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Lithium ion batteries: active electrode materials based on manganese dioxide

K. Banov[1,2], D. Ivanova[2], L. Fachikov[2], V. Kotev[4], T. Stankulov[1], B. Banov* [1,3]

[1] Institute of Electrochemistry and Energy Systems, IEES, 1, Acad. G. Bonchev str., bl. 10, 1113 Sofia
[2]University of Chemical Technology and Metallurgy – UCTM, bul. "Kl. Ohridski" 8, 1756 Sofia
[3] European Polytechnical University – EPU, 23, "St. St. Cyril and Methodius" str., 2300 Pernik
[4] Institute of Mechanics, IM, 1, Acad. G. Bonchev str., bl. 4, 1113 Sofia

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Lithium cobaltate used in commercial rechargeable lithium ion batteries possesses good cyclability, high discharge potential and acceptable energy density. Its synthesis is easy and can be realized on a large industrial scale. However, the price of cobalt is very high and determines the end user price of the lithium battery. Cobalt and its oxides are very toxic. Lithium manganese dioxide spinel combines high specific energy density – volumetric and gravimetric, high coulomb efficiency - close to the theoretical one, long cycle life. It is non-toxic, environmentally friendly and with low cost but possesses some disadvantages as low starting capacity and low stability at elevated temperatures. Optimising the synthesis methods and elucidating the factors influencing the electrochemical stability, we have obtained manganese dioxide spinel, which is very attractive and prospective cathode material for large scale application. Cathode materials based on manganese dioxide spinel with high coulomb efficiency close to 90%, discharge rates of 4C and cycle life up to 1000 cycles are presented.

Keywords: Lithium ion batteries, Manganese dioxide spinel, Elevated temperatures stability

INTRODUCTION

Commercially available rechargeable lithium batteries refer to the Li-Ion battery, which uses carbon powder as negative active electrode material and lithiated metallic oxides as cobaltate and nickelate for positive active electrode material. For the moment only $LiCoO_2$ (lithium cobaltate) is present at the market as positive electrode material. However, the cost of this material is so high that it would take up too much of the battery cost and besides, its specific energy density is not the highest, therefore, it may be replaced by the concurrent $LiNiO_2$. The price of $LiNiO_2$ (lithium nikelate) is less because of the highest specific gravimetric capacity but it is difficult for synthesis and treatment. Both materials are not environmentally friendly.

Thus the nearest future is devoted to the development of positive electrode materials with the following features:

- High specific energy density – volumetric and gravimetric;
- Improved coulomb efficiency close to the theoretical one;
- Cycle life, meeting the requirements;
- Easy for synthesis and treatment;
- Non-toxic and environmentally friendly;
- Low cost.

There is only one group of candidates that can meet these requirements - cathode materials based on manganese dioxide working in the 3 and 4 volts range.

The success of lithium batteries in the last 20 years is due to their big advantages over classical electrochemical systems as high specific energy density, stable and flat discharge profile, long storage life and wide operating temperature range.

Electrode components – general assumptions

The electrochemical parameters of lithium battery electrodes depend on the active mass (AM) and applied technology. Twenty years ago our lab (IEES former CLEPS) successfully developed a dry technique for electrode preparation [1, 2]. The electrode typically consists of active electrode materials (AM) mixed with electronic conductor and some amount of polymer playing the role of binder. The ratio between all above-mentioned compounds in general is as follows: 80% active electrode material (AM), 10% electronic conductor – graphite for example and 10% PTFE as a binder. We use preliminary prepared mixture of acetylene black and PTFE transformed in the so-called Teflonized Acetylene Black (TAB-2). The abbreviation TAB-2 denotes the content of PTFE in the dry mixture (typically 5%). In this way the test electrodes consist of 85% AM and 15% CB. Reduction in the content of PTFE is very important especially from a practical point of view.

The main factor for the electrochemical

- * To whom all correspondence should be sent.
- E-mail: bbanov@iees.bas.bg

behavior of AEM in use is the stoichiometry and the purity of the used compounds: cobaltate, nickelate and manganese dioxide spinel. The particles size together with porosity and micro and macro pore distribution plays a decisive role for the electrochemical features [3, 4, 5]. A summary of the chemical and physicochemical properties for an improved active electrode material is given below.

Chemical characteristics

- Chemical formula - $LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$ - strict stoichiometry;
- Purity of active electrode material (avoiding impurities generated during the synthesis process, which deteriorate the electrochemical performance);
- Correctly selected starting chemical compounds (including purity grade);
- Appropriate thermal treatment & gas atmosphere;
- Modification of the basic structure with the aim to improve some characteristics: thermal stability, enhanced lithium diffusion coefficient, cycleability.

Physico-chemical properties

- Specific Surface Area SSA (the higher the SSA, the lower the polarization), higher delivered capacity, improved reversibility and longer cycle life;
- Particles size - nanoparticles - balance of size depending on the specific application (the smaller the particles size the higher the discharge rate but delivered capacity is lower);
- Porosity of the particles and pore distribution - suitable micro- and macro pore ratio;
- Conductive binder ensuring an appropriate porosity and suitable electronic conductivity.

MANGANESE DIOXIDE SPINEL

During the last 10 years a high-energy demand has existed at the lithium battery market. Lithium cobaltate and lithium nickelate have successfully found a niche in this growing market. Some non-toxic, environmentally friendly, low cost candidates with specific energy density close to 450 Wh g^{-1} are under intensive investigation for replacement of the cathode materials based on Ni and Co. Lithium manganese spinel $LiMn_2O_4$ is very attractive and prospective cathode material, combining the advantages to be non-toxic, environmentally friendly, with low cost and theoretical specific energy density of 475 Wh g^{-1} [3, 6-8]. It has been under investigation since the beginning of the new century, but displays the big disadvantage of premature capacity loss especially at elevated temperature – over room temperature (RT) [9-11, 13, 15-17].

The same problem exists also in regard to cathode materials based on lithiated nickel and cobalt oxides, however, less pronounced.. Various authors have proposed two different solutions to the problem, which can be summarized in three directions:

- *Increased lithium content in the initial structure, the so-called overlithiated manganese dioxide spinel;*
- *Modification of the manganese dioxides spinel with foreign ions*

The main instability of $LiMn_2O_4$ is due to the so-called Mn^{3+} disproportion described by the equation:

$$2Mn^{3+} = Mn^{4+} + Mn^{2+}_{(sol)}$$

The increased lithium content in the overlithiated manganese dioxide spinel of $Li_{1+x}Mn_{2-x}O_4$ type stabilizes the crystal structure and suppresses the dissolution of Mn^{3+}. This reflects in increased stability during cycling at elevated temperatures. However, the gain in cycleability is accompanied by diminishing of the delivered reversible capacity of the material.

The next option is to substitute small amount of Mn^{3+} ions by another ion. Some authors [9-16] propose stabilization of the structure by partially replacing Mn^{3+} ions by Ni or Co ones. We have also piled up experience in this regard. The obtained stability of Co doped spinel with chemical formula $LiCo_{0.1}Mn_{1.9}O_4$ is excellent during long term cycling at room temperature [7, 18-21] but is not satisfactory at elevated temperatures. This substitution can also be performed using Mg. The result is improved cycleability but reduced initial reversible capacity.

OVERLITHIATED MANGANESE DIOXIDE SPINELS

Manganese dioxide spinels of the type $Li_{1+x}Mn_{2-x}O_4$ ($0.01<x<0.15$) with increased Li content.

Expected results:

- Starting capacity 100 mAh g^{-1} (65% Q_{th}) - 135mAh g^{-1}(90% Q_{th});
- Cycleability of 300 cycles at RT (up to 50% from the initial capacity);
- Improved cycleability at elevated temperatures (55°C).

The overlithiation of manganese dioxide spinel is the simplest way to increase the stability of the active electrode material at elevated temperatures.

We have prepared a series of overlithiated manganese dioxide and subjected it to high temperature tests (Table 1). As it was already mentioned, this approach offers reduced reversible capacity in the beginning but the cycle life is improved significantly. The capacity fade at room temperature (RT) decreased from 0.4% to 0.032% per cycle – more than ten times. On the other hand the starting delivered capacity was reduced from 135 mAh g$^{-1,}$ to 101 mAh g^{-1}. The capacity fade at elevated temperatures (55°C) starts form 1.3% (three times higher than at RT) per cycle and drops to 0.067%, which is very close to the value displayed at RT for the spinel with chemical formula $Li_{1.11}Mn_{1.89}O_4$. The graphical presentation of the capacity changes at long term cycling for the investigated overlithiated samples is given in Fig. 1.

Taking into account the so-called “accumulated capacity” the best choice would be the sample “IEES”, because the accumulated capacity, graphically represented by the area limited by the cycling curve is the biggest one.

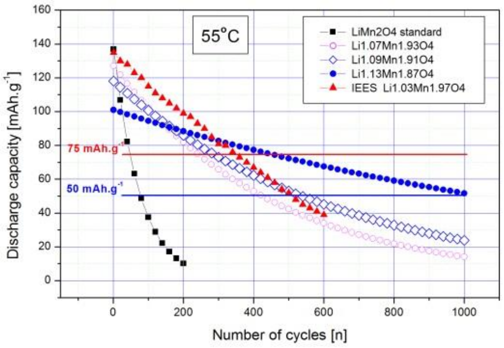

Fig. 1. Discharge capacity at long term cycling of overlithiated $Li_{1+x}Mn_{2-x}O_4$ samples at 55°C

If the cycle life is set to 1000 cycles, the leader would be the sample with chemical formula $Li_{1.13}Mn_{1.87}O_4$. For middle cycle life (for example 400 cycles), there is no best choice, because all tested samples offer nearly the same accumulated capacity, excluding the spinel with maximum lithium content - $Li_{1.13}Mn_{1.87}O_4$.

Table 1. Theoretical and observed capacity dependence on extra lithium content in manganese dioxide spinel

Spinel Formula $Li_{1+x}Mn_{2-x}O_4$	RT Initial Capacity, [mAh g^{-1}]	Fade %/cycle at 50th cycle	55° C Initial Capacity, [mAh g^{-1}]	Fade %/cycle at 50th cycle	(a) [Å]
Standard $LiMn_2O_4$	135	0.4	135	1.300	8.248
$Li_{1.02}Mn_{1.98}O_4$	123	0.11	134	0.770	8.243
$Li_{1.05}Mn1_{.95}O_4$	121	0.11	133	0.450	8.235
$Li_{1.07}Mn_{1.93}O_4$	121	0.11	120	0.290	8.228
$Li_{1.09}Mn_{1.91}O_4$	118	0.06	118	0.170	8.222
$Li_{1.11}Mn_{1.89}O_4$	101	0.05	101	0.080	8.218
$Li_{1.13}Mn_{1.87}O_4$	101	0.032	101	0.067	8.207

CONCLUSIO*Ns*

- A series of overlithiated manganese dioxide spinel $Li_{1+x}Mn_{2-x}O_4$are successfully synthesised and tested as cathode material for prospective LIB;
- Overlithiated manganese dioxide spinel $Li_{1+x}Mn_{2-x}O_4$with different overlithiation ratios are suitable for different applications;
- There are no universal overlithiated active electrode materials solving all customer requirements without any compromise;
- Different approach for each specific application is needed;

Overlithated samples tested present very good and promising cycleability at elevated temperature.

SUBSTITUTED MANGANESE DIOXIDE SPINEL

Manganese dioxide spinels of the type $LiMe_xMn_{2x}O_4$ $(0.01<x<0.20)$ modified with Mg ions.

Expected results

- Starting capacity 100 mAh g^{-1} (65% Q_{th}) – 120 mAh g^{-1} (80% Q_{th});
- Improved thermal stability & electrochemical characteristics;
- Improved cycleability up to 700 cycles;
- Target: batteries for EV&HEV.

The advantages of doping with foreign ions are investigated on manganese dioxide spinel $LiMg_{0.05}Mn_{1.95}O_{4,}$ i.e. the selected doping ion is Mg. Based on our previous investigations, lithium acetate and manganese carbonate have been chosen as lithium and manganese source, and magnesium nitrate - as Mg doping agent ($CH_3COOLi.2H_2O$, $MnCO_3$, $Mg(NO_3)_26H_2O$). These initial compounds are not widely used in lithium manganese spinel preparation. The optimal conditions to obtain a high quality active cathode material for lithium batteries operating in the 4 volts region are published in [1, 3, 19-21].

EXPERIMENTAL

The newly proposed method of synthesis is based on two different techniques: impregnation and decomposition inside the particle. $MnCO_3$ with mean particle size about 20 μmis chosen as starting compound and manganese source [2, 3, 6, 7,]. Magnesium nitrate is introduced in the reaction composition as an aqueous solution. The manganese carbonate is well soaked with the magnesium nitrate. After drying and good mixing, lithium acetate is introduced and the mixture is again dried at temperature of 120ºC. The real synthesis starts with a thermal pretreatment at 250ºC for 24h. The temperature is selected according to the decomposition temperatures of $Mg(NO_3)_26H_2O$ and $CH_3COOLi.2H_2O$. During the initial thermal pretreatment at relatively low temperature (about 120ºC) the composite mixture is subjected to impregnation by the lithium acetate and magnesium nitrate. The final thermal decomposition of manganese carbonate/lithium acetate/ magnesium nitrate takes place at high temperatures (750ºC). Doped llithium manganese spinel with high purity and perfect crystal structure has been obtained as a result of this synthesis. The XRD of thus prepared samples is presented on Fig. 2a. It can be seen no difference in the XRD patterns of pure ($LiMn_2O_4$) spinel and substituted one ($LiMg_{0.05}Mn_{1.95}O_4$). This is due to the occupation of 16(d) places by the Mg ions. For comparison apure manganese spinel is synthesized by standard solid-state procedure. Chemical manganese dioxide (CMD) with high purity and high specific surface area (SSA) about 100 m^2 g^{-1} and lithium acetate $CH_3COOLi.2H_2O$ are mixed in an appropriate molar ratio 2:1 [4, 5, 8]. The medium particle size of the used MnO_2 is about 100 μm. Lithium acetate is chosen due to its low decomposition temperature, which is around 70ºC. Thermal pre-treatment for 24 hours at 750ºC is done. The syntheses are performed in a tube furnace with 0.5 dm^3 total volume under a constant air flow of 25 dm^3 h^{-1}. The gas flow is very important because of the generated carbon dioxide. The synthesis reaction of $LiMn_2O_4$ requires oxygen for the end product synthesis. The sample is cooled at 10ºC min^{-1} cooling rate. In both cases - with and without doping, an active cathode material with SSA (measured by the B.E.T. method) about 10 m^2 $g^{-1}$is obtained [2-4, 19-21]. The phase composition of the samples is determined by X-ray diffraction analysis using Philips APD 15 powder diffractometer with ***Cu-Kα*** radiation. The electrochemical characteristics are tested in a three-electrode glass cell with lithium reference electrode in excess of electrolyte and with a floating test electrode, described in [4, 5]. The electrolyte consists of 1M $LiClO_4$ solution in a mixture of EC:PC:DMC in 1:1:2 volume ratio. The composite test electrode material is a mixture of the investigated compounds with *Teflonized Acetylene Black*(TAB-2) [1, 3-5] at a 1:1 ratio by weight, pressed on expanded nickel grid with 15 mm diameter. The test electrodes weight is typically 50 mg without the nickel grid. To carry out the electrochemical tests a standard charge/discharge current of C/3 is applied.

Results and discussions

The XRD pattern of the manganese spinel doped with 5 atomic percent Mg is equal to those of the pure $LiMn_2O_4$, i.e. the phase of the doped spinel is also *Fd3m*. The doping agent cannot be detected on the XRD patterns sown on Fig. 1b of $LiMg_{0.05}Mn_{1.95}O_4$ spinel.

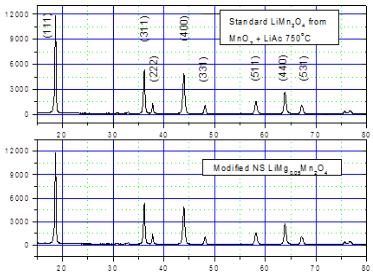

Fig. 2. XRD diagram of pure $LiMn_2O_4$ and Mg doped spinel $LiMg_{0.05}Mn_{1.95}O_4$

That confirms that Mg occupies 16(d) places. The morphology of the obtained powdered active electrode material is presented on Fig. 3.

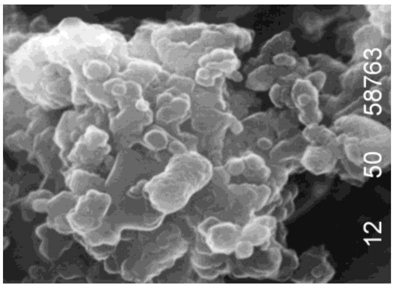

Fig. 3. SEM micrograph of $LiMg_{0.05}Mn_{1.95}O_4$ powder

The micrograph shows that the lithium spinel preserves in maximum the shape of the initial manganese source - $MnCO_3$ [8, 20-22]. The obtained doped and non-doped spinels possess specific SSA of ~ 10 m^2 g^{-1}. The combined impregnation - decomposition process leads to the formation of particles with high porosity and spherical shape. XRD and SEM micrographs show that the preparation technique is very suitable. The charge/discharge profiles of pure $LiMn_2O_4$ active electrode material are presented in Fig. 4.

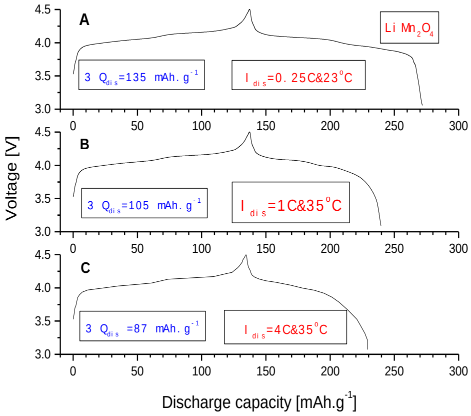

Fig. 4

Charge/discharge profiles of pure lithium manganese spinel $LiMn_2O_4$ at different temperatures and discharge rates: 0.25C/23ºC; 1C/35ºC and 4C/35ºC

The electrochemical tests are performed at different discharge rates and temperatures - room temperature (RT) 23ºC and elevated one 35ºC, respectively. The first curve (Fig. 4A) shows the pure spinel behavior applying 4h charge/discharge (0.25C)rate at 23ºC (RT). Due to the high SSA of the sample (10 m^2 g^{-1}), the charge/discharge profile is very flat. The delivered capacity is 135 mAh g^{-1}. When a charge/discharge rate of 1C is applied and the temperature is increased to 35ºC, the obtained capacity is 105 mAh g^{-1}. The discharge profile at high current density (4C) and 35ºC is presented inFig. 4C. In this case the exhibited discharge capacity is only 87 mAh g^{-1}. The reduction is 35% in regard to RT and about 18% against 1C/35ºC. The displayed results are interesting and promising. Fig. 5 shows the charge/discharge profiles of newly prepared $LiMg_{0.05}Mn_{1.95}O_4$ active electrode material.

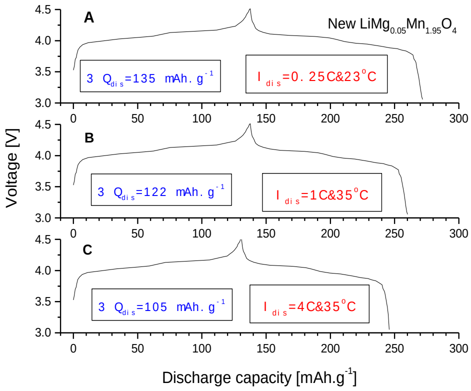

Fig. 5. Charge discharge profiles of lithium manganese spinel doped with Mg ($LiMg_{0.05}Mn_{1.95}O_4$) at different temperatures and discharge rates: 0.25C/23ºC, 1C/35ºC and 4C/35ºC

Three discharge/charge profiles: at 0.25C/RT, 1C/35ºC and 4C/35ºC are presented again for comparison with the pure spinel. At 0.25C rate and room temperature there is no difference in the discharge capacity due to the low discharge current and the high SSA of the sample [1-5, 19-21]. The sample exhibits capacity close to that of the pure material, which means that the very small amount of doping agent does not affect the discharge capacity. At elevated temperature 35ºC and discharge rate of 1C the delivered capacity is 122 mAh g^{-1}. The displayed reversible capacity decreases to 105 mAh g^{-1} when a high current drain and temperature are applied (4C/35ºC). Compared to the tested pure spinel, the value increases about 16% and 20%, respectively. In all of the tests the charge current rate is kept constant (0.25C) to ensure optimal conditions for low polarization charging. The obtained results confirm our assumption that combining different techniques and starting compounds it is possible to prepare a highly efficient cathode material.

Conclusions

- $LiMg_{0.05}Mn_{1.95}O_4$ is successfully synthesised as cathode material with improved stability at elevated temperatures;
- A very high rate (4C) active electrode material ($LiMg_{0.05}Mn_{1.95}O_4$) for lithium batteries is obtained by our cathode preparation technique;
- The overall efficiency of $LiMg_{0.05}Mn_{1.95}O_4$ is enhanced by 20% at high rate (4C) and elevated temperature (35ºC);
- Combining different techniques of preparation and modification, it is possible to prepare highly efficient, environmentally friendly cathode material with high charge and discharge rates at elevated temperatures.

ELECTROCHEMICAL BEHAVIOUROF $LiMn_2O_4$ ACTIVE ELECTRODE MATERIAL IN THE 3 VOLTS REGION

The lithium manganese spinel $LiMn_2O_4$ possesses twodischarge plateaux, at 4 volts and at 3 volts one. So far the efforts of R&D has been oriented to improve the discharge capacity and the cycleability of the high potential region – the 4 volts one. We have already demonstrated that it is possible to obtain $LiMn_2O_4$ with 90% (Fig. 1) of the theoretical capacity in the 4 volts region during long term cycling at high charge/discharge rate of C/3 [1, 3, 8]. The techniques of preparation, sol-gel or solid-state syntheses, the influence of the starting compounds on the obtained precursor and final product, and the physicochemical properties and electrochemical behavior of the active electrode materials have been discussed 1-3, 13-16, 18-21]. The challenge is to improve the electrochemical characteristics of lithium manganese spinel $LiMn_2O_4$ working in the low potential region of 3 volts, modifying the physicochemical parameters and applying an appropriate synthesis method.

Experimental

Based on our previous investigations, lithium spinel is prepared by a new synthesis approach. The standard solid-state reaction is applied for comparison. Lithium acetate is used in both methods to avoid the influence of the starting compounds. The new synthesisis based on a two-step technique: impregnation and decomposition. The particles of manganese carbonate with average particle size of 20 μm are impregnated by lithium acetate at about 150ºC. The final thermal decomposition of the manganese carbonate takes place at temperature about 550ºC. Thus lithium manganese spinel is obtained at relatively low temperature [18-21]. Lithium spinel prepared at low temperature possesses low discharge capacity at 4 volt range.

Results and Discussion

XRD patterns of materials prepared at 550ºC and 750ºC are the same, *Fd3m* space group, i.e. a spinel was successfully obtained at relatively low temperature (550ºC). The pattern of the new synthesis shows only a little lower intensity of the peaks. The morphology of the obtained active electrode material powders is presented on Fig. 6. It can be seen that the lithium spinel preserves in maximum the spherical shape of the starting manganese source, the CMD Faradizer M. The SEM picture (Fig. 6 a, b) shows that the particles are built from fine nanosized needles, at 750ºC Fig. 6 a and at 550ºC Fig. 6 b. A small difference appears in the particles dimensions Fig.6 a, b resulting in different SSA of thus prepared samples.

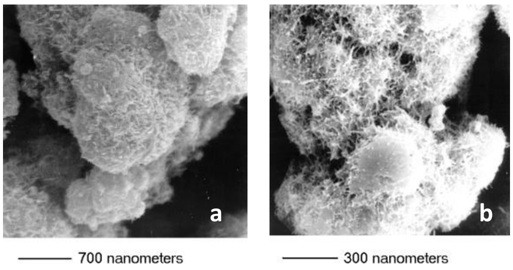

Fig. 6. SEM pictures of pure $LiMn_2O_4$ powders obtained by: (a) solid-state reaction; (b) new complex synthesis (impregnation) method

The measured SSA ($10 m^2 g^{-1}$) is three times higher than that of the reference material (standard lithium spinel prepared at 550ºC). The discharge profile in the 3 volts region of active electrode material prepared by the standard synthesis way (750ºC) is presented in Fig.7.

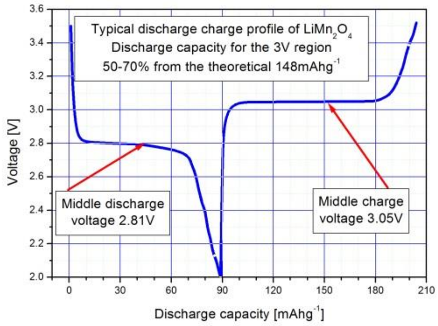

Fig. 7. Discharge/charge profile of standard lithium manganese spinel in the 3 volts region

It has capacity of 90 mAh g^{-1} with discharge plateau at 2.81 V. From theoretical point of view the plateau must be situated at 2.95 V. The observed difference is due to the discharge polarization. The charge plateau is at 3.05 V and the charge capacity is 115 mAh g^{-1}. The efficiency of the total electrochemical reaction discharge/charge is 78% and the calculated specific energy density - 253 Wh g^{-1}. In the 4 volts region the same active electrode material displays a reversible capacity of 135 mAh g^{-1} at the 3rd cycle. The cycleability in the same region is pretty good, 115 mAh g^{-1} at the 100th cycle. The discharge/charge profile of the active electrode material prepared by the new synthesis procedure is presented in Fig. 8.

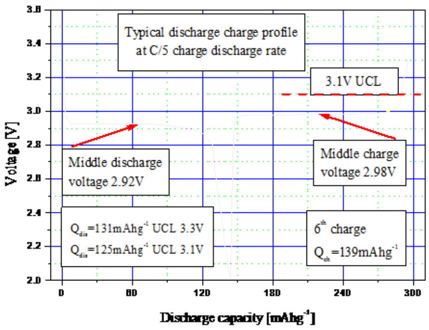

Fig. 8. Discharge/charge profile of electrode material prepared by the new complex synthesis (impregnation) method

The first difference between both syntheses is observed in the discharge plateau. It is situated at 2.92 V, a value very close to the theoretical one - 2.95 volts. The second difference is in the displayed discharge capacity-131mAh g^{-1}. Normally the capacity in the 3 V region is close to 60 % from the theoretical one, i.e. around 90 mAh g^{-1}. In our case the obtained value is 1.4 times higher. A specific energy density of 375 Wh.g^{-1} is achieved. The charge plateau shows reduced polarization – the middle charge voltage is 2.98 volts. The charge capacity of the new material is 139 mAh g^{-1} with an efficiency of about 94%, a very high and attractive value. As described above (Fig. 8), its microstructure is characterized with very fine particles, which cause increase in the SSA and porosity, thus allowing more electrolyte to be in contact with the active electrode material, not only on the surface but in the whole volume. According to similar investigations [13,14], the higher SSA and porosity bring to higher discharge capacity and to lower polarization, which is in agreement with our results. They are summarized in Table 2**.**

Table 2. Comparison of specific capacity and coulomb efficiency of $LiMn_2O_4$ synthesized by different methods and $LiCoO_2$ as reference

Cathode material	Type material [V]	Cycling limits [V]	Theoretical capacity [mAh g^{-1}]	Practical Specific Capacity [mAh g^{-1}] 5th	25th	50th	***CE**** [%]
$Li_{0.3}MnO_2$	3	3.5-2.0	200	180	165	155	90-75
Standard $LiMn_2O_4$	3	3.5-2.0	148	90	75	60	60-40
New synthesis $LiMn_2O_4$	3	3.5-2.0	148	131	95	80	85-55
$LiMn_2O_4$	4	4.5-3.0	148	135	120	115	85-75
$LiCoO_2$	4	4.5-3.0	275	160	155	150	60-52

CE* coulomb efficiency

For comparison, the electrochemical performance of other types of active electrode materials working in the 3 and the 4-volt regions are given. The obtained results show that the lithium spinel in the 3 volts region is very attractive cathode material for practical use in lithium batteries.

Conclusions

- Applying an appropriate synthesis method, the 3 volts region of $LiMn_2O_4$ spinel becomes very attractive for practical use, with specific energy density more than 375 Wh g^{-1};
- The synthesis techniques and the starting precursors play preponderant role for the electrochemical behaviour of the active electrode materials;
- The charge discharge profile of the active electrode material is improved with the increasing of the SSA;
- The overall efficiency of manganese dioxide spinel working in the 3 volts region is increased up to 94% from the theoretical one.

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ЛИТИЕВО ЙОННИ БАТЕРИИ
АКТИВНИ МАТЕРИАЛИ НА БАЗАТА НА МАНГАНОВИ ДИОКСИДИ

Кр. Банов [1,2], Д. Иванова [2], Л. Фачиков [2] , В. Котев [4], Т. Станкулов [1],
Бр. Банов* [1,3]

[1]. *Институт по Електрохимия и Енергийни Системи, ИЕЕС, ул. "Акад. Г. Бончев" Бл. 10. 1113 София*
[2] *Химико Технологичен и Металургичен Университет, бул. "Кл. Охридски" 8, 1756 София*
3) Европейски Политехнически Университет, ЕПУ, ул. "Св. Св. Кирил и Методи" N:23, 2300 Перник
[4] *Институт по Механика, ул. "Акад. Г. Бончев" N:1, Бл. 4. 1113 София*

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(Резюме)

Литиевият кобалтат използван в болшинството комерсиални литиево йонни акумулаторни батерии притежава добра циклируемост, висок разряден потенциал и приемлива плътностна енергията. Лесно се синтезира и може да бъде изготвян в големи индустриални количества. За съжаление цената на кобалта расте с непредвидими темпове, а тя е определяща в основната си част за цената на крайния продукт – литиево йонната батерия. Кобалтът, както и неговите оксиди са изключително токсични. Литиево мангановодиоксидния шпинел притежава, висока специфична енергийна плътност, тегловна и обемна, както и висока Кулонова ефективност, близка до теоретичната и дълъг цикличен живот. Той не е токсичен, екологично приемлив, с ниска цена, но притежава и някои недостатъци, като нисък начален разряден капацитет и понижена стабилност при повишена температура. Оптимизирайки методите на синтез и вниквайки в дълбочина на факторите, влияещи върху електрохимическата стабилност, успешно е изготвен литиран маганово диоксиден шпинел, който е много привлекателен и перспективен катокатоден материал за широко индустриално използване. В това изследване е представен успешно синтезиран и изследван катоден материал на основата на манганово диоксиден шпинел с висока Кулонова ефективност близо до 90% спрямо теоретичната, работещ в режим от 4C и показващ стабилна циклируемост от повече от 1000 цикъла.

Ключови думи: литиево йонни батерии, манганово диоксиден шпинел, стабилност при повишена температура.