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Review Article

Redox flow battery technology development from perspective of patent applications: A review

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Abstract: With the continuous increase in global energy consumption, the development and utilization of renewable energy become imperative. However, the intermittency and fluctuation of wind and solar power generation prevent direct grid integration, resulting in energy waste. As a large-scale electrochemical energy storage technology, redox flow batteries (RFBs) can effectively store renewable energy and smooth power output. In this paper, the development history of RFB technology in China is summarized by analyzing relevant patent application data and elaborating on the working principles, advantages and disadvantages of various RFBs, and their latest research progress. The technical challenges in current RFB research are analyzed and the application prospects of RFB commercialization are presented. The results showed that although RFB technology has made significant progress in China, it still faces issues, such as high battery cost and limited cycle life. To realize the efficient utilization of renewable energy and green low-carbon development, RFB technology needs continuous optimization and upgrade. This paper can provide references for the development of RFB technology.

Keywords: redox flow batteries; ion exchange membranes; electrolytes; electrodes; bipolar plates

1. Introduction

As the fundamental resource for human survival and development, energy is becoming increasingly scarce with growing consumption. It is predicted that the global energy consumption will double during 2010–2050. To face the energy crisis, the development of new energy technologies is imperative. Renewable power generation using wind and solar is affected by natural conditions, such as sunlight, weather, and terrain. Also, their power output is intermittent and discontinuous, which prevents direct integration into power grids and causes energy waste, and making modifications directly at the generator end will also further increase the cost[1]. Developing grid systems independent of fossil fuels is of top priority. Currently, there are various energy storage technologies available. While compressed air energy storage has the capacity to manage peak demand and store excess energy, it is constrained by the need for larger installation spaces, limiting its suitability based on geographical location. Energy losses and inefficiencies occur during the compression of air at high temperatures. Pumped energy storage offers several advantages, including low maintenance costs in the long run, scalability, extended lifespan, and rapid response times. However, it faces limitations related to the availability of water sources and the substantial construction costs, which necessitate alternative solutions to overcome terrain restrictions. Battery energy storage currently stands as the most widely utilized technology for energy storage. Nevertheless, it encounters certain inherent challenges, such as environmental pollution, high manufacturing costs, restricted material resources, and primary suitability for only smaller-scale applications, such as automotive and mobile devices. Redox flow batteries (RFBs) realize electrical energy storage and release through the change of ionic valence states and electron transfer in the electrolyte. As a large-scale energy storage technology, RFBs have become one of the most promising candidates for a new era of energy storage, owing to their high efficiency, low initial and

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maintenance costs, flexible capacity with the storage level, and long cycle life[2,3]. Using RFBs as the intermediate link between renewable power generation and power grids helps realize functions such as power smoothing, peak shaving, scheduled power generation, and surplus energy storage, which further improves the continuity, stability, and controllability of renewable power generation.

2. Development history and current situation of RFBs

The earliest theory of RFB was proposed by Kangro[4] in 1949, which realized electrical energy storage in electrolytes through redox reactions using $Cr_2(SO_4)_3$ as the reactant for both positive and negative electrodes and 2mol.L^{-1} sulfuric acid as the electrolyte. In 1976, Thaller[5] from NASA patented the concept of a rechargeable redox flow battery, which used Fe^{3+} and Fe^{2+} for the positive electrode and Cr^{3+} and Cr^{2+} for the negative electrode for redox reactions. This patent systematically elucidates the basic structure and working principles of flow batteries. The typical structure of modern RFBs is shown in **Figure 1**.

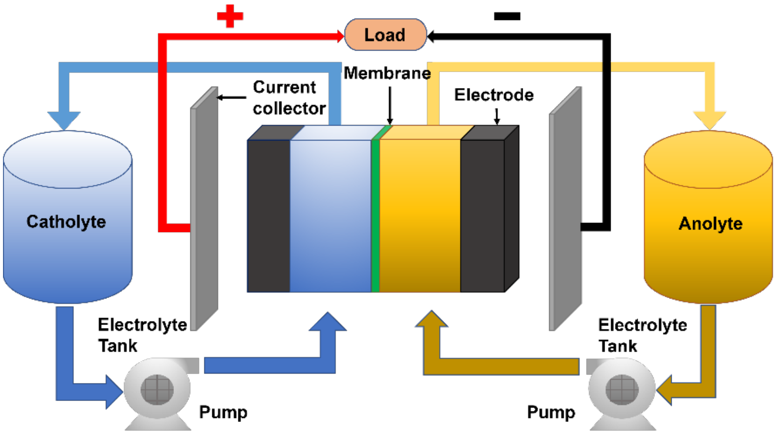

Figure 1. Basic structure of modern RFBs.

According to the European Patent Office (EPO) database, the first RFB-related patent in China was filed by Xiao and Xiao[6] in 2002 for a vanadium redox flow battery system, which was authorized in 2004 with patent No. CN1319207C. From the conception of RFBs in the 1970s to the early 21st century, RFB research in China remained dormant. In the early 21st century, RFB research in China was gradually carried out by domestic universities and companies, and the domestic RFB industry began to develop.

The number of RFB patents in China has been increasing annually since 2000. During 2003–2010, the number of patent applications grew slowly, but after 2010, China's RFB industry entered a rapid development stage with a steadily and rapidly increasing number of patents. In 2010 alone, the application number approached the sum of the previous decade. The number of Chinese RFB patents reached 6181 during 2010–2023, which represents an increase of 3987.74% compared with that in 2000–2010, with the total number up to 6344. The number of global RFB patents strongly correlated with that in China, where both experienced a surge in 2010 and steady growth afterward. The global RFB patents numbered 1195 before 2010 and reached 10,710 by 2023, with a growth rate of 896.23%, as shown in **Figure 2**.

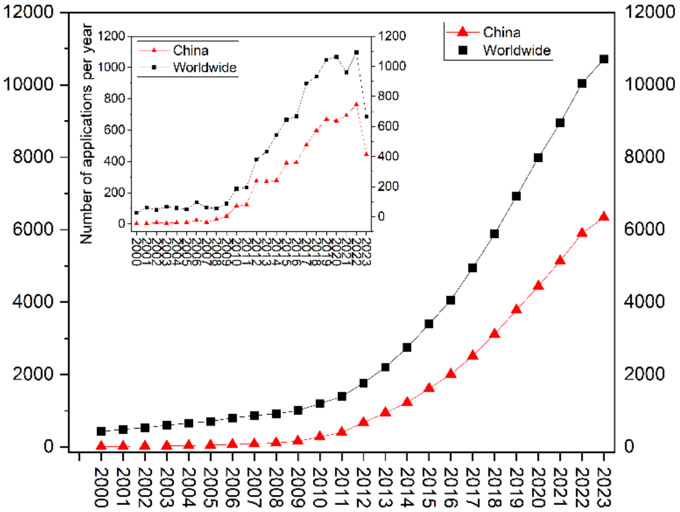

Figure 2. Annual patent publications and total growth trends in China and globally.

The slow development of China's RFB industry in the early 21st century was mainly due to the following factors:

1) Small market demand: The proportion of renewable power generation was small in the early 21st century, as fossil fuels met the electricity demand. The awareness of environmental protection and the energy crisis promoted renewable power generation technologies, which were replacing fossil fuel power generation at an annual rate of 0.4%[7]. By 2020, the global renewable power generation capacity reached 2839 GW. Problems such as the inability to directly integrate renewable power generation into grids also drove the development of large-scale energy storage technologies[8].
2) Technical barriers: The electrochemical energy storage technologies were proposed by foreign professors and belong to emerging industries. Research personnel were unwilling to disclose core technologies. In 2000, the Dalian Institute of Chemical Physics of the Chinese Academy of Sciences began to enter the RFB industry. After more than ten years of research, Dalian Rongke Power Co., Ltd., in which the Dalian Institute of Chemical Physics has a technology share, established the then world's largest 5MW/10MWh demonstration project in December 2012 at Woniushi Wind Farm, Faku County, Liaoning[9].
3) Insufficient capital investment: The early large-scale energy storage technologies were immature, and only a few research institutions stepped into the RFB industry. With the gradual maturity of technologies and increasing market demand, a large number of companies, investment institutions, and universities have entered this industry, further promoting industry development.

After these problems were solved, the number of authorized RFB patents in China increased annually. The proportion of global patents fluctuated slightly in the first decade of the 21st century but showed an upward trend in the second decade. By July 2023, the total number of RFB patents in China reached 6344, accounting for 59.23% of the global patents, ranking first globally.

3. Analysis of major global RFB patent applicants

Out of approximately 10,710 global RFB patents, China leads with the highest number, totaling 6344, thus securing the first position worldwide. Japan, the USA, and the World Intellectual Property Organization (WIPO) followed with 2576, 2519, and 2458 patents, accounting for 23.77%, 23.52%, and 22.96% of the total, respectively. South Korea and EPO also exhibit a substantial number of applications, with 1805 and 1459 patents, making up 16.85% and 13.62% of the total, respectively. The remaining top 10 applicants hold fewer than 500 patents each, collectively contributing no more than 5%. Specific data can be found in **Table 1** and **Table 2**.

Table 1. Ranking of major global RFB patent applicants (by application volume).

Country	Total
China	6344
Japan	2576
United States	2519
WIPO	2458
Korea	1805
EPO	1459
Australia	490
Taiwan	304
Germany	300
Spain	68

Table 2. Number of patents held by institutions worldwide (top 10 by filing volume).

Institution name	Total
Sumitomo Electric Industries, Ltd. (Japan)	514
Dalian Institute of Chemical Physics (China)	392
Dalian Rongke Power Co., Ltd. (China)	208
Kansai Electric Power Co., Ltd. (Japan)	182
LG Chemical Ltd. (Korea)	178
Lotte Chemical Corp. (Korea)	115
State Grid Corporation of China (China)	104
Dongfang Electric Corporation (China)	81
Toray Industries, Inc (Japan)	75
Showa Denko K.K. (Japan)	73

Japan’s RFB industry ranks first globally, mainly due to its limited resources and urgent need to develop renewable energies, such as wind and solar power, thus driving the demand for energy storage technologies. Sumitomo Electric (514 patents) is a leader in the RFB industry. It started getting involved in this field in the late 1980s and began collaborating with Hokkaido Electric Power on R&D in the early 1990s. Sumitomo has built redox flow battery energy storage power stations in many countries, mainly for grid-side and load-side applications. In 2015, Sumitomo Electric and Hokkaido Electric Power jointly built the then world’s largest 15MW/60MWh energy storage station in Japan; in 2022, they built a 17MW/51MWh station[10]. Driven by Sumitomo Electric, many Japanese companies, including Kansai Electric Power (182 patents), Toray Industries (75 patents), and Showa Denko (73 patents), have joined the R&D and application of RFBs.

In South Korea, LG Chemical (178 patents) entered the electrochemical energy storage field in 1992, with a focus on addressing RFB electrodes, flow fields, and permeation resistance structures, resulting in significant achievements. Its products find wide applications in grid peak shaving, smoothing power generation output, load power supply, and emergency scenarios. By 2012, LG Chemical had accumulated 21.6 GWh of energy storage installations globally[11]. Closely following it is Lotte Chemical (115 patents), which started its electrochemical energy storage business in 2002 and focused on electrolyte R&D. In 2011, Lotte Chemical began studying vanadium RFBs and zinc-bromine RFBs. It commenced trials with organic electrolytes in 2021, thus opening the door to organic RFB R&D[12].

In the wave of electrochemical energy storage, the Dalian Institute of Chemical Physics and other research institutes engaged multiple institutions in parallel RFB research and development[13]. After more than a decade of development, China’s RFB technology has matured. Starting in 2010, researchers began to develop RFB systems, structures, controls, and equipment and applied for numerous related patents, making China a global leader in RFB patents and holding a leading position in the industry.

According to the analysis of RFB patent applications, applicants in China mainly come from companies, research institutes, and universities. Among them, companies (including industry-academia collaboration) account for 61%, while research institutes and universities account for 17% and 19%, respectively, and individual applications only account for 3%, as shown in **Figure 3**.

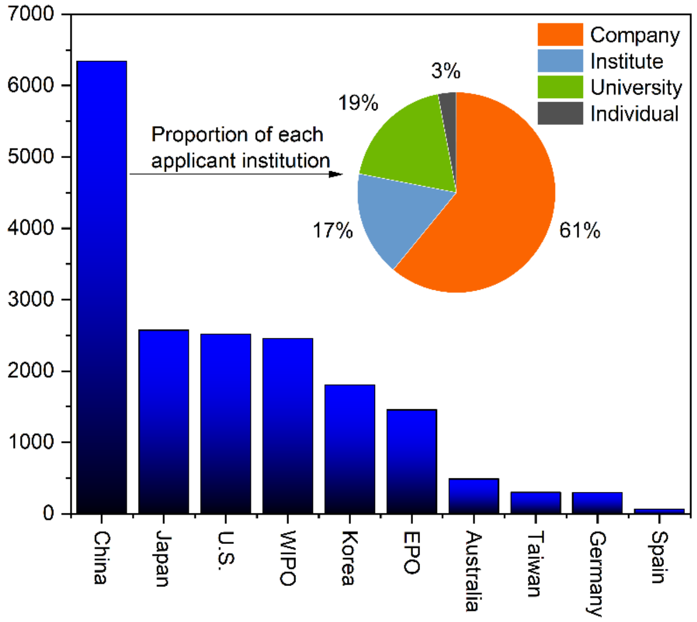

Figure 3. Proportions of RFB patent applications in global Top 10 countries and different sectors in China.

Considering the large base number of companies, as detailed in **Table 3**, this paper only analyzed the top three companies, two research institutes, and one university in terms of application volume.

Table 3. Ranking of major RFB patent applicants in China (by application volume).

Institution name	**Total**
Dalian Rongke Power Co., Ltd.	208
State Grid Corporation of China	104
Dongfang Electric Corporation Ltd.	81
Dalian Institute of Chemical Physics	392
Institute of Metal Research	45
Dalian University of Technology	51

The company with the most applications is Dalian Rongke (208 patents), which is a technology transfer from the Dalian Institute of Chemical Physics. Founded in 2008, Dalian Rongke is one of the earliest companies in China to get involved in electrochemical energy storage. With strong R&D capabilities, it has undertaken the construction of the world's largest 100MW energy storage power stations, promoting the rapid development of China's RFB industry[14].

The second is the State Grid Corporation (104 patents). State Grid has strong R&D teams on RFBs and has established demonstration projects in different regions of China since 2010. It has now started the construction of several 100MW energy storage power stations[15]. The third is Dongfang Electric (81 patents). As a leading power equipment company, its "six-power" strategy promotes the development of flow battery energy storage technology[16]. The Dalian Institute of Chemical Physics (392 patents) and the Institute of Metal Research (45 patents) also started RFB research early on and established multiple pilot systems in regions rich in wind and solar resources, achieving breakthroughs in commercialization[17].

Neighboring the two institutes, the Dalian University of Technology (51 patents) has also become one of the Chinese universities with the most RFB patents by leveraging its geographical advantages.

With joint efforts from all parties, the National Energy Administration has approved the construction of the world's largest 200MW/800MWh RFB energy storage power station. The first 100MW/400MWh phase passed commissioning in 2022. At the same time, a 300MWh/year manufacturing base was established, signifying the in-depth development of China's RFB technologies and industry[18].

4. RFB type classification

4.1. Classification by reaction mechanism

RFBs can be divided into the liquid-liquid type (such as all-vanadium redox flow batteries (VRFBs), iron/chromium redox flow batteries (ICRFBs), and Na-S flow batteries) and the deposition type according to the redox reactions of the positive and negative electrodes. The deposition type can be further divided into the semi-deposition type, such as Zn-Br and Zn-Ce flow batteries, and the full-deposition type, such as soluble lead-acid redox flow batteries (SLFBs).

In liquid-liquid RFBs, the active materials of both positive and negative electrodes are dissolved in the electrolyte, and redox reactions take place in the electrolyte without a phase change. An ion exchange membrane is required to separate the positive and negative electrodes. Inevitable ion permeation occurs in liquid-liquid RFBs during charging-discharging, resulting in contamination and a decline in energy density. Choosing an appropriate membrane can alleviate this problem to some extent.

In semi-deposition RFBs, the positive electrode reaction takes place in the electrolyte without a phase change, while the negative electrode undergoes metal deposition/dissolution reactions with a phase change. A membrane is required to separate the positive and negative electrodes. Taking Zn-Br as an example, during charging, Zn^{2+} is reduced and deposited on the negative electrode, while during discharging, the solid Zn is oxidized to generate Zn^{2+}. However, the interfacial Zn is difficult to be fully oxidized and long-term cycling will reduce the electrode-electrolyte contact area and the electrolyte ion concentration. Resolving Zn deposition is key to improving the performance of Zn-based RFBs.

In full-deposition RFBs, both positive and negative electrodes undergo deposition reactions with phase changes, without the need for membrane separation. Currently, only SLFBs are relatively prominent, but their cycle life is limited and commercialization has not yet been achieved. The short life of SLFBs is mainly due to the deposition of Pb and PbO_2 and the fall off of PbO_2. Incomplete dissolution of PbO_2 leads to passivation and efficiency decrease. After falling off, PbO_2 loses its reduction capability, affecting the oxidation reaction of Pb, resulting in a rapid efficiency decline after several cycles[19].

4.2. Classification of RFBs based on redox couples

At present, there are many types of RFBs, with different classification methods. According to the different redox reaction pairs, they can be divided into all-vanadium redox flow batteries, zinc/bromine redox flow batteries, iron/chromium redox flow batteries, zinc/nickel redox flow batteries, polysulfide bromide redox flow batteries, all-iron redox flow batteries, lead-acid redox flow batteries, etc. Referring to the patent application status in the past 20 years, the current research hotspot for RFBs is all-vanadium redox flow batteries, as shown in **Figure 4**.

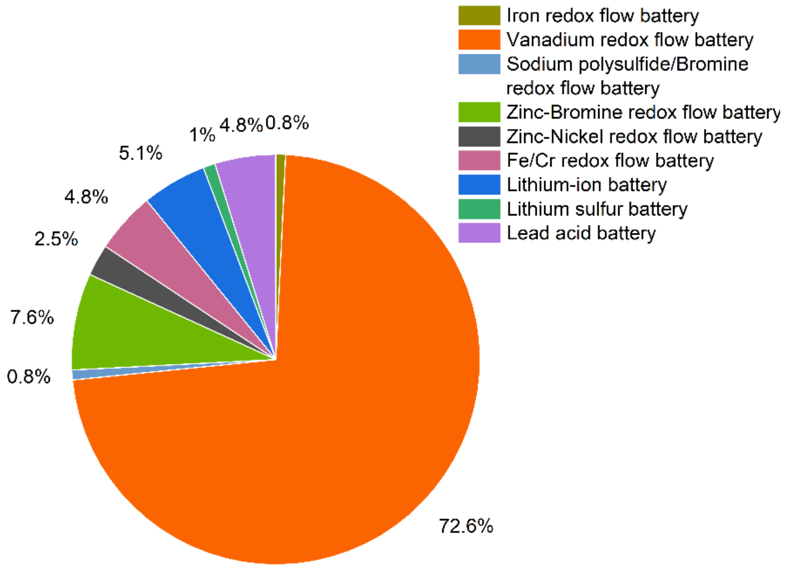

Figure 4. Proportion of patent applications for RFBs of different electricity.

4.2.1. All-vanadium redox flow battery (VRFB) system

The positive electrolyte solution of VRFBs contains tetravalent vanadium ions (VO^{2+}) and pentavalent vanadium ions (VO_2^+), while the vanadium valence in the negative electrolyte solution consists of divalent vanadium ions (V^{2+}) and trivalent vanadium ions (V^{3+}). The conversion between electrical energy and chemical energy is achieved through the redox reactions of vanadium ions with different valences on the electrode surface, thus realizing the release and storage of electrical energy. During charging, VO^{2+} on the positive electrode loses electrons and is converted to VO_2^+, while V^{3+} on the negative electrode gains electrons and is converted to V^{2+}. Meanwhile, H^+ migrates to the negative electrode through the ion exchange membrane. The electrode reaction formulas are as follows:

Positive reaction:

$$VO^{2+} + H_2O - e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} VO_2^+ + 2H^+ \tag{1}$$

Negative reaction:

$$V^{3+} + e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} V^{2+} \tag{2}$$

Overall reaction:

$$VO^{2+} + V^{3+} + H_2O \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} VO_2^+ + V^{2+} + 2H^+ \tag{3}$$

In 1985, Skyllas-Kazacos et al. from the University of New South Wales in Australia began researching VRFBs and made significant contributions to the development of VRFBs[20]. VRFBs account for 3/4 of the chemical energy storage technology research, with the following advantages:

- The energy storage system is safe and reliable with little environmental pollution during its life cycle.
- The output power and energy storage capacity of VRFB systems are independent of each other. The output power is related to the size and number of cell stacks, while the energy storage capacity is related to the volume of the electrolyte.

- It has high energy efficiency, fast start-up speed, and no contamination caused by active species crossing over the ion exchange membrane, which would result in performance degradation. The switching between charging and discharging states is rapid.
- It has strong overload and deep discharge capabilities.
- The electrode reaction is highly active with small polarization.

At present, VRFBs are in the early stage of commercialization that mainly focuses on grid-side applications. In December 2012, Rongke Power installed a 5MW/10MWh energy storage power station at the Woniushan Wind Power Plant in Longyuan, Liaoning. By 2021, although its energy storage capacity has decreased after being in operation for nine years, its capacity was restored to 10 MWh after an online capacity recovery[21], demonstrating the excellent performance of VRFB energy storage systems in terms of long-life cycle and recyclable electrolytes. According to current statistics, the total installed capacity of VRFBs in China has reached 0.1 GWh in 2020 and is expected to reach 4 GWh by 2025. In 2021, the installed VRFB energy storage systems worldwide reached 750 MWh, including a 200MW/400MWh gigawatt-level power station in Dalian. In 2022, the world's first 100MWh VRFB energy storage power station invested and constructed by Rongke Power was put into operation, and the first GWh VRFB project was officially started in China. With the further development of energy storage power stations, the single-cell power of VRFBs has reached 50 kW, which is expected to increase to 1 MW, accelerating the industrialization of VRFBs[22,23].

4.2.2. Zinc/bromine redox flow battery (ZBB) system

The positive and negative electrolytes of ZBBs both adopt $ZnBr_2$, which reduces cost and increases its energy density[24]. The positive electrode redox pair is Br^-/Br_2, while the negative electrode redox pair is Zn^{2+}/Zn. During charging, Br^- on the positive electrode undergoes an oxidation reaction to generate Br_2, which then forms polybromide complexes. Zn^{2+} on the negative electrode undergoes a reduction reaction to generate metallic Zn deposited on the electrode surface. During discharging, Br_2 on the positive electrode is reduced to Br^-, and metallic Zn on the negative electrode is oxidized to Zn^{2+}. The electrode reaction formulas are as follows:

Positive reaction:

$$2Br^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} Br_2 + 2e^- \tag{4}$$

Negative reaction:

$$Zn^{2+} + 2e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} Zn \tag{5}$$

Overall reaction:

$$Zn^{2+} + 2Br^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} Zn + Br_2 \tag{6}$$

The advantages of ZBBs are their high theoretical energy density (440 $Wh.kg^{-1}$), high theoretical capacity (335 $mAh.g^{-1}$), and high output voltage (1.85 V), meeting the requirements of grid-scale energy storage[25]. The disadvantages are that (i) the use of $ZnBr_2$ as an electrolyte has a large environmental burden and is not conducive to recycling at the end of its life cycle, (ii) the existence of two storage tanks and two pumps leads to a large volume and heavy weight of ZBBs, and (iii) bromine permeation through the ion exchange membrane causes cross-contamination, resulting in self-discharge that severely degrades the performance of ZBBs.

Recent research has focused on the performance degradation of ZBBs. Lee et al.[26] added bromide 1,2-dimethylimidazole (DMEIM•Br, $C_7H_{13}BrN_2$) to the electrolyte to increase the speed of zinc plating/stripping and the binding and reduction of bromine with the complexing agent, which improved the reversibility of the redox reactions. This indicates that suitable organic additives have a positive effect on the redox reactions in redox flow batteries, laying the foundation for further improving battery performance.

Currently, while the main problems of ZBBs have been initially solved, industrial applications still need to be explored. Benergy Technology implemented a hybrid system in the Yellow River Gigawatt PV Power Plant, incorporating a 1MWh ZBB system. However, ZBB energy storage power stations cannot operate independently at present. In 2022, researchers from the Dalian Institute of Chemical Physics integrated a 30kW single ZBB cell stack with a measured discharge capacity of 31.6 kW[27]. This achievement is expected to change the current situation and enable the independent application of ZBB systems independently in energy storage power stations. Wenzhou Zinc Era Energy Co., Ltd., which was established in 2022, successfully developed a 40kW/100kWh zinc-bromine flow battery module, further advancing the development of zinc-bromine flow batteries[28].

4.2.3. Iron/chromium redox flow battery (ICRFB) system

Proposed in 1975, the ICRFB is the first true redox flow battery. NASA explored the feasibility of RFBs in 1979 after the proposal of ICRFBs. The positive electrode of ICRFBs uses ferric chloride with the redox pair Fe^{2+}/Fe^{3+}, while the negative electrode uses chromium-rich compounds with the redox pair Cr^{2+}/Cr^{3+}. Hydrochloric acid dissolved in water is used as the electrolyte. During charging and discharging, H^+ migrates through the ion exchange membrane and electrons migrate through the external circuit to complete the reactions. The electrode reaction formulas are as follows:

Positive reaction:

$$Fe^{2+} \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} Fe^{3+} + e^- \tag{7}$$

Negative reaction:

$$Cr^{3+} + e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} Cr^{2+} \tag{8}$$

Overall reaction:

$$Fe^{2+} + Cr^{3+} \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} Fe^{3+} + Cr^{2+} \tag{9}$$

The main disadvantages of ICRFBs include (i) a significant active species crossover between the positive and negative electrodes during the reaction, leading to a shortened life cycle; (ii) serious side reactions (hydrogen evolution) that cause an imbalance of the state of charge (SOC) between the positive and negative electrodes, resulting in reduced battery capacity; and (iii) the reactions possibly leading to an elevated temperature (up to 65 °C), which accelerates crossover and side reaction rates when the temperature is too high[29]. On the other hand, ICRFBs offer advantages, such as good performance and long discharge times under low cost and high current density conditions. Recent research on ICRFBs has focused on addressing side reactions and high temperatures by using additives, such as catalysts, to mitigate these issues. In the literature, Wan et al.[30] proposed electrolyte purification as a solution to address hydrogen evolution.

The Dalian Institute of Chemical Physics began researching ICRFBs in the 1990s, but it was temporarily paused due to issues, such as excessive side reactions and cross-contamination. The research was later resumed in 2011. With the gradual alleviation of problems, such as ICRFB side reactions and active species cross-contamination, through technological advances, various energy storage projects have been also gradually implemented. In 2017, China's first large-scale commercial ICRFB energy storage project with a total installed capacity of 200 MWh was started in Zhangjiakou, Hebei. In 2020, the Zhaoqing municipal government in Guangdong cooperated with German company Stornetic to build a 50MWh ICRFB energy storage project in Zhaoqing. In 2021, the Nanyang municipal government in Henan cooperated with Shenzhen Energy Storage Technology to carry out a 20MWh ICRFB energy storage project in Nanyang. In 2023, the first megawatt-level ICRFB energy storage system invested and constructed by the State Power Investment Group was successfully tested in Inner Mongolia[31].

4.2.4. Soluble lead-acid redox flow battery (SLFB) system

In lead-acid batteries (LABs), which are used for grid energy storage, the electrolyte is sulfuric acid. During charging, Pb^{2+} is released from solid lead sulfate, while during discharging, PbO_2 and Pb dissolve into Pb^{2+} at the positive and negative electrodes and are subsequently deposited as solid lead sulfate. The poor ion diffusion of this solid phase release limits battery performance[32].

SLFBs were proposed by Hazza et al.[33] from the University of Southampton in 2004 based on lead-acid batteries. Both positive and negative electrodes use highly soluble divalent lead compounds with a methylsulfonic acid (MSA) solution as the electrolyte. During charging, Pb^{2+} undergoes a reduction reaction to deposit metallic lead on the negative electrode. During discharging, PbO_2 and Pb dissolve into Pb^{2+} at the positive and negative electrodes. The electrode reaction formulas are as follows:

Positive reaction:

$$Pb^{2+} + 2H_2O - 2e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} PbO_2 + 4H^+ \tag{10}$$

Negative reaction:

$$Pb^{2+} + 2e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} Pb \tag{11}$$

Overall reaction:

$$2Pb^{2+} + 2H_2O \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} Pb + PbO_2 + 4H^+ \tag{12}$$

Research on SLFBs started later than that on other RFBs, but they exhibit advantages over most RFBs. First, the positive and negative electrodes use the same electrolyte, and hence no ion exchange membrane is needed to separate the active species, which greatly reduces equipment costs. Second, the electrolyte can be recycled and reused after the end of life. Third, the electrolyte has relatively low acidity and degradability, greatly reducing environmental hazards[34]. Fourth, the battery performance is excellent. Na et al.[35] found through experiments that SLFBs can operate normally between 20 °C and 40 °C and that the coulombic efficiency still remained at 92% after 800 cycles at 25 °C, with energy density maintained at 86%.

However, SLFBs also have some disadvantages that have slowed down their trend of commercialization. First, it is difficult to prepare pure PbO_2. Second, a long-term deposition of Pb on the electrode surface can lead to passivation, reducing battery efficiency and the overall lifecycle. Bates et al.[36] found through experiments that temperature has a significant effect on battery voltage, while current density affects the Pb deposition rate, which is significantly reduced at low current densities. Therefore, choosing suitable operating conditions promotes the commercialization of SLFBs. SLFBs have huge application potential in energy storage projects that require low current densities.

4.3. Classification based on organic solvents

According to the electrolyte solvent, redox flow batteries can be divided into organic and aqueous systems. The addition of organic solvents in RFB electrolytes changes the molecular structure and functional groups of the electrolyte, resulting in different degrees of change in the discharge mechanism, which directly or indirectly improves the energy efficiency, voltage efficiency, coulombic efficiency, and energy density of RFBs[37]. Representative active species include small molecules and macromolecules. Small-molecule active species do not contain inert backbones, have a large number of active groups, and can undergo definite redox reactions due to the high flexibility in the molecular structure design. However, they have poorer solubility and cyclic stability compared with those of macromolecules. Macromolecular active species can introduce active groups into the main/side chains to facilitate reactions. Representative substances are quinone derivatives, whose conjugated carbonyl groups make reactions highly reversible and also have high specific capacity[38]. In recent years, with the development of organic RFBs, the application of organics is no longer limited to the electrolyte. Researchers have found that the addition of organics to components, such as the ion exchange membrane, electrodes, and catalysts, also improves battery performance. Hence, organic RFB research has more options, and organic RFBs have also attracted increasing research attention due to their advantages, with the domestic patent application proportion also slowly rising. In this section, the research hotspots of RFB patents involving organic modifications applied during 2011–2023 through patent data mining are analyzed. The small base before 2010 lacks referential significance. As shown in **Figure 5**, the research hotspots and growth trends of organic RFBs are presented.

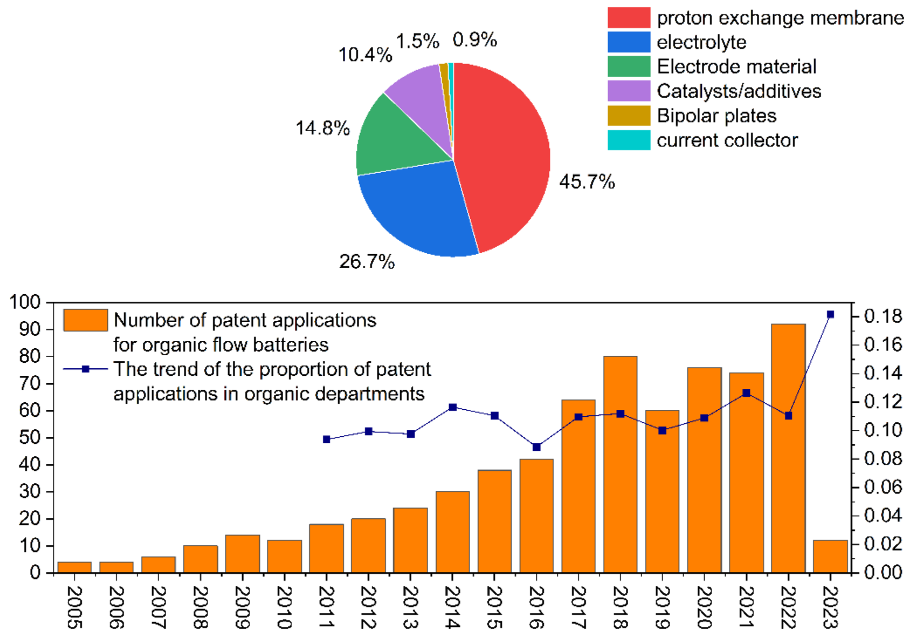

Figure 5. Number of patent applications, proportion trends, and research subject ratios for organic RFBs (2011–2023).

4.3.1. Organic-modified ion exchange membranes

Due to their functional requirements, structure, and other factors, ion exchange membranes have received more research attention than electrolytes in the past decade, constituting 46% of patent applications.

Park et al.[39] dissolved dabazol in N,N-dimethylacetamide (DMAc) to prepare a polybenzimidazole (PBI) membrane and compared its performance with that of the widely used Nafion® 212 membrane. The battery system using the Nafion® 212 membrane exhibited greater cross-contamination, and so the system using the PBI membrane demonstrated higher energy density. The PBI membrane had lower anion/cation selectivity, making the RFB discharge process more stable with higher cyclic stability. Comparisons between control groups using membranes with thicknesses of 15 μm, 30 μm, and 45 μm revealed that the PBI membrane with 30 μm of thickness had less than 3% capacity decay after 100 cycles.

McCormack et al.[40] grafted phenoxyamine sulfonated (POATS) aromatic compounds obtained from the reaction of phenoxyamine and aromatic sulfonation onto the backbone of poly(phenylene oxide) (PPO) to obtain a POATS-PPO membrane. Compared with the system using the Nafion® 117 membrane, the use of the POATS-PPO membrane resulted in an ionic conductivity of 0.061 $mS.cm^{-2}$, higher than those in systems using current non-aqueous membranes, and good ion selectivity. The POATS-PPO membrane maintained a good structure and resulted in a higher organic electrolyte uptake compared with that of the system using the Nafion® 117 membrane when dimethyl carbonate was used as the organic solvent, and it also in higher conductivity than that of the system using the Nafion® 117 membrane.

Pang et al.[41] grafted sulfated UIO-66 (UIO-66OSO_3) onto the PBI backbone to obtain a PBIU-0.40 membrane. Compared with Nafion® 212, PBIU-0.40 had lower vanadium ion permeability (7.88×10^{-9} $cm^2.s^{-1}$, about 1/42 that of Nafion® 212) and lower area resistance (0.23 $\Omega.cm^{-2}$). After 100 cycles at a high current density (100 $mA.cm^{-2}$), the energy efficiency of the system using the PBIU-0.40 membrane remained at 86.1%, with a capacity decay of 0.15% per cycle. After 2000 cycles (>2500 h), there was no phase change (the system using the Nafion® 212 membrane had an energy efficiency of 74.9% and capacity decay of 0.71% under the same condition), and hence the PBIU-0.40 membrane was shown to outperform most porous, dense, and hybrid membranes, greatly improving RFB performance.

4.3.2. Organic-modified electrolytes

Compared with inorganic electrolytes, organic RFB electrolytes have the following advantages[42]:

a) Battery voltage can be increased to improve energy density by adjusting the molecular structure to add or remove electron-donating (electron-withdrawing) functional groups.
b) Organic compounds can be extracted from plants/biowastes at lower costs than inorganic synthetics and are more environmentally friendly than inorganic compounds.
c) The low freezing point of organic solvents allows battery operation at low temperatures, avoiding overheating problems.

Pahlevaninezhad et al.[43] extracted tetraaminopyrene (DB-1) from organics and dissolved it in dimethyl sulfoxide to obtain an organic electrolyte. With metal lithium electrodes, up to six electron transfers occurred, with a peak voltage of up to 4.4 V and a theoretical battery capacity of 1858 $Wh.kg^{-1}$. At a current density of 20 $mA.cm^{-2}$, the battery retained about 100% capacity with an energy efficiency of 71%.

Liu et al.[44] synthesized a new bipolar water-soluble organic compound: mono-N-alkylated viologen iodide ($[(bpy\text{-}(CH_2)_3NMe_3)]I_2$). It had a water solubility of up to 1.76 M and good electrochemical stability, and it could be used as both positive and negative electrolytes, with a theoretical capacity of 32.5 $Wh.L^{-1}$. After 100 cycles at 10 $mA.cm^{-2}$, energy efficiency was maintained at above 72%, with 0.5% capacity decay per cycle. Capacity was restored to the initial level after electrode replacement, and no phase change occurred after 2900 cycles, making the system suitable for low current density energy storage needs.

Guiheneuf et al.[45] synthesized 2,3-dihydroxyanthraquinone (2,3-DHAQ) as a negative electrolyte solvent. It had a solubility of 0.7 M at pH > 13.5 with an energy density of 17 $Wh.L^{-1}$. At an energy density of 25 $mA.cm^{-2}$, current efficiency exceeded 99.7% after 180 cycles, with 0.022% capacity decay per cycle (recoverable). 2,3-DHAQ had better electrochemical stability than those of other dihydroxyanthraquinones. After 3000 cycles, the major product was still 2,3-DHAQ, with a small portion transformed into 1,2-DHAQ (solubility of 0.19 M), resulting in a very slight capacity decrease.

4.3.3. Organic-modified electrodes

RFB electrodes have evolved from metal electrodes to predominantly carbon-felt electrodes currently. Common organic electrode methods include organic coatings, slurry electrodes, and carbon nanotube-based composites.

Tan et al.[46] synthesized 2,4,6-tris(4-pyridyl)-1,3,5-triazine (TPT) with multiple active sites in one molecule. They prepared a cathode slurry electrode using TPT as the raw material. During reactions, TPT could accept and release four charges, transforming into a biradical after accepting two charges and into a quinoid structure after accepting four charges. The four aromatic rings effectively reduced side reactions and increased cyclic stability. The experiments showed 66% capacity retention after 6000 RFB cycles using TPT, exhibiting excellent rate capability.

Zhu et al.[47] introduced quaternary ammonium groups into anthraquinone to synthesize an anthraquinone derivative (QAAQ). The strong intermolecular interactions between the quaternary ammonium groups and anthraquinone carbonyls greatly improved cyclic stability. After 500 cycles, the capacity retention was 81% with 0.041% decay per cycle, lower than those of other anthraquinone derivatives. QAAQ was suitable for neutral aqueous RFBs, with water solubility of 1.4 M and solubility of 1.2 M in a 2.4M neutral NaCl solution. The maximum battery capacity reached 64.3 $Ah.L^{-1}$. QAAQ provided new ideas for subsequent practical application of anthraquinone derivatives.

Lei et al.[48] synthesized covalent organic frameworks (COFs) grown on carbon nanotubes (CNTs) by reacting CNTs and COF precursors at room temperature. The COF@CNTs exhibited excellent electrochemical performance. The reversible capacity continuously increased before 320 cycles, reaching a stable reversible capacity of 1021 $mAh.g^{-1}$ between 320–500 cycles and stable cycling over 500 cycles at 100 $mA.g^{-1}$.

4.3.4. Organic additives/catalyst

Factors decreasing RFB system performance include incomplete redox reactions, slow reaction rates, side reactions (such as hydrogen/oxygen evolution and other substances hindering reactions), and electrolyte chemical phase changes affecting subsequent reactions. Choosing suitable additives based on needs can mitigate the effects on battery performance. Currently, additives used in RFBs are mostly metal-based, but these can only positively affect certain aspects and have greater environmental pressures, imposing considerable limitations. The discovery and preliminary application of organic additives have proven their superiority in improving battery performance in multiple aspects, as well as their environmental-friendliness, prompting more researchers to explore the feasibility and advantages of other organic substances as additives.

Park et al.[49], considering the high costs of energy storage, proposed a new membrane-free zinc-bromine battery system and improved the dendritic growth of Zn and cross-diffusion of Br^-. They mixed metal salts, such as lithium sulfate and 1-bromoethylpyridinium bromide (1-EPBr), with the electrolyte. Metal ions formed a shielding layer during Zn^{2+} deposition to inhibit Zn dendrite growth. 1-EPBr suppressed Br^- cross-diffusion and promoted bromine complexation. After 700 cycles at 20 $mA.cm^{-2}$ of current density and 2 $mAh.cm^{-2}$ of areal capacity, the coulombic efficiency remained at 98.5%. At 1 $mA.cm^{-2}$ of current density and 1 $mAh.cm^{-2}$ of areal capacity, the coulombic efficiency approached 100% after 1600 cycles, achieving low-cost grid-scale energy storage.

Zinc nickel batteries also face electrode passivation due to zinc deposition. Zhang et al.[50] added tetraethylammonium bromide and poly(ethylene oxide) (PEO) to the electrolyte, respectively. Results showed the coulombic efficiency remained close to 100% after 386 cycles (450 h) with the PEO addition. This was because the additive provided more active sites in the deposited Zn, enabling full re-oxidation. The additive also inhibited hydrogen and oxygen evolution to some extent, increasing the corrosion current density and improving corrosion resistance. After the PEO group was cycled for over 40 days, the system remained stable at discharge power of 27.7 mW.cm^{-2}, energy density of 39.2 mW.h.cm^{-2}, and temperature of 60 °C, indicating significant performance enhancement by the organic additive.

5. Research progress on single-cell structure

The single cell of RFBs is the most basic unit for evaluating battery system performance, optimizing structural design, and operating energy storage systems. As shown in **Figure 6**, the ion exchange membrane for ion/proton exchange is in the middle. To the right of the membrane are the electrode frame for fixing the electrodes, the electrodes that provide the site for redox reactions, the seal to prevent electrolyte leakage, the bipolar plate with flow channels, the current collector for current transmission, and the end plate for fixing the single cell. The left and right sides symmetrically form a complete single cell.

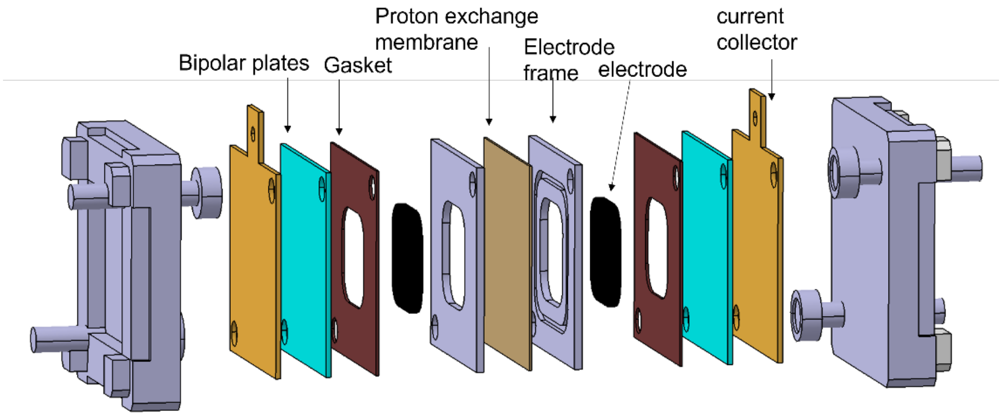

Figure 6. Structure of RFB single cell.

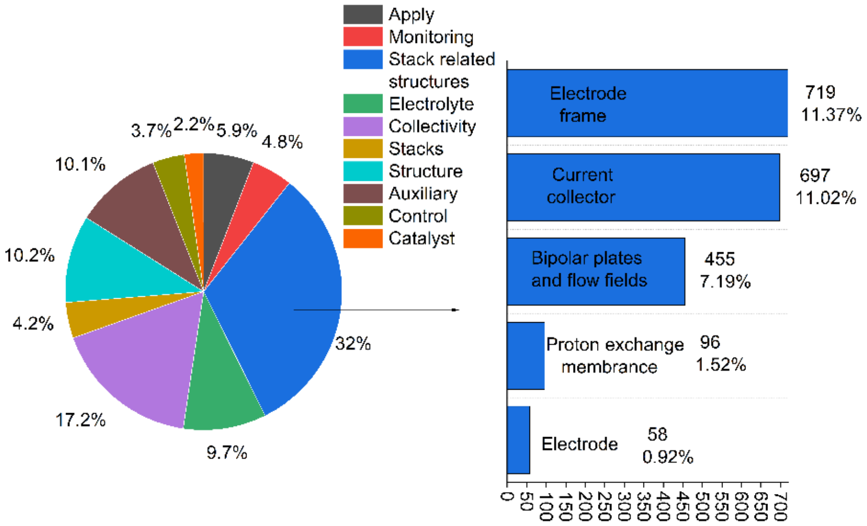

Figure 7. Number of patent applications and percentages for various RFB research topics.

To improve single-cell RFBs' performance, researchers are currently studying the above components to varying degrees. According to the number of patent applications, the research hotspots and research on parts that improve single-cell RFBs' performance the most can be seen in **Figure 7**. New RFB systems and applications account for 23% of the total. Ion exchange membranes and electrodes each account for 11%, bipolar plates and flow fields account for 7%, current collectors account for 2%, electrode frames account for

1%, and the rest are related patents that help improve RFB system stability, such as improving battery structure (10%), assisting stable battery operation (10%), monitoring battery operation (5%), controlling battery operation (4%), etc. In this section, the latest articles involving the above structures are referenced, the patents related to single-cell RFB structures (electrodes, ion exchange membranes, bipolar plates (flow fields), current collectors) are analyzed, and the latest development status of each RFB structure and the overall development status of RFBs are demonstrated.

5.1. Latest electrode research progress

Electrodes are one of the key components of RFBs. Their role is to provide a site for redox reactions without participating in the reactions. Electrolytes undergo electron acceptance and donation at the electrode-electrolyte interface to carry out electrochemical reactions, achieving mutual conversion between electrical energy and chemical energy. Electrode materials affect the electrochemical reaction rate, battery internal resistance, and uniformity of electrolyte distribution, thereby affecting the three major polarizations (activation, ohmic, and concentration), further influencing battery performance[51].

Graphite felts (GFs) and carbon felts (CFs) currently used in VRFBs have defects, such as small specific surface area, low catalytic activity, and poor conductivity. In recent research, scholars have introduced noble metals and carbon nanomaterials to modify the surface to enhance the active potential, thereby improving these issues. However, high costs prevented commercialization. Fu et al.[52] proposed a new electrode suitable for VRFBs. The graphene-improved carbon felt electrode (CF) was treated with Ar plasma after chemical vapor deposition (CVD) to obtain a highly improved Ar-GCF electrode, which effectively enhanced the electrochemical performance of the VRFBs. The experiments showed that VRFBs assembled with Ar-GCF electrodes improved the energy efficiency by 7.10% and the voltage efficiency by 6.98%. After 800 cycles, the charge transfer resistance (R_{ct}) of the VRFBs using Ar-GCF electrodes increased by 15.79%, while for the VRFBs using CF electrodes, R_{ct} increased by 102.40% after 600 cycles, demonstrating greatly improved cyclic stability.

The semi-solid electrode (SSE) is a new type of electrode proposed by Duduta et al.[53] in 2011. Its physicochemical properties are different from those of traditional solid electrodes. The main feature is fluidity, and the electrochemical performance can be adjusted by adding active materials to meet different needs. For example, this method was found to improve the cyclic stability of aqueous Prussian blue derivatives and Zn-$LiFePO_4$ electrolytes. Borlaf et al.[54] proposed the 3D printed battery concept based on additive manufacturing (AM) and SSE technologies. For demonstration, the experiments used an aqueous zinc-manganese battery (Zn-MnO_2). Stereolithography (SLA) printing fabricated the overall battery structure, and then the SSE was injected to obtain a complete battery system. This new concept changed the traditional manufacturing method of RFBs, accelerating commercialization.

5.2. Latest ion exchange membrane research progress

Ion exchange membranes (IEMs) are another key component of RFBs. Their role is to separate the active species in the positive and negative electrolytes to prevent cross-mixing while allowing target ions to pass through to enable normal operation of the internal conductive circuit. Excellent IEMs should have excellent ionic conductivity, high ion selectivity, high mechanical and chemical stability, low swelling, and low cost. But in practice, it is impossible to fully consider all these properties. Some or even most of the demanding properties have to be abandoned to pursue overall performance improvement by satisfying the remaining properties.

The most commonly used membranes on the market are dense and porous membranes, with dense membranes accounting for 64% and porous membranes accounting for 42% (with overlap)[55]. Dense membranes are composed of multiple dense layers and have good ion selectivity and mechanical/chemical stability, but the extremely low ionic conductivity means they are only suitable for low current density conditions. Porous membranes work by utilizing pores to screen ions, allowing smaller ions to pass through while blocking larger ions, resulting in extremely low ion selectivity. Accordingly, their ionic conductivity, mechanical/chemical stability, and swelling are superior to those of other commercial membranes.

In recent years, researchers have been committed to improving existing membranes to add or enhance other properties beneficial to battery performance on the basis of original capabilities. Chen et al.[55] obtained an intrinsic dense membrane by solution casting, which showed good structural and chemical stability in organic solvents, with an ionic conductivity of 0.105 $mS.cm^{-1}$, a current efficiency of 91.7% after 20 cycles at 0.1 $mA.cm^{-2}$, and a voltage density of 95.7%. Cheng et al.[56] added active materials to synthesize multilayer membranes in a two-layer film. Through experiments, it was found that membrane design can be tailored for various needs and different battery systems to achieve maximum efficiency. Modified composite membranes can be synthesized by surface coating and pore filling. Chen et al.[57] synthesized a modified composite membrane by surface coating. Compared with those of unmodified membranes, its charge transfer resistance decreased from 418.9 $\Omega.cm^2$ to 35.6 $\Omega.cm^2$, greatly reducing ohmic polarization. After 1000 cycles at 1.0 $mA.cm^{-2}$, the current density remained at 90%. Yuan et al.[58] synthesized a modified composite membrane by pore filling. The current density reached 91.0% and the voltage density reached 93.7%. At the ultrahigh current density of 4.0 $mA.cm^{-2}$, the average discharge capacity remained at 1.30 $Ah.L^{-1}$, with overall performance improvement compared with those of unmodified membranes.

Fang et al.[59] synthesized a new hydrogen bond-rich membrane (SP-TiON) suitable for iron-chromium redox flow batteries by adding titanium oxynitride (TiON) to a sulfonated poly(ether ether ketone) (SPEEK) matrix. The TiON generated -OH and $-NH_2$ functional groups. The interactions between these two functional groups and water molecules form abundant and continuous hydrogen bonds, improving ionic conductivity. The data showed that the ICFRBs assembled with SP-TiON had a current density close to 100%. The interaction force between $-NH_2$ groups and $-SO_3H$ groups on the SPEEK surface reduced the swelling rate of SP-TiON to 9.9% (19.24% for the original membrane), significantly improving stability.

As the structure is in direct contact with the electrolyte, improving the ion exchange membrane performance is inextricably linked with the electrolyte. Therefore, measures can be taken in the redox reactions, such as adding functional groups and coating with catalysts that promote the reactions, to directly or indirectly enhance battery performance rather than just limiting to ion transfer and circuit continuity.

5.3. Latest bipolar plate and flow field research progress

Bipolar plates (BPs) serve functions such as conducting current, supporting electrodes, providing flow fields, and connecting cells in series in RFBs. Therefore, good BP materials must have high conductivity, high structural stability, good gas tightness, and good chemical stability[60]. Graphite plates currently used in the market, despite advantages such as good conductivity, chemical stability, and low cost, have a complex preparation, a loose porous structure, and a low production efficiency, indicating room for further improvement.

In recent years, BP material research has focused on coating graphite plates with a resin layer, sacrificing some original advantages, such as conductivity, to overcome disadvantages, such as loose porous structure and poor gas tightness, to improve the overall RFB performance.

Jiang et al.[61] hot-pressed a resin layer onto a BP surface with cactus-like carbon nanofibers (C-CNFs) and graphitized cactus carbon nanofibers (G-C-CNFs). The needle-like fibers of G-C-CNFs penetrated the resin layer to reach the graphite layer, forming an efficient conductive network. For BPs treated with C-

CNFs, the area-specific resistance (ASR) was 37.7 mΩ.cm^2 and the conductivity was 162.0 S.cm^{-1}. For BPs treated with G-C-CNFs, the ASR decreased to 25.4 mΩ.cm^2 and the conductivity increased to 198.7 S.cm^{-1}, which was lower than that of pure graphite plates (324.9 S.cm^{-1}) but with significantly decreased ASR (38.2 mΩ.cm^2). At 40 mA.cm^{-2}, the energy density was 91.81% for C-CNFs and 92.88% for G-C-CNFs. At the high current density of 200 mAcm^{-2}, the energy densities were 71.61% and 75.23% for C-CNFs and G-C-CNFs, respectively, demonstrating improvement at different current densities.

Flow fields are channels on the bipolar plates for electrolyte circulation. Reasonable flow field designs can reduce pressure drops, improve mass transfer, and evenly distribute ion concentrations. The flow field shape affects the flow rate, which in turn affects mass transfer. Losses in mass transfer lead to overpotential, further reducing battery capacity[62]. Therefore, selecting suitable flow channel shapes is an important way to improve RFB performance. Zigzag, interdigitated, serpentine, composite, and other flow fields have all shown good performance.

Pan et al.[63] added a slope (GSFF) to a serpentine flow field, with the channel depth gradually decreasing from the inlet to the outlet to increase the electrolyte flow velocity near the outlet. Simulations tested slopes of 75%, 50%, 25%, and 5%. A 25% depth reduction gave the biggest performance improvement. At a current density of 400 mA.cm^{-2} and flow rate of 12 mL.min^{-1}cm^{-2}, the energy density was 73.1%, 5% higher than that of the traditional serpentine flow channel, and the electrolyte utilization reached 59.5%, a 27.7% increase.

The proven performance of serpentine flow channels means that current research focuses on improving them. Gundlapalli et al.[64] proposed a flip-flop serpentine (FFS) flow field based on triple serpentine and enhanced interdigitated serpentine flow fields. The electrolyte separates the FFS inlet into three reaction zones. The experiments showed that the electrolyte distribution was more uniform in the FFS flow field compared with those of the above two flow fields, resulting in lower pressure drops. At flow rates above 50% of the single-serpentine (SS) flow field, the energy density and discharge capacity in the FFS flow field exceeded that of the SS flow field, with other performances comparable to those of the SS flow field. Comparing the SS flow field and the FFS flow field at 90 mA.cm^{-2} and 120 mA.cm^{-2}, the discharge energy in the FFS flow field increased by about 12% and the charge/discharge efficiency improved by 3%, with the energy density exceeding 30 Wh.L^{-1}. Huang et al.[65] compared different channels, establishing a relationship between channels and performance enhancement, thereby demonstrating the necessity of well-designed channels.

As support structures and electrolyte circulation channels, bipolar plates and flow fields are especially important for improving battery performance. Suitable bipolar plate materials and flow field designs can enable more uniform electrolyte distribution during circulation, greatly promoting the commercialization of large-scale RFB energy storage systems.

5.4. Latest current collector research progress

As the structure conducting current in RFBs, current collectors must have good conductivity and corrosion resistance. Current collectors allow metal and active particles to enter the electrolyte and participate in the reactions in the electric field, and so improvements can be made using inert particles (C) that do not participate in reactions but form a conductive network to improve conductivity or using organic active particles that promote redox reactions to enhance battery performance.

Chen et al.[66] proposed using carbon felt as the substrate and embedding lithium particles in the carbon felt to design a 3D current collector for lithium-ion flow batteries based on the lithium-ion flow battery system. During reactions, the lithium particles replaced carbon particles in the slurry electrolyte to reduce viscosity and increase the active material volume ratio, hence improving volume capacity and energy density. The experiments demonstrated that the battery system with this current collector achieved an energy density of over 230 $Wh.L^{-1}$, with the coulombic efficiency still exceeding 95% after 100 cycles.

Zhang et al.[67] also reconstructed the 3D current collector structure. Using a carbonized polymer "magic sponge", they prepared a 3D macroporous carbon sponge current collector suitable for hybrid sodium-seawater flow batteries, with an open framework structure and good flexibility and customizability. The introduced nitrogen and oxygen-containing groups provided abundant active sites on the carbon backbone. The macroporous structure facilitated the transport of O_2, OH^-, and H_2O, enhancing oxygen evolution reaction and oxygen reduction reaction. The 3D framework also showed good stability, remaining stable after 100 cycles. The experiments showed this 3D macroporous carbon sponge current collector gave small charge/discharge voltage gaps, high voltage efficiency, large power density, and good cyclic stability for the hybrid sodium-seawater flow battery, with potential as a commercial structural component.

RFB electrolytes are usually acidic corrosive compounds. Corrosion resistance is also a major indicator of suitability as current collectors. Tekaligne et al.[68] proposed the concept of coating current collectors with organics to enhance corrosion resistance. Aluminum foils are commonly used in aqueous RFBs for excellent conductivity but they still face corrosion challenges. The researchers added 8-hydroxyquinoline (HQ) and 5-formyl-8-hydroxyquinoline (FHQ) as corrosion inhibitors, finding inhibition rates of 84.07% and 94.03% for HQ and FHQ, respectively. After 60 cycles at 1 C, the average coulombic efficiency (ACE) values were 97.46% and 98.63% for HQ and FHQ, respectively, compared with 93.4% without inhibitors. After 400 cycles at 0.2 C, the capacity values were 127.9 $mAh.g^{-1}$, 117.17 $mAh.g^{-1}$, and 49.5 $mAh.g^{-1}$ and the ACE values were 99.82%, 99.2%, and 98.02% for FHQ, HQ, and without inhibitors, respectively. The polarization tests showed corrosion rates of 1.37×10^{-3} mm/year, 3.66×10^{-3} mm/year, and 2.29×10^{-2} mm/year for FHQ, HQ, and without inhibitors, respectively. The active formyl group in FHQ enabled better corrosion inhibitor adsorption through interactions with the metal, further reducing aluminum foil corrosion.

5.5. Latest electrode frame research progress

As the structure carrying the electrodes, electrode frames need to be adjusted according to electrode shape, thickness, etc. Some frames have etched flow channels that directly provide reaction sites, so structural improvements to electrode frames are necessary to design more efficient frames.

A 2023 patent application by the University of Science and Technology of China (public number CN115732716A) proposed adding disturbance zones in the electrode frame to adjust the electrolyte flow velocity, improving electrolyte distribution uniformity on the electrodes, effectively reducing dead flow zones, lowering concentration polarization, and increasing battery energy efficiency.

A 2023 authorized patent (number CN219226324U) for the Dalian Institute of Chemical Physics proposes a new electrode frame structure. Communicating branch pipes are set between the positive and negative electrolyte inlets and outlets around the frame, with necking structures of different numbers and cross-sectional areas on the pipes. This slightly increases flow resistance, while reducing leakage current, improving actual output voltage and system safety to some extent. There are many other optimization design patents for various single-cell RFB components. The latest developments in major structures are briefly summarized here.

The above structures all improve overall battery performance to varying degrees. Currently, RFB energy storage systems face technical bottlenecks, such as low energy density and high environmental impact. In addition to trying new materials, structural optimization of battery components is also crucial. The proposed research methods and patented inventions all improve battery performance in aspects such as energy efficiency, cyclic stability, and system safety to some extent, enabling qualitative leaps in RFB performance and promoting the commercialization of RFB energy storage systems.

6. Discussion

RFB energy storage technology promotion from scientific research to practical application involves many stages. With several decades of unremitting efforts by scientific researchers, China's redox flow battery technology and industry have developed rapidly, reaching an internationally leading level. The National Development and Reform Commission and the National Energy Administration's Guiding Opinions on Promoting Development of New Energy Storage proposed adhering to diversified energy storage technologies, enabling commercialization of long-duration storage technologies, such as compressed air and redox flow batteries. It can be predicted that the next few years will be a period of rapid development for various new energy storage technologies.

Therefore, for China to meet the national demand for large-scale electrochemical energy storage systems and improve RFB storage system adaptability and efficiency, continued strengthening of R&D into new materials and technologies is needed, along with solving issues, such as RFB costs, lifespan, and scalability, to achieve healthy and orderly development of the entire RFB industry chain. This will make electrochemical energy storage a key supporting technology in the energy sector for carbon peaking and neutrality goals.

The rapid development of RFB technologies in China also faces some challenges. Firstly, the core technologies are still controlled by foreign companies, restricting domestic commercialization. Secondly, manufacturing costs are still high, limiting large-scale applications. Thirdly, there are still technical bottlenecks, such as insufficient cycle life, that need breakthroughs. Fourthly, supporting facilities for recycling and reusing RFB electrolytes need improvement.

To overcome these challenges, we propose the following recommendations: (i) increase investment and policy support for domestic R&D to break foreign monopolies, (ii) optimize manufacturing and system integration to reduce costs, (iii) develop new electrode and membrane materials to improve cycle life, and (iv) establish a complete recycling system to reduce environmental impact. With joint efforts from the government, industry, and academia, the promising prospects of RFBs for sustainable energy development can be fully realized.

7. Conclusion and prospects

This paper started with a discussion on the number and trends of RFB patent publications in China, and then the latest domestic and foreign research were reviewed and the development process and latest research results that demonstrate the latest progress in RFB research and the energy storage industry were summarized. Beginning with RFB principles and historical development, data were presented on current pioneering companies, universities, research institutes, etc., in the industry. Different classification methods of RFBs were summarized, such as the mechanisms of different reaction pairs to different reactions, systematic analysis of organic and inorganic RFBs, and summaries of the latest research from various perspectives. According to different research topics, the single-cell stack structure was analyzed, covering electrodes, ion exchange membranes, bipolar plates/flow fields, and current collectors, showcasing the domestic and foreign research methods and results on different components.

In summary, with the continuous development of research both domestically and internationally, flow battery technology is poised to become more mature and energy storage systems will become more efficient.

The flow battery industry will benefit from the ongoing growth in research and innovation, while playing an increasingly significant role in the field of energy storage. This technology holds the potential to achieve further breakthroughs in areas such as renewable energy integration, grid balancing, and industrial applications, thereby providing vital support for the future of sustainable energy.

Author contributions

Conceptualization, AM and WW; methodology, WW; validation, WW and AM; writing—original draft preparation, WW and AM; writing—review and editing, AM, BY, JW and YW; supervision, AM; project administration, AM. All authors have read and agreed to the published version of the manuscript.

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Conflict of interest

The authors declare no conflict of interest.

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