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Internal Friction Characterization of Positive Electrode of Lithium Ion Battery by Using Vibrating Reed Technique

振動リード法を用いたリチウムイオン電池正極内部摩擦の評価

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1. Introduction

Organic materials are used to lithium ion battery (LIB) to adhere the active materials on metal electrode as well as the grains of the active materials. Recently, a novel organic coating method to enhance the performance of the battery by surface modification on a molecular scale was reported, and significant improvement in electrochemical properties of $LiMn_2O_4$-based cathodes was obtained by applying a direct coating of PEDOT[1].

The organic binder plays an important role on both performance and lifetime of the LIB. In this work, we will report a useful way, vibrating reed technique, to characterize the viscous properties of organic component in the LIB.

2. Experimental

The positive-electrode was composed of a sandwich structure of the $Li(NiCoAl)O_2$/Alminium/$Li(NiCoAl)O_2$. The active materials with thickness of 79 μm were coated on the surfaces of Al foil with thickness of 27μm. The electrode was cut to the reeds having dimensions of $5.0\times0.185\times l$ mm^3, where l is 27 mm, 29 mm, 31 mm and 39 mm, corresponding to resonance frequencies of 75.8, 64.7, 53.3 and 38.6 Hz at room temperature, respectively.

The vibrating reed was set in a copper box in a vacuum chamber under residual gas pressure below 3×10^{-4} Pa. One end of the reed was fixed on ground electrode, the copper box, as shown in **Fig.1**. An alternating voltage was applied on the free end of the reed to vibrate the reed.

The displacement of the free end was measured using a laser/CCD camera displacement sensor with accuracy of 10 nm. Temperature of the reed sample set in the copper box was changed from 100 K to 400 K in steps of 5 K. The amplitude, A, of vibration of the free end can be decreased exponentially with time t, $A=A_0e^{-\alpha t}$ due to the viscous loss. Internal friction Q^{-1} was determined from the α, $Q^{-1}=\alpha/\pi f$, where f is the resonance frequency of the reed.

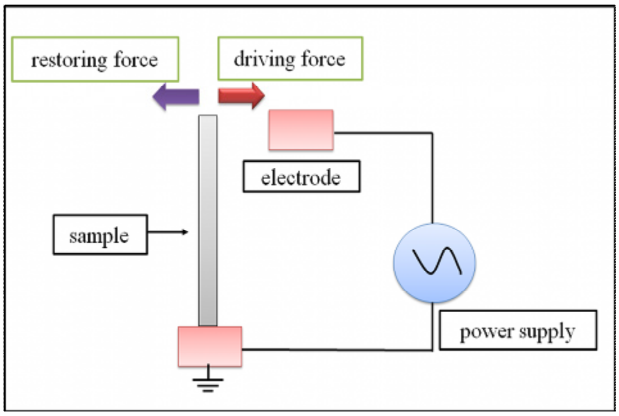

Fig.1 Schematic diagram of the vibrating reed measurement system.

3. Results and Discussion

Fig.2 shows the x-ray diffraction pattern of the positive-electrode sample. Diffraction peaks from (003), (101) and (104) planes of $Li(NiCoAl)O_2$ structure are observed.

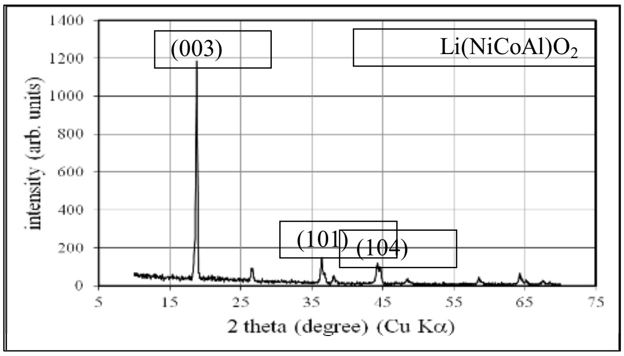

Fig.2 X-ray diffraction pattern of the positive-electrode of the lithium ion battery.

The grain size of the active material was estimated by using Scherrer equation, $\tau=K\lambda/\beta\cos\theta$. The average grain size was 32 nm. Compositional analysis using transmission electron microscopy shown that carbon, oxygen nitrogen and fluorine are observed from the active material. They may be from organic components as such binder.

Resonance frequencies of the vibrating reeds with various lengths are shown in **Fig. 3** as a function of temperature. The resonance frequencies decrease with increasing temperature, and there are two minimums at about 185 K and 260 K.

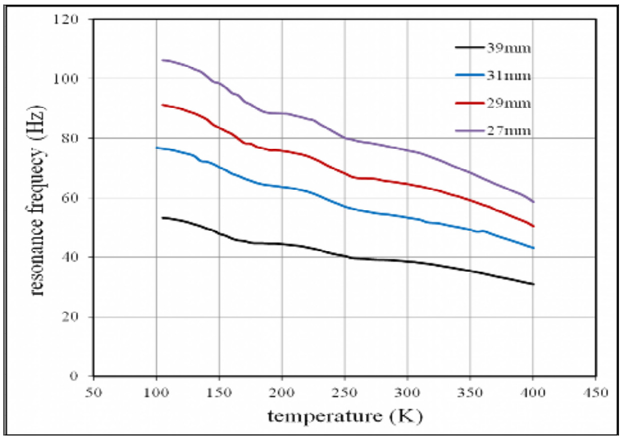

Fig.3 Resonance frequencies of the positive-electrode samples as a function of temperature.

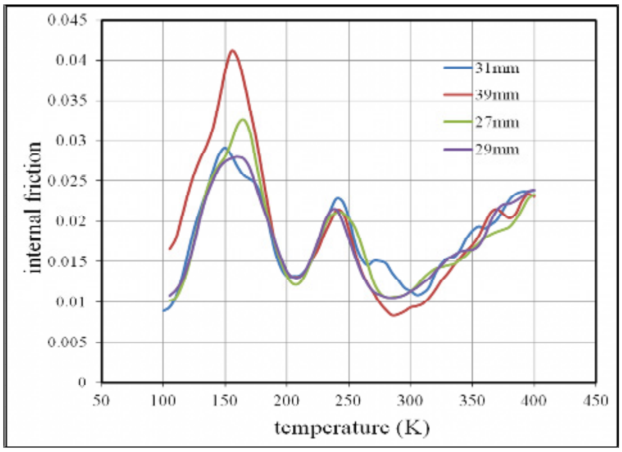

Fig.4 Internal friction of the positive-electrode sample as a function of temperature.

The internal frictions of the positive-electrode at various resonance frequencies are shown in **Fig. 4** as a function of temperature. Two peaks are observed on the temperature dependences. Also, an increase is seen at temperatures above 300 K. It is clear in Fig. 4 that intensities of the internal friction at the peaks are independent of the resonance frequency. This suggests a viscous damping process in the samples at temperatures below room temperature.

We are now in a position to discuss the mechanisms of the internal friction in the positive-electrode of lithium ion battery. First, the strong internal friction peaks with good signal/noise (S/N) ratio can be observed on the positive-electrode at various resonance frequencies as a function of temperature. This suggests that the vibrating reed technique is a useful tool to characterize the properties of organic components in the electrode material, namely, the binding of active material and lifetime of the electrode material.

Second, the intensity of the internal friction peak is independent of resonance frequency of the electrode sample. This fact indicates that the friction is not thermal activation type and is due to a viscosity from the electrode material. Temperature dependences of resonance frequency of the sample also show the same conclusion. The resonance frequency decreases at temperature where the internal friction takes a maximum. The resonance frequency due to a viscosity can be described by $\omega' = \omega(1-\alpha^2)^{1/2}$.

Third, the internal friction peaks are observed at low temperatures but cannot be observed at high temperatures over the wide temperature range of 300~400 K. In general, organic component becomes more fluid at temperatures above room temperature.

Finally, we have also measured the internal friction of the negative-electrode composed of crystalline graphite and organic binder as a function of temperature. Several peaks are also observed at temperatures below 300 K. Our results indicate that the internal friction of the electrodes from grain boundaries and crystalline defects do not be measured when the grains are coated with organic component at temperatures below 300 K.

4. Conclusions

We have measured the internal friction properties of the positive-electrode of lithium ion battery by using vibrating reed technique. Strong friction peaks are observed at temperatures below 300 K. It is a useful method to characterize the properties of organic materials in the electrodes.

Acknowledgements

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References

[1] C. Arbizzani, A. Balducci, M. Mastragostino, M. Rossi and F. Soavi, J. Electroanal. Chem. 553 (2003) 125..

[2] C. Remillat, Mechanics of Materials 39 (2007) 525.

[3] Z. Zhang and G. Hartwig, Cryogenics 38 (1998) 401.

[4] U. Harms, M. Gaertner, A. Schutze, K. Bewilogua, and H. Neuhauser, Thin Solid Films 385 (2001) 275.

[5] F. B. Klose, U. Harms, H. Neuhauser, A. Bakin, I. Behrens, E. Peiner, H. H. Wehmann, A. Schlachetzki and J. Rosler, J. Appl. Phys. 91 (2002) 9031.