Temperature dependence of XRD for hybrid chiral metal complexes and its applications as energy materials (in 2013)

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1 Introduction

In recent development of rechargeable lithium (or larger sodium, if possible) ion battery materials, decomposition of regular crystal structures of metal oxide materials during charge/discharge is pointed out as one of serious problem to attain desirable functions. In order to overcome this issue, we have proposed hybrid composition of metal oxide materials such as $LiMnO_2$, a typical lithium ion battery material, and chiral metal complexes, such as flexible Cu(II) ones associated with Jahn-Teller distortion, exhibiting anisotropic (thermal) lattice distortion to control changing crystal structures.

In last year (2012), we have successfully proved this concept for composite materials composed of anatase TiO_2 as an anode material and chiral Cu(II) complexes, $[CuL_2]_3[Co(CN)_6]_2 \cdot 4H_2O$ and $[CuL_2(H_2O)_2](NO_3)_2$ (L = (*1R, 2R*)-cyclohexanediamine) [1]. However, because of isotropic crystal structure of TiO_2, the effect of structural regulation by surface adsorption of anisotropic additives between their grains or domains could not be observed clearly. In this time, herein, we have employed a cathode material $LiMnO_2$ with anisotropic and layered crystal structure. We have investigated thermally-accessible lattice strain of $[CuL_2]_3[Fe(CN)_6]_2 \cdot 4H_2O$ and $[CuL_2(H_2O)_2](NO_3)_2$ (L = (*1R, 2R*)-cyclohexanediamine), by means of variable temperature PXRD measurements in which the former was compared with H_2O and D_2O for isotope effect.

2 Experiment

For example, composite materials composed of $[CuL_2(H_2O)_2](NO_3)_2$ and $LiMnO_2$ of molar ratios of 0:10 (pure $[CuL_2(H_2O)_2](NO_3)_2$), 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, 9:1, 10:0 (pure $LiMnO_2$) were prepared by grinding in the solid states. IR spectra were measured to confirm surface adsorption of the compounds. Variable temperature PXRD patterns were obtained at KEK PF BL-8B (8 keV, at 100-300 K every 10 K).

3 Results and Discussion

By increasing the ratios of $[CuL_2(H_2O)_2](NO_3)_2$ in the composite materials, IR bands at 611 cm^{-1} (Mn-O) indicated low-wavenumber shift gradually. The corresponding PXRD patterns at constant 300 K exhibited the (010) peaks shifts of due to elongation of lattice constants of the *b*-axis of $LiMnO_2$. Variable temperature PXRD patterns of the 5:5 composite at 300-100 K exhibited gradual shifts for predominant (010), (011), and (002) peaks, which were different from that of pure $LiMnO_2$.

In order to discuss interplanar distance changes by temperature changes, we have proposed the following evaluation function of approximation straight line.

$$\ln K = a/T + b$$

where K $= d(T)\text{-}d(0)/d(T)$, $d(T)$ and $d(0)$ are $d = n\lambda/(2\sin\theta)$ at T K and 0 K (extrapolated), respectively. Fig. 1 suggested that direction of (011) indicated remarkable s changes.
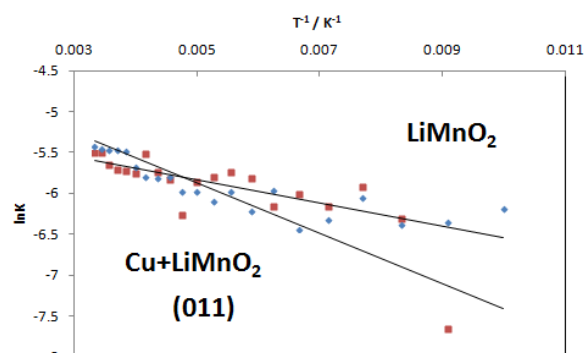

Fig. 1. The lnK vs T^{-1} plot for the 5:5 composite.

For comparison, we also evaluated temperature dependence of each lattice constant with a Rietveld software. The *b*-axis direction (along the layered stacking of the crystal structure of $LiMnO_2$) indicated remarkable s changes.
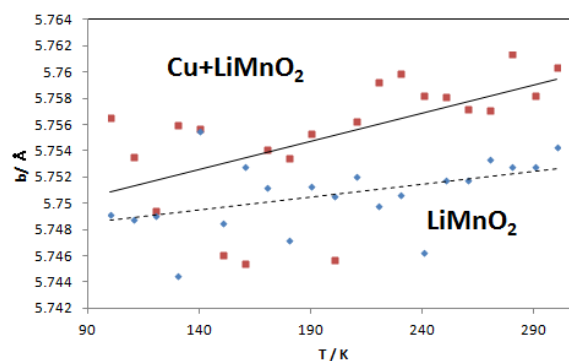

Fig. 2. The *b*-axis vs T plot for the 5:5 composite.

References

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