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Electrochemical Performance of Nano-structured $LiM_xMn_{2-x}O_4$(M= Cr and Fe) Powders at High Charge-discharge Operation

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Introduction

Among three promising candidates for the cathode materials of lithium ion batteries ($LiCoO_2$, $LiNiO_2$, and $LiMn_2O_4$), the spinel $LiMn_2O_4$ has economical and environmental advantages as compared with the layered compounds ($LiCoO_2$ and $LiNiO_2$). Thus, the lithium ion batteries, used the spinel $LiMn_2O_4$ as a cathode material, are under consideration for the electric vehicle and the hybrid electric vehicle application. However, the capacity fading during long-term cycling limits this application. To improve the cycle performance of the spinel $LiMn_2O_4$, many researchers have investigated the partially substituted lithium manganese oxides, which the manganese atom was partially replaced by some transition metals such as Co and Ni, and non-transition metals such as Al and Mg. As the results, the substitute part of the manganese with another metal may increase the stability of the spinel structure. Recently, Lee et al. [1] prepared nano-structured $LiNi_{0.5}Mn_{1.5}O_4$ powders by composite carbonate process and reported that the nano-structured particles improved the cycling performance. In our previous work [2], it was reported that the nano-structured $LiMn_2O_4$ powders could be easily synthesized by ultrasonic spray pyrolysis method. In this work, we prepare the nano-structured $LiM_xMn_{2-x}O_4$ (Cr and Fe) powders by ultrasonic spray pyrolysis and investigate their electrochemical performance at high charge-discharge operation.

Experimental

The experimental set-up and sample preparation were described in our previous work [2]. The powder characteristics, such as crystallite size, specific surface area and particle size, have been examined with X-ray diffraction (XRD), the Brunauer-Emmett-Teller (BET) method, field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). The electrochemical performance of the obtained $LiM_xMn_{2-x}O_4$(Cr and Fe) powders was examined in a two-electrode cell. The electrochemical cell consisted of 10 wt.% PVdF, 20 wt.% acetylene black and 80 wt.% active material $LiM_xMn_{2-x}O_4$(Cr and Fe). The cells were assembled in an argon-filled glove box using Li metal as a counter electrode, microporous polypropylene as a separator, and 1M solution of $LiClO_4$ in EC:DEC=1:1. The electrochemical measurements were carried out galvanostatically at various C-rates over a potential range between 3.5 and 4.4 V.

Results and discussion

Figure 1 shows the X-ray diffraction patterns of the $LiCr_xMn_{2-x}O_4$ (x=0, 0.05, 0.1, 0.2 and 0.3) powders. All the peaks in each pattern of $LiCr_xMn_{2-x}O_4$(x=0, 0.05, 0.1, 0.2 and 0.3) can be indexed as those of single-phase spinel structure. The Mn site in $LiMn_2O_4$ is substituted fully by Cr doping, and no other Cr-containing phase is formed. The same results have been obtained in case of Fe substitution.

Figure 2 shows SEM photographs of partially substituted spinel $LiM_{0.2}Mn_{1.8}O_4$ (M=Cr and Fe) powders. All the as-prepared particles are spherical in shape and non-agglomerated. However, spinel $LiMn_2O_4$ powders had a porous surface morphology, while the partially substituted spinel $LiM_{0.2}Mn_{1.8}O_4$ powders exhibit a smooth surface morphology. The surface morphology of as-prepared particles changes from porous to smooth surface one with the amount of Cr or Fe substitution.

Figure 3 shows the variation of the discharge capacity with cycle number for Li/$LiClO_4$ in EC: DEC =1:1/$LiCr_xMn_{2-x}O_4$ cells with various *x* values. The electrochemical measurements were carried out galvanostatically at 5C-rates and room temperature. All the Cr-doping samples exhibit extremely stable performance at high C-rate, while the non-doping material ($LiMn_2O_4$) has a capacity fading upon cycling.

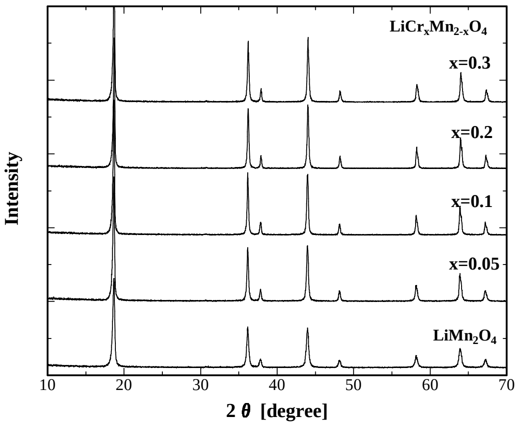
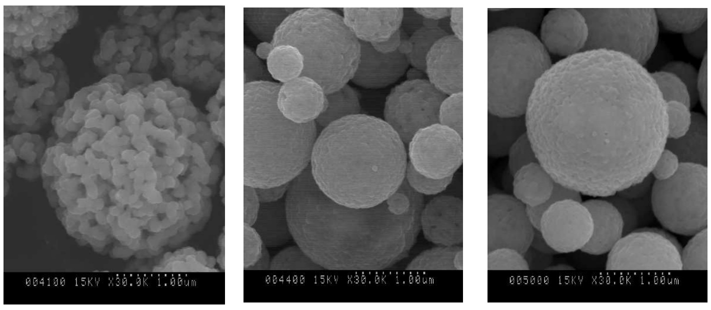


Fig. 1 X-ray diffraction patterns of substituted $LiCr_xMn_{2-x}O_4$ (x=0,0.05,0.1,0.2 and 0.3) spinels



$LiMn_2O_4$ $LiCr_{0.2}Mn_{1.8}O_4$ $LiFe_{0.2}Mn_{1.8}O_4$

Fig. 2 SEM picture of as-prepared samples

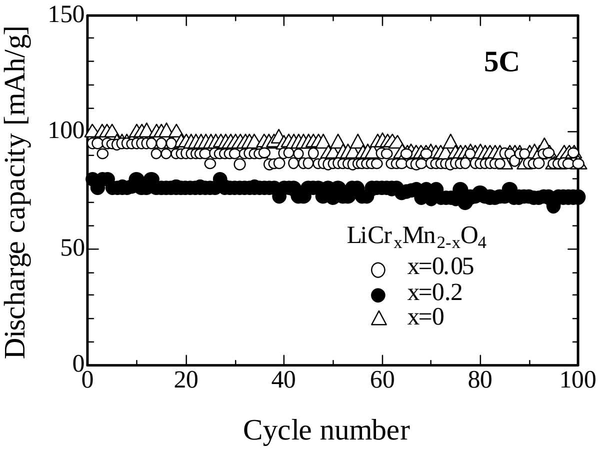


Fig. 3 Cycling performances of Li/$LiCr_xMn_{2-x}O_4$ cells at 5C charge-discharge rate

References

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2. I. Taniguchi, D. Song, M. Wakihara, J. Power Sources, 109, 333-339(2002).