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Mechanical Properties of LIB Electrodes Measured by Vibrating Reed Method

振動リード法による LIB 電極の機械的特性評価

Syogo Hatake, Tsuyoshi Noge, Ryo Inagaki, Kenta Kirimoto[1], and Yong Sun
(Kyushu Institute of Technology, [1]Ariaki National College of Technology)
畠 祥悟，野下 剛，稲垣 遼，桐本賢太[1]，孫 勇
(九州工業大学大学院・先端機能システム，[1]有明工業高等専門学校・電子情報)

1. Introduction

In the pursuit of high-perfprmance lithium ion batteries (LIBs), significant effort has been expended to study high-performance cathode and anode materials[1,2]. The ideal architecture of electrode materials for providing efficient ion and electron transport consists of a three-dimensional (3D) interpenetrating network of ion and electron pathways[3,4]. In general, the elastic properties of materials depend sensitively on its architecture such as 3D structure, composition and crystallinity. We have studied the ageing properties of LIB's electrode by measuring its mechanical parameters and showed that the binder PVdF in the electrode plays an important role in the ageing processes[5].

In this study, we measured both resonance frequency and internal friction of electrode reeds of LIB as a function of temperature. The relationships between the remaining useful life (RUL) and the mechanical parameters of LIB electrodes such as resonance frequency and internal friction are studied. Our results indicate that characterization of vibrating reed is a powerful technique to design architecture in new battery development and to measure RUL of the used LIBs.

2. Experimental

The electrodes of LIB were composed of a sandwich structure of the active material/collector/ active metal. The active materials were 80 µm thick for positive-electrode and 60 µm for negative-electrode, respectively. The Al foil (30µm) and Cu foil (20µm) were used as collectors of the positive and negative-electrode. Those electrodes were cut to the reeds having dimensions of $5.0 \times h \times l$ mm^3, where h is electrode's thickness and l is length of the reed. The l was fixed at 25~39 mm in this study. The resonance frequency of the reeds depends on the length l, the thickness h and temperature.

The electrode reed was set in a copper box in a vacuum chamber under residual gas pressure below 1.0×10^{-6} Torr. One end of the reed was fixed on ground electrode, the copper box. An alternating voltage was applied on the free end of the reed to vibrate the electrode sample at a resonance frequency. The displacement of the free end was measured using a laser/CCD camera displacement sensor system with accuracy of 10 nm. Schematic diagram of the measurement system is shown in **Fig. 1**. Temperature of the vibrating reed sample was changed from 100 K to 400 K in steps of 5 K. The vibrating amplitude, A, of the free end can be expressed by $A = A_0 e^{-\alpha t}$ where α the constant of the decay curve and t is time. The amplitude decreases as an exponential of time due to viscous loss, internal friction Q^{-1}, in the reed sample. The Q^{-1} was determined from $Q^{-1} = \alpha/\pi f$ where f is the resonance frequency of the reed sample.

E-mail address: o350924s@mail.kyutech.jp

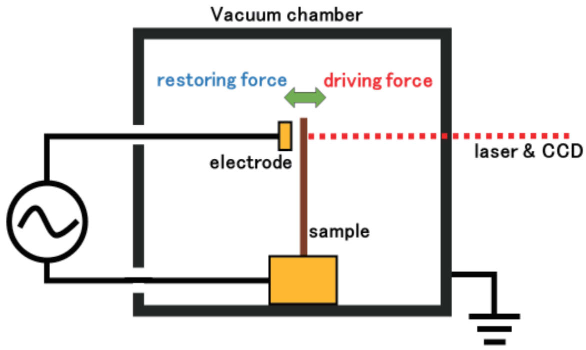

Fig. 1 Schematic diagram of measurement system

3. Results and Discussion

Resonance frequencies of the positive-electrode reeds, which are before charged and discharged cycles, at various lengths are shown in **Fig. 2** as a function of temperature. There are a proportional decrease in the temperature range from 100 K to 400 K and sharp decreases at temperatures at 150 K and 240 K. The sharp decrease corresponds to an internal friction process occurred in the samples.

Internal friction of the positive-electrode reeds which are before charged and discharged cycles, at various lengths are shown in **Fig. 3** as a function of temperature. Two peaks on internal friction curves are observed at temperatures of 150 K and 240 K, and an increase trend is also observed above 300 K. This result is agree with that on the temperature dependences of the resonance frequency as shown in **Fig. 2**.

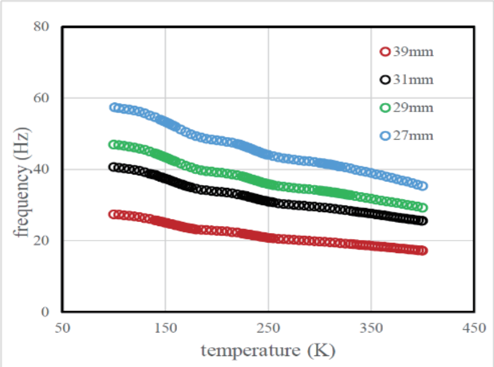

Fig. 2 Resonance frequencies of positive-electrode reeds at various lengths as a function of temperature.

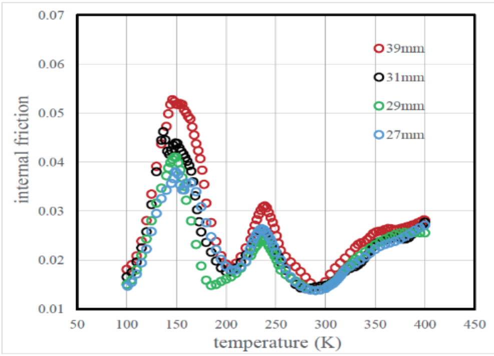

Fig. 3 Internal frictions of positive-electrode at various lengths as a function of temperature.

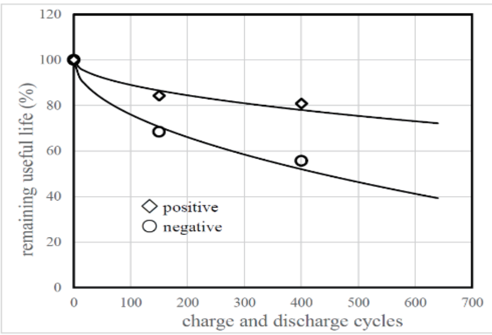

Fig. 4 Remaining useful life of the electrodes as a function of charge and discharge cycle.

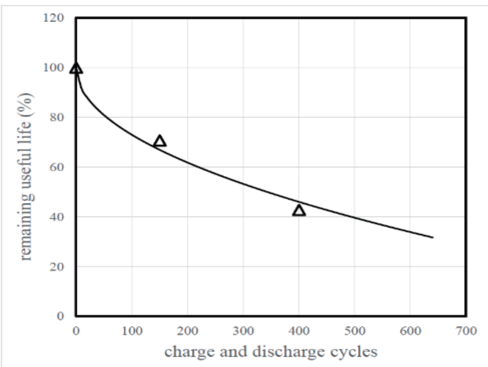

Fig. 5 Remaining useful life of negative-electrode as a function of charge and discharge cycle.

We can obtain the RUL of the electrodes from their resonance frequencies after various charge and discharge cycles. The RUL of the positive and negative electrodes, which are obtained from variations of the resonance frequencies after charge and discharge cycles, are shown in **Fig. 4** as a function of charge and discharge cycles. The solid lines show the results of root fitting, $y = 100 - \beta\sqrt{N}$ where β is a constant and N is number of the charge and discharge cycles. The constant β is 1.1 for positive electrode and 2.4 for negative electrode, respectively. This result indicates that the negative electrode is degraded faster.

The RUL of the negative electrode, which is obtained from activation energies on internal friction processes, are shown in **Fig. 5** as a function of the charge and discharge cycles. The activation energy decreases as a root function with increasing charge and discharge cycle. The constant β is 2.7 for the root fitting. We also must pointed out that no significant results were obtained for the positive electrode due to a large temperature steps of 5.0 K in this study.

4. Conclusions

On the basis of the above experiment results we can conclude as following.

✧ The resonance frequency and activation energy on internal friction process for LIB's electrodes change as a root function of the charge and discharge cycle. This is agree to the RUL of general LIB cell. Therefore, mechanical parameters of the electrodes can be use to characterize properties of the LIB cell, such as life time and architecture of the electrodes.

✧ There is clear difference on the RULs between the positive and negative electrodes. The RUL of the negative electrode is small to that of the positive electrode for the LIB cell used in this study. Therefore, this method is effective for the evaluation of balance of the life time between the positive and negative electrodes.

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