

R&D for Safe and Reliable Solvent-free Lithium-Ion Polymer Batteries

Background and Objective

Lithium secondary batteries are expected to develop from electric vehicles to stationary applications. Large rechargeable battery systems for energy storage are required for safer and longer life systems than those that have been used in electric vehicles.

Our project aims to realize energy storage system using all-solid-state lithium secondary batteries with high energy efficiency and reliable safety for the upcoming large amount of renewable energies installation to the grid. In addition, the project also focuses on sophistication of the battery evaluation technology to suggest long life operation procedure of the batteries.

Main results

1. Improvement of the cathode performance of all-solid-state lithium secondary battery using novel additives in electrodes

Carboxyl methyl cellulose (CMC) was introduced at the interface between cathode and SPE as a buffer layer to suppress the side reaction and found 10 times longer cycle life based on 50% retention than that of the conventional electrode without CMC additive. Obtained cycle performance using all-solid-state battery with 4 V class cathode materials ($\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$) was the longest one among the previously reported (Fig. 1) [Q10029].

2. Development of solid polymer electrolyte film preparation condition using printing process

A developed printing process, in which SPE precursor was coated on the cathode and anode surface, was applied for the low cost forming of SPE layer. The prepared SPE film showed sufficient mechanical strength to prevent internal short circuit. The proposed process enabled the film formation using printing and subsequent chemical cross-link of SPE with sufficient reversible capacity of anode (Fig. 2) [Q10017].

3. Determination of capacity degradation mechanism of commercialized lithium-ion cell using each electrode potential analysis

Cathode and anode materials were obtained by disassembling after the constant cell voltage condition in the glove box which prevented deterioration of the materials. The correlation between cathode / anode potential profiles and capacity decrease of the battery was determined. Then we found that the shift of cathode / anode operation region due to the consumption of lithium-ion at anode-side was a major trigger of the degradation of the Mn-type lithium-ion battery in collaboration with the cathode capacity decrease (Fig. 3) [Q10026].

4. Validation of the main reason of capacity decrease in commercialized lithium-ion battery using highly sensitive surface temperature measurement of the battery

We developed 30 times highly sensitive temperature measurement procedure during charging and discharging by the thermal insulation of the battery. The temperature change obtained using the developed procedure showed good correlative profiles with each electrode potential curve. The proposed procedure can apply to various kinds of batteries such as large batteries without disassembling so that it will be a novel internal analysis approach to the batteries (Fig. 4) [Q10030].

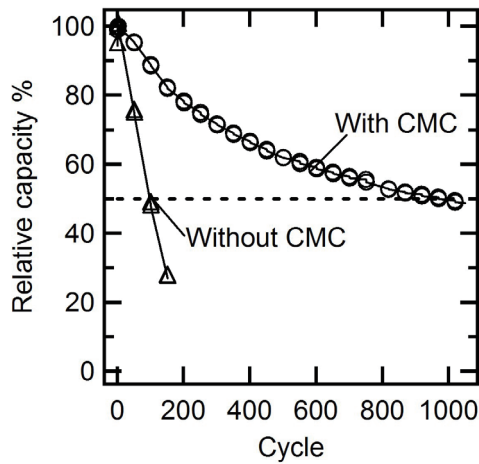


Fig. 1 Cycle properties of [Li|SPE|NMC] battery

The battery without CMC buffer in the cathode reached 50% capacity at 100 cycles. On the other hand, the battery with CMC exhibited long life of 1000 cycles under the same conditions.

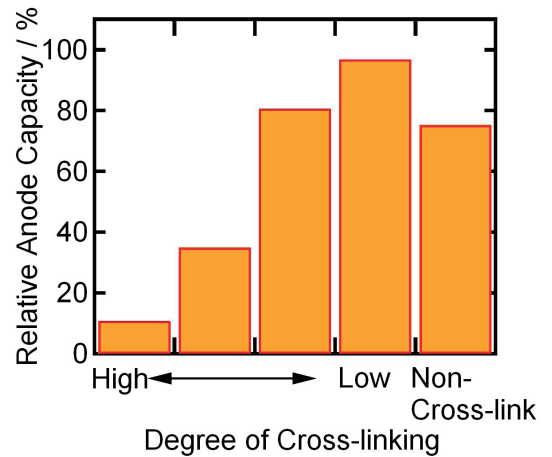


Fig. 2 Correlation between obtained reversible capacity of graphite and the degree of cross-linking of SPE in [Li|SPE|Graphite] battery at the 50th cycle

Optimized cross-link condition of sufficient strength of SPE film formation was found with high reversible capacity of graphite.

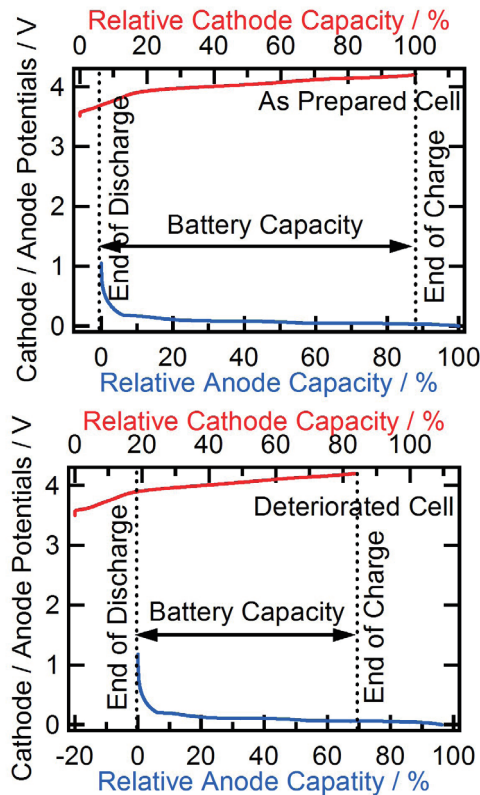


Fig. 3 Electrode potential profiles of as-prepared (top) and deteriorated (bottom) cells

The cathode capacity was decreased to 80% versus initial while the anode capacity maintained similar capacity versus initial condition. In addition, the cathode potential was shifted to the higher value after the degradation despite the same battery disassembling condition of 3.0 V. We found that the shift of the cathode operation region played a significant role in the battery degradation in addition to the capacity fading of cathode itself.

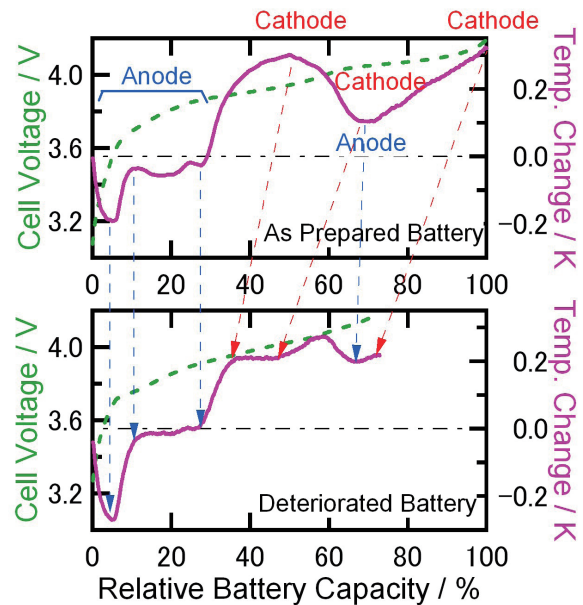


Fig. 4 The attribution of capacity decrease of the battery using the comparison of the temperature profiles during charging between as-prepared (top) and deteriorated (bottom) cells

Cell voltage: dashed line, temperature change: solid line. The capacity decrease of the cell could be described by the cathode capacity decrease and the misalignment of cathode / anode operation region without decrease of anode capacity from the thermal profiling of the battery during charging.