

THE EFFECT OF SURFACE MODIFICATION OF CATHODE MATERIALS ON THEIR ELECTROCHEMICAL CHARACTERISTICS

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A literature review has been undertaken with the aim of analyzing the state-of-the-art in coating the LiMn_2O_4 spinel with various materials to enhance its cycling stability and improve electrochemical characteristics. To examine the influence that the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ coating has on the spinel, samples have been synthesized containing 7 and 14 wt. % of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Studying the charge/discharge characteristics will help improve our understanding of the properties of the materials in question.

The specific properties that allow the stoichiometric lithium-manganese spinel LiMn_2O_4 to reversibly intercalate lithium ions make this compound a very promising cathode material for lithium-ion batteries. Contrary to other popular cathode materials of today, for example, LiCoO_2 and LiNiO_2 , the lithium manganese spinel has a lower price, higher thermal stability, and is environmentally friendly and less toxic [1]. In spite of these advantages, the stoichiometric spinel LiMn_2O_4 demonstrates a considerable decrease in stability upon long-term cycling, especially at elevated temperatures. This restricts the use of this material in energy storage applications [2].

The main reasons for capacity fading of the stoichiometric LiMn_2O_4 spinel upon cycling include electrolyte decomposition, dissolution of Mn^{2+} ions in organic electrolytes, the decrease in the diffusion rate of Li^+ ions due to the formation of a resistive solid electrolyte interface layer [3], oxygen deficiency in the spinel [4], and the Jahn-Teller effect during the final discharge stages [5]. A significant amount of research was conducted to find ways of mitigating the decrease in stability of the material upon cycling. A promising method involves doping the compound with other ions by substituting Mn with other cations. Another way of solving the problem is modifying the surface of the LiMn_2O_4 particles with other compounds to create a protective shell on their surface. Many materials have been tested with such a purpose: ZnO , TiO_2 , SnO_2 , Al_2O_3 , Cr_2O_3 , SiO_2 , Sb_2O_3 , Fe_2O_3 , Co_3O_4 , LiAlO_2 , ZrO_2 , Li_2MnO_3 , LiCoO_2 , LiFePO_4 , $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, and others. A core-shell structures made out of each of these compounds influence the stability

and electrochemical performance of the lithium-manganese spinel LiMn_2O_4 in a certain way.

It has been shown previously that a citric acid aided method is advantageous for obtaining spinels with exceptionally good high-rate properties [6-8]. Recently, we have obtained a surface modified material constituted of the LiMn_2O_4 core and a shell containing 10 wt. % of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and studied its electrochemical characteristics [9]. It has been shown that covering surface of the mother compound (LiMn_2O_4) improves the high-rate properties of the material by 30%.

Therefore, the aim of our investigations is to analyze the effects of surface modification of the LiMn_2O_4 spinel with various amounts of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ on the electrochemical properties of the core-shell material by means of varying the amount of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ in the shell.

Research Methodology

The stoichiometric lithium-manganese spinel LiMn_2O_4 was synthesized by means of the citric acid method using solutions of lithium nitrate, nickel (II) nitrate, manganese (II) nitrate, and citric acid mixed in calculated molar ratios [6,7]. For surface modification, the pyrolyzed LiMn_2O_4 precursor was soaked with a solution containing lithium, nickel, manganese, and the citric acid. After the annealing process, a $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ surface layer was formed. The mass ratio of LiMn_2O_4 to $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ in the two samples synthesized was calculated to be 1:0.07 and 1:0.14. The pyrolysis and annealing temperatures were 400 °C and 700 °C respectively.

CR2016 coin cells were assembled to obtain electrochemical characteristics of the synthesized materials. Cyclic voltammetry (CV) and galvanostatic charge/discharge cycling were performed on a home-made automated electrochemical workstation. The “dry” component ratio of the analyzed material, the conductive additive, and the PVdF binder for the cathodes was 82:10:8. The cells were assembled in a dry glove box and consisted of a cathode made from the synthesized material, a lithium metal anode used as a counter and reference electrode, a Celgard 2500 separator membrane, and 1 mol/L solution of LiPF_6 in the 1:1 mass ratio mixture of EC and DMC.

Results and Discussions

A literature review has been undertaken on the field of surface-modified LiMn_2O_4 spinel, so as to understand the effects such treatment has on the electrochemical characteristics of the material. Following is the analysis of some of the research articles on surface modification with various materials.

Surface Modification with Anode Materials

In Ref. [10], an experiment has been carried out whereby the surface of the spinel LiMn_2O_4 has been coated with ZnO. The authors state that even though various coatings have increased the long-term cycling stability of the spinel at room temperature, the spinel still demonstrates significant capacity losses during cycling at elevated temperatures, which restricts its use in lithium-ion batteries. Therefore, the effectiveness of the ZnO-coating has been examined under elevated temperature conditions.

The samples were cycled with 1 C current in the 3.0-4.4 V potential range at 55 °C. The initial capacity of the pure LiMn_2O_4 spinel was higher than that of the surface-modified material, viz. 124 $\text{mAh}\cdot\text{g}^{-1}$ and 121 $\text{mAh}\cdot\text{g}^{-1}$, respectively. However, after 60 charge/discharge cycles, the specific capacity of the LiMn_2O_4 with a ZnO core decreased only by 3% (117 $\text{mAh}\cdot\text{g}^{-1}$), whereas the capacity of the pure LiMn_2O_4 was lowered by 21% (98 $\text{mAh}\cdot\text{g}^{-1}$).

This investigation proves that the cycling stability of LiMn_2O_4 at elevated temperatures can be significantly improved by coating the spinel particles with ZnO. The obtained core-shell aided in protecting the spinel from contacting with the electrolyte, lowered the catalytic influence of the cathode material surface on the electrolyte oxidization process, and decreased the amount of Mn^{2+} ions dissolving in the electrolyte [10].

The effects of Al_2O_3 -coating of the commercial spinel $\text{LiMn}_{2-x}\text{M}_x\text{O}_4$ (M=Zr) were examined by Lee et al. [11]. Four samples of the material were prepared and each of them had a different mass ratio of spinel to Al_2O_3 (0.56%, 1.27%, 1.61%, and 2.11%).

Charge/discharge cycling of the assembled systems was conducted under 0.5 C current in the potential range of 3.0-4.2 V at room temperature. Samples 1 and 2 of the Al_2O_3 -coated spinel showed a considerable drop in capacity after first 40 cycles. However, sample 3 not only exhibited a higher initial capacity (110 $\text{mAh}\cdot\text{g}^{-1}$) than the unmodified spinel (100 $\text{mAh}\cdot\text{g}^{-1}$), but also lowered its capacity only by a few percent after 120 cycles, whereas the capacity of the pure spinel decreased to 95 $\text{mAh}\cdot\text{g}^{-1}$. Sample 4 demonstrated a high specific capacity during the first 60 cycles as well, but after that the capacity losses became much more significant. Therefore, it can be concluded that surface coating of the $\text{LiMn}_{2-x}\text{M}_x\text{O}_4$ spinel with Al_2O_3 can be beneficial for increasing the cycling stability and specific capacity of the material. The increased capacity is attributed to the structural changes that occur due to the Al_2O_3 coating. The core-shell material exhibits improved interfacial properties between the electrode and the electrolyte [11].

The first examination of Cr_2O_3 as a possible shell material for the LiMn_2O_4 spinel was made by Şahan et al. [12]. The experiment was conducted at room temperature and 1 C current rate in the potential

range of 3.5-4.5 V. It was concluded that the optimal mass ratio of Cr_2O_3 to LiMn_2O_4 is 0.01:1. Even though initial capacity of the modified sample was lower than that of the pure spinel ($107.5 \text{ mAh}\cdot\text{g}^{-1}$ and $118.1 \text{ mAh}\cdot\text{g}^{-1}$ respectively), after 70 charge/discharge cycles the Cr_2O_3 -coated material still maintained 94.6% of its initial capacity whereas the pure spinel retained only 84.5%.

The improved cycling stability of the surface-modified LiMn_2O_4 was even more evident after cycling the samples at an elevated temperature ($55 \text{ }^\circ\text{C}$). With an identical initial capacity of $105 \text{ mAh}\cdot\text{g}^{-1}$ the discharge capacity of the pure spinel decreased to $55 \text{ mAh}\cdot\text{g}^{-1}$ after 70 cycles whereas the core-shell LiMn_2O_4 spinel only experienced capacity fading to $72 \text{ mAh}\cdot\text{g}^{-1}$. Capacity retention at $55 \text{ }^\circ\text{C}$ for the pure LiMn_2O_4 was observed to be 52.4%, and 68.6% for the Cr_2O_3 -coated. These results indicated that the protective Cr_2O_3 shell is effective in improving the capacity retention of the LiMn_2O_4 spinel at elevated temperatures [12].

The effects of Co_3O_4 -coating on the electrochemical properties of stoichiometric lithium-manganese spinel were studied by Lee et al. [13]. The mass ratio of the Co_3O_4 coating to the spinel was 0.3 wt. %. Charge/discharge characteristics were obtained in the potential range of 3.0-4.3 V at 1 C current rate and $55 \text{ }^\circ\text{C}$. The initial capacity of the pure LiMn_2O_4 spinel was $103 \text{ mAh}\cdot\text{g}^{-1}$ whereas that of the Co_3O_4 surface-modified sample was $105 \text{ mAh}\cdot\text{g}^{-1}$. However, after 100 charge/discharge cycles, the capacity retention of the pure LiMn_2O_4 sample was 87.9% while that of the Co_3O_4 core-shell material was 97.1%.

Examining the effects Co_3O_4 coating had on the cycling stability of the spinel LiMn_2O_4 showed that the obtained samples exhibit an increased capacity towards long-term cycling, especially at elevated temperatures. The paper also provided evidence that the Co_3O_4 surface-modified spinel provided improved electrochemical properties during cycling at high current rates (5 C and 10 C).

Surface Modification with Cathodic Materials

The main difference between using anodic and cathodic materials for surface modification is that not only the capacity retention may be improved due to such a change, but also the specific capacity may increase because of it. Contrary to anodic materials that simply form a shell around the spinel particles and protect them from harmful effects of the electrolyte, cathodic materials can also take part in the intercalation/deintercalation process. This, in turn, may lead to an increase in the initial capacity of the system and make the cell more powerful. In 1999, Korean researchers have hypothesized that coating LiMn_2O_4 spinel particles with another cathodic material, namely LiCoO_2 , could increase the structural stability of the obtained material during cycling at elevated temperatures [14].

Cycling of the assembled cells was conducted under 0.2 C (1 C=120 mA·g⁻¹) current in the potential range of 3.4-4.5 V at 55 °C. For the stoichiometric LiMn₂O₄ spinel, the irreversible capacity loss after the first cycle constituted 17 mAh·g⁻¹ whereas the LiCoO₂-coated sample lost only 4 mAh·g⁻¹. After 100 charge/discharge cycles, the surface-modified material showed capacity retention at 91% while the pure spinel only maintained 49% of its capacity after 50 cycles.

With the help of this experiment it was proven that a LiCoO₂ core-shell on LiMn₂O₄ can aid in capacity retention and increasing stability during cycling at elevated temperatures. Even though morphology examinations showed that after heat treatment at 800 °C the external layer of Co-coating disappeared, the newly-formed Li_{1+x}Mn_{2-x}Co_xO₄ compound with a higher concentration of Co particles close to the surface of the mother particles demonstrated an improved structural stability compared to the pure LiMn₂O₄ spinel.

Chan et al. published a paper [15] examining the influence of coating Li_{1+x}Mn₂O₄ powder with amorphous Li₂O-2B₂O₃ (LBO) glass film. The following experiment was performed to evaluate the decrease in Mn²⁺ dissolution and to lower the number of side-reactions on the cathode surface.

The assembled cells were cycled at a 0.2 C current rate in the potential range of 3.0-4.2 V at room temperature. Initial discharge capacity recorded for the unmodified LiMn₂O₄ sample was 123.5 mAh·g⁻¹ and after 25 cycles it lowered to 103.7 mAh·g⁻¹ showing a capacity retention of 84%. From several LBO coated samples the best cycling characteristics exhibited the one with a 0.3 wt % of coating. The initial capacity for this sample constituted 116.2 mAh·g⁻¹, and upon 25 cycles it retained 93% of its capacity. Therefore, the authors showed that it was possible to considerably lower the amount of dissolving Mn ions and decrease the intensity of the interaction between electrode and electrolyte by coating the spinel with LBO.

Recently, researching cathode coatings led scientists to examining the properties of a new material, the lithium nickel manganese oxide spinel LiNi_{0.5}Mn_{1.5}O₄ [16]. It was analyzed whether the structural similarities between the stoichiometric and the nickel manganese oxide spinel would help to improve the electrochemical properties of a cathode material with such a shell. A citric acid aided method was used to synthesize coated materials. The obtained samples contained 3, 5, and 10 wt. % of LiNi_{0.5}Mn_{1.5}O₄. According to TEM data, particles were of 2-3 μm in size.

Cells with the synthesized samples were cycled at room temperature and at 60 °C in the voltage range of 3.2-4.5 V. The optimal properties were exhibited by the sample coated with 10 wt % of LiNi_{0.5}Mn_{1.5}O₄. It was evident from the results of both experiments that

the cycling stability of the LiMn_2O_4 spinel coated with $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was much higher than that of the pure compound. Even though the modified material showed lower initial capacity during the first several cycles, it retained 96.3% of its initial capacity upon 50 charge/discharge cycles whereas the unmodified sample demonstrated capacity retention of 81.7%.

During cycling at an elevated temperature the differences between the materials became even more apparent. The initial capacity of the pure spinel was recorded to be $124.1 \text{ mAh}\cdot\text{g}^{-1}$, however, after 40 cycles it decreased to $82.8 \text{ mAh}\cdot\text{g}^{-1}$ (66.6% capacity retention). Contrary to the unmodified material, the spinel coated with 10 wt. % of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ showed a $98.6 \text{ mAh}\cdot\text{g}^{-1}$ specific capacity and exhibited capacity retention of 90% even after 100 charge/discharge cycles. Besides the elevated cycling stability, the surface-coated spinel also demonstrated increased rate performance [16].

This experiment provides evidence that coating stoichiometric LiMn_2O_4 with $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ improves the cycling stability of the material and amends its electrochemical characteristics.

Conclusions

In this paper, a literature review was presented examining the effects various surface coatings could have on the electrochemical properties of the LiMn_2O_4 spinel. Two samples of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ coated LiMn_2O_4 were synthesized to further examine how this type of coating might influence the cycling stability, specific capacity, and other characteristics of the stoichiometric spinel. The results of the forthcoming experiments would provide more information about the optimal mass ratio of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ coating of the core LiMn_2O_4 spinel.

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