Synergetic action of doping and coating on electrochemical performance of lithium manganese spinel as an electrode material for lithium-ion batteries

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Abstract. Spinel LiMn_2O_4 and multidoped spinel $\text{LiMn}_{1.9}\text{Co}_{0.025}\text{Cr}_{0.025}\text{Ni}_{0.025}\text{Fe}_{0.025}\text{O}_4$ were synthesized by the glycine-nitrate method and coated with lithium borosilicate (LBS) in order to enhance the electrochemical performance at room temperature. The structure and electrochemical performance of all samples were characterized by inductively coupled plasma-mass spectrometer (ICP-MS), X-ray diffraction (XRD), differential thermal analysis/thermogravimetry (DTA/TG), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), atomic force microscopy (AFM) and galvanostatic charge–discharge measurements. The XRD analysis shows that the samples exhibit a pure spinel phase. The SEM results indicated that LBS particles had encapsulated the surface of the undoped and multidoped LiMn_2O_4 without causing any structural change. The charge–discharge tests showed that $\text{LiMn}_{1.9}\text{Co}_{0.025}\text{Cr}_{0.025}\text{Ni}_{0.025}\text{Fe}_{0.025}\text{O}_4$ displays better cycling performance than the pristine LiMn_2O_4 at room temperature. However, in the same conditions, LBS-coated $\text{LiMn}_{1.9}\text{Co}_{0.025}\text{Cr}_{0.025}\text{Ni}_{0.025}\text{Fe}_{0.025}\text{O}_4$ and LiMn_2O_4 have better cycling performance than uncoated samples. The results suggest that multidoped and LBS-coated LiMn_2O_4 could develop into a promising cathode material for lithium ion batteries.

Keywords. Lithium ion battery; LiMn_2O_4 ; cation doping; surface modifications; electrochemical cycling performance.

1. Introduction

Lithium ion batteries which have high energy and power density, are important for consumer electronic devices, portable power tools and vehicle electrification.^{1–4} Li_xCoO_2 is a commonly used cathode material in commercial lithium ion batteries and has a charge capacity of 140 mAh g^{-1} with a practical value of x from 0.5 to 1. However, the high cost, toxicity and limited abundance of cobalt have been recognized to be disadvantageous. As a result, alternative cathode materials have attracted much interest. One of the most promising candidates is spinel LiMn_2O_4 , which has a charge storage capacity of 148 mAh g^{-1} .^{5–9} Spinel LiMn_2O_4 has the advantages of low-cost, environmental friendliness and high abundance.

However, early work soon identified that stoichiometric LiMn_2O_4 shows considerable capacity fading on cycling, associated with structural degradation and poor rate performance.^{10–19}

Although the reason for the poor cycling performance is not fully understood, several possible mechanisms have been

suggested including Mn dissolution, Jahn–Teller distortion and changes in crystallinity.^{20–26}

Several methods for the improvement of cycle life have been suggested. Among these, the substitution of small amount of a ion doping at the Mn sites is the most commonly used.^{27–30} In this case, the basic idea of doping is to stabilize the spinel structure against lattice breakdown or Jahn–Teller distortion during cycling. In particular, the problem of capacity fading in LiMn_2O_4 electrodes, which is believed to be at least partly due to the formation of domains of the tetragonally distorted Mn^{3+} rich phase at high levels of reduction, has been successfully solved by substitution to decrease the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio.³¹ Although ion substitution can improve the stability of the spinel structure, and suppress the Jahn–Teller distortion, studies indicate that the dissolution of Mn occurs mainly at the interface between spinel LiMn_2O_4 and electrolyte.^{32,33} Therefore, surface modification with various metal oxides^{34–38} such as Al_2O_3 , Co_3O_4 or ZnO , is considered as one effective method to solve the problem, because these oxides can suppress Mn dissolution by scavenging HF which may originate from the electrolyte.

In a previous study³⁹ we successfully coated lithium borosilicate (LBS) on the surface of LiMn_2O_4 and obtained

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satisfactory improvement in capacity retention. In the present study, to improve the capacity fade of the cathode, we used two different modification methods. Firstly, to decrease Jahn–Teller distortion in the compound we tried to substitute part of the manganese site with four typical elements, designated as $\text{LiMn}_{1.9}\text{Co}_{0.025}\text{Cr}_{0.025}\text{Ni}_{0.025}\text{Fe}_{0.025}\text{O}_4$, by the glycine nitrate combustion method. Secondly, to avoid Mn dissolution in the cathode, LBS was coated on the surface of $\text{LiMn}_{1.9}\text{Co}_{0.025}\text{Cr}_{0.025}\text{Ni}_{0.025}\text{Fe}_{0.025}\text{O}_4$ particles *via* the simple solution method. In addition, the correlation of the $\text{LiMn}_{1.9}\text{Co}_{0.025}\text{Cr}_{0.025}\text{Ni}_{0.025}\text{Fe}_{0.025}\text{O}_4$ coating layer on the electrochemical performance and structural stability of the LiMn_2O_4 cathode material is elucidated and discussed.

2. Experimental

All the samples, LiMn_2O_4 , $\text{LiMn}_{1.9}\text{Co}_{0.025}\text{Cr}_{0.025}\text{Ni}_{0.025}\text{Fe}_{0.025}\text{O}_4$, were synthesized by the glycine-nitrate combustion process.⁴⁰ Stoichiometric amounts of LiNO_3 (Riedel-de Haen) and $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (Sigma), $\text{Co}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Surechem), $\text{Cr}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ (Merck), $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Merck) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck) were dissolved in distilled water. Glycine (Merck) was added to the solution either as a solid or as a water solution. Its role was to serve both as a fuel for combustion and as a complexant to prevent inhomogeneous precipitation of individual components prior to combustion. Finally, nitric acid with the same mole of acetate anions was added to the solution. The molar ratio of glycine to nitrate was 1:4. The solution was heated continuously without any previous thermal dehydration. Later the solution became a transparent viscous gel which auto-ignited automatically, giving a voluminous, black, sponge-like ash as the product of combustion. The resulting ash was heated at 800°C for 12 h.

In order to coat LiMn_2O_4 with LBS, xerogels of lithium borosilicate (LBS) were prepared by the sol–gel process using precursors of analar grade tetraethylorthosilicate ($\text{Si}(\text{C}_2\text{H}_5\text{O})_4$, TEOS) (Merck), boric acid (Panreac) and lithium nitrate (Riedel–de Haen). The precursors were mixed according to their calculated molecular weight percentage under 0.1 N nitric acid concentration as a catalyst, using the following chemical composition:

The above composition and synthesis of LBS samples was proposed by Muralidharan and Venkateswarlu⁴¹ in earlier studies. In order to obtain the LBS compound, different solutions, labeled from A to C, were prepared separately by mixing the appropriate amount of precursors. Calculated amounts of ethanol, water and TEOS were mixed in a 250 ml conical flask with a magnetic pellet. The mixture was found to be turbid initially but on stirring a clear solution was obtained. The water:TEOS ratio was maintained at 16:1 to form solution A. Solution B, containing boric acid in ethanol,

was added to solution A with continual stirring and $x = 0.1$ N nitric acid was also added as an acid catalyst to the above mixture (A + B). The mixture of solutions A and B was stirred for half an hour and later solution C, lithium nitrate in water, was added and stirred continuously at room temperature (RT) for about an hour. The temperature of the mixed solution was raised to 65°C and maintained for about 3 h with continual stirring. The sol was cast into plastic beakers covered with aluminum foil and maintained at 65°C in the oven. Aging of the gel was maintained at the same temperature (65°C) and resulted in transparent/opaque dried gels.

The mixture of the LBS precursor and LiMn_2O_4 powders was thoroughly mixed in a agate mortar and pestle, and the mixed powders were then calcined at 425°C for 5 h. The weight ratio of the precursor of LBS glass to the LiMn_2O_4 powders for this method was 2 wt%.

The cation composition of the base and surface-treated LiMn_2O_4 powders was determined by inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7500a) after dissolving the powders in a solution of 0.1 M 10 ml sulphuric acid of 0.1 M oxalic acid.

The phase identification and evaluation of the lattice parameters of the base and surface-treated LiMn_2O_4 powders were carried out by powder X-ray diffraction (XRD) using CuK_α radiation (Bruker AXS D8). The diffractometer was equipped with a diffracted beam graphite monochromator. The diffraction data were collected at 40 kV and 40 mA over a 2θ range from 10° to 90° with a step size of 0.02° and a count time of 10 s per step. The DiffracPlus and Win-Metric programs were used to obtain the lattice parameters of the powders. The particle morphology of the powders was examined by means of scanning electron microscopy (SEM) (LEO 440), operated at 20 kV.

Tapping-mode atomic force microscopy (TP-AFM) was conducted with a multi-mode coupled with a nanoscope controller, Veeco, which gave the surface information of the prepared materials.

LiMn_2O_4 particle samples were prepared by isolated particles on a silicon wafer *via* the following steps. First, LiMn_2O_4 powder was dispersed in absolute ethyl alcohol suspension with a ratio of 1 wt% by using an ultrasonic wave for 15 min, then the LiMn_2O_4 particles were placed onto a silicon wafer from a drop of suspension and then dried at room temperature.

The thermogravimetry (TG) and differential thermal analysis (DTA) measurements were conducted by a Perkin-Elmer (Diamond) high temperature thermal analyzer with 5–20 mg samples and a heating rate of $10^\circ\text{C min}^{-1}$ from 50 to 700°C in air.

The electrochemical studies were carried out in two-electrode Teflon cells. The cells were fabricated by using the bare and surface-treated LiMn_2O_4 as a cathode and lithium foil as an anode. A glass fiber separator soaked in electrolyte separated the two electrodes in the Teflon cells. The electrolyte consisted of an 1 M solution of LiPF_6 dissolved in ethylene carbonate (Aldrich)/diethyl carbonate (Merck)

(EC/DEC, 1:1 ratio by volume). For the preparation of the cathode composite, a slurry mixed with 86 wt% of cathode active material, 9 wt% of acetylene black conductor (Alfa Aesar) and 5 wt% of polyvinylidene fluoride (PVDF, Fluka) binder in 1-methyl-2-pyrrolidone (NMP, Merck) was pasted on the aluminum foil current collector which had a diameter of 13 mm, followed by vacuum drying at 120°C overnight in a vacuum oven and uniaxial pressing between two flat plates at 2 tons for 5 min. The electrode loading consisted of about 4 mg of cathode active material. Diethyl carbonate, ethylene carbonate and acetylene black were used after being purified according to the methods given in the literature.⁴² **Diethyl carbonate:** 100 ml DEC was washed with an aqueous 10% Na_2CO_3 (20 ml) solution, saturated CaCl_2 (20 ml), then water (30 ml). After drying by standing over solid CaCl_2 for 1 h (note that prolonged contact should be avoided because slow combination with CaCl_2 occurs), it was fractionally distilled. **Ethylene carbonate:** this was dried over P_2O_5 then fractionally distilled at 10 mmHg pressure and crystallized from dry ethyl ether, respectively. **Acetylene black:** this was leached for 24 h with 1:1 HCl to remove oil contamination, then washed repeatedly with distilled water. It was then dried in air, and eluted for 1 day each with benzene and acetone. It was again dried in air at room temperature, then heated in a vacuum for 24 h at 600°C to remove adsorbed gases.

Table 1. Elemental analysis results of bare LiMn_2O_4 and cation-doped LiMn_2O_4 samples.

Theoretical cation composition	Experimental cation composition
LiMn_2O_4	$\text{Li}_{0.95}\text{Mn}_{1.89}\text{O}_4$
$\text{LiMn}_{1.90}\text{Co}_{0.025}\text{Cr}_{0.025}\text{Ni}_{0.025}\text{Fe}_{0.025}\text{O}_4$	$\text{Li}_{0.99}\text{Mn}_{1.90}\text{Co}_{0.023}\text{Cr}_{0.026}\text{Ni}_{0.026}\text{Fe}_{0.024}\text{O}_4$

Figure 1. X-ray diffraction patterns of (a) LBS glass produced from calcination of the precursor powder of coating material, (b) bare LiMn_2O_4 , (c) LBS-coated LiMn_2O_4 , (d) $\text{LiMn}_{1.9}\text{Co}_{0.025}\text{Cr}_{0.025}\text{Ni}_{0.025}\text{Fe}_{0.025}\text{O}_4$ and (e) LBS-coated $\text{LiMn}_{1.9}\text{Co}_{0.025}\text{Cr}_{0.025}\text{Ni}_{0.025}\text{Fe}_{0.025}\text{O}_4$.

Charge–discharge tests were performed galvanostatically at a current rate of 1 C with cut-off voltages of 3.5–4.5 V (vs. Li/Li^+) at room temperature. All electrochemical experiments were performed using a multi-channel battery tester (PAR, Versa STAT MC Multichannel Potentiostat /Galvanostat). All processes of assembling and dismantling the cells were carried out in an argon-filled dry glove box.

3. Results and discussion

The composition of the synthesized samples was obtained through the ICP-MS analysis. As shown in table 1, it was found that the data were close to what we were expecting for the targeted formula. The structures of all these samples were characterized using XRD. The XRD patterns of the as-prepared samples, namely, undoped spinel (LiMn_2O_4), LBS-coated LiMn_2O_4 , doped spinel ($\text{LiMn}_{1.9}\text{Co}_{0.025}\text{Cr}_{0.025}\text{Ni}_{0.025}\text{Fe}_{0.025}\text{O}_4$) and LBS-coated

Table 2. The cubic lattice parameters for LiMn_2O_4 and doped and LBS-coated samples.

Compounds	Lattice parameter ($\text{\AA}$)
Bare LiMn_2O_4	8.239(2)
LBS-coated LiMn_2O_4	8.234(2)
$\text{LiMn}_{1.9}\text{Co}_{0.025}\text{Cr}_{0.025}\text{Ni}_{0.025}\text{Fe}_{0.025}\text{O}_4$	8.237(2)
LBS-coated $\text{LiMn}_{1.9}\text{Co}_{0.025}\text{Cr}_{0.025}\text{Ni}_{0.025}\text{Fe}_{0.025}\text{O}_4$	8.234(2)

Figure 2. (a) Thermal gravimetric curve of LBS precursor powder as the coating medium obtained from evaporation of solution.³⁹ (b) Thermal gravimetric curve of LBS precursor mixed cathode powders.

$\text{LiMn}_{1.9}\text{Co}_{0.025}\text{Cr}_{0.025}\text{Ni}_{0.025}\text{Fe}_{0.025}\text{O}_4$ spinel are shown in figure 1a–d, respectively. It is obvious that the diffraction patterns of the four samples are characteristic of the spinel crystal structure, in which lithium ions occupy the $16a$ positions of the tetrahedra, manganese ions (Mn^{3+} and Mn^{4+}) occupy the $16d$ positions of the octahedra and oxygen ions occupy the $32e$ positions, the vertices of the tetrahedra and octahedra. The same diffractions of spinel structure for the samples with and without doping indicate that the doped chromium, cobalt, iron and nickel has inserted the lattice of $16d$ positions to replace manganese. The crystal lattice constants of all samples, as listed in table 2, clearly reveal that the values remain nearly unchanged with doping and coating. The ionic radius of six coordinate Mn^{4+} is $0.530 \text{ \AA}$, but the ionic radius of six coordinate Mn^{3+} is $0.645 \text{ \AA}$, while the ionic radii of sixth coordinate Cr^{3+} , Fe^{3+} , Co^{3+} and Ni^{2+} are 0.615 , 0.645 , 0.610 and $0.690 \text{ \AA}$, respectively.⁴³ Because the average of the ionic radius of these cations is approximately equal to the Mn^{3+} cation, the calculated lattice parameter of the substituted spinel was not different from the undoped spinel LiMn_2O_4 . In addition, almost no change in the lattice parameter for uncoated and coated samples existed suggesting that the LBS coating medium was not incorporated into the spinel

structure but only presented on the surface of LiMn_2O_4 , since Li^+ , B^{3+} and Si^{4+} introduction into the spinel structure leads to significant change in the lattice parameter. If Li^+ , B^{3+} and Si^{4+} ions were substituted for Mn^{3+} ions in the crystal lattice, the lattice parameter of the substituted spinel would be smaller than that of the undoped spinel LiMn_2O_4 . This is due to the smaller size of Li^+ ($0.59 \text{ \AA}$), B^{3+} ($0.27 \text{ \AA}$) and Si^{4+} ($0.40 \text{ \AA}$) as compared with the larger Mn^{3+} ($0.645 \text{ \AA}$).⁴⁴

To determine the possible chemical composition of the coating layer, a thermal gravimetric examination of the precursor powder of the coating material, obtained from the evaporation of the LBS xerogel solution, was carried out and the results can be seen in figure 2. The precursor obviously displays three important weight losses. The initial sharper endothermic peak occurred from 50 to 120°C , attributed to the adsorbed water. The second, endothermic peak appeared at $150\text{--}300^\circ\text{C}$. This peak was attributed to the thermal decomposition of nitrates. Finally, the third endothermic peak occurred between 350 and 500°C . This last stage weight loss was due to thermal decomposition of organic species. Later, only a small amount of weight was lost, and the TG curve became smooth and flat, indicating that a stable complex had formed above 500°C . Actual weight ratio of LBS

Figure 3. SEM images of (a) the uncoated LiMn_2O_4 , (b) LBS-coated LiMn_2O_4 , (c) $\text{LiMn}_{1.9}\text{Co}_{0.025}\text{Cr}_{0.025}\text{Ni}_{0.025}\text{Fe}_{0.025}\text{O}_4$ and (d) LBS-coated $\text{LiMn}_{1.9}\text{Co}_{0.025}\text{Cr}_{0.025}\text{Ni}_{0.025}\text{Fe}_{0.025}\text{O}_4$.

Figure 4. AFM images obtained in height mode of cathode surface in air at $3\ \mu\text{m}$ scan sizes. Samples were obtained from (a) uncoated LiMn_2O_4 , (b) LBS-coated LiMn_2O_4 , (c) $\text{LiMn}_{1.9}\text{Co}_{0.025}\text{Cr}_{0.025}\text{Ni}_{0.025}\text{Fe}_{0.025}\text{O}_4$ and (d) LBS-coated $\text{LiMn}_{1.9}\text{Co}_{0.025}\text{Cr}_{0.025}\text{Ni}_{0.025}\text{Fe}_{0.025}\text{O}_4$ powder.

to pristine and doped LiMn_2O_4 samples were determined as a 1.9 wt%. As can be seen from figure 1a calcination of the precursor powder at 425°C for 5 h exhibited a mixture of amorphous–semicrystalline LBS. Therefore, it is believed that the spinels shown in figure 1 are coated with LBS.

According to the morphological investigation of the uncoated LiMn_2O_4 and $\text{LiMn}_{1.9}\text{Co}_{0.025}\text{Cr}_{0.025}\text{Ni}_{0.025}\text{Fe}_{0.025}\text{O}_4$ the particles are smooth, as shown in figure 3a and c, but as shown in figure 3b and d, they become rough and aggregated after coating with LBS. Figure 4 shows the AFM images obtained in tapping mode of the cathode surface in air. Samples were obtained from uncoated and LBS-coated LiMn_2O_4 , $\text{LiMn}_{1.9}\text{Co}_{0.025}\text{Cr}_{0.025}\text{Ni}_{0.025}\text{Fe}_{0.025}\text{O}_4$ particles. As shown in figure 5, the surface of the cathodes appears smooth and homogeneous. However the particles of LBS-coated cathodes were more aggregated than the uncoated ones.

Figure 5 shows the charge–discharge curves of LiMn_2O_4 , $\text{LiMn}_{1.9}\text{Co}_{0.025}\text{Cr}_{0.025}\text{Ni}_{0.025}\text{Fe}_{0.025}\text{O}_4$, LBS-coated LiMn_2O_4 and LBS-coated $\text{LiMn}_{1.9}\text{Co}_{0.025}\text{Cr}_{0.025}\text{Ni}_{0.025}\text{Fe}_{0.025}\text{O}_4$ cathode materials at the 1 C rate in the voltage range of 3.5–4.5 V at room temperature, respectively. It can be seen that

they have similar charge–discharge profiles, exhibiting two pseudoplateaus at around 3.9 and 4.1 V, which represents the typical electrochemical behavior of spinel LiMn_2O_4 .⁴⁵ It means that Cr, Co, Fe and Ni multi-doping did not change the intrinsic charge–discharge behaviour of LiMn_2O_4 . The initial discharge capacities of the uncoated LiMn_2O_4 and doped samples are about 114.7 and 105.6 mAh g^{-1} , respectively. The initial discharge capacities of doped LiMn_2O_4 decreases because of a decrease in the amount of extractable Li^+ ion in the spinel. For $\text{LiMn}_{1.9}\text{Co}_{0.025}\text{Cr}_{0.025}\text{Ni}_{0.025}\text{Fe}_{0.025}\text{O}_4$, all doped cations replaced the place occupied originally by Mn^{3+} and the amount of Mn^{3+} in the spinel was reduced by the increasing amount of doped cations. Since Co^{3+} , Cr^{3+} , Ni^{2+} and Fe^{3+} ions cannot be oxidized in this potential range, the amount of removable Li^+ is determined by the amount of Mn^{3+} .⁴⁶ Briefly, the initial capacity can be estimated for the compound $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ by the following formula: $C=148(1-(4-Z)X)$,¹³ where Z is the valance of the doped ion and X the molar fraction of the dopant. Apparently, for the same doping level, M^{3+} shows much higher initial capacity. Therefore, in the following studies,

Figure 5. Continuous charge–discharge curves during 70 cycles: (a) the uncoated LiMn_2O_4 and (b) LBS-coated LiMn_2O_4 , (c) $\text{LiMn}_{1.9}\text{Co}_{0.025}\text{Cr}_{0.025}\text{Ni}_{0.025}\text{Fe}_{0.025}\text{O}_4$ and (d) LBS-coated $\text{LiMn}_{1.9}\text{Co}_{0.025}\text{Cr}_{0.025}\text{Ni}_{0.025}\text{Fe}_{0.025}\text{O}_4$. The applied current density is 148 mA g^{-1} (1 C-rate) at room temperature. Li metal was used as the anode.

theoretical capacity of $\text{LiMn}_{1.9}\text{Co}_{0.025}\text{Cr}_{0.025}\text{Ni}_{0.025}\text{Fe}_{0.025}\text{O}_4$ cathode material was calculated as 129.5 mAh g^{-1} .

It can be seen from figure 5c and d that the modification of LiMn_2O_4 and $\text{LiMn}_{1.9}\text{Co}_{0.025}\text{Cr}_{0.025}\text{Ni}_{0.025}\text{Fe}_{0.025}\text{O}_4$ with LBS does not change their charge and discharge characterization: two potential platforms for the lithium ion intercalation or de-intercalation into or from the spinel, for Li_xMnO_4 $0 \leq x \leq 0.5$ and $0.5 < x \leq 1$, respectively. It is found that there is a small loss in the charge or discharge capacity of the treated samples compared with the untreated samples, the discharge capacity is 102.3 and 105.6 mAh g^{-1} , respectively. This can be explained by the fact that the LBS layer forms a barrier to the movement of Li ions, which impedes the extraction and insertion of Li ions from the spinel resulting in the low initial specific capacity of the cathode.⁴⁷

CV measurements were carried out to further clarify the origin of multiple doping with Cr, Co, Fe and Ni and LBS coating did not change the intrinsic charge–discharge

behaviour of coated LiMn_2O_4 . Figure 6 shows the CV profiles of the pristine, multidoped and LBS-coated LiMn_2O_4 samples between 3.5 and 4.45 V with a scan rate of 0.1 mV s^{-1} . It can be clearly observed that all products display two pairs of redox peaks between 3.8 and 4.3 V , indicating Li^+ are extracted and inserted into spinel LiMn_2O_4 by a two-step process. These results are strongly consistent with the first charge–discharge capacity curves, corresponding to two charge–discharge plateaus in the potential region of 3.9 – 4.1 V .

Figure 7 shows the result of discharge cycling at 1 C rate between 3.5 and 4.5 V for LiMn_2O_4 , $\text{LiMn}_{1.9}\text{Co}_{0.025}\text{Cr}_{0.025}\text{Ni}_{0.025}\text{Fe}_{0.025}\text{O}_4$, LBS-coated LiMn_2O_4 and LBS-coated $\text{LiMn}_{1.9}\text{Co}_{0.025}\text{Cr}_{0.025}\text{Ni}_{0.025}\text{Fe}_{0.025}\text{O}_4$ carried out at room temperature. The discharge capacities and percentage of capacity fading rate of all cathode materials as a function of cycle numbers are shown in table 3. It should be noted that there is a significant difference in the discharge capacity vs. cycle numbers between these samples

Figure 6. Cyclic voltammetry (CV) curves of (a) the pristine LiMn_2O_4 and $\text{LiMn}_{1.9}\text{Co}_{0.025}\text{Cr}_{0.025}\text{Ni}_{0.025}\text{Fe}_{0.025}\text{O}_4$ and (b) LBS-coated LiMn_2O_4 and $\text{LiMn}_{1.9}\text{Co}_{0.025}\text{Cr}_{0.025}\text{Ni}_{0.025}\text{Fe}_{0.025}\text{O}_4$ at a scan rate of 0.1 mV s^{-1} .

(figure 7). The percentage of discharge capacity fading rate of the undoped spinel sample abruptly declines to 25.4% at the 70th cycle at 1 C. For the doped sample, the discharge capacity fading ratio (16.1%) is smaller than that of the undoped one over 70 cycles at the same C-rate. By contrast, the initial capacity of the undoped sample is higher than that of the doped sample which can be attributed to the small variations of manganese amount in the lattice frame. As expected, the doped spinel displays good cycle performance in terms of discharge capacity and cycle-life. The good cyclability is probably due to the substitution of some Mn–O linkages in the spinel by $M\text{--O}$ (M : Co, Cr, Ni and Fe). The doped Co^{3+} , Cr^{3+} , Ni^{2+} and Fe^{3+} cations enhance the stability of the octahedral sites in the spinel skeleton structure.⁴⁸ As for the LBS-coated cathode materials, in the same conditions, the initial discharge capacity of LBS-coated LiMn_2O_4 declined from 102.3 to 91 mAh g^{-1} with a capacity fading ratio of 11% after 70 cycles. However,

Figure 7. Cycling performance of all cathode materials at current level of 1 C (148 mAh g^{-1}) in the voltage range of 3.5–4.5 V at room temperature.

LBS-coated $\text{LiMn}_{1.9}\text{Co}_{0.025}\text{Cr}_{0.025}\text{Ni}_{0.025}\text{Fe}_{0.025}\text{O}_4$ assures an initial discharge capacity of 105.6 mAh g^{-1} and remains at 96.6 mAh g^{-1} after 70 cycles, with a capacity fading ratio of 8.5%. Electrochemical charge–discharge test results showed that the electrochemical cycling performance of LiMn_2O_4 enhanced with multication (Co, Cr, Ni and Fe) doping. However, the LBS-coated and multication-doped LiMn_2O_4 had the better cycling performance than the others. The LBS coating protected the spinel from electrolyte degradation. As we know,^{12–14,49,50} capacity loss caused by the dissolution of manganese accounted for 23% of overall capacity loss at room temperature. HF, generated during cycling when using LiPF_6 -based electrolyte, was responsible for the dissolution of manganese. In fact, preparation of H_2O -free electrolyte containing LiPF_6 in organic solvent is difficult. A small amount of water (though the amount is less than 20 p.p.m) facilitates the decomposition of electrolytic salt, LiPF_6 . Thus, HF is formed as a by-product by the following reaction:

HF contamination drastically increases the dissolution of manganese cations through the disproportionation of Mn^{3+} , as reported by Jang *et al*⁴⁹

Therefore the contact of the cathode with electrolyte would result in the dissolution of the cathode and do great harm to its performance. As we obtained in our previous study,³⁹ the LBS coating prevented direct contact between the spinel and the electrolyte and therefore reduced the dissolution of manganese and the oxidation of electrolyte. These results indicate that Jahn–Teller distortion and the reaction of Mn dissolution in the cathode material were suppressed *via* the synergetic effect of multication doping and LBS coating.

Table 3. Discharge capacity performance of bare LiMn₂O₄ and surface-treated LiMn₂O₄ cells^a.

Cathode material	1st	10th	30th	50th	70th	Capacity loss (%)
LiMn ₂ O ₄	114.7	101.1	92.9	88.8	85.5	25.4
LiMn _{1.9} Co _{0.025} Cr _{0.025} Ni _{0.025} Fe _{0.025} O ₄	105.6	99.1	98.6	94.5	85.5	16.1
LBS-coated LiMn ₂ O ₄	102.3	101.5	97.0	93.7	91.0	11.0
LBS-coated LiMn _{1.9} Co _{0.025} Cr _{0.025} Ni _{0.025} Fe _{0.025} O ₄	105.6	103.1	99.5	97.8	96.6	8.50

^aLoss of discharge capacity at the last cycle is compared with that at maximum discharge capacity.

4. Conclusions

New Co-, Cr-, Ni- and Fe-substituted compounds were synthesized by using the glycine-nitrate combustion method and coated with LBS via the solution method. The effects of doping and coating on the electrochemical properties of LiMn₂O₄ were studied using electrochemical charge-discharge tests and XRD, SEM, AFM and ICP-MS methods. The XRD pattern for Co-, Cr-, Ni- and Fe-doped and LBS-coated spinel did not show any change in the 2θ value of the peaks and no impurities were detected. The similar lattice parameters of the coated and uncoated samples indicated that the LBS layer only coated the surface rather than diffusing into the crystal. Compared with the uncoated LiMn₂O₄ and LiMn_{1.9}Co_{0.025}Cr_{0.025}Ni_{0.025}Fe_{0.025}O₄, on line the LBS-coated LiMn_{1.9}Co_{0.025}Cr_{0.025}Ni_{0.025}Fe_{0.025}O₄ sample exhibited an improved cycling stability at room temperature compared with the undoped and doped one. The capacity losses in the first 70 cycles between 3.5 and 4.5 V decrease significantly from 25.4%, 16.1% and 11% for uncoated LiMn₂O₄, LiMn_{1.9}Co_{0.025}Cr_{0.025}Ni_{0.025}Fe_{0.025}O₄ and LBS-coated LiMn₂O₄, respectively. The LBS-coated LiMn_{1.9}Co_{0.025}Cr_{0.025}Ni_{0.025}Fe_{0.025}O₄ showed 8.5% capacity loss of the initial discharge capacity. The results suggested that the as-prepared LBS-coated LiMn_{1.9}Co_{0.025}Cr_{0.025}Ni_{0.025}Fe_{0.025}O₄ could be a promising cathode material for lithium ion batteries.

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