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Effects of LiNi_{0.5}Mn_{1.5}O₄ cathode thickness on the LiNi_{0.5}Mn_{1.5}O₄/Li₄Ti₅O₁₂ lithium ion batteries

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The lithium ion batteries based on $\text{LiNi}_{0.5}\text{Mn}_{1.5}O_4$ cathode and $\text{Li}_4\text{Ti}_5O_{12}$ anode are prepared by controlling the cathode thickness to optimize cell balancing. The relationship between N/P ratios (0.58, 0.83 and 1.07) and electrochemical performances are investigated. The capacity, rate performance are proportional to the cathode thickness while cycle performance decrease with increasing cathode thickness. It can be explained by high cycling stability of $\text{Li}_4\text{Ti}_5O_{12}$ anode compared to $\text{LiNi}_{0.5}\text{Mn}_{1.5}O_4$ cathode. These results clearly indicate that N/P ratio affects the electrochemical performances of lithium ion batteries.

Key words: Lithium ion batteries, LiNi_{0.5}Mn_{1.5}O₄ cathode, Li₄Ti₅O₁₂ anode, N/P ratios, Electrochemical performances.

Introduction

It is well known that energy storage devices (ESDs) are common in consumer electronics and among the most promising electro-chemical cells which are expected to replace the traditional fossil fuels in transportation, as well as energy storage for renewable energy such as solar or wind power [1].

Among them, the electrochemical performances of lithium-ion batteries (LIBs) are mainly determined by the electrodes. Graphite anode is the most widely used in commercial LIBs along with lithiated metal oxide cathodes, i.e. $LiCoO_2$, $LiMn_2O_4$ and $LiFePO_4$ and so on. However, the graphite has a critical drawback of lithium plating, which cause the serious problem in reliability and safety by the dendrite-induced internal short circuit. This phenomenon is closely related to the reversible potential is in close proximity to that of Li⁺/ Li [2, 3].

 $Li_4Ti_5O_{12}$ (LTO) has been demonstrated to be a promising alternative to graphite for high performance LIBs because of its zero volume change, high working petential (1.55 V vs. Li/Li⁺), superior safety and thermal stability, superlong cycle life in the wide operating temperature range [4]. In recent years, many 2 V-class LIBs have been studied continually, such as LiCoO₂/LTO, LiMn₂O₄/LTO, LiFePO₄/LTO, LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂/LTO and so on [5-9]. In order to obtain an operating

voltage of more than 3 V, the combination of 5 V-class $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) cathode and LTO anode has attracted considerable attention.

LNMO cathode is the most promising candidate among the cathode materials for LIBs due to its flat plateau at 4.7 V (vs. Li/Li^+) and superior capacity of 147 mAh/g, arising from the Ni²⁺/Ni⁴⁺ redox couple [10]. In addition to the high voltage plateau, the intrinsic structure of the spinel phase allows fast lithiation and de-lithiation kinetics [11, 12].

In this paper, we fabricated LIBs using LNMO cathode and LTO anode and investigated the effect of negative to positive electrode (N/P ratio) on electrochemical performances of LIBs.

Experimental

The LNMO cathode and LTO anode electrode (86 wt%), carbon black (7 wt%) and polyvlidene fluoride (PVdF) (7 wt%) were made by casting process on aluminium etching foils, respectively. N-Methyl pyrrolidiznone (NMP) was used as a solvent. The slurry obtained from the mixture was coated by an aluminium etching foils and dried at 150 °C to remove the NMP solvent. The thickness and loading density of LNMO electrode were prepared to investigate the effect of different N/P ratio (0.58, 0.83 and 1.07) on the electrochemical performance. The width and length of cathode and anode electrodes were 5 cm and 200, respectively. The charge and discharge measurements were performed on a cylindrical cell (3560 size). The battery cell was assembled by using Li₄Ti₅O₁₂ as an anode and LiNi_{0.5}Mn_{1.5}O₄ as cathode. The electrolyte

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was a 1.5 M solution of $LiBF_4$ in carbonate solvent mixture including ethylene carbonate (EC), ethyl methyl carbonate (EMC) and diethyl carbonate (DEC). The structural properties were observed by X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM). The electrochemical performance was evaluated using a programmable multichannel battery tester (Arbin Instruments).

Results and Discussion

Fig. 1 shows the XRD patterns of as-prepared (a) $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) and (b) $Li_4Ti_5O_{12}$ (LTO). Both diffractions of LNMO and LTO well match with the cubic spinel with a space group of Fd3m. For LNMO, it was reported that Li^+ ions are in the 8*a* tetrahedral



Fig. 1. XRD patterns of (a) $LiNi_{0.5}Mn_{1.5}O_4$ and (b) $Li_4Ti_5O_{12}$.

sites, Ni²⁺ and Mn⁴⁺ ions are randomly distributed the 16*d* octahedral sites, and O²⁻ ions occupy the 32*e* sites while Li⁺ ions occupy all the 8*a* sites and 1/6 of the 16*d* sites while the Ti⁴⁺ ions occupy the other 16*d* sites, and all the 32*e* sites are filled by O²⁻ ions in the LTO [13, 14]. Both samples have strong and sharp diffraction peaks with no impurity phase, indicating highly crystallized LNMO and LTO.

The SEM micrographs of LNMO cathode and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) anode coated on etched Al foil, were shown Fig. 2. The average particle size of LNMO was 1-3 µm in diameter and that of granule LTO was 5-10 µm., which were composed of primary particles with average size between 200 and 300 nm. The mixed slurry using LNMO and LTO was coated to Al etching foils and then pressed compression ratio of 25%. During the compression process, the LNMO and LTO were evenly distributed on the Al etching foils and a dense electrode was obtained.

Fig. 3 shows cyclic voltammetry (CV) curve of the LNMO/LTO battery prepared with different N/P ratios at a scan rete of 1mV/s with potential widow from 2.1 to 3.7 V. The CV curves with different N/P ratios showed similar shape and a pair of redox peak, indicating working potential, appeared at approximately 3.5 V and 2.9 V. All cells show excellent reversibility. The charge/discharge curves of LNMO/LTO battery with different N/P ratios were shown Fig. 4 and it shows the ideal battery behaviour. The plateau voltage range of LNMO/LTO was between 2.9~3.2 V, indicating that



Fig. 2. The SEM images of electrode of $LiNi_{0.5}Mn_{1.5}O_4$ and $Li_4Ti_5O_{12}$ ((a) 130µm cathode, (b) 100µm cathode, (c) 85µm cathode, (d) 100µm anode).



Fig. 3. The cyclic voltammetry (CV) curves for $LiNi_{0.5}Mn_{1.5}O_4$ / $Li_4Ti_5O_{12}$ battery prepared with different N/P ratios at a scan rete of 1 mV/s.



Fig. 4. The charge/discharge curves of $LiNi_{0.5}Mn_{1.5}O_4/Li_4Ti_5O_{12}$ battery with different N/P ratios during 1^{st} cycle at 1A.

the cell stores the most energy in the voltage range of $2.9 \sim 3.2$ V. It is clearly demonstrated that the cell with low N/P ratio can enhance the discharge capacity in comparison with a cell with low N/P ratio. Therefore, we can conclude that the electrolyte decomposition and electrode collapse of the cell can be effectively suppressed at the low N/P ratio [15].

The rate performance of LNMO/LTO battery with different N/P ratios were shown Fig. 5. Three chargedischarge cycles were carried out for each current density. With increasing charge/discharge current rate, the retention of discharge capacity and DC-ESR of LNMO battery was decreased. It is found that the cell with N/P ratio of 0.58 shows the best retention than other cells regardless of current density (C-rate). The cells with N/P ratio with 0.83 and 1.07 exhibited small difference. In case of graphite anode, the cell with



Fig. 5. The cycle performance of $LiNi_{0.5}Mn_{1.5}O_4/Li_4Ti_5O_{12}$ battery as a function of N/P ratios at different charge/discharge current rates.

small N/P ratio was preferred due to lithium plating. However, the cell with high N/P ratio can be designed to maximize the electrochemical performances because LTO does not cause lithium plating [16]. The retention of discharge capacity increased with decreasing of the N/P ratios. These results could be attributed to the increase in the amount of LNMO that can participate in the reaction, which could be evaluated by the N/P ratios. Moreover, the decrease in rate performance can be explained by the side reaction at the surface of LNMO and the passivation layer [17]. This result is consistent with the charge/discharge curves, as shown above.

The capacity and DC-ESR retentions of the LNMO/ LTO battery at 25 °C under 5 C were shown in Fig. 6. All cells exhibit excellent retention regardless of N/P ratio up to 800 cycles. However, the retention of cell with an N/P ratio of 0.58 rapidly degrades and the retention after 15000 cycles is approximately 46.5 %. The discharge capacity was decreased due to the different capacity of LNMO and LTO with decreasing of N/P ratio. On the other hand, the retentions of the cell with N/P ratio of 0.83 and 1.07 are well maintained without obvious fading during cycling test since discharge capacity and cycle stability of LTO were higher than that of LNMO. With increasing of N/ P ratios, LNMO electrode loading density was decreased with same LTO electrode density. Although they lost similar capacity (about 14%) 1500 cycles, we can confirm that cell with N/P ratio of 0.83 shows slightly high retention than 1.07, as shown in Fig. 6(a). The retention degradation of cell can be explained by



Fig. 6. The cycle performance of $LiNi_{0.5}Mn_{1.5}O_4/Li_4Ti_5O_{12}$ battery as a function of N/P ratios at 5C ((a) discharge capacity, (b) DC-ESR).

Mn²⁺ ion dissolution of LNMO cathode. Fig. 6(b) shows the DC-ESR of cell with different N/P ratio. The ESR of LNMO/LTO battery was decreased with increasing of N/P ratios. These results could be attributed to the decreasing of LNMO electrode thickness. The DC-ESR has a similar tendency with retention and it is composed of ionic resistance, electronic resistance and interfacial resistance, resulting in reduction in electrochemical performance due to sluggish kinetics of Li ion. Consequently, internal resistance is the one of the most important factor for the electrochemical performance, especially cycle performance [18, 19].

Conclusions

In this study, the effect of LNMO cathode thickness on the LNMO/LTO battery was investigated. With increasing of N/P ratios, the discharge capacity and DC-ESR were decreased due to decrease in LNMO thickness. The discharge capacity retention increased with decrease in N/P ratios as a function of charge/ discharge current. These results could be attributed to the increase in the amount of LNMO that can participate in the electrochemical reaction, which could be evaluated by the N/P ratios. After 1500 cycles, discharge capacity retentions were approximately 46.5%, 86.8% and 86.1% for N/P ratio of 0.58, N/P 0.83 and N/P 1.07, respectively. From these results, we can confirm that the cell using LNMO/LTO electrode can deliver superior electrochemical performances at the optimized N/P ratio.

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