Parameter Determination of Lithium Titanate Battery for Rail Transit Based on OCV-SOC Characteristic Curve

Long Wu[*], Guoshi Yang, Wenjun Dai

Huainan Normal University, Anhui 232038, China
longwu557429@126.com

The properties of lithium titanate battery for rail transport in different states are tested based on OCV-SOC characteristic curve in order to achieve the homogeneity of rail transit facilities. Here a study case is cited to reveal how about some parameters for battery under test such as the pressure and the capacity, etc. The results show that this approach has a good effect on the lithium titanate battery charge-discharge control with the best voltage limit determined. It is concluded that the best voltage limits for floating charge are favorable for the charge and discharge control of lithium titanate battery in rail transit.

1. Introduction

The traditional rail transit system usually adopts batteries as a power source, mainly in attempt to use it as an emergency device. Since many advanced technologies sprung up, the battery has fallen well short of what's needed in modern times no matter in which ways such as stability, functionality and so on. In response to this challenge, a kind of lithium titanate battery is developed to replace the common batteries. Lithiumtitanate battery, in theory, completely outperforms any common battery in term of functions, but it has been found from part of the studies that lithium titanate batteries in different states present jagged functions which, in practices, may cause a certain degree of instability against the practical application under normal service conditions.

This paper aims to achieve the homogeneity and stability of rail transit, takes a lithium titanate battery shelved for a year as a case to allow it in a different state of charge, where all parameters are tested. The test results tell us that in which state, the function of lithium titanate batteries reach the peak to be in line with single standard.

2. Literature review

As all kinds of negative materials have been reported to be difficult to overcome, with the continuous development of rail traffic, the requirements for lithium ion batteries are increasingly demanding, and the existing negative electrode materials are difficult to meet the requirements.

The research on lithium titanate battery mainly include: Hannan et al. took lithium lactate as carbon source and lithium source and TiO_2 as the titanium source, prepared the carbon coated lithium titanate composite ($Li_4Ti_5O_{12}$/C) with the help of solid phase reaction. The influence of sintering temperature and Li/Ti molar ratio on the synthesis process was also studied. The crystal structure, microstructure and electrochemical properties of the samples were characterized by constant current charge discharge, cyclic voltammetry, X-ray diffraction and scanning electron microscopy. The results show that the optimum synthesis process is that the Li/Tim molar ratio is 4:5 and sintering temperature is 800 DEG C, and the $Li_4Ti_5O_{12}$/C samples prepared under the optimum process show excellent performance of multiplication and cycle stability. The discharge specific capacity of $Li_4Ti_5O_{12}$/C composites synthesized under 1C is 168.0mAhg^{-1}, and the capacity retention rate of cyclic 50 times is 97.9% under this rate. Especially under the 10C rate, the discharge capacity of the sample is as high as 140.0mAhg^{-1}. After 200 times cycles, the capacity retention rate is 90.2% (Hannan, et al., 2017). Zhai and so on took Li_2CO_3 and TiO_2 as the materials, and synthesized the high crystallinity lithium titanate materials by high temperature ball milling assisted high-temperature solid-state reaction. The effects of ball milling and synthetic temperature on the morphology and electrochemical properties of $Li_4Ti_5O_{12}$ were studied.

The results show that the dispersed particle size distribution is between 0.5–2μm. The constant current charge discharge test shows that the A2 sample synthesized at 750 DEG C shows excellent electrochemical performance, the first discharge ratio at 0.1C ratio is 170.313mAh/g, and the capacity retention rate is 91.6% after 16 cycles (Zhai et al., 2017).

Jaguemont et al. synthesized porous $Li_4Ti_5O_{12}$ materials with LiCl, TiCl4 and 70% oxalic acid as raw materials by one-step solid-state reaction. The material is cubic spinel structure and only one voltage platform appears in 1.5V. The capacity of porous $Li_4Ti_5O_{12}$ materials under 0.5C and 1C discharge rates is 167mAh/g and 133mAh/g, respectively. The charge and discharge is cycled for 20 times, and the capacity retention rate is over 98%. The material exhibits excellent rate performance, and its capacity is still 70Ah/g under 10C cycled for 20times. In addition, the study shows that the material has excellent cycling performance under 50C rate (Jaguemont et al., 2016). Li et al. prepared mesoporous $Li_4Ti_5O_{12}$ materials with $TiOSO_4 \cdot H_2O$ and $LiOH \cdot H_2O$ as raw materials assisted by solid phase reaction assisted by high-energy ball milling. Solid phase reaction results in the formation of mesoporous structure after removal of impurities after high temperature synthesis. This method can ensure that the product is a very fine mesoporous structure with very fine particles. The particle size of $Li_4Ti_5O_{12}$ synthesized by this method is 8nm. When the current density is 1750mAg-1(10C), the first discharge specific capacity is 174.5mAh/g, and after 50 times cycles, the capacity remains 143.4mAh/g (Li et al., 2018). Liu and others investigated the effect of P123 surfactants on the performance of the synthetic $Li_4Ti_5O_{12}$ by sol-gel method. The results showed that the $Li_4Ti_5O_{12}$ material synthesized by adding P123 surfactants showed high specific capacity and excellent performance. In addition, the dispersive nano size $Li_4Ti_5O_{12}$ particles and carbon black are very homogeneous, increasing the contact area between the active materials and electrolytes, shortening the diffusion path of the lithium ion, and having a good high rate performance (Liu et al., 2015). Panchal et al. regarded carbon spheres as templates, and synthesized the spinel structure of lithium titanate spheres with spinel structure by sol-gel method and high temperature calcined xerogels. It is found that the hollow sphere structure and the thickness of the hollow sphere have great influence on the lithium storage property and the high rate cycling performance of the material. Especially the thin-walled hollow lithium titanate ball has a great improvement in its multiplying performance at high magnification. It is concluded that lithium titanate with large pore hollow spheres can greatly shorten the diffusion path of lithium ion and increase the contact surface between lithium titanate and electrolyte. As a result, the mixing of active materials and conductive carbon black is more uniform, which makes lithium titanate have good performance ratio (Panchal et al., 2017). Veneri and others used Li2CO3 and tetrabutyltitanate as the materials and oxalate as chelating agent, and synthesized the $Li_4Ti_5O_{12}$ material by sol-gel method. The material applied differential thermal gravimetry (TG-DTA) and X-ray diffraction (XRD) characterization and found that the samples synthesized were spinel structure. Search engine marketing (SEM) analysis showed that the synthesized $Li_4Ti_5O_{12}$ powder was a uniform cubic shape particle with an average size of 200nm. When the ratio of oxalic acid to titanium is 1, the first discharge capacity of $Li_4Ti_5O_{12}$ material is 171, and the capacity after 35 cycles is 150. The material shows a flat charging and discharging platform and excellent cycling performance (Veneri et al., 2017). Xie et al. used tetrabutyltitanate and Li_2CO_33 as raw materials and EDTA- citric acid as chelating agent, and synthesized $Li_4Ti_5O_{12}$ samples by sol-gel method. The raw materials and powder samples were sintered at different temperatures for a certain time. The samples were characterized by XRD, Fourier transform infrared (FT-IR), and SEM. The sample is a high purity nanometer $Li_4Ti_5O_{12}$, and pure $Li_4Ti_5O_{12}$ can be obtained by sintering at 750 DEG C or higher temperatures. The synthesized $Li_4Ti_5O_{12}$ exhibited a network structure and good dispersion. At 1C and 10C ratio, the discharge specific capacity of the material is 164mAh/g and 108mAh/g, respectively. At 25 DEG C, the capacity retention rate of 1000 cycles is up to 97% under the charge discharge ratio of 1C, and the $Li_4Ti_5O_{12}$ sample synthesized by this method has a high ratio of multiplication and capacity retention (Xie et al., 2018).

To sum up, the above research is mainly on lithium titanate battery. The content involved is how to prepare lithium titanate battery, but it is not combined with OCV-SOC characteristics curve. Therefore, based on the above situation, the test of lithium titanate battery parameters used in rail transportation based on OCV-SOC characteristics curve is studied. In addition, OCV-SOC characteristics curve analysis, external parameter characterization analysis of battery units, and internal mechanism analysis are carried out, respectively, and then the results are discussed. The experimental results show that this study is of great help for testing the performance of lithium titanate battery used in rail transportation in different states.

3. Method

3.1 Analysis of OCV-SOC characteristics

Lithium titanate battery uses lithium titanate material instead of graphite as the battery cathode, which makes up for the defects of graphite such as easy to precipitate lithium, volatile structure, and the formation of SEI

membrane, etc., thus to ensure a higher safety and longer cycle life; the lithium titanate material is higher in diffusion coefficient, and can withstand high rate charge and discharge. It fully meets the requirements of high safety, high reliability, wide temperature range in rail transit. The OCV-SOC curve of Ah- lithium titanate batteries is shown in Figure 1. Since the negative voltage level of lithium titanate is higher than that of graphite, the voltage level of lithium titanate battery decreases and the open circuit voltage falls within 2 and 2.7V, the voltage of battery at the time of charge-discharge basically coincides with open circuit voltage, which shows that the battery polarization is tiny. External voltage of battery more depends on the SOC and DC internal resistance deviations. When SOC is greater than 50%, the battery voltage approaches to a linear growth as the SOC increases. At this time, the battery SOC deviation can be directly determined via the external voltage.
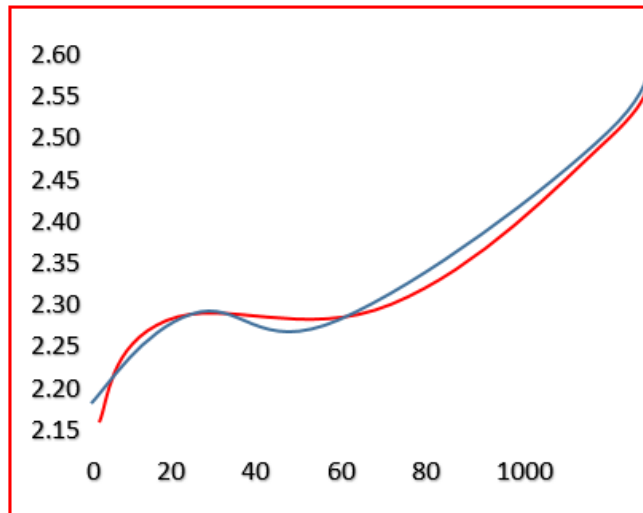

Figure 1: lithium batteryOCV-SOCcurve

The above analysis shows that in a high charge state, the SOC deviation caused by self-discharge rate between batteries can be roughly judged from external voltage of a battery cell with shelf life of a year; further analysis can be made on the deviations of battery capacities # internal resistances after the battery cell and module charge-discharge tests. Due to the OCV-SOC curve plateau exists, if it falls within 0-50%, a capacity increment is suitable. The subtle change in voltage can be amplified to determine whether the chemical reaction in the battery is complete, by which the health state of the battery can be evaluated.

3.2 External parameter characterization of shelved battery cells

The voltage level of lithium battery is lower, the batteries are always packed in series and in parallel in rail transit. As the self-discharge and internal resistance deviations exist, there will be inconsistencies between the monomers, usually characterized by differences in battery capacities and internal resistances. In this paper, six unused battery cells with rated capacity of 8.5Ah were selected and divided into two packs based on their initial capacities. The pack A is 100% in SOC, pack B is 50%. In order to observe the external difference of batteries, keep the battery in a place at a same temperature for one year, record their open circuit voltages, initial SOCs, capacities, calculate the DC internal resistances, calibrated battery capacities, and compare the differences between the parameters.

As shown in Table 1, the characteristic parameters of three batteries in pack A are compared. Three individual batteries are characterized by voltage, capacitance and internal resistance. The open circuit voltage difference manifests the inconsistency of SOCs between batteries. The battery capacity reflects its energy retention and recession, while its internal resistance compares aging and other properties. It is obvious from Table 1 that the three batteries hold voltage at about 2.57V. As can be seen from Figure 2, the battery gets an open circuit voltage of 2.57V in a state of 100% SOC with a minor voltage difference, which shows that the SOC difference also falls within a lower range. Three batteries have an actual capacity of above 8.5Ah, which implies that the difference among the maximum available capacities of three batteries is much lower; the internal resistance of battery 3 is low, so that their internal resistances differ.

Table 1: Comparison of initial information parameters of three batteries in group A

Number of monomers	1	2	3
Open circuit voltage/V	2.575	2.601	2.554
Capacity/Ah	8.790	8.708	8.682
internalresistance/mO	1.80	1.90	1.48

As shown in Figure 2, three batteries are calibrated for capacitance at different rates. 1/3C is the standard capacity; 1/20C is the maximum available capacity; the polarization effect under 1/20C is negligible. The curve is close to the battery open circuit voltage. As shown in Figure 2, the discharge capacity of No. 1 battery is 9.04Ah3 under 1/3C, and 9.28Ah under 1/20C; that of No. 2 battery is 8.97Ah under 1/3C, and 9.2Ah under 1/20C; that of No. 3 battery is 9.18Ah under 1/3C, and 9.18Ah under 1/20C. The difference between discharge capacities at a low rate shows that battery shelved after a year does not manifest recession. 1/3C discharge capacity shows a little difference between the internal resistances of the batteries, no impact on its rate characteristics.
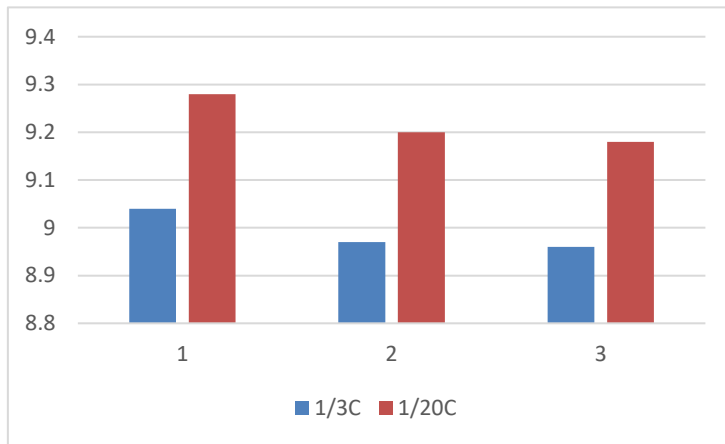

Figure 2: capacity parameters at different rates of three batteries in group A

As shown in the Table 2, the characteristic parameters of three batteries in pack B are compared. Three batteries have a pre-shelf SOC of 50%, and maintain a voltage of about 2.36V; the difference between the batteries is less than 20mV. It is found from OCV-SOC curve that, when SOC is 50%, the open circuit voltage is 2.357V at a low difference; the capacitances of three batteries are all around 4.54Ah, and the difference of capacitances between individuals is lower. There are differences in internal resistance since the battery 3 presents lower.

Table 2: Comparison of initial information parameters of three batteries in group B

Number of monomers	1	2	3
Open circuit voltage/V	2.368	2361	2.358
Capacity/Ah	4.541	4.535	4.578
internalresistance/mO	1.56	1.61	1.25

As shown in Figure 3, the three batteries in pack B are calibrated for capacities after shelving at 50% SOC. 1/3C is the standard capacity; 1/20C is the maximum available capacity; as shown in Figure 3, the discharge capacity of No. 1 battery is 8.93Ah under 1/3C, and 9.16Ah under 1/20C; that of No. 2 battery is 8.91Ah under 1/3C, and 9.14Ah under 1/20C; that of No. 3 battery is 8.93Ah under 1/3C, and 9.12Ah under 1/20C. In contrast with Figure 2, the capacity of battery stored at 50%SOC is lower than that at full, but still greater than 8.5Ah; three batteries have a minor difference in their capacities.
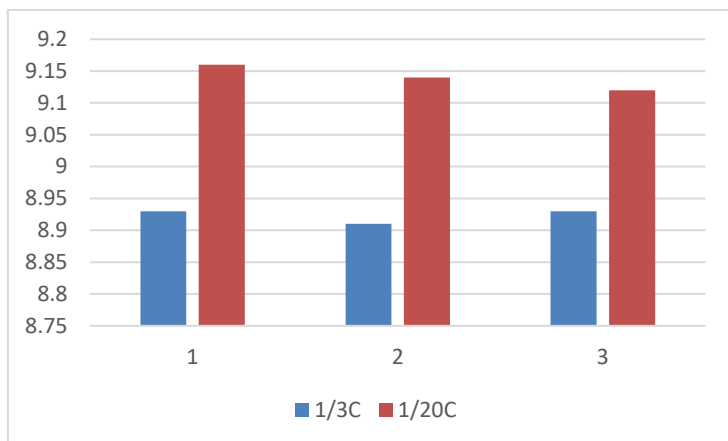
Figure 3: Comparison of three battery capacity parameters in group B

3.3 Internal mechanism

The reactive state of battery at different voltage can be observed from the capacitance increment curve. The unit voltage variation in this paper takes a fixed value of 5mV. The curve of incremental capacitance of lithium titanate battery is shown in Figure 4, where the horizontal axis represents the voltage variation; the vertical axis represents the reaction rate; the area represents the capacity variation. Battery in the initial charge has a moderate reaction rate, and a minor capacitance change. After the battery voltage reaches 2.3V, the reaction rate shows a sharp rise, up to the peak and then rapidly decays to the initial state, i.e. 2.3V-2.4V. The battery reaction rate changes rapidly, and its capacitance change is also reflected in the voltage peak. We can learn from the material properties that cathode material is mainly reflected in the lithium cobalt oxides.
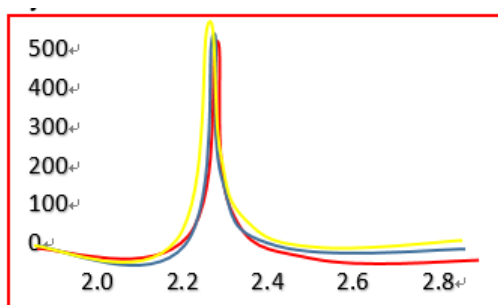

Figure 4: capacity increment curve under 1/20 C of group A battery

As shown in Figure 4, the overlap ratio of the three curves is high, which suggests that there is a little difference between the battery voltage levels and the internal chemical reaction rates are consistent. The peak of battery 1 is significantly higher than that of the other two batteries, which implies that the battery reacts intensely in the vicinity of the voltage level. The overlap ratio of the three curves is high, so that there is a little difference between the voltage levels and the internal chemical reaction rates are similar. The peak of battery 1 is obviously higher than that of the other two batteries, thus the battery 1 reacts more violently near the voltage level.

4. Results and analysis

As above, it is possible to determine how the lithium titanate battery changes in a different shelf life. If the initial SOC is 100%, a great difference does not occur at least in a one-year shelf life, and performs well at battery rates. On the contrary, if the initial SOC fall at 50% or less, they will significantly decay after a one-year shelf.

From the perspective of internal mechanism, similarly, batteries will be divided into packs A, B. The internal mechanism of pack A is to react violently, i.e. from the initial moderate value to the peak at a high speed, which suggests that the internal mechanisms of batteries in pack A differ a little after a shelf life of one year,

but just the other way around, the pack B shows moderate and flat, climbs from the initial value to the peak at a slower rate, which shows that there may be a certain aging phenomenon in internal mechanism, also demonstrates that there is a difference between them in this regard.

5. Conclusion

Inconsistency between lithium titanate batteries are characterized by voltage, capacitance, internal resistance and other factors. The charge-discharge tests at different rates are conducted to compare these batteries. The results show that the difference between capacitances and SOCs of batteries after a shelf life is not obvious, and battery self-discharge rate is lower; it turns out by the capacitance increment that the batteries differ a little at voltage level, chemical reaction rate as characterized, and in phase transition, so that long shelf life has a minimal impact on the service life; packs A, B get a similar results after the tests, which shows that how much the battery capacity after a shelf life loses has nothing to do with the initial value of battery. It is known from the capacitance increment curve that the batteries in the pack show a little difference, and a better consistency. The capacitance curve tells us that the peak inflection points are not consistent, which suggests that there is a slight difference between the initial SOCs of the batteries, so does between the internal resistances. Lithium titanate battery has a good prospect of application due to its better properties. This paper primarily probes into the inconsistent performance of the lithium titanate batteries after a long shelf life under special working conditions of auxiliary power sources by virtue of the battery characterization of voltage, internal resistance and by the capacitance increment analysis from internal mechanism. The floating charge voltage limit is set at 90% SOC based on how the charge voltage of the whole pack of batteries change in order to lay a groundwork for floating charge test to be done next time; since there are limited test data at this stage, further in-depth study is still required to reveal the specific impact of floating charge on the batteries.

Acknowledgement

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