Application and Development of Lead-Carbon Battery in Electric Energy Storage System

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***Abstract*—*Lead-carbon battery is a kind of new capacitive lead-acid battery, which is based on the traditional lead-acid battery, using the method of adding carbon material to the negative electrode to improve the specific capacity and charge-discharge characteristics of the battery. Lead-carbon battery solves the defects of low charge-discharge rate of traditional lead-acid battery, improves the phenomenon of negative sulfate, and has the advantages of good charge-discharge performance and long battery life. This paper firstly starts from the principle and structure of lead-carbon battery, then summarizes the research progress of lead-carbon battery in recent years, and finally looks forward to the development direction and trend of lead-carbon battery in the future.*

***Keywords*—*lead-carbon battery,lead-acid battery,electric energy storage system*

I. Introduction

In recent years, electrochemical energy storage systems have developed rapidly, and the energy storage industry market under the "Carbon neutrality and emission peak" goal has great potential for development, and the application prospects are more extensive. As a mature and widely used technical product, lead-acid battery has been widely used in many fields such as navigation, transportation, electric power, and communications. However, with the popularity of lithium battery, photovoltaic cells and other batteries, lead-acid battery has inevitably been affected to some extent. When the lead-acid battery operates in a high-rate partial state of charge (HRPSoC), the sulfation of the negative electrode is exacerbated by the increase in the number of cycles, and it is irreversible. In order to make the charge-discharge performance of the lead-acid battery better, extend the working time of the battery, completely or partially replace the active substance of the negative electrode of the lead-acid battery with carbon material to provide the specific surface area required for the reaction and increase the specific capacitance, which is the origin of the lead-carbon battery. Lead-carbon battery improves the insufficient charge-discharge capacity and stability on the basis of lead-acid battery, while retaining the advantages of lead-acid battery such as cheap price, safe, reliable, and recyclable, so it has broad market prospects and research value.

II. *The Principle of Lead Carbon Battery*

Lead-acid battery uses sponge lead (Pb) and lead dioxide (PbO_2) as the active substances of the negative and positive electrodes of the battery respectively, and ensures the reciprocating electrochemical reaction by realizing the conversion between Pb^{2+} and Pb. When the battery is discharged, the PbO_2 at the positive electrode and the Pb at the negative electrode react with H_2SO_4 to form $PbSO_4$, respectively; When the battery is charged, the PbSO4 at the positive electrode and the negative electrode reacts again to form PbO_2 and Pb. The specific formula of the charge-discharge reaction of the lead-acid battery is as follows:

Discharge reaction:

$$\mathrm{PbO_2 + HSO_4{}^- + 3H^+ + 2e^- \longrightarrow PbSO_4 + 2H_2O} \quad (1)$$

$$\mathrm{Pb + HSO_4{}^- \longrightarrow PbSO_4 + H^+ + 2e^-} \quad (2)$$

Charge reaction:

$$\mathrm{PbSO_4 + 2H_2O \longrightarrow PbO_2 + HSO_4{}^- + 3H^+ + 2e^-} \quad (3)$$

$$\mathrm{PbSO_4 + H^+ + 2e^- \longrightarrow Pb + HSO_4{}^-} \quad (4)$$

Lead-carbon battery is a kind of capacitive hybrid energy storage device which inherits some of the characteristics of lead-acid battery. The carbon material is added to the negative electrode as a negative electrode collector, completely or partially replaces the original Pb active substance of the lead-acid battery, and then the lead-carbon composite electrode is matched with the PbO_2 positive electrode to assemble, finally the lead-carbon battery is obtained. There are many kinds of carbon materials that can act as an anode collector of lead-carbon battery, such as: graphene, activated carbon, carbon nanotubes and much more. Figure 1.1 is a brief structural diagram of a lead-carbon battery.

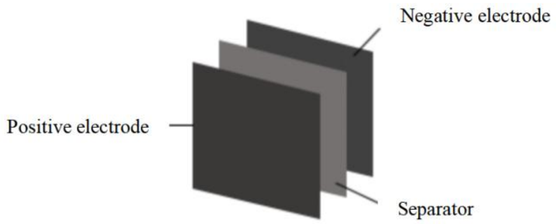

Fig. 2.1 *Schematic diagram of the structure of a lead-carbon battery*

Lead-carbon battery works similarly to lead-acid battery, The main difference comes from the negative electrode of the battery. The $PbSO_4$ crystallization produced during the reaction process of traditional lead-acid battery will make charge-discharge reversibility of the battery worse, so the cyclic life of lead-acid battery isn't long enough. Lead-carbon battery plays a buffering role by incorporating carbon materials into the negative active substance witch has the functions in conducting electricity, increasing capacitance, limiting the crystallization of $PbSO_4$, increasing the active action site, etc., thus delaying the accumulation of $PbSO_4$ crystals, improving the charge-discharge reversibility of the battery, reducing the weight and the cost while prolonging the battery life, and greatly improving the battery performance.

III. *HISTORY AND CURRENT SITUATION*

A. Development of Lead-carbon Battery

The earliest lead-acid batteries appeared in the 19th century, invented by the French physicist Plante [1] in 1859, and have a history of more than 160 years. Plante compared the metal electrodes of different materials and found that the battery composed of the lead electrode immersed in dilute sulfuric acid had the highest voltage and current, and finally determined that lead was used as the positive and negative electrodes, rubber strips as the separator, and sulfuric acid as the electrolyte, forming the initial chemical power source - lead-acid batteries. Before 1873, the battery was only a laboratory product, in 1873, the French engineer Gramme mistakenly connected the electricity from one DC generator to the output of another DC generator, and the DC generator that was crucial to the practicalization of lead-acid batteries was introduced. In 1881, Sellon proposed a lead-antimony alloy plate grid, in the same year, Faure proposed a method that coat the lead paste on the lead plate to form an active substance, the lead antimony alloy plate grid combined with this powder coating method to form a paste-type plate, laying the foundation for the continuous production of lead-acid batteries.In 1882, Cladstone and Tribe proposed the double-sulfate theory, which elaborated the reaction mechanism of lead-acid batteries in the process of charging and discharging, and confirmed the working principle and process route of lead-acid batteries. In the 20th century, lead-acid battery entered a period of rapid development, and its materials and manufacturing processes were greatly improved. In 1910, the Exide Company of the United States introduced the tubular cathode plate. In 1924, Shimadzu invented the ball mill to make lead powder, which effectively improved the manufacturing process of lead powder. In 1935, Haring and Thomas invented the lead-calcium alloy grid, which greatly improved the maintenance needs of batteries. In the same year, Slegler invented the glass wire tube to replace the rigid hose used in the past for tubular plates. In 1957, Otto Jache invented a gel electrolyte that improved the problem of hydrogen evolution in the battery. In 1970, Deviff built a valve-regulated battery with a lean-liquid structure. In 1975, GatesRutter invented a D-type sealed lead-acid dry battery, which is a prototype of a valve-regulated sealed lead-acid battery (VRLA). In 1980, VRLA batteries were first introduced to the market. In 1996, VRLA batteries were recognized by the majority of users, replacing the traditional liquid-rich batteries.

Lead-acid battery as a mature process, widely used technology, with its low price, easily obtained raw materials, safety, reliability and other advantages, from the first generation of liquid-rich battery to the second generation of valve-controlled sealed battery, is widely used in navigation, transportation, electricity, communications and other fields. With the rapid progress and development of society, science and technology, especially the maturity of new energy technology, new requirements and challenges have been put forward for the technology of lead-acid battery, so that the third generation of lead-acid battery - lead-carbon battery can be born. In 1997, scientists at the Japanese battery company found that adding a higher than the usual amount of carbon material to lead-acid batteries can improve the problem of sulfation of the negative electrode in the battery under HPCSoC. In 1998, the Advanced Batteries Consortium (ALABC) identified the lead-carbon battery research project. At present, scientists from various countries have carried out a lot of in-depth research on the material, structure and mechanism of action of lead-carbon batteries. So far, lead-carbon batteries have been developed for more than 20 years.

B. Research Progress of the Grid of Lead-carbon Battery

The grid of lead-carbon batteries is roughly the same as that of lead-acid batteries, and its function is to distribute the current evenly on the plate and is the support carrier of the active substance. The positive plate gate material is usually lead alloy, and the most used positive plate grid is lead antimony alloy plate and lead-calcium alloy plate. The traditional negative electrode alloy plate grid mainly includes lead and antimony alloy plate grid, lead-calcium alloy plate grid, lead-tin alloy plate grid, etc. In recent years, researchers have tried to improve the the specific energy of the battery by reducing the quality of the grid, so the light grid has developed rapidly.

The lightweight grating uses less dense materials as the substrate and lead or lead-based alloy materials as the coating on the surface of the grating substrate. Lannelongue J [2] et al. use titanium substrates such as dioxide fin coated foils or expansion meshes as positive grids, and the results show that titanium substrates have excellent mechanical strength, corrosion resistance and abundance, and the use of titanium cathode plates can reduce electrode thickness and weight and effectively slow down the corrosion of positive collectors. Naresh V et al. [3] inhibit the corrosion of the positive lead alloy plate grid by adding a polypyrrole (ppy) coating to the surface of the lead alloy grid, and the experimental results show that the presence of ppy coating significantly improves the corrosion resistance and inhibits the oxygen release rate, and the charge-discharge rate is increased by 10% to 20% compared with traditional lead-acid batteries. Yang T [4] et al. use bronze mesh plated with lead and tin as the negative plate, compared with the traditional negative plate, the weight is reduced by about 17 g, and the experimental results show that the high electronic conductivity of the bronze-based negative plate can inhibit the sulfate phenomenon of the negative electrode, and the specific capacity of the battery has also been significantly increased. Figure 2.1 and Figure 2.2 are the comparison curves of charge and discharge performance of tin bronze grid battery (TBGC) and conventional grid battery (CGC). It can be seen that the charging voltage of TBGC is lower than that of CGC, and its hydrogen evolution reaction occurs later, during discharge, the discharge voltage and discharge time of TBGC are higher than those of CGC, and the charge-discharge performance of TBGC is better. In addition, after 450 cycles of 100% discharge, the disassembled lead-tinned bronze mesh negative plate is still intact and can be directly recycled and reused, opening up a new direction for the lightweight development of lead-carbon batteries.

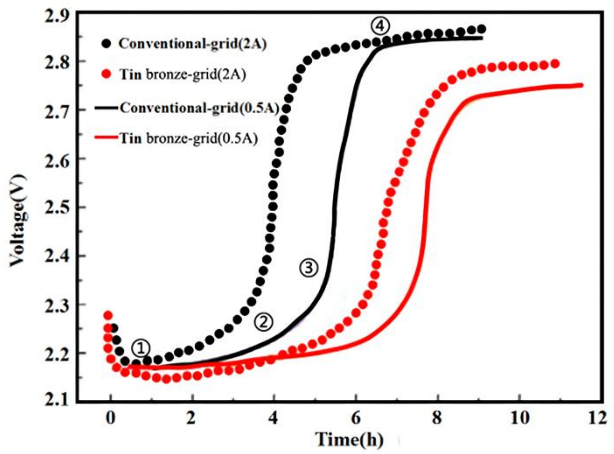

Fig. 3.1 *The charging curves of TBGC and CGC at different charging currents*

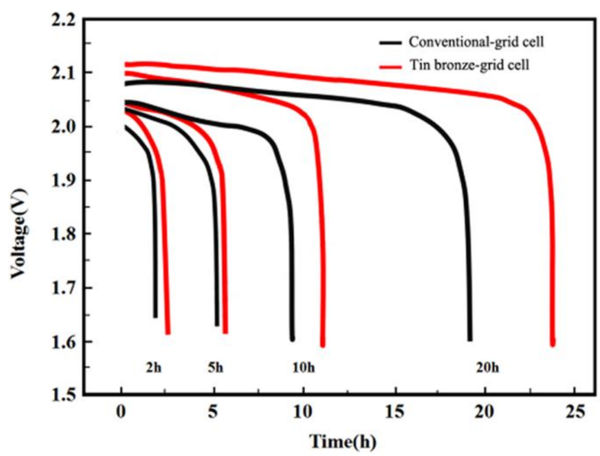

Fig. 3.2 *The discharge curves of TBGC and CGC at different discharge rates*

C. *Research Progress on the Negative Active Substance of Lead-carbon Battery*

The negative active substances in lead-carbon batteries include sponge lead and carbon materials, lead loses electrons during discharge and is converted into the form of lead ions, and lead sulfate gets electrons reduced to lead during charging, forming an electric current, forming an electric current; Carbon materials with electrochemical activity can play a role in inhibiting the sulfation of the negative electrode, which is of great significance for optimizing battery performance.

The following is a discussion on the research progress of the negative active substances in lead-carbon batteries from four perspectives: preparing carbon composite materials, changing the binding method of lead-carbon materials, adding other additives to the battery negative electrode, and recycling and reuse of waste lead paste.

1) Preparing carbon composite materials

Although the addition of carbon materials can inhibit the sulfation of the negative electrode, the hydrogen evolution overpotential of the carbon material surface is lower than that of the lead surface, which leads to aggravation of the hydrogen evolution reaction. Combining carbon materials with other materials can slow down the hydrogen evolution reaction, thereby improving the capacity and electrochemical performance of the battery.

Jiang Z Y et al. [5] prepared nitrogen-doped activated carbon material by high-temperature pyrolysis, and used it for the negative electrode of lead-carbon battery. Electrochemical measurement results showed that since nitrogen is easy to bind to hydrogen atoms during hydrogen evolution reaction, thereby inhibiting hydrogen atoms from entering hydrogen, so nitrogen-doped activated carbon has a higher hydrogen evolution reaction potential than activated carbon in sulfuric acid solution, and more importantly, the specific capacitance value of nitrogen-doped activated carbon is 51.57% higher than that of raw activated carbon in sulfuric acid solution, which can inhibit the precipitation of hydrogen , improve specific capacitance and cycle life.

2) Changing the binding method of lead-carbon materials

Generally, The preparation of lead-carbon composites is to mechanically mix activated carbon, graphite and other carbon materials directly with lead paste, although this method can improve the sulfation of the negative electrode of the battery, but it will lead to uneven distribution of lead and carbon particles, incompatibility between the interface between the carbon material and the negative active substance, etc., and ultimately affect the electrochemical properties of the negative active substance.

Since the birth of lead-carbon battery, various types and structures of carbon materials have emerged in an endless stream, and the application of porous carbon materials to the negative electrode of lead-carbon batteries can optimize battery performance. BLWA et al. [6] proposed and prepared a new type of nano-lead-doped mesoporous carbon composite material as a negative electrode additive, and experimental results showed that through NaOH activation and air oxidation, porous carbon can obtain more mesoporous volume and appropriate acidic groups, enabling the mesoporous system to load more nano-lead deposits, and limit the size of the deposits to the nanometer level through its local effects, thereby ensuring more significant inhibition of hydrogen evolution and better $Pb/PbSO_4$ reversibility; Li J et al. [7] synthesized a lead-carbon composite NSCG@PbO with nano-lead oxide and multifunctional porous carbon nucleated on the graphene framework by sol-gel pyrolysis, and applied it to the negative electrode of lead-carbon batteries, the unique three-dimensional porous lead-carbon network structure of NSCG@PbO limits the formation of large $PbSO_4$ particles, effectively increases the porosity of lead-carbon electrodes, maintains the electrochemically active surface area of lead-carbon batteries, and PbO functional groups and COO functional groups embedded in the graphene framework further enhance the interfacial performance of electrode and electrolyte, inhibited the hydrogen evolution during the long cycle, and successfully enhanced the reversibility of the deep discharge of the battery; Zhang Y S et al. [8] synthesized three-dimensionally constructed graphene/nano-lead (SCG-Pb) composites by electrodeposition, the study showed that SCG-Pb has good electrical conductivity, rich pore structure and excellent dispersion, an efficient conductive network can be constructed in the negative electrode active material, which is beneficial to the ion exchange between the negative electrode active material and the electrolyte, accelerates the dynamic process of the negative electrode, and effectively suppresses the irreversible sulfation of the negative electrode, thereby improving the capacity and cycle life of the battery; Xie JM et al. [9] prepared lead oxide and carbon composites (LC) by pyrolysis of highly graphitized porous carbon and $PbCO_3$ mixtures, the test results show that the density difference between Pb and C can be eliminated by using LC materials, thus, they are uniformly mixed, effectively limiting the accumulation of irreversible PbSO4, and the presence of -Pb-COO chemical bonds can enhance the stability of the lead-carbon electrode. Compared with the control battery, when the LC material is added to the negative electrode active material, the initial specific discharge capacity increased by 16.5%; Gao Y [10] prepared a new lead-modified phenolic resin-based carbon material (Pb/PRC) with lead-modified phenolic resin (Pb/PR) as precursor, toluene as pore-forming agent, and KOH as activator, he hierarchical porous nanosphere structure exhibited by it helps to prolong its cycle life under HRPSoC, effectively suppress hydrogen evolution and improve specific capacitance; Yi T H et al. [11] synthesized hierarchically porous carbon with in-situ grown carbon nanotube clusters (HPC-CNTs) by transition metal catalytic cracking, and used as an additive to suppress the irreversible sulfation of the negative electrode. This synthetic method not only established a stable connection point between HPC and carbon nanotubes, but also avoided the aggregation of carbon nanotubes.

3) Adding other additives to the battery negative electrode

Pavlov D et al. [12] incorporated the carboxylic acid aromatic ester compound benzyl benzoate ($C_6H_5CH_2O_2CC_6H_5$) as an additive into the negative electrode active material of the battery, the research results show that $C_6H_5CH_2O_2CC_6H_5$ can effectively inhibit the hydrogen evolution reaction and improve the cycle life and electrochemical performance of the battery.

4) Recycling and reuse of waste lead paste

Recycling lead resources from waste batteries for remanufacturing lead-carbon batteries is a very green process. In recent years, many researchers have carried out research on the recycling and reuse of waste lead paste.

Hjd A et al. [13] used waste batteries and waste high-density polyethylene (HDPE) plastics as raw materials to prepare PbO/C composites, and proposed an energy storage application that can be used in lead-carbon batteries by extracting value-added products from waste plastics and waste lead-acid batteries; Ali A [14] successfully synthesized a porous carbon material based on silkworm dung (SEPC) by metal catalytic cracking method. The SEPC and desulfurization waste lead slurry were mixed and calcined to obtain a composite material SEPC-PbO of SEPC and PbO， which is used as a negative electrode additive to inhibit irreversible sulfation of batteries. The synthesis of bio-carbon materials and the combination of waste lead paste recycling industry are discussed, which can help reduce the pollution risk of silkworm breeding and lead-carbon battery recycling industry and realize the sustainable use of carbon resources.

D. Research Progress on the Positive Active Substance of Lead-carbon Battery

The positive active material of the lead-carbon battery is PbO_2, and the positive electrode of the battery will form $PbSO_4$ crystals during the discharge process, causing the phenomenon of sulfation and reducing the utilization rate of PbO_2.

Reasonable selection of positive electrode additives can effectively improve the softening and shedding of the active materials of the positive electrode, and the early capacity loss caused by grid corrosion interface oxidation barrier layer. Bao J P et al. [15] prepared nano-SiO_2-doped PbO_2 electrodes by co-electrodeposition, the experimental results show that inert nano-SiO_2 can establish electrolyte diffusion channels in the positive electrode, thereby improving the effective utilization of active materials, which provides new ideas for the design and development of positive electrode materials for lead-carbon batteries.

E. Research Progress of Electrolyte Additives for Lead-carbon Battery

In lead-carbon batteries, the main function of the electrolyte is to act as a medium for conducting current and ions, and to participate in the battery reaction. Therefore, parameters such as the concentration, quality, and temperature of the electrolyte can affect the progress of the reaction and the performance of the lead-carbon battery. There are two kinds of electrolytes that are widely used at present, one is an ordinary sulfuric acid aqueous solution, which uses a separator to fix the electrolyte, and the other is a colloidal electrolyte containing sulfuric acid, which uses a silica gel to fix the electrolyte.

1) Research progress of liquid electrolyte additives

Adding suitable additives to the sulfuric acid aqueous electrolyte can improve the solubility of $PbSO_4$ in the electrolyte, inhibit the early capacity loss, prevent the softening and shedding of active materials, and inhibit the hydrogen evolution reaction. The additives in liquid electrolytes can be mainly divided into two categories: inorganic additives and organic additives.

a) Inorganic additives

Inorganic substances used in lead-acid battery electrolyte additives mainly include inorganic acids and metal salts. Wu Z A et al. [16] used boric acid as an additive in lead-acid electrolyte, and studied the key effect of boric acid on battery performance. The experimental results show that boric acid can increase the hydrogen evolution overpotential and oxygen evolution overpotential of the lead grid, thereby reducing the water loss phenomenon during battery operation; Hosseini S et al. [17] studied the effect of sodium hexametaphosphate (SHMP) as an electrolyte additive on the performance of batteries, the results show that SHMP can increase cycle life and can be used with a variety of additives to improve the overall performance of batteries.

b) Organic additives

Pavlov D et al. [12] incorporated the carboxylic acid aromatic ester compound benzyl benzoate ($C_6H_5CH_2O_2CC_6H_5$) as an additive into the electrolyte of lead-acid batteries, the results show that C6H5CH2O2CC6H5 has an inhibitory effect on the growth process of PbSO4 crystals, which is manifested as hindering the growth of PbSO4 crystals during the recrystallization process and promoting the formation of small-sized $PbSO_4$ crystals with high solubility.

2) Research progress of colloidal electrolyte additives

Adding suitable additives to the colloidal electrolyte can prolong the gel time, improve the gel strength, improve the performance of the colloidal electrolyte, and improve the discharge capacity of the colloidal battery. The additives in colloidal electrolytes can be mainly divided into three categories: surfactants, inorganic additives and organic additives.

a) Surfactants

The surfactant in the colloidal electrolyte can be combined with the silica (SiO_2) particles to prevent aggregation between the silica particles, prevent the interaction between some silica particles and solvent molecules and silica particles, extend the gel time of the colloidal electrolyte, which is conducive to filling the battery with glue.

Nahidi S et al. [18] tested two surfactants, polyethylene glycol octyl phenyl ether (Triton X100) and sodium dodecyl sulfate (SDS) as electrolyte additives, , the experimental results show that the battery capacity is increased by 16% and 10%, respectively; Abdulmecit M et al. [19] used nitrogen-doped graphene oxide powder (N-GrOP) as an additive in fumed silica-based gel electrolytes for valve-regulated lead-acid batteries, and performed cyclic charge-discharge tests to determine the discharge capacity of the electrolyte , the results showed that N-GrOP can interact with hydrolyzed fumed silica particles to increase the discharge capacity of fumed silica-based gel electrolytes.

b) Inorganic additives

Gencten M et al. [20] used gibbsite and pseudo-boehmite as additives for gel VRLA batteries, and determined the optimal amount of each additive to be 0.6wt% by cyclic voltammetry and electrochemical impedance spectroscopy, the study showed that with the use of additives, the anode peak current and capacity increased and the charge transfer resistance decreased. Compared with non-gel electrolytes and fumed silica-based gel electrolytes, the gel system composed of additives has a lower corrosion tendency.

c) Organic additives

Binh P T et al. [21] used liquid glass and sulfuric acid as the basis and polyaniline as the organic additive to prepare gel electrolyte, then studied the electrochemical properties of gel electrolytes. The results show that polyaniline can inhibit the water loss phenomenon of the electrolyte, and the charge transfer resistance of the lead electrode in the gel electrolyte environment is lower than the charge transfer resistance in sulfuric acid, which improves the electrochemical performance of the electrolyte.

IV. *THE APPLICATION OF LEAD CARBON BATTERY IN POWER STORAGE SYSTEM*

In recent years, in order to achieve the goal of low-carbon, environmental protection and green development, the worldwide energy structure has undergone great changes. The proportion of electricity generated from fossil energy has gradually declined, and new energy sources such as wind energy and solar energy have gradually replaced fossil energy as the focus of development in the energy field. Because the power generated by new energy sources such as wind energy and solar energy has the characteristics of randomness, volatility and discontinuity, accessing it to the power grid on a large scale can easily cause operational safety problems, even lead to large-scale vicious accidents when serious. Therefore, in the future low-carbon energy system, the power system needs to be flexibly adjusted to a greater extent with the grid-connected new energy power stations.

As an important technology in the field of renewable energy power generation, energy storage system (ESS) can smooth out load power fluctuations caused by the connection of new energy power stations to the grid, and effectively improve the quality of electricity generated by renewable energy. At the same time, energy storage technology can also be used for the "peak shaving and valley filling" of the power grid, Reduce the pressure on the peak-to-valley gap of the power supply, which is of great significance for the adjustment of the future energy structure and the construction of the smart grid.

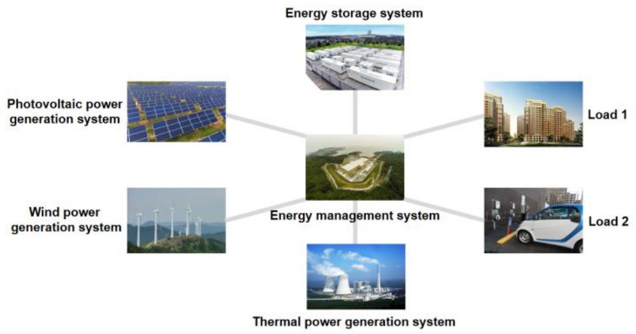

Fig. 4.1 *Application of energy storage system in the field of electric energy storage*

Conventional energy storage technology includes electromagnetic energy storage technology, mechanical energy storage technology and battery energy storage technology. Compared with other energy storage systems, battery energy storage system can play different roles in power supply side, power grid side and user side of the power system by virtue of its advantages such as stable input and output, fast response speed, strong controllability, good environmental adaptability, frequency regulation, peak shaving ability, etc. At present, the more mature energy storage batteries in the field of new energy storage mainly include lead-carbon battery, lithium-ion battery and sclerophore battery, all kinds of batteries have their own different characteristics. The cost of lithium-ion battery is relatively high, and the security is poor. The cost of vanadium redox flow battery is also very high, which is difficult to apply on a large scale. As a new generation of lead batteries, lead-carbon battery has high development potential in the field of battery energy storage because of its low cost, safety, stability, mature technology and long service life. In addition, because solar energy, wind energy and other intermittent energy requires batteries to work in a partially charged state, and lead-carbon battery just has the characteristics of excellent performance in high-rate partially charged states, so lead-carbon battery has a very good application prospect in power energy storage systems.

At present, the application of lead-carbon battery in the field of energy storage has a large number of successful examples.

The main producer of lead-carbon battery in the world is AxionPower in the United States, AxonPower has manufactured the PowerCube battery energy storage system based on the patented technology of mixed batteries of lead-acid/carbon chemical materials, and applied the energy storage system to the FM market field of the US power grid operator PJM Company; Ultrabattery from Furukawa, East Penn and Ecoult has been used in a large number of grid and microgrid stationary energy storage units in the United States, Australia and Asia. China's Tianneng Group completed the State Grid's12mw/24mwh lead carbon energy storage project of pheasant city, which is the first super-large lead-carbon energy storage power station project in China; El Paso, Texas, USA, will build a parallel off grid switching project supported by large-scale photovoltaic power stations, energy storage and power grids, of which the planned 4 million kWh of energy storage part will all use lead carbon batteries, scheduled for 2021-2025 phased implementation.

V. *SUMMARY AND OUTLOOK*

Battery energy storage technology is currently in a critical period when the technology is gradually maturing and the market is developing with high quality. Lead-carbon battery combines the advantages of lead-acid battery and supercapacitor, with their mature technology, safe and reliable performance, low cost and other advantages, is currently one of the relatively economical and feasible battery energy storage technologies. Lead-carbon batteries have a very good development potential and application prospects in the power energy storage system.

Although lead-carbon battery has great advantages in terms of energy density and power density, there is also a lot of room for improvement. In the future research and application of lead-carbon battery, more attempts can be made from the preparation methods of lead-carbon composites, because different preparation methods may bring changes in the microstructure and morphology of composites, which will bring new improvements to the performance of lead-carbon battery; It is meaningful to further clarify the relationship between the physicochemical properties of carbon additives and the performance of lead-carbon battery, especially the effect of mesoporous carbon, macroporous carbon and the surface chemistry of carbon on the performance of lead-carbon electrode, and conduct more in-depth research on the structure of carbon additives; The softening of the positive active substance at high temperature and the corrosion phenomenon of the plate grid will also make the battery capacity decay rapidly, so how to reduce the grid corrosion and maintain the structure of the positive plate will also be the focus of future research; According to the inherent mechanism of the attenuation of battery capacity, the impact of additives on battery performance can be further studied; It is also necessary to appropriately simplify the system of lead-carbon battery and optimize the battery preparation process, thereby develop lead-carbon batteries with longer life and higher energy storage stability, and promote the industrialization of high-performance lead-carbon battery and the application in power systems.

REFERENCES

[1] G. Plante, C.R. Acad. Sci. Paris 50 (1860), pp. 640-642.

[2] J Lannelongue，M Cugnet，N Guillet，ED Vito，A Boulineau，A Kirchev, "Operation of thin-plate positive lead-acid battery electrodes employing titanium current collectors," The Journal of Energy Storage 20.DEC. 2018:230-243.

[3] V Naresh，L Elias，SA Gaffoor，SK Martha, "Corrosion Resistant Polypyrrole Coated Lead-Alloy Positive Grids for Advanced Lead-Acid Batteries," 2019.

[4] T Yang，S Qian，Y Luo，X Wang，Z Wang,"Direct re-usability of lead-plated tin bronze as negative plate for lightweight lead-acid battery," Journal of Electrochemical Energy Conversion and Storage , 2021:1-24.

[5] Zhongyi，Jiang，Tao，Wang，Li，Song，Hu，Guo，Wei，Xia, "High over-potential nitrogen-doped activated carbon towards hydrogen evolution inhibition in sulfuric acid solution," Journal of Materials Science Materials in Electronics, 2018.

[6] Leying Wang a b，Hao Zhang c，Wenfeng Zhang c，Hao Guo d，Gaoping Cao c，Hailei Zhao b , et al., "A new nano lead-doped mesoporous carbon composite as negative electrode additives for ultralong-cyclability lead-carbon batteries - ScienceDirect," Chemical Engineering Journal, 2018, 337:201-209.

[7] J Li，Y Hu，Y Zhang，J Xie，PK Shen, " Construction of a novel three-dimensional porous lead-carbon network for improving the reversibility of deep discharge lead-carbon batterie," Journal of Alloys and Compounds, 2021:158822.

[8] YS Zhang，A Ali，J Li，J Xie，PK Shen, "Stereotaxically constructed graphene/nano lead composite for enhanced cycling performance of lead-acid batteries," The Journal of Energy Storage, 2021, 35:102192.

[9] J Xie，Y Hu，X Wu，A Ali，P Shen, " Positive Effects of Highly Graphitized Porous Carbon Loaded with PbO on Cycle Performance of Negative Plates of Lead-Acid Batteries," Applied Sciences. 2021; 11(18):8469.

[10] Gao Y, " Preparation of Hierarchically Porous Lead/Carbon Composite and Its Application in Lead-Carbon Battery," ChemPlusChem, 2018, 83.

[11] Hu YT, Li JC, Wu XL, Shen PK, "Inhibition of irreversible sulfation of lead-acid batteries by hierarchal porous carbon with in-situ grown carbon nanotube clusters," Energy Storage. 2022:104420.

[12] D Pavlov，V Naidenov，Y Milusheva，S Vassilev，T Shibahara，M Tozuka, "Benzyl benzoate as an inhibitor of the sulfation of negative electrodes in lead-acid batteries," Journal of Energy Storage, 2018, 17:336-344.

[13] HJD A，AS B，LRS A，MM B, "Waste derived low cost PbO-Carbon nanocomposite and its energy storage application - ScienceDirect," 2021.

[14] Ali A, "Using silkworm excrement and spent lead paste to prepare additives for improving the cycle life of lead-acid batteries," The Journal of Energy Storage, 2021, 41.

[15] J Bao，N Lin，Y Dan，W Gao，H Lin, "Anodic co-electrodeposition of hierarchical porous nano-SiO2+PbO2 composite for enhanced performance of advanced lead-carbon batteries," The Journal of Energy Storage, 2021, 35:102285.

[16] ZA Wu，YB Liu，CB Deng，HB Zhao，RAC Zhao，HAC Chen, "The critical role of boric acid as electrolyte additive on the electrochemical performance of lead-acid battery - ScienceDirect," Journal of Energy Storage, 27.

[17] Hosseini S , Farhadi K , Banisaeid S, "Sodium hexa meta phosphate impact as electrolyte additive on electrochemical behavior of lead-acid battery," The Journal of Energy Storage, 2018, 17:170-180.

[18] Gencten M , " Investigation the Effects of Boehmite and Gibbsite on the Electrochemical Behaviours of Gel-VRLA Batteries,"

International Journal of Electrochemical Science, 2018, 13(12):11741-11751.

[19] S Nahidi，IJ Gavzan，S Saedodin，M Salari，B Maddah, “Influence of Surfactant Additives on the Electrolyte Flow Velocity and Insoluble Gas Bubbles Behavior within a Lead-Acid Battery,” Journal of The Electrochemical Society, 2020, 167(12):120524 (9pp).

[20] Abdulmecit M, Caner K, Barışhan S, Alperen A , Metin G, Sahin M, et al., “N-Doped Graphene Oxide as Additive for Fumed Silica Based Gel Electrolyte of Valve Regulated Lead Acid Batteries,” Journal of The Electrochemical Society, 2021, 168(6):060512 (11pp).

[21] PT Binh，NTV Anh，TTT Mai，TX Mai，LT Thanh, “ Electrochemical properties of antimony lead electrode in gelled electrolyte prepared by liquid glass and sulfuric acid using polyacrylamide together with polyaniline,” Vietnam Journal of Chemistry, 2019, 57(4).