Charge/Discharge Property and Cycle Life of $Li_4Ti_5O_{12}/LiCoO_2$-$LiNi_{1-x-y}Co_xAl_yO_2$ Cell for Electricity Storage Applications: Effect of Cell Design Parameters

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ABSTRACT

$Li_4Ti_5O_{12}$ is a promising anode material in lithium-ion batteries for electricity storage applications operating at high charge/discharge rates due to its excellent cyclability and rate-capability. $Li_4Ti_5O_{12}$(LTO) and $LiCoO_2$-$LiNi_{1-x-y}Co_xAl_yO_2$(LCO-NCA) was used as an anode and cathode material, respectively, for the fabrication of three-electrode cells. The cells were designed to LTO-limited cell (reversible capacity of LTO anode (N) < reversible capacity of LCO-NCA cathode (P)) and LCO-NCA-limited cell (N > P). The capacity of the cell was found to be strongly dependant on the reversible capacity of LTO anode rather than N/P ratio except for the very low N/P ratio (N/P << 1). The cyclic characteristic of the cell varied with N/P ratio. LTO-limited cell showed a fabulous cyclic performance (~ 100 % capacity retention at 1000th cycle) at a high charge/discharge rate of 4C (*i.e.*, current extracting the full capacity of cell in 15 min), while LCO-NCA-limited cell exhibited relatively poor cyclic performance (~ 87 % capacity retention at 1000th cycle). The marginal region of electrode for the alignment of electrodes played an important role in changing the charge/discharge behavior of the cell.

Keywords: $Li_4Ti_5O_{12}$, three-electrode cell, N/P ratio, cyclic performance, charge/discharge behavior

1 INTRODUCTION

Carbonaceous materials such as graphite are the anode of choice for commercial lithium-ion batteries, but there are still critical problems that need to be overcome. For example, the redox potential is so close to the potential of metallic lithium that lithium precipitation occurs on the surface upon overcharge.[1] Furthermore, the solid electrolyte interphase (SEI) is usually formed on the carbonaceous materials at the potentials below 0.8 V vs. Li/Li^+, resulting in the degradation of cycle life and rate-capability.[2]

On the other hand, $Li_4Ti_5O_{12}$ with spinel structure undergoes no significant SEI formation due to a relatively high operating voltage of 1.5 V vs. Li/Li^+. This results in improved cyclability and rate-capability during the charge/discharge process as compared with carboneous materials.[3-4]

In this work, $Li_4Ti_5O_{12}$ has been used as an anode material in lithium-ion batteries for electricity storage applications, which operate under intermittent cycling conditions with higher charge/discharge rates than 4C (*i.e.*, current extracting the full capacity of cell in 15 min). $Li_4Ti_5O_{12}/LiCoO_2$-$LiNi_{1-x-y}Co_xAl_yO_2$ cells for electricity storage applications have been designed and constructed with different cell parameters (N/P ratio, electrode dimension, materials loading level, etc.), and then the effect of design parameters on the capacity, cycle life and charge/discharge behavior has been analyzed using various physical and electrochemical techniques.

2 EXPERIMENTAL

$Li_4Ti_5O_{12}$ (LTO) anode and $LiCoO_2$-$LiNi_{1-x-y}Co_xAl_yO_2$ (LCO-NCA) cathode electrode were prepared by slurry casting process. The calculated amounts of active materials were loaded in the electrodes for the fabrication of LTO-limited cell (N/P < 1) and LCO-NCA-limited cell (N/P > 1). (In N/P ratio, N and P are defined as reversible electrode capacities in anode and cathode, respectively.)

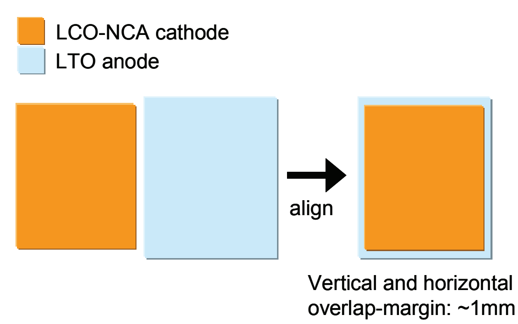


Figure 1. Schematic diagram of electrode-alignment.

The LTO anode and LCO-NCA cathode were dried for several hours at 120 ◦C under vacuum and then pressed under the optimum pressure. The pressed electrodes were cut into calculated size (Figure.1). Jelly-roll and pouch-type three-electrode cells containing Li-metal reference electrode were assembled in a dry room and tested under Galvanostatic conditions at 0.1C (initial two cycles for electrode formation) and 4C (standard cycles after the two formation cycles) current rate within a fixed voltage window between 1.5 and 2.8 V.

3 RESULTS AND DISCUSSION

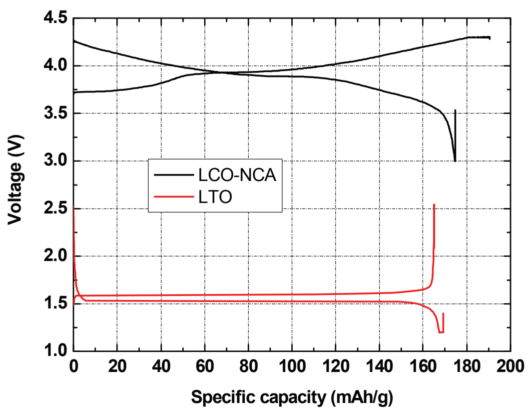


Figure 2. Charge/discharge profiles of Li/LTO and Li/LCO-NCA half cell.

The charge/discharge profiles of Li/LTO and Li/LCO-NCA half cell are displayed in Figure 2. The reversible capacities of LTO and LCO-NCA are 167 and 173 mAh/g, respectively. The reversible capacities obtained from the half cell test were used to design the LTO or LCO-NCA-limited cell.

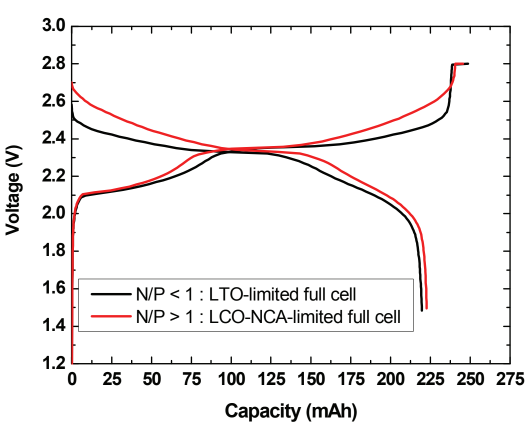


Figure 3. Initial Charge/discharge profiles of LTO/LCO-NCA cell at 0.1C charge/discharge rate.

Figure 3 shows the initial charge/discharge profiles of LTO/LCO-NCA jelly-roll-type cell. LTO-limited cell (N/P < 1) has the discharge capacity of 220 mAh and the coulombic efficiency of 90%. LTO/LCO-NCA-limited cell (N/P > 1) has slightly better performance than LTO-limited cell, 223 mAh and 92%. It is inferred from these results that the cell capacity is strongly dependant on the reversible capacity of LTO anode rather than N/P ratio except for the very low N/P ratio (N/P << 1).

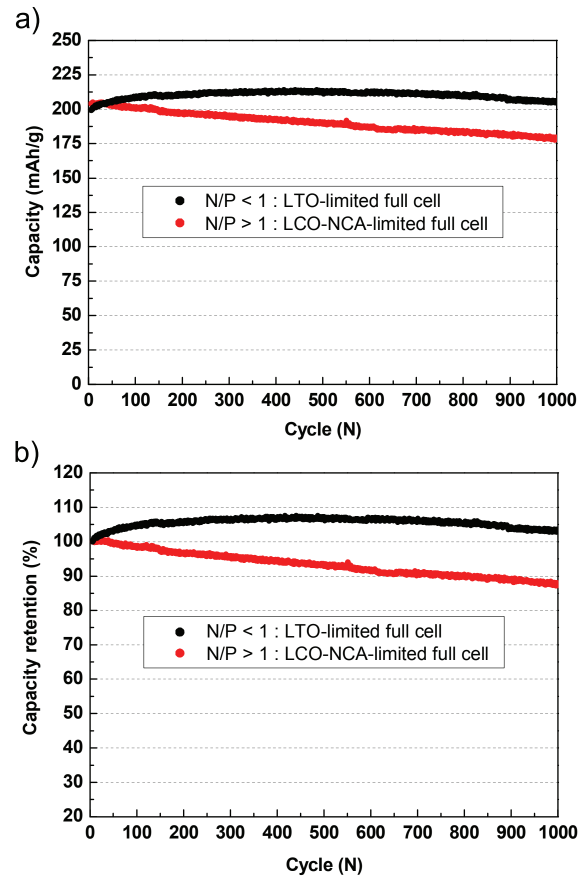


Figure 4. Cyclic characteristics of LTO/LCO-NCA cell at 4C charge/discharge rate; a) capacity vs. cycle number, b) capacity retention vs. cycle number

In contrast to the capacity results, the cyclic characteristics of the cell show a large difference between the LTO-limited and the LCO-NCA-limited cell. The cyclic characteristics of the cells are described in terms of capacity vs. cycle number and capacity retention vs. cycle number. LTO-limited cell featured a fabulous cyclic performance (~ 100 % capacity retention at 1000^{th} cycle) at a high charge/discharge rate of 4C, while LCO-NCA-limited cell exhibited relatively poor cyclic performance (~ 87 % capacity retention at 1000^{th} cycle). It is highly likely that the cyclic characteristic of the cell varies with N/P ratio.

In order to clarify the effect of N/P ratio on the cyclic performance, a change in the charge/discharge cut-off potential of each anode and cathode was examined using in-situ three-electrode profile. The three-electrode profile in Figure 5 represents the general cathode-limited profile. The

LCO-NCA-limited cell operates within the LTO plateau region and the potential of LCO-NCA cathode rises up to 4.36 V vs. Li^+/Li during charge process. A gradual decrease in the discharge capacity of LCO-NCA-limited cell can result from high charge cut-off potential because charging the cathode up to more than 4.3 V vs. Li^+/Li does not guarantee the structural stability of LCO-NCA cathode.

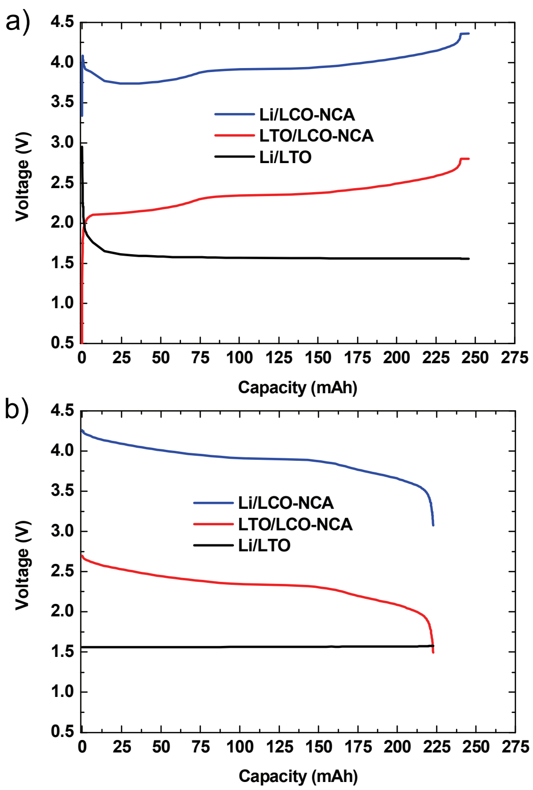


Figure 5. In-situ three-electrode profiles of LCO-NCA-limited cell (N/P > 1); a) charge profiles, b) discharge profiles.

Contrary to our expectations, the three-electrode profile of LTO-limited cell in Figure 6 also represents the general cathode-limited profile, which is contradictory to the LTO-limited cell design. Eventually, the potential of LCO-NCA cathode also increases up to 4.36 V vs. Li^+/Li during charge process and the charge cut-off potential does not account for better cyclic performance of LTO-limited cell. For the elucidation of better cyclic performance of LTO-limited cell, the open-circuit potentials of LCO-NCA cathodes upon cycling (Figure 7) were investigated. It is observed from Figure 7 that the open-circuit potential of LTO-limited cell is lower than that of LCO-NCA-limited cell at every cycle. This means that the cathode in the LTO-limited cell operated under milder charge/discharge condition, resulting in the better cyclic performance.

The cathode-limited behavior of LTO-limited cell is very peculiar phenomenon. In order to verify the reason for that behavior, three-electrode charge profiles of LTO-limited pouch-type cell with and without LTO-anode-margin were examined (Figure 8). LTO-limited behavior was observed in no margined cell, signifying that the marginal region of electrode plays an important role in changing the charge/discharge behavior of the cell. The investigation for the explanation of this phenomenon is under way in our laboratory.

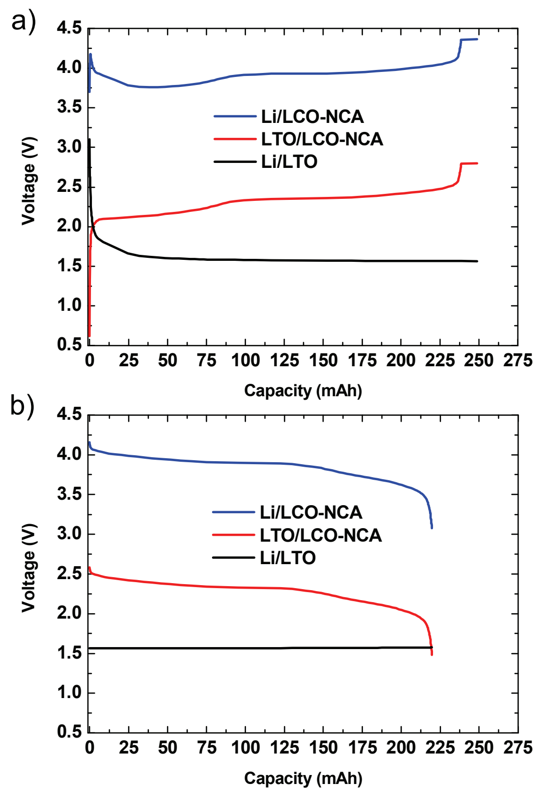


Figure 6. In-situ three-electrode profiles of LTO-limited cell (N/P < 1); a) charge profiles, b) discharge profiles.

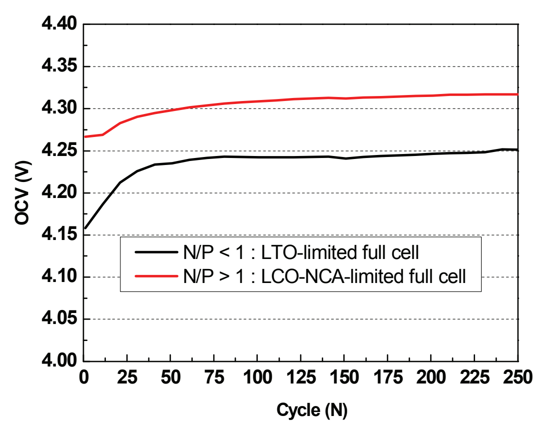


Figure 7. Open-circuit potentials of LCO-NCA cathodes upon cycling.

The charge/discharge test of LTO-limited cell with LCO-NCA cathode margin was performed for the

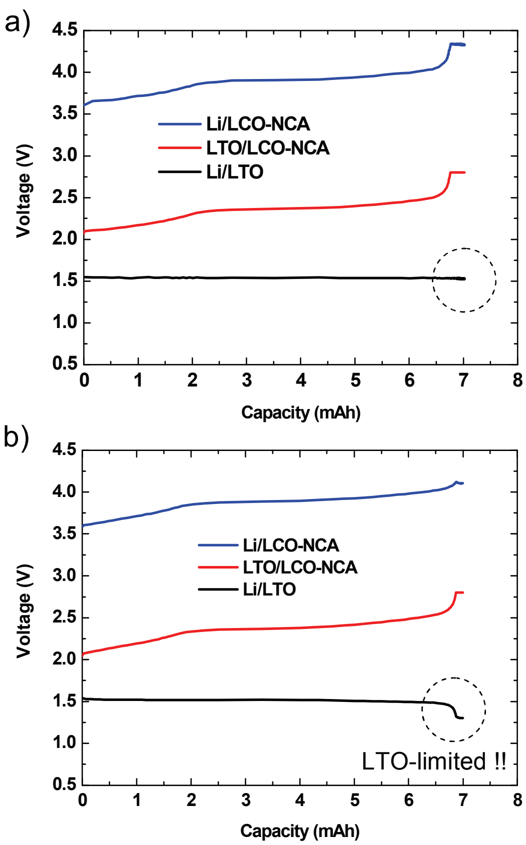
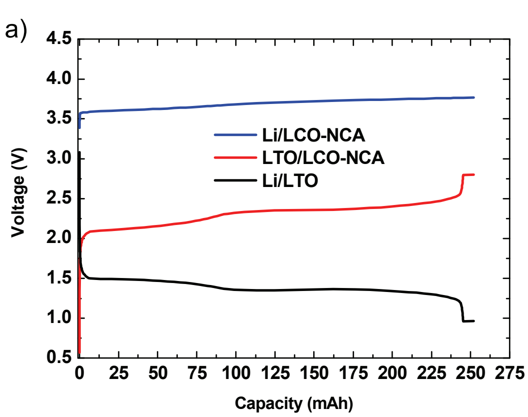


Figure 8. In-situ three-electrode charge profiles of LTO-limited pouch-type cell (N/P < 1); a) LTO-anode-margined cell, b) No margined cell.

examination of a change in the charge/discharge behavior. It is observed from Figure 9 that LTO-limited cell shows the general cathode-limited charge/discharge behavior due to the cathode margin. The test of the cyclic characteristic of this cell is now going on in our laboratory.



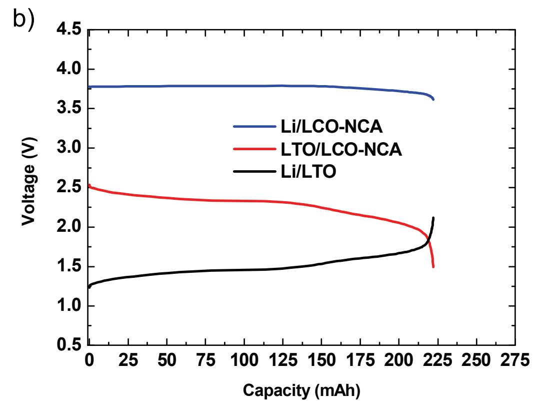


Figure 9. In-situ three-electrode profiles of LTO-limited cell (N/P < 1) with LCO-NCA-cathode margin; a) charge profile, b) discharge profile.

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