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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.

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 0 V 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 μm) as a current collector of positive electrode. The positive electrodes are pressed to obtain a desired thickness (thickness = 122 μm, 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 μm). 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 μm 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) × 72 mm (length) × 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.

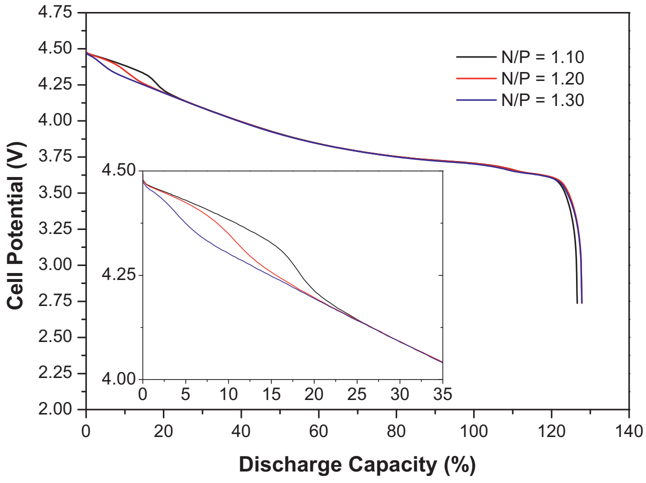

Fig. 1. Discharging profiles at 4.50 V of charging voltage condition. The inset is the magnification of the initial range of discharging profiles to show the voltage overshoot by over-potential.