

Effects of Capacity Ratios between Anode and Cathode on Electrochemical Properties for Lithium Polymer Batteries



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ABSTRACT

The areal capacity ratio of negative to positive electrodes (N/P ratio) is the most important factor to design the lithium ion batteries with high performance in the consideration of balanced electrochemical reactions. In this study, the effect of N/P ratio (1.10, 1.20, and 1.30) on electrochemical properties has been investigated with a lithium polymer battery with PVdF-coated separator and 1.40 Ah of capacity. The N/P ratio is controlled by adjusting the anode thickness with a fixed anode density. The cell with an N/P ratio higher than 1.10 effectively suppresses the lithium plating at the 0.85C-rate charging at 25 °C and the cell with 1.20 of N/P ratio shows the enhanced cycle performance in comparison with other cells. Among the cells with differently designed N/P ratios, significant difference was not observed in the aging test with fully charged batteries at 25 and 45 °C. The effect of N/P ratio on electrochemical properties of lithium batteries can help to design the safe full cell without lithium plating.

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1. Introduction

The current lithium ion batteries (LIBs) have high energy density, flexible and lightweight design, and long cycle life property [1] in comparison with other secondary batteries. However, there have been a lot of efforts to find novel materials [2,3] with higher energy and power density to satisfy the new requirements for future LIBs for personal electronic devices, electric vehicles (EVs), energy storage systems (ESSs), and so on. In addition, there are many systematic researches on the properties of electrode itself (cathode [4,5] and anode [6,7]) to design a high performance full cell. The density and thickness of electrode is considered as an important factor in commercial batteries to get higher energy density [8]. Even though many researches of electrode-design parameters have focused on individual electrodes such as cathode or anode, only limited works have been done for the parameter such as the capacity ratio of negative to positive electrode (N/P ratio). The capacity ratio is practically important to achieve the targeted performance and the reduction of cost since it

affects the properties of full cell [9–11]. One of electrochemical properties closely related with N/P ratio is lithium plating during a charging process. Lithium plating causes irreversibility and is accumulated during cycling, and it ultimately results in capacity loss, mechanical swelling, and potentially internal short-circuit. It is commonly expected that lithium plating is not frequently occurred when anode potential is positive (versus Li/Li⁺). However, lithium plating can be formed even if anode potential versus a reference electrode in the battery is above 0V because local electrochemical potential of electrode can be often changed by dynamic environmental parameters such as edge effect which may induce side reactions [12]. However, there is lack of practical studies of the N/P ratio for lithium ion batteries whereas the effect of N/P ratio on electrochemical reaction is very important parameter in full cell performance.

In this study, we have studied the effect of N/P ratio on electrochemical properties such as capacity, cycleability, and lithium plating by charging to higher voltage of the cells with various N/P ratios (1.10, 1.20, and 1.30). The N/P ratio is controlled by increasing the anode thickness and loading level with a fixed anode density. The tested battery is a winding type lithium polymer battery with PVdF-coated separator. The effects of N/P ratio on electrochemical properties of lithium batteries have been discussed in detail and this study can help to design the safe and high performance full cell without lithium plating.

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2. Experimental

2.1. Battery construction

The positive electrode consists of LiCoO_2 as a positive active material, acetylene black as a conductive agent, and poly(vinylidene fluoride) (PVdF) as a binder with the weight ratio of 97.4, 1.3, and 1.3%, respectively. The slurry was prepared by mixing them with N-methylpyrrolidone (NMP), and then, it is coated on an aluminum foil (thickness = $13.5\text{ }\mu\text{m}$) as a current collector of positive electrode. The positive electrodes are pressed to obtain a desired thickness (thickness = $122\text{ }\mu\text{m}$, electrode density of 3.90 g cm^{-3}) and they are cut into a desired width and then vacuum-dried. The negative electrode is prepared with natural graphite as a negative active material and a styrene-butadiene rubber-carboxymethylcellulose (SBR-CMC) as a binder. The slurry is made by dissolving them in distilled water with the weight ratio of 98.0, 1.0, and 1.0%, respectively. Then it is coated onto a copper foil (thickness = $10\text{ }\mu\text{m}$). The negative electrodes are pressed and the thickness of anodes (N/P ratio = 1.10, 1.20, and 1.30) are 124, 135, and $146\text{ }\mu\text{m}$ with the same electrode density (1.60 g cm^{-3}), respectively. The resulting electrode is cut into a desired width and then vacuum-dried.

The battery assembly from winding is carried out in the dry-room under the control of humidity. Electrode assembly, so-called jelly-roll is wound by winding machine with positive and negative electrodes controlled with desired N/P ratio (1.10–1.30) after tab welding. The separator is coated by PVdF polymer on both side of polyethylene (PE). The battery has 1.4 Ah of capacity and the dimension is 29 mm (width) $\times$ 72 mm (length) $\times$ 5.1 mm (thickness). The electrolyte is 1.10 M LiPF_6 dissolved in the mixed organic solvents consisting ethylene carbonate (EC), propylene carbonate (PC), ethyl propionate (EP) in the volume ratio of 3:1:6 with some additives such as fluoro ethylene carbonate (FEC) and vinylene carbonate (VC). This electrolyte is battery grade and used without further treatment. The electrolyte is injected into the open side inlet of pouch after the jelly-roll is inserted into a pouch and then the pouch is sealed by heat sealer. The assembled battery is kept at room temperature for about one day. Subsequently, the battery is pre-charged to 20% state of charge (SOC) and degassed to eliminate internal gas and pressed by heat-press. In a formation process, heat-pressed battery is charged by constant-current (CC) mode to 4.20 V and by the constant-voltage (CV) mode to 0.05C-rate of current and discharged to 3.00 V and then charged to 50% of SOC by CC mode.

2.2. Electrochemical characterization

All the electrochemical properties are characterized with the aluminum pouch cells without external safety devices such as PCM (protect circuit module) and PTC (positive temperature coefficient). The prepared battery was connected to the TOYO charging/discharging cycler to control and monitor their current and voltage during charging and discharging periods. The batteries are charged at 0.85C-rate by CC mode until its voltage reaches the desired charging (cut-off) voltage from 4.20 V to 4.50 V followed by CV charging mode until the current reduces to 0.05C-rate of current and then discharged at 0.20C-rate until cut-off voltage of 2.75 V. All the rate discharge performance was examined with a rest time of 10 minutes in between charging and discharging processes. The cycle life tests are performed with the same procedure as described above, but only the differences are that discharge condition was 1.0C-rate of current with cut-off voltage of 2.75 V and the cell is discharged with 0.20C-rate of current at 24th and 49th cycle. For the aging tests, the fully charged cells ($n=5$) for various N/P ratio (1.10, 1.20, and 1.30) were aged for 1 month at two different

temperatures (25 and 45°C) and physic-chemical and electrochemical properties of the cells are measured prior to and after aging.

3. Results and discussion

Even though lithium plating is not frequently occurred under normal operation condition, it can often occur on the anode instead of normal intercalation of lithium under severe charging conditions such as charging at high current density and/or low temperature due to the slow intercalation kinetics of lithium. Especially, graphite electrode, which is the most widely used in commercial lithium ion batteries, is vulnerable to lithium plating because the reversible potential of graphite is in close proximity to that of Li^+/Li [13]. The plated lithium causes degradation in capacity and performance. More seriously, lithium plating brings about the formation of dendrite to induce an internal short-circuit which can results in serious problems in reliability and safety of lithium ion battery [13]. Another factor increasing the formation of lithium plating is the electrolyte. The electrolyte with high concentration of EC exhibits the acceleration of lithium plating and low N/P ratio causes to polarize the anode to lithium deposition potentials and increase lithium plating [14]. Hence, the anode has to be designed to hold higher N/P ratio more than 1.0 and/or higher dimensions to avoid edge effect resulting in lithium plating. Fig. 1 shows the discharging profiles of full-cell with various N/P ratio (charging voltage = 4.50 V) and it obviously shows plateaus in the initial range of discharging profile as shown in the inset. This high voltage plateau is the evidence of the presence of metallic lithium over graphite anode (shown in Fig. S1), which is a semi-quantitative indication for the lithium plating, because the lithium plating can make a voltage overshoot by over-potential in the initial range of the discharging profile [13]. In addition, the length of this plateau is proportional to the amount of metallic lithium over graphite electrode [13]. Based on our capacity data as shown in Fig. 1, the actual N/P ratios at 4.50 V charging voltage are 0.87, 0.94, and 1.02 for 1.10, 1.20, and 1.30 of the designed N/P ratio, respectively. Voltage overshooting in discharging profile after charging at 4.50 V covers ~ 25 , 17, and 10% of discharging capacity for 1.10, 1.20, and 1.30 of designed N/P ratio, respectively. It is clearly demonstrated that the cell with high N/P ratio suppresses lithium plating under a given charging voltage condition.

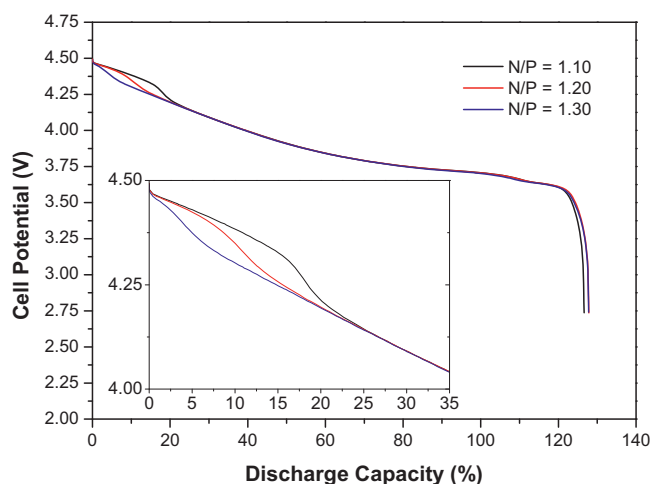


Fig. 1. Discharging profiles at 4.50 V of charging voltage condition. The inset is the magnification of the initial range of discharging profiles to show the voltage overshoot by over-potential.

The detailed data for the cells with various N/P ratios are summarized in Table 1. Charging process is proceeded through CC-CV mode with 0.85C-rate up to each desired cut-off voltage (4.20–4.50 V) followed by 0.05C-rate cut-off condition, and the discharging is proceeded by CC mode with 0.20C-rate and 2.75 V of cut-off voltage. There is rest time for 10 minutes in between charging and discharging processes. The designed N/P ratio is a target value based on 4.20 V of charging voltage and the actual N/P ratio is obtained from measuring the capacities at different charging voltages. For the series A, the reference (A1) has the N/P ratio of 1.10 which is obtained at the charging voltage of 4.20 V and the discharging capacity of 1463 mAh and the discharging capacity is the second cycle capacity at 0.20C-rate after the first formation charging and discharging process at 25 °C. For the higher voltage charging (4.25–4.50 V), the actual N/P ratios are varied from 1.09 (A2) to 0.87 (A7). For the series B and C, the actual N/P ratios are varied from 1.18 (B1) to 0.94 (B7) and from 1.28 (C1) to 1.02 (C7) at a charging voltage of 4.20–4.50 V, respectively. It is unambiguous that the specific capacity of the cathode at the charging voltage of 4.20 V becomes higher with an increase in N/P ratio. For a cell with a high N/P ratio, charging voltage of cathode should be slightly higher in comparison with a cell with a low N/P ratio to reach at 4.20 V of full cell due to the high anode voltage by low charging depth from high anode capacity. To investigate lithium plating in detail, discharging profiles are measured as a function of charging voltage (4.20–4.50 V) and the results are shown in Fig. 2 and Table 1. Fig. 2 shows the discharge profiles after charging with various voltages (4.20–4.50 V) and designed N/P ratios in second cycle. For the cell with N/P ratio = 1.10 (A series), as shown in Fig. 2(a), the high voltage plateaus are observed with a charging at low voltage. The lithium plating is observed from the charging voltage of 4.25 V and the actual N/P ratio is 1.09. For the cells with 1.20 (B-series) and 1.30 (C-series) designed N/P ratios, the lithium plating begins from the charging voltage of 4.35 and 4.45 V and the actual N/P ratios are 1.08 and 1.06 under each charging condition, respectively. Lithium plating noted in the right side column of Table 1 is assessed from the voltage overshoot in the initial range of the discharge profile shown in Fig. 2. It is evident that a cell with

lower N/P ratio experiences lithium plating at lower charging voltage.

Fig. 3 (a) shows the growth rate of discharging capacity for the cells under various conditions in comparison with the capacity for the cell with N/P = 1.10 (at the charging voltage of 4.20 V; A1 in Table 1) as a function of charging voltage. The growth rate of discharging capacity gradually increases as the charging voltage increases. However, the abrupt reduction of growth rate of discharge capacity is observed and it is attributed to the lithium plating. The decrease in the discharging capacity only at the point starting lithium plating are 3.5, 2.3, and 2.1% by trend-line analysis for the cells with N/P ratio 1.10, 1.20, and 1.30, respectively. Fig. 3 (b) shows the actual N/P ratio for the cells under various conditions as a function of charging voltage. The actual N/P ratios are obtained from the discharging capacity on the basis of the cell with N/P ratio = 1.10 (at the charging voltage of 4.20 V; A1 in Table 1) and the designed capacity of anode. The results show that the actual N/P ratios become gradually reduced as an increase in the charging voltage because the capacity of cathode increases with increasing the charging voltage. The red dashed window shown in Fig. 3(b) indicates the range of 1.06–1.09 in the actual N/P ratio and the starting points for the formation of lithium plating points are noted by the green arrows. The lithium plating is occurred in between 1.06 and 1.09 of actual N/P ratios for the cells with the designed N/P ratios of 1.10–1.30 under 0.85C-rate of charging condition at 25 °C. The designed N/P ratio higher than 1.1 suppresses the lithium plating under the same charging/discharging condition (0.85C-rate charging with the same cut-off voltage at 25 °C). As shown in Fig. 3(b), as the designed N/P ratio increases, the charging voltage to form lithium plating increases and the actual N/P ratio for the formation of lithium plating decreases.

Fig. 4 shows the discharging capacity for the cells with various N/P ratios as a function of the number of cycle at 25 °C. As already discussed, the initial discharging capacity increases as an increase in the charging voltages. However, all the cells experience the substantial capacity fading under high charging voltage condition (charging voltage > 4.40 V) and the capacities of the cells are significantly reduced as an increase in the number of cycle. The

Table 1

The summary of data for the cells with various designed N/P ratios (1.10–1.30) as a function of charging voltages

	No.	Charging Voltage (V)	Charging Capacity (mAh)	Discharging Capacity (mAh)	Efficiency (%)	Capacity Ratio (%)	Actual N/P ratio	Note
N/P = 1.10	A1	4.20	1455	1463	100.6	100	1.10	Reference
	A2	4.25	1492	1480	99.2	101	1.09	(Li-Plating)
	A3	4.30	1553	1538	99.0	105	1.05	Li-Plating
	A4	4.35	1631	1609	98.7	110	1.00	Li-Plating
	A5	4.40	1708	1682	98.5	115	0.96	Li-Plating
	A6	4.45	1786	1755	98.3	120	0.92	Li-Plating
	A7	4.50	1891	1852	97.9	127	0.87	Li-Plating
N/P = 1.20	B1	4.20	1487	1488	100.1	102	1.18	
	B2	4.25	1556	1545	99.3	106	1.14	
	B3	4.30	1613	1599	99.1	109	1.10	
	B4	4.35	1635	1622	99.2	111	1.08	(Li-Plating)
	B5	4.40	1705	1686	98.9	115	1.04	Li-Plating
	B6	4.45	1794	1772	98.8	121	0.99	Li-Plating
	B7	4.50	1897	1870	98.6	128	0.94	Li-Plating
N/P = 1.30	C1	4.20	1486	1490	100.3	102	1.28	
	C2	4.25	1558	1552	99.6	106	1.23	
	C3	4.30	1631	1622	99.4	111	1.17	
	C4	4.35	1699	1687	99.3	115	1.13	
	C5	4.40	1773	1757	99.1	120	1.08	
	C6	4.45	1809	1791	99.0	122	1.06	(Li-Plating)
	C7	4.50	1892	1870	98.8	128	1.02	Li-Plating

* Capacity is second cycle results after the first formation charge and discharge at 25 °C and test method is CC-CV 0.85 C, each voltage, 0.05 C cut-off/rest 10 min/CC 0.2 C, 2.75 V cut-off at 25 °C. (Li-plating) is starting point of lithium plating.

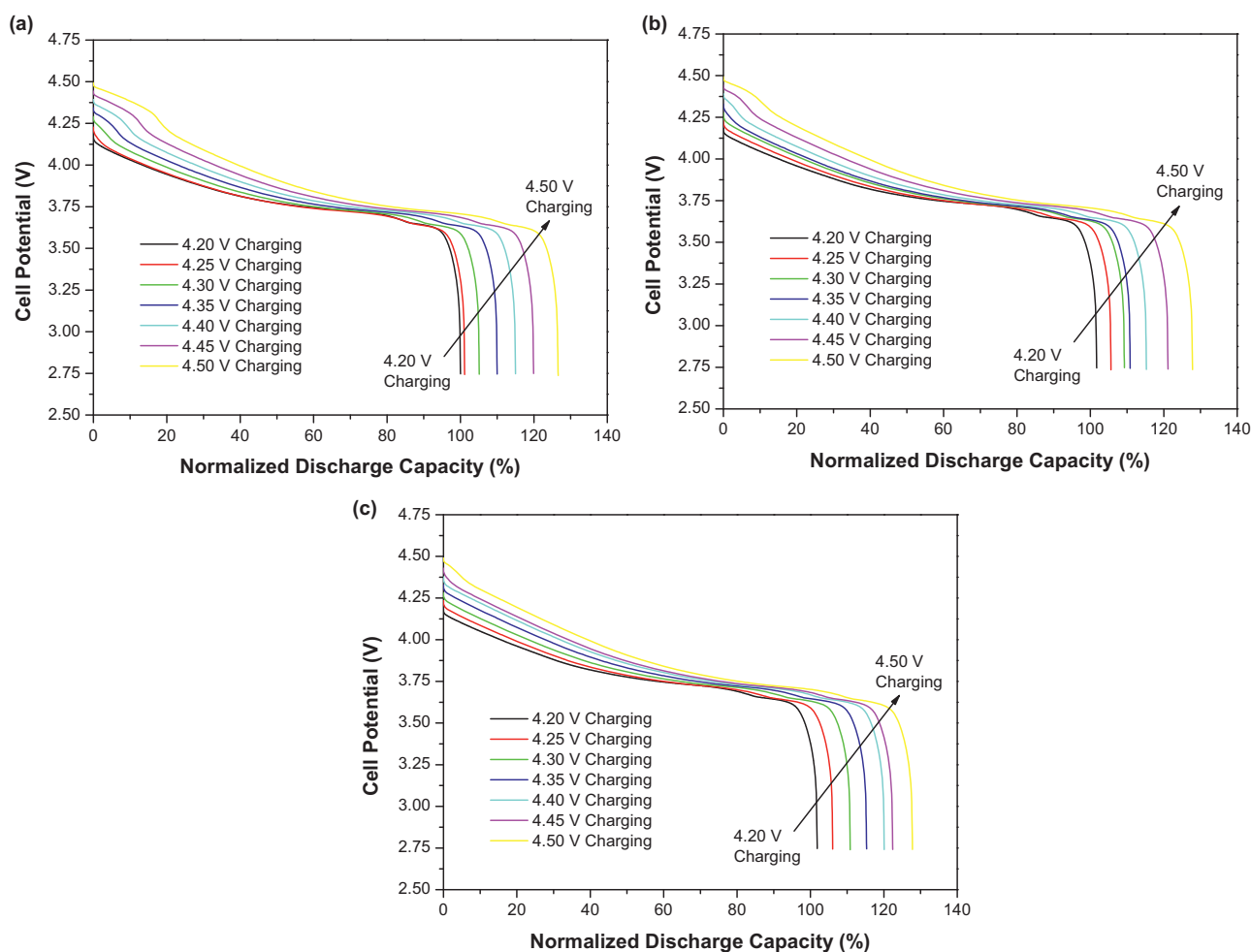


Fig. 2. Discharging profiles after charging up to each cut-off voltage from 4.20 to 4.50 V for the cells with the designed N/P ratio of (a) 1.10, (b) 1.20, and (c) 1.30.

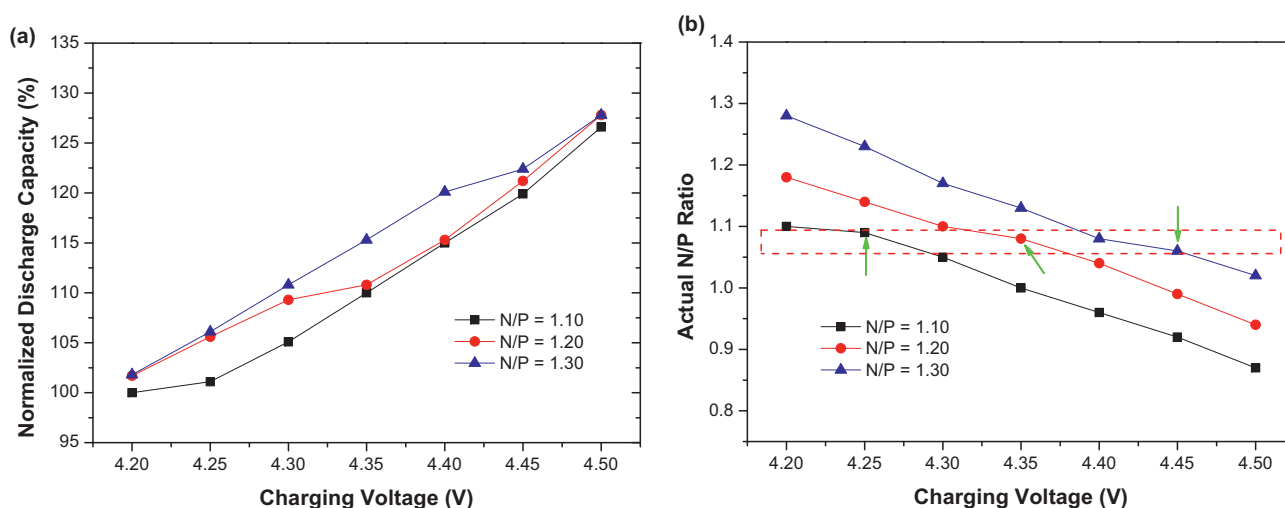


Fig. 3. (a) The normalized discharging capacity and (b) the actual N/P ratio of the cells with various designed N/P ratios as a function of charging voltages.

basic trends for the discharging capacity of the cells with different designed N/P ratio are very similar under nominal charging conditions (charging voltage ≤ 4.40 V) except the cell with 1.10 N/P ratio at 4.40 V of charging voltage although the cells with higher N/P ratios show higher discharging capacity than the cell with 1.10 of N/P ratio. Over all of the charging conditions, the cell with 1.20 of N/P

ratio has better cycleability than others in that the one with 1.10 of N/P ratio is degraded and the one with 1.30 of N/P ratio shows a slightly rapid capacity reduction slope. Moreover, under the higher charging voltage conditions (>4.40 V), the cell with 1.20 of N/P ratio shows the enhanced performance as a function of the number of cycle as shown in Fig. 4. The capacity retention ratios at 60 cycles under the 4.40 V

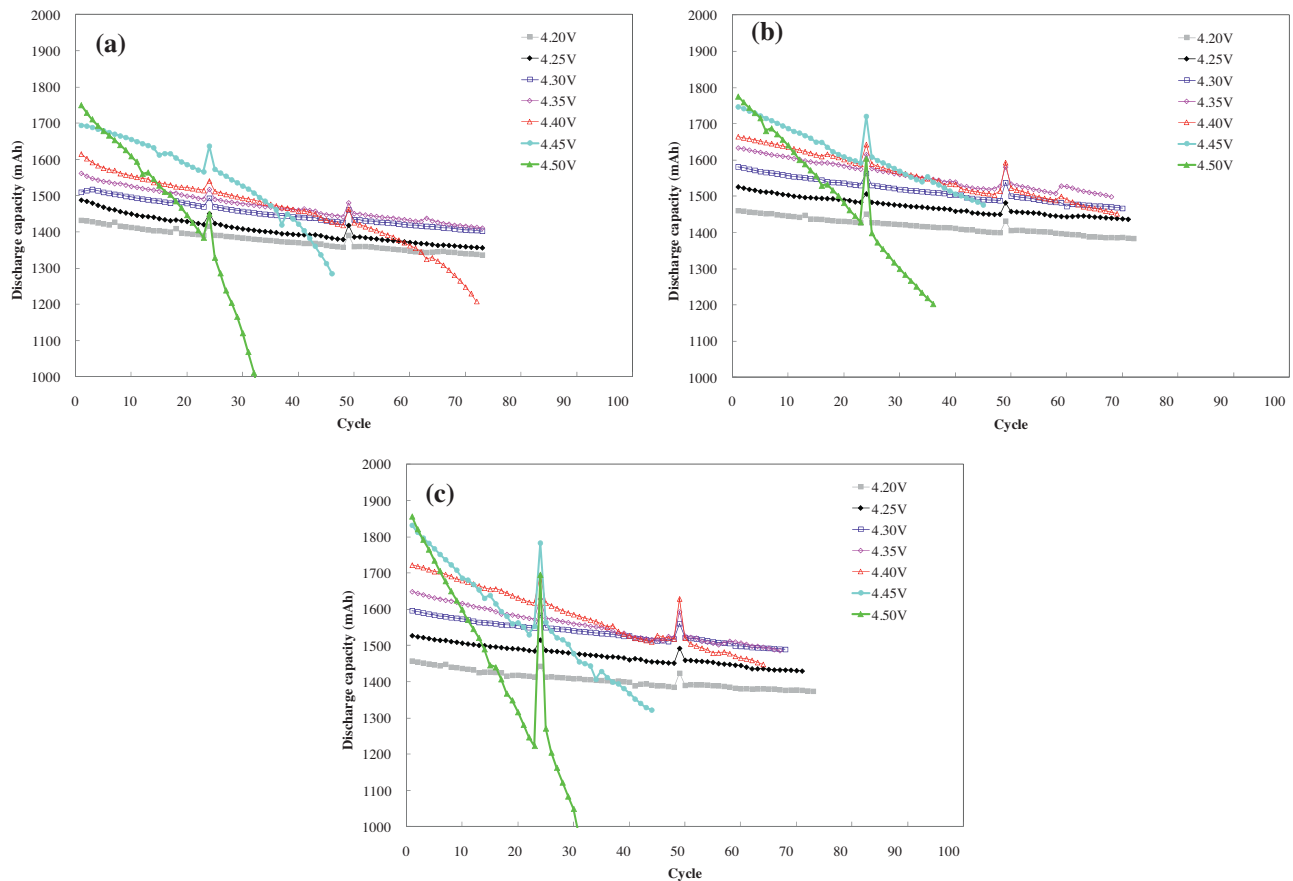


Fig. 4. The cycleability data for the cells with designed N/P ratios of (a) 1.10, (b) 1.20, and (c) 1.30 as a function of charging voltages.

charging voltage condition are 84.35, 89.54, and 85.10% for the cells with 1.10, 1.20, and 1.30 of N/P ratios, respectively.

Fig. 5 shows the physical and electrochemical properties for aging tests and the cells with various N/P ratios (1.10, 1.20, and 1.30) are aged for one month at two different temperatures (25 and 45 °C). Five cells for each N/P ratio are aged and the physico-chemical and electrochemical properties are measured prior to and after aging. As shown in Fig. 5(a), the open-circuit voltages (OCVs) of fully charged fresh batteries are 4.1596–4.177 V regardless of their N/P ratios. The aged batteries for one month show lower OCV in comparison with fresh batteries. For the aging at 25 °C, OCVs drop to 4.143–4.160 V and the difference from that of fresh battery is 0.016 V on average. However, for the aging at 45 °C, the difference of OCV between aged and fresh batteries increases to 0.061 V which is 4 times higher than that of batteries stored at 25 °C due to an increase in the rate of side reactions at high temperature. These phenomena are observed in the change of internal resistance (not shown in brevity) and the differences between fresh and aged batteries at 25 and 45 °C are 0.33 and 3.57 mΩ on average, respectively. The difference at 45 °C is ~11 times higher than that at 25 °C. The thickness changes for the cell stored at 25 and 45 °C are 0.016 and 0.119 mm on average, respectively. Even though the difference stored at 45 °C is 7.5 times larger than that at 25 °C, the rate of change before and after the aging at 45 °C is only ~2.238%. The capacity recovers for the cell stored at 25 °C are 97.43, 98.67, and 100% for the cells with N/P ratio = 1.10, 1.20, and 1.30, respectively, and the average is 98.7%. On the other hands, the capacity recoveries for the cell stored at 45 °C are much lower in comparison with the cell stored at 25 °C due to the increase in the irreversibility at high temperature. The recoveries for the cell with N/P ratio = 1.10, 1.20, and 1.30 are 92.99, and 92.71, and 94.66%,

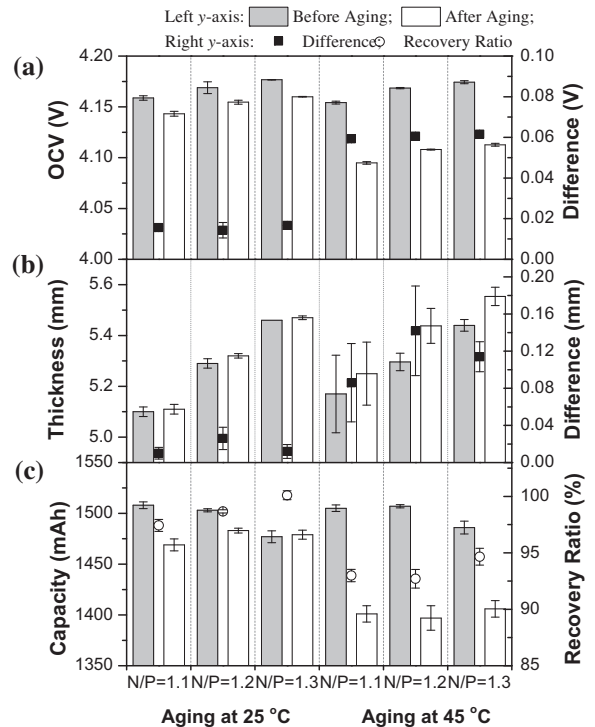


Fig. 5. The experimental results of the aging tests for (a) OCV, (b) cell thickness, and (c) capacity. The aging tests are carried out at two different temperature (25 and at 45 °C) for one month. The data shown in this figure are average values ($n = 5$) and error bar indicates the standard deviation of data.

respectively. Among the cells with differently designed N/P ratios (1.10–1.30), significant difference was not observed in the aging test with fully charged batteries for one month at 25 and 45 °C. The cells aged at high temperature demonstrate lower performance. Specifically, OCV and recovery capacity are reduced but internal resistance and thickness are increased after aging test.

4. Conclusions

Because negative-to-positive capacity ratio is one of the most important parameters in battery performance, the effect of areal capacity ratio of negative-to-positive capacity (N/P ratios = 1.10, 1.20, and 1.30) on electrochemical properties has been studied in this study. The areal capacity ratios of the electrodes were adjusted by controlling the anode thickness and loading level under fixed anode density. The N/P ratio should be considered as the most critical factor for designing a full cell since it is closely related to the lithium plating and lithium plating affect to the life-time and performances of the battery. It is found that the cell with a high N/P ratio can decrease the actual N/P ratio when lithium plating is occurred. The cell having N/P ratio higher than 1.10 suppresses the lithium plating under 0.85C-rate of charging condition at 25 °C. In addition, the cell with 1.20 of N/P ratio shows the enhanced cycle performance in comparison with other cells in that the cell with N/P ratio = 1.10 is degraded by lithium plating and the cell with N/P ratio = 1.30 has lower capacity retention as an increase in the number of charge/discharge cycle. Among the cells with differently designed N/P ratios (1.10–1.30), significant difference was not observed in the aging test with fully charged batteries for one month at 25 and 45 °C. The cells aged at high temperature demonstrate lower performance. Specifically, OCV and recovery capacity are reduced but internal resistance and thickness are increased after aging test. It is believed that this study of the effect

of N/P ratio on electrochemical properties of lithium batteries can help to design the safe full cell without lithium plating.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.electacta.2014.12.005>.

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