

**$\text{Li}_{1\pm\delta}[\text{Mn}_{2-x}\text{Li}_x]\text{O}_4$ 전극의 망간 산화수가 전기화학적 리튬
인터칼레이션에 미치는 영향에 대한 연구**

**Effects of Oxidation State of Manganese Ion
on the Electrochemical Lithium Intercalation
into $\text{Li}_{1\pm\delta}[\text{Mn}_{2-x}\text{Li}_x]\text{O}_4$ Electrode**

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The effect of Mn valence on lithium intercalation reaction into porous $\text{Li}_{1\pm\delta}[\text{Mn}_{2-x}\text{Li}_x]\text{O}_4$ electrodes with various excess lithium contents of $x=0$ to 0.2 was investigated in 1M LiClO_4 propylene carbonate(PC) solution by using galvanostatic intermittent titration technique(GITT), electrochemical impedance spectroscopy(EIS) and charge-discharge experiment. $\text{Li}[\text{Mn}_{2-x}\text{Li}_x]\text{O}_4$ powders with various compositions were prepared by solid state reaction at 800°C for 18 h in air, and their crystal structure and the degree of occupation of lithium ion in 8a(tetrahedral) and 16d(octahedral) sites were identified by Rietveld refinement analysis. Electrochemical impedance measurements were carried out by superimposing an ac voltage of 10 mV amplitude ranging between 1 mHz and 100 kHz on a dc potential range 3.0 to 4.4 $V_{\text{Li/Li}^+}$. From the results of impedance measurements for $\text{Li}_{1\pm\delta}[\text{Mn}_2]\text{O}_4$ electrode, absorption resistance associated with the arc in the middle frequency range of 50 mHz to 50 Hz increases abruptly at $(1\pm\delta)$ above 1.0. This is presumably due to Jahn-Teller distortion occurred when the average oxidation state of manganese ion is below 3.5. In contrast, $\text{Li}_{1\pm\delta}[\text{Mn}_{2-x}\text{Li}_x]\text{O}_4$ electrodes with excess lithium contents of $x=0.1$ and 0.2 , showed smaller absorption resistance above $(1\pm\delta)=1$ because of high average oxidation state of manganese ion. The GITT and EIS results showed that the factors affecting the absorption reaction into the $\text{Li}_{1\pm\delta}[\text{Mn}_{2-x}\text{Li}_x]\text{O}_4$ electrode are not only the number of vacant sites available for lithium ion diffusion and size of diffusion path, but also oxidation state of manganese metal ion in the host lattice. The discharge capacities of $\text{Li}_{1\pm\delta}[\text{Mn}_2]\text{O}_4$ and $\text{Li}_{1\pm\delta}[\text{Mn}_{2-x}\text{Li}_x]\text{O}_4$ electrodes with respect to cycling of the cell were measured by using charge-discharge experiment. From the experimental results, it was found that $\text{Li}_{1\pm\delta}[\text{Mn}_2\text{Li}_x]\text{O}_4$ has smaller initial capacity but better rechargeability than $\text{Li}_{1\pm\delta}[\text{Mn}_2]\text{O}_4$.

References

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