

A Study on Electrochemical Reaction Mechanism of RuO₂ Using Synchrotron Based X-Ray Techniques.

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Abstract

Recently, various transition metal oxides (M= Fe, Ni, Co, Cu) have been studied as alternative anode materials for lithium ion batteries. Focusing on the higher energy density of anode materials, reinvestigation of conversion reaction in Li-ion battery using a representative material RuO₂ has shown an important evolution in the reaction mechanism. Ruthenium oxide is a well known as anode material for its high capacity (1130mAh/g) and high coulombic efficiency (98%, at the first cycle). RuO₂ stored 5.6M Li during the first discharge. Li up to 4mol per mole RuO₂ is stored by the insertion and conversion reaction. Generally, additional capacity of RuO₂ explained is related to the interfacial reaction^{1,2}.

Although electrochemical reaction mechanism of RuO₂ is suggested in previous report, it is still difficult to prove the mechanism perfectly. For explaining the additional capacity, it is important to know the insertion and conversion reaction clearly. In this work, we have tried to explain the electrochemical reaction mechanism of RuO₂ by using *in situ* X-ray Diffraction (XRD) and X-ray Absorption Spectroscopy (XAS) during first discharge.

Ruthenium oxide powder is purchased from Alfa and annealed in air at 350°C. The working electrode was consisted of annealed RuO₂ powder, polyvinylene difluoride (PVDF) in 10 : 1 weight ratio. *In situ* cell is assembled with Li foil, Celgard separator, and 1.3M LiPF₆ dissolved in a 3:7 volume mixture of EC (ethylene carbonate): DEC (diethyl carbonate) in the argon-filled glove box.

This electrochemical reaction mechanism is studied by *in situ* XRD pattern. Appearance of new peak could be attributed to formation of LiRuO₂ phase and at the same time, RuO₂ phase disappears during discharge in the Fig 1(a). The change of XRD pattern is reflected in the results of insertion reaction.

We tried to combine *in situ* XAS for getting closer insight into the reaction mechanism. After insertion reaction, there is an appearance of Ru metal peak

which is due to effect of conversion reaction.

This study suggests that, Li storage in RuO₂ takes place via phase transformations. RuO₂ transformed into LiRuO₂ by Li insertion, intermediate LiRuO₂ turns to Li₂O and Ru metal by conversion reaction. It is clearly evidenced by the *in situ* XRD, XAS studies.

The more detailed mechanism of RuO₂ during discharge will be presented at the time of meeting.

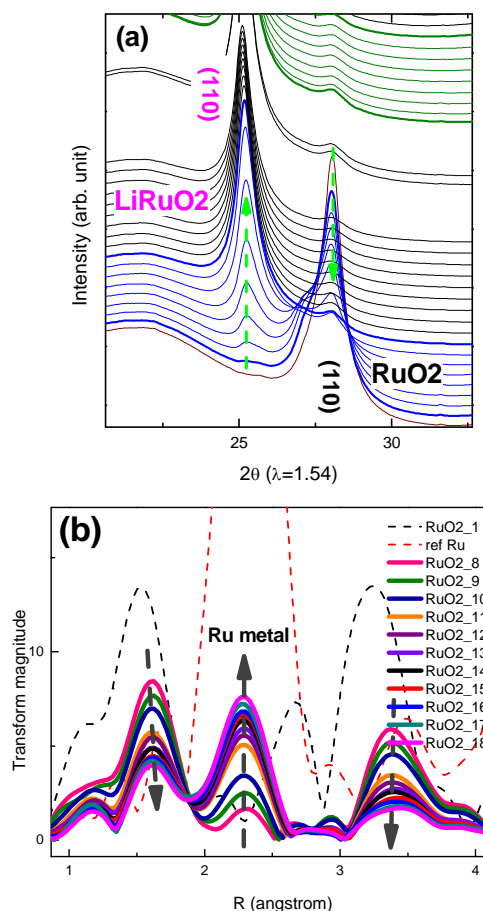


Fig.1 (a) *in situ* XRD, (b) *in situ* EXAFS pattern (Fourier transforms(FTs) of the K³-weighted Ru K-edge, FT range is 2.0 – 13.8Å⁻¹) during the first discharge at constant current density 100mA/g, voltage range : 0.05-4.3V.

Reference

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