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Structure Principle and Experimental Study of energy storage station with soft carbon anode at megawatt level

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At present, due to limited storage power stations at more than a megawatt, it is lack of operational data. As a core element, energy storage battery plays an important role in the development of energy storage power station. The negative electrode material has a great influence on the overall battery performance. The traditional LiFePO₄ battery uses graphite material as the negative electrode and has poor multiplying power performance and poor cycle performance. Because soft carbon is an excellent material, the battery in which the anode is made of soft carbon has excellent rate performance and large energy density. Compared with the traditional graphite anode material, soft carbon has better properties. In this paper, a set of megawatt-level energy station, the container type energy station, is studied. A novel structure of soft carbon anode lithium iron phosphate battery is developed as the energy battery. The 400KWh capacity charge and discharge experiments with low load power are carried out for the energy storage power station. The results show that the charging efficiency reaches 93% and the discharge efficiency reaches 97%. The experiments also verify the charge and discharge characteristics battery with soft carbon anode. The new structure of soft carbon material battery has good rate performance and the level of the platform is low and stable during charging and discharging. The experimental results are compared with the simulation results and they match very well. Results from this study are the valuable guide for the actual power station operation.

Keywords: Solar; Energy storage; Soft carbon; Rate capability

1. INTRODUCTION

The development of society consumes a large amount of energy and causes serious environmental pollution. The development and utilization of clean energy has become a top priority. Solar energy is undoubtedly the most important one. It is clean, environmental friendly, and inexhaustible. At present, the application of solar energy is mainly based on the photovoltaic (PV) effect to achieve photoelectric conversion. It is estimated that the total installed capacity of PV will reach 700GW[1]in 2020 and solar energy will account for 10% of the world's energy consumption, reaching 50% in 2050 when the fossil fuels are no longer used. These trends have also led to the development and application of large energy storage plants. Currently the development and application of energy storage plants below a megawatts (MW) level has already had many successful engineering cases[2],but the actual operation of megawatt level power station still needs a large amount of data and practical experience to support[3-6].

The battery is the most important part of the energy storage, and the performance of the anode material has a great influence on the performance of the battery[7]. There are many improvements and utilizations of the traditional graphite materials with different structures[8], however, as a new type of anode material, soft carbon materials have more advantages than traditional anode materials. Pan[9] prepared a new type of composite carbon material, which has the characteristics of soft carbon and hard carbon, to improve the specific capacity and rate performance of the battery; Zhang[10] improved the configuration of soft carbon material through the change of particle size and material coating process and the rate performance has been greatly improved than traditional graphite material. A new structure(micro-nano sphere structured)soft carbon is proposed based on soft carbon anode material. Its spherical structure is beneficial to improve the battery performance and the high rate charge discharge performance and low temperature performance are better than traditional graphite materials. Both chemical and electrical properties are more stable. All above mentioned properties ensure that the new structure of soft carbon is ideal to be used for the establishment and operation of MW level power station. This work will develop a megawatt level energy storage station and conduct experimental tests for verification.

2. ENERGY STORAGE STATION

2.1 Energy storage system

The key to the deep development and utilization of solar energy lies in the development of energy storage technology[11]. This paper presents the structure of a container energy storage station as shown in Figure 1. The container energy storage system (CESS) consists of battery cabinet, battery management system (BMS), and container moving ring monitoring system. In addition, based on user's need the energy storage converter and energy management system[12]can be integrated. Battery management system (BMS) uses three layers of modular structure, composed of battery management unit (BMU), main battery management system (MBMS), and battery array management system (BAMS). The power conversion system (PCS) of energy storage station is composed of main power part, signal detection part, control part, drive part, monitor display part, and auxiliary power supply part. The PCS system has the mode of "grid connected operation" and "off grid operation", which controls whether the energy storage power station is integrated into the power grid or not. At the same time, the PCS adopts grid voltage oriented vector control, the orthogonal decoupling of active power, and reactive power is realized so that the active power and reactive power can be separately controlled.

The active power of the system is set up through the PCS system, which can monitor the charging and discharging process and parameters of the battery in real time.

An improved BP network algorithm, the combination of back-propagation (BP) neural network and genetic algorithm (GA), and ant algorithm, is implemented in battery management system to estimate the capacity of the battery under different discharge conditions. At the same time, the battery management system is based on the controller area network (CAN) bus. The internal communication of the battery box is collected and processed by the internal CAN bus and the communication between the battery box and the control center is carried out through the external CAN bus. In this way, the voltage of each lithium ion battery monomer can be detected in real time, which is convenient for monitoring and also reduces the security risk[13].And the management system has the function of selfdiagnosis and self-protection. When any problem occurs, the alarm can be sent out in real time, and the fault battery pack will be put out of operation, which will be beneficial to the protection of the whole system.



Figure 1. Structure diagram of energy storage system

As shown in Fig.2 the set of megawatt level energy storage system consists of 6528 3.2V-50Ah single cell, composes 272 19.2V-200Ah battery modules. Two battery modules are connected in series to form a 38.4V-200Ah battery module. 17 battery modules are connected in series to form a clusters of 652.8V-200Ah basic energy storage system, and the 8 clusters of basic energy storage systems are connected in parallel to form a large capacity energy storage system with a distributed 1 MW capacity. The basic energy storage system can be divided into 8 clusters of batteries, and the MBMS can control the BMU in each cluster. Each cluster consists of 12 clusters of batteries and each BMU is responsible for managing 12 battery packs. The structure of the BMS system is shown in Figure 3. Eight cluster battery heaps are formed through interconnection and eight clusters are summed up in the main control box to form a complete control system. The whole BMS system collects and monitors the charging and discharging voltage and current of each battery in real time, completes the full charging and discharging of the battery pack under the cooperation of PCS, and realizes the capacity calibration of the battery system and the function calibration of SOC.



Figure 2. Schematic diagram of BMS system



Figure 3. BMS system structure

The container energy storage station has the characteristics of simplifying infrastructure construction cost, short construction period, high modularization, easy transportation and installation. It can be used in power plants, wind power plants, solar power plants, islands, residential areas, schools, scientific research institutions, factories, large load centersand other applications. The design capacity of the container energy storage station is 1MWh, which puts forward high requirements for the construction of energy storage station. In the solar energy storage station, the development and application of energy storage battery is the key. The traditional lead-acid battery has small energy density and serious pollution[14-15].Lithium ion battery has high energy density and high efficiency but the cost is high[16].The battery with soft carbon anode, as a new type of lithium ion battery, has the characteristics of high energy density and high life expectancy of the traditional lithium-ion battery. Its low preparation cost makes it possible to apply this type of battery in a wide range. The

container energy storage station uses a kind of spherical soft carbon anode material for lithium iron phosphate battery, which has advantages over the traditional lithium battery.



2.2. Battery with soft carbon anode

Figure 4. Schematic diagram of spherical soft carbon with micro-nano structure

Soft carbon material is a kind of graphitized carbon which is easy to be graphitized after the heat treatment temperature reaches the graphitization temperature. Soft carbon material has low and stable charge/discharge platform, good rate performance, good cycle charging and discharging performance, and high first time coulombic efficiency. Through the adjustment of raw material treatment technology and process parameters, we can control the particle size of the material and improve the conductive ability of soft carbon through doping appropriate additives[17]. As shown in Fig.4, the soft carbon and the pyrolytic carbon are organically compounded by the composite technology, and then the surface modification of the material is carried out in the process of forming the composite material, and the micro-nano structure spherical soft carbon is obtained. The spherical structure can provide rich nano pores for soft carbon materials and it is beneficial to the rapid diffusion of lithium ion and to increase the rate performance. The low temperature charging and discharging performance is superior. The interface stability of electrode/electrolyte is enhanced after carbonization at low temperature, forming a solid electrolyte interface (SEI)[18]. The selectivity of the solvent in the electrolyte is low, which is beneficial to the long-term cycle performance of the battery. When the material is spherical the bulk density increases, which is beneficial to the increase of the bulk energy density of the cell, and the specific surface area is low, which is beneficial to reduce the side reactions during charging and discharging to improve the safety performance of the battery. Because the soft carbon of spherical structure is easy to be prepared, the cost control can be done at a lower level, which is beneficial to the popularization and wide application of this new material. The actual parameters of the developed micronano spherical soft carbon anode are as follows: the discharge capacity is of more than 350mAh/g for the first time, and the efficiency is not less than 87%; the particle size is 6.0 to 15.0

 μ m; the true density is greater than or equal to 2.10g/cm3; the tap density is larger than 1.0g/cm3; the specific surface area is less than or equal to 3.0m2/g; the ash content is less than or equal to 0.10%

The system uses a kind of Lithium iron phosphate battery whose anode material is made of micro-nano composite structure with mesophase spherical soft carbon doped with about 40% graphite. In Chen[19]'s research, the charge-discharge performance of graphite anode is poor, and doping can improve its charge-discharge performance to a certain extent. So compared with the traditional anode material battery, it should have better charge and discharge characteristics.

3. EXPERIMENTAL VERIFICATION

Due to the high cost of the storage power station, it is still limited to the demonstration application stage[20]. The accumulation of experimental research and original operation data is of great significance for the future industrial application. Experiments were carried out to investigate the charging and discharging performance of the power station with small storage energy and power. The energy storage is 400kWh and the power is 100kW.

3.1 Charging experiment



Figure 5. Relationship curve between monomer voltage and time in charging process

In the charging process, the process curve between the monomer voltage and charging time is shown in Figure 5. The relationship curves of the voltage for a single cell with time are given in the four groups of charging process. With the charging process, the battery voltage begins to rise sharply because of capacitive voltage. But with the change of the charged state of the power station the rate slows down, because the lithium iron phosphate in the battery quickly reacted, and the lithium ions moved to the negative electrode, the ions began to transform. With the increase of heat in the charging process, the internal resistance of the battery changes, the internal resistance becomes larger, so the high speed of the voltage rise is slowed down[21], forming the "inflection point", the corresponding platform effect appears. However, the platform is not obvious when charging the battery with soft carbon anode. As a contrast, Zhai[22]get the conclusion through the experiment that graphite anode material has higher lithium ion insertion and stripping potential, so it has a higher voltage platform. So for the energy storage station it just reflects the better charging characteristics.

It can also be seen from Figure 5 that the lithium iron phosphate battery has poor consistency and this is mainly due to the lithium iron phosphate battery manufacturing process[23].From the single aspect of material preparation, the synthesis reaction of lithium iron phosphate is a complex heterogeneous reaction. There are solid phosphates, iron oxides and lithium salts, carbon precursors, and reductive gas phases. In this complex reaction process it is difficult to ensure the consistency of the reaction[24].In order to better demonstrate the inconsistency of the battery, the relationship between the voltage and time for each battery is illustrated in Figure 6 to test the fitting degree of the data. The X axis represents the battery number, the Y axis represents the charging time, and the Z axis represents the voltage value of the monomer. Results show that the consistency of the battery and the variance (sum square error-SSE) is 9.928e-28 and the coefficient of determination (R-square) is 1. The data fitting degree is very high and the consistency of the battery is also quite good.



Figure 6. Fitting curve of battery consistency

3.2. Discharging experiment

Battery discharge performance is also a very important application performance characteristic of batteries. The biggest difference between soft carbon anode and traditional graphite anode is that

soft carbon has a low and stable charging and discharging platform and excellent rate performance[25]. The discharge curves of soft carbon cells at different rates are shown in Figure 7.



Figure 7. Comparison of discharge curves of the battery at different rates



Figure 8. Fitting discharge curve of experimental data

In Fig.7, the battery discharges to the cut-off voltage at different rates, we can get that the higher the discharge rate is, the lower the discharge capacity is. Tang[26] discovered a rule of discharge capacity change of lithium ion battery at high rate discharge through experiments, the higher the discharge rate, the higher the discharge capacity. So this is consistent with Tang's conclusion. The discharge capacity of 2C(C is the capacity of the battery)has been significantly reduced, but can still achieve more than 90% of the discharge capacity of 0.5C. However, in Li's study of graphite negative materials, the data can only reach about 31.6% [27]. Therefore, the battery with soft carbon anode has

good rate performance and basically meets the design expectation. The discharge curve of the single soft carbon cell is fitted by the experimental data as shown in Figure 8. The process is relatively smooth.

From above results the charge/discharge characteristic curves of this type of battery basically meet the requirements of experimental design. In order to verify the charging and discharging characteristics of the whole energy storage system, the experimental data are fitted as one curve of the energy storage system and the system characteristics is analyzed as shown in Figure 9 and 10.



Figure 9. Voltage and time fitting curve of system charging and discharging



Figure 10. Fitting curve of charge and discharge voltage and SOC

Figure 9 shows the relationship between the overall voltage and time of the energy storage system during charging and discharging. Figure 10 denotes the relationship between the charge/discharge voltage and the SOC. The charging and discharging voltage trends of the energy storage system are the same as those for the single battery with soft carbon anode and this shows that the single cell has good consistency.

The efficiency of battery charging and discharging directly affects the fast response output of the energy storage system. It can be seen from Figure 9 that the charge and discharge curves with respect to time do not overlap. The time difference between coordinate axes directly reflects the difference between charge and discharge efficiency. According to the experimental data, the charging efficiency of the energy storage system can reach 93% and the discharge efficiency can reach 97%. As a comparison, Wang[28] experimented with the existing energy storage power station and found that the charging efficiency varied from 83% to 91%, while the discharge efficiency was about 93%. The results basically meet the design needs.

4. CONCLUSION

A micro spherical composite lithium iron phosphate storage battery with micro-nano composite structures was developed .Xu[29] prepared a kind of soft carbon--the nanoporous carbon microspheres (NCM). The porous spherical structure of NCM possesses noticeably lithium-ion storage capability, which exhibits high discharge capacity and excellent cycling stability at different current density. The conclusion is in agreement with the results obtained in this experiment (during the experiment, when the current density is 20mA/g, the first discharge capacity is 312.6mAh/g, and the first coulombic efficiency is 80.7%). Gao[30]prepared a kind of carbon by in-situ polymerization and pyrolysis, in which the carbon-coated layer had complete micropores. After 40 cycles, the composite still has a reversible capacity of more than 1200mAh/g with a capacity retention of 95.6% and excellent cycling performance. But the soft capacity of the prepared soft carbon material is 97.7% after 600 cycles, so the system had good charge and discharge characteristics. A megawatt power station was built and the characteristics of the station were verified through experiments: (1)In the charging process, the voltage of the battery with soft carbon anode was stable and low. Qiu[31]pointed out that when charged at high rate, the charge performance of graphite anode battery is poor, and the charging platform is obviously higher than that of soft carbon material prepared by experiment. So the charging performance of the soft carbon battery is good. And with the progress of chemical reaction the high speed rate gradually decreased. The charging process showed good consistency; (2)In the discharge process, the battery showed a low and stable discharge platform and the discharge trend had a low and stable platform at different rates. Although the capacity decreased greatly, it could still meet the requirements of the experimental design (the discharge capacity of 2C was decreased, but still more than 90% of the 0.5C discharge during the experiment). As a contrast, in Wang[32]'s research, it was found that the discharge performance of graphite negative electrode was poor under high magnification, and the discharge platform was very low. Because of the change of graphite layer structure and the increase of lithium ion diffusion rate at high rate, the high rate discharge ability of graphite is poor. So the rate performance of the soft carbon was excellent; (3)Through the analysis of the experimental data, the overall energy storage performance of the power station was excellent. The power station charging efficiency reached 93% and the discharge efficiency reached 97%. While Chen[33]carried on the experiment to the traditional energy storage power station, and obtained that the charging and discharging efficiency of the energy storage power station is about 92.2%, the maximum is not more than 94%. So the station had high efficiency of charging and discharging. The data processing results were highly consistent with the theoretical values. Therefore, the basic index of the power station so that it can serve the network with better output characteristics; At the same time, large energy storage and high power charge discharge experiment should be carried out to verify its operation reliability and accuracy.

References

- 1. M. Sanehez, Overview of microgrid research and development activities in the EU in Montreal 2006-Symposium on Microgrids, 1 (2006) 22.
- 2. C.T. Ana, B.M. Eduard, Renewable and Sustainable Energy Reviews, 59 (2016) 309-319.
- 3. X.C. Fan, W.Q. Wang, R.J. Shi, Renewable & Sustainable Energy Reviews, 72 (2017) 950-960.
- 4. S. Mandelli, J. Barbieri, R. Mereu, *Renewable & Sustainable Energy Reviews*, 58 (2016) 1621-1646.
- 5. J.L. Li, S.H. Xu, W.T. Jin, Low Voltage Apparatus, 13 (2017) 1-7.
- 6. T. Lockwood, I. Renda-Tanali, *Engineering economist*, 55 (2010) 1-37.
- 7. Y. Li, S. Wang, Y.B. He, Journal of Materials Chemistry A, 9 (2017) 4359-4367.
- 8. P.X. Han, B. Zhang, G.L. Cui, *Electrochemistry Communications*, 44 (2014) 70–73.
- 9. G.H. Pan, Y.B. Zhao, K.Z. Zhang, *Energy Storage Science and Technology in chinesecxksama*, 6 (2017) 94-100.
- 10. H. Zhang, Journal of Fudan University, (2014) 1-64.
- 11. F. Ausfelder, C. Beilmann, M. Bertau, ChemBioEng Reviews, 4 (2017) 144-210.
- 12. X.T. Shi, B. Yin, Y.P Cong, B Li, A new method for power scheduling management of distributed energy storage system based on multi-agent structure in 4th International Conference on Mechanical Materials and Manufactring Engineering, 4 (2016) 411-414.
- 13. J. Jousse, N. Ginot, C. Batard, Lemaire Elisabeth, *IEEE Transactions on Smart Grid*, 8 (2017) 2129-2137.
- 14. B. Hariprakash, A.U. Mane, S.K. Martha, S.A. Gaffoor, S.A. Shivashankar, A.K. Shukla, *Electrochemical and Solid State Letters*, 7 (2004) 66-69.
- 15. V.V. Bayunov, G.V. Krivchenko, Podalinskii, A. Yu, *Russian Electrical Engineering*, 75 (2004) 78-80.
- 16. B.I. Banov, H.C. Vasilchina, Bulgarian Chemical Communications, 43 (2011) 7-16.
- 17. X.Q. Han, P.X. Han, J.H. Yao, S. Zhang, X.Y. Cao, J.W. Xiong, J.N. Zhang, G.L. Cui, *Electrochimica Acta*, 196 (2016) 603–610.
- 18. J.M. Zheng, J.A. Lochala, A. Kwok, Z.Q.D. Deng, J. Xiao, Advanced Science, 4 (2017) 1-19.
- 19. M. Chen, B. Xiao, C. Yang, Chinese Battery Industry, 11 (2006) 125-127.
- 20. Z.Q. Tang, H.T. Zhou, Chinese J Power Sources, 1 (2014) 185-188.
- 21. F. Yang, Y.L. Qiao, D.G. Gan, Transactions of China Electrotechnical Society, 12 (2017) 171-178.
- 22. Y.M. Zhai, Journal of Tianjin University, (2000) 1-70.
- 23. S.M. Zhang, Journal of Shanghai Jiaotong University, (2015) 1-144.

- 24. T. Li, C.T. Lin, Q.S. Chen, Journal of Tsinghua University Science and Technology, 52 (2012) 1001-1006.
- 25. Y.J. Zhang, Z.Y. Zhu, P. Dong, *Chemical Industry and Engineering Progress*, 11 (2017) 4106-4115.
- 26. Z.Y. Tang, C.Y. Tan, Y.H. Chen, Chinese J Power Sources, 5 (2006) 383-387.
- 27. L.X. Fu, Journal of Harbin Institute of Technology, (2013) 1-57.
- 28. H.B. Wang, H. Chen, J.M. Dong, North China Electric Power, 3 (2016) 8-17.
- 29. S.T. Xu, Z.F. Zhang, T.Y. Wu, Y. Xue, Ionic, 24 (2018) 99-109.
- 30. P.F. Gao, J.W. Fu, J. Yang, Physcal Chemistry Chemical Physics, 47 (2009) 11101-11105.
- 31. W.H. Qiu, G. Zhang, S.G. Lu, Q.G. Liu, Chinese journal of power sources, 23 (2000) 7-10.
- 32. J. Wang, L. Qi, J.H. Li, Study on properties of MCMB and artificial graphite as anode materials for lithium ion batteries on the Eighth National Annual Meeting of Applied Chemistry in Chinese society of Chemistry, 8 (2003) 395-397.
- 33. H. Chen, J. Diao, K. Bai, Electric Power, 5 (2016) 149-156.

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