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Ageing behaviors of LiB positive electrode by characterizing mechanical properties

機械特性によるリチウムイオン電池正極の劣化特性評価

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1. Introduction

The changes in the cathode due to the ageing processes are recognized as ageing of active materials, degradations of binder and conducting agents, corrosion of current collector , and so on. These effects do not occur separately and therefore cannot be analyzed independently each other. In order to realize a balance between lifetimes of electrode, electrolyte and separator, it is necessary to provide a technique to separately measure ageing behaviors of these lithium ion batteries (LiB) parts.

Since elastic properties of materials depend sensitively on internal friction due to lattice distortion and its thermodynamic behaviors, elastic parameters can be anticipated as good indicators for characterization of ageing behaviors of the LiB electrode as a whole.

In this study, we measure both resonance frequency and internal friction of positive-electrode reed samples as a function of temperature. Finally, we will discuss mechanisms of the internal friction on the positive electrode through comparison with the measurement results of the negative electrode.

2. Experimental

Two kinds of LiBs, not filled and filled with electrolyte, having dimensions of 230×200×7mm^3, were obtained from Nissan Motor Co, Ltd. The filled battery was prepared by charge/discharge for 150 cycles at 20 % depth-of-discharge (DOD). The measurement system of the elastic parameters of the positive electrode is that, one end of the reed sample was fixed on the copper box to assure an electrical ground lead and to control its temperature. An alternating voltage with variable frequency and amplitude was applied to the free end of the sample to vibrate it at its resonance frequency. Temperature of the sample set in the copper box was changed from 100 K to 400 K with a rate of 0.2 Kmin^{-1} and in a stepwise with 5.0 K step.

3. Results and discussion

3.1 Experimental results

The resonance frequencies of the reed sample with length of 39 mm before and after the charge/discharge cycling show that the resonance frequency drops markedly at temperatures of ~150 K and ~240 K. The resonance frequencies decrease 17% at 150 K and 19% at 240 K after the cycling. In general, the sharp decrease in the temperature-dependent resonance frequency results in a peak in the temperature-dependent internal friction.

The internal frictions of the reed sample with length of 39 mm before and after the charge/discharge of 150 cycles are shown in **Fig. 1**. Changes on the internal friction after the cycling, the increase of the Q^{-1} value and the shift of the Q^{-1} peaks, can be seen in the figure. The Q^{-1} peak values at 150 K and 240 K increase 40% and 16% after the cycling. It suggests a structure change occurred on molecular level of the active materials.

The shifts of the Q^{-1} peaks suggest a change in activation energies of the thermally activated relaxation processes. The activation energy is 901 meV for the process at ~150 K and 289 meV for the process at ~240 K, respectively. They become large after the charge/discharge cycling (before the cycle, 208 meV and 104 meV, respectively).

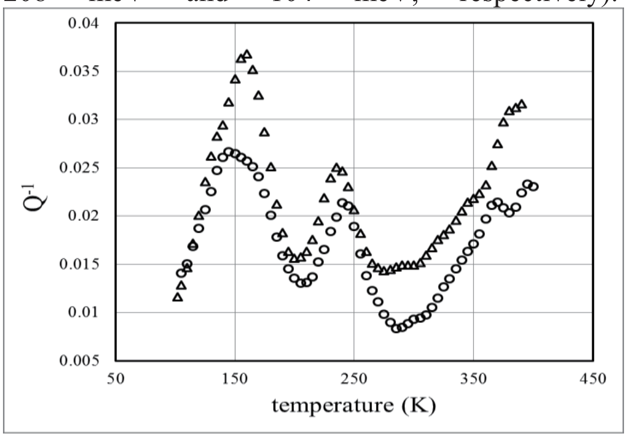

Fig 1 the internal friction with length of 39 mm before and after the charge/discharge of 150 cycles as a function of temperature

The internal frictions of both negative and positive electrode reeds with the length of 31 mm are plotted in **Fig. 2**. Two new peaks at ~190 K and ~370 K are also observed in addition to the peaks at ~150 K and ~240 K. The peak at ~150 K is weak and that at ~240 K is broad.

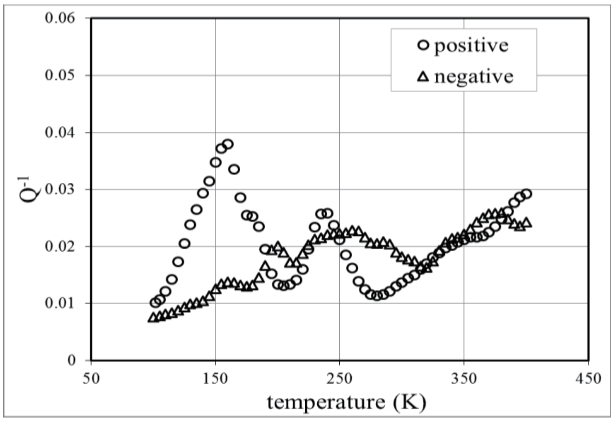

Fig 2 the internal frictions of both negative and positive electrode reeds with the length of 31 mm as a function of temperature

We are now in the position to discuss the ageing behaviors and the mechanisms of internal friction appeared in the positive electrode on the basis of the above experimental results.

3.2 Discussion on internal frictions

Low-temperature internal friction on the PVDF polymer has been reported by Callens *et al* [1]. They measured the internal friction spectra of the PVDF polymer by using a torsion pendulum technique. Nine peaks were observed on temperature-dependent internal friction spectra of the PVDF polymer at temperatures of ~140, ~190, ~220, ~236, ~270, ~330, ~350, ~386 and ~413 K in the range of 70−450 K.

Inelastic behaviors of the polycrystalline $LiMn_2O_4$ sample synthesized by a solid-state reaction have been characterized using a vibrating-reed technique [2]. In general, the elastic behaviors of the $LiMn_2O_4$ materials depend strongly on crystal structure, volume of amorphous phase and defects. Therefore, the internal friction peak is always asymmetric and much broad over a wide temperature range, 100~200 K. Hardness of the $LiMn_2O_4$ crystal and the PVDF polymer is 11 GPa and 0.15 GPa, respectively [3]. Therefore, the internal friction can be observed in the PVDF polymer more easily due to larger strain.

The nature of internal friction revealed in this study are not match to the results reported about the $LiMn_2O_4$ crystal, we can conclude that the internal friction peaks at ~150, ~240 and ~410 K are related to the PVDF polymer.

The internal friction of bulk graphite material has been measured in the temperature range of 150−680 K [4]. Two internal friction peaks were observed at 385 and 620 K. The internal friction of nanocrystalline diamond-like carbon films in the range of 0.4-300 K showed that there is a peak at approximately 1.7 K. The internal friction of amorphous diamond-like carbon films has also been measured at temperatures between 0.3 K and 300 K. The internal friction increases with increasing temperature but no any peaks were observed in this temperature range.

In the temperature range of 100−400 K, the internal friction of Al metal maybe mainly due to movement of point defects, the interaction between dislocation with point defect and impurity. Therefore, the internal friction on the Al current detector of LiB in this study does not change after the cycling. Also, the internal friction on the Al current detector is smaller than that from the active materials because the 30 μm Al foil is much thinner than that of the active materials, 160 μm. Therefore, we can conclude that the internal friction peaks at ~150 K and ~240 K do not origin from the Al current detector of the positive electrode.

4. Conclusion

Mechanical parameters of both resonance frequency and internal friction of the positive-electrode reed samples of LiBs were measured for temperature range of 100−400 K. Two thermally-activated relaxation processes are observed at ~150 K and ~240 K. The experimental results for the positive electrode before and after the charge/discharge of 150 cycles showed that the cycling process leads to the decrease in the resonance frequency of the electrode samples and the increase in their internal friction. The activation energies of the internal friction processes increased after the charge/discharge cycling. The resonance frequency, the internal friction and the activation energy of the internal friction processes are expected as new parameters for characterizing the ageing behaviors of positive electrode of LiBs.

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