리튬 이차전지용 전극재료인 Li[Li_{1/3}Ti_{5/3}]O₄ 에서의 전기화학적 리튬 인터칼레이션에 대한 연구

A Study on the Electrochemical Lithium Intercalation into Li[Li_{1/3}Ti_{5/3}]O₄ as an Electrode Material for Rechargeable Lithium Battery

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The electrochemical lithium intercalation into porous Li[Li_{1/3}Ti_{5/3}]O₄ electrode has been investigated in 1M LiClO₄ propylene carbonate solution by using galvanostatic intermittent titration technique(GITT) in combination with electrochemical impedance spectroscopy(EIS) and potentiostatic current transient technique. Li[Li_{1/3}Ti_{5/3}]O₄ powder was synthesized by solid state reaction at 800 °C for 24 h in air, and then identified as a defect spinel-framework structure with a space group Fd3 m by X-ray diffractometry. From the results of GITT, the apparent chemical diffusivity of lithium ion in the porous oxide electrode was determined to be $10^{-9} \sim 10^{-10} \text{ cm}^2 \text{s}^{-1}$ at room temperature in the lithium content range of 1.1 to 1.5. The charge-discharge curve displayed a wide potential plateau near 1.56 $V_{\rm Li/Li^+}$ in the (1+ δ) range of 1.0 to 1.6 in $\text{Li}_{(1+\delta)}[\text{Li}_{1/3}\text{Ti}_{5/3}]O_4$ electrode. The occurrence of the plateau is due to the coexistence of two pseudo-phases of a Li-diluted phase a and a Li-concentrated phase B. The impedance spectra of the electrode consisted of two separated arcs in the high and intermediate frequency range 1 Hz to 100 kHz, and a line inclined at approximately 45° to the real axis in the low range 10 mHz to 1 Hz. The typical current transients during the lithium intercalation were divided into three stages, and the third stage disappeared below the lithium charging potential of 1.50 $V_{\text{Li/Li+}}$. However, the third stage was not observed clearly during the lithium deintercalation over the whole potential range investigated. The lithium transport through porous Li[Li_{1/3}Ti_{5/3}]O₄ electrode was discussed in terms of diffusion-controlled phase boundary movement and variation of lithium ion diffusivity with lithium content.

References

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