Capacity Fade and Mn Dissolution of $LiMn_2O_4$

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Introduction

The lithium ion rechargeable batteries are used as power sources of portable computers, cellular phones, and so on today, and $LiCoO_2$ have been used as the cathode materials in almost all of them. Nevertheless, in the case of large-scale batteries for electric vehicles or load leveling systems, $LiMn_2O_4$ is preferred, because of its low cost, low toxicity and good stability at the overcharged state. However, $LiMn_2O_4$ has two big problems at elevated temperatures: capacity fade over charge-discharge cycling, and dissolution of Mn into the electrolyte. Recent studies have focused on the relationship between capacity fade or dissolution of manganese and the Depth Of Discharge (DOD). In this work, we present the capacity fade and Mn dissolution from $LiMn_2O_4$ at elevated temperatures and their dependence on the DOD.

Experimental

The electrochemical properties of the samples were evaluated as cathode materials in 2016 coin type cells (diam. 20mm, height 1.6mm) consisted of a lithium anode and an electrolyte of 1M $LiPF_6$ in mixture of ethylene carbonate and dimethyle carbonate. Cells were assembled in dry air atmosphere, and cycled between the voltage limits of 4.25V and 3.00V at a current of 1.0mA.

Results and Discussion

The capacity retention of a coin type cell with spinel manganese oxides (A:$Li_{1.05}Mn_{1.95}O_{4.00}$ B:$LiCr_{0.15}Mn_{1.85}O_{4.00}$) after 125 hours storage in a 60 ºC oven at different DOD are shown in Fig. 1. Capacity retention is almost constant below 50%, decreases with the proceeding of DOD in the range of 50% to 80% and increases with proceeding of DOD at over 80%.

The concentration of manganese dissolved from $Li_{1.05}Mn_{1.95}O_{4.00}$ stored at different DOD in 60 ºC for 125 hours is shown in Fig. 2. The amount of dissolved Mn depends on the DOD, and obviously relates to the capacity retention shown in Figure 1.

It is suggested from above mentioned results that capacity fade and Mn dissolution are caused by the same mechanism. This phenomenon is considered to be the essential deterioration of spinel manganese oxides.

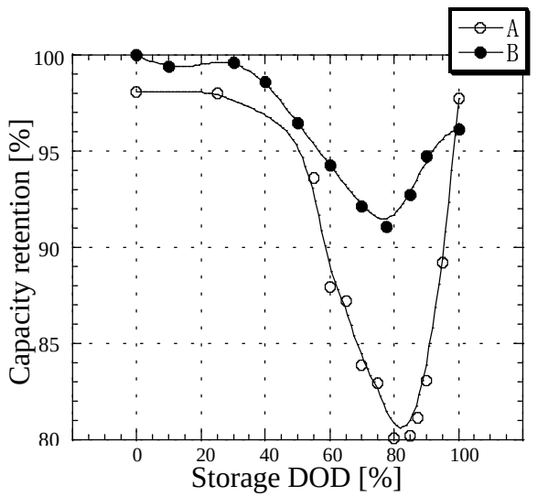

Fig.1 Storage performances of manganese spinel cathodes at different DOD, at 60 ºC for 125 hours.
A:$Li_{1.05}Mn_{1.95}O_{4.00}$
B:$Li_{1.00}Cr_{0.15}Mn_{1.85}O_{4.00}$

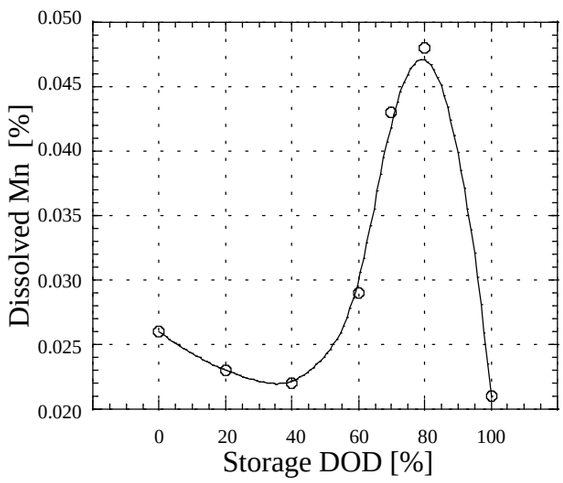

Fig.2 Amount of dissolved Mn from $Li_{1.05}Mn_{1.95}O_{4.00}$ after storage in electrolyte at 60 ºC for 125 hours.