Review Article

Progress and Perspective of the Cathode Materials towards Bromine-Based Flow Batteries

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Received 12 September 2021; Accepted 12 January 2022; Published 17 February 2022

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Bromine-based flow batteries (Br-FBs) have been one of the most promising energy storage technologies with attracting advantages of low price, wide potential window, and long cycle life, such as zinc-bromine flow battery, hydrogen-bromine flow battery, and sodium polysulfide-bromine flow battery. The research and development of aqueous Br-FBs are very fast and many achievements have been realized. However, Br-FBs suffer from the sluggish kinetics of Br_2/Br^- redox couple and serious self-discharge caused by the diffusion of bromine, which hinder the further commercialization and industrialization of the aqueous Br-FBs. A series of mitigation strategies have been developed to figure out these challenges, especially the modifications on electrode materials. Electrode, one of the critical components in a Br-FB, provides the reactions sites for redox couples, upon which its properties exert a significant effect on the performance of Br-FBs. Up to now, extensive research has been carried out on electrode modifications to solve the aforementioned notorious issues of Br-FBs, including surface treatment and surface modification. In this review, various electrode materials and relevant modification approaches used for Br-FBs are overviewed and summarized. Moreover, the relevant mechanisms are illustrated deeply, providing comprehensive and available instruction to pursue and develop high-performance cathodes for Br-FBs with high power density and long lifespan.

1. Introduction

The increasingly severe energy crisis and environmental problems lead to the rapid development of renewable energies and their raised proportion in the energy supply structure [1]. However, the unstable, discontinuous, and uncontrollable characteristics of renewable energies make the large-scale energy storage technologies imperative to realize grid safety and high reliability when using renewable energies to generate electricity. That is because large-scale energy storage technologies can enhance the frequency and peak regulation capacity of the power grid, enabling the smooth integration of renewable energies into the grid. Therefore, the research and development of large-scale energy storage technologies are the keys to realize the wide utilization of renewable energies. Electrochemical energy storage (EES) technologies are not limited by geographical conditions and are easy to be scaled up, which are thus widely applied in energy storage. In particular, flow battery

(FB) technology has attracted much attention owing to its fantastic advantages of the independent regulation of energy and power, high safety, long cycle life, and outstanding environmental benignity [2, 3]. Up to now, FB technologies have been extensively utilized in large-scale energy storage and distributed generation.

Bromine redox couple (Br_2/Br^-) is often used as the positive active species of FBs because Br_2/Br^- couple has high electrode potential, high solubility, and rich source [4, 5]. When matching a suitable negative electrode, a bromine-based flow battery (Br-FB) is constructed (Figure 1), which has the advantages of wide voltage window, high energy density, low cost, and reliability when compared with other FBs, which are as follow:

- (i) Wide voltage window: Br_2/Br^- couple has a high electrode potential of 1.08 V
- (ii) High solubility: The solubility of Br_2 in water is 0.43 mol/L at 20°C, but when there are halogen ions

FIGURE 1: Schematic diagrams of Br-FBs with different negative redox couples: (a) metallic redox couple and (b) nonmetallic redox couple or organic molecular redox couple.

such as Br^- in the solution, Br_2 will complex with halogen ions to form complex ions such as Br_3^- and Br_5^- , thus significantly improving its solubility

- (iii) High energy density, which is mainly caused by the high potential of Br_2/Br^- couple and the high solubility of Br_2
- (iv) Low cost: Bromine resources are abundant enough for bromine-based FBs, since bromine, a “marine element,” can be extracted directly from seawater
- (v) High reliability: The potential safety hazard of Br-FBs mainly comes from volatile bromine molecules, which will be quickly complexed by complexing agent to form oily bromine complexes. Combined with the optimization of battery system, almost no bromine can be released into the environment, guaranteeing the safety and reliability of Br-FBs

The negative redox couples can be metallic, such as Zn^{2+}/Zn (Figure 1(a)), or nonmetallic (or organic molecules), such as sodium polysulfide (Figure 1(b)). Notably, when constructed with metallic redox couples, the reactions at negative side are based on the dissolution/deposition mechanisms, as shown in Figure 1(a). The traditional Br-FBs include zinc-bromine flow battery (ZBFB), hydrogen-bromine flow battery (HBFB), sodium polysulfide-bromine flow battery (PBFB), and vanadium-bromine flow battery (VBFB). In recent years, many novel Br-FB systems have also been proposed, such as quinone-bromine flow battery (QBFB), lithium-bromine flow battery (LBFB), tin-bromine flow battery (TBFB), and titanium-bromine flow battery (TiBFB) [6, 7].

The features of different Br-FBs are shown in Table 1.

At present, ZBFB technology together with HBFB technology has been at the demonstration stage. Especially, in the past few years, the ZBFB technology has achieved rapid development in China, the United States, Japan, Australia, etc. In 2017, the first 5 kW/5 kWh zinc-bromine single flow

battery energy storage demonstration system was developed in China [8]. Nevertheless, the further commercialization and industrialization of Br-FBs still suffer from many thorny problems as follows:

- (i) Bromine is highly corrosive and oxidizing, which brings about higher requests for the chemical stability of various components of Br-FBs, including the electrode and the membrane materials [9–12]
- (ii) The high diffusivity of bromine will reduce the safety and lifespan of batteries. In general, bromine will easily migrate to the negative side, which may react with the negative active materials to result in the self-discharge, thus decreasing the efficiency, causing the capacity decay, and shortening the lifespan of batteries [12].
- (iii) The sluggish kinetics of Br_2/Br^- reactions is believed to be one of the major factors that result in higher electrochemical polarization and lower battery power density of Br-FBs [13]
- (iv) Bromine has high volatility, which will easily volatilize to pollute the environment and lead to safety issues. Meanwhile, it also gives rise to the reduced content of active species in the battery, reducing the efficiency, capacity, and cycle life of the battery [14]
- (v) The key to overcome these challenges is to modify and optimize the key materials of Br-FBs, which mainly include the electrolyte, the membrane, and the electrode. Up to now, a series of strategies to overcome these challenges have been researched and developed, mainly including:
 - (i) To modify membrane materials to inhibit the diffusion of bromine by sieving effect but commonly increase the membrane impedance [14–16]. In fact, there are limited membrane materials suited for Br-

TABLE 1: Summary of various Br-FBs systems.

Br-FBs	Advantages	Disadvantages
ZBFB	High energy density Low cost	Zinc dendrite Large polarization Lower working current density Limited area capacity Short cycling life
HBFB	High energy density High power density	Catalyst deterioration
PBFB	Low cost	Cross-contamination of active substances Sluggish kinetic of anodes Polysulfide shuttle
VBFB	High energy density Wide operating temperature range Low cost	Self-discharge Corrosivity of Br ₂
QBFB	Various quinones and quinone-based derivatives Flexible functionalized modification of quinones	Poor temperature adaptability Poor chemical/electrochemical stability
LBFB	High theoretical voltage High energy density Low cost	Capacity attenuation Poor cycling stability Lithium dendrite
TBFB	High solubility Low cost	Cross-contamination Low power density
TiBFB	Outstanding cycle stability	Low theoretical voltage

FBs, due to the particular operating conditions of Br-FB systems

- (ii) Adding complexing agent into the electrolyte is an effective way to reduce the concentration of Br₂ in the water phase and further reduce its diffusion rate [17–20]. The complexing agent will complex with bromine to form larger polybromide ion complexes, facilitating the exclusion of the membrane to bromine and consequently reduce the self-discharge of batteries [9–12]. However, the introduction of additives will affect the conductivity of the electrolyte or reduce the reaction kinetics [20]. The battery polarization is therefore improved
- (iii) To develop electrode materials with high activity, which can effectively increase the reaction activity of Br₂/Br⁻ couple [21, 22]

Electrode, the place where the electrochemical reactions happen, plays a role in transporting electrons, providing the reaction sites, transporting the electrolyte, and so forth. The physical and chemical properties of electrodes are directly related to the performance of batteries. Therefore, it is important for cathode materials of Br-FBs to have high conductivity to accelerate the electron transport, high electrocatalytic activity to boost Br₂/Br⁻ reactions, great hydrophilicity to reduce the electrode-electrolyte interface resistance, and high chemical and electrochemical stability to resist the bromine corrosion [23]. At present, the commonly used bromine cathode materials include metals and metal oxides, carbon materials, and their corresponding composite materials.

Among them, carbon felts (CFs) or graphite felts (GFs) with three-dimensional (3D) porous structures have been widely used as the cathodes in Br-FBs on account of their superior advantages of large specific surface area, good electronic conductivity, excellent stability, good chemical stability, and so on [24, 25]. However, in consideration of their relatively poor hydrophilicity and low electrochemical activity, CFs and GFs need to be modified purposefully to enhance their overall properties. So far, many modification methods have been carried out on cathodes of Br-FBs, such as surface treatment and surface modification (Figure 2). Herein, we will overview the commonly used cathode materials in Br-FBs. The advantages, disadvantages, and corresponding modification methods on them will be summarized, including the surface treatment, metallic element modification, nonmetallic element modification, and structure decoration (Figure 2). Furthermore, prospective directions for the future exploration of Br-FBs cathode materials will be proposed. Therefore, this review will be helpful to instruct the construction of high-performance and long lifespan Br-FBs.

2. Overview of Br-FBs

In a typical Br-FB, the positive and negative electrolytes are stored in two external storage tanks, which are driven by pumps into the battery body to complete the circulation of electrolytes in Br-FBs (Figure 1). At the same time, the positive and negative electrolytes are separated by a membrane to avoid the cross-contamination of the active materials in the positive and negative electrolytes, respectively. During the charge process, Br⁻ is oxidized to Br₂, which will further

FIGURE 2: An overview on the modification methods of cathode materials for Br-FBs.

complex with bromide ion to form polybromides and be captured by the bromine complexing agent to form bromine complexes and then enriched in the oil complexes (Figure 1) [26, 27]. When the negative active materials are metal ions, they are reduced to metals and deposited on the surface of negative electrodes simultaneously (Figure 1(a)). If the negative active materials are nonmetal ions, they are reduced to their corresponding reduction products (Figure 1(b)). During the discharge process, the reverse electrode reactions occur. The current Br-FB systems include ZBFB, HBFB, PBFB, VBFB, QBFB, LBFB, TBFB, and TiBFB, upon which their redox reactions during the charge-discharge process are as shown in Table 2 [7, 28–33]:

In a typical Br-FB, the electrode is a place where the electrochemical reactions of redox couples occur (Figures 1 and 3). Notably, the electrode only provides reaction sites but does not participate in redox reactions. Generally, during the charge-discharge process, positive redox reactions of Br-FBs are exhibited in Figure 3. The formation of bromine in the adsorbed state is considered as the rate-determining step [34]. As a result, the ideal cathode materials of Br-FBs should meet the following requirements:

- (i) Excellent chemical and electrochemical stability. The strong corrosivity of Br_2 means that cathode materials must have high chemical and electrochemical stability, which is the vital assurance of the long-term and stable battery operation
- (ii) High electrochemical activity. Cathode materials should be highly electrochemically reactive to Br_2/Br^- couple, thus reducing the electrochemical polarization and increasing the power density of batteries
- (iii) Good electronic conductivity, which is beneficial to transport electrons rapidly and reduce the ohmic polarization of batteries
- (iv) Outstanding hydrophilic property. Br-FBs normally use aqueous electrolytes. The high hydrophilicity of cathode materials is favorable to the reduction of

TABLE 2: Current Br-FB systems and their corresponding redox reactions.

Systems	Reactions
ZBFB	$\text{Zn}^{2+} + 2\text{Br}^- \rightleftharpoons \text{Zn} + \text{Br}_2$
HBFB	$2\text{H}^+(\text{aq}) + 2\text{Br}^-(\text{aq}) \rightleftharpoons \text{H}_2(\text{g}) + \text{Br}_2(\text{aq})$
PBFB	$2\text{NaBr} + (x-1)\text{Na}_2\text{S}_x \rightleftharpoons x\text{Na}_2\text{S}_{x-1} + \text{Br}_2, x = 2 \sim 4$
VBFB	$2\text{V}^{3+} + 3\text{Br}^- \rightleftharpoons 2\text{V}^{2+} + \text{Br}_3^-$
QBFB	$\text{AQDS} + 2\text{H}^+ + 2\text{Br}^- \rightleftharpoons \text{AQDSH}_2 + \text{Br}_2$
LBFB	$2\text{Li}^+ + 2\text{Br}^- \rightleftharpoons 2\text{Li} + \text{Br}_2$
TBFB	$\text{Sn}^{2+} + 2\text{Br}^- \rightleftharpoons \text{Sn} + \text{Br}_2$
TiBFB	$2\text{TiO}^{2+} + 4\text{H}^+ + 2\text{Br}^- \rightleftharpoons 2\text{Ti}^{3+} + 2\text{H}_2\text{O} + \text{Br}_2$

the interfacial resistance, because the electrochemical reactions exactly occur at the interface between the electrode and the electrolyte (Figure 3)

3. The Cathode Materials of Br-FBs

Based on the requirements as mentioned above, the commonly used cathode materials for Br-FBs are classified as metal-based compounds (such as Pt) together with carbon-based materials (such as graphite, CF, and GF) [24, 35–39]. In this review, we will first overview the properties, advantages, and disadvantages of different types of cathode materials for Br-FBs.

3.1. Metal-Based Materials. Metal-based materials have been studied as electrodes for Br_2/Br^- redox couple due to their high electrochemical activity, good electronic conductivity, and excellent mechanical properties. However, except for some precious metals and oxides, most metals and metal oxides are unstable in the presence of highly corrosive bromine. So far, metal-based cathode materials currently available for Br-FBs are Pt, TiN, ZrO_x , TiO_x , WO_x , AlO_x , etc., which show high activity on Br_2/Br^- redox reactions and improve the reversibility of Br_2/Br^- redox reactions [38, 40, 41].

Among them, Pt exhibits good adsorption characteristics towards Br_2 , Br^- ions, and Br_3^- ions, which significantly affects the electrochemical reactions of Br_2/Br^- couple on Pt cathode [42, 43]. In 1963, Breiter [44] found that Br^- could adsorb on Pt electrode, which strongly inhibited the adsorption of oxygen-containing substances on the surface of Pt electrode in the double-layer potential region. On the contrary, Johnson and Bruckens [45] reported that the adsorption of Br^- would not occur when oxides covered the surface of Pt electrode. Thus, the surface natures of the electrodes are essential for the adsorption of Br^- ions. Lane and Hubbard [46] further showed that the adsorption of Br^- on Pt was irreversible and the electrochemical oxidation activity of the adsorbed Br^- was much lower than that of Br^- in the bulk solution. In addition, Cooper and Parsons [47] showed that Pt was highly active and reversible on Br_2/Br^- redox couple. Moreover, the study of reaction kinetics of Br_2/Br^- indicated that the determining step was the

FIGURE 3: The mechanism of Br_2/Br^- reactions on the cathode.

formation of the adsorbed Br atoms or the combination of the two adsorbed bromine atoms to form a Br_2 molecule. Williams et al. [38] found that amorphous metal oxides with good conductivity were more likely to adsorb bromine complex, thus improving the rate capacity of batteries. They proved that ZrO_x was superior in preventing side reactions with the complexing agent through deep charge cycle tests (Figure 4(a)). The ZrO_x prevented the overcharge and was conducive to a three-phase interaction to adsorb more bromine from the complex phase through a thin layer of aqueous phase directly on the electrode surface.

However, minimal percentages of Pt have been used as a catalyst in Br-FBs because the expensive nature of Pt limits its large-scale accessibility. Thereby, metals or metal oxides are not well suited for Br-FBs, which are scarcely used as cathode materials for Br-FBs. In most instances, metal and metal-based electrodes are often used to investigate the kinetics of Br_2/Br^- reactions. Nevertheless, it is worth noting that the research on the adsorption process and reaction mechanism of Br_2/Br^- redox couples on metal-based electrodes will exhibit great guiding significance for the study of electrochemical reaction characteristics of Br_2/Br^- on other types of cathode materials [46, 48–50].

3.2. Carbon Materials. Carbon materials have been widely used for the cathode materials of Br-FBs because of their low price, good electronic conductivity, and outstanding corrosion resistance as well as controllable structure and surface properties [24, 51, 52]. Up to now, the commonly utilized carbon-based cathode materials for Br-FBs include intrinsically porous carbon materials and porous (2D or 3D) carbon fiber-based materials [21, 35, 53].

3.2.1. Intrinsically Porous Carbon Materials. Intrinsically porous carbon materials are carbon materials with intrinsic pore structures, which are commonly powdery. The intrinsically porous carbon materials used in Br-FBs can have micropores (<2 nm), mesopores (2–50 nm), or macropores (>50 nm). The intrinsically porous carbon materials com-

monly have high specific surface area, good electronic conductivity, and easy structure control, thereby are widely used in Br-FBs. Their utilization in Br-FBs can improve the adsorption ability of bromine to a certain extent and thus accelerate the rate-determining step of Br_2/Br^- redox reactions, such as carbon nanotubes (CNTs), activated carbon (AC), and biomass-derived porous carbon. Among them, CNTs are concentric circular tubes composed of several layers of carbon atoms arranged in a hexagonal pattern, with the radial and axial dimensions in the micrometer range. The distance between the sheets is fixed at about 0.34 nm. The carbon atoms adopt sp^2 hybridization, which has a larger s orbital component than that of sp^3 hybridization, endowing CNTs' good mechanical properties [54]. CNTs can be viewed as sheets of graphene coiled in layers, which provides plentiful freely moving electrons to result in good electronic conductivity. Benefiting from the advantages of CNTs, they have been used as cathode materials for Br-FBs [55–59]. Engelhard and co-workers first compared the difference of the $\text{Br}^-/\text{BrCl}_2^-$ redox reactions between CNTs and graphite electrodes (Figure 4(b)) [3, 58]. They found that CNTs showed higher activity than that of graphite because of high electronic conductivity and high surface area (Figure 4(c)) [58]. Moreover, the functional groups and structure defects (pentagon, heptagon, dangling structures, etc.) on CNTs are usually considered as the electrocatalytic sites [60, 61]. According to the number of layers, CNTs can be classified as single-walled CNTs (SWCNTs) and multiwalled CNTs (MWCNTs) (Figure 4(d)) [57]. The walls of MWCNTs are usually rich in defects because trap centers are easy to form between the layers, which can then trap all kinds of defects [62]. In contrast, SWCNTs have a smaller distribution of diameter sizes, a higher degree of uniformity, and a larger specific surface area, accordingly exposing more active sites. Worth noting is that SWCNT electrodes have better electrochemical activity, which results from the presence of abundant basal surfaces. However, the reversibility of Br_2/Br^- reactions on MWCNT electrodes was better because of numerous edge planar active sites in MWCNTs.

FIGURE 4: (a) Nyquist plots of AC and ZrO_x-coated AC. (b) Comparison of CNTs and graphite electrodes. (c) Cyclic voltammograms (CV) on CNTs and graphite electrodes in 1.0 M HCl + 0.5 M NaBr solution (20 mV s⁻¹). (d) Comparison of SWCNTs and MWCNTs. (e) CVs of CNT-modified electrodes and glassy carbon (GC) at 20 mV s⁻¹ in 0.05 M ZnBr₂ + 1 M HClO₄. (f) SEM picture of the megaloporous carbon cryogel and energy yield as a function of the number of cycles, for three different charge densities applied to the cell for 5 mA g⁻¹.

Munaiah et al. [56] investigated the catalytic activity of SWCNTs with different purity for Br₂/Br⁻ redox reactions. For SWCNTs, higher purity meant more active sites, which were beneficial to the charge transfer and showed higher catalytic activity on Br₂/Br⁻ redox reactions. They also applied MWCNT electrodes in ZBFBs, and they exhibited remarkable electrochemical behaviors due to plenty of basal planes and edge planes (Figure 4(e)) [58]. Nonetheless, CNTs are expensive, which are not suited for large-scale applications.

Moreover, Ayme-Perrot et al. [63] adopted megaloporous carbon cryogels as the cathodes for ZBFBs, which could act as a good bromine storage tank by the capillary trapping effect. Thus, the corrosion of bromine to the zinc anode could be avoided effectively by preventing bromine diffusion. Meanwhile, the high specific surface area of megaloporous carbon cryogels led to excellent charge transfer properties and provided abundant active sites for Br₂/Br⁻ reactions. Therefore, the assembled ZBFB was capable of reversibly storing substantial amounts of bromine and maintained a constant energy yield after running multiple cycles (Figure 4(f)). Furthermore, many carbon-based materials

with intrinsic pores, such as AC, have rich micropores, large specific surface area (2314 m² g⁻¹), and strong adsorption capacity, which is expected to exhibit sufficiently high electrochemical activity in Br-FBs. However, such powdery carbon materials exhibited significant concentration polarization and cannot be prepared as self-supported electrodes, which are usually loaded on porous carbon fiber-based materials. That will be discussed in detail in the following parts.

3.2.2. Porous Carbon Fiber-Based Materials. Different from the intrinsically porous structures of carbon materials, the porous (2D or 3D) carbon fiber-based materials, such as CF, GF, carbon paper (CP), and carbon cloth (CC), are constructed by interweaving carbon fibers with a diameter of tens of micrometers and length of several centimeters (Figure 5(a)) [40]. First, the self-supported 3D porous structures with high porosity facilitate the electrolyte flow, meaning smaller concentration and diffusion polarization [37, 64]. Second, the excellent mechanical properties, high corrosion resistance, and good conductivity of 3D carbon fiber-

FIGURE 5: (a) Schematic diagram of CF or GF. (b) CVs of GC, GF, and CP at 20 mV s⁻¹. (c) Charge-discharge profiles of ZBFBs using GF and CP as the electrode at 40 mA cm⁻². (d) Schematic representation of surface treatment of electrodes. (e) Proposed reaction mechanism of Br₂/Br⁻ couple on functionalized CP.

based materials make them especially suited as cathode materials for Br-FBs [37]. Zhou et al. [24] have compared the performance of AC and CF as cathodes in PFBF. Compared with CFs, AC had low porosity, poor mass transfer behavior, and low utilization rate of surface area, which led to the poor discharge performance of the battery. In contrast, the high porosity and large pores of CF formed by interlacing fibers allowed the electrolyte to flow through the felts fluently. Thus, the forced convection was the primary flow mode, most favorable for mass transport. However, the hydrophobic nature of CFs and GFs caused by hydrophobic C-C bond and lack of hydrophilic functional groups will lead to relatively poor aqueous wettability. Moreover, the smooth surface of carbon fibers lacks sufficient catalytic sites, resulting in high resistance and poor electrocatalytic activity [65, 66]. To this end, Wu et al. [23] used a thin CP to replace the conventional thick GF electrode in ZBFBs. Thick GFs led to a large internal resistance when the assembled battery operated at a high current density. While CP was very thin, therefore, the electrical resistance was lower and the electrolyte transport through CP could be facilitated (Figure 5(b)). The enhanced electrocatalytic activity of CP on Br₂/Br⁻ reactions and the reduced internal resistance of the thinner electrode significantly decreased the battery polarization as well as improved the energy efficiency (EE) of ZBFBs, which was up to 83.5% at 40 mA cm⁻² (GF: 73.0%, Figure 5(c)).

The summary of different cathode materials for Br-FBs is shown in Table 3. Of note, although the activity of carbon materials is commonly lower than that of Pt, their electrochemical activity can be enhanced by regulating the internal structure and surface properties. At present, porous (2D or 3D) carbon fiber-based materials, especially CFs and GFs, are the most widely used cathode materials in Br-FBs.

4. Modification of Electrodes

As shown in Table 3, the currently used electrode materials still suffer from many challenges, which cannot fully meet the demand of commercializing and industrializing Br-FBs. Therefore, it is necessary to modify the existing electrode materials to improve their performance, especially the electrochemical activity and hydrophilicity, thereby increasing the power density and lifespan of the batteries. Considering that CFs and GFs are the most widely used cathode materials in Br-FBs at present, this part will largely focus on the modification methods of CFs and GFs, which will be referential to instruct the modifications on other kinds of cathode materials of Br-FBs. The usually used modification methods mainly include surface treatment and surface modification.

4.1. Surface Treatment. The surface treatment is to construct intrinsically porous structures on the electrode surface by oxidizing etching, which can increase the specific surface

TABLE 3: The summary of different cathode materials for Br-FBs.

Types	Materials	Advantages	Disadvantages
Metals and metal oxides	Pt, ZrO_x , TiO_x , WO_x , AlO_x , etc.	High electrochemical activity	Expensive Instability
Intrinsically porous carbon materials	CNTs, megaloporous carbon cryogels, etc.	Good conductivity Large specific surface area High adsorption capacity	Low electrochemical activity Large concentration polarization
Porous carbon fiber-based materials	CF, GF, CP, etc.	Excellent mechanical properties Good conductivity High corrosion resistance Low cost	Poor hydrophilicity Low specific surface area

area and introduce oxygen-containing functional groups (Figure 5(d)) [2]. In general, according to the operating conditions, surface treatment can be categorized into heat treatment, acid treatment, and electrochemical oxidation treatment [67]. The heat treatment method involves the oxidation etching of the felt surfaces by heating them in an air or water vapor atmosphere at high temperatures. The acid treatment uses strongly oxidizing acids to oxidize the felt surfaces. Differently, the electrochemical oxidation method needs to be carried out in the presence of electric fields [68]. First, the surface of the electrodes becomes rough and porous after oxidation, thereby leading to the increased specific surface area and the formation of vacancies. More reactive sites are provided, thus improving the electrochemical activity of the modified electrodes. Second, the oxygen-containing and nitrogen-containing groups and defects on the surface increase the electrode hydrophilicity, which is beneficial to accelerate the mass transference and decrease the concentration polarization in Br-FBs [66]. Moreover, oxygen-containing and nitrogen-containing groups can catalyze Br_2/Br^- reactions. Notably, these three methods differ in the degree of etching, bringing about differences in enhancing the catalytic activity and hydrophilicity of electrodes. For instance, when using the heat treatment method, after being heated to 500°C , more pores and oxygen-containing functional groups will be created on the surface of CFs [69]. Moreover, the CFs used in the novel TBFBs were pretreated in the air at 500°C for 5 h to achieve higher electrophilicity [33]. Suresh et al. [70] employed H_2SO_4 -treated CPs (SM-CP) at the positive side of the ZBFBs. The introduction of oxygen-containing functional groups improved the hydrophilicity of CPs and provided more electrochemical active sites to catalyze Br_2/Br^- redox reaction (Figure 5(e)). Similarly, the surface area of GFs increased after being electrochemically oxidized. Furthermore, the content of carboxyl functional groups was also increased simultaneously, beneficial to higher electrochemical activity [71]. Zhang et al. [36] also found that both acid oxidation and thermal oxidation methods could increase the number of oxygen-containing functional groups on GFs. However, it should be noted that excessive oxygen-containing functional groups may increase the ohmic impedance and charge transfer impedance of GFs [72].

In summary, surface treatment methods are designed to increase the specific surface area of electrodes and introduce oxygen-containing functional groups to improve their hydrophilicity and electrochemical activity. However, surface treatment is an uncontrolled process, leading to different sizes of the pores and uneven distribution. Moreover, the breakage of C-C bonds leads to the reduced electronic conductivity and deteriorated mechanical properties of the electrodes. The improvement in battery performance is thus limited. Furthermore, the effects that surface treatment exerts on increasing the specific surface area and introducing the suited amount of favorable functional groups are not enough. Upon most occasions, surface treatment is used as a pretreatment method due to their insignificant effect and damage to the electrodes.

4.2. Surface Modification. Different from surface treatment, surface modification is to increase the electrochemical activity and hydrophilicity of the electrodes by introducing active materials. Based on the properties of introduced active materials, surface modifications can be classified into metallic element modification, nonmetallic element modification, and structure decoration. Metallic element modification means introducing metal-based electrocatalysts on the electrode, while nonmetallic modification introduces active nonmetallic elements through element doping or compounding carbon-based electrocatalysts. Structure decoration is to design materials with unique structures to modify the electrodes, thus achieving higher electrochemical activity or better ability to inhibit the diffusion of bromine. The effects or mechanisms, advantages, and disadvantages of different modification methods will be described in detail in this part.

4.2.1. Metallic Element Modification. Metallic element modifications aim at improving the electrocatalytic activity through introducing active metal-based compounds, including metals, metal oxides, and metal nitrides, such as Pt, RuO_2 , ZrO_x , TiO_x , WO_x , AlO_x , and TiN [73–75]. The loaded metals or metallic compounds act as catalysts, which can improve the catalytic activity of electrodes on Br_2/Br^- redox reactions and increase the specific surface area of the electrodes (Figure 6(a)). Analogously, Pt particles with high activity were deposited on GF as an electrocatalyst to improve the

FIGURE 6: (a) Schematic representation of metallic element modification of electrodes. (b) Schematic representation of the Pt-coated GF preparation using pulsed laser deposition (PLD) process.

kinetics of Br_2/Br^- redox reactions (Figure 6(b)) [76]. When the Pt-coated GF was used as the cathode material of a ZBFB, its average coulombic efficiency (CE) and EE were up to 99.96% and 88% at 50 mA cm^{-2} , respectively (original GF: CE = 89.79% and EE = 67.93%). The low load of Pt minimized the electrochemical polarization and improved the kinetics of Br_2/Br^- redox reactions to a certain extent (Figure 6(b)). Therefore, the low Pt-loaded GF is considered as potential candidate electrodes for Br_2/Br^- redox couple. Sivasubramanian et al. [77] loaded RuO_2 on the CC electrode to improve its electrochemical activity, but the high load and low utilization rate of RuO_2 in the catalytic layer increased the cost. In addition to depositing metal-based electrocatalysts on felts, carbon fibers can also be coated with metal oxide protective layers by spinning technology [38]. Different from the deposition of metal-based particles, adding metal-based precursors during the preparation of CF can not only coat a layer of metal-based substance on the carbon fibers uniformly but control the thickness of the coatings. Moreover, Williams et al. [38] coated metal oxides on the carbon electrodes to prevent their degradation, which was evidenced by the formation of C-Br bond [78, 79].

Noble metal-decorated electrodes can also accelerate the kinetics of Br_2/Br^- redox reactions, but the increased cost and decreased stability will impede their commercialization and industrialization. Nonnoble metal materials used as electrocatalysts to boost the battery performance of Br-FBs still need further investigation. The electrode modified by the deposition of metal-based catalysts suffers from weak structure stability because the binding force between the catalyst particles and the electrode is weak [80]. The process of coating metal-based materials on the electrode by spinning

is complicated. Moreover, there is no report on improving the catalytic activity of electrodes with metal-based coatings. Hence, metal-based catalysts with relatively low price, excellent catalytic activity, and high cyclic stability for Br-FBs need to be further developed.

4.2.2. Nonmetallic Element Modification. The methods to modify the electrode with nonmetallic elements include heteroatom doping and introduction of carbon-based electrocatalysts [66].

(1) Heteroatom Doping. Heteroatom doping can break the conjugated system between C atoms by heteroatoms different in size and electronegativity [65]. By doping or codoping O-, N-, S-, B-, and P-containing functional groups with catalytic activity, heteroatoms are covalently bound to adjacent C atoms in carbon lattices [66]. Some carbon atoms are replaced by heteroatoms, creating defects and vacancies on the surface of the electrode as well as introducing hydrophilic polar bonds. As a result, heteroatom doping is an effective strategy to introduce defect sites and changes the distribution of electron clouds around the adjacent C atoms. Therefore, heteroatom doping can expand the catalytic interface and expose more electrocatalytic active sites, which is favorable to the fast mass transfer and better electrocatalytic activity (Figure 7(a)) [81, 82].

Nitrogen is one of the most commonly used dopants because of its strong electronegativity and superior hydrophilicity [83, 84]. Coating with nitrogenous substances on the carbon-based electrodes and then pyrolysis is a common and facile method to introduce N element into electrodes

FIGURE 7: (a) Schematic illustration of heteroatom doping of electrodes. (b–c) SEM images of pristine GF (PGF) and CTPPy-modified GF (CTPPy-GF). (d) Schematics of Br conversion/storage mechanism of NGF electrode. (e) Schematic representation of proposed Br species capture and storage mechanisms for NGF electrodes. (f) Bromine adsorption behavior of CF, TCF, and NTCF (TCF represents thermally treated pristine CF at 900°C for 3 h). (g) Reaction mechanism of Br₂/Br⁻ couple on NTCF.

[85]. For example, N-doped carbon-based cathodes with a large specific surface area and abundant heteroatomic functional groups were synthesized for ZBFBs, which were conducive to the formation and exposure of active sites of Br₂/Br⁻ redox reactions [86]. At 80 mA cm⁻², the voltage efficiency (VE) and EE of ZBFBs with the N-doped cathode were 83.0% and 82.5%, respectively, higher than that of using the undoped cathode. The introduction of N element can also be achieved by coating polymers with better electronic conductivity such as polyaniline (PANI) and polypyrrole (PPy). Recently, GFs were successfully doped with N element and O element by decorating carbonized tubular PP (CTPPy) with abundant nitrogen- and oxygen-containing functional groups (Figures 7(b) and 7(c)) [87]. The functional groups showed good electrocatalytic activity on Br₂/Br⁻ redox reactions, and the more electronegative nature facilitated the adsorption of bromine. In the meantime, the graphitic-N, which referred to the nitrogen atoms

that replace the carbon atoms in the graphene hexagonal ring, was the major nitrogen doping type. The existence of graphitic-N was beneficial to the higher electronic conductivity and stability of the framework. Therefore, the performance of ZBFBs was promoted when utilizing such modified GFs. Actually, the introduction of N elements plays a prominent role in catalyzing electrochemical redox reactions of Br₂/Br⁻ redox couples. Lee et al. [27] modified GFs with protonated nitrogen pyridine-doped microporous carbon (NGF-T, T represents carbonization temperature) and utilized the adsorption effects to prevent bromine crossover (Figure 7(d)). In an acidic environment of ZBFBs, pyridinic N is converted to hydrogenated form (hPL), which is more effective to adsorb bromide and polybromides than other N-doped structures. Considering the dipole-dipole interaction, the radius of the atomic adsorption site should be sufficiently smaller than that of the adsorbent [88]. They carried out theoretical calculations to prove that protons

FIGURE 8: (a) Schematic illustration of introducing carbon-based electrocatalysts to electrodes. (b) CV curves of AB, CNT, EG, and BP at 10 mV s⁻¹ in 0.005 M ZnBr₂ + 0.005 M Br₂. (c) Relationship between I_p and S_{BET}. (d) CV curves of pristine CP (PCP), GO-modified PCP (PCP-GO), and rGO-modified PCP (PCP-rGO) (PCP was used as a current collector in the three electrodes system only). (e) CV curves of BDG and rGO at 20 mV s⁻¹. (f) CV curves of FGs in 1 M H₂SO₄ electrolyte at 100 mV s⁻¹ (the FGs synthesized in 1 M, 2 M, 3 M, and 4 M KF aqueous electrolytes were termed as FG-M1, FG-M2, FG-M3, and FG-M4, respectively).

bound to pyridine N with a radius of 120 pm were smaller than that of carbon (170 pm), providing a stronger adsorption site for bromine (185 pm) (Figure 7(e)). Lu et al. [21] fabricated CFs with N-rich defects (NTCF) for high power density and long cycle life ZBFBs by nonmetallic element modification method. The N-rich defects increased the hydrophilicity and specific surface area of the modified CFs, meaning more active reaction sites and enhanced adsorption capacity of bromine (Figures 7(f) and 7(g)). The NTCF thereby demonstrated excellent electrochemical activity on Br₂/Br⁻ reactions, enabling ZBFBs to realize higher power density and longer lifespan. Moreover, N-doping was also carried out by a simple pyrolytic urea method [22] or a nanocasting method [89], both of which improved the electrocatalytic activity of electrodes. Apart from doping N element into electrodes, B-doping is also adopted to enhance Br₂/Br⁻ redox reactions by inducing defect sites and destruction in the carbon lattice [90].

As clarified above, the hydrophilicity, electronic conductivity, and adsorption properties of electrodes can be improved by heteroatom doping. The porous structure and stable heteroatom functional groups are formed simultaneously due to the structural characteristics of the dopant itself. Therefore, under the premise of ensuring sufficient specific surface area, the nonmetallic element doping effectively promotes the electrochemical activity on Br₂/Br⁻ redox reactions. However, this modification method is designed to

improve the catalytic activity of the electrodes without considering the problem of bromine diffusion. The effective utilization of different dopants and the effects of the content of doped elements on the catalytic activity of electrodes still need to be further investigated. More than that, the reported dopants used for cathodes of Br-FBs are also used in other catalytic systems and the selection principles of dopants are not definite, leading to that the reaction mechanisms are unclear and remain further in-depth understanding.

(2) *Introduction of Carbon-Based Electrocatalysts.* As mentioned above, carbon materials with large specific surface area, good conductivity, and good electrochemical stability are applicable enough for electrode materials. In like manner, they can also be used as electrode-modifying materials, such as graphene, graphene oxide (GO), reduced graphene oxide (rGO), CNTs, carbon nanofibers, carbon nanosheets, and AC (Figure 8(a)) [51, 91, 92].

Wang et al. [53] firstly introduced acetylene black (AB), expanded graphite (EG), CNTs, and BP 2000 as electrocatalysts for ZBFBs (Figure 8(b)). They concluded that the carbon materials with high specific surface, large pore size, and high electronic conductivity showed higher electrochemical activity (Figure 8(c)). Additionally, among carbonaceous materials, graphene, a two-dimensional carbon nanomaterial composed of C atoms hybridized by sp², has

FIGURE 9: (a) The catalytic mechanism on the improved activity of pure SWCNTs and FSWCNTs toward Br_2/Br^- redox reaction. (b) CV curves of the pristine graphite, MWCNTs, SWCNTs, and FSWCNTs at 50 mV s^{-1} in the electrolyte of 2 M $\text{V}^{3.5+}$, 8 M HBr, 2 M HCl, and 0.75 M QBr (methyl ethyl morpholinium bromide (MEM) + methyl ethyl pyrrolidinium bromide (MEP)). (c) CV curves of GC, three-dimensional NOMC (NOMC-3D), and two-dimensional NOMC (NOMC-2D) at 50 mV s^{-1} in the electrolyte of 0.10 M $\text{ZnBr}_2 + 0.10 \text{ M B r}_2$. (d) CV curves of the AC and CF at 20 mV s^{-1} . (e) CV curves of AC-GF and bare GF at 5 mV s^{-1} .

a large specific surface area, excellent electronic conductivity, and good chemical stability. GO, prepared by proper oxidation of graphene, is rich in oxygen-containing functional groups and exhibits higher electrocatalytic properties. As a result, graphene-based carbon materials are considered as one of the most promising electrocatalysts in Br-FBs. For example, GO and rGO were loaded on CFs as cathodes for ZBFBs [93]. The highly enhanced kinetics and improved reversibility of Br_2/Br^- redox reactions were achieved, favoring higher CE and VE (Figure 8(d)). The outstanding performance was due to the enhanced electronic conductivity and overwhelmed electrochemical active sites. Wu et al. [22] synthesized N-doped graphene nanoplatelets (N-GnP) and applied them as electrocatalysts in ZBFBs. They exhibited remarkable catalytic activity on Br_2/Br^- redox reactions. The electronic properties of the nearby C atoms were modulated because of the strong electronegativity of the incorporated nitrogen. Accordingly, the adsorption of polybrominated ions and the charge transfer between the adsorbed ions and the electrode were promoted, boosting the kinetics of Br_2/Br^- redox reactions. Thus, ZBFBs were able to reach an EE of 84.2% at 80 mA cm^{-2} (original CF: 71.8%). Boron-doped graphene (BDG) with high surface area and high electrocatalytic activity was used as the electrocatalyst in ZBFBs as well

[90]. The introduction of B element in the graphene matrix greatly increased the peak current and reduced the double-layer charge storage due to defect sites and destruction in the carbon lattice (Figure 8(e)). The ZBFBs assembled with the modified CF demonstrated better cycling performance at 20 mA cm^{-2} . Furthermore, the functionalized graphene can improve the kinetics of Br_2/Br^- redox reactions as well. Br_2 and Br^- could be selectively adsorbed on the surface of the functionalized graphene, which was dependent on the degree of functionalization. The degree of edge stripping was increased and more effective active sites were created during the fluorination process. Consequently, the fluorinated graphene-modified CFs showed higher reversibility and better electrocatalytic activity on Br_2/Br^- redox reactions (Figure 8(f)) [94].

When CFs modified with CNTs were used as cathodes, the assembled ZBFBs also showed better electrochemical performance in terms of efficiency and durability [95]. In order to further improve the performance of CNT-modified electrodes, some modification methods are needed. For instance, Rui et al. [96] modified the SWCNTs with oxygen-containing functional groups (FSWCNTs) to reduce the charge transfer resistance and improve the catalytic activity on Br_2/Br^- redox reactions (Figures 9(a) and 9(b)). Of note, metal impurities like iron, cobalt, and nickel may

TABLE 4: Summary of carbon-based electrocatalysts in Br-FBs.

Catalysts	Features	Advantages	Disadvantages
Graphene, GO, rGO	2D carbon nanomaterial composed of C atoms hybridized by sp ²	Large specific surface area Excellent electronic conductivity Good chemical stability Abundant O-containing groups High catalytic activity	High cost
CNTs	Sheets of graphene coiled in layers	Large specific surface area Excellent electronic conductivity Good chemical stability High catalytic activity	High cost
AC	Carbon consists of graphite microcrystalline, single planar reticulated carbon and amorphous carbon	Abundant micropores Large specific surface area Strong adsorption capacity	Low porosity low specific surface area
Biomass-derived carbon	Rough and porous structure	Abundant active functional groups Rich sources Low cost	Complex preparation process Uneven pore distribution

exist in some of the CNTs. As a consequence, pretreatment is required for purification. Moreover, the catalytic mechanisms of CNTs remain to be further studied. Even so, CNTs are still promising electrode electrocatalysts for Br-FBs. Furthermore, Jin et al. [89] introduced low-dimensional nitrogen-doped carbon (NOMC) as electrocatalysts for the Br_2/Br^- redox couple. The heteroatom-activated carbon could act as active sites, and its structure promoted the exposure of active sites and accelerated the mass transfer of reactive species. Thus, the electrochemical activity was significantly improved (Figure 9(c)). As mentioned above, AC is suitable for Br-FBs because of its large specific surface area and good adsorption capacity. L. Zhang et al. [97] used AC as cathode electrocatalysts in ZBFBs, which promoted the formation of Br_{ads} , thus exhibiting comparatively high activity to Br_2/Br^- redox reactions (Figures 3 and 9(d)). A highly electrochemically active layer on the electrode was constructed, significantly reducing the resistance of the battery. Wu et al. [98] used mesoporous carbon materials (PPC/NiPPC) with high specific surface area as the cathode electrocatalyst in ZBFBs. The resultant mesoporous carbon materials showed an extraordinary activity on Br_2/Br^- redox reactions, which was ascribed to sufficient active sites, fast mass transport, and facile electron transfer. Thus, the assembled ZBFBs could operate at 80 mA cm^{-2} with an EE up to 84.2% (original GF: 78.4%). Naresh et al. [99] reported AC derived from *Phyllanthus emblica* leave's biomass as an electrocatalyst to Br_2/Br^- redox reactions. The high specific surface area and defects provided more active sites and ensured strong adsorption capacity of AC, accelerating the formation of Br_{ads} (Figure 3). Accordingly, the AC-anchored GFs (AC-GFs) showed significant improvement in electrochemical activity on Br_2/Br^- redox reactions and reinforced the overall performance of ZBFBs (Figure 9(e)). As a matter of fact, bio-

mass materials possess great potential in the applications of Br-FBs due to their porous structure with abundant active functional groups, rich sources, and low cost.

In summary, carbon-based materials with large specific surface area, good conductivity, electrochemical stability, and low cost are proper as advanced electrocatalysts for Br-FBs. The morphology and pore structures of carbon materials can be controllably designed, and the surface properties can be easily regulated. However, the powdery carbon materials will bring about a certain concentration polarization. Although they have good stability in the bromine-containing system, they are easy to fall off from the electrode under the flow of electrolytes. Furthermore, the introduced carbon-based electrocatalysts unevenly distribute in the felts, leading to increased local polarization and poor battery performance. The summary of different carbon-based electrocatalysts in Br-FBs is exhibited in Table 4.

4.3. Structure Decoration. Engineering the physical structure of the electrode with advanced materials having unique and regular structures is a critical approach to enlarge the specific surface area and build appropriate pathways for mass and charge transport (Figure 10(a)). Profiting from the synergistic effect of the nanostructure and active surface, metal-based nanomaterials can provide more active sites for electrochemical reactions. For example, Wang et al. [41] constructed a CF-supported TiN nanorod array (CTN) 3D hierarchical composite electrode (Figures 10(b) and 10(c)). The CF provided a 3D electron conductive framework to guarantee the high electronic conductivity. At the same time, TiN nanowires exhibited excellent catalytic activity on Br_2/Br^- redox reactions (Figure 10(d)). In addition, such a unique 3D hierarchical nanorod array alignment structure and improved hydrophilicity facilitated the ion transfer

FIGURE 10: (a) Schematic illustration of the electrode structure decoration. (b) Schematic illustration of the fabrication of CTN. (c) SEM images of (b) CF and CTN. (d) CV curves for CF, HCF, CTO, and CTN at 10 mV s^{-1} in an electrolyte composed of $0.1 \text{ M ZnBr}_2 + 0.1 \text{ M Br}_2$ (HCF and CTO represent the CF after the same heat treatment without the TiO₂ growth process and TiO₂ nanorod array-coated CF, respectively). (e) The efficiency of the ZBFB with CF and CTN at 160 mA cm^{-2} .

and contributed to a high electrolyte penetration, resulting in reduced diffusion polarization (Figure 10(b)). As a result, the overall performance of the assembled ZBFB was significantly improved, showing a VE of 68% and an EE of 66% at an ultrahigh current density of 160 mA cm^{-2} (Figure 10(e)).

The good electronic conductivity and adjustable structure of carbon materials make it practical to regulate the structures of the electrode by the structure decoration methods. For instance, Wang et al. [100] prepared a sandwich-like multiscale pore-rich hydroxylated carbon (SPHC), which consisted of a highly activated porous mesoporous layer assembled between a pair of protuberances-rich compact outer layers (Figure 11(a)). First, the porous interlayer structure provided abundant active sites, while the outer layer had a dense surface to protect the internal pores in the middle layer for electrolyte transport (Figure 11(b)). Second, the high content of hydroxyl functional groups improved the electrochemical activity of the electrodes by improving their hydrophilicity and electronic properties. As a result, the obtained carbon material-modified GF delivered remarkable electrochemical properties towards Br_2/Br^- redox reactions. Moreover, Wang et al. [101] prepared porous nanosheet carbon (PNSC) materials with abundant nitrogen and oxygen functional groups

(Figure 11(c)). The porous and loose structure together with in-plane nanopores provided 3D transport channels, enhancing the mass diffusion. Additionally, the large specific surface area ($2085 \text{ m}^2 \text{ g}^{-1}$) of PNSC could provide more reactive sites, showing excellent activity to Br_2/Br^- redox reactions (Figure 11(d)). A possible mechanism was also proposed: Br^- and Br_3^- ions could be absorbed on the carbon at edge and ions exchanged with the O- or N-containing functional groups to form adsorbed bromine species, which was because of the higher electronegativity of the O element and N element (Figure 11(e)). Moreover, Wang et al. designed bimodal highly ordered mesoporous carbon materials (BOMC) with pore sizes of 2 nm and 5 nm (Figure 11(f)) [102]. The smaller pores provided more active sites for Br_2/Br^- reactions and promoted bromine adsorption, thus speeding up the rate-determining step of Br_2/Br^- redox reactions. Meanwhile, the pores with a size of 5 nm played a role in shortening the mass transfer path, reducing the diffusion resistance, and improving the mass transfer rate (Figure 11(g)). As a result, the materials demonstrated ultrahigh electrochemical activity. The ZBFBs with the prepared cathode achieved a VE of 82.9% and an EE of 80.1% at 80 mA cm^{-2} , much better than those of batteries without the bimodal highly ordered mesoporous carbon materials (Figure 11(h)).

FIGURE 11: (a) Schematic diagram of the SPHC. (b) SEM images of the SPHC. (c) SEM images of the PNSC. (d) CV curves of NSC and PNCS at the scan rate of 10 mV s^{-1} in the electrolyte of $0.1 \text{ M ZnBr}_2 + 0.1 \text{ M Br}_2$ (NSC represents no CO_2 etching process). (e) Catalytic mechanism of the prepared materials to bromine redox reactions. (f) Electrochemical reactions on the surface of BOMC. (g) Pore size distribution curves and TEM pictures of BOMCs. (h) The efficiency of Blank ZBFB and ZBFB with BOMCs at 80 mA cm^{-2} .

Of note, the better adsorption capacity of cathode materials to bromine can possibly prevent bromine diffusion. However, almost no research about electrodes concentrates on preventing bromine diffusion. As a matter of fact, the self-discharge caused by the bromine diffusion seriously affects the performance and lifespan of Br-FBs. However, Wang et al. [103] achieved the inhibition to bromine migration by the surface decoration method (Figure 12(a)). They controlled the primary pore size of the cage porous carbon material (1.1 nm) precisely between the size of Br^- ions (4.83 Å), MEP^+ (9.25 Å), and bromine complex (MEPBr_3 ; 12.4 Å) (Figure 12(b)). When Br^- ions were oxidized to Br_2 , Br_2 complexed with the complexing agent to form a large-sized bromine complex immediately, which was entrapped in the cage via the pore size exclusion effect. Moreover, the prepared cathode materials exerted excellent bromine entrapping ability due to their hollow structure and specific pore size. These features were efficient in alleviating bromine diffusion and slow down the self-discharge of Br-FBs. As a

result, the assembled ZBFB could still maintain a high CE (98%) and a high EE (81%) at 80 mA cm^{-2} after running for 300 cycles (Figure 12(c)). This work provided a new idea for the structural design of cathode materials for Br-FBs. Moreover, Lee et al. [27] utilized the geometric trapping effect and adsorption effect of microporous carbon to prevent the diffusion of bromine. They modified GF with the N-doped microporous carbon to create micropores (<2 nm) for effectively absorbing and confining bromine and polybromide ions (NGF-T). According to theoretical calculations, the characteristic dimensions of Br_2 , Br_3^- , Br_5^- , Br_7^- , and Br_2 complexes are 2.354, 5.270, 9.212, 14.205, and 17.856 Å, respectively (Figure 12(d)). It was verified that the bromide ions were transformed into polybromide anions smaller than 2 nm. The strong adsorption site within the micropores facilitated the conversion of bromine and the capture of polybromide ions (Figure 7(e)). The Br species can be further confined within the entangled micropores on the electrode surface, leading to significant suppression

In summary, engineering the physical structure of the electrode by designing unique structured materials can improve their performance from different aspects:

- (iv) To promote the reaction kinetics of Br_2/Br^- redox reactions by introducing catalytic groups, creating active sites, and improving electronic conductivity

The comparison of different electrode modification methods is shown in Table 5.

With the advantages of high energy density and low cost, Br-FBs have made a series of outstanding achievements. In addition to the ZBFB system which have been at the demonstration stage, several new Br-FB systems with broad

TABLE 5: Comparison of electrode modification methods.

Methods	Advantages	Disadvantages
Surface treatment	Simplicity Low cost	Uncontrollability Decreased mechanical properties High temperature
Metallic element modification	High catalytic activity	Weak stability High cost
Nonmetallic element modification	Low price Abundant source Controllable surface properties High catalytic activity	Weak bonding force Uneven distribution Concentration polarization
Structure decoration	Inhibited Br_2 diffusion High catalytic activity Flexible structure design	High complexity Weak bonding force

application prospects have emerged in recent years, such as QBFB, LBFB, and TBFB. Nevertheless, there is still a long way to go for the industrialization of Br-FBs, due to the existence of many technical bottlenecks. The main technical bottlenecks include low power density and serious self-discharge of batteries. In order to solve these challenges, to promote the reaction kinetics of Br_2/Br^- , to reduce the battery polarization, and to suppress the diffusion of bromine through different ways are very important. Thus, the research and development of cathode materials with high activity, stability, and bromine fixing/retention ability are significant to promote the performance of Br-FBs effectively. The main modification methods are surface treatment, metallic element modification, nonmetallic element modification, and structure decoration. Surface treatment can create defects on the electrode surface, which increases the electrode-specific surface area and introduces oxygen-containing functional groups. However, uneven distribution of these pores and deteriorated mechanical properties are inevitable. Metallic element modification costs much and the modifier is not stable enough in Br-FBs. Although element doping contributes to improved activity and good wettability, nonmetallic element modification suffers from poor mechanical stability and nonuniform element distribution. As for structure-decorating electrodes, the active sites are indeed increased with the enlarged specific surface area and the mass transfer is expedited with designed specific pores or channels. However, the stability of the structure and simplicity of the preparation process need to be further improved. Of note, the strategies to modify electrodes reported in the literature could mostly be found to catalyze other reactions as well. The reasons for choosing these materials for Br-FBs cathodes are not explicit. Considering that the rate-determining step of Br_2/Br^- reactions is the formation of Br_{ads} , the selection principles of cathode materials for Br-FBs mainly include (i) strong adsorption capacity for bromine to accelerate the formation of Br_{ads} ; (ii) good conductivity to promote electron transfer; and (iii) excellent stability to resist bromine corrosion. Above all, electrodes prepared by the aforemen-

tioned modification methods still confront with the challenges of poor bromine retention ability and unclear mechanisms of Br_2/Br^- redox reactions. Thus, there still exists a huge potential for the development of advanced cathode materials of Br-FBs and further research on the mechanisms of Br_2/Br^- reactions. The further development directions are as follows:

- (i) To continually develop advanced electrodes of Br-FBs with high activity and bromine retention capacity by enhancing their chemical surfaces and improving their physical structures. As described above, porous carbon fiber-based materials, such as CF or GF, play an irreplaceable role in constructing effective electrodes, which benefits from their porous structures, excellent electronic conductivity, great chemical stability, and superior corrosion resistance. To introduce active substances or electronegative heteroatoms on the surface of their carbon fibers is considered to be an effective method to improve the electrochemical activity. Moreover, engineering novel surface morphology on the porous carbon fiber-based electrodes to expose reaction sites, accelerate the mass transport, and prevent bromine diffusion is especially worthy of further exploration and investigation
- (ii) The reaction mechanisms on the electrode are not clear and need in-depth investigations. The electrochemical activity of the electrode was significantly enhanced after modification with various active substances like metal-based electrocatalysts and carbon-based electrocatalysts. However, catalytic mechanism and synergistic effect have not been studied qualitatively and quantitatively, and there are no clear explanations. In particular, the kinetics of Br_2/Br^- reactions are not so clear. Hence, more efforts need to be made to fundamentally understand the specific reaction mechanism of electrodes to the kinetics of Br_2/Br^- reactions both theoretically

and experimentally, which is beneficial to guide the design of high activity electrodes of Br-FBs. In the practical application of Br-FBs, the chemical and structure stability of electrodes is very important for the long-term charge-discharge cycles. However, it is also a tricky problem that the active substances easily fall off caused by the electrolyte circulating flowing. The interface between the electrode and the modifying materials should be chemically and physically stable to ensure the long-term stable operation of batteries. The stable interface may also favor the lower interfacial resistance. As a result, to enhance the bonding force between the electrodes and the electrocatalysts while maintaining a low contact resistance, further efforts on improving the interfacial stability of electrodes need to be made

- (iii) To improve the bromine fixing/retention capacity of electrodes by structural design, namely, to inhibit the diffusion and migration of bromine species to the negative side. In general, the commonly used methods to inhibit bromine diffusion/migration mainly include the electrolyte optimization and the membrane modification. To add bromine complexing agent in the electrolyte to form bromine complexes with larger size can effectively prevent the bromine migration across the membrane based on the pore size effect of the porous membrane. However, Br-FBs still suffer from serious self-discharge issue caused by bromine migration. Notably, as for the membrane modification, the strongly oxidizing bromine conditions lead to that the proper membrane matrixes and modifying materials for Br-FBs are actually very rare. According to the previous report, the structural design on electrodes for Br-FBs can make electrodes exhibit bromine fixing/retention capacity as mentioned above. Thus, the bromine diffusion from the electrode surface to the bulk electrolyte and the bromine migration through the membrane to the negative side are effectively avoided. Thus, the electrode modification is very promising in overcoming the bromine diffusion/migration issue of Br-FBs. By introducing modifying substances which can adsorb or complex with bromine, or carrying out intrinsic modifications on the electrode structures, bromine can be fixed/entrapped in the electrode by the adsorption effect, complexing effect, pore size effects, or their synergies. Then, the bromine diffusion to the bulk electrolyte and the bromine migration to the other side can be depressed, thus inhibiting the battery self-discharge. Therefore, the further structure design of electrodes and investigations on the corresponding mechanisms about inhibiting bromine diffusion/migration are imperative

Conflicts of Interest

The authors declare no competing financial interest.

Authors' Contributions

Luyin Tang wrote the original draft. Wenjing Lu and Xianfeng Li wrote, reviewed, and edited the manuscript. Huamin Zhang carried out the discussion.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (Grant No. 21206158), Key Project of Frontier Science, CAS (QYZDBSSW-JSC032), DICI funding (DICI I202026 and DICI I201928), and Liaoning Natural Science Foundation.

References

- [1] Z. G. Yang, J. Liu, S. Baskaran, C. H. Imhoff, and J. D. Holladay, "Enabling renewable energy-and the future grid-with advanced electricity storage," *JOM*, vol. 62, no. 9, pp. 14–23, 2010.
- [2] "Nano-catalytic layer engraved carbon felt via copper oxide etching for vanadium redox flow batteries," *Carbon*, vol. 153, pp. 674–681, 2019.
- [3] M. Park, I.-Y. Jeon, J. Ryu, J.-B. Baek, and J. Cho, "Exploration of the effective location of surface oxygen defects in graphene-based electrocatalysts for all-vanadium redox-flow batteries," *Advanced Energy Materials*, vol. 5, no. 5, p. 1401550, 2015.
- [4] A. Jameson and E. Gyenge, "Halogens as positive electrode active species for flow batteries and regenerative fuel cells," *Electrochemical Energy Reviews*, vol. 3, no. 3, pp. 431–465, 2020.
- [5] L. Gao, Z. Li, Y. Zou et al., "A high-performance aqueous zinc-bromine static battery," *iScience*, vol. 23, no. 8, article 101348, 2020.
- [6] P. Vanysek and V. Novak, "Redox flow batteries as the means for energy storage," *Journal of Energy Storage*, vol. 13, pp. 435–441, 2017.
- [7] X. Li, C. Xie, T. Li, Y. Zhang, and X. Li, "Low-cost titanium-bromine flow battery with ultrahigh cycle stability for grid-scale energy storage," *Advanced Materials*, vol. 32, no. 49, article 2005036, 2020.
- [8] H. Zhang, W. Lu, and X. Li, "Progress and perspectives of flow battery technologies," *Electrochemical Energy Reviews*, vol. 2, no. 3, pp. 492–506, 2019.
- [9] M. Schneider, G. P. Rajarathnam, M. E. Easton, A. F. Masters, T. Maschmeyer, and A. M. Vassallo, "The influence of novel bromine sequestration agents on zinc/bromine flow battery performance," *Advances*, vol. 6, no. 112, pp. 110548–110556, 2016.
- [10] J. H. Yang, H. S. Yang, H. W. Ra, J. Shim, and J. D. Jeon, "Effect of a surface active agent on performance of zinc/bromine redox flow batteries: improvement in current efficiency and system stability," *Journal of Power Sources*, vol. 275, pp. 294–297, 2015.
- [11] M. C. Wu, T. S. Zhao, L. Wei, H. R. Jiang, and R. H. Zhang, "Improved electrolyte for zinc-bromine flow batteries," *Journal of Power Sources*, vol. 384, pp. 232–239, 2018.
- [12] W. Kautek, A. Conradi, C. Fabjan, and G. Bauer, "In situ FTIR spectroscopy of the Zn-Br battery bromine storage

- complex at glassy carbon electrodes," *Electrochimica Acta*, vol. 47, no. 5, pp. 815–823, 2001.
- [13] H. Lin, T. Jiang, Q. Sun, G. Zhao, and J. Shi, "The research progress of zinc bromine flow battery," *Journal of New Materials for Electrochemical Systems*, vol. 21, no. 2, pp. 063–070, 2018.
 - [14] S. C. Yang, "An approximate model for estimating the faradaic efficiency loss in zinc/bromine batteries caused by cell self-discharge," *Journal of Power Sources*, vol. 50, no. 3, pp. 343–360, 1994.
 - [15] K. J. Cathro, D. C. Constable, and P. M. Hoobin, "Performance of porous plastic separators in zinc/bromine cells," *Journal of Power Sources*, vol. 22, no. 1, pp. 29–57, 1988.
 - [16] R. Kim, H. G. Kim, G. Doo et al., "Ultrathin Nafion-filled porous membrane for zinc/bromine redox flow batteries," *Scientific Reports*, vol. 7, no. 1, p. 10503, 2017.
 - [17] G. P. Rajarathnam, M. E. Easton, M. Schneider, A. F. Masters, T. Maschmeyer, and A. M. Vassallo, "The influence of ionic liquid additives on zinc half-cell electrochemical performance in zinc/bromine flow batteries," *RSC Advances*, vol. 6, no. 33, pp. 27788–27797, 2016.
 - [18] D. Kim, Y. Kim, Y. Lee, and J. Jeon, "1,2-Dimethylimidazole based bromine complexing agents for vanadium bromine redox flow batteries," *International Journal of Hydrogen Energy*, vol. 44, no. 23, pp. 12024–12032, 2019.
 - [19] X. Li, T. Li, P. Xu, C. Xie, Y. Zhang, and X. Li, "A complexing agent to enable a wide-temperature range bromine-based flow battery for stationary energy storage," *Advanced Functional Materials*, vol. 31, no. 22, p. 2100133, 2021.
 - [20] L. Hua, W. Lu, T. Li, P. Xu, H. Zhang, and X. Li, "A highly selective porous composite membrane with bromine capturing ability for a bromine-based flow battery," *Materials Today Energy*, vol. 21, article 100763, 2021.
 - [21] W. Lu, P. Xu, S. Shao, T. Li, H. Zhang, and X. Li, "Multifunctional carbon felt electrode with N-rich defects enables a Long-cycle zinc-bromine flow battery with ultrahigh power density," *Advanced Functional Materials*, vol. 31, no. 30, p. 2102913, 2021.
 - [22] M. C. Wu, H. R. Jiang, R. H. Zhang, L. Wei, K. Y. Chan, and T. S. Zhao, "N-doped graphene nanoplatelets as a highly active catalyst for Br₂/Br⁻ redox reactions in zinc-bromine flow batteries," *Electrochimica Acta*, vol. 318, pp. 69–75, 2019.
 - [23] M. Wu, T. Zhao, R. Zhang, H. Jiang, and L. Wei, "A zinc-bromine flow battery with improved design of cell structure and electrodes," *Energy Technology*, vol. 6, no. 2, pp. 333–339, 2018.
 - [24] H. Zhou, H. Zhang, P. Zhao, and B. Yi, "A comparative study of carbon felt and activated carbon based electrodes for sodium polysulfide/bromine redox flow battery," *Electrochimica Acta*, vol. 51, no. 28, pp. 6304–6312, 2006.
 - [25] P. Zhao, H. M. Zhang, H. T. Zhou, and B. L. Yi, "Nickel foam and carbon felt applications for sodium polysulfide/bromine redox flow battery electrodes," *Electrochimica Acta*, vol. 51, no. 6, pp. 1091–1098, 2005.
 - [26] Y. Wu, P. W. Huang, J. D. Howe et al., "In operando visualization of the electrochemical formation of liquid polybromide microdroplets," *Angewandte Chemie International Edition*, vol. 58, no. 43, pp. 15228–15234, 2019.
 - [27] J. H. Lee, Y. Byun, G. H. Jeong et al., "High-energy efficiency membraneless flowless Zn-Br battery: utilizing the electrochemical-chemical growth of polybromides," *Advanced Materials*, vol. 31, no. 52, p. 1904524, 2019.
 - [28] H. S. Lim, A. M. Lackner, and R. C. Knechtli, "Zinc-bromine secondary battery," *Journal of the Electrochemical Society*, vol. 124, no. 8, pp. 1154–1157, 1977.
 - [29] K. T. Cho, P. Ridgway, A. Z. Weber, S. Haussener, V. Battaglia, and V. Srinivasan, "High performance hydrogen/bromine redox flow battery for grid-scale energy storage," *Journal of the Electrochemical Society*, vol. 159, no. 11, pp. A1806–A1815, 2012.
 - [30] D. P. Scamman, G. W. Reade, and E. P. L. Roberts, "Numerical modelling of a bromide-polysulphide redox flow battery: Part 1: Modelling approach and validation for a pilot-scale system," *Journal of Power Sources*, vol. 189, no. 2, pp. 1220–1230, 2009.
 - [31] M. Skyllas-Kazacos, "Novel vanadium chloride/polyhalide redox flow battery," *Journal of Power Sources*, vol. 124, no. 1, pp. 299–302, 2003.
 - [32] Q. Chen, M. R. Gerhardt, L. Hartle, and M. J. Aziz, "A quinone-bromide flow battery with 1 W/cm² Power density," *Journal of the Electrochemical Society*, vol. 163, no. 1, pp. A5010–A5013, 2016.
 - [33] Y. Zeng, Z. Yang, F. Lu, and Y. Xie, "A novel tin-bromine redox flow battery for large-scale energy storage," *Applied Energy*, vol. 255, article 113756, 2019.
 - [34] Y. A. Hugo, W. Kout, F. Sikkema, Z. Borneman, and K. Nijmeijer, "Performance mapping of cation exchange membranes for hydrogen-bromine flow batteries for energy storage," *Journal of Membrane Science*, vol. 566, pp. 406–414, 2018.
 - [35] R. Wang, Y. Li, Y. Wang, and Z. Fang, "Phosphorus-doped graphite felt allowing stabilized electrochemical interface and hierarchical pore structure for redox flow battery," *Applied Energy*, vol. 261, p. 114369, 2020.
 - [36] L. Zhang, Z.-G. Shao, X. Wang, H. Yu, S. Liu, and B. Yi, "The characterization of graphite felt electrode with surface modification for H₂/Br₂ fuel cell," *Journal of Power Sources*, vol. 242, pp. 15–22, 2013.
 - [37] S. Suresh, M. Ulaganathan, N. Venkatesan, P. Periasamy, and P. Ragupathy, "High performance zinc-bromine redox flow batteries: role of various carbon felts and cell configurations," *Journal of Energy Storage*, vol. 20, pp. 134–139, 2018.
 - [38] B. P. Williams, G. L. Shebert, and Y. L. Joo, "Metal oxide coatings on carbon electrodes with large mesopores for deeply charged zinc bromine redox flow batteries," *Journal of the Electrochemical Society*, vol. 166, no. 10, p. A2245-A 2254, 2019.
 - [39] R. Banerjee, N. Bevilacqua, A. Mohseninia et al., "Carbon felt electrodes for redox flow battery: impact of compression on transport properties," *Journal of Energy Storage*, vol. 26, article 100997, 2019.
 - [40] K. Mariyappan, R. Velmurugan, B. Subramanian, P. Ragupathy, and M. Ulaganathan, "Low loading of felt for enhancing multifunctional activity towards achieving high energy efficiency of Zn-Br₂ redox flow battery," *Journal of Power Sources*, vol. 482, article 228912, 2021.
 - [41] C. H. Wang, W. J. Lu, Q. Z. Lai, P. C. Xu, H. M. Zhang, and X. F. Li, "A TiN nanorod array 3D hierarchical composite electrode for ultrahigh-power-density bromine-based flow batteries," *Advanced Materials*, vol. 31, no. 46, p. e1904690, 2019.

- [42] V. S. Bagotzky, Y. B. Vassiyev, J. Weber, and J. N. Pirtskhala, "Adsorption of anions on smooth platinum electrodes," *Journal of Electroanalytical Chemistry*, vol. 27, no. 1, pp. 31–46, 1970.
- [43] S. Gottesfeld and B. Reichman, "Coverage and field components in optical effects measured during halide ion adsorption on platinum," *Journal of Electroanalytical Chemistry*, vol. 67, no. 2, pp. 169–189, 1976.
- [44] M. W. Breiter, "Voltammetric study of halide ion adsorption on platinum in perchloric acid solutions," *Electrochimica Acta*, vol. 8, no. 12, pp. 925–935, 1963.
- [45] D. C. Johnson and S. Bruckens, "A ring-disk study of HOBr formation at platinum electrodes in 1.0M H₂SO₄," *Journal of the Electrochemical Society*, vol. 117, no. 4, p. 460, 1970.
- [46] R. F. Lane and A. T. J. J. Hubbard, "Electrochemistry of chemisorbed molecules. III. Determination of the oxidation state of halides chemisorbed on platinum. Reactivity and catalytic properties of adsorbed species," *The Journal of Physical Chemistry*, vol. 79, no. 8, pp. 808–815, 1975.
- [47] W. D. Cooper and R. J. T. Parsons, "Kinetics of the bromine/bromide electrode on platinum in aqueous sulphuric acid," *Transactions of the Faraday Society*, vol. 66, pp. 1698–1712, 1970.
- [48] F. Marques Mota, J.-H. Kang, Y. Jung et al., "Mechanistic Study Revealing the Role of the Br₃[−]/Br₂ Redox Couple in CO₂-Assisted Li-O₂ Batteries," *Advanced Energy Materials*, vol. 10, article 1903486, no. 9, 2020.
- [49] N. E. Kuleshova, A. V. Vvedenskii, and E. V. Bobrinskaya, "Adsorption of serine anion on smooth and platinized platinum," *Russian Journal of Electrochemistry*, vol. 54, no. 11, pp. 949–955, 2018.
- [50] L. G. Verga, J. Aarons, M. Sarwar, D. Thompsett, A. E. Russell, and C.-K. Skylaris, "DFT calculation of oxygen adsorption on platinum nanoparticles: coverage and size effects," *Faraday Discussions*, vol. 208, pp. 497–522, 2018.
- [51] T. Y. Jiang, H. Lin, Q. Y. Sun, G. Z. Zhao, and J. Y. Shi, "Recent progress of electrode materials for zinc bromide flow battery," *International Journal of Electrochemical Science*, vol. 13, no. 6, pp. 5603–5611, 2018.
- [52] S. Zhang, S.-F. Jiang, B.-C. Huang et al., "Sustainable production of value-added carbon nanomaterials from biomass pyrolysis," *Nature Sustainability*, vol. 3, no. 9, pp. 753–760, 2020.
- [53] C. Wang, X. Li, X. Xi, P. Xu, Q. Lai, and H. Zhang, "Relationship between activity and structure of carbon materials for Br₂/Br[−] in zinc bromine flow batteries," *RSC Advances*, vol. 6, no. 46, pp. 40169–40174, 2016.
- [54] I. Jeon, R. Xiang, A. Shawky, Y. Matsuo, and S. Maruyama, "Single-walled carbon nanotubes in emerging solar cells: synthesis and electrode applications," *Advanced Energy Materials*, vol. 9, no. 23, p. 1801312, 2019.
- [55] A. Kaliyaraj Selva Kumar, R. Miao, D. Li, and R. G. Compton, "Do carbon nanotubes catalyse bromine/bromide redox chemistry?," *Chemical Science*, vol. 12, no. 32, pp. 10878–10882, 2021.
- [56] Y. Munaiah, S. Dheenadayalan, P. Ragupathy, and V. K. Pillai, "High performance carbon nanotube based electrodes for zinc bromine redox flow batteries," *ECS Journal of Solid State Science and Technology*, vol. 2, no. 10, pp. M3182–M3186, 2013.
- [57] Y. Shao, M. Engelhard, and Y. Lin, "Electrochemical investigation of polyhalide ion oxidation-reduction on carbon nanotube electrodes for redox flow batteries," *Electrochemistry Communications*, vol. 11, no. 10, pp. 2064–2067, 2009.
- [58] Y. Munaiah, S. Suresh, S. Dheenadayalan, V. K. Pillai, and P. Ragupathy, "Comparative electrocatalytic performance of single-walled and multiwalled carbon nanotubes for zinc bromine redox flow batteries," *The Journal of Physical Chemistry C*, vol. 118, no. 27, pp. 14795–14804, 2014.
- [59] W. Li, J. Liu, and C. Yan, "Multi-walled carbon nanotubes used as an electrode reaction catalyst for VO₂⁺/VO₂²⁺ for a vanadium redox flow battery," *Carbon*, vol. 49, no. 11, pp. 3463–3470, 2011.
- [60] S. Carrara, "Nano-bio-technology and sensing chips: new systems for Detection in personalized therapies and cell biology," *Sensors*, vol. 10, no. 1, pp. 526–543, 2010.
- [61] E. Yeager, "Dioxygen electrocatalysis: mechanisms in relation to catalyst structure," *Journal of Molecular Catalysis*, vol. 38, no. 1–2, pp. 5–25, 1986.
- [62] D. Schindler, M. Gil-Sepulcre, J. O. Lindner et al., "Efficient electrochemical water oxidation by a trinuclear Ru (bda) macrocycle immobilized on multi-walled carbon nanotube electrodes," *Advanced Energy Materials*, vol. 10, no. 43, p. 2002329, 2020.
- [63] D. Ayme-Perrot, S. Walter, Z. Gabelica, and S. Valange, "Evaluation of carbon cryogels used as cathodes for non-flowing zinc-bromine storage cells," *Journal of Power Sources*, vol. 175, no. 1, pp. 644–650, 2008.
- [64] L. Zhang, J. Yue, Q. Deng et al., "Preparation of a porous graphite felt electrode for advance vanadium redox flow batteries," *RSC Advances*, vol. 10, no. 23, pp. 13374–13378, 2020.
- [65] S. E. Park, S. Y. Yang, and K. J. Kim, "Boron-functionalized carbon felt electrode for enhancing the electrochemical performance of vanadium redox flow batteries," *Applied Surface Science*, vol. 546, article 148941, 2021.
- [66] T. Liu, X. F. Li, H. M. Zhang, and J. Z. Chen, "Progress on the electrode materials towards vanadium flow batteries (VFBs) with improved power density," *Journal of Energy Chemistry*, vol. 27, no. 5, pp. 1292–1303, 2018.
- [67] X. G. Li, K. L. Huang, S. Q. Liu, N. Tan, and L. Q. Chen, "Characteristics of graphite felt electrode electrochemically oxidized for vanadium redox battery application," *Transactions of Nonferrous Metals Society of China*, vol. 17, no. 1, pp. 195–199, 2007.
- [68] K. S. Archana, R. P. Naresh, H. Enale et al., "Effect of positive electrode modification on the performance of zinc-bromine redox flow batteries," *Journal of Energy Storage*, vol. 29, article 101462, 2020.
- [69] M. C. Wu, T. S. Zhao, H. R. Jiang, Y. K. Zeng, and Y. X. Ren, "High-performance zinc bromine flow battery via improved design of electrolyte and electrode," *Journal of Power Sources*, vol. 355, pp. 62–68, 2017.
- [70] S. Suresh, M. Ulaganathan, R. Aswathy, and P. Ragupathy, "Enhancement of bromine reversibility using chemically modified electrodes and their applications in zinc bromine hybrid redox flow batteries," *ChemElectroChem*, vol. 5, no. 22, pp. 3411–3418, 2018.
- [71] W. Zhang, J. Xi, Z. Li et al., "Electrochemical activation of graphite felt electrode for VO₂²⁺/VO₂⁺ redox couple application," *Electrochimica Acta*, vol. 89, pp. 429–435, 2013.

- [72] A. Di Blasi, O. Di Blasi, N. Briguglio et al., "Investigation of several graphite-based electrodes for vanadium redox flow cell," *Journal of Power Sources*, vol. 227, pp. 15–23, 2013.
- [73] Y. Li and N. Trung Van, "Core-shell rhodium sulfide catalyst for hydrogen evolution reaction/hydrogen oxidation reaction in hydrogen-bromine reversible fuel cell," *Journal of Power Sources*, vol. 382, pp. 152–159, 2018.
- [74] K. Saadi, P. Nanikashvili, Z. Tatus-Portnoy et al., "Crossover-tolerant coated platinum catalysts in hydrogen/bromine redox flow battery," *Journal of Power Sources*, vol. 422, pp. 84–91, 2019.
- [75] K. Amini, J. Gostick, and M. D. Pritzker, "Metal and metal oxide electrocatalysts for redox flow batteries," *Advanced Functional Materials*, vol. 30, no. 23, p. 1910564, 2020.
- [76] L. Zhang, Z.-G. Shao, H. Yu, X. Wang, and B. Yi, "IrO₂ coated TiO₂ nanopore arrays electrode for SPE HBr electrolysis," *Journal of Electroanalytical Chemistry*, vol. 688, pp. 262–268, 2013.
- [77] P. Sivasubramanian, R. P. Ramasamy, F. J. Freire, C. E. Holland, and J. W. Weidner, "Electrochemical hydrogen production from thermochemical cycles using a proton exchange membrane electrolyzer," *International Journal of Hydrogen Energy*, vol. 32, no. 4, pp. 463–468, 2007.
- [78] Y. Yi, G. Weinberg, M. Prenzel et al., "Electrochemical corrosion of a glassy carbon electrode," *Catalysis Today*, vol. 295, pp. 32–40, 2017.
- [79] L. Coustan, G. Shul, and D. Bélanger, "Electrochemical behavior of platinum, gold and glassy carbon electrodes in water-in-salt electrolyte," *Electrochemistry Communications*, vol. 77, pp. 89–92, 2017.
- [80] R. Wang and Y. Li, "Carbon electrodes improving electrochemical activity and enhancing mass and charge transports in aqueous flow battery: status and perspective," *Energy Storage Materials*, vol. 31, pp. 230–251, 2020.
- [81] G. F. Long, X. H. Li, K. Wan, Z. X. Liang, J.-H. Piao, and P. Tsiakaras, "Pt/CN-doped electrocatalysts: superior electrocatalytic activity for methanol oxidation reaction and mechanistic insight into interfacial enhancement," *Applied Catalysis B-Environmental*, vol. 203, pp. 541–548, 2017.
- [82] S. Liu, I. S. Amiinu, X. Liu et al., "Carbon nanotubes intercalated Co/N-doped porous carbon nanosheets as efficient electrocatalyst for oxygen reduction reaction and zinc-air batteries," *Chemical Engineering Journal*, vol. 342, pp. 163–170, 2018.
- [83] S. Wang, X. Zhao, T. Cochell, and A. Manthiram, "Nitrogen-doped carbon nanotube/graphite felts as advanced electrode materials for vanadium redox flow batteries," *The Journal of Physical Chemistry Letters*, vol. 3, no. 16, pp. 2164–2167, 2012.
- [84] A. Dinesh, M. S. Anantha, M. S. Santosh, M. N. Kumar, K. Venkatesh, and H. B. Muralidhara, "Nitrogen-doped carbon spheres-decorated graphite felt as a high-performance electrode for Fe based redox flow batteries," *Diamond and Related Materials*, vol. 116, p. 108413, 2021.
- [85] G. R. Bhadu, B. Parmar, P. Patel et al., " carbon nanomaterial derived by simple pyrolysis of mixed-ligand MOF as an active and stable oxygen evolution electrocatalyst," *Applied Surface Science*, vol. 529, article 147081, 2020.
- [86] H. X. Xiang, A. D. Tan, J. H. Piao, Z. Y. Fu, and Z. X. Liang, "Efficient nitrogen-doped carbon for zinc-bromine flow battery," *Small*, vol. 15, no. 24, p. e1901848, 2019.
- [87] M. C. Wu, T. S. Zhao, R. H. Zhang, L. Wei, and H. R. Jiang, "Carbonized tubular polypyrrole with a high activity for the Br₂/Br⁻ redox reaction in zinc-bromine flow batteries," *Electrochimica Acta*, vol. 284, pp. 569–576, 2018.
- [88] T. Z. Hou, X. Chen, H. J. Peng et al., "Design principles for heteroatom-doped nanocarbon to achieve strong anchoring of polysulfides for lithium-sulfur batteries," *Small*, vol. 12, no. 24, pp. 3283–3291, 2016.
- [89] C. X. Jin, H. Y. Lei, M. Y. Liu et al., "Low-dimensional nitrogen-doped carbon for Br₂/Br⁻ redox reaction in zinc-bromine flow battery," *Chemical Engineering Journal*, vol. 380, p. 122606, 2020.
- [90] N. Venkatesan, K. S. Archana, S. Suresh et al., "Boron-doped graphene as efficient electrocatalyst for zinc-bromine redox flow batteries," *ChemElectroChem*, vol. 6, no. 4, pp. 1107–1114, 2019.
- [91] A. W. Bayeh, D. M. Kabtamu, Y. C. Chang, T. H. Wondimu, H. C. Huang, and C. H. Wang, "Carbon and metal-based catalysts for vanadium redox flow batteries: a perspective and review of recent progress," *Sustainable Energy & Fuels*, vol. 5, no. 6, pp. 1668–1707, 2021.
- [92] W. I. Jang, J. W. Lee, Y. M. Baek, and O. O. Park, "Development of a PP/carbon/CNT composite electrode for the zinc/bromine redox flow battery," *Macromolecular Research*, vol. 24, no. 3, pp. 276–281, 2016.
- [93] S. Suresh, M. Ulaganathan, and R. Pitchai, "Realizing highly efficient energy retention of Zn-Br₂ redox flow battery using rGO supported 3D carbon network as a superior electrode," *Journal of Power Sources*, vol. 438, article 226998, 2019.
- [94] M. Yeddala, T. N. Narayanan, R. Pitchai, and V. K. Pillai, "Electrochemical exfoliation of graphite to fluorographene: an effect of degree of functionalization on 2Br⁻/Br₂ redox reaction," *ChemistrySelect*, vol. 4, no. 38, pp. 11385–11393, 2019.
- [95] Y. Popat, D. Trudgeon, C. Zhang, F. C. Walsh, P. Connor, and X. Li, "Carbon materials as positive electrodes in bromine-based flow batteries," *ChemPlusChem*, vol. 87, no. 1, pp. 1–3, 2022.
- [96] X. Rui, A. Parasuraman, W. Liu et al., "Functionalized single-walled carbon nanotubes with enhanced electrocatalytic activity for Br⁻/Br₃⁻ redox reactions in vanadium bromide redox flow batteries," *Carbon*, vol. 64, pp. 464–471, 2013.
- [97] L. Zhang, H. Zhang, Q. Lai, X. Li, and Y. Cheng, "Development of carbon coated membrane for zinc/bromine flow battery with high power density," *Journal of Power Sources*, vol. 227, pp. 41–47, 2013.
- [98] M. C. Wu, R. H. Zhang, K. Liu, J. Sun, K. Y. Chan, and T. S. Zhao, "Mesoporous carbon derived from pomelo peel as a high-performance electrode material for zinc-bromine flow batteries," *Journal of Power Sources*, vol. 442, p. 227255, 2019.
- [99] R. P. Naresh, K. Mariyappan, K. S. Archana et al., "Activated carbon-anchored 3D carbon network for bromine activity and its enhanced electrochemical performance in Zn-Br₂ hybrid redox flow battery," *ChemElectroChem*, vol. 6, no. 22, pp. 5688–5697, 2019.
- [100] R. Wang, Y. Li, H. Liu, Y.-L. He, and M. Hao, "Sandwich-like multi-scale hierarchical porous carbon with a highly hydroxylated surface for flow batteries," *Journal of Materials Chemistry A*, vol. 9, no. 4, pp. 2345–2356, 2021.

- [101] C. Wang, Q. Lai, K. Feng, P. Xu, X. Li, and H. Zhang, "From zeolite-type metal organic framework to porous nano-sheet carbon: high activity positive electrode material for bromine-based flow batteries," *Nano Energy*, vol. 44, pp. 240–247, 2018.
- [102] C. Wang, X. Li, X. Xi, W. Zhou, Q. Lai, and H. Zhang, "Bimodal highly ordered mesostructure carbon with high activity for Br_2/Br^- redox couple in bromine based batteries," *Nano Energy*, vol. 21, pp. 217–227, 2016.
- [103] C. Wang, Q. Lai, P. Xu, D. Zheng, X. Li, and H. Zhang, "Cage-like porous carbon with superhigh activity and Br_2 -complex-entrapping capability for bromine-based flow batteries," *Advanced Materials*, vol. 29, no. 22, 2017.