

Establishment of Evaluation Technologies for High Performance Secondary Batteries

Background and Objective

A large scale secondary battery system is expected to be used for leveling operation in grid systems with renewable power generation such as photovoltaic and wind power generation. It is important to evaluate the life of the battery in order to operate such secondary battery systems for long periods of time.

In light of this, we clarified the degradation mechanism of the lithium-ion battery, which

is expected to have high energy density and high energy efficiency. The methods are novel techniques in order to measure each electrode's behavior and postmortem analysis techniques in order to establish the non-destructive and accurate evaluation of battery performance. In addition, we investigate an advanced battery for the potential of improving safety and production cost compared with the conventional lithium-ion battery.

Main results

1 Development of a measurement method of electrode behavior during capacity fading of the battery using a pseudo reference electrode

In the lithium-ion battery, the cathode and anode potential changes during charge and discharge, and the obtained voltage of the lithium-ion battery is different from both the cathode and anode potential; thus, it is difficult to obtain the profile of each electrode potential from measurement of the cell voltage. Therefore, we could not obtain useful information about the determining factors of the capacity fading from each electrode profile. As such, we proposed a method to introduce a pseudo

reference electrode, which shows stable and constant potential and no significant influences on cell performance (Fig. 1). We introduced the proposed pseudo reference electrode to the all-solid-state lithium ion cell manufactured by CRIEPI, and confirmed a long stable operation of over 500 cycles (over 1 year). The rise in cathode potential at the end of discharge and the decrease of the low potential region of the anode were observed using a pseudo reference electrode (Fig. 2).

2 Analysis of the capacity fading mechanism through cell disassembly

Commercially available lithium-ion batteries (manganese oxide based cathode, graphite based anode) were disassembled after capacity fading and the half cells were reconstructed with the extracted cathode and anode using lithium metal as a counter electrode. Both reversible capacities were measured and compared with the original cell capacity in order to clarify the capacity fading mechanism. Moreover, quantitative lithium consumption in anode was measured using chemical analysis. These actions made it possible to estimate the change in reversible capacities and the operation region of the cathode and anode. As a result, we found that

the cathode operation region decreased* with the rise of the cathode potential at the end of discharge due to the irreversible consumption of the lithium at the anode. In addition, we confirmed that the acceleration of the capacity fading of the cell in high temperature operation derived from the degradation of the cathode while the degradation of the anode exhibited little influence on the capacity fading of the cell (Fig. 3). In conclusion, the capacity fading of the cell could be explained by decreasing of the operation region of the cathode and degradation of the cathode active material.

3 Development of a low cost all-solid-state Na battery with reliable safety

Na batteries, which use Na ion instead of Li as a mobile ion species, have the potential to be applied to various kinds of cathode crystalline structures. Na as an element has lower resource restriction than Li. We investigated the possibility of developing an all-solid-state Na battery, which has more potential of improving safety compared with the conventionally used flammable organic electrolytes. The

demonstrated cell, which consisted of NaCoO₂ cathode and Na metal anode, showed results as per the designed initial charge and discharge capacity (Fig. 4). In addition, we confirmed the viable use of Ni and Fe oxides as cathode material instead of resource restricted Co. Therefore, we demonstrated that the proposed all-solid-state Na battery has potential as a low cost battery system with reliable safety.

* The capacity operation region depends on the operation voltage between charge and discharge. When the cathode potential at the end of discharge increases, the potential gap between the end of charge and discharge becomes small, and operation region becomes narrow. This causes capacity fading due to the decrease in mobile lithium ion inside the cell.

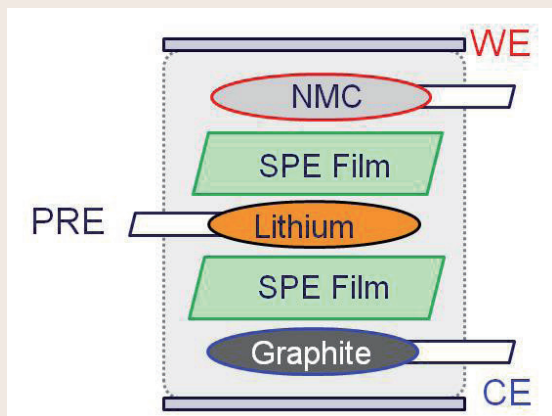


Fig. 1: All-solid-state lithium-ion battery with pseudo reference electrode

Isometric lithium metal (pseudo reference electrode: PRE) was introduced in the location of between cathode ($\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$: NMC) as a working electrode (WE) and anode (Graphite) as a counter electrode (CE). Long term uniform electrochemical reaction was demonstrated using PRE. Each electrode potential and interfacial impedance can be monitored by the proposed cell configuration.

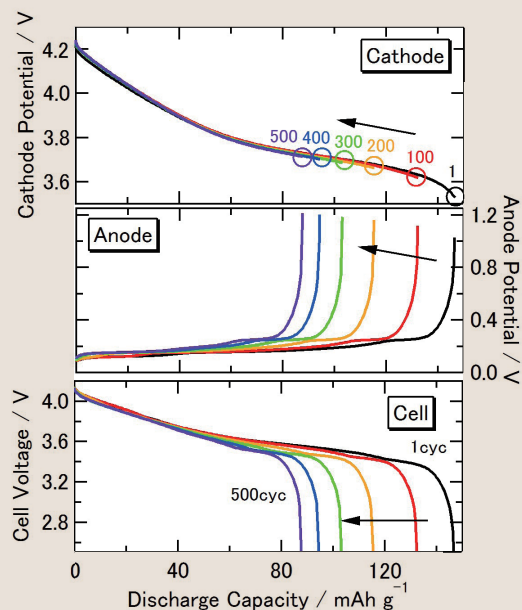


Fig. 2: Cathode and anode potential variation during charge and discharge cycle operation

Voltage profiles of each electrode in the proposed all-solid-state lithium-ion battery using a pseudo reference electrode were successfully demonstrated over 500 cycles (over 1 year). We confirmed that the cathode potential at the end of discharge rises with the capacity fading of the battery.

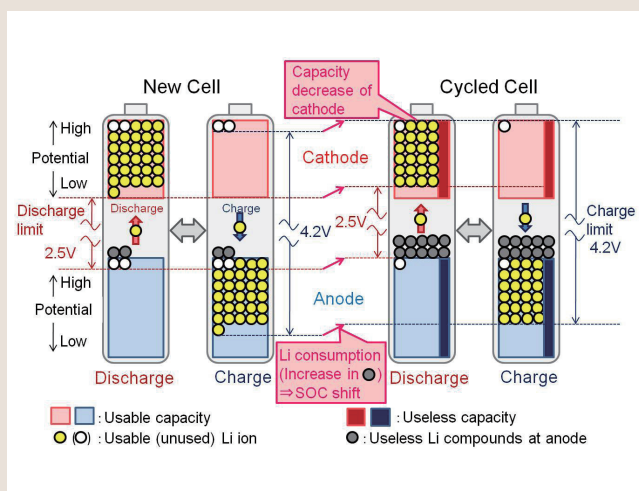


Fig. 3: Capacity fading mechanism presumed from the cell disassembly

The reversible capacity of lithium-ion battery is determined by the number of usable active lithium-ions (●) between electrodes supplying from the cathode. We confirmed that the capacity fading of the battery can be explained by the irreversible consumption of Li at the anode (increase in ●) and the degradation of the cathode (increase in useless inactive capacity of the cathode, ■). The increase in the cathode potential at the end of discharge with capacity fading of the battery was explained as follows. The increase of the irreversible Li at the anode was larger than the degradation of the cathode active material. As a consequence, the decrease in the number of Li-ion triggered the increase in rise of the cathode potential at the end of discharge.

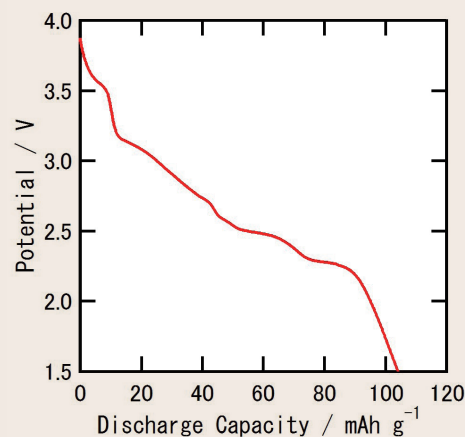


Fig. 4: Discharge voltage profile of prepared all-solid-state Na battery

The prepared all-solid-state Na battery consisted of NaCoO_2 cathode, Na metal anode, and solid polymer electrolyte (SPE) demonstrated near the designed discharge capacity (110mAhg^{-1}) at 60°C .