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# FORMATION OF SPINEL STRUCTURE IN SYNTHESIS PROCESS OF $Li_{1.37}Mn_2O_4$ USING HYDROTHERMAL METHOD

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## ABSTRACT

**FORMATION OF SPINEL STRUCTURE IN SYNTHESIS PROCESS OF $Li_{1.37}Mn_2O_4$ USING HYDROTHERMAL METHOD** $Li_{1.37}Mn_2O_4$ is one form of $Li_{1+x}Mn_2O_4$ which is engineered from $LiMn_2O_4$ phase which is commonly used as a lithium cathode active ingredient. The crucial thing from $Li_{1.37}Mn_2O_4$ synthesis is the spinel structure that is formed. This study aims to observe when the spinel structure of $Li_{1.37}Mn_2O_4$ starts and when the transformation from a tetragonal structure into spinel occurs. The raw materials used are tetragonal LiOH and tetragonal $MnO_2$. The synthesis was carried out using a hydrothermal method with a temperature of 200 °C with a variation of holding times of 50, 70, 90 and 110 hours. Observation of spinel structure was carried out using XRD and TEM. The results obtained were at the holding times of 50 and 70 hours, the spinel structure had not been formed. The spinel structure begins to form at 90 hours holding time which also indicates that the transformation from the tetragonal structure to spinel occurs at such holding time. The result of a 90-hour holding time is a regular spinel structure but there are still many Mn and Mn-O –based impurities. While the results of the 110-hour holding time produce a perfect yet irregular transformation of the spinel structure.

***Keywords***: $Li_{1.37}Mn_2O_4$, Spinel, Crystal structure, Hydrothermal

## ABSTRAK

**PEMBENTUKAN STRUKTUR SPINEL PADA PROSES SINTESIS $Li_{1.37}Mn_2O_4$ MENGGUNAKAN METODE HIDROTERMAL.** $Li_{1.37}Mn_2O_4$ merupakan salah satu bentuk dari $Li_{1+x}Mn_2O_4$ yang merupakan rekayasa dari fasa $LiMn_2O_4$ yang biasa digunakan sebagai bahan aktif katoda baterai lithium. Hal krusial dari sintesis $Li_{1.37}Mn_2O_4$ adalah struktur spinel yang terbentuk. Studi ini bertujuan untuk mengamati kapan mulai terbentuknya struktur spinel $Li_{1.37}Mn_2O_4$ dan kapan transformasi dari struktur tetragonal menjadi spinel terjadi. Bahan baku yang digunakan adalah LiOH tetragonal dan $MnO_2$ tetragonal. Sintesis dilakukan menggunakan metode hidrotermal dengan temperatur 200 °C dengan variasi waktu penahanan 50, 70, 90 dan 110 jam. Pengamatan struktur spinel dilakukan menggunakan XRD dan TEM. Hasil yang diperoleh adalah [illegible] ai terbentuk pada [illegible] al menjadi spinel terjadi pada waktu penahanan tersebut. Hasil dari waktu penahanan 90 jam adalah struktur spinel yang teratur namun masih ditemukan banyak impuritas berbasis Mn dan Mn-O. Sementara hasil dari waktu penahanan 110 jam menghasilkan transformasi sempurna struktur spinel namun tidak teratur.

***Kata kunci:*** $Li_{1.37}Mn_2O_4$, Spinel, Struktur kristal, Hidrotermal



## INTRODUCTION

$LiMn_2O_4$ is one of the materials used as cathode lithium active material. $LiMn_2O_4$ has a relatively inexpensive price and good thermal stability, but has a weakness on low specific capacities [1,2]. For this reason, various efforts have been made by scientists to increase their specific capacity, one of which is to convert it to $Li_{1+x}Mn_2O_4$. The $Li_{1+x}Mn_2O_4$ cathode is engineered from $LiMn_2O_4$ which has more lithium content. This cathode

type is included in the category of lithium-rich cathode oxides. Lithium-rich cathode oxides are candidates for new generation of cathode lithium batteries with the superiority of oxidation-reduction reactions of transition metals (cations) and multivalent anions so that theoretically it potentially produces a higher specific capacity compared to the usual lithium oxide cathode [3]. However, the weakness of this material is a less stable cyclic behavior. Therefore efforts to improve the current cycle behavior are mostly done by increasing the composition of the spinel structure and modifying its particle surface [4], where these two crucial things depend heavily on the synthesis method used.

Basically, the synthesis method of $Li_{1+x}Mn_2O_4$ is the same as that of $LiMn_2O_4$. Such synthesis method includes solid reaction with raw materials of $Li_2CO_3$ and $MnO_2$ calcined in two stages 500 °C and 780 °C [5], solid reactions with raw materials of α-$MnO_2$ nanotubes and $Li_2CO_3$ calcined at 900 °C [6], sol-gel with calcination temperature of 650 °C [7], dynamic process [8], combustion method with a temperature of 800 °C [9], synthesis method with precursor polyvinylpyrrolidone or poly (vinyl alcohol) [10], a combination of mechanical alloying and rotating heating methods [11], etc.

The composition of the spinel structure on $LiMn_2O_4$ cathode will affect the performance of lithium batteries. The greater the spinel composition, the specific capacity will increase due to a decrease in irreversible capacity loss [12]. Irreversible capacity loss is a phenomenon where some lithium irons do not return to the spinel structure during the discharging process before being extracted during the charging process.

This study attempts to synthesize $Li_{1+x}Mn_2O_4$ with a spinel structure in the form of $Li_{1.37}Mn_2O_4$ from the raw material of tetragonal LiOH and tetragonal $MnO_2$ using the hydrothermal method. A crucial problem in this synthesis is when the spinel structure begins to form and when the transformation of the tetragonal structure into spinel begins to occur. The spinel structure has an indication of having a Fd-3m space group [13]. Therefore, controlling the formation of Fd-3m space group is the main objective of this synthesis.

## EXPERIMENT METHOD

### Materials and Equipment

The raw materials used are tetragonal LiOH (Merck, purity > 99%) and tetragonal $MnO_2$ (Merck, purity > 99%).

Synthesis equipment used is magnetic stirrer and Morey type autoclave. While the characterization equipment used is the Rigaku Smart Lab XRD 3 kW in continuous scan mode with an angle range of 2θ from 10° to 90° and step width of 0.02°. The TEM used is Tecnai G2-STWIN FEI with an acceleration voltage of 200 kV and uses bright plane mode.

### Procedure

$Li_{1.37}Mn_2O_4$ synthesis in this study follows the ideal reaction equation as follows:

LiOH and $MnO_2$ are mixed and dissolved using distilled water and added carbon black (purity > 99%) then stirred with a magnetic stirrer for one hour to produce slurry solution. The slurry solution was then put into an autoclave with a volume of 50 cc and heated with a temperature of 200 °C with a variation of holding time of 50 hours, 70 hours, 90 hours and 110 hours. After heating, the samples are removed from the autoclave to be dried in an oven at a temperature of 100 °C.

The samples are then characterized using X-ray diffractometer (XRD) and transmission electron microscope (TEM).

## RESULTS AND DISCUSSION

Spinel structure is one variant of the cubic structure with certain crystal planes such as (111), (220), (311), (400), (331), (422), (511), (333), (440), (531) and (620) [14]. The spinel structure in this system has Fd-3m space group [13]. The X-ray diffraction pattern in Figure 1 shows that the spinel structure has not been formed at 50 and 70 hours of holding time. However, the spinel structure has been detected at 90 and 110 hours of holding time (see Figure 1). Spinel crystal planes detected at 90 hours of holding time are (111), (220), (311) and (440) while at 110 hours of holding time are (111), (311), (400) and (440) (as seen in Figure 1, Tables 1 and 2). Both the 90-hour and 110-hour holding times found three similarities in the crystalline plane formed, namely (111), (311) and (440). The difference between the two is that at the holding time of 90 hours, a plane (220) is found, while at the holding time of 110 hours, the plane (220) does not appear and a new plane (400) is found.

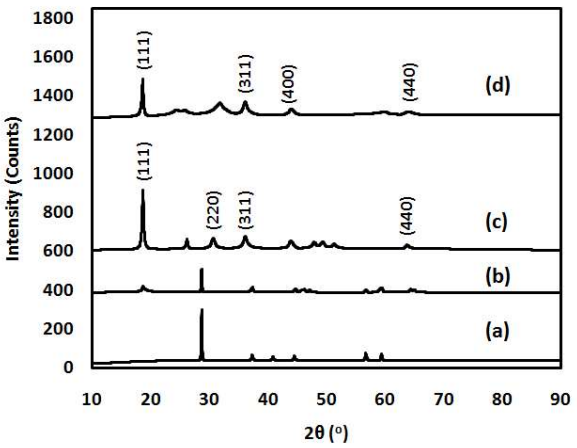


***Figure 1.*** X-ray diffraction pattern in hydrothermal synthesis samples with a temperature of 200 °C along with Miller index in the emerging spinel structure planes (a). 50-hour holding time (b). 70-hour holding time (c). 90-hour holding time (d). 110-hour holding time.

***Table 1.*** Identification of spinel structure on the samples with a 90-hour holding time.

| 2θ (°) | $Sin^2θ$ | $(Sin^2θ)/3$ | $(Sin^2θ)/8$ | $(Sin^2θ)/11$ | $(Sin^2θ)/32$ | hkl | *a* (Å) |
|---|---|---|---|---|---|---|---|
| 18.620000 | 0.026171 | 0.008724 | 0.003271 | 0.002379 | 0.000818 | 111 | 8.253951 |
| 30.610571 | 0.069676 | 0.023225 | 0.008709 | 0.006334 | 0.002177 | 220 | 8.260742 |
| 36.070000 | 0.095851 | 0.031950 | 0.011981 | 0.008714 | 0.002995 | 311 | 8.258741 |
| 63.700000 | 0.278464 | 0.092821 | 0.034808 | 0.025315 | 0.008702 | 440 | 8.264292 |

***Table 2.*** Identification of spinel structure on the samples with a 110-hour holding time.

| 2θ (°) | $Sin^2θ$ | $(Sin^2θ)/3$ | $(Sin^2θ)/11$ | $(Sin^2θ)/16$ | $(Sin^2θ)/32$ | hkl | *a* (Å) |
|---|---|---|---|---|---|---|---|
| 18.61 | 0.026144 | 0.008715 | 0.002377 | 0.001634 | 0.000817 | 111 | 8.258347 |
| 36.06 | 0.095799 | 0.031933 | 0.008709 | 0.005987 | 0.002994 | 311 | 8.260955 |
| 43.93 | 0.139906 | 0.046635 | 0.012719 | 0.008744 | 0.004372 | 400 | 8.244367 |
| 63.81 | 0.279325 | 0.093108 | 0.025393 | 0.017458 | 0.008729 | 440 | 8.251546 |

When a lattice parameter values are plotted of all spinel planes detected in Table 1 against the Nelson-Riley function [15], a linear regression line will be obtained with a gradient of -0.001053 and interception of 8.266664 (Figure 2(a)). The linear regression line has an R2 value of 0.899057. That line can still be fixed so that it has a R2 value above 0.9 by dividing the two combinations of spinel constituent planes into groups (440), (311) and (111) (Figure 2(b)) and (440), (220) and (111) (Figure 2(c)) so that we can obtain two different cut off points, i.e. 8.266219 (Figure 2(b)) and 8.267704 (see Figure 2(c)). The cut off point in the linear regression line shows the precision lattice parameter value $a_0$ [14]. Thus, it can be assumed that there are two order-cell spinel structures that are ordered in the sample resulted from 90 hours of holding time, each of which has a grid parameter of 8.266219 Å and 8.267704 Å.

Although the spinel structure is formed at 90-hour holding time, Mn-O and Mn-based impurities are still found. The first impurity phase was an orthorhombic-structured non-hausmanite $Mn_3O_4$ characterized by identification of d values of 3.41 Å, 1.84 Å and 1.78 Å (PDF # 75-0765). The second impurity phase is a primitive-cubic-structured Mn with detected d value of 1.90 Å (PDF # 33-0887). This shows that the function of carbon black as a reaction catalyst to prevent the formation of the Mn-O-based impurity phase has not functioned optimally at this 90-hour holding time.

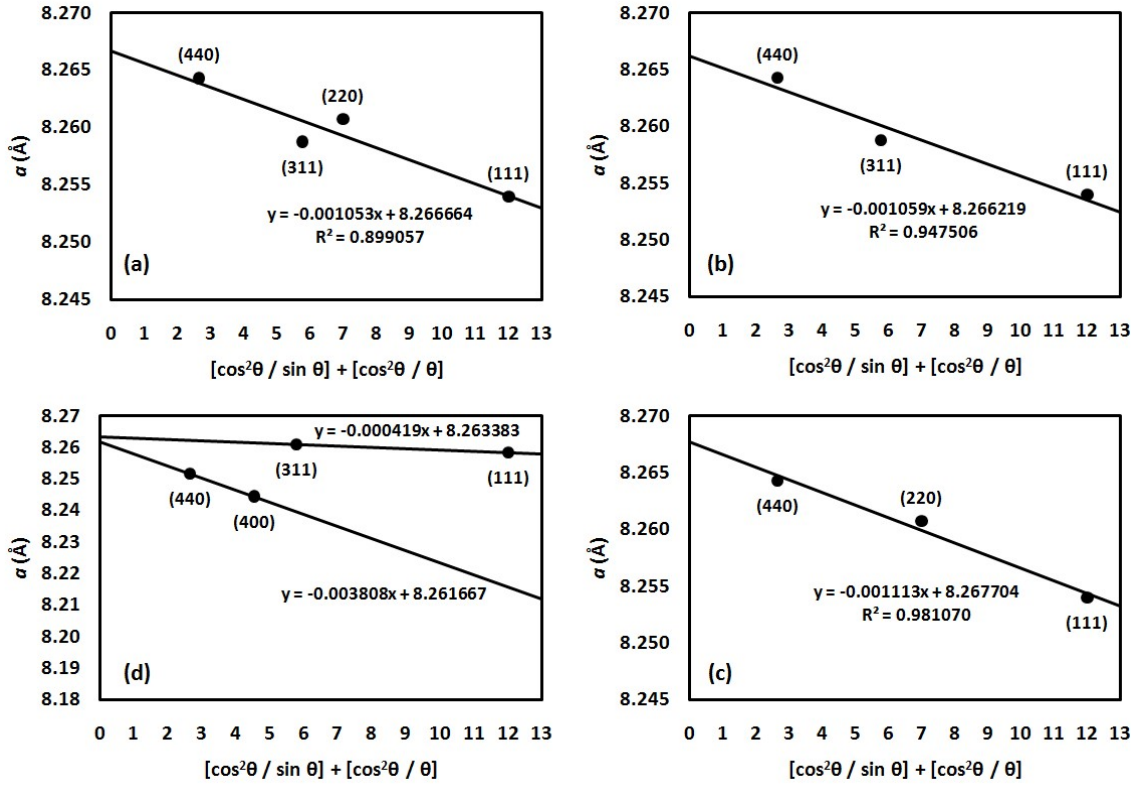


***Figure 2.*** The plot of the lattice parameter a spinel structure as a function of $(\cos^2θ/\sin θ) + (\cos^2θ/θ)$ (a). 90-hour holding time with spinel planes (440), (311), (220), and (111) (b). 90-hour holding time with spinel planes (440), (311) and (111) (c). 90-hour holding time with spinel planes (440), (220), and (111) (d). 110-hour holding time.

With the discovery of the impurity phases of $Mn_3O_4$ and Mn, it can be as-certained even though the spinel structure is formed under ordered conditions, the results obtained were not $Li_{1.37}Mn_2O_4$ but experienced a deficiency of Mn to be $Li_{1.37}Mn_2O_4$.

Thus, it is very likely that the loss of some Mn occupancy in the spinel structure will be filled by Li atoms which are indeed made more in composition so that the spinel structure resembles the form of $LiMn_2O_4$ spinel. However, as some of Li functions change to fill Mn occupancy, it is feared that it will reduce the effectiveness of Li intercalation-deintercalation so that the initial function of adding Li from $LiMn_2O_4$ to $Li_{1.37}Mn_2O_4$ in order to increase the specific capacity of lithium batteries will not be achieved.

Meanwhile, when a lattice parameter values are plotted in Table 2 against Nelson-Riley function [16], a linear regression line formed by a minimum of three spinel constituent planes will not be obtained. However, if we extrapolate the linear regression line by grouping each of the two constituent planes, namely group (111) with (311) and group (400) with (440), an interception point will be found between the two linear regression lines at almost the same range, i.e. 8.26 (see Figure 2(d)). This shows that indeed there is actually a spinel structure with a precision lattice parameter of about 8.26 Å in the synthesis result with 110-hour holding time, but the condition is a disorder. This disorder condition shows that even though the spinel structure is formed, the occupancy arrangement of Li, Mn and O atoms is messy and there is a possibility of exchanging positions with each other [14]. However, even though the spinel structure formed is in a disorder condition, the impurity based on Mn-O and Mn is no longer found. It shows the function of the carbon black as a reaction catalyst to prevent the emergence of Mn-O based phase to work well at this 110-hour holding time. The first impurity that appears in the synthesis results at a 110-hour holding time is C60 carbon with an indication of d values of 2.81 Å and 1.53 Å (PDF # 79-1715). While the second impurity is d at 3.44 Å which is assumed to be a transition phase between C60 with a cubic structure (d = 3.40 Å, PDF # 79-1715) and C70 with a hexagonal structure (d = 3.46 Å, PDF # 48-1206). The presence of carbon-based impurity shows that at 110-hour holding time, the amorphous carbon black structure undergoes a recrystallization process towards the crystalline form.

Thus, it is difficult to determine the best holding time parameters for the formation of $Li_{1.37}Mn_2O_4$ spinel structures by hydrothermal synthesis method at a temperature of 200 °C. From the point of view of the spinel crystal structure formed, a 90-hour holding time

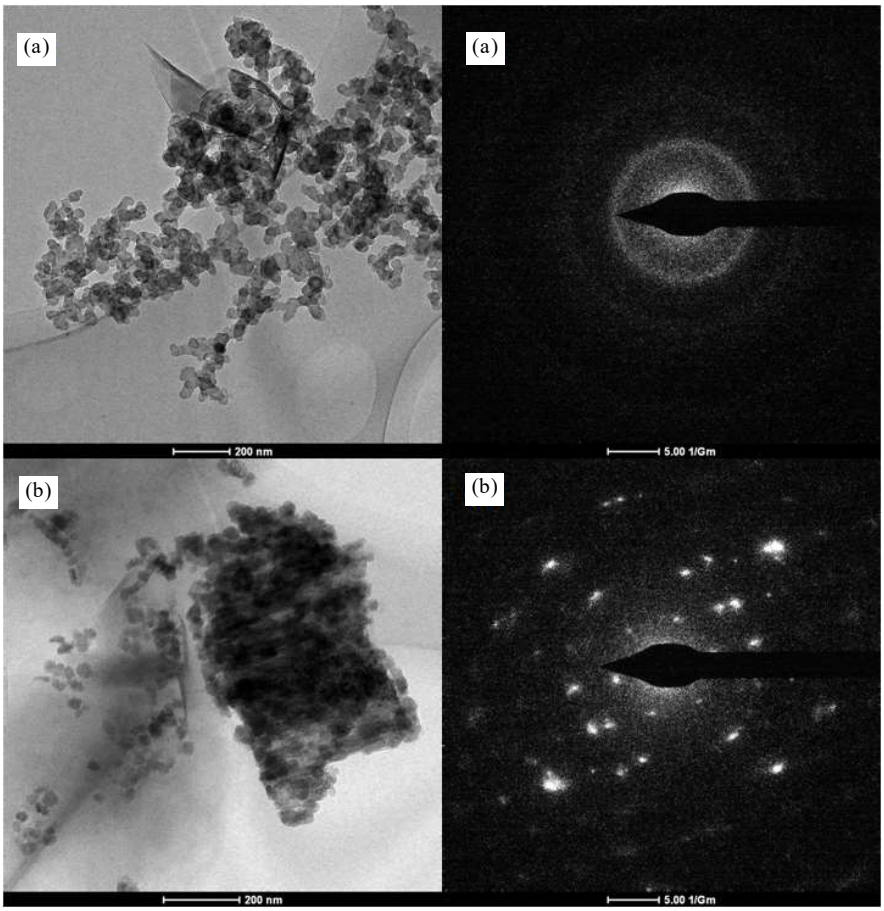


***Figure 3.*** Images of TEM and SAED on hydrothermal synthesis particles with a temperature of 200 °C and a holding time of 90 hours.

is more recommended. This reasoning is strengthened from the results of TEM testing, where apart from obtaining nanoscale spinel crystallites (see Figure 3), the SAED diffraction pattern is clearly obtained in polycrystalline form (see Figure 3(a) on the right) and in the form of single crystalline (see Figure 3(b) on the right). The SAED single crystalline pattern of spinel structures cannot be found in synthesized spinel disorder structures with a holding time of 110 hours and only found in synthesis results with a 90-hour holding time. This pattern (see Figure 3(b) on the right) is identical to the arrangement of atoms forming the $LiMn_2O_4$ spinel structure, especially in the first ring which is identical to the arrangement of Mn and O at the viewpoint of {001 } <100> and {010} <001> (see the simulation in Figure 4 then compare with Figure 3.b on the right).

Meanwhile, at holding times of 50 and 70 hours, the phase formed is a $MnO_2$ tetragonal which is indicated by the detected d values (PDF # 81-2261). At the 50-hour holding time, d values are detected namelyt 3.11 Å, 2.41 Å, 2.21 Å, 1.62 Å and 1.55 Å. While at 70-hour holding time, detected d values include 3.11 Å, 2.40 Å, 1.96 Å, 1.62 Å, 1.55 Å and 1.44 Å. Thus, at the 90-hour holding time there is a transformation of the crystal structure from tetragonal to cubic spinel.

## CONCLUSION

The transformation of tetragonal structure into $Li_{1.37}Mn_2O_4$ spinel has been successfully synthesized using a hydrothermal process at 200 °C with a holding time of 90 hours. At 90-hour holding time, the spinel structure is formed under order conditions, but there are still Mn and Mn-O-based impurities. At 110-hour holding time, Mn and Mn-O-based impurities are no longer found so that the synthesis takes place completely and produces $Li_{1.37}Mn_2O_4$ spinel structure, but the spinel structure that is formed has a disorder condition.

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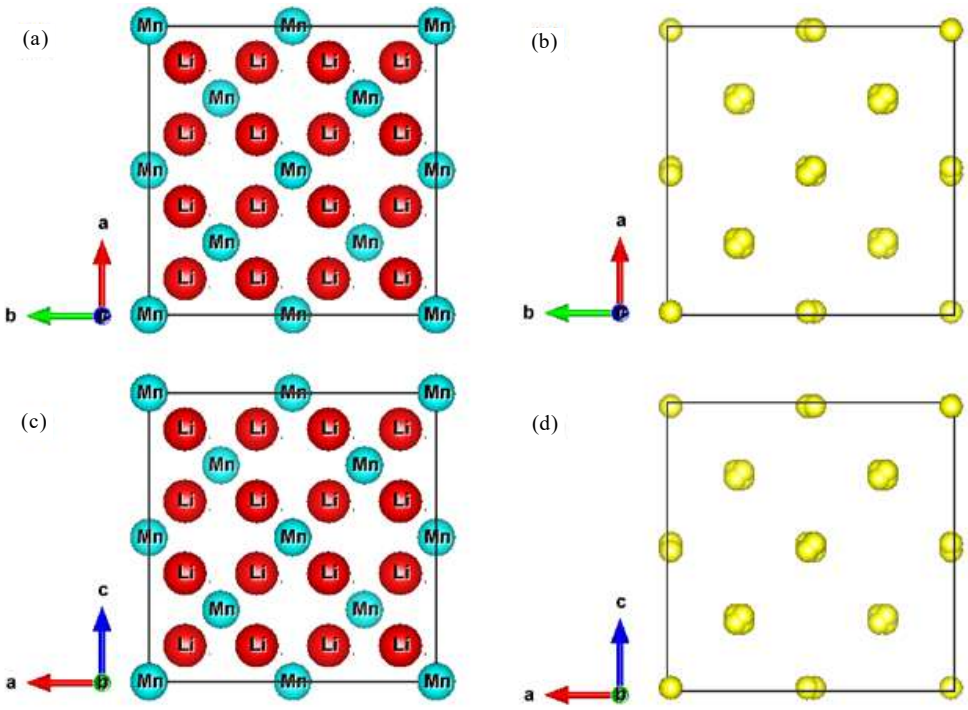


***Figure 4.*** Simulation of the atom arrangement in the ideal $LiMn_2O^4$ spinel phase [15]. (a). Distribution of Mn and Li atoms in the viewpoint of {001} <100> (b). Distribution of O atoms in the viewpoint of {001} <100> (c). Distribution of Mn and Li atoms in the viewpoint of {010} <001> (d). Distribution of O atoms in the viewpoint of {010} <001>.

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