

Environmentally friendly cathode materials for Li-ion batteries

B. I. Banov*, H. C. Vasilchina

Institute of Electrochemistry and Energy Systems, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bl №:10, 1113 Sofia, Bulgaria

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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 applied 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 Coulombic efficiency, close to the theoretical, and long cycle life. It is non-toxic, environmentally friendly, and low cost, but possesses some disadvantages such 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 a prospective cathode material for large-scale application. Cathode materials are presented based on manganese dioxide spinel with high Coulomb efficiency close to 90% at temperatures of 55°C, discharge rates of 4C and cycle life up to 500 cycles. The obtained results show that our approach could also be applied for enhancing the efficiency of other active electrode materials.

Keywords: Highly efficient lithium batteries, manganese dioxide spinel, elevated temperature stability, high rates, coating

1. 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 a positive electrode material. However, the cost of this material is so high that it would take up too much of the battery cost and its specific energy density is not of the highest. Therefore, it may be replaced by the competitive LiNiO_2 . The price of the LiNiO_2 (lithium nickelate) is less due to the highest specific gravimetric capacity but the LiNiO_2 (lithium nickelate) 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 Coulombic efficiency close to the theoretical;*
- ✓ *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, the cathode materials which are based on manganese dioxide, working in the 4 volt range – the manganese spinel.

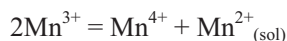
2. MANGANESE DIOXIDE SPINEL

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 of theoretical specific energy density of 475 Wh.g^{-1} . It has been under investigation since the beginning of the new century, but displays the big disadvantage of premature capacity loss, especially in the high temperature range of 30–60°C [1–8].

The same problem also exists in regard to the cathode materials, based on lithiated nickel and cobalt oxides. It is, however, less pronounced. The

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

solubility of those active cathode materials is increased at elevated temperatures, and the cathodes dissolve in the electrolyte during storage and long time cycling. The main instability of LiMn_2O_4 is due to the so-called Mn^{3+} disproportionation, described by the equation:



The increased lithium content in the overlithiated manganese dioxide spinel of $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ 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.

Another way to solve the problem is to envelop the active electrode material with metal oxides in order to prevent the Mn^{3+} dissolution. In this way the high temperature characteristics of the LiMn_2O_4 spinel are enhanced but the lithium diffusion coefficient is reduced, which reflects in deterioration of the overall electrochemical behaviour of the lithium cell. In the literature [4] the MgO is proposed as an almost universal coating agent for LiCoO_2 and LiNiO_2 , which are from the same-layered crystallographic group. The manganese dioxide spinel belongs to the *Fd3m* crystallographic space group, so it is difficult to apply the same method of stabilization.

The third option is to substitute small amount of Mn^{3+} ions by another metal ion. Some authors [2, 3] propose stabilization of the structure by partially replacing Mn^{3+} ions by Ni or Co ions. We have also piled up experience in this regard. The obtained stability of Co doped spinel with chemical formula of $\text{LiCo}_{0.1}\text{Mn}_{1.9}\text{O}_4$ is excellent during long term cycling at room temperature [18–19] but it is not satisfactory at elevated temperatures. This substitution can also be performed using Mg and Al. The result is an improved cycleability but a reduced initial reversible capacity.

In a series of papers [10–18] we have demonstrated that if an appropriate method and manner of synthesis are applied, it is possible to obtain LiMn_2O_4 , delivering up to 80% of the theoretical capacity in the 4 volt region during long term cycling at high charge/discharge rate (C/3) and room temperature. The techniques of preparation, sol-gel or solid-state syntheses, the influence of the initial compounds on the obtained precursor and the final product, the thermal treatment, the physicochemical properties and the electrochemical behaviour of the active electrode materials (AEM)

have been largely discussed in our previous papers [10–19].

The general principles to overcome the problems, concerning the stability of manganese dioxide spinel, numbered below, are illustrated by the next three possible steps:

- Overlithiated Manganese Dioxide Spinels, $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$
- Foreign ions substituted manganese dioxide spinel, $\text{Li}_{1+x}\text{Me}_y\text{Mn}_{2-x-y}\text{O}_4$
- Coated Manganese Dioxide Spinel
- LiMn_2O_4 coated with inactive metal oxide – ZnO
- LiMn_2O_4 coated with active lithiated metal oxide – LiMeO_2 .

The typical physicochemical properties of active electrode materials also affect the material electrochemical behaviour:

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

The role of all chemical and physicochemical parameters which influence the electrochemical performance is elucidated hereafter by simple examples, and the obtained results are discussed.

3. OVER-LITHIATED MANGANESE DIOXIDE SPINELS

Manganese dioxide spinels of the type $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ are regarded with the following expected results:

- Starting capacity of $100 - 135\text{mAh.g}^{-1}$ ($65-90\% Q_{\text{th}}$);
- Cycleability of 300 cycles at RT ;
- Improved cycleability at elevated temperatures (55°C).

The over-lithiation 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 over-lithiated manganese dioxide and subjected it to high temperature tests (cf. Table 1).

As already mentioned, this approach offers reduced reversible capacity but the cycle life is

improved significantly. The capacity fades 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 fades at elevated temperatures (55°C), starting from 1.3%

Table 1. Theoretical and observed capacity dependence on extra lithium content in over-lithiated manganese spinel

Spinel	RT	Fade	55° C	Fade
Formula	Initial	%/cyc.	Initial	%/cyc.
	Cap	at 50 th	Cap	at 50 th
Li _{1+x} Mn _{2-x} O ₄	mAh/g	cycle	mAh/g	cycle
LiMn ₂ O ₄	135	0.42	135	1.40
Li _{1.02} Mn _{1.98} O ₄	125	0.13	125	0.75
Li _{1.05} Mn _{1.95} O ₄	123	0.12	123	0.45
Li _{1.07} Mn _{1.93} O ₄	121	0.11	120	0.27
Li _{1.09} Mn _{1.91} O ₄	118	0.08	118	0.18
Li _{1.11} Mn _{1.89} O ₄	101	0.05	101	0.08
Li _{1.13} Mn _{1.87} O ₄	100	0.04	101	0.07

(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 the chemical formula of Li_{1.11}Mn_{1.89}O₄. 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

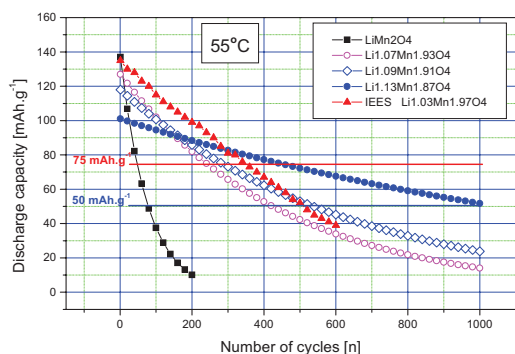


Fig. 1. Discharge capacity at long term cycling of overlithiated samples at elevated temperature.

‘accumulated capacity’, the best choice would be the ‘IEES’ sample because the accumulated capacity, graphically represented by the area limited by the cycling curve, is the biggest one. If the cycle life is set to 1000 cycles, the leader would be the sample with the chemical formula of Li_{1.13}Mn_{1.87}O₄. There is no best choice for the middle cycle life (for example 400 cycles) because all tested samples offer nearly the same accumulated capacity, excluding the

spinel with maximum lithium content - Li_{1.13}Mn_{1.87}O₄.

CONCLUSIONS

- Small amount of extra lithium, incorporated in the initial crystal structure, stabilizes the spinel during cycling and suppresses the Mn³⁺ dissolution;
- The cycleability of over-lithiated samples is improved by more than 50% but the reversible capacities are lower;

The capacity of the over-lithiated samples fade at room temperatures, drastically reduces at elevated temperatures.

4. MANGANESE DIOXIDE SPINEL

Li Me_xMn_{2-x}O₄ (0.01<X<0.20) MODIFIED WITH FOREIGN IONS (Me = Mg, Al)

Expected features:

- Starting capacity of 100 – 120 mAh.g⁻¹ (65 – 80% Q_{th});
- Improved thermal stability & electrochemical futures;
- Improved cycleability of 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}O₄, i.e. the selected doping ion is the 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 (CH₃COOLi.2H₂O, MnCO₃, Mg(NO₃)₂·6H₂O). The optimal conditions to obtain a high quality active cathode material for lithium batteries, operating in the 4 volt region, are published in [10]. The AEM should be optimized specifically for reaching maximum efficiency [10–14]. The dissolution of manganese ions in the electrolyte can be reduced by diminishing the specific surface area (SSA) to a value of about 1–3 m².g⁻¹. When this approach is applied, the stability is improved but the electrochemical properties of the manganese spinel based cathode material are deteriorated. It is well known that the SSA of the active electrode material plays an important role for the electrochemical performance of the electrode [10–17]. In this work we tried to find a compromise between both parameters: the stability and the electrochemical performance using the Mg as a doping agent.

4.1. 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 of about $20 \mu\text{m}$ is chosen as starting compound and manganese source [10]. Magnesium nitrate is introduced in the reaction composition as an aqueous solution. Doped lithium manganese spinel with high purity and perfect crystal structure has been obtained as a result of this synthesis. In both cases, with and without doping, an active cathode material with SSA (measured by the B.E.T. method) of about $10 \text{ m}^2 \cdot \text{g}^{-1}$ is obtained [10 – 18]. The phase composition of the samples is determined by X-ray diffraction analysis using Philips APD 15 powder diffractometer with Cu-K α 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 [12, 13]. The electrolyte consists of 1M LiClO_4 solution in a mixture of EC:PC:DMC in a 1:1:2 volume ratio. The composite test electrode material is a mixture of the investigated compounds with Teflonized Acetylene Black (TAB-2) [10 – 13] at a 1:1 ratio by weight, pressed on expanded nickel grid with diameter of 15 mm. The test electrodes weight is typically 50 mg without the nickel grid.

4.2. Results and Discussion

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* and the crystallinity of the sample is very high. The doping agent cannot be detected on the XRD patterns of $\text{LiMg}_{0.05}\text{Mn}_{1.95}\text{O}_4$ spinel. That confirms that the Mg occupies **16(d)** places. The obtained doped and non-doped spinels possess specific SSA of $\sim 10 \text{ m}^2 \cdot \text{g}^{-1}$. The charge/discharge profiles of pure LiMn_2O_4 active electrode material are presented in Fig. 2. The electrochemical tests are performed at different discharge rates and temperatures. The first curve (Fig. 2A) shows the pure spinel behaviour applying 4h charge/discharge (0,25C) rate at 23°C (RT). Due to the high SSA of the sample ($10 \text{ m}^2 \cdot \text{g}^{-1}$), the charge/discharge profile is very flat. The delivered capacity is $135 \text{ mAh} \cdot \text{g}^{-1}$. When a charge/discharge rate of 1C is applied and the temperature is increased to 35°C , the obtained capacity is $105 \text{ mAh} \cdot \text{g}^{-1}$. The discharge profile at high current density (4C) and 35°C is presented in Fig. 2C. In this case the exhibited discharge capacity is only of $87 \text{ mAh} \cdot \text{g}^{-1}$. The reduction is 35% in regard to RT and about 18% against 1C/ 35°C . Fig.

3 shows the charge/discharge profiles of a newly prepared $\text{LiMg}_{0.05}\text{Mn}_{1.95}\text{O}_4$ AEM. Three discharge/charge profiles: at 0.25C/RT, at 1C/ 35°C , and at 4C/ 35°C , are presented again for comparison with the pure spinel. There is no difference in the discharge capacity at 0.25C rate and RT due to the low discharge current and the high SSA of the sample. 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 of 35°C and discharge rate of 1C the delivered capacity is $122 \text{ mAh} \cdot \text{g}^{-1}$. The displayed reversible capacity decreases to $105 \text{ mAh} \cdot \text{g}^{-1}$ when a high current drain and temperature are applied (4C/ 35°C). Compared to the tested pure spinel, the value increases with 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 charge. The obtained results confirm our assumption that it is possible to prepare a highly efficient cathode material.

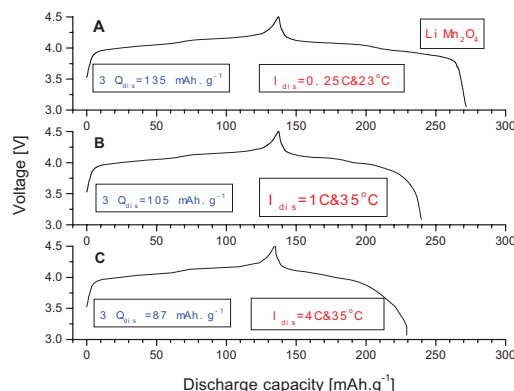


Fig. 2. Charge discharge profile of spinel sample at 0.25C/ 23°C , 1C/ 35°C and 4C/ 35°C .

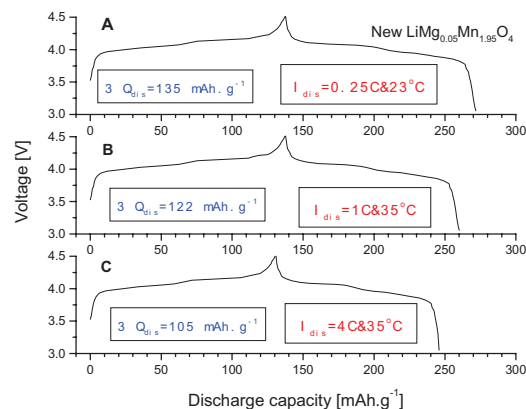


Fig. 3. Charge discharge profile of Mg doped spinel sample at 0.25C/ 23°C , 1C/ 35°C and 4C/ 35°C

CONCLUSIONS

- $\text{LiMg}_{0.05}\text{Mn}_{1.95}\text{O}_4$ is successfully tested as cathode material with improved stability at elevated temperatures;
- A very high rate of (4C) AEM ($\text{LiMg}_{0.05}\text{Mn}_{1.95}\text{O}_4$) is obtained;
- The overall efficiency of $\text{LiMg}_{0.05}\text{Mn}_{1.95}\text{O}_4$ is enhanced by 20% at high rate (4C) and elevated temperature (35°C);

5. MANGANESE DIOXIDE SPINEL $\text{Li}_{1+x}\text{Al}_y\text{Mn}_{2-x-y}\text{O}_4$ MODIFIED WITH Al

Expected characteristics:

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

The same procedure was applied for testing Al-doped manganese dioxide sample of the $\text{Li}_{1+x}\text{Al}_y\text{Mn}_{2-x-y}\text{O}_4$ type. In this experiment the Al substitution was made with the same idea for improvement of the high temperature stability and the electrochemical performances of the active electrode material.

5.1 Results and Discussion

The XRD patterns of pure LiMn_2O_4 spinel and samples, doped with 25 atomic percent Al, do not differ from the XRD of pure manganese spinel. This is true especially in our case. Both substituting agents were especially chosen due to the fact that they make spinel of the same type, MgAl_2O_4 - Mn_2O_4 (λ - MnO_2). This is the reason that the XRD diagram of substituted spinel does not differ from the well known theoretical spinel XRD diagrams. The synthesis gives pure **Fd3m** phase (without any extra peaks). The XRD patterns of Al doped spinel, $\text{Li}_{1.05}\text{Al}_{0.25}\text{Mn}_{1.70}\text{O}_4$, overlap the pure one and the doping agent cannot be XRD detected. That confirms that the Al occupies **16(d)** places and the XRD pattern does not differ from the original. The obtained doped and non-doped spinels possess specific SSA of about $\sim 10 \text{ m}^2.\text{g}^{-1}$. The samples with Al substitution show a little bit higher SSA of about $12\text{-}15 \text{ m}^2.\text{g}^{-1}$, but in order to be accurate we chose the samples of SSA within $10\text{-}12 \text{ m}^2.\text{g}^{-1}$ for our investigation. The charge/discharge profile of the Al substituted material does not differ from the pure manganese spinel. The cycleability of the new prepared compound, $\text{Li}_{1.05}\text{Al}_{0.25}\text{Mn}_{1.70}\text{O}_4$, is given in Fig.4. We can see that the sample shows a very

good stability over cycling. We estimated the capacity fade based on the first 80 cycles. During cycling the samples are subjected to load tests. The results of these tests are shown in Fig.5. The plotted results are obtained on the base of 5 successive charge/discharges performed with 1-hour pause after the load discharge.

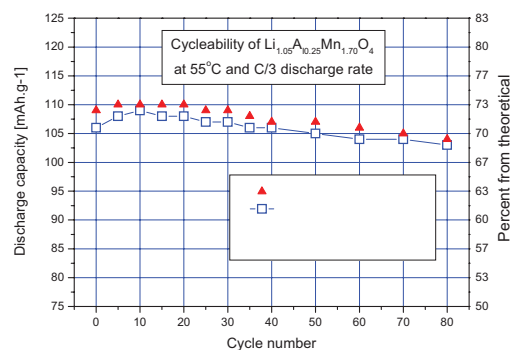


Fig. 4. Long term cycleability of Al doped spinel sample

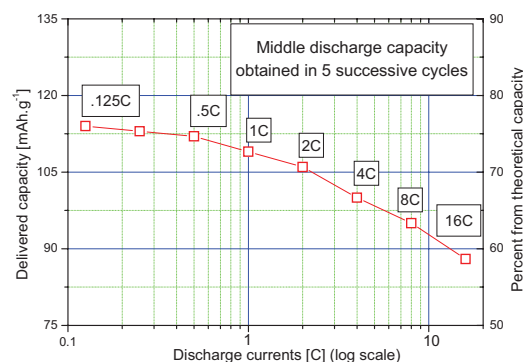


Fig. 5. Load characteristics obtained after 5 successive charge discharges and 1 hour relaxation time.

Each time the charge is effectuated with constant current of C/3. It can be seen from the graph that the aluminum-substituted material is very powerful. When a 4C discharge rate is applied, the material delivers about 90% from the base discharge capacity, delivered at C/3 (about 110 mAh.g^{-1}). Just to remind: a 4C discharge rate corresponds to starting of a car engine! At 8C the delivered capacity is 85% and even at 16C(!) the material withstands and delivers 80% from the capacity at C/3. All these results are very promising and attractive on a large-scale application. To our knowledge, by far no one has reported comparable data about power capabilities of the manganese oxide spinel. The long-term stability and cycleability at elevated temperatures (55°C) are

presented in the next Fig.6. The Figure summarizes the tests of the previously investigated and developed overlithiated manganese oxides against the winner in this experiment, the $\text{Li}_{1.05}\text{Al}_{0.25}\text{Mn}_{1.70}\text{O}_4$. The overall improvement in stability and cycleability is in the range of about 20-25%. The lower starting capacity leads to a very long and stable cycle life. Table 2 presents summary of both, Mg and Al doped active electrode materials, prepared and tested in the same laboratory.

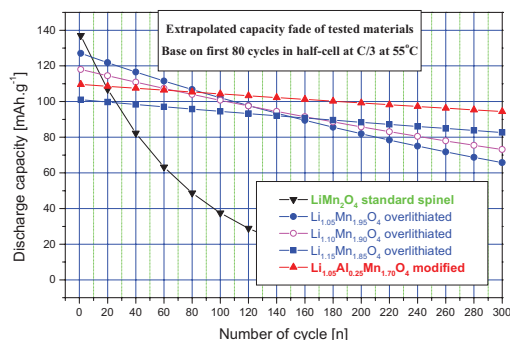


Fig. 6. Long term cycling of tested samples compared with over-lithiated ones.

Table 2. Reversible capacity and capacity fade at RT and elevated temperature of Mg and Al doped spinel.

Spinel Formula	RT		55° C	
	Init Cap	Fade %/c 50 th cycle	Init Cap	Fade %/c 50 th cycle
$\text{Li}_{1+x}\text{M}_y\text{Mn}_{2-x-y}\text{O}_4$	mAh/g		mAh/g	
$\text{Li}_{1.05}\text{Al}_{0.1}\text{Mn}_{1.85}\text{O}_4$	119	0.04	117	0.05
$\text{Li}_{1.1}\text{Al}_{0.1}\text{Mn}_{1.8}\text{O}_4$	103	0.01	102	0.03
$\text{Li}_{1.05}\text{Al}_{0.15}\text{Mn}_{1.8}\text{O}_4$	109	0.04	109	0.06
$\text{Li}_{1.05}\text{Mg}_{0.1}\text{Mn}_{1.85}\text{O}_4$	114	0.06	112	0.08
$\text{Li}_{1.1}\text{Mg}_{0.1}\text{Mn}_{1.8}\text{O}_4$	108	0.03	108	0.07
$\text{Li}_{1.05}\text{Mg}_{0.15}\text{Mn}_{1.8}\text{O}_4$	105	0.08	105	0.09

It can be seen in the table that there are solutions which are appropriate for different cases, a high stability with low starting capacity, or higher starting capacity with acceptable cycle life. All of the above results are very interesting from theoretical point of view because they demonstrate the ability of the research group to set the requirements and to find the adequate solutions for them. Once again, the obtained result confirms our idea that it is possible to prepare cathode material, attractive for practical application by combining different techniques like over-lithiation and substitution with different starting compounds and appropriate thermal treatment (the way of synthesis).

CONCLUSIONS

- The AEM of $\text{Li}_{(1+X)}\text{Al}_Y\text{Mn}_{(2-X-Y)}\text{O}_4$ type is successfully synthesized and tested as a cathode material;
- The efficiency of the new prepared AEM is enhanced by 20% at high discharge rates of the 8C;
- The capacity fade at elevated temperature (55°C) of aluminum-substituted spinel is comparable with this at 25°C.

6. MANGANESE DIOXIDE SPINEL, $(\text{MeO})_x\text{LiMn}_2\text{O}_4$, COATED WITH ELECTROCHEMICALLY INACTIVE MeO, IN OUR CASE (Me= Zn)

- Starting capacity of 100 – 120mAh.g⁻¹ (65-80% Q_{th});
- Improved thermal stability;
- Deteriorated discharge characteristics;
- Improved cycleability, over 500 cycles;
- Best in small batteries for 3C products at RT and above.

This part of the work demonstrates the results, obtained on nanosized ZnO covered manganese spinel LiMn_2O_4 . The approach for stabilization, proposed in literature, is covering of the active electrode material particles by a very thin coating, preventing the dissolution of Mn^{3+} ions. Consequently, a small deterioration of the electrochemical parameters is also expected. The aim of the study is to find a compromise between the stability and the electrochemical performance.

6.1. Experimental

The applied way of synthesis is based on a two-step technique: impregnation and decomposition inside the particle which was already described above. In the second step of the synthesis, the particles are covered with ZnO. Thus, two samples with thickness of the ZnO of about 30 and 50 nm (according to our calculations) are prepared.

6.2. Results and Discussion

The XRD pattern of the coated spinel does not differ from the theoretical. The proposed synthesis gives pure **Fd3m** phase. The ZnO cover cannot be detected by the XRD patterns, which shows that the ZnO cover is very thin and the XRD is amorphous. The presence of ZnO on the surface is proven only by Atomic Absorption Spectroscopy (AAS). The obtained spinel possesses a SSA of about 10 m².g⁻¹. When the particles of AEM are covered with ZnO, the SSA is almost the same, ~8 m².g⁻¹. The charge/discharge profiles of the pure and ZnO

covered active electrode material are presented in Fig.7. The electrochemical tests are performed at the same charge/discharge rate (C/3) and at temperatures of 30°C and 55°C, respectively. The first curve (Fig.7A) shows the pure spinel, tested at 30°C. Due to the high SSA of the sample ($8 \text{ m}^2 \cdot \text{g}^{-1}$), the charge/discharge profile is very flat. The charge/discharge profiles of the samples, covered

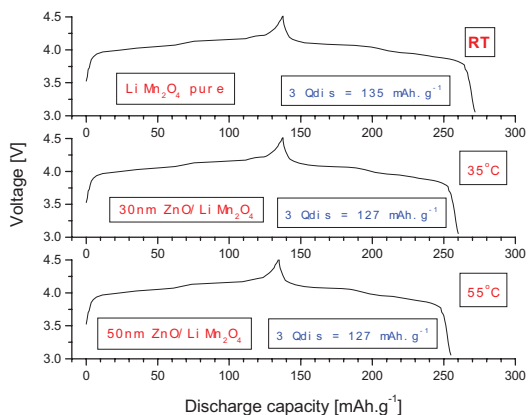


Fig. 7. Charge discharge profile of pure and coated with 30 and 50 nm ZnO spinel at 30 and 55°C.

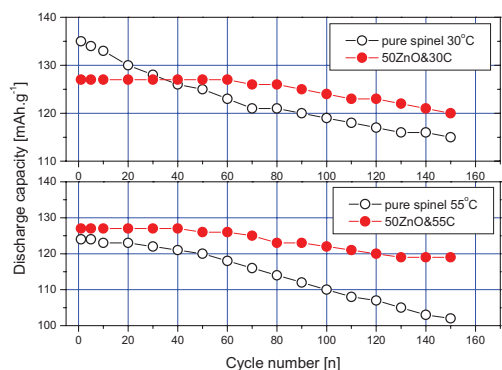


Fig. 8. Long term cycling test of pure and coated with 50 nm ZnO spinel at 30 and 55°C.

with 30 and 50 nm, are shown in Figs.7B and 7C. They indicate no significant difference between the discharge profiles of the pure and the coated samples. The initial discharge capacity of the pure spinel is $135 \text{ mAh} \cdot \text{g}^{-1}$ versus $125 \text{ mAh} \cdot \text{g}^{-1}$ for the covered one. The capacity decline versus cycle number is displayed in Fig.8. Since there is no difference in the voltage profile of both samples, covered with 30 or 50 nm of ZnO, in the next experiments only the latter is considered. Fig.8a shows the cycle life of the pure LiMn_2O_4 , compared to that of the covered spinel at 30°C. The initial capacity of the pure spinel is higher and declines

slowly, reaching a value of about $115 \text{ mAh} \cdot \text{g}^{-1}$ against $120 \text{ mAh} \cdot \text{g}^{-1}$ for the coated material. The difference is less than 5% for 150 cycles. Fig.8b presents the same comparison for 55°C. The initial capacity of the pure spinel at 55°C is $124 \text{ mAh} \cdot \text{g}^{-1}$, which is close to the coated. After cycling, the difference between the two samples increases (102 against 119 at the 150th cycle). The data show that the 50 nm ZnO coated lithium spinel is of interest for practical application in 3C products at elevated temperatures (of up to 50°C).

CONCLUSIONS

- Manganese dioxide spinel, covered by inactive electrode material (ZnO) is successfully prepared;
- Electrochemical performances are not deteriorated;
- The stability of the cathode material is improved by 10%;
- Even very fine coating of 50 nm thickness, prevents the Mn^{3+} dissolution and stabilizes the electrochemical features at an elevated temperature.

7. MATERIAL PHYSICO-CHEMICAL PROPERTY EFFECT ON THE ELECTROCHEMICAL BEHAVIOUR

- SSA (the higher the SSA is, the lower the polarization is), higher delivered capacity, improved reversibility and long cycle life;
- Particles size – nanoparticles – balance of size depending on the specific application (the smaller the particle size is the higher the discharge rate and long cycle life are);
- Porosity of the particles and pore distribution – suitable micro and macro pore ratio.

The lithium manganese spinel, LiMn_2O_4 , possesses two discharge plateaus, a 4 volt and a 3 volt. So far the efforts of R&D have been oriented to improve the discharge capacity and the cycleability of the high potential region, the 4 volt and the 3 volt regions have been forgotten.

We have already demonstrated [10–18] that it is possible to obtain LiMn_2O_4 with 90% of the theoretical capacity in the 4 volt region during a long term cycling at high charge/discharge rate of C/3. The techniques of preparation, sol-gel or solid state syntheses, the influence of the starting compounds on the obtained precursor and the final product, and the physicochemical properties and electrochemical behaviour of the active electrode materials have been discussed [10–19]. The challenge is to improve the electrochemical

characteristics of lithium manganese spinel working in the low potential region of 3 V.

7.1. Experimental

Based on our previous investigations, lithium spinel is prepared by the same synthesis approach. The final thermal treatment in this case takes place at a temperature of about 550°C. The solid-state reaction synthesis, the physicochemical and electrochemical investigation procedures are described above.

7.2. Results and discussion

XRD patterns of both syntheses are the same, of the *Fd3m* space group, i.e. a spinel was successfully obtained at a relatively low temperature (550°C). The XRD pattern of the new synthesis shows only a little lower intensity of the peaks. The material obtained by the combined impregnation decomposition process, forms highly porous particles. The measured SSA (10 m².g⁻¹) is five times higher than that of the other reference materials. The discharge profile in the 3 volt region of the active electrode material, prepared by the standard synthesis, is presented in Fig.9. It has

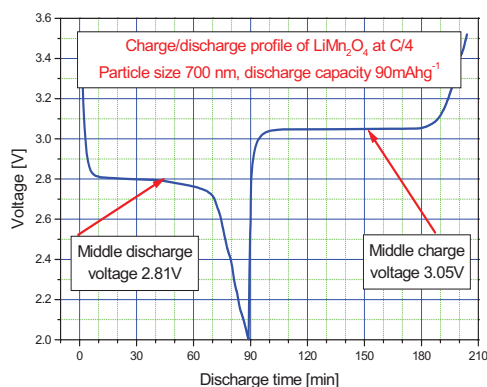


Fig. 9. Discharge charge profile of standard lithium spinel.

capacity of 90 mAh.g⁻¹ with a discharge plateau at 2.81 V. From a 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 is 253 Wh.g⁻¹. In the 4 volt 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.

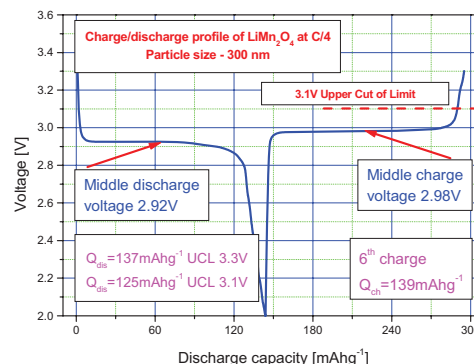


Fig. 10. Charge discharge profile of 3 volts spinel prepared according to new technique.

The discharge/charge profile of the active electrode material, prepared by the new synthesis process, is presented in Fig.10. 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. it is around 90 mAh.g⁻¹. In our case the obtained value is 1.5 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%.

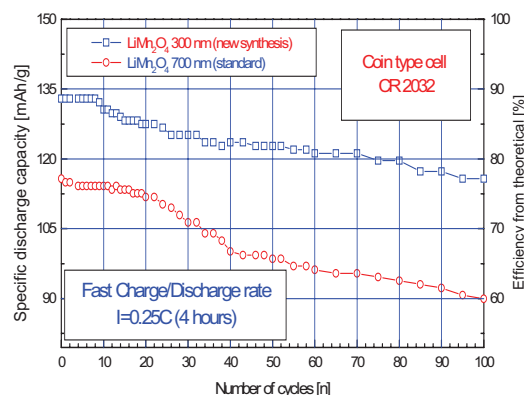


Fig. 11. Long term cycling of 3 volts spinel with particle size 300 and 700nm.

Table 3. Comparison of delivered capacity and columbic efficiency of AEM working in 3 and 4 volts range.

Cathode material	TheoCap. mAh/g	Practical Specific Capacity			CE* [%]
		5 th	25 th	50 th	
Li _{0.3} MnO ₂	200	180	165	155	90-75
St LiMn ₂ O ₄	148	90	75	60	60-40
New LiMn ₂ O ₄	148	131	95	80	85-55
LiMn ₂ O ₄	148	135	120	115	85-75
LiCoO ₂	275	160	155	150	60-52

According to similar investigations [5, 6], 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 3. For comparison, the electrochemical performance of other types of active electrode materials, working in the 3-volt and the 4-volt regions, is given.

Obtained results show that the lithium spinel thus prepared is very attractive cathode material for practical use in the 3 volt region. The long-term cycleability of both samples with different particle size is presented in Fig. 11. Active electrode materials with small particle size exhibit high cycleability, good and stable electrochemical performances, and improved total efficiency. Thus, again it was demonstrated no negligible improvement of electrical characteristics by simple technique based on good knowledge of chemistry and electrochemistry of processes of tested material.

CONCLUSIONS

Applying an appropriate synthesis method, the 3 volt region of the LiMn₂O₄ spinel becomes very attractive for practical use, with specific energy density of more than 375Whg⁻¹;

The charge/discharge profile of the active electrode material is improved with the SSA increase and the porosity;

The overall efficiency of manganese dioxide spinel, working in the 3 volt region, is increased up to 94%.

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ЕКОЛОГИЧНО-СЪВМЕСТИМИ КАТОДНИ МАТЕРИАЛИ ЗА ЛИТИЕВО-ЙОННИ БАТЕРИИ

Б.И. Банов*, Х.К. Василчина

Институт по електрохимия и енергийни системи, Българска академия на науките, ул. Акад. Г. Бончев, бл. 10, 1113 София

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(Резюме)

Литиевият кобалтат, най-широко използвания катоден материал в произвежданите широко литиево йонни батерии, притежава добра циклируемост, високо разрядно напрежение и приемлива енергийна плътност. Неговата синтеза е лесна и може да бъде изготвян в широк промишлен мащаб. Цената обаче на кобалта е висока и е определяща за крайната цена на батерията. Кобалтът и неговите соли са високо токсични. Литиевият манганово диоксиден шпинел, притежава висока специфична тегловна и обемна енергия, висока кулонова ефективност, близка до теоретичната и добра циклируемост. Той не токсичен, не замърсява природата, цената му е ниска, но притежава някои недостатъци като нисък начален капацитет и понижена стабилност при повишена температура. Оптимизирайки методите на синтез и изяснявайки основните фактори влияещи върху електрохимичната стабилност, ние получихме литиево манганово диоксиден шпинел, притежаващ много атрактивни електрохимични характеристики, особено при широка употреба. В работата са представени изследванията на широка гама катодни материали на основата на модифицирани литиево манганово диоксидни шпинели с кулонова ефективност близка до 90% при температура от 55°C, разрядни скорости от 4С и живот над 500 цикъла. Получените резултати показват правилността на нашия подход, като методът може да бъде приложен и при други активни електродни материали за подобряване на техните електрохимични характеристики.