Zinc–Bromine Flow Batteries

Subjects: Electrochemistry

Contributor: Uxua Jiménez-Blasco , José Carlos Arrebola , Alvaro Caballero

The development of energy storage systems (ESS) has become an important area of research due to the need to replace the use of fossil fuels with clean energy. Redox flow batteries (RFBs) provide interesting features, such as the ability to separate the power and battery capacity. This is because the electrolyte tank is located outside the electrochemical cell. Consequently, it is possible to design each battery according to different needs. In this context, zinc–bromine flow batteries (ZBFBs) have shown suitable properties such as raw material availability and low battery cost. To avoid the corrosion and toxicity caused by the free bromine (Br_2) generated during the charging process, it is necessary to use bromine complexing agents (BCAs) capable of creating complexes.

redox flow battery   zinc–bromine flow battery

1. Introduction

Renewable energy sources are very important to reduce greenhouse gas emissions and to fight against climate change. As a complement to renewable energy sources, energy storage systems that can be used to regulate power generation are necessary to balance and guarantee the continuity of operation, since renewable energies are intermittent sources [1][2]. Regarding these energy storage systems, during off-peak hours, when the demand is lower than generation, energy is stored, and, at peak times, when the demand is higher than generation, the remaining load is supplied by the energy storage system [3][4][5].

Among energy storage systems, there are different technologies [4][6], such as mechanic, thermal, magnetic or electrochemical. The latter transform electrical energy into chemistry via redox chemical reactions. There three types of these systems: batteries (including non-rechargeable primary and rechargeable, or secondary batteries), electrochemical capacitors (electric double layer capacitors and pseudo-capacitors) and fuel cells [7][8][9].

As for batteries, they are used both as a storage system and as an energy transformation system. This type of electrical storage system features a high specific energy and a constant output voltage. There are different technologies within secondary batteries, depending on the redox pair. The best known and most commercialized are those based on Pb, Li, Ni and Na, but, in recent years, flow batteries, more specifically those based on Zn-Br (ZBFBs), have gained great importance. Batteries based on Li have a higher energy density, energy efficiency and power density compared to the rest of the technologies, followed by those based on Na, Pb and Ni. In the case of ZBFBs, their values are above Ni and Pb batteries, although the most interesting thing about this technology, in addition to the energy values, is the low cost of the materials and their abundance and availability. In addition to this, because the electrolyte tanks are located outside the electrochemical stack, they have high scalability. As mentioned above, one of the advantages of ZBFBs is their use of abundant and available materials, which makes their price per kW/h lower compared to other technologies, and the cost is estimated between 350 to 600 dollars [10]. The environmental impact associated with the assembly of ZBFBs has been studied by He et al. [11], and has been seen to be less compared to other technologies [12][13][14][15].

Redox flow batteries (RFBs) are rechargeable devices which are used for energy storage and the electrolytes are pumped through the electrochemical cell to transform the chemical energy into electric energy. A typical RFB usually has two electrolyte tanks for energy storage, a cell or several cells (stack) for the electrochemical reaction and pumps for the flow of the electrolyte between the tanks and the stack. The difference between RFB technology and other battery systems is that in RFBs, the energy is stored in electrolyte solutions, and the system capacity is determined by the redox pair concentration and the volume of the electrolytes. In addition, the system's power is determined by the electrode's surface. Consequently, the power and the capacity are separated and offer flexibility to build battery systems under different working conditions [16][17][18]. If RFB technology is compared with other technologies, RFBs have a lower power and current density that is not appropriate for traction and mobile applications. Usually, RFBs are used in stationary applications such as homes, smart grids, or telecommunications [17][18][19].

1.1. RFB Description

The transformation of chemical energy into electrical energy occurs by pumping the electrolyte from the reservoir to the stack, where the redox reactions occur. The anolyte (negative electrolyte) flows in the negative semi-cell, the catholyte (positive electrolyte) flows in the positive half-cell and the reduction–oxidation reactions occur at the electrode–electrolyte interface. In the oxidation reaction, electrons are generated and moved by the external circuit. For the reduction reaction to happen, the electrons are accepted into the other half-cell. For secondary batteries, the chemical reactions must be reversed during discharge. In this way, as one solution reduces, the other oxidizes, creating an electric current that passes through the externally installed electrical circuit. The potential difference between the redox pair of both half-cells determines the electromotive force or voltage of the cell. Both half-cells are separated by a membrane, to prevent the self-discharge of the battery. Across the membrane, electrolytes exchange ions to maintain electroneutrality and electrolyte balance [18][20].

1.2. RFB Classification

RFB classification can be carried out according to the structure of the cell or according to the type of redox couple used. Considering the structure of the cell, four types of RFB have been developed [6]: true or redox flow batteries, type 1 hybrid redox flow batteries, type 2 hybrid redox flow batteries and flow batteries without membranes.

The first type is characterized by all the active materials being dissolved in the electrolyte [21][22][23], so that the capacity of the battery is totally independent of its power. One of the best-known examples is the vanadium flow battery (VFB).

Those of type 1 are characterized by there being one phase change in the active species in the chemical reaction, depositing material in the solid phase on one of the electrodes. Consequently, the surface of the electrode limits the storage capacity as well as the amount of electrolyte. A typical example is zinc–bromine flow batteries (ZBFBs), in which during the charging stage, solid zinc is deposited on the anode surface [21][24].

In type 2, both half-reactions involve phase changes in the charge or discharge phase. An example of this type is a soluble lead flow battery (SLFB), in which during charging, the Pb^{2+} ions pass into solid compounds that are deposited on the surface of both electrodes [21][24][25].

Finally, in flow batteries without membranes [26][27], two liquids are pumped through a channel, storing or releasing energy via electrochemical reactions. Both solutions flow in parallel without mixing, without the need for a membrane. This technology is the least developed of all those cited.

2. Zinc–Bromine Flow Batteries (ZBFBs)

A zinc–bromine flow battery (ZBFB) is a type 1 hybrid redox flow battery in which a large part of the energy is stored as metallic zinc, deposited on the anode. Therefore, the total energy storage capacity of this system depends on both the size of the battery (effective electrode area) and the size of the electrolyte storage tanks. For this reason, in this type of battery, the capacity and power are not totally decoupled [28][29].

During charge, the electrolyte is pumped into the cell, where bromine gas is formed in the cathode part due to the oxidation of the bromide, while in the anodic part, the zinc ions are reduced into metallic zinc and is deposited on the surface of the electrode [28][30][31].

Bromine has limited solubility in water, so a bromine complexing agent (BCA) or quaternary amine is added to the electrolyte to capture the bromine formed and prevent its evaporation (the boiling point of bromine is 58.8 °C). As the bromine–BCA complex forms, a denser and more viscous organic liquid phase immiscible with aqueous electrolyte is formed, which sinks to the bottom of the positive electrolyte (catholyte) tank [32].

In discharge, the organic phase must be mixed with the rest of the catholyte to transport and release the bromine molecules on the surface of the positive electrode. During discharge, the metallic zinc that has formed at the anode is oxidized into Zn^{2+} ions, dissolving in the anolyte (negative electrolyte) and releasing two electrons that are transported by the external circuit. The electrons return to the cathode and reduce the bromine molecules into bromide ions, which are soluble in the catholyte. The chemical process used to generate the electric current increases the concentration of zinc and bromide ions in both electrolytes [33].

These are the reactions that occur during charge [28][29][31][34][35]:

$$\text{Cathode: } 2Br^{-} \leftarrow\rightarrow Br_2 + 2e^{-} \qquad E^0 = 1.06\ V$$

$$\text{Anode: } Zn^{2+} + 2e^{-} \leftarrow\rightarrow Zn^0 \qquad E^0 = -0.76\ V$$

$$\text{Global reaction: } 2Br^- + Zn^{2+} \leftarrow\rightarrow Br_2 + Zn^0 \qquad E^0 = 1.86\ V$$

As mentioned above, the energy efficiency of this battery is around 70%, and it also offers one of the highest voltages of the redox pairs used in flow batteries (1.8 V), releasing two electrons per atom of zinc. In having such a high energy density, the weight and cost are reduced for the same storage capacity as a similar battery. However, since bromine is a highly toxic compound to inhale or absorb, it is necessary for a complete bromine capture process to take place within the cell. This is essential for the safety and efficiency of the system [36].

ZFBF Components

ZBFBs consist of three main components: the electrochemical stack, the hydraulic circuit and the battery control system (BMS). The electrochemical cell is built of two half-cells, each of which is made up of electrodes in which the active materials are charged and discharged and supported by a suitable fluid dynamic design, through which the electrolyte flows. Both half-cells are separated by a membrane or separator [37]. Stacks are made up of several cells placed in parallel one on top of the other and electrically connected in series.

As for the electrodes, in ZBFBs, they are mostly composed of carbon-based materials such as graphite, carbon fibers or carbon nanotubes. The choice of appropriate materials is really important to obtain the desired behaviors. In this regard, several properties are essential, such as the conductivity or the surface characteristics to correctly deposit the metallic zinc during charging. On the other hand, the use of composites made up of carbonic-polymeric materials for the electrodes or the doping of graphene materials using heteroatoms is common to increase efficiency [29][35][38].

Another main component is the membrane. A selective porous membrane pulls apart both half-cells and allows the crossing of ions without allowing the species to mix, avoiding self-discharge. There are several types of membranes, in the form of fabrics, microporous paper, polymer, etc. [36][39].

As for the electrolyte, it must be remarked that it is the most essential component of the ZBFB, due to the fact that it contains the active species, responsible for the redox reaction and therefore for the difference in voltage or power generated. To avoid net species transfer, both electrolytes (positive or catholyte and negative or anolyte) have the same composition. Zinc bromide is the main component of the electrolyte. Its ions participate in the redox reaction that occurs on the surface of the electrode. $ZnBr_2$ is usually used in concentrations between 1 and 3 M, while the pH is generally kept between 1 and 3.5 to avoid dendritic zinc deposition [40][41]. Furthermore, it is common to use other additional salts as support and to increase the conductivity of the electrolyte, which causes the pH to vary until reaching pH 4. Usually, salts with chlorides are used, due to the changing lability of the protons in the solution and charge transfer impedances at the anode surface [31][38]. Furthermore, the use of a complexing agent is essential to trap the free bromine (Br_2) formed. Its importance lies in the fact that free bromine causes corrosion and toxicity, both among the main problems in ZBFBs. These complexing agent materials are extensively addressed shortly.

Finally, a characteristic element of this system is the hydraulic circuit, and consists of the electrolyte storage tanks (positive and negative) and pumps to pump the electrolyte flow through the electrochemical cell. The tanks are connected to the electrochemical cell via a series of valves and conduits. The electrolytes flow into the circuit, which contains the active species [16][42][43]. To conclude, it is essential to have electronic management over all electronic and hydraulic parameters (power control, valve opening, flow control and loading–uploading protocol), as carried out by the BMS, which allows this control in each of the cells that make up the stack, as well as in the full flow battery [44].

References

1. Dong, K.; Dong, X.; Jiang, Q.; Zhao, J. Assessing energy resilience and its greenhouse effect: A global perspective. Energy Econ. 2021, 104, 105659.
2. Xu, Y.; Cui, G. Influence of spectral characteristics of the Earth's surface radiation on the greenhouse effect: Principles and mechanisms. Atmos. Environ. 2021, 244, 117908.
3. Dunn, B.; Kamath, H.; Tarascon, J.-M. Electrical Energy Storage for the Grid: A Battery of Choices. Science 2011, 334, 928–935.
4. Jiao, Y.; Månsson, D. Greenhouse gas emissions from hybrid energy storage systems in future 100% renewable power systems—A Swedish case based on consequential life cycle assessment. J. Energy Storage 2023, 57, 106167.
5. Olabi, A.G.; Wilberforce, T.; Sayed, E.T.; Abo-Khalil, A.G.; Maghrabie, H.M.; Elsaid, K.; Abdelkareem, M.A. Battery energy storage systems and SWOT (strengths, weakness, opportunities, and threats) analysis of batteries in power transmission. Energy 2022, 254, 123987.
6. Arabkoohsar, A. Chapter One—Classification of energy storage systems. In Mechanical Energy Storage Technologies; Arabkoohsar, A., Ed.; Academic Press: Cambridge, MA, USA, 2021; pp. 1–12.
7. Dixit, M.; Muralidharan, N.; Parejiya, A.; Essehli, R.; Belharouak, I.; Amin, R. 9—Electrochemical energy storage systems. In Emerging Trends in Energy Storage Systems and Industrial Applications; Kumar, N.P., Ed.; Academic Press: Cambridge, MA, USA, 2023; pp. 259–282.
8. Bhattacharjee, U.; Ghosh, S.; Bhar, M.; Martha, S.K. 6—Electrochemical energy storage part I: Development, basic principle and conventional systems. In Emerging Trends in Energy Storage Systems and Industrial Applications; Kumar, N.P., Ed.; Academic Press: Cambridge, MA, USA, 2023; pp. 151–188.
9. Miller, J.R.; Butler, S. Storage system design based on equivalent-circuit-model simulations: Comparison of eight different electrochemical capacitor storage systems. J. Power Sources 2021, 491, 229441.

10. Tang, L.; Leung, P.; Mohamed, M.R.; Xu, Q.; Dai, S.; Zhu, X.; Flox, C.; Shah, A.A.; Liao, Q. Capital cost evaluation of conventional and emerging redox flow batteries for grid storage applications. Electrochim. Acta 2023, 437, 141460.

11. He, H.; Tian, S.; Tarroja, B.; Ogunseitan, O.A.; Samuelsen, S.; Schoenung, J.M. Flow battery production: Materials selection and environmental impact. J. Clean. Prod. 2020, 269, 121740.

12. Tian, S.; He, H.; Kendall, A.; Davis, S.J.; Ogunseitan, O.A.; Schoenung, J.M.; Samuelsen, S.; Tarroja, B. Environmental benefit-detriment thresholds for flow battery energy storage systems: A case study in California. Appl. Energy 2021, 300, 117354.

13. Xiong, D.; Yang, L.; Cao ZLi, F. In Situ Construction of High-Density Solid Electrolyte Interphase from MOFs for Advanced Zn Metal Anodes. Adv. Funct. Mater. 2023, 33, 2301530.

14. Liu, C.; Deng, L.; Li, X.; Wu, T.; Zhang, W.; Cui, H. Metal–organic frameworks for solid-state electrolytes: A mini review. Electrochem. Commun. 2023, 150, 107491.

15. Tao, S.; Momem, R.; Luo, Z.; Zhu, Y.; Xiao, X.; Cao, Z.; Xiong, D.; Deng, W.; Liu, Y.; Hou, H.; et al. Trapping Lithium Selenides with Evolving Heterogeneous Interfaces for High-Power Lithium-Ion Capacitors. Small 2023, 19, e2207975.

16. Sayed, E.T.; Shehata, N.; Abdelkareem, M.A.; Ramadan, M.; Olabi, A.-G. Redox Flow Batteries. In Encyclopedia of Smart Materials; Olabi, A.-G., Ed.; Elsevier: Oxford, UK, 2022; pp. 176–185.

17. Tang, L.; Leung, P.; Xu, Q.; Mohamed, M.R.; Dai, S.; Zhu, X.; Flox, C.; Shah, A.A. Future perspective on redox flow batteries: Aqueous versus nonaqueous electrolytes. Curr. Opin. Chem. Eng. 2022, 37, 100833.

18. Adeniran, A.; Bates, A.; Schuppert, N.; Menon, A.; Park, S. Recent advances in aqueous redox flow battery research. J. Energy Storage 2022, 56, 106000.

19. Yang, I.; Lee, S.; Jang, D.; Lee, J.-E.; Cho, S.Y.; Lee, S. Enhancing energy efficiency and long-term durability of vanadium redox flow battery with catalytically graphitized carbon fiber felts as electrodes by boron doping. Electrochim. Acta 2022, 429, 141033.

20. Doetsch, C.; Pohlig, A. 13—The Use of Flow Batteries in Storing Electricity for National Grids. In Future Energy, 3rd ed.; Letcher, T.M., Ed.; Elsevier: Amsterdam, The Netherlands, 2020; pp. 263–277.

21. Arenas, L.F.; de León, C.P.; Walsh, F.C. Engineering aspects of the design, construction and performance of modular redox flow batteries for energy storage. J. Energy Storage 2017, 11, 119–153.

22. Guo, Y.; Huang, J.; Feng, J.-K. Research progress in preparation of electrolyte for all-vanadium redox flow battery. J. Ind. Eng. Chem. 2023, 118, 33–43.

23. Trovò, A.; Poli, N.; Guarnieri, M. New strategies for the evaluation of Vanadium Flow Batteries: Testing prototypes. Curr. Opin. Chem. Eng. 2022, 37, 100853.
24. Flox, C.; Monllor-Satoca, D. Hybrid Flow Batteries: Advances, Scientific Challenges and Market. In Encyclopedia of Energy Storage; Cabeza, L.F., Ed.; Elsevier: Oxford, UK, 2022; pp. 443–452.
25. Krishna, M.; Fraser, E.J.; Wills, R.G.A.; Walsh, F.C. Developments in soluble lead flow batteries and remaining challenges: An illustrated review. J. Energy Storage 2018, 15, 69–90.
26. Chaabene, N.; Ngo, K.; Turmine, M.; Vivier, V. Ionic liquid redox flow membraneless battery in microfluidic system. J. Energy Storage 2023, 57, 106270.
27. Wang, X.; Lashgari, A.; Chai, J.; Jiang, J. A membrane-free, aqueous/nonaqueous hybrid redox flow battery. Energy Storage Mater. 2022, 45, 1100–1108.
28. Jiménez-Blasco, U.; Moreno, E.; Cólera, M.; Díaz-Carrasco, P.; Arrebola, J.C.; Caballero, A.; Morales, J.; Vargas, O.A. Enhanced Performance of Zn/Br Flow Battery Using N-Methyl-N-Propylmorpholinium Bromide as Complexing Agent. Int. J. Mol. Sci. 2021, 22, 9288.
29. Jin, C.; Lei, H.; Liu, M.; Tan, A.; Piao, J.; Fu, Z.; Liang, Z.; Wang, H. Low-dimensional nitrogen-doped carbon for Br2/Br− redox reaction in zinc-bromine flow battery. Chem. Eng. J. 2020, 380, 122606.
30. Archana, K.S.; Naresh, R.P.; Enale, H.; Rajendran, V. Effect of positive electrode modification on the performance of zinc-bromine redox flow batteries. J. Energy Storage 2020, 29, 101462.
31. Wu, M.C.; Zhao, T.S.; Wei, L.; Jiang, H.R.; Zhang, R.H. Improved electrolyte for zinc-bromine flow batteries. J. Power Sources 2018, 384, 232–239.
32. Lee, Y.; Yun, D.; Park, J.; Hwang, G.; Chung, D.; Kim, M.; Jron, J. An organic imidazolium derivative additive inducing fast and highly reversible redox reactions in zinc-bromine flow batteries. J. Power Sources 2022, 547, 232007.
33. Schneider, M.; Rajarathnam, G.P.; Easton, M.E.; Masters, A.F.; Maschmeyer, T.; Vassallo, A.M. The influence of novel bromine sequestration agents on zinc/bromine flow battery performance. RSC Adv. 2016, 6, 110548–110556.
34. Wu, M.C.; Zhang, R.H.; Liu, K.; Sun, J.; Chan, K.Y.; Zhao, T.S. Mesoporous carbon derived from pomelo peel as a high-performance electrode material for zinc-bromine flow batteries. J. Power Sources 2019, 442, 227255.
35. Wu, M.C.; Jiang, H.R.; Zhang, R.H.; Wei, L.; Chan, K.Y.; Zhao, T.S. N-doped graphene nanoplatelets as a highly active catalyst for Br2/Br− redox reactions in zinc-bromine flow batteries. Electrochim. Acta 2019, 318, 69–75.
36. Zhang, L.; Zhang, H.; Lai, Q.; Li, X.; Cheng, Y. Development of carbon coated membrane for zinc/bromine flow battery with high power density. J. Power Sources 2013, 227, 41–47.

37. Rajarathnam, G.P.; Vassallo, A.M. The Zinc/Bromine Flow Battery. In SpringerBriefs in Energy; Springer: Singapore, 2016.

38. Wu, M.C.; Zhao, T.S.; Jiang, H.R.; Zeng, Y.K.; Ren, Y.X. High-performance zinc bromine flow battery via improved design of electrolyte and electrode. J. Power Sources 2017, 355, 62–68.

39. Hua, L.; Lu, W.; Li, T.; Xu, P.; Zhang, H.; Li, X. A highly selective porous composite membrane with bromine capturing ability for a bromine-based flow battery. Mater. Today Energy 2021, 21, 100763.

40. Yang, H.S.; Park, J.H.; Ra, H.W.; Jin, C.-S.; Yang, J.H. Critical rate of electrolyte circulation for preventing zinc dendrite formation in a zinc–bromine redox flow battery. J. Power Sources 2016, 325, 446–452.

41. Kim, M.; Yun, D.; Jeon, J. Effect of a bromine complex agent on electrochemical performances of zinc electrodeposition and electrodissolution in Zinc–Bromide flow battery. J. Power Sources 2019, 438, 227020.

42. Tomazic, G.; Skyllas-Kazacos, M. Chapter 17—Redox Flow Batteries. In Electrochemical Energy Storage for Renewable Sources and Grid Balancing; Moseley, P.T., Garche, J., Eds.; Elsevier: Amsterdam, The Netherlands, 2015; pp. 309–336.

43. Weber, A.Z.; Mench, M.M.; Meyers, J.P.; Ross, P.N.; Gostick, J.T.; Liu, Q. Redox flow batteries: A review. J. Appl. Electrochem. 2011, 41, 1137–1164.

44. Trovò, A.; Guarnieri, M. Battery Management Systems for Redox Flow Batteries and Controllers for Fuel Cells. In Encyclopedia of Energy Storage; Cabeza, L.F., Ed.; Elsevier: Oxford, UK, 2022; pp. 557–567.