

Electrochemical performance and cyclability of $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ as a 5 V cathode material for lithium batteries

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Abstract

Electrochemical behavior of a thin film of $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel deposited on a Pt substrate electrode in nonaqueous medium of LiBF_4 in ethylene carbonate/dimethyl carbonate (EC/DMC) solution was investigated using cyclic voltammetric technique. In addition, the chemical diffusion coefficients of Li^+ at different states of charge (different electrode potentials) in the system under investigation were estimated using chronoamperometric technique. The charge/discharge characterization of the lithium secondary cell employing this 5 V cathode material shows an acceptable electrochemical performance with high-voltage and specific capacity. The disadvantage of the material was related to significant capacity fades at elevated temperature. It was demonstrated that the capacity fading in this electrolyte solution is significantly lesser than common electrolyte solutions, e.g. LiPF_6 . In addition, an approach viz. surface modification of the spinel with aluminum oxide was utilized to reduce the capacity fade at elevated temperatures. The sources for the appearance of such capacity fades appearing at both 4 and 5 V performance of the cathode material were discussed.

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Keywords: Lithium battery; Cathode material; $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$; LiBF_4 ; Cyclability; Capacity fade; Al_2O_3 coating

1. Introduction

Among three main candidate materials (LiCoO_2 , LiNiO_2 and LiMn_2O_4) for cathodes of lithium secondary batteries, there is a great attention to LiMn_2O_4 , due to its lower cost and nontoxicity of Mn in comparison with Co and Ni. However, there are some serious problems, which should be overcome, before commercialization of LiMn_2O_4 as a cathode material. The main obstacle in this context is the significant capacity fades of LiMn_2O_4 at elevated temperature, which is mainly related to Mn dissolution. Due to the noticeable advantages of LiMn_2O_4 as a cathode material, considerable efforts have been paid to this subject. It has been reported that substituting manganese ions with monovalent lithium ions ($\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$) [1] or by other metal cations, such as Ni [2], Co [3], Cr [4], Cu [5] and Fe [6] can significantly improve cyclability of LiMn_2O_4 at elevated temperatures.

Interestingly, it has been found that this approach is also accompanied by a higher voltage plateau at about 5 V as a result of the redox system provided by the transition metal substituted. The possibility for the fabrication of 5 V

rechargeable batteries is very desirable and is the subject of a numerous researches to achieve an acceptable situation, as there are some problems to be solved. The lack of sufficient knowledge is due to novelty of this type of cathode materials, as they (as 5 V cathode materials) have just been introduced a few years ago [4]. Thus, studies of their electrochemical properties are now an active area of research.

The most of investigations in this context is related to $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [7–15]. Although, this material has excellent properties for the preparation of 5 V cathodes, the problem of toxicity of Ni is problematic, similar to LiNiO_2 . In the present research, we examine $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ as an excellent cathode material due to its lower cost and lesser toxicity in comparison with the similar materials ($\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$; M: substituted transition metal). $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was first introduced as a 5 V cathode material by Kawai et al. [6]. Shigemura et al. [16] have studied this material with spectroscopic techniques in detail.

Another important problem about this class of cathode materials, which is not usually addressed in the literature, is their significant capacity fades at elevated temperatures. Although, substituting Mn ions in LiMn_2O_4 with transition metal ions can improve cyclability of $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ as a 4 V cathode material, the problem of capacity fading is still strong when such materials are used in 5 V cathodes. Sun

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et al. [12–14] have recently paid attention to the capacity fading of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at elevated temperatures.

2. Experimental

$\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel was synthesized based on a solid-state reaction according to Shigemura et al. [16]. Briefly, a stoichiometric mixture of MnCO_3 , FeOOH and $\text{LiOH}\cdot\text{H}_2\text{O}$ was heated at 650°C for 12 h to drive off CO_2 and then pressed into a pellet and heated at 750°C for 72 h followed by an additional annealing at 550°C for 72 h. Finally, the sample was cooled slowly to room temperature in 24 h. Similar procedure was employed to synthesize $\text{LiFe}_x\text{Mn}_{2-x}\text{O}_4$ (where $x = 0.1, 0.3$ and 0.5). To fabricate thin-film cathodes, the spinel was deposited onto an Al current collector at room temperature by a RF power 100 W under an Ar atmosphere with 1.4 Pa pressure using a conventional RF magnetron sputtering system. The amount of the spinel attached to the substrate surface was determined by weighting the electrode before and after sputtering. Similar to other transition metal-substituted LiMn_2O_4 spinels, sputtering deposition process has no significant effect on the structure of $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel. All electrochemical measurements were performed using thin-film cathodes prepared in accordance with the above-mentioned procedure.

A nonaqueous solution of 1 M LiBF_4 in 3:7 ethylene carbonate/dimethyl carbonate (EC/DMC) was used as the electrolyte solution of the secondary cell. Some experiments were performed using 1 M LiPF_6 in 3:7 EC/DMC for the investigation of the electrolyte effects. All chemicals including EC and DMC were of analytical grade. A lithium foil was employed as both counter (anode) and reference electrodes. In galvanostatic experiments, the cell was charged and discharged at $C/10$ rate ($C = 1 \text{ Li mol}^{-1} \text{ h}^{-1}$). The electrochemical measurements were performed using a homemade potentiostat connected to a computer running CorrView software.

3. Results and discussion

The spinel was prepared according to the method proposed by Shigemura et al. [16], thus the XRD pattern of the spinel was similar to that reported previously [16]. As electrochemical properties of high-voltage cathode materials based on composite electrodes cannot be well investigated due to the existence of organic polymeric binders and high surface area carbons, it is of interest to prepare thin film-based cathodes to investigate the intrinsic properties of the active material due to their well-defined geometries of pure active electrode materials. Indeed, this failure (i.e. lack of appropriate investigations of thin film-based high-voltage cathode materials) is applicable for all metal-substituted LiMn_2O_4 spinels, as the preliminary investigations of this class of high-voltage materials are just related to compos-

ite electrodes. More recently, Mohamedi et al. [15] have investigated the electrochemical properties of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ thin-film electrode. Due to the lack of appropriate reports on the electrochemical properties of $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$, we first attempt to investigate the electrochemical behavior of a thin-film of $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel deposited on the substrate surface in nonaqueous medium.

Fig. 1 shows a typical cyclic voltammogram of the $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ film electrode recorded in the potential range 3.0–5.3 V versus Li/Li^+ . The material presents a well-defined cyclic voltammetric behavior displaying a redox couple at high-voltage region (about 4.9 V versus Li/Li^+). The reason for the occurrence of such high-voltage pair of peaks has been proposed in [16]. It can be attributed to the oxidation of trivalent Fe ions incorporated into the spinel to replace 25% of Mn in LiMn_2O_4 . There is also a weaker redox couple appeared at about 4.1 V versus Li/Li^+ as the result of $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox system. The curve shows that the high-voltage redox couple of $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ occurs at about 0.1 V higher than $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [15]. In addition, the high-voltage redox system appeared as a single couple, whereas $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ may display two redox couples as the result of two-step Ni^{2+} oxidation to Ni^{4+} ($\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Ni}^{3+}/\text{Ni}^{4+}$ redox systems) [15].

The curve indicates that deintercalation process during charge occurred as the result of the oxidation of both trivalent ions (Mn and Fe), as judged from similar anodic peaks. Whereas, the intercalation process during discharging is mainly due to the reduction of high-valent Fe, which is accompanied by a strong cathodic peak at 4.9 V in comparison with the other cathodic peak appearing at 4.1 V. This means that the most of Li^+ is intercalated during the Fe reduction process at the second redox system.

A problem of LiMn_2O_4 cathodes is low rate capability due to slow diffusion of Li^+ . Thus, it is appropriate to determine the chemical diffusion coefficient of Li^+ for the high-voltage cathode material to verify its applicability for battery applications. The importance of diffusion coefficient is related to the fact that the kinetics of a solid-state diffusion system limit the total reaction. Chronoamperometry is an applicable technique for the determination of the chemical diffusion coefficient of Li ions in lithium battery media. It has been described [17,18] that for the time domain of $t \gg h^2/\pi^2 D_{\text{app}}$, the time-dependency of the current is expressed as

$$\ln(i) = \ln\left(\frac{2nFAD \Delta C}{h}\right) - \left(\frac{\pi^2 D_{\text{app}}}{4h^2}\right)t \quad (1)$$

where h and A are the thickness and the surface area of the electroactive film, and ΔC is the variation of lithium concentration in the film during the potential step applied. Thus, two different approaches can be employed to estimate the value of the chemical diffusion coefficient based on the first and second terms of Eq. (1). As measuring the precise value of ΔC is difficult, the approach using the second sentence

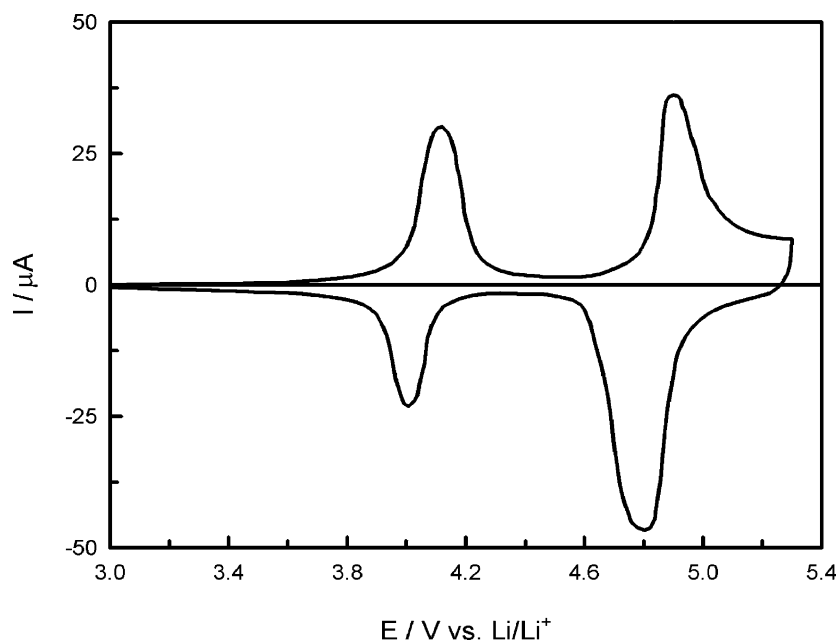


Fig. 1. Typical cyclic voltammogram of the $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ film electrode in a nonaqueous solution of LiBF_4 . Scan rate 0.1 mV s^{-1} .

is more suitable. This approach has been used for LiMn_2O_4 [19,20]. Thus, the chronoamperometric curve (Fig. 2a) was transformed to a semi-logarithmic plot (Fig. 2b). By performing such chronoamperometric measurements at different applied potentials, the chemical diffusion coefficient of the system at different electrode potentials across the electrochemical redox couples, can be estimated. The data obtained from such experiments are illustrated in Fig. 3. As expected, the curve exhibit minima at the potential regions of the peaks observed in the CV. Interestingly, the values estimated for the chemical diffusion coefficients of the system under investigation were located in the range 10^{-10} to $10^{-12} \text{ cm}^2 \text{ s}^{-1}$. This is satisfactory for the lithium battery performance, as the values are comparable with other cathode materials. Consequently, it can be concluded that $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ does not suffer from slow diffusion to Li^+ , that would result in weak rate capability.

Preliminary electrochemical studies of the system under investigation indicate excellent electrochemical properties of the $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel as a 5 V cathode material. To investigate the battery performance of this cathode material, charge/discharge characteristic of a lithium battery employing $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel was examined as a 5 V secondary cell (Fig. 4). As expected from the cyclic voltammetric results, the charge/discharge characteristic is accompanied by two different plateaus appearing at about 4.1 and 4.9 V versus Li/Li^+ . The results provide another evidence for excellent battery performance of the 5 V cathode material. In addition, it is observable that thin-film $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ can be used as well as composite spinel (in comparison with the results reported in [16]). This may come from the fact that thin-film spinel electrodes have rough structures with high fractal dimensions [21]. On the other hand, it

is known that nanostructured spinels provide better 5 V performance. This was the reason to use carbon black additives to spinel composites to act as temporal dispersing agent to yield a finely dispersed solid. The variation of the coulombic efficiency of the cathode during cycling shows that like LiMn_2O_4 -based cathode materials, the coulombic efficiency increases to reach a limitation values (Fig. 5). Moreover, the results indicates a sufficiently high value for the coulombic efficiency of the first cycle.

Let recall that the main problem of LiMn_2O_4 as a (4 V) cathode material for lithium batteries is its weak cyclability at elevated temperatures displaying significant capacity fades. Thus, it is also necessary to inspect this problem for the 5 V cathode materials prepared by Fe substituting in LiMn_2O_4 spinel. The data presented in Fig. 6 shows that in LiPF_6 nonaqueous medium, which is the common electrolyte solution of lithium batteries (widely employed in commercial batteries), the battery designed loses about 50% of its capacity after 50 cycles at 55°C . Whereas, employing the electrolyte solution used in this research (LiBF_4) significantly improves the cyclability of lithium battery.

The results suggest that LiBF_4 is an excellent electrolyte with sufficient stability for 5 V cathode materials to reduce their capacity fading at elevated temperatures. It can be concluded from the results obtained from electrochemical performance of $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ in LiPF_6 electrolyte with those reported in the literature for $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_4$ in the same electrolyte that $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ has a better cyclability in comparison with $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Although, reporting such improvement is satisfactory from an applied research point of view, further investigations on the source of such capacity fade are needed to clarify the problem. It should be emphasized that it cannot be claimed that using LiBF_4

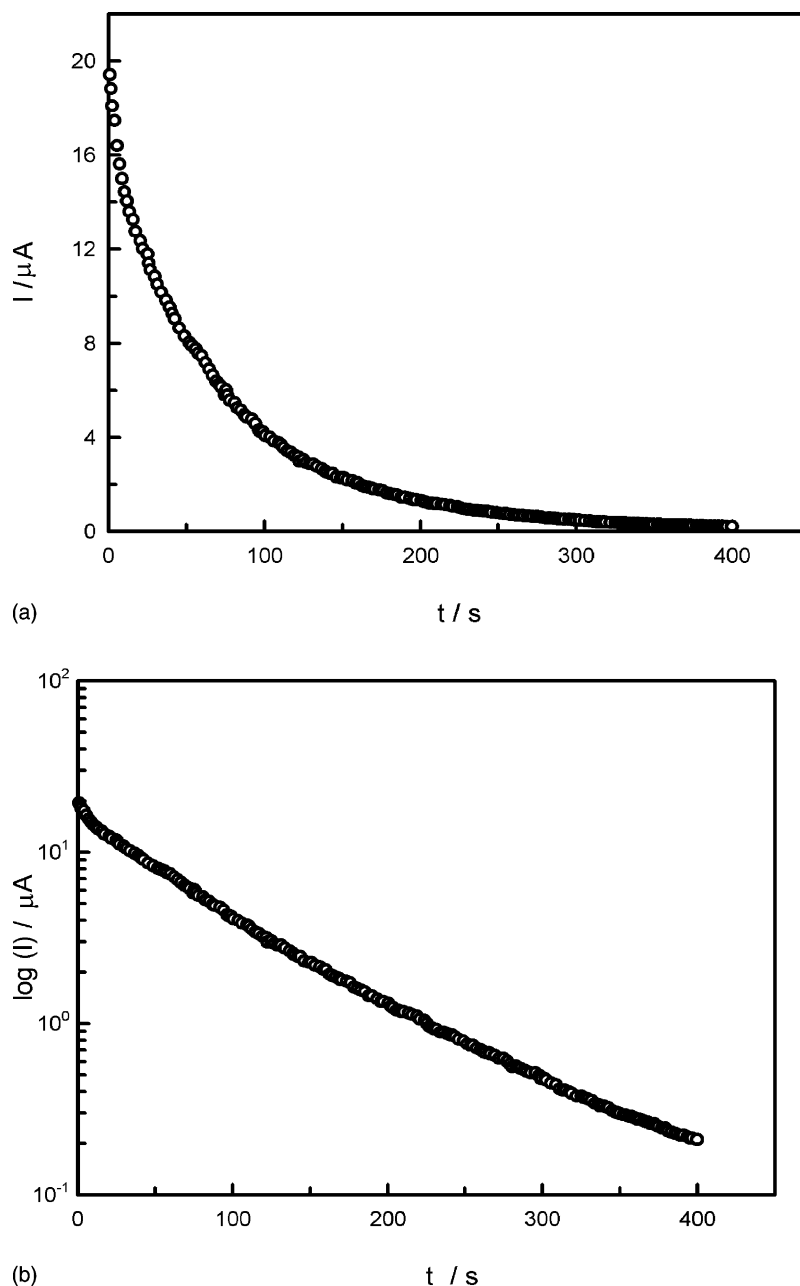


Fig. 2. (a) Chronoamperogram of the film electrode recorded at 4.0 V by a potential stepping from 3.95 V and (b) semi-logarithmic plot of the chronoamperogram employed for the determination of the chemical diffusion coefficient.

could completely satisfy the problem related to instability of electrolyte solution at high-voltage operation, however, the results suggest LiBF_4 as a promising alternative to LiPF_6 .

It is known that the main reason for the appearance of capacity fades in LiMn_2O_4 particularly at elevated temperatures is due to Mn dissolution. Sun et al. [12] have assumed that this is also the main reason for capacity fading of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel as a 5 V cathode material at elevated temperatures. Based on numerous studies of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel as a 5 V cathode material, it has been understood that the plateau appearing at about 4.8 V is related to $\text{Ni}^{2+}/\text{Ni}^{4+}$ redox. Indeed, the formal charges of Ni

and Mn in $\text{LiNi}_{0.5}\text{Mn}_{1.5}$ are +2 and +4, respectively. As the Mn dissolution of LiMn_2O_4 is referred to the disproportionation reaction: 2Mn^{3+} (insoluble) \rightarrow Mn^{4+} (insoluble) + MnO (soluble) [22], the Mn dissolution does not seem to be the main reason for capacity fading of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel, due to the absence of Mn^{3+} .

However, $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is different from $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Based on Mössbauer spectroscopic measurements, it has been reported that Fe in $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is trivalent [16]. The first plateau appearing at 4.1 V is related to the oxidation of available trivalent Mn to tetravalent Mn and the second plateau at 4.9 V is due to the oxidation of trivalent Fe.

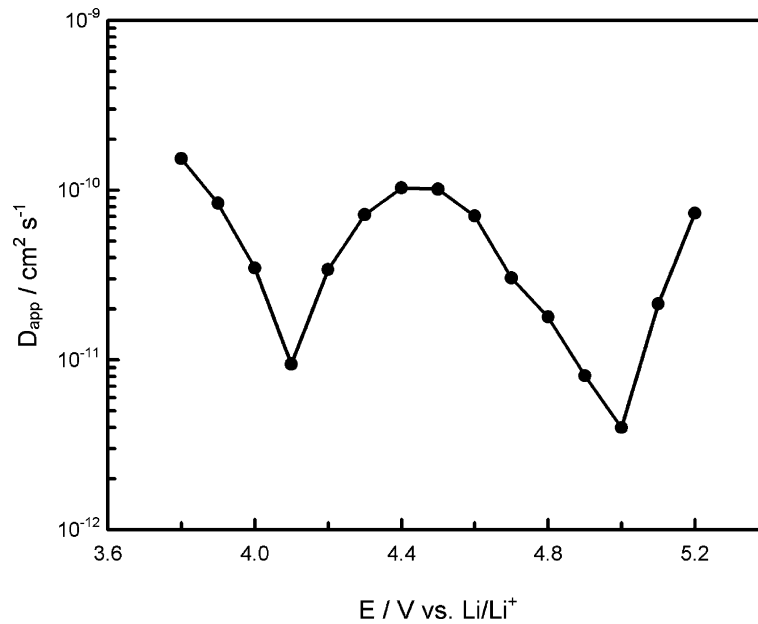


Fig. 3. Dependence of the chemical diffusion coefficient on the electrode potential.

Shigemura et al. [16] have concluded this mechanism from the existence of mixed valency state of $\text{Fe}^{+3.5}$, also reported previously [23]. As they have proposed this mechanism based on detailed spectroscopic studies and also the electrochemical behavior of the spinel (appearing two plateaus) confirm this mechanism, it seems to be correct. Based on this mechanism, Mn dissolution is possible due to the existence of trivalent Mn. As all of Mn in the spinel is oxidized to tetravalent Mn at the 4.1 V redox system, Mn dissolution-based capacity fading should be related to charging/discharging during 4 V performance.

Fig. 7 shows cyclability data obtained from charge/discharge profiles of the $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel as a 4 V cathode material, where cycled between 3.0 and 4.4 V. In this voltage range, the spinel acts as a 4 V cathode material similar to LiMn_2O_4 , but with 1.5 ions of Mn instead of 2 ions (0.5 Fe^{3+} is not active at this potential range). As seen, the capacity fade appeared in this potential range is significant, which can be attributed to the Mn dissolution. It can be understood by comparison of the results obtained for two different electrolyte solutions. It is known that Mn dissolution is lesser in LiBF_4 in comparison with LiPF_6 [24]. As

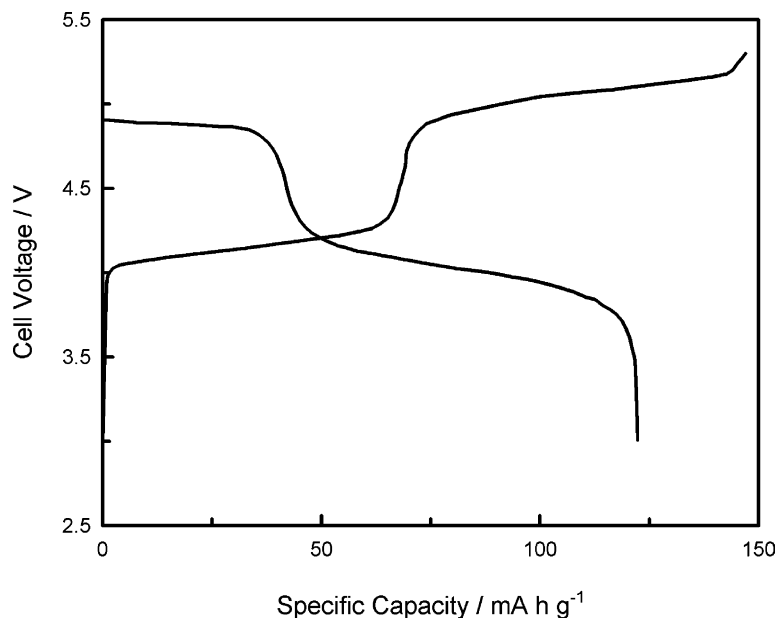


Fig. 4. Charge/discharge characteristic of $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ as a 5 V cathode material investigated in the potential range 3.0–5.3 V vs. Li/Li^+ with the rate of 0.1 mA cm^{-2} .

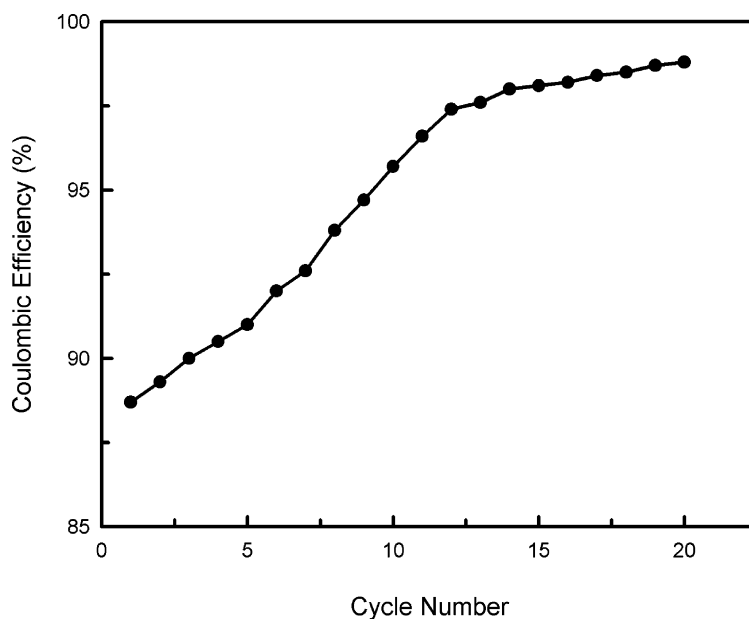


Fig. 5. Coulombic efficiency of the cathode upon cycling.

reported by Mohamedi et al. [24], the capacity fading of LiMn_2O_4 (which is mainly due to Mn dissolution) in LiBF_4 and LiPF_6 electrolyte solutions after 36 cycles at 60°C is 10 and 50%, respectively.

It can be understood from the cyclability data that the weak cyclability observed in Fig. 5 is not only related to the capacity fade at 3.0–4.4 V potential range as the result of Mn dissolution. Another significant capacity fading occurs at higher potentials, where the total Mn content of the spinel is tetravalent. Thus, Mn dissolution is not responsible for this capacity fading. Other reasons, such as Jahn–Teller

distortion is also inappropriate due to the absence of any trivalent Mn.

Thus, this problem should be related to the electrolyte instability at such high-voltage. The influence of electrolyte decomposition on capacity fading of LiMn_2O_4 has also been reported [25]. However, such effect is not very strong as observed for $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$. In a trial to solve this problem, we increased the amount of the electrolyte solution, although, it is not of practical interest. However, this action did not result in any improvement, thus indicating that the electrolyte decomposition is not responsible for the capacity

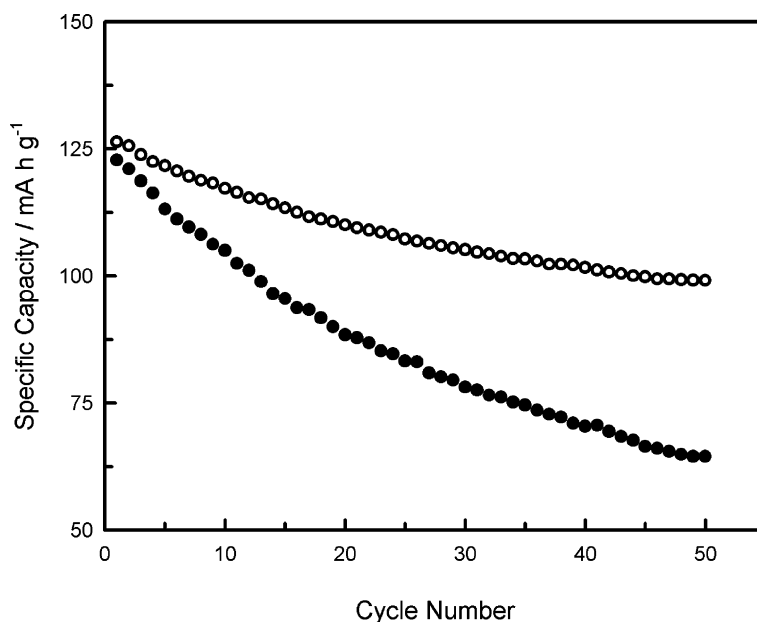


Fig. 6. Cyclability of the $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ film electrode in nonaqueous medium containing LiBF_4 (○) or LiPF_6 (●). $T = 55^\circ\text{C}$.

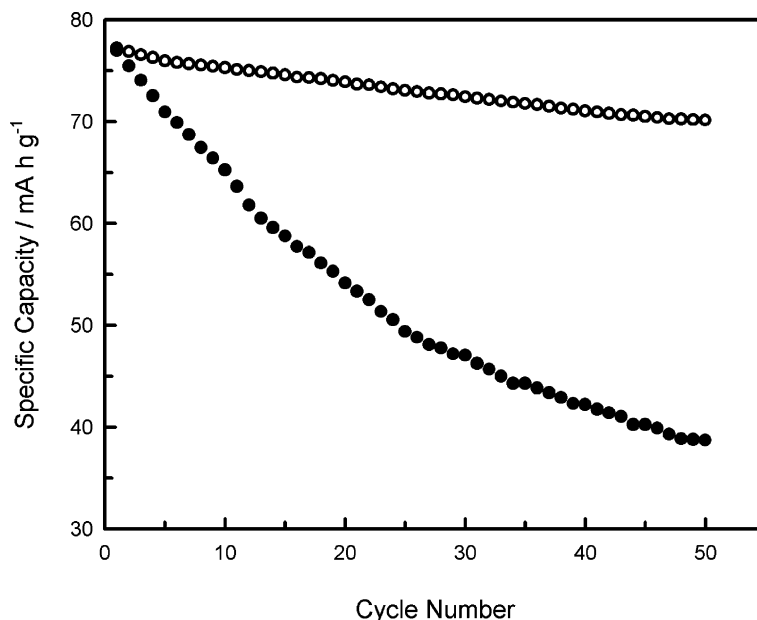


Fig. 7. Cyclability data of the $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ film electrode obtained from charging/discharging in the potential region 3.0–4.4 V in the electrolyte solutions containing LiBF_4 (○) or LiPF_6 (●) at 55°C .

fading of the 5 V $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode. Therefore, it can be concluded that there is a process occurring at the electrolyte/electrode interface, which causes the appearance of such significant capacity fading at high voltages.

Surprisingly, in the final stage of the present research searching for a possible process occurring at the electrolyte/electrode interface, we found an interesting paper by Sun et al. [14] suggesting surface contamination as the result of electrolyte decomposition at the electrode surface during 5 V performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The formation of carbonaceous nanostructures on the electrode surface [14] recalls that decomposition of organic molecules, such as ethylene, CO_2 , etc. on metallic catalysts is a common method for the preparation of carbon nanofibers [26,27]. The most probable mechanism for the formation of such carbonaceous film is the direct reaction of organic materials from the nonaqueous medium with high-valent Fe generated at 5 V performance. Thus, this phenomenon should be dependent on the amount of high-valent Fe. If we assume that the formation of such carbonaceous films is just due to electrolyte instability, the effect should be observable in such high-voltage without dependency on the amount of Fe. On the other hand, the latter assumption seems to be inappropriate, as LiBF_4 is relatively stable at such high-voltage (as can be judged from Fig. 1).

To examine this hypothesis, the influence of the amount of Fe in $\text{LiFe}_x\text{Mn}_{2-x}\text{O}_4$ was investigated. Table 1 depicts cyclability data for $\text{LiFe}_x\text{Mn}_{2-x}\text{O}_4$ with different amounts of Fe ($x = 0.1, 0.3$ and 0.5). For lower amounts of Fe, the capacity fade appearing at 4 V is higher (due to larger amounts of trivalent Mn) accompanied by a lower capacity fading at 5 V performance. This provides a strong evi-

dence for the hypothesis proposed, indicating the direct role of high-valent Fe on the formation of such carbonaceous films. In other words, the 5 V operation of the cathode material cause the generation of high-valent Fe, which is the reason for the occurrence of a side reaction that decreases the cathode capacity. This means that 5 V operation alone is not responsible for the capacity fading at 5 V in the absence of high-valent Fe reactant at the electrolyte/electrode interface. Investigating the exact reaction occurring at the electrolyte/electrode interface and the nature of the carbonaceous film growth on the electrode surface is very useful, however is out of the aim of the present study as it needs a different strategy.

Table 1
Cyclability data obtained from charge/discharge characterization of $\text{LiFe}_x\text{Mn}_{2-x}\text{O}_4$ with different values of x at 55°C

	$x = 0.1$	$x = 0.3$	$x = 0.5$
Total charging/discharging			
Initial capacity (mA h g^{-1})	123.96	127.42	126.38
Capacity after 50 cycles	97.98	98.87	99.11
Capacity fading (%)	20.96	22.41	21.58
Charging/discharging between 3.0 and 4.4 V			
Initial capacity (mA h g^{-1})	108.67	93.27	77.21
Capacity after 50 cycles	89.36	80.92	70.14
Capacity fading (%)	17.77	13.24	9.10
Charging/discharging between 4 and 5.3 V			
Initial capacity (mA h g^{-1})	15.71	35.43	48.87
Capacity after 50 cycles	8.78	31.69	42.15
Capacity fading (%)	4.41	10.55	13.75

Note: the total capacity is not equal to the sum of subdivided capacities, as they are recorded during different experiments.

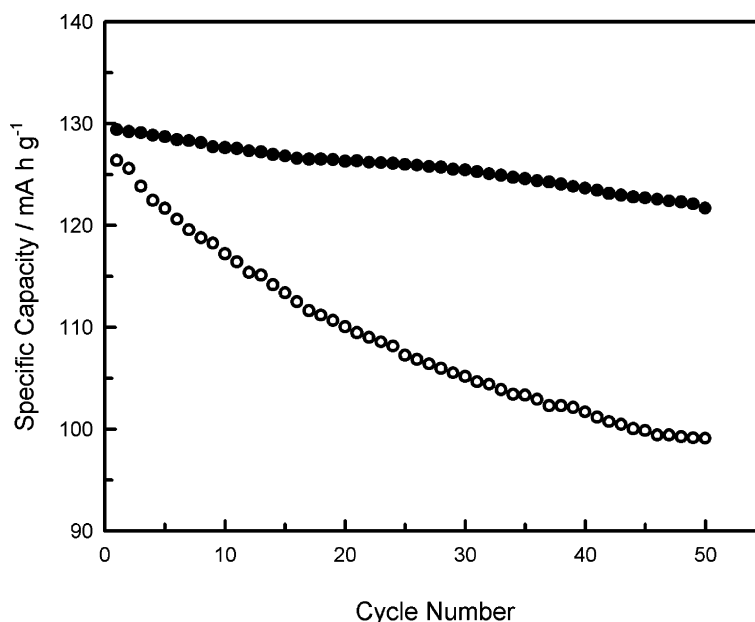


Fig. 8. Enhanced cyclability of the Al_2O_3 -coated $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ film electrode in the electrolyte solution containing LiBF_4 (●). The data related to uncoated $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ film electrode is also presented for comparison (○). $T = 55^\circ\text{C}$.

Sun et al. [16] have suggested that coating the spinel surface with ZnO hinders the formation of such carbonaceous film, but no reason was given for the observation of such improvement. Metal oxide coating of the spinel surface is an efficient approach to reduce capacity fades of LiMn_2O_4 by protecting the trivalent Mn ion against dissolution [28,29]. Due to its simplicity, this approach is considered as one of the best methods for the cyclability improvement of LiMn_2O_4 . It has also been reported that metal oxide coating can be performed during electrodeposition (via Au-codeposition method) of the spinel [30]. Here, we examine the usefulness of the metal oxide coating on the 5 V performance of the $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel. To this aim, a thin layer of aluminum oxide (ca. 10 nm) was deposited on the $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel by reactive sputtering of an Al target, and the resultant product was subject of heating at 300°C for 4 h. The amount of aluminum oxide added to the sample was about 2 wt.%.

Comparison of the uncoated and coated $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes (Fig. 8) indicates that metal oxide coating is also useful to reduce the capacity fade of $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel at high voltages. As stated before, Mn dissolution is not responsible for the capacity fading during 5 V performance; thus, a difference mechanism is expected for the improvement provided by the metal oxide cover. It is thought that the metal oxide coated onto the electrode surface avoids the reaction of the electrolyte with the high-valent Fe generated during 5 V operation. However, Al_2O_3 has some particular properties in comparison with other metal oxides. Al_2O_3 is an excellent coating material to protect the substrate against corrosion and stabilize the deposits. It has been described that the corrosion of the substrate surface is an important factor for the capacity fading of 5 V cathode materials [10].

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ deposited on Al current collector has a significant better cyclability in comparison with that deposited on Ti current collector. It is due to the protecting properties of the Al_2O_3 formed by the substrate passivation [10]. On the other hand, it has been described for the deposition of a variety of materials on Al substrate that formation of aluminum oxide layer on the substrate surface provides more suitable sites for the deposition of the electroactive material [31–35]. Thus, the electroactive film deposited is accompanied by a higher stability. It has been described [29] that aluminum oxide formed on the spinel surface is likely to consist of AlOOH rather than Al_2O_3 . However, at high voltages, AlOOH is oxidized to form Al_2O_3 . Since the amount of the aluminum oxide added to the sample is very small (less than 2 wt.%); the exact form could not be determined by XRD.

Now, it is possible to generalize the capacity fading of $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ 5 V cathode materials. The overall fade is split in the two processes occurring at 4 and 5 V operations. The first one is related to the common Mn dissolution similar to LiMn_2O_4 . Although, substituting Mn by transition metals increases the Mn valency accompanied by a lower capacity fading, another source of capacity fading is generated due to the transition metals substituted. The generation of highly reactive high-valent transition metals at high potentials (during 5 V operation) is the second reason for the capacity fading of $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ 5 V cathode materials.

Although, we believe that electrolyte instability at high-voltage performance is still problematic for 5 V cathode materials, however, it was demonstrated that the electrolyte decomposition as a result of instability at high-voltages is not responsible for significant capacity fading of such 5 V cathode materials. Indeed, the high reactivity of the

high-valency state metal generated during the process is the reason. Therefore, this problem can be overcome by avoiding the direct reaction of such high-valency metal with the electrolyte. This is possible by covering the spinel surface with some materials (e.g. metal oxides) with membrane properties.

Finally, it is useful to compare $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ that is the most famous of the 5 V cathode materials. First of $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ shows a higher voltage in comparison with $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ for 5 V operation, which is desirable for battery applications. Oxidation of Fe^{3+} in $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is a one-step process, whereas Ni^{2+} oxidation may occur during two steps displaying two plateaus at about 5 V. $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ displays a redox system at 4.1 due to $\text{Mn}^{3+/4+}$ system, whereas this redox system is absent in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. However, some researchers have reported the appearance of 4 V redox system for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, which can be attributed to the existence of defects in the spinel [10]. $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ provides high specific capacity close to its theoretical capacity as well as $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (their theoretical capacities are approximately the same). It should be taken into account that the excellent capacity of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ recently reported in the literature has been achieved as the result of numerous investigations by using some approaches, such as excess lithium content [11], etc. Finally, although the Mn dissolution is larger in $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$, however, the total capacity fading of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is higher.

4. Conclusion

$\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was introduced as a promising candidate for 5 V cathode materials of lithium batteries. In addition, it was demonstrated that LiBF_4 is a relatively stable electrolyte for 5 V performance. Capacity fading of the $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel at elevated temperatures was investigated in the two voltage regions corresponding to the 4 and 5 V operation. The capacity fading at 4 V operation is mainly due to Mn dissolution, which the fading observed at 5 V is related to the direct reaction of the organic species in the electrolyte with the high-valent Fe at the electrolyte/electrode interface. Interestingly, the use of LiBF_4 in the electrolyte significantly reduced both capacity fades. Moreover, an additional approach viz. surface modification of spinel surface with metal oxide (Al_2O_3) was utilized. The metal oxide coating avoids Mn dissolution and acts as a membrane to avoid the direct reaction of the high-valent Fe with the electrolyte solution. Based on the experimental results, the present research (i) shows excellent properties of $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ as a 5 V cathode material and (ii) describes the sources of capacity fading in this class of 5 V cathode materials.

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