INFLUENCE OF ANNEALING TEMPERATURE AND SUBSTITUTION OF Mn WITH Al IN THE SPINEL $LiMn_2O_4$ CATHODE POWDERS

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Introduction

The spinel structure of $LiMn_2O_4$ can be slightly changed with the reaction temperature of the initial reactive chemical compounds or by partially substituting manganese with other metallic elements [1-4]. The main idea is to replace Mn^{4+} ions with metal ions having mainly M^{3+} in order to keep the Average Oxidation State, AOS, of the Manganese higher than 3.5. This way it is very possible that the Jahn Teller phenomenon can be avoided in the spinel structure. In this work the substitution of Mn is made with Al, since the ionic radius of Al^{3+} is very close to the ionic radius of Mn^{4+} [4].

Experimental

The spinel structures of $LiMn_2O_4$ and $LiMn_{1.5}Al_{0.5}O_4$ were prepared with the solid state reaction method by mixing powders of λ-MnO_2, LiOH and $Al(OH)_3$. Two reactive temperatures were tried, 750 and 800 ^oC. Grinding of the materials is following the first reaction for about 24 hours in the atmosphere and subsequent annealing at the same temperature for about 45 hours. Before starting slow cooling of the material, O_2 atmosphere is introduced and the cooling rate is kept quite low, 0.83 $^oC.min^{-1}$. The oxygen atmosphere is needed for receiving spinels with the right stoichiometry. The resulted powders were studied with x-rays, electrochemical and AC impedance spectroscopy measurements.

Results and Discussion

Figure 1 presents the x-ray powder diffraction patterns. In all cases, either by changing the reaction temperature or by partially substituting Mn with Al, the structure of the powders was that of the space group Fd3m. The influence of the reaction temperature on both chemical compounds was a very small increase of the lattice parameter by increasing the reaction temperature from 750 to 800 ^OC. The sharpness of the peaks indicates that the average crystal size increases at higher reactive temperatures. In the $LiMn_{1.5}Al_{0.5}O_4$ powders, though, traces of the initial reactive compounds were detected. The lattice parameters of the $LiMn_{1.5}Al_{0.5}O_4$ compounds were slightly smaller than those of the $LiMn_2O_4$ powders, which is an strong indication that Al^{3+} ions replace Mn^{4+} ions.

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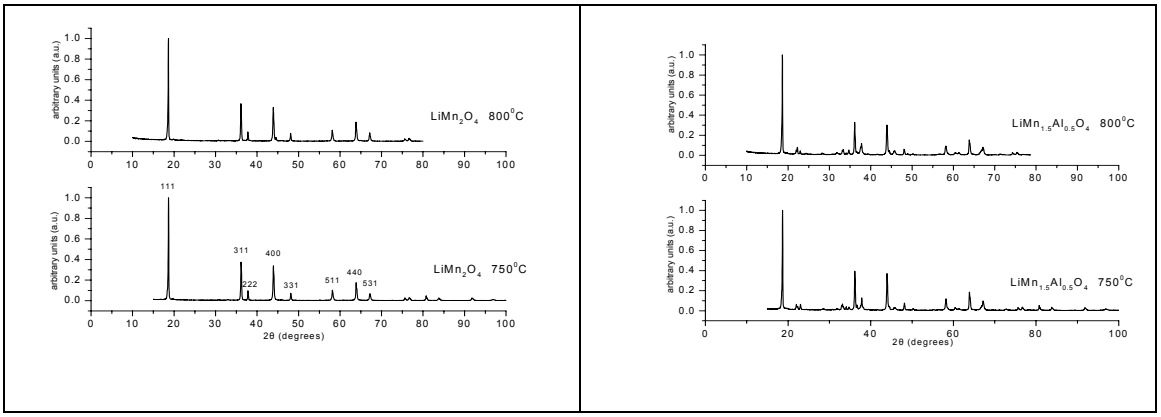

Fig. 1 *X-ray powder diffraction patterns of the $LiMn_2O_4$ and $LiMn_{1.5}Al_{0.5}O_4$ spinel compounds prepared at 750 or 800°C.*

Figure 2 shows the electrochemical measurements of the $LiMn_2O_4$ compounds prepared at the two different reaction temperatures. The specific capacity of the powder prepared at 800 °C is higher than in the other compound in the voltage range of 3.2 - 4.4 V. Similar behavior was obtained for the $LiMn_{1.5}Al_{0.5}O_4$ compounds but the initial capacities were lower than the respective ones of the clearly spinel manganese structures.

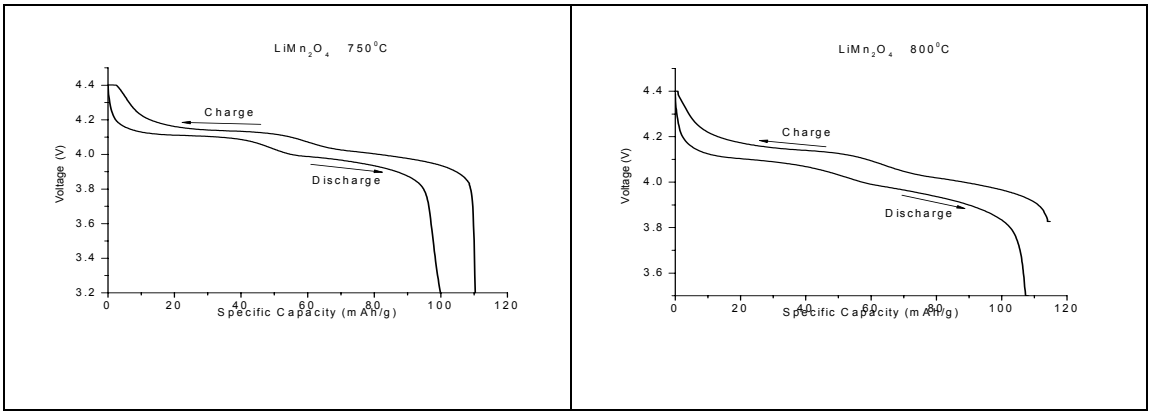

Fig. 2 *Specific capacity measurements of the $LiMn_2O_4$ powders prepared at 750 and 800 °C.*

Figure 3 presents the normalised specific capacities of discharge, with the number of cycles, of all prepared powders in the voltage range of 3.2 - 4.4 V. Within the first 20 cycles the capacity decreases by almost 20% in all samples. The Al doped samples, though, are more stable in the first cycles. After these cycles, the powders prepared at 800 °C seam to loose their capacity much slower, especially after substitution of Mn with Al. The $LiMn_2O_4$ samples, prepared at 800 and 750 °C reactive temperature and after 100 cycles, keep 70% and 54% of their capacity, respectively. The corresponding reduction percentage, for the same number of cycles, of the Al doped samples is approximately 70.5% and 66%. The decrease of the capacity during the first cycles is due to the formation of the interface between the electrode and the electrolyte. The continuous decrease of the capacity in the $LiMn_2O_4$ powders is because of the Jahn Teller distortion,

which is more obvious at the high discharge, for voltages lower than 3.5 V. The substitution of Mn with Al, though, improves the stability of the capacity considerably.

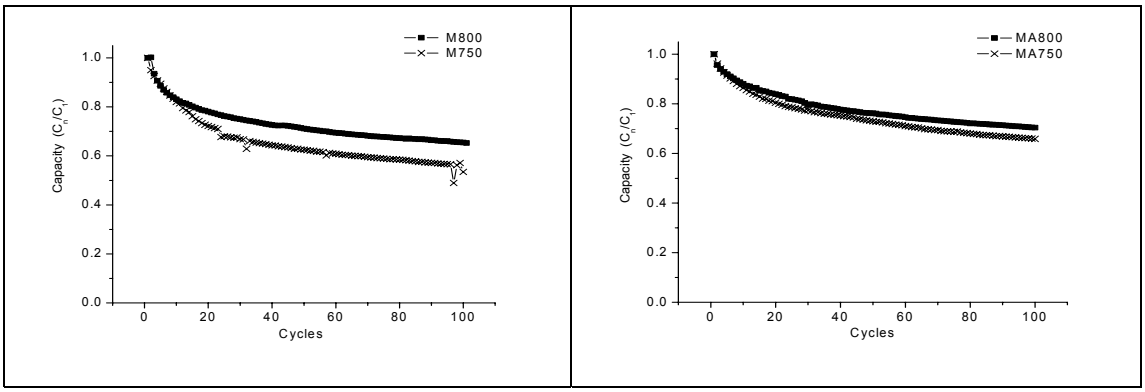

Fig. 3 *Normalised capacity with the cycles for all samples (M for the $LiMn_2O_4$ and MA for the $LiMn_{1.5}Al_{0.5}O_4$ powders) - voltage range 3.2 - 4.4 V.*

Conclusions

Higher reactive temperatures during the preparation of the powders, either in the original Manganese spinel or in the partially substituted of Mn with Al, results to slight increase of the lattice parameter and larger average crystal size. The lattice parameter, though, decreases after the substitution of Mn with Al, which is a strong indication that Al^{3+} ions replace Mn^{4+} ions. Even though the substitution of Mn with Al decreases the specific capacity of the material, the stability with the cycles of the $LiMn_{1.5}Al_{0.5}O_4$ is improved considerably compared to the $LiMn_2O_4$ spinel cathode and this is attributed to keeping the AOS of the manganese higher than 3.5. This prevents the appearance of the Jahn Teller distortion.

References

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