Stabilized Oxygen Stoichiometric Lithium Manganese Oxide Spinel Cathode $(Li,Mn,M)_3O_{4+\delta}$ at Elevated Temperatures

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Presently, much interest has been focused on applying lithium ion batteries for the electricity of power storage systems and hybrid electric vehicles (HEV) because of their high gravimetric and volumetric energy density In these applications, lithium manganese oxide spinel compounds $(Li,Mn,M)_3O_4$, M = metal ions) is the most promising alternatives as the cathode for lithium ion batteries, because of its low cost, less toxicity and material safety in the charged state in addition to the high rate capability (over than 20C). .

We reported previously that capacity fading during cycling of the spinel electrode at room temperature occurred only in the high-voltage region and it was caused mainly by the unstable two-phase structure co-existing in this region for lithium ion insertion/extraction [1]. To overcome the problem is doping the foreign metal ion (M) in to the spinel structure as reported in elsewhere.

One of the important problems for commercial use of spinel compounds as a cathode is the capacity fading at elevated temperatures (2).

Recently we have demonstrated that main reason of the capacity fading at the elevated temperature is due to the oxygen deficiency in the spinel structures and oxygen stoichiometric spinel shows the excellent cycle performance even in the elevated temperatures (3,4).

The other problem using spinel cathodes would be the manganese ion dissolution at the elevated temperature, which cause degradation of the graphite anode. Soluble manganese species diffuse through the electrolyte to reach the carbon anode and deposited Mn at the surface of the graphite induces the degradation on the anode side. We believe that the solubility of Mn ion in the electrolyte at the elevated temperatures should be less than 10 ppm and/or no structure change in XRD. It was reported that the solubility of conventional spinel are around 100 ppm (5).

From these viewpoints, we have developed the new preparation method of stabilized spinel in the elevated temperature application, as follows.

First heating process:

Using rather high heating temperature for suppressing the surface area, which causes the low solubility of manganese ion.

Second heating process:

Using lower heating temperature under additives and/or O_2 atmosphere for making oxygen stoichiometric spinels.

Fig.1 shows the charge-discharge tests, which was carried out at constant current ($0.4mA \cdot cm^{-2}$) between 3.5V and 4.5V at 60°C. The cathodes were consisted of 25mg of oxygen stoichiometric spinel, $(Li,Mn,Mg)3O_{4+\delta}$, and oxygen deficient spinel, $(Li,Mn,Mg)3O_{4-\delta}$. The anodes were consisted of graphitized mesophase carbon (MCMB6-28). The CR2032 type coin cells were constructed and 1M $LiPF_6$ EC-DMC(1:2 by volume) as electrolyte solution.

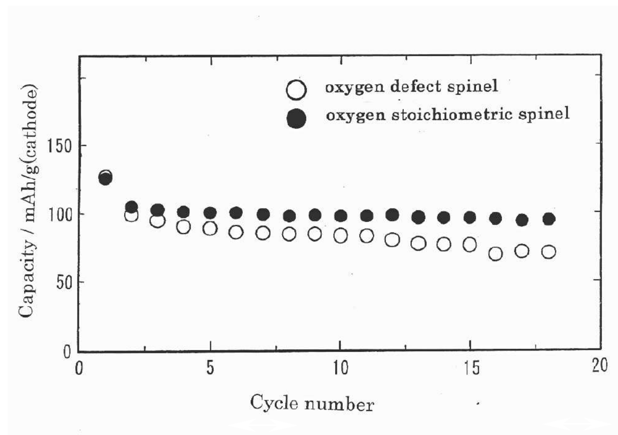

Fig.1. Cycle performance of Li-Ion batteries at 60°C:(●) oxygen stoichiometric spinel, $(Li,Mn,Mg)3O_{4+\delta}$, and (○) oxygen deficient spinel $(Li,Mn,Mg)3O_{4-\delta}$, as a cathode.

Our conclusion is as follows; No structure change by XRD after several weeks' storage in the electrolyte at the elevated temperature is important factor. We have developed the new stabilized spinel in the elevated temperature performance by the two-step heating process. .

References

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