Superior Anode for Li-Ion Batteries; Journal of The Electrochemical Society, 158 (2011), p. E119–E123

[18] K. Nishio, S. Tagawa, T. Fukushima, H. Masuda: Highly Ordered Nanoporous Si for Negative Electrode of Rechargeable Lithium-Ion Battery; Electrochemical and Solid-State Letters, 15 (2012), p. A41–A44

[19] M. Green, E. Fielder, B. Scrosati, M. Wachtler, J.S. Moreno: Structured Silicon Anodes for Lithium Battery Applications; Electrochemical and Solid-State Letters, 6 (5) (2003), p. A75–A79

[20] N. S. Hieu, J. C. Lim, J. K. Lee: Free-standing silicon nanorods on copper foil as anode for lithium-ion batteries; Microelectronic Engineering, 89 (2012), p. 138–140

[21] M.-H. Park, M. G. Kim, J. Joo, K. Kim, J. Kim, S. Ahn, Y. Cui, J. Cho: Silicon Nanotube Battery Anodes; Nano Letters, 9 (11) (2009), p. 3844–3847

[22] T. Song, J. Xia, J.-H. Lee, D. H. Lee, M.-S. Kwon, J.-M. Choi, J. Wu, S. K. Doo, H. Chang, W. I. Park, D. S. Zang, H. Kim, Y. Huang, K.-C. Hwang, J. A. Rogers, U. Paik: Arrays of Sealed Silicon Nanotubes as Anodes for Lithium Ion Batteries; Nano Letters, 10 (2010), p. 1710–1716

[23] C.-M. Park, J.-H. Kim, H. Kim, H.-J. Sohn: Li-alloy based anode materials for Li secondary batteries; Chemical Society Reviews, 39 (2010), p. 3115–3141

[24] H. Bin Wu, J. S. Chen, H. H. Hng, X. W. D. Lou: Nanostructured metal oxide-based materials as advanced anodes for lithium-ion batteries; Nanoscale, 4 (2012), p. 2526–2542

[25] J. S. Chen, X. W.(D) Lou: SnO2-Based Nanomaterials: Synthesis and Application in Lithium-Ion Batteries; Small, 9 (2013), p. 1877–1893

[26] G.-L. Xu, S.-R. Chen, J.-T. Li, F.-S. Ke, L. Huang, S.-G. Sun: A composite material of SnO2/ordered mesoporous carbon for the application in Lithium-ion Battery; Journal of Electroanalytical Chemistry, 656 (2011), p. 185–191

[27] S. Ivanov, L. Cheng, H. Wulfmeier, D. Albrecht, H. Fritze, A. Bund: Electrochemical behaviour of anodically obtained titania nanotubes in organic carbonate and ionic liquid based Li ion containing electrolytes; Electrochimica Acta, 104 (2013), p. 228–235

[28] D. Albrecht, H. Wulfmeier, S. Ivanov, A. Bund, H. Fritze: Electrochemical performance of ionic liquid-molybdenum disulfide Li-ion batteries; Journal of Applied Electrochemistry, 43 (2013), p. 559–565

[29] C. Yu, G. Li, X. Guan, J. Zheng, L. Li: Composite $Li[Li_{0.11}Mn_{0.57}Ni_{0.32}]O_2$: Two-step molten-salt synthesis, oxidation state stabilization, and uses as high-voltage cathode for lithium-ion batteries; Journal of Alloys and Compounds, 528 (2012), p. 121–125

[30] X. Rui, X. Zhao, Z. Lu, H. Tan, D. Sim, H. H. Hng, R. Yazami, T. M. Lim, Q. Yan: Olivine-type nanosheets for lithium ion battery cathodes; ACS Nano, 7 (2013), p. 5637–5646

[31] Y. Zhou, C. D. Gu, J. P. Zhou, L. J. Cheng, W. L. Liu, Y. Q. Qiao, X. L. Wang, J. P. Tu: Effect of carbon coating on low temperature electrochemical performance of LiFePO4/C by using polystyrene sphere as carbon source; Electrochimica Acta, 56 (2011), p. 5054–5059

[32] C. Wei, J. Deng, L. Xi, H. Zhou, Z. Wang, C. Y. Chung: High Power LiMn2O4 Hollow Microsphere Cathode Materials for Lithium Ion Batteries; International Journal of Electrochemical Science, 8 (2013), p. 6775–6783