

Studies on the Capacity Fading of $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_{4\pm\delta}$ Spinels in Half Cell and Li-ion Batteries at Elevated Temperature

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Introduction

LiMn_2O_4 -type spinels are very attractive to be used as alternative materials for LiCoO_2 because of their low cost, low toxicity and safer performance in the charged states. However, capacity fading especially at elevated temperatures of the half cells and Li-ion batteries based on manganese spinel cathodes has impeded their wide application. Recently we have demonstrated that the oxygen stoichiometry for the original materials is necessary for Mn spinels to obtain improved cycleability,¹ and succeeded to prepare a new kind of Mg-doped spinels with excellent cycleability and very little Mn dissolution at 60°C.² The materials are oxygen stoichiometric with metal vacancies in the 16d sites as written by an ideal formula of $[\text{Li}]_{8a}[\text{Li}_n\text{Mg}_m\text{Mn}_{2-n-m-p}\square_p]_{16d}[\text{O}_4]_{32e}$. Here, we present our new insights on this kind of materials by preparing Mn spinels with Li doping only, and the capacity fading during cycling and storage at elevated temperature for the half cells and Li-ion batteries is discussed in more details based on their special structure.

Experimental

The new kind of spinel designated Li010-N600 is prepared by the method described elsewhere with 0.10 LiOH for 1.0 LiOH in the starting material is added in the second step.² The determined chemical composition of Li010-N600 is $\text{Li}_{1.094}\text{Mn}_{1.906}\text{O}_{4.025}$ and it can be written in $[\text{Li}]_{8a}[\text{Li}_{0.087}\text{Mn}_{1.894}\square_{0.019}]_{16d}[\text{O}_4]_{32e}$. Another two spinels designated Li010-C800 and Mn800 were prepared by conventional method with composition of $\text{Li}_{1.10}\text{Mn}_{1.90}\text{O}_4$ and LiMn_2O_4 respectively (calculated from the starting mixture of LiOH and MnO_2). The electrochemical performance of half cells and ion batteries based on these materials were evaluated at elevated temperatures with 1M LiPF₆ in EC/DMC by making CR2032 coin cells.

Results and discussions

Although Li-doped spinels have been investigated intensively, significant capacity loss upon cycling at elevated temperature still could be observed by other researchers.³ In contrast, excellent cycling performance for our material Li010-N600 with about 3% capacity loss after 50 cycles at 60°C was shown in Figure 1. As for the conventional material Li010-C800, about 8% capacity is lost after 50 cycles although their Li-doping content is almost the same as Li010-N600. Until now, several theories including the Jahn-Teller distortion, Mn dissolution, two-phase coexistence and oxygen defect had been proposed for the capacity fading at room temperature or elevated temperature, but no consensus had yet been reached. Despite these different mechanisms, resultant change of partial spinel from active for reversible Li^+ storage to inactive is sure. In the dynamic evolution process, some Mn cations may emigrate from the 16d sites to 8a or 16c sites to form inactive impurities such as $\beta\text{-MnO}_2$. It is proposed that existence of vacancies in the 16d sites as well as partial substitution of Mn cations can suppress the going-on of deactivation process

especially at elevated temperatures. Therefore, cycling performance at both ambient and elevated temperatures was improved.

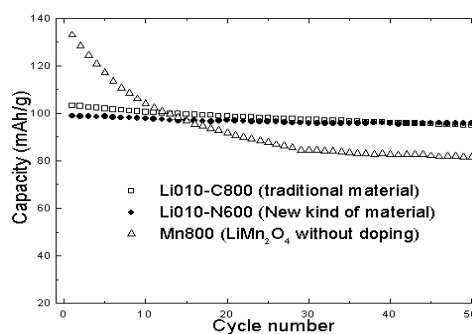


Figure 1. Comparison of the cycling performance of Li010-N600, Li010-C800 and Mn800 materials at 60°C. The charge /discharge current is 0.8 mA/cm².

Li-ion batteries based on Li010-N600 cathodes were evaluated by using MCMB6-28 as anodes to fabricate coin cells. The cycling performance of Li010-N600 ion batteries is observed to be comparable with that of $\text{LiCoO}_2/\text{MCMB}$ at both room temperature and 60°C, although the initial capacity of the latter one is larger. Judging from our preliminary results, our new spinels showed promising future in the practical application of replacing LiCoO_2 .

References

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