Enhancing Lithium-Manganese Oxide Electrochemical Behavior

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Lithium manganese oxide is regarded as a capable cathode material for lithium-ion batteries, but it suffers from relative low conductivity, manganese dissolution in electrolyte and structural distortion from cubic to tetragonal during elevated temperature tests.

lithium manganese oxide | surface modification | doping | stability | long cycling ability | discharge capacity

1. Introduction

Since their introduction to market by Sony, in 1990, lithium-ion batteries (LIBs) became the most popular power source for consumer electronics (smartphones, laptops, portable medical devices) and electric vehicles too [1][2][3]. Lithium-ion batteries are preferred for current electrically powered devices because of their advantages over the classic energy storage devices: better gravimetric density, higher working potential, large number of charge/discharge cycles and small self-discharge rate [4][5].

The most studied cathode materials are lithium cobalt oxide ($LiCoO_2$) [6][7][8], lithium iron phosphate ($LiFePO_4$) [9][10][11] and lithium manganese oxide ($LiMn_2O_4$) [5][12][13]. The anode consists of carbonaceous materials [12][14], silicon [15][16] or transition metal oxides [17] and the electrolyte mainly contains $LiPF_6$ dissolved in a mixture of organic solvents (ethylene carbonate and dimethyl carbonate) [18].

Lithium manganese oxide (LMO) is considered an appropriate cathode material for lithium-ion batteries because of plenty raw materials, environmental friendliness, low cost, relatively facile manufacturing process and higher potential (4.1 vs. Li/Li^+) than $LiCoO_2$ (4 V vs. Li/Li^+) and $LiFePO_4$ (3.45 V vs. Li/Li^+) [4][19]. The theoretical capacity of LMO is 148 mAh g^{-1}, lower than $LiCoO_2$ (274 mAh g^{-1}) and $LiFePO_4$ (170 mAh·g^{-1}). However, lithium cobalt oxide fails to deliver more than half of the theoretical capacity because of structural deformation [2][8]. Pristine LMO managed to deliver more than 95% of its theoretical capacity [20].

$LiMn_2O_4$ has a close cubic package (*ccp*) spinel structure within the *Fd*3*m* space group. Manganese ions are located in the 16 d octahedral positions, oxygen ions in 32 e sites, while the lithium ions from the 8a tetrahedral positions can diffusive through the interstitial space of the 3D diamond shaped framework formed by $[MnO_6]$ octahedrals [21][22][23][24].

It is well known that lithium manganese oxide's performance in organic electrolyte solution at elevate temperatures, suffers from manganese dissolution into electrolyte [25][26][27], Jahn-Teller distortion [28] and electrolyte oxidation on the surface of LMO particles [29]. Another problem related to Li-ion battery functioning is the electrolyte stability. Normally, LIBs are assembled in chambers with controlled atmosphere and humidity. If any water traces remain in the cell's assembly, it can react with lithium hexafluorophosphate ($LiPF_6$) to form hydrofluoric acid (HF), which has a harmful effect on LMO particles, thus the cycling ability of the cathode material is drastically affected [30].

Two main strategies have been employed to diminish LMO's disadvantages: structure doping (cations [31][32], anions [33][34] or multiple ions [29][35][36]) and surface modification of the particles [37][38][39]).

Cation doping stabilizes the LMO spinel structure, by reducing the amount of electrochemically active Mn^{3+} [40], which is responsible for manganese disproportionate reaction into electrolyte [41]. However, in the case of doped $LiMn_2O_4$ a longer cycle life has been noticed at both room and elevated temperature as well, due to lower capacity loss during charge-discharge cycles, because of the more stable unit cell [42][43]. In addition, the anions inserted into LMO's lattice do not reduce the content of Mn^{3+}, therefore the good discharge capacities of anion-doped $LiMn_2O_4$ spinels were recorded [44][45].

Jahn Teller distortion (JT) occurs on the particle surface and it is a phase transition from cubic ($c/a = 1$) to tetragonal ($c/a > 1$), which reduce the structure stability due to a change in volume [46]. JT occurs especially by the end of the discharge process, when the average Mn oxidation state decreases from 3.5 to 3.0 [47][48]. Surface modification of the LMO particles proved to be an efficient way to hinder the JT's effect on cathode performance, by shielding the active material particles from the electrolyte solution, where Mn^{3+} can easily disproportionate into Mn^{2+} and Mn^{4+} [49].

2. Improving $LiMn_2O_4$ by Coating

Surface modification of $LiMn_2O_4$ particles proved to be an efficient way to diminish the harmful activity of electrolyte solution during cell cycling. As mentioned before, one important drawback of LMO spinel is related to manganese dissolution. The coatings not only improve the material stability by reducing its contact area with the electrolyte solution, but also enhance the electrochemical characteristics by reducing the charge transfer resistance and providing a better samples-cycling stability, for instance [50][51]. Throughout the years, many different coatings, which include organic and inorganic compounds like carbon, oxides, perovskites, solid solutions, have been studied [52][53][54][55].

2.1. Carbon

Lithium ions diffusion and rate capability life of lithium manganese oxide can be enhanced by using high conductive carbon-based materials [56][57]. Different carbonaceous coatings like hard carbon [12], activated carbon [58][59], carbon nanotubes [60][61][62][63][64][65], graphene [66][67], amorphous carbon [65][66][67][68][69][70], carbon nanospheres [71] were studied in the last years.

Reduced graphene oxide (rGO) nanosheets were employed as support for LMO uniform deposition by a low temperature microwave assisted hydrothermal reactions method [72]. The rGO presence prevented LMO agglomeration and low range particle distribution (10–40 nm). High crystalline LMO samples with stable 3D framework behaved remarkably at low and high c-rates, as well. Delivering an initial discharge capacity of 137 mAh·g^{-1} at 1 C, LMO/rGO hybrid material exhibited 85.4% (117 mAh·g^{-1}) and 73.7 (101 mAh·g^{-1}) of its initial discharge capacity, at 50 and 100 C, respectively. The improvement in material's performance was strongly related to the properties of rGO: high surface area, protecting barrier against the electrolyte solution and the channels presence for permitting faster lithium ions diffusion [14].

$LiMn_2O_4$/graphene composite electrodes were proposed as suitable cathode materials for Li-ion batteries [56][57][67][73][74][75][76][77][78]. The unique and amazing graphene properties, such as high electrical conductivity, thermal and mechanical stability and high surface area, provided an efficient method for improving lithium manganese oxide's electrochemical properties [14][55][56][77][79]. Brief characteristics about the electrochemical behavior of lithium manganese oxide/graphene composite materials are presented in Table 8, while a more advanced description about graphene influence on LIB's cathode materials has been described elsewhere [80]. The challenges related to graphene-based materials usage in energy storage devices have been discussed in [14].

Table 1. Graphene-coated LMO and its electrochemical properties.

No.	Material	Synthesis	Discharge Capacity (mAh g^{-1})	Coulombic Efficiency (%)	Discharge Capacity/N Cycles (mAh g^{-1} N^{-1})	Capacity Retention (%)	Ref
1	$LiMn_2O_4$/graphene	Hydrothermal method	143.6 (x) *	-	137.4/50	95.7	[67]
			141.5 (x) **		133.4/50	94.3	
2		Sputtering + CVD	131.6 ***	-	119/750 ***	90.4	[57]
3		Ball-milling method	78.8	93.7	64.6/500	82	[74]
4		Solution method	131.1 (b)	-	125.3/50	96	[66]
5		Electrophoretic deposition	49.6 (r)	-	-	-	[75]
6		Spray drying combustion process	139 (b)	92.5	121	87	[81]
7		Hydrothermal method	139.2 (i)	98.2	117.5/200	84.5	[82]
8		Self-assembly process+Solid-	155 (d)	94.9	149.8/80	96.6	[56]

No.	Material	Synthesis	Discharge Capacity (mAh g^{-1})	Coulombic Efficiency (%)	Discharge Capacity/N Cycles (mAh g^{-1} N^{-1})	Capacity Retention (%)	Ref
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Zhu et al. [79] published an ample review about novel carbon-based coatings (graphene, carbon nanotubes) for enhancing the behavior of $LiMn_2O_4$ in Rechargeable Hybrid Aqueous Batteries (ReHAB).

2.2. Oxides

Many researchers drove their attention to the usage of metal oxides as surface coatings for lithium manganese oxide [83].

Several research groups focused their studies on the influence of different lanthanide oxides on LMO particles. Since 2007, several studies were concentrated on CeO_2 behavior as coating for lithium manganese oxides [52][53][84][85].

In order to modify the pristine samples, disparate approaches were made. Arumugam et al. [85] employed a polymeric process followed by a high temperature heat treatment (850 °C for 6 h), in order to obtain the modified samples. As expected, the initial discharge capacity of the pristine sample (135 mAh·g^{-1}) was slightly higher than the one of 1 wt.% CeO_2 (126 mAh·g^{-1}), but the latter sample exhibited improved stability during cell's cycling in both room and elevated temperature (60 °C) tests, providing 120 and 117 mAh·g^{-1}, respectively, after 100 cycles at 0.5 C. While the pristine samples failed to offer more than 60% capacity retention at 30 °C and 50% at 60 °C, the coated material provided astonishing capacity retention of at least 93%, in both cases. Not only the cycle performance is important, but also the material ability to work at higher current rates is important. The 1 wt.% CeO_2-$LiMn_2O_4$ was cycled for 100 times at higher current rate (5, 10, 15, 20 C, respectively) and its performance was compelling in all the case, because the initial discharge capacities were relatively high (102 mAh g^{-1} at 20 C) and small capacity fades were recorded (between 12%–17%). For a better understanding of coating layer importance, the electrochemical impedance spectra of LMO-based electrodes were studied. It was noticed that the charge transfer resistance was greatly decreased by coating, while the side reactions between the electrode material and electrolyte solution were minimized. Despite the fact that the initial R_{ct} of the bare sample was slightly smaller than the one of coated material (21 Ω vs. 26 Ω), after 100 cycles it increased for more than four times, up to 98 Ω, while a R_{ct} of only 42Ω was recorded for the coated LMO.

The precipitant influences, namely $(NH_4)_2CO_3$ and NH_4OH, in a precipitation synthesis of CeO_2 modified $LiMn_2O_4$ particles were studied by Cho et al. [84]. Small particles size and a uniform coating layer were obtained when NH_4OH was involved in the synthesis process, while the usage of $(NH_4)_2CO_3$ favored particle agglomeration, when the coating amount increased. The precipitant used during the coated materials synthesis enhanced its capacity retention, from 50% for the pristine up to 88% for 5 wt.% CeO_2 upon cycling for 200 times, at 60 °C and 1 C. Even though the lowest capacity fade was recorded for the 5 wt.% CeO_2 (about 12%), its discharge capacity is still too low to be used in practical batteries (~70 $mAh{\cdot}g^{-1}$. Due to uniform coating layer formed when NH_4OH was used, the electrode material was less exposed to electrolyte solution and thus the sample electrochemical characteristics were improved, with decreased recorded capacity fade (12–24%). In contrast, higher capacity fades were observed for the samples with $(NH_4)_2CO_3$ as precipitant (32–40% of initial discharge capacity).

Michalska et al. [52] employed another investigation on CeO_2 coating layer. The modified samples were obtained through a sol-gel synthesis followed by a low-temperature calcination (350 °C). The resultant particles presented relatively clear surface, with wide size interval (between 100 and 600 nm), which agglomerated into larger clusters. Compared to the previous studies, the initial discharge capacity of the modified sample was higher (115 $mAh{\cdot}g^{-1}$) than the pure $LiMn_2O_4$ ($mAh{\cdot}g^{-1}$), thus the lithium intercalation-deintercalation processes were not negatively influenced. In addition, the capacity loss of LMO/CeO_2 sample was just 2% after 100 cycles (1 C), in comparison with 10% for bare LMO. Another benefit of the cerium oxide coating can be correlated with material performance at high current rates (Table 2).

Table 2. Comparative data of pristine and CeO_2 modified LMO at high current rates.

Material	**Initial Discharge Capacity (mAh g^{-1})**					**Ref.**
	5 C	**20 C**	**15 C**	**20 C**	**30 C**	
Pristine $LiMn_2O_4$	88	79	-	-	23	[52]
CeO_2 1 wt.%-$LiMn_2O_4$	108	100	-	-	35	
	125	121	117	102	-	[85]

Among the lanthanide oxides, La_2O_3 was another oxide studied by Amurugam et al. [86][87]. Uniform grains with average diameters of 200–300 nm and clear surface were obtained. During the electrochemical tests at 30 and 60 °C, respectively, the coated LMO samples exhibited higher capacity retentions than the pristine sample and among all the samples the performance of LMO/2 wt.% La_2O_3 had been highlighted. 2 wt.% La_2O_3 coated LMO not only showed good discharge capacity, but also possessed a high coulombic efficiency at high c-rates (2 and 5 C), which increased with the number of cycles. In the case of discharge rate of 2 C, a coulombic efficiency of 100% was obtained after 80 cycles and it remained unchanged even after 100 cycles. In the other situation, at 5 C, the highest coulombic efficiency (95%) was noted after 50 cycles and it did not modify until the experiment's end.

Lithium manganese oxide modified with 5% La_2O_3 was synthesized by a classical solid-state reaction method by Feng et al. [88]. The SEM analysis of the sample showed rough surface for the coated spinel, which tended to form agglomerations. Similar discharge capacity with Ref. [87] (116.4 $mAh{\cdot}g^{-1}$) was recorded when the cell was cycled at a temperature of 25 °C and a c-rate of 1 C. In contrast with the pure $LiMn_2O_4$, there was no sudden capacity loss, and the material was able to provide 90.1% of its initial capacity after 200 cycles. Since $LiMn_2O_4$ suffers from elevate temperature instability, 5 wt.% La_2O_3 demonstrated that it could be an efficient spinel coating when the cell was tested at 55 °C. Like in similar studies, the capacity retention of the current modified sample was at least 82% after 200 cycles.

Lanthanum oxide synthesized by a combustion method, was coated on LMO particles in neopentyl glycol [89]. In contrast with the previous reported article related to La_2O_3 modified lithium manganese oxide, 3 wt.% La_2O_3 improved the cycling ability of LMO and a capacity loss of 8.3% was seen after 100 cycles at elevated temperature (60 °C).

Due to its interesting properties like thermal and structural stability and fast kinetics, titanium dioxide was employed as coating for lithium manganese oxide [90][91][92][93]. In one of the first studies about the TiO_2 effect upon the improvement of electrochemical properties of $LiMn_2O_4$, it was noticed that it did not modify the spinel structure, but a spinel $LiTi_xMn_{2-x}O_4$ formed on the pristine particles [93]. In contrast, when TiO_2-B particles with nano-belts morphology were coated, no intermediary Li-Ti-Mn-O layer was obtained. The TiO_2 (B) porous coating hindered manganese dissolution and enhanced the lithium ions transport, throughout their network, fact proven by smaller charge-transfer and solid electrolyte interface (SEI) resistances, in comparison with bare sample [90].

Different mass weight percentages for possible coatings were studied, in order to determine de optimal amount of TiO_2 coating for $LiMn_2O_4$. Zhang et al. [91] synthesized modified spinel with 0.5, 1, 2 and 3 wt.% TiO_2, respectively. The charge-discharge curves and cycling performance emphasized that the optimal amount was 2 wt.% TiO_2, because of its highest initial discharge capacity (129 $mAh \cdot g^{-1}$) and low-capacity loss after 50 cycles (5.5%). Using the same percentage of TiO_2, Shang et al. [90] studied long time cycling of LMO/TiO_2 materials at elevated temperature (55 °C), in order to determine the improvement done by the oxide coating. After 300 cycles, the modified sample furnished a capacity of 77.4 $mAh \cdot g^{-1}$ (74% of initial discharge capacity), while the LMO offered only 63% of the initial capacity (66.1 $mAh \cdot g^{-1}$). Walz et al. [94] used ZrO_2 and TiO_2 as coatings for bare $LiMn_2O_4$ and proposed a possible mechanism ZrO_2 and TiO_2 protection of LMO during cycling at elevated temperature (55 °C). The HF, which has such a harmful effect on lithium manganese oxide, can appear as a reaction's product between $LiPF_6$ and water traces during cell's assembly [95]. TiO_2 may react with HF and form a compound with the formula of $TiO_2 \cdot 2HF$ and it prevents the manganese dissolution, improving spinel's stability over repeated cycling. Having an average diameter of only 4.8 nm and pores size around 0.7 nm, TiO_2 coating reduced to half the internal resistance of the cell (81 Ω), which remained lower than for the pristine $LiMn_2O_4$ cell (168 Ω). The discharge capacity of the modified LMO decreased with about 10% (from 120 to 103 $mAh \cdot g^{-1}$), while a serious severe capacity fading of ~75% was recorded for pristine material.

For the TiO_2 (B)-nano belts $LiMn_2O_4$, two synthesis approaches were made. One of them [91] consisted of facile phase liquid mixing, while the other one was a two-steps synthesis, which employed a preliminary hydrothermal method stage, followed by electrostatic attraction [90]. In the case of the latter suggested synthesis method, the heat treatment for the obtaining of modified sample was also studied and it was clearly noticed that a heat treatment of 2 h would be enough to synthesis a porous coating layer on the pristine LMO. When a longer heat period (4 h) was tested, it was observed that a dense compact layer formed and it did not improve the electrochemical performance of the sample.

LMO/V_2O_5 particles were easily obtained by a solid-state method, followed by a calcination at 500 °C, for 2 h in air atmosphere [96]. The XRD patterns of the synthesized samples showed that the vanadium oxide did not modify LMO spinel structure and no remarkable differences between pristine and modified samples XRD peaks were noticed. The main reason of applying vanadium oxide coating on the pristine sample was, like in other case, the improvement of LMO spinel's stability. The coating layer was not dense, so the modified sample solid electrolyte interphase resistance (R_{SEI}) had a slightly higher value (8.52 Ω) than the pristine LMO (8.35 Ω) and the LMO charge-transfer resistance was greatly decreased from 69.72 to 26.51 Ω, demonstrating the development brought by V_2O_5 coating. During cycling at elevated temperature (>55 °C) and since the electrode material is in contact with the electrolyte on wide area, the possible presence of HF in the electrolyte tends to encourage the disproportionate reaction of manganese ions (Mn^{3+}). Inductively coupled plasma atomic emission spectroscopy (ICP-AES) studies showed that the manganese concentration in electrolyte solution, in certain conditions (30 days' samples immersion at 55 °C), was five times smaller (88 ppm) for the coated LMO, than for bare LMO, proving the coating efficiency again manganese dissolution. The best results were for 2.5 wt.% V_2O_5 when discharge capacities of 107.3 and 92 $mAh{\cdot}g^{-1}$, respectively, were provided after the materials were cycled for 200 times at room and elevated temperatures. In spite the fact that it was not such a large difference between LMO and 2.5 wt.% V_2O_5/LMO (~1%), the low discharge capacity exhibited by the pristine sample synthesized makes it unsuitable for practical devices.

In one of the latest studies on oxide coating for $LiMn_2O_4$, Tao et al. [97] coated MoO_3 through a wet chemical method. Throughout this synthesis process, a uniform coating layer with a thickness of about three nm was deposited. The cyclic voltammetry tests revealed the two peak pairs, specific for $LiMn_2O_4$ spinel, but in the case of LMO/MoO_3, the peaks were slightly shifted to the right, with about 0.05 V. Both pairs of peaks of the modified sample were sharper than the ones of bare LMO. The main characteristic of the modified samples was the ability to provide almost 70% of its initial discharge capacity (101.6 $mAh{\cdot}g^{-1}$) after long time cycling (900 times) at a current density of 2 C. All the results mentioned above were recorded for the sample modified with three-weight percentage of molybdenum oxide. A higher oxide amount did not lead to improved electrochemical results, except cycling performance. From EIS spectra, it was confirmed that the lowest slope of LMO/5 wt.% MoO_3 provided the lowest lithium ions diffusion, lower even than pristine sample, owing the highest value of charge-transfer resistance (265.1 Ω).

Lithium manganese oxide thin films coated by manganese oxide exhibited an outstanding life cycle and only 20% capacity fade was calculated after 3000 cycles [98]. The bixbyite-type Mn_2O_3 coating layer was deposited on the LMO/Pt substrate by a spin-coating technique, followed by an annealing treatment at 750 °C for 6 h. The relatively large thickness of Mn_2O_3 porous layer (~600 nm) did not block the lithium ions during tests, and a slightly improved discharge capacity (~3 $mAh{\cdot}g^{-1}$) was recorded for coated sample in comparison pristine LMO. In order to demonstrate the efficiency of Mn_2O_3 layer against the electrolyte attack over the LMO modified electrode, pristine and coated LMO were immersed in 1 M $LiPF_6$ electrolyte solution for seven days. The $Mn_2O_3/LiMn_2O_4$ electrode barely showed dissolution proofs, while the pristine LMO completely dissolved. While the Mn^{3+} ions inside $LiMn_2O_4$ spinel structure are exposed for reduction to Mn^{2+}, fact that hinders material's performance, it was determined that Mn^{3+} ions from bixbyite structure are more stable.

Recently, Yao et al. [99] suggested that tert-butanol addition during the synthesis of Al_2O_3 coated LMO enhanced the stability and electrochemical properties of the sample. Due to the fact that Al_2O_3 is inactive in the range between 3.0–4 V, the LMO-Al_2O_3 composite delivered a lower specific discharge capacity in the first cycle (105.46 mAh·g^{-1}, c = 0.2 C), in comparison with the bare lithium manganese spinel (114.69 mAh·g^{-1}), but the elevated temperature (55 °C) test proved a better capacity retention (90.78%). This cyclability improvement is related to the protective coating layer, which is strongly attached to the LMO particles. Al^{3+} has the role of an anchor ion between polymeric functional groups formed by tert-butanol's hydroxyl groups and the hydrogen bonds from the aluminum salt precursor (aluminum sulfate octadecahydrate). In addition, the ageing tests showed less manganese content in LMO-Al_2O_3 sample (62.3 ppm) compared to bare LMO (218.5 ppm). For the ageing tests, the samples were immersed in electrolyte for 20 days at a temperature of 55 °C.

Al_2O_3-coated $LiMn_2O_4$ have been synthesized by a co-precipitation method [100]. In contrast with the previous reported LMO-Al_2O_3 composite, the current modified sample showed a higher capacity in the first cycle (133.5 mAh g^{-1}, c = 0.5 C) and the recorded capacity faded with only 0.014% per cycle. Al_2O_3 uniform nano-coating can be considered efficient to prevent the apparition of Jahn-Teller structural distortion and also to hinder the electrolyte attack over the active LMO particles, because of the lower specific area (2.3 m^2 g^{-1}), four times lower than for pristine LMO (13.6 m^2·g^{-1}). In addition, Al_2O_3 strengthened the high discharge rate performance, at 5 C (55 °C), thus, the 100th cycle capacity of LMO-Al_2O_3 remained ~92% of the initial one (~108 mAh·g^{-1}), much better than the bare spinel (73.5% capacity retention and ~90 mAh·g^{-1} in the first cycle).

In another research article [101], Al_2O_3 was coated on pre-sintered and calcined $LiMn_2O_4$, through a wet process, followed by heat treatment at 750 and 350 °C for 10 h, respectively. During the electrochemical test, it was noticed an improved cycle life for Al_2O_3 pre-coated LMO compared to other samples. The Al_2O_3 layer acted like an inhibitor layer and prevented large growth of $LiMn_2O_4$ particles, thus the smaller sized material owned better kinetics during tests. Moreover, during ageing tests, 0.05 mg of manganese from the Al_2O_3 pre-coated LMO dissolved into in electrolyte, which was four times lower than for bare spinel and with 25% less than Al_2O_3-coated LMO.

Guo et al. [102] have reported lithium manganese oxide coated by a wet process implying electrostatic attraction forces method. By adjusting the pH of a mixture of water and ethanol to 8, a Zeta potential difference of 44 mV has been recorded. After that, LMO spinel powder was added, while nano-silica sol was poured drop wise. The resulted sol was heated at 90 °C for 10 h and then calcined at 700 °C for 6 h. Different weight percentages of SiO_2 were tested, but the best results were measured for 2 wt.% SiO_2-LMO. The XRD patterns of coated samples were slightly shifted to the left, which can be attributed to a possible replacement of Mn^{4+} from 16d sites by Si^{4+} ions. During the cell's cycling at room temperature (25 °C), 2 wt.% SiO_2-LMO retained 97.6% of the initial capacity (101.2 mAh·g^{-1}) after 100 cycles. Even though a low-capacity loss of only 2.4% was calculated, the achieved discharge capacity was too low for a possible practical application (only 68.73% of LMO's theoretical capacity), whereas higher discharge capacities were recorded for LMO coated with CeO_2 [85], Li_2ZrO_3 [103] or AlP [30]. SiO_2 had benefic effect over the $LiMn_2O_4$ performance at elevated temperature (55 °C), which is considered a critical parameter for spinel. Moreover, silicon oxide coating reduced the amount of dissolved manganese into the electrolyte by 36% and increased the lithium diffusion coefficient by one magnitude order, which determined faster lithium ions migration throughout the electrochemical tests. Another improvement brought by the SiO_2 coating was related to reducing the R_{ct} increasing rate after 100 cycles, thus, in the case of surface modified sample, R_{ct} increased by ~8 times (from 125.9 to 970.1 Ω), while bare sample's R_{ct} value dramatically raised by almost 20 times, reaching an enormous value of 11,800 Ω.

2.3. Other Surface Changes

Coatings that are more complex were studied in the last years (Table 3). Metal phosphates [104][105][106] and fluorides [51] were among the most investigated coatings. Among other possible coatings, layered material $LiCoO_2$ [107], spinel type material ($LiNi_{0.5}Mn_{1.5}O_4$) [1] or pervoskite-type oxide [108] were also tested.

Table 3. Other surface modification of LMO.

Nr. Crt.	Material	Synthesis Method	Discharge Capacity (mAh g^{-1})	Coulombic Efficiency (%)	Discharge Capacity/N Cycles * (mAh·g^{-1})	Capacity Retetion (%)	D_{Li} × 10^{10} (cm^2·s^{-1})	R_{ct} (Ω)	Ref
1	3 wt.% $FePO_4$-$LiMn_2O_4$	Chemical deposition method	122.0 $^{(d)}$	-	83/80	68	-	-	[104]
			118.2 $^{(d)}$		78/80	66		-	
2	1 wt.% $FePO_4$-$LiMn_2O_4$		124.0 $^{(d)}$	98%	118.7/100	93.5	-	-	[105]
			127.0 $^{(g)}$	-	68/100	53.5		-	
3	3% LaF_3-$LiMn_2O_4$		118.7 $^{(i)}$	99.9	107/100	90.1	-	-	[51]
			117.1 $^{(i)}$	99.5	98.6/100	84.2		-	
4	3% AlP-$LiMn_2O_4$		124.2 $^{(i)}$	-	116.7/100	94		66/100 cycles *	[30]
				-	108.1/100	87			
5	2% AlF_3-$LiMn_2O_4$		103.4 $^{(i)}$	90	92.9/50	89.8	-	-	[109]
6	1% Li_3PO_4-$LiMn_2O_4$	Ball milling method450 °C (5 h)	114.2$^{(i)}$		97.1/100	85	-	293	[110]
7	10% $LiNi_{0.5}Mn_{1.5}O_4$-$LiMn_2O_4$	Sol-gel	112.0 $^{(q)}$	-	107.8/50	96.3	-	-	[1]
			109.5 $^{(q)}$	-	98.6/100	90			

Nr. Crt.	Material	Synthesis Method	Discharge Capacity (mAh g^{-1})	Coulombic Efficiency (%)	Discharge Capacity/N Cycles * (mAh·g^{-1})	Capacity Retetion (%)	D_{Li} × 10^{10} ($cm^2 \cdot s^{-1}$)	R_{ct} (Ω)	Ref
8	0.3% Li_3BO_3-$LiMn_2O_4$		118.2 $^{(d)}$	90	108.7/40	92		14.3/20	[111]
			119.3 $^{(d)}$	-	104.5/40	87.8		22/20	
9	5% FeF_3-$LiMn_2O_4$		110.7 $^{(d)}$	-	75.5/200	68.2	-	-	[112]
			108.1 $^{(d)}$	-	66.5/100	61.5			
10	3% YPO_4-$LiMn_2O_4$		107.0 $^{(d)}$	-	90.0/200	84.1	-	151.7	[106]
			107.2 $^{(d)}$	-	86.1/100	80.3			
11	3% LaF_3-$LiMn_2O_4$		115.9 $^{(d)}$		84.3/200	72.7	-		[113]
			115.3 $^{(d)}$		81.1/100	70.3			
12	$LiCoO_2$-$LiMn_2O_4$		117.7 $^{(j)}$	-	111.1/100	94.4	-	-	[107]
			117.2 $^{(j)}$	97.6	110.1/100	93.6			
13	0.5% Li_2CuO_2-Li_2NiO_2 solid solution-$LiMn_2O_4$		121.2 $^{(i)}$	-	113/300	93.2			[54]
			12 1 **	96	98.1/200	81.1	-	49.23	
14	3% Li_2ZrO_3-$LiMn_2O_4$		126.7 $^{(i)}$	97.5	125.5/100	99.0	-	34.2	[103]
			129.5 $^{(i)}$	99.8	116.8/100	90.2			
15	La-Sr-Mn-O-LMO		129.9 $^{(b)}$120.0 $^{(i)}$	90.7	108.1/500/1 C	90.6	2.54 × 10^2	42.1	[114]
16	2% $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$-$LiMn_2O_4$		107.3 $^{(i)}$	-	97.4/130	90.8	-	192.6/100 cycles	[26]
			116.6 $^{(i)}$	-	111.8/200	95.88			
				-	/200	89.74			
17	3% $LaMnO_3$-$LiMn_2O_4$		114.0 $^{(g)}$106.0 $^{(l)}$	95.0	97/500	91.5	5.12 × 10^{-1}	-	[37]
18	3% Li_2MnO_3-$LiMn_2O_4$		113.3 $^{(i)}$	-	106.7/500	94.17	-	75.2/50 cycles	[115]
			115.0 $^{(i)}$	-	103.2/200	89.75			

Nr. Crt.	Material	Synthesis Method	Discharge Capacity (mAh g^{-1})	Coulombic Efficiency (%)	Discharge Capacity/N Cycles * (mAh·g^{-1})	Capacity Retention (%)	D_{Li} × 10^{10} (cm^2·s^{-1})	R_{ct} (Ω)	Ref
19	$LiNi_{0.5}Mn_{1.5}O_4$-$LiMn_2O_4$		101.0 $^{(i)}$	94.4	-	-	-	-	[116]
20	3% $La_{0.7}Sr_{0.3}Mn_{0.7}Co_{0.3}O_3$-$LiMn_2O_4$ *		123 $^{(d)}$ 108.0 $^{(x)}$	95.8	101/100 $^{x)}$	93.5	2.15	4.05	[108]
21	$LiMn_{1.912}Ni_{0.072}Co_{0.016}O_4$	Co-precipitation	118.0 $^{(i)}$	97	113.4/200	96.1	8 × 10	45.31	[117]
22	3% LaF_3-LMO		118.4 $^{(i)}$	97.5	118.04/50	99.7	4.67 × 10^2	-	[118]
23	3% $FePO_4$-$LiMn_2O_4$		105.3 $^{(g)}$	-	93.3/100	88.6	9.85	171/20	[119]
24	3% $LiMnPO_4$-$LiMn_2O_4$	Hydrothermal reaction	112.4 $^{(g)}$	94.5	104/300	92.5	5.32 × 10^{-2}	400.6	[120]
			115.7 $^{(g)}$	94.2	111.7/100	96.6			
			107.0 $^{(g)}$	83	75.1/500	70.2			
25	2 wt.% $LaPO_4$-$LiMn_2O_4$	Polymeric process	123.9 $^{(g)}$ 103.0 $^{(g)}$	95.4	-	-	-	0.5 - 1.5	[121]

oxide's was able ately, at s of the d lesser e, lithium terial for the LMO uring the calcined nation of cts were s^{-1}) was perature NMO) on not very common, LNMO influenced the capacity retention of the pristine sample, especially at high temperature. While the bare LMO exhibit 82.8 mAh·g^{-1} (66.7% of its initial discharge capacity) after 40 cycles, the LNMO/LMO composite had 98.6 mAh·g^{-1} (~90% of the first cycle capacity). Changes in the structure of LMO cycled at 60 °C were noticed and peaks corresponding to tetragonal $Li_2M_2O_4$ were identified after analyzing the sample by XRD. No similar peaks were observed for the modified sample, fact that proved the efficiency of 10% LNMO to suppress the Jahn-Teller distortion. The $LiNi_{0.5}Mn_{1.5}O_4$ structure, which greatly favors the Li^+ diffusion, was an important factor in reducing the charge-transfer resistance of the composite.LNMO/LMO composite material has been synthesized trough a citric acid sol-gel route [116]. The core-shell material presented an initial lower discharge capacity (101 mAh·g^{-1}) and only after five cycles, the structure has been stabilized along with the formation of LNMO's SEI layer. Charge/discharge tests at different rates (from 1 to 65 C), demonstrated the high-rate ability of the modified sample, due to its discharge capacity of approximately 25 mAh·g^{-1} at 65 C. In comparison, the pristine sample exhibited a similar capacity, but for a lower discharge rate (45 C).$LiCoO_2$ established as a good cathode material since the appearance of the Li-ion batteries. In the last years, it was suggested as a potential coating material for spinel type LMO, in order to improve the high-temperature behavior of the latter [107]. Commercial LMO sample was modified with $LiCoO_2$ throughout a sol-gel process, employing a two-stage heat treatment, at 350 and 650 °C, respectively. The initial discharge capacities of $LiCoO_2$-LMO sample were higher than the ones for unmodified sample, both at room and elevated temperature. The reason for this aspect is related to the electrochemical activity of the lithium cobalt oxide in the tests' voltage area (3.4–4.2 V). $LiCoO_2$ improved the capacity retention of LMO by 6%, from 87.5% to 93.6%, after 100 cycles at 55 °C. In addition, the $LiCoO_2$ coating layer acted as a barrier and halved the manganese dissolution into the electrolyte; the dissolved quality of manganese ions (determined by ICP-AES analysis) from $LiCoO_2$-$LiMn_2O_4$ electrode was 10.17µg/cm^2, in comparison to 22.54 µg/cm^2 for pristine $LiMn_2O_4$ electrode.Among the newly studied core-shell material, LMO coated with $LiMnPO_4$ (LMP) indicated suitable performance for log lasting heavy-duty devices [120]. During the test at room temperature, the LMO coated with 3% LMP showed good capacity retention of ~96% after 100 cycles. 3 wt.% LMP was not enough to suppress the structural modifications, which occurred at elevated temperature (55 °C), thus high-capacity fade (30%) was recorded after 500 cycles. The LMP layer notably improved $LiMn_2O_4$′s cyclic performance, especially at high discharge rates of 10 and 20 C, respectively. After long time cycling (1000 cycles) at 20 C, the discharge capacity for 3 wt.% LMP (76.3 $mAh \cdot g^{-1}$) was 1.6 times higher than for the pristine sample (45.8 $mAh \cdot g^{-1}$). As a drawback, due to low electronic conductivity of $LiMnPO_4$ material, the modified samples presented a lower D_{Li} (5.32×10^{-12} $cm^2 \cdot s^{-1}$) than in other reported studies [117][119]. LMP layer did not suppress the disproportionate reaction of Mn^{3+}, but it successfully blocked the dissolution of Mn^{2+} into the electrolyte.Feng et al. [30] developed an aluminum phosphide (AlP) coating. An interesting aspect related to aluminum phosphide is its ability to react with the harmful HF, which promote Mn^{3+} disproportionate reaction, and the resulted product, AlF_3, was also successfully tested as coating for $LiMn_2O_4$ [122][109].AlF_3 was deposited on already modified LMO by an Al^{3+} and F^- co-doping sample via a co-precipitation method [122]. The aluminum fluoride coating protected the $LiAl_{0.04}Mn_{1.96}O_{3.96}F_{0.04}$ particles from electrolyte action, resulting in a more stable structure during charge-discharge cycles. Moreover, it reduced the charge-transfer resistance growth rate calculated, which was calculated to be from 67 to 197 Ω for pristine $LiAl_{0.04}Mn_{1.96}O_{3.96}F_{0.04}$, to only 6 Ω (from 87 to 93 Ω) after the same number of cycles (100 cycles). However, a minor improvement related to D_{Li+} was noticed for AlF_3-coated LMO ($1.4 \cdot 10^{-8}$ cm^2 s^{-1}) in comparison with $LiAl_{0.04}Mn_{1.96}O_{3.96}F_{0.04}$ ($1.2 \cdot 10^{-8}$ cm^2 s^{-1}), but the lithium diffusion coefficients of the latter samples was ten times higher than for pristine $LiMn_2O_4$ ($1.1 \cdot 10^{-9}$ cm^2 s^{-1}).Modified LMO samples were tested with good results in ARLB cells. For example, 2 wt.% LaF_3-$LiMn_2O_4$ exhibited an insignificant capacity fade after 50 cycles [118]. Due to LaF_3′s structure, its large channels enhance the lithium migration to and from the electrode material, while an optimum amount of lanthanum fluoride coating may prevent the side reaction that can occur between LMO and electrolyte. The calculated lithium diffusion coefficient ($4.67 \cdot 10^{-8}$ $cm^2 \cdot s^{-1}$) was two magnitude higher than the one obtained for iron phosphate modified $LiMn_2O_4$ in organic electrolyte [119] and similar to D_{Li} calculated for La-Sr-Mn-O coating [114]. The protective LaF_3 layer acted like a barrier and protected the electrode surface, by reducing the contact area between LMO and aqueous electrolyte; therefore, the manganese dissolution into $LiNO_3$ was barely noticed.Solid electrolytes, like Li_3BO_3 [111] or La-Sr-Mn-O (LSM) [114], with good ionic conductivity demonstrated to be adequate coating materials for enhancing the cycle ability of $LiMn_2O_4$. The higher ionic conductivity of LSM thin uniform layer played an essential role in the higher initial discharge capacity (129.9 $mAh \cdot g^{-1}$, 0.1 C) and promoted a capacity retention (90.6%) with up to 50% higher than the pristine sample. LSM coating decreased the charge-transfer resistance, enhanced the lithium-ion diffusion and the calculated diffusion coefficient for lithium ions had the same magnitude order as for LaF_3-coated $LiMn_2O_4$ tested in an ARLB [123]. Another improvement brought by the LSM was related to electrical conductivity ($8.42 \cdot 10^{-4}$ S/cm), which was larger than for pristine sample ($5.31 \cdot 10^{-5}$ S/cm).An isostructured Li_2CuO_2-Li_2NiO_2 solid solution has been considered as a coating for lithium manganese oxide [54]. During the electrochemical investigations at room temperature, it was demonstrated that a low amount of solid solution (0.5 wt.%) was enough to increase the rate capability (93.2% capacity retention after 300 cycles) and to maintain a reasonable discharge capacity (113 $mAh \cdot g^{-1}$ in the first cycle). However, taking in consideration that the elevated temperature performance is a key demand, it was noticed that 0.5 wt.% was not enough to stabilize the $LiMn_2O_4$ at 55 °C, thus the capacity retention was only 81.2% after 200 cycles. In comparison, 2% *w*/*w* Li_2CuO_2-Li_2NiO_2 solid solution exhibited an improved electrochemical performance. By having higher amount of coating, the contact area between the electrolyte and $LiMn_2O_4$ was reduced, so the manganese dissolution was hindered.Multiple doped $LiCo_{0.025}Cr_{0.025}Ni_{0.025}Fe_{0.025}Mn_{1.90}O_4$ and pristine $LiMn_2O_4$ were coated by lithium borosilicate (LBS) through a facile solution method [124][125]. LBS-based glass was proposed as a coating due to its improved ionic conductivity. Surface modified samples exhibited lower initial discharge capacity (109.7 $mAh·g^{-1}$) than pristine LMO, because the coating layer slightly decreased the lithium diffusion. However, LBS reduced the contact surface between the electrode active material (LMO) with the electrolyte (1 M $LiPF_6$ solution), and superior capacity retention (93.3%) was observed after 70 cycles (25 °C). At elevated temperature (55 °C), LBS-coated $LiMn_2O_4$ performed better than bare LMO, showing a higher initial discharge capacity (120 $mAh·g^{-1}$ vs. 104.2 $mAh·g^{-1}$). In addition, the capacity fade per cycle was slightly lower for coated LMO spinel (0.708 $mAh·g^{-1}$ $cycle^{-1}$ vs. 0.728 $mAg·g^{-1}$ $cycle^{-1}$).Perovskite-type $LaMnO_3$ was successfully deposited on lithium manganese oxide, without modifying the spinel structure [37]. The improved electronic conductivity of $LaMnO_3$ determined a higher initial discharge capacity of the modified sample (114 mAh g^{-1}) and better coulombic efficiency (95%) than for pristine lithium manganese oxide (106 mAh g^{-1} and 89.1%).Titanium carbide ($Ti_3C_2T_x$) nanosheets, a MXene 2D layered structured material, has been recently used as a protective coating layer for LMO particles by their encapsulation through facile electrostatic self-assembly method. Similar synthesizes methods can be using for other cathode materials like $LiCoO_2$ or $LiFePO_4$ [126]. MXene layered material, with the general formula of $M_{n+1}AX_n$ (n = 1, 2, 3), where M is a transition metal (Sc, Ti, Zr, Nb, Mo), A corresponds to elements from the 13th or 14th groups (Al, Si, for example) and X represents either C or N atoms. Namely, in the case of titanium carbide, T_x is attributed to functional group –OH and atoms like –O and –F [126][127]. $Ti_3C_2T_x$ is obtained by selective removal of Al from Ti_3AlC_2 in dilute HF solution media. Details about the synthesis procedure of titanium carbide along with other aspects related to MXene materials can be found in Ref [128]. Three samples were tested: pristine LMO, $Ti_3C_2T_x$-LMO (obtained using CTAB as decorator for charging the surface of LMO) and $Ti_3C_2T_x$-$LiMn_2O_4$ (synthesized in similar conditions but replacing CTAB with deionized H_2O). During the electrochemical tests, at both room temperature and 55 °C, $Ti_3C_2T_x$–coated LMO (with CTAB) performed better than the other two tested samples and delivered higher specific capacity of 114.1 $mAh·g^{-1}$ (c = 1 C, RT) and 115.9 mAh g^{-1} (c = 1 C, 55 °C), respectively. In addition, the capacity fade was not as broad as in other case, and at 55 °C, $Ti_3C_2T_x$–coated LMO (with CTAB) showed a discharge capacity with more than 18% than the pristine sample (63%), after 200 cycles. Titanium carbide layered hampered the manganese dissolution into the electrolyte by reducing the contact area between the working electrode and electrolyte. By coating the pristine LMO with $Ti_3C_2T_x$, which possesses low Li^+ diffusion barrier (0.007 eV), good electronic conductivity and high Li^+ diffusion coefficient, determined lower charge-transfer resistance (133.4 Ω) than 370.7 Ω for $Ti_3C_2T_x$-LMO (deionized water) and 552.6 Ω for bare spinel (at room temperature).$Li_4Ti_5O_{12}$(LTO) is a characteristic material which can be used as anode in Li-ion batteries [129][130], but, lately, it was successfully employed as a coating layer for enhancing the performance of $LiMn_2O_4$ [130]. LTO–LMO nanorods were manufactured by a three-step synthesis method: in the first stage, β-MnO_2 were obtained by a hydrothermal process, followed a solid stage reactions method, when as-synthesized β-MnO_2 were mixed with lithium hydroxide and calcined to result lithium manganese oxide. Afterwards, the composite material resulted through a sol-gel process, where a key parameter was to control the hydrolysis and condensation of titanium precursor (titanium tetrabutoxide). LTO-coated LMO was electrochemically tested for a long number of cycles (500 cycles, *c* = 1 C), at room (25 °C) and elevated temperature (55°), respectively. In the first cycles, the tested working electrode provided 119.7 mAh·g^{-1} and a capacity of 17.8% was recorded after 500 cycles, while an initial discharge of 119.2 mAh·g^{-1} and a 74.8% capacity retention was calculated after an identical number of cycles, at 55 °C. The results obtained by $Li_4Ti_5O_{12}$ overcome other coatings like Li_3PO_4 [110], $LiMnPO_4$ [120] or Li_2CuO_2-Li_2NiO_2 [54], but performed slightly worse than Li_2MnO_3 [115] or La-Sr-Mn-O [114]. Despite the fact that lithium titanium oxide improved the cycling ability of the LMO by preventing manganese solution, no significant enhancement was observed in the case of lithium diffusion coefficient (5.33 × 10^{-12} m^2 s^{-1}), which was lower than in other cases: $La_{0.7}Sr_{0.3}Mn_{0.7}Co_{0.3}O_3$ [108], $FePO_4$ [119], La-Sr-Mn-O [114] or LaF_3 [118]. However, electrochemical impedance spectra demonstrated that LTO helped lithium diffusion and composite's R_{ct} did not increased so much (from 6.58 to 54.2 Ω) after 100 cycles, as in the case of pristine sample (from 8.45 to 156.27 Ω).Uniform thin layer of hexafluorotitanic lithium (Li_2TiF_6) with high lithium conductivity has been deposited on commercial $LiMn_2O_4$ by a co-precipitation method, using precursors like lithium carbonate (Li_2CO_3) and hexafluorotitanic acid (H_2TiF_6) [131]. Low amount of hexafluorotitanic lithium was enough to stabilize and improve the lifetime of LMO. It was showed that high weight amount (10 wt.% Li_2TiF_6) of coating determined the formation of a thick coating layer. It managed to constrain capacity fade, although the delivered discharge capacity was not sufficient. Usually, the coatings do not have excellent lithium conductivity and this drawback affects the performance of the working electrode at high discharge rates, because the adequate lithium diffusion paths are available. However, Li_2TiF_6 improved the high discharge rate performance of bare spinel; thus, the specific capacity for composite material was 99.4 mAh·g^{-1} in the 200th cycle, much greater than 65.7 mAh·g^{-1} for pristine LMO. The results were superior to the ones obtained by $La_{0.7}Sr_{0.3}Mn_{0.7}Co_{0.3}O_3$-coated lithium manganese spinel [108].

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