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Effect of lanthanum dopant on the structural and electrical properties of LiCoVO_4 cathode materials investigated by EXAFS

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Abstract

The effect of lanthanum dopant on the structural and electrical properties of LiCoVO_4 cathode materials was investigated by X-ray absorption spectroscopy (XAS). The conductivity of LiCoVO_4 was increased from 8.44×10^{-9} to 7.17×10^{-8} S/cm by doping proper amounts of La_2O_3 . The doping of La results in slightly decreasing the oxidation states of Co and V and the intensity of Fourier transform (FT) around absorbing atom Co and V. It may result from the distortion of the inverse spinel structure of LiCoVO_4 . It was suggested that La dopant located in interstitial site near vanadium atom to make the tetragonal distortion. This distortion is contributed to the generation of the defects in the doped LiCoVO_4 and the enhancement of its conductivity. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: LiCoVO_4 ; Conductivity; La-doped; XAFS

1. Introduction

Since the discovery of both of LiNiVO_4 and LiCoVO_4 as new systems of cathode materials for secondary lithium batteries [1], interest in inverse spinel materials has arisen due to their high voltage behavior. It is necessary to mix them with some good electrical conductor such as carbon black to ensure that the electrode has sufficient electrical conductivity during electrode preparation [2] because the electrical conductivity of these materials is poor. However, the addition of carbon black lowers the electrode material's energy density. The use of a dopant to a material of interest is a widely used method to improve its electrical conductivity. The dopant effects of introducing rare earth atoms into the LiNiVO_4 inverse spinel structure were reported in our previous paper [2]. The conductivity of LiNiVO_4 increased significantly with the incorporation of trace amounts of the La_2O_3 [2]. It is interesting to establish the relationship between the structure and state changes and the enhancement of the conductivity of these materials prepared at various level of dopant. Unfortunately, it is difficult to distinguish the change of the structure by powder diffraction techniques.

X-ray absorption fine structure (XAFS) spectroscopy has been applied in lithium batteries to study lithium insertion transition metal oxides LiCoO_2 [3,4] and LiNiO_2 [5,6]. XAFS is able to probe not only the electronic but also local structural environment around a selected absorbing atom. It is a powerful tool to investigate the variation of the local structure and the oxidation state of an absorbing metal.

In this study the local structure changes and the oxidation state of Co and V in LiCoVO_4 doped with different concentration of La_2O_3 were investigated by XAFS. The relationship between the conductivity and the changes of the local structure was also discussed.

2. Experimental

2.1. Powder preparation

The doping process of LiCoVO_4 with trace amounts of rare earth elements was conducted as follows. First, $\text{LiOH}\cdot\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, NH_4VO_3 , La_2O_3 (available from Aldrich, 99% purity) were weighted according to the mole ratio of $\text{Li}:\text{Co}:\text{V}:\text{La} = 1:1:1:y$, where $y = 10^{-1}$, 10^{-2} , 10^{-3} , 10^{-4} , 10^{-5} . Since La_2O_3 is air-sensitive, it was weighted in the glove box filled with argon. Then, La_2O_3 was dissolved into dilute nitric acid, forming a colorless

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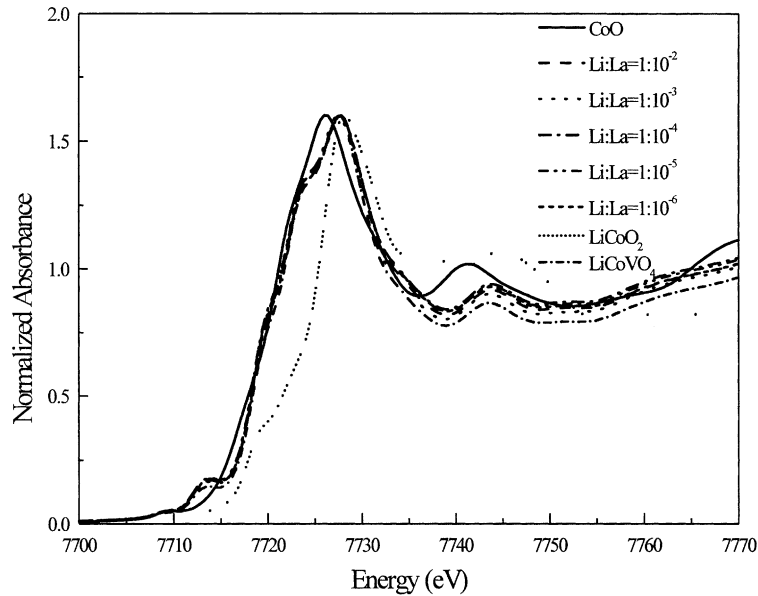


Fig. 1. Normalized absorbance of Co K-edge for CoO, LiCoO₂ and LiCoVO₄ doped with different mole ratio of La₂O₃.

solution of trivalent cations of rare earth element. The acidic solution of La₂O₃ was added to a red solution containing LiOH, Co(NO₃)₂, NH₄VO₃, and a yellowish-brown precipitate was readily formed with sufficient stirring. After filtration, the precipitate was dried at 100°C and then heated at 700°C for 2 h. A yellowish-brown solid was obtained.

A weighted amount of powdery sample was pressed into a thin pellet under a pressure of 10 t. The resistivity values were measured by means of a Keithley 617 programmable electrometer using a two-probe technique. The conductivity of the pellet was calculated from the measured resistance and physical dimensions of the pellet.

2.2. XAS measurement

The X-ray absorption experiments were performed on the beamline of wiggler C (S5C) in the Synchrotron Radiation Research Center (Taiwan) with the electron storage ring operating at an electron energy of 1.5 GeV and stored current in the range 100–200 mA. The samples were ground finely and spread uniformly onto an adhesive tape of Kepton. The tape was folded into a few layers to obtain an appropriate absorption edge ($\mu x = 1$). Spectra of Co K-edge (7709 eV) and V K-edge (5465 eV) were obtained in the transmission mode at room temperature (300 K). Data analysis of the

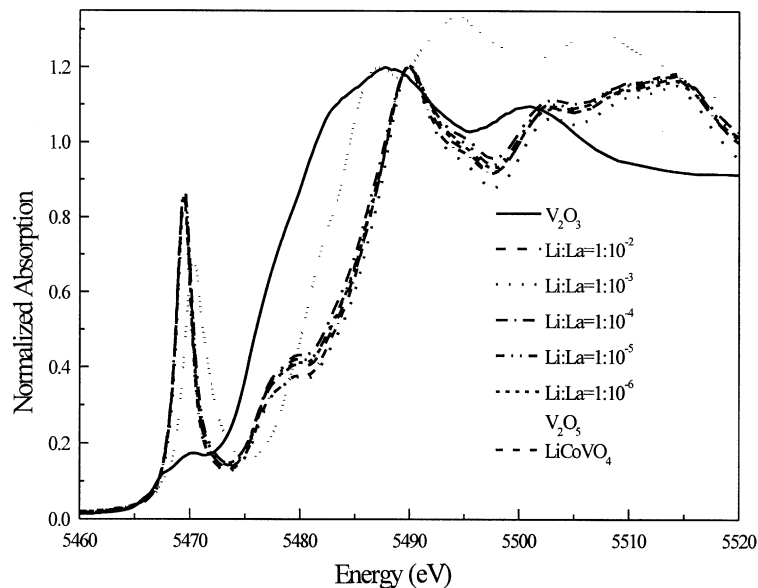


Fig. 2. Normalized absorbance of V K-edge for V₂O₃, V₂O₅ and LiCoVO₄ doped with different mole ratio of La₂O₃.

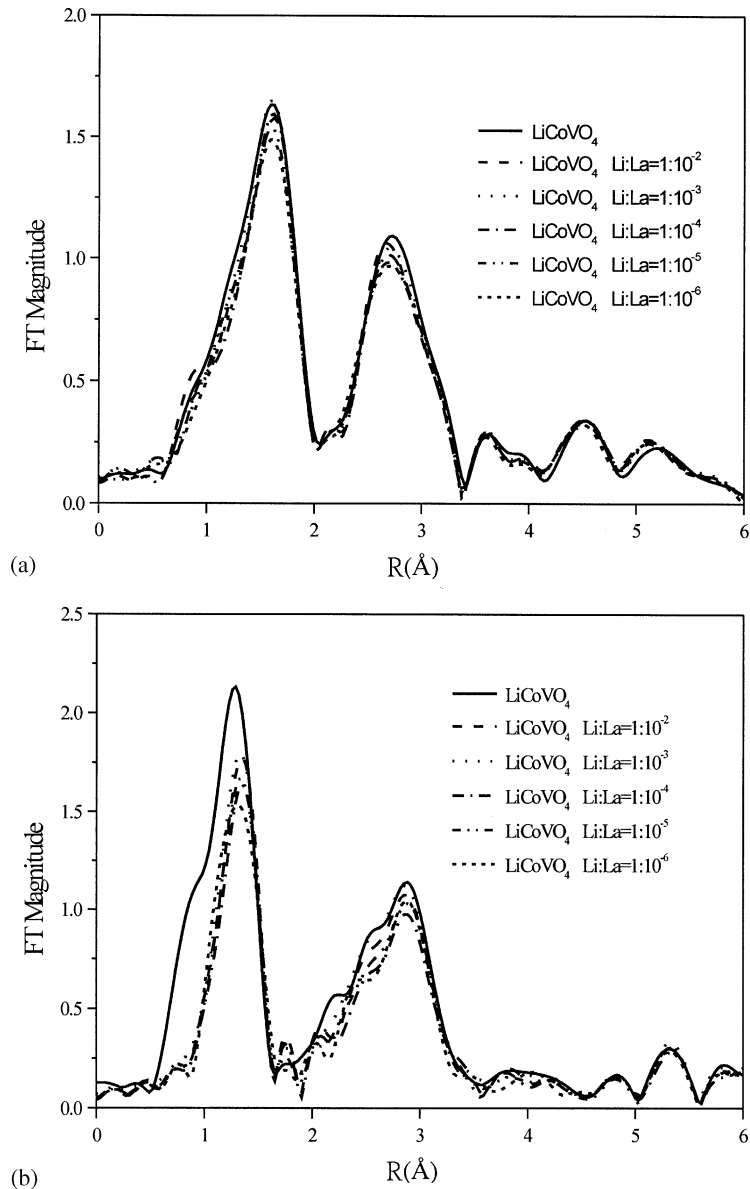


Fig. 3. Fourier transform of X-ray absorption spectra for (a) Co and (b) V K-edges.

experimental spectra was performed with the computer program, UWXAFS 3.0, which employed curved wave theory using the scattering parameters obtained by ab initio FEFF7 code.

2.3. Data analysis

Local structure parameters such as the coordination number (N), coordination distance (R), and the mean square relative displacement (σ^2) were extracted using non-linear least-squares fitting procedures based on FEFFIT. The fits of Co K-edge and V K-edge spectra were performed over the r -space range 0.49–3.53 and 0.58–3.41 Å, which were generated by Fourier filtering over the k -space range 2.04–13.67 and 2.08–11.82 Å⁻¹ with k^2 -weighting and a Hanning win-

dow ($dk_1 = dk_2 = 1.5 \text{ Å}^{-1}$). Initially, a three-shell fit was used to analyze each data set. The first shell was used to account for Co–O distance. The second and third shells were used to account for Co–Co and Co–V distances. In all fits, the sum of the coordination numbers for the Co–O bonds was constrained to be 6. The fit of V K-edge is in process.

3. Results and discussion

The conductivity data of lanthanum-doped LiCoVO₄ at room temperature were measured. The data collected were the initial conductivity values measured by a pseudo ac non-polarization method with minimum influence attributable to polarization. The initial value was an average of 10

measurements by manually alternating electrode polarity back and forth continuously. The electrical conductivity values measured in this way represent sums of ionic and electronic conductivity, actually higher than those measured by a dc method which reduces ionic conductivity significantly due to extensive measuring time. The pure LiCoVO_4 showed conductivity in 8.44×10^{-9} S/cm. The electrical conductivity of La-doped LiCoVO_4 were 4.03×10^{-10} , 5.02×10^{-10} , 7.17×10^{-8} , 1.16×10^{-8} , and 2.01×10^{-8} S/cm as the mole ratios of LiCoVO_4 :La were from 10^2 to 10^6 , respectively.

The Co and V K-edge XANES spectra of LiCoVO_4 doped with different content of Lanthanum were shown in Figs. 1 and 2, respectively. CoO , LiCoO_2 , V_2O_3 , and V_2O_5 were used as reference compounds. The edge will shift to the high energy as the oxidation state of the absorbed atom increased. Since the Co K-edge of the doped LiCoVO_4 is located between that of CoO and LiCoO_2 , it can be concluded that its oxidation state of the Co atom is between +2 and +3 (approaches +2). Similarly, the oxidation state of the V in the doped LiCoVO_4 compared with V_2O_3 (+3) and V_2O_5 (+5) is between +4 and +5 (approaches +5). From the edge structure, it can be seen that the Co and V edge of the doped LiCoVO_4 shifts to lower energy compared to that of the undoped LiCoVO_4 . It implies that valence of Co and V tends to +2 and +4 for the doped LiCoVO_4 , respectively.

The Fourier transforms (FTs) of the Co and V K-edge EXAFS spectra of La-doped LiCoVO_4 were shown in Fig. 3(a) and (b). It was found that the magnitude of FTs at both edges decreased as LiCoVO_4 was doped with La. It implies that the local structure of LiCoVO_4 around the Co and V absorbing atoms changed slightly with the addition of La element. The depression of the magnitude of FTs around absorbing atom Co and V may result from the distortion of the inverse spinel structure of LiCoVO_4 . The FTs' peak of the first shell V–O was significantly reduced as LiCoVO_4 was doped with La, as shown in Fig. 3(b). It was suggested that La dopant located in interstitial site near vanadium atom to make the tetragonal distortion. Since the doped La is in interstitial site, the oxidation states of Co and V will decrease due to the charge balance. This conclusion is

consistent with the results of the XANES. Meanwhile, the distortion will generate more defects in the structure of LiCoO_4 and enhance its conductivity. The distance of Co–O, Co–Co and Co–V are 2.07 ± 0.01 , 3.07 ± 0.01 and 3.45 ± 0.01 Å, respectively.

4. Conclusion

The structural change and oxidation state of La-doped LiCoVO_4 were investigated by X-ray absorption spectroscopy (XAS). The valence of Co and V in undoped LiCoVO_4 is close to +2 and +5, respectively. The valence of absorbing atom Co and V shifts to lower value because the charge of La^{3+} will be balanced by the oxygen atoms around Co and V. Since the intensity of Fourier transform of the first shell V–O was decreased more significantly, it was concluded that La dopant located in interstitial site near vanadium atom to make the tetragonal distortion. This distortion is contributed to the generation of the defects in the doped LiCoO_4 and the enhancement of its conductivity.

Acknowledgements

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