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Research Progress of Zinc Bromine Flow Battery

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Abstract: *Zinc bromine redox flow battery (ZBFB) has been paid attention since it has been considered as an important part of new energy storage technology. This paper introduces the working principle and main components of zinc bromine flow battery, makes analysis on their technical features and the development process of zinc bromine battery was reviewed, and emphasizes on the three main components of zinc bromine battery, and summarizes the materials and applications of electrolyte, membrane and electrode. At the same time, the solution to the technical problems of zinc bromine flow battery is also briefly analyzed. Finally, the future development of zinc bromine battery system is prospected.*

Keywords: Zinc bromine redox flow battery; electrolyte; membrane; electrode

In today's society, the industry is highly developed, but it has caused a series of negative impacts, resulting in the world's three major crises: shortage of resources, environmental destruction and ecological destruction. Therefore, today's industrial development is focused on low carbon, environmental protection and sustainability, and the problems faced by traditional fossil fuels are becoming increasingly serious[1]. In order to solve the above problems and realize low carbon sustainable development, we must vigorously develop new energy sources. Whether taking the road to sustainable development or protecting the ecological environment of human survival, it is of strategic importance to develop new energy resources.

At present, new energy technologies such as wind energy and solar energy are used more and more in power grid[2], but their volatility have a big impact on the grid. Therefore, the application of large-scale energy storage technology in the power grid is the technical support of the new energy stable power supply[3,4]. Flow battery as a type of large-scale energy storage technology[5], The electrolyte is circulated in and out of the battery through the action of the pump, and the electrolyte flowing out is stored in another tank so as to carry out cyclic charging and discharging, which increases the capacity of the battery, but also guarantee the stability and safety.

The flow zinc battery has great potential and attraction in commercial development, be attribute to the high energy density and low cost of zinc. The zinc bromide flow battery (ZBFB) is the representative of a zinc containing battery, in addition to the advantages of low cost, it also has the characteristics of high energy density, good power performance, rich raw materials, strong ability of deep discharge and so on[6]. In recent years, more and more attentions have been paid to it. People believe that this technology has great potential and competitive advantages in large-scale energy storage applications[7]. But as a mature commercial battery, there are two technical problems in the zinc bromide battery: (1) The tendency of dendrite formation when zinc deposition occurs, which puncture the membrane, causing the battery to short-circuit[8]. (2) Bromine has a high solubility in aqueous zinc bromide[9], and the rapid mass transfer to the zinc surface leads to the self-discharge of the battery[10], reducing the coulombic efficiency of the system[11].

1. Basic introduction and principle of ZBFB

1.1. Electrochemical reaction equation

In order to promote the commercial use of zinc bromide flow battery, we must understand its component components and functional states, including system performance levels, operating mechanisms, and the raw materials and methods required for the component. The zinc bromine flow battery is a modular system consisting of three main parts: electrodes, electrolytes, and membrane. The electrochemical reaction equation of the electrode is as follows:

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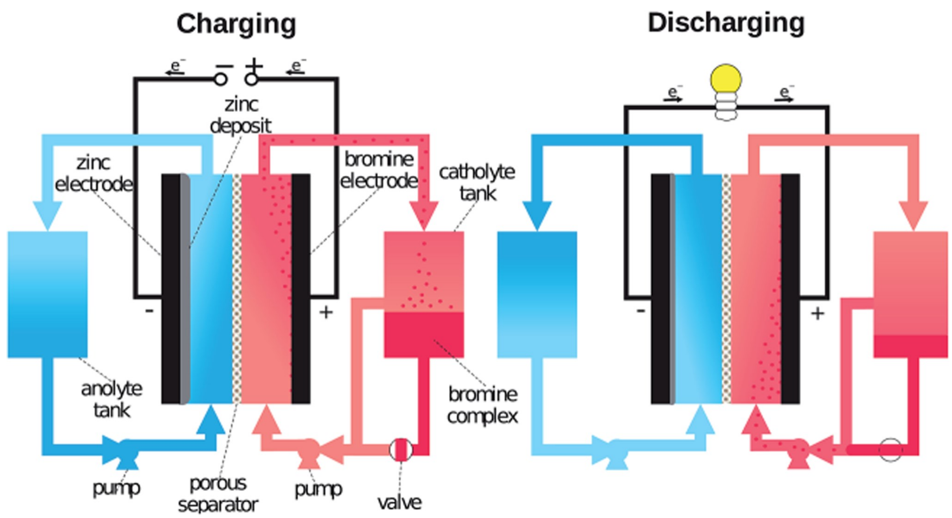

Figure 1. Schematic of a zinc bromine redox flow battery[12].

$$Negative: Zn^{2+} + 2e \Leftrightarrow Zn \qquad E_0 = -0.76V$$

$$Positive: 2Br^- \Leftrightarrow Br_2 + 2e \qquad E_0 = +1.07V$$

$$Overall: ZnBr \Leftrightarrow Zn + Br_2 \qquad E_0 = +1.83V$$

1.2. Principle of ZBFB

The zinc bromine flow storage battery is a new and efficient electrochemical energy storage device. As shown in Fig.1, the electrolyte solution (the energy storage medium) is stored in an electrolyte tank outside the battery, The positive and negative electrodes of the battery are separated by a micro-porous membrane into two chambers (positive and negative sides) that are independent of each other, When the battery is working, the positive and negative electrolyte are forced by their respective power pumps to circulate in the closed loop composed of the liquid storage tank and the battery. During charging process, the battery is connected with an external power supply, and the electric energy is converted into chemical energy and stored in electrolyte solution; During discharging, the battery is connected with the load, and the chemical energy stored in the electrolyte solution is converted into electric energy for use by the load.

2. DEVELOPMENT TREND AND APPLICATION STATUS OF ZBFB

The concept of ZBFB was first proposed by C. S. Bradley in 1885. From the mid 1970s to the early 1980s, Exxon and Gould made a series of technical improvements, and the problem of dendrite formation in zinc electrode is solved effectively. 1980s medium term, Exxon transfer ZBFB technology to the US Johnson Control Inc (JCI), Europe SEA, Japan's Toyota Auto Body Co, and Meidensha, as well as Australia's Sherwood Industries. In 1994, JCI sold its company's zinc bromide battery technology to ZBB Energy, After more than 20 years of development, ZBB Energy has made great progress in the technology of zinc bromide bromide battery, and it is in the leading position in the world[13].

ZBB announced that it will sign a cooperation agreement with Eaton electric, in which ZBB will provide a 500 kW h energy storage system for use in micro grid systems in April 4, 2011. The micro grid system is used to connect the operation of electric power facilities Ft.Sill army Oklahoma in the United States. The system uses a new generation of zinc storage (ZESS) technology, the ZESS system is based on 50 kWh module as the foundation, it combines all the software and hardware and works like a complete

Table 1. Comparison of battery performance parameters of main zinc bromide flow battery manufacturers

	ZBB energy	RedFlow	Premium Power
Model	EnerStore	M120	ZF45
Capacity	25kW/50kWh	120kW/240kWh	30kW/45kWh
Operating temperature	-30~50ºC	Under 50ºC	-25~60ºC
Efficiency	70%	75%	73%
Voltage	118V	-	48V
Cycle life	Over 20 years of design life	>1500 times	Thousands of times
Cost	~$390/kWh	-	-
Energy density	34Wh/kg	15Wh/kg	28Wh/kg

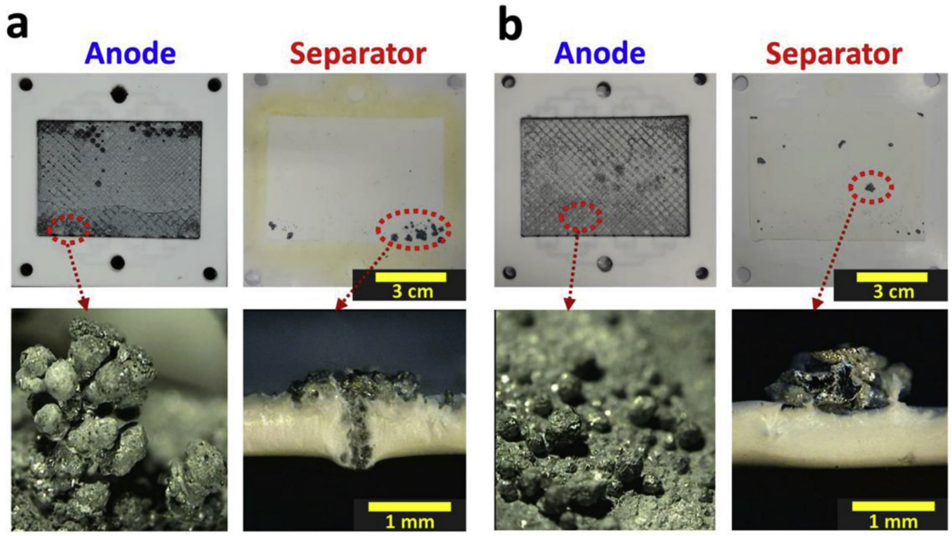

Figure 2. Photographs of the negative electrode surface (top left), negative side of the separator (top right), and micrographs of the negative electrode surface (bottom left) and separator cross-section (bottom right) at 100 x magnification after complete charging in the ninth cycle at circulation rates of (a) 50 and (b) 100 mL min^{-1}[16].

energy storage system that can be connected to the grid or work with an independent power supply system. Each module can be connected to provide greater storage capacity.

Japan is also committed to developing zinc bromide battery technology for power utilities. In 1990, Kyushu power company and Meidensha company installed 1MW /4MWh batteries in the Imajuku substation of Kyushu power company in Fukuoka. The battery has completed 1300 cycles, with a total energy efficiency of 65.9%. However, there has been no relevant report on the recent progress in the zinc bromide flow battery technology in japan.

Austria SEA has been working on ZBFB for electric vehicles since 1983, and has now produced batteries ranging in size from 5 to 45kWh. SEA installed a set of 45kWh and 216V batteries on a bus, the quality of the battery is about 700kg, the car has a top speed of 100km/h, and the maximum distance to travel at 50km/h is 220km. Its efficiency is 2-3 times that of lead-acid batteries.

In China, the research of zinc bromide flow battery started late. By 1990s, the problem of non circulating zinc bromide battery was only being carried out in some universities and enterprises. But the zinc bromide flow battery is developing rapidly in China. In the case of the localization of the parts, the cost is equivalent to that of the lead-acid battery, and the energy density is 3-5 times of that of the lead-acid battery. Anhui Meineng Store Energy System Co., Ltd is a provider of leading-edge energy storage systems and solutions to the greater China market. Meineng's products enable improved efficiency of energy distribution, and include 3rd generation Zinc-Bromide flow batteries and power electronics and control systems, for a total storage and management system level solution. Meineng's energy storage batteries are self-contained, modular units and are easy to transport, enabling delivery of an expandable solution that is virtually "plug and play". Beijing baineng Huitong Technology Co. Ltd. is a professional engaged in power storage with high performance and low cost, large capacity energy products and solutions for high-tech companies. Through independent innovation, the company successfully developed China's first zinc bromide liquid storage battery, which fills China's technical gaps in this field. At present, in the field of battery key materials, stack processing, assembly, battery management systems, leading domestic and foreign level.

Generally speaking, zinc bromide battery has attracted a lot of attention because of its high energy density and low cost. Study on the technology of zinc bromine flow battery although started late, but rapid development. Mature commercial products are shown in table 1. At present, the technology of self-discharge and dendrite formation of zinc bromine battery has been greatly improved. In the aspect of battery performance, the frontier research focuses on the application of ordered mesoporous materials in the electrode of zinc bromine battery, in order to reduce the internal resistance and increase the power density of the stack, so that the zinc bromide battery is expected to become an important pillar of large-scale energy storage.

3. THE MAIN COMPONENTS OF ZBFB

3.1. Electrolyte and quaternary ammonium salt

As a large-scale energy storage system, the storage capacity of the zinc bromide battery and the concentration of electrolyte determine the energy storage capacity. Therefore, the storage tank can be flexibly designed to meet the requirements of various sizes of electrical energy storage. Under the condition of a certain output power, the storage capacity of the zinc bromine battery can be improved by increasing the volume of the storage tank or the concentration of the zinc bromide electrolyte. Zito has studied the influence of changes in the solubility of bromine on the changes in ion resistivity, from his research, it is known that the conductivity of zinc bromide is highest when the molar concentration is 2mol/L. But the minimum solubility of bromine in zinc bromide concentrate is 7mol/L[14]. The concentration of the zinc bromide solution is too high, the high solubility bromine causes the bromine diffusion problem to be serious, and the rapid mass transfer to the zinc surface and its direct reaction will lead to the self-discharge of the battery and be corrosive to the anodic zinc. The concentration of zinc bromide is too low, the internal resistance of the battery will be too large, resulting in energy consumption. Therefore, the concentration of zinc bromide electrolyte should be guaranteed within a reasonable range. A better solution is to adjust the zinc bromide solution concentration reached 5mol/L, then reached the ideal conductivity and solubility of bromide as worthy of half[15]. Moreover, the study of Hyeon Sun Yang shows that the cycle rate of electrolyte affects the formation of zinc dendrites[16]. As the positive Br/Br- reaction matches the negative zinc deposition, the inhomogeneous redox reaction of the positive electrode is accompanied by an uneven zinc deposition and zinc dendrite formation. Fig.2 compares photographs of the negative electrode surface and separator after complete charging in the ninth cycle at circulation rates of 50 and 100 mL min^{-1}. Obviously, the zinc deposition of cycle at circulation rates of 50 mL min^{-1} is much more serious than that of cycle at circulation rates of 100 mL min^{-1}, and with the flow rate of 100 mL min^{-1} zinc depositions were loosely attached to the electrode or the separator. At the same time, in order to reduce the level of self discharge of zinc bromine battery and increase the coulombic efficiency and energy efficiency of battery, tungsten-cobalt heteropoly acid can be added into the electrolyte of cathode and anode of flow battery. Liu and his team have done research on it[17].

Bromine in the electrolyte of zinc bromide flow battery has the characteristics of being volatile. During the charging process, bromine vapor will be formed when the temperature increases, which is corrosive, toxic and easy to cause safety hazard. Generally, quaternary ammonium salt is added into electrolyte to solve the above problems[12]. The usual quaternary ammonium salts are shown in table 2. After adding quaternary ammonium salt, the positive reaction equation of ZBFB is: $2Br^{-} + QBr^{-} \rightarrow QBr^{3-} + 2e^{-}$. Researchers in the United States and Japan have studied it[18,19]. The quaternary ammonium salt reacts with bromine to form a solid bromine complex (QBr_3^-) and is deposited at the bottom of the electrolyte tank of the positive electrode. During discharge, the bromine complex of solid is released again to form bromine ion. By adding quaternary ammonium salt to reduce bromine volatilization, and the bromine complexes deposited at the bottom, reduces the bromine to the cathode diffusion, prevent direct reaction of zinc bromide and self discharge occurred, increasing the energy efficiency of zinc bromine battery. The addition of Tetra-n-butylammonium (TBAb) bromide can alleviate the self discharge of the zinc bromine battery, and has a restraining effect on the formation of dendrites of the negative electrode zinc, and does not affect the discharge behavior of the zinc bromine battery, so the technical problem of the zinc bromine battery can be well solved.

As a storage system, zinc bromide battery has the advantages of low cost and high cost performance, mainly due to the low price of zinc bromide electrolyte. The price of zinc bromide electrolyte is mainly affected by the price fluctuation of zinc and bromine, the price of bromine is about $1620 per ton, and the price of zinc per ton is about $2837. According to the price of the raw material, the price of 3M zinc bromide electrolyte is about US $875 per ton. In some countries, such as China[20], the commercial costs of zinc bromide flow batteries will also decline as raw material prices decline and manufacturing processes improve. To sum up, with the gradual reduction of costs and the effective solution of technical problems, zinc bromide batteries will have unlimited potential in the energy storage market.

Table 2. Types of Quaternary ammonium salt

The type of Bromine complexing agent
N- methyl -N- ethyl bromide bromide
N- methyl -N- brominated butyl pyrrole
N- propyl -N- brominated butyl pyrrole
N- methyl -N- bromide hexyl pyrrole
N- ethyl -N- brominated butyl pyrrole
N- methyl -N- brominated butyl morpholine
Tetra-n-butylammonium bromide

3.2. Membrane

The bromine diffused from the cathode to the anode, and the reaction between bromine and anodic zinc results in self discharge of the battery. In order to avoid these problems, an ion exchange membrane or a microporous membrane is needed to separate the anode and cathode electrolyte into two relatively independent cavities[21]. The main function of ion exchange membrane for liquid flow battery is to separate the positive and negative electrolyte, and also to allow the ion carrying charge to pass through to realize the complete current loop.

Ion exchange membrane is the key component of ZBFB. It not only has the function of separating positive and negative electrolyte, but also provides proton conduction channel for positive and negative electrolyte. For different ion exchange membrane for comparison results show that the diffusion coefficient is larger in the range of bromine, which is between $1.44 \times 10^{-10} \sim 3.74 \times 10^{-10}$ cm^2 s^{-1} and $1.52 \times 10^{-8} \sim 2.28 \times 10^{-8}$ $cm^2 s^{-1}$[22, 23]. Therefore, reducing the porosity and resistivity of the membrane is the bottleneck of the study on the membrane of zinc bromide flow cell. Meanwhile, the high selectivity of the cation exchange membrane to separate positive and negative electrolyte of zinc bromine flow battery, and only through the cation, prevent bromine to the cathode diffusion, and reduce the direct reaction of zinc and bromine leads to the self discharge of zinc bromine battery. British scientist F.G.Will first proposed the use of ion-exchange membranes as a zinc bromide flow cell separator[24], and investigated the practical use of Nafion membrane in ZBFB. The performance test of the Nafion membrane shows that can effectively prevent bromine from passing through the membrane[25], which may be attributed to the bromine exists mainly in the form of Br_3^- and Br_5^- ionic states[26]. Table 3 shows the modification of the Nafion membrane. After that, scientists in various countries have done a lot of research on the modification of membranes[27, 28], membrane permeation and doping ions to find out the membrane which can improve the performance of ZBFB. At present, the research direction of ion exchange membrane is mainly concentrated in two aspects: (1) Modification of commercial ion-exchange membranes; (2) Preparation and study of novel ion exchange membranes.

Owing to the commercial use of cation exchange membrane expensive, and ohmic resistance is higher. Therefore, zinc bromide flow batteries can be made of inexpensive microporous polymer membrane. For example, polyolefin film[29, 30], which is mainly made of high molecular polyethylene, amorphous silica and special hydrocarbon oil, low ionic resistance[31, 32], flexibility and sealing excellent, can be made into rolls or flakes. But the drawback is that it does not completely prevent bromine from passing through[33]. The permeation rate of bromine was reduced by two assistant methods: (1) The quaternary ammonium salt is added to the electrolyte to make the bromine deposit[34]; (2) The membranes were treated by anionic polyelectrolyte impregnation, however it might increase the ohm resistance of the film. The experiment of different dosage of quaternary ammonium salt in solution shows that the coulombic efficiency of the flow cell is directly affected by the change of the membrane resistance[35], which may be caused by the negatively charged groups repel negatively charged bromide complexes in anionic polyelectrolytes[34]. There are also studies have shown that with propionitrile organic solution treatment microporous polymer membrane, may can reduce self discharge rate of zinc bromine battery. Experimental results demonstrate that the energy efficiency of ZBFB is up to 93% by use both treated-membrane and quaternary ammonium salt, the only problem is propionitrile reduced conductivity of microporous membrane[36]. There is also a functionalized membrane, the sulfonated polysulfone membrane, which has proved superior in performance to membranes grafted on organic substrates[37].

In general, the membrane of the flow battery should meet the following requirements: low cost, low diaphragm resistance, long cycle life, high water content, etc. At present, the commercial cation membrane is excellent in performance, but higher in cost, resulting in higher cost of the flow battery. The microporous separator is low in price, but poor in performance, which may leads to self discharge of the 5% power of the battery. Therefore, it is necessary to find the balance between cost and performance, not only to meet the zinc bromide battery low cost characteristics, but also to effectively solve its technical problems, and improve its system performance.

3.3. Electrode

The electrode is the core component of the zinc bromide flow battery, and also has a close relationship with the performance of ZBFB. The research of the electrode material is one of the hot spots of the current battery research. There are many kinds of electrode materials, such as metal, graphite and so on. Metals are often used as battery electrodes, As a result of the metal has low resistivity. But in the zinc bromine bromide flow battery system, because of the corrosive environment of bromine, the metal electrode will be corroded and decomposed during the operation of the battery[42]. Even titanium (Ti) is oxidized to titanium dioxide (TiO_2)[43], or brominated to titanium bromide ($TiBr_2$)[44]. The carbon based electrode materials for corrosion of bromine has good resistance, although its resistance is slightly higher than the metal electrode. Indeed, the use of carbon based material electrodes is also a reason for the low energy efficiency of zinc bromide flow battery.

The use of carbon based material electrodes has become a hot topic in recent years for flow battery research[45]. There are many kinds of carbon based materials, glass carbon or conductive carbon black is a better choice for electrode materials, and they have better charge transfer capability than other carbon materials[46,47]. But in practice, they also have their limitations, such as the ductility of a single carbon material is poor. A good solution is to develop carbon composite electrode materials and increase the electrochemical active sites on the electrode surface. On this basis, the active carbon embed carbon - plastic composite electrode made by high density polypropylene, not only increased the mechanical strength of the electrode, and the cost is low, which has attracted a lot of attention. There is also a good choice of electrically conductive activated carbon powders covering the surface of a poorly conductive carbon plastic electrode, and increase the electrochemical active sites on the electrode surface when redox reactions occur, thereby increasing the conductivity of the electrodes. In order to enhance the mechanical properties of the electrode, glass fiber can be added to modify the electrode, or press the metal mesh on the conductive plastic layer[48]. The electrode does not participate in the reaction but only acts as the substrate for the reaction. Thus, unlike most rechargeable batteries, the loss of metal electrodes due to cyclic cycling results in loss of performance.

Carbon nanotubes have large pore size and unique hollow structure, which is the same as the lamellar structure of graphite. Therefore, carbon nanotubes have good conductivity, which is one of the focuses of current research[49,50]. Graphite electrodes doped with carbon nanotubes have improved greatly in terms of conductivity and mechanical strength. Therefore, carbon nanotube electrodes are considered as ideal electrode materials for high-power storage bat-

Table. 3 Method for modifying Nafion membrane

Who	Method for modifying Nafion membrane
Jingyu Xi	1. Preparation of Nafion/SiO2 composite film by sol-gel method, the membrane shows almost the same ionic conductivity and proton conductivity as fresh Nafion117[38]. 2. Nafion/ organic silicate composite film was prepared by combining TEOS and DEDMS mixture with Nafion film in situ sol-gel method.
TENG X G	The Nafion/Si/Ti composite film was prepared by combining TiO2 modified organic silicate with Nafion in situ sol-gel method, the coulombic efficiency of the single cell composed of the film is higher than that of the untreated Nafion film[39].
LUO Q T	A cationic layer was polymerized on the surface of Nafion117 by interfacial polymerization, the coulombic efficiency is increased from 93.8% to 96.2% to 97.3%[40].
Jie Zeng	Polypyrrole was polymerized onto Nafion 117 surface by electrodeposition to form polypyrrole /Nafion composite film[41].
KIM J G	Synthetic (Psf/PPSS/TPA) cation exchange membranes were found by thermal analysis to have higher thermal stability as compared to Nafion117.

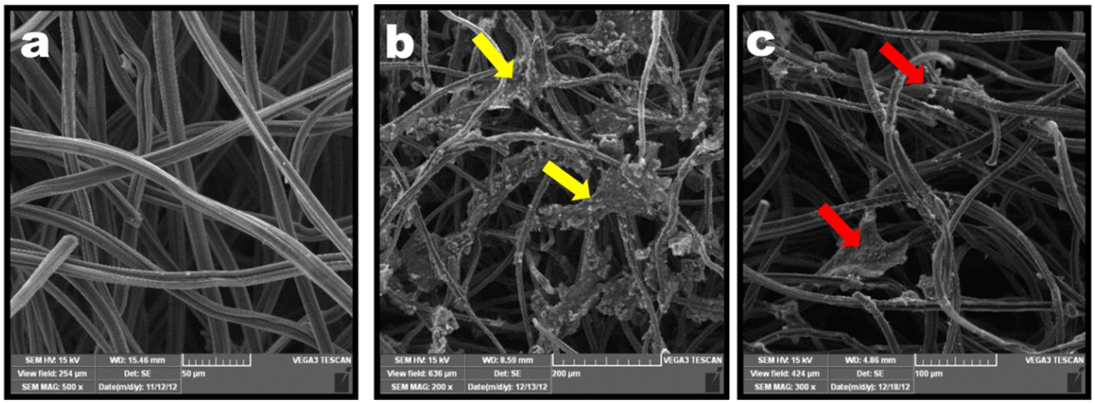

Figure 3. SEM images of Carbon Felt (a), SWCNT (b), and MWCNT (c) modified CF. Arrow marks show the CNT anchored on CF[53].

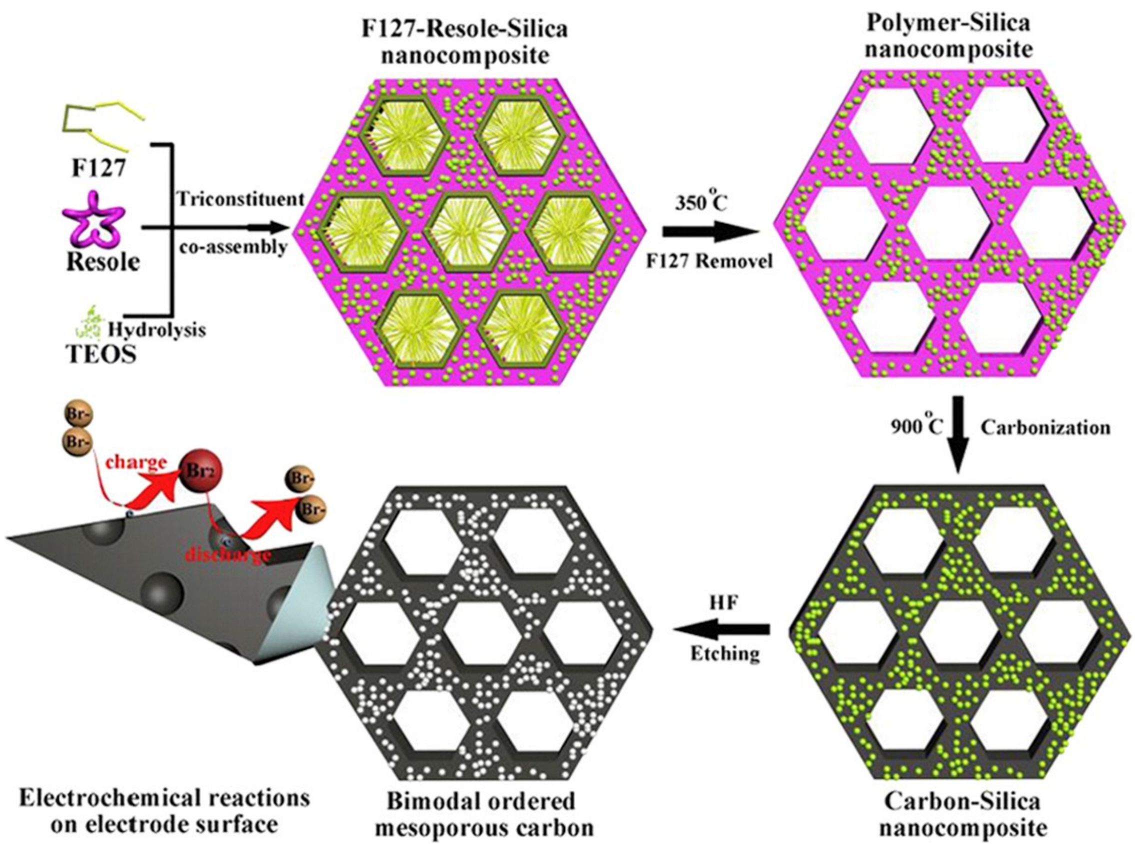

Figure 4. Principle of bimodal highly ordered mesostructure carbon applicated in bromine based batteries[55].

teries[51,52]. With regard to the application of carbon nanotube electrodes in the zinc bromide flow battery, the performance of the modified electrode with single walled carbon nanotubes and multi walled carbon nanotubes has been compared by experiments with Y. Munaiah team[53]. The results show that the electrocatalytic activity of SWCNTs is better than that of MWCNTs, which provides more active sites for the reaction of Br_2/Br^-. Of course, both SWCNTs and MWCNTs exhibit superior electrochemical performance compared to other carbon materials, thereby improving the energy efficiency of the zinc bromide flow battery. Fig.3 shows their differences. Hu Wendi, Key Laboratory of polarized materials and devices, Ministry of education, East China Normal University, starting from the treatment of carbon nanotubes with different processes on graphite electrodes, the structure of graphite /CNT electrode applied to zinc bromide redox flow battery was obtained. Woo In Jang and his team[54], explored the effect of different mass fraction of CNT on the performance of polypropylene / graphite electrodes. The experimental results show that the polypropylene /

graphite electrode with CNT added 5%wt has the best electrochemical and mechanical properties.

Recently, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Zhang Huamin and his team[55], They have made new progress in the research of electrode materials for zinc bromide flow battery. The project has been funded by the National Natural Science Foundation of China. According to reports, the research team has developed a highly ordered mesostructure carbon cathode material through structural design. The scheme is displyed in Fig.4. The electrode material provides more active sites for the reaction of Br_2/Br^-. The energy efficiency of single cell assembled by the electrode is over 80%, which breaks through the bottleneck of low power density, and lays a foundation for the development and application of zinc bromide battery with high power density and low cost.

From the point of view of the application of carbon based material electrode in zinc bromide flow battery, porous carbon showed superior performance in the application of electrode due to its good porosity and large specific surface area. Whether activated carbon, carbon nanotube, graphene or other porous carbon materials have high specific surface area and excellent charge transfer capacity, so they become promising electrode materials for batteries. The current research focuses on the development of highly ordered mesoporous carbon materials for zinc bromide redox flow batteries, it provides more active sites for the reaction of Br_2/Br^- and matches the reaction rate of zinc electrode, which greatly improves the power density of the battery. Moreover, because of the matching of two electrode reaction rates, the formation of dendrite in the anodic zinc crystal is well relieved, which not only improves the performance of the battery, but also solves the technical problems effectively.

4. CONCLUSION AND PROSPECT

The zinc bromide flow battery has an inherent advantage of low cost, high energy density and high cost performance. After nearly 40 years of technological development, has achieved remarkable technological development, and become an important part of new energy storage technology. Different from the traditional physical energy storage, the zinc bromine battery system has the advantages of small footprint, low one-time investment, long service life, high safety and reliability. All of these provide technical support for the solution of the zinc bromide flow battery system to solve the new energy power generation and grid connection. Indeed, zinc bromide battery also has the problem that zinc deposition is easy to form dendrites and self discharge, but these problems have been effectively solved by the optimization of zinc bromide battery materials and technical improvement. Zinc bromide battery needs to be studied deeply to break the monopoly of technology and develop the key material on the basis of maintaining the advantage of cost, optimize the performance of zinc bromine battery and realize mass production. Improving the manufacturing process and product safety reliability while substantially reducing the cost. Through the combination of scientific research, education and production, the docking and coupling of the upper, middle and lower reaches of technological innovation can be realized, which provides a theoretical basis for the study of zinc bromide flow battery, and finally realizes the large-scale application of zinc bromide flow battery technology in energy storage technology.

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