Redox Flow Batteries

Subjects: Energy & Fuels
Contributor: João Sousa

Redox Flow Batteries (RFB) are electrochemical energy storage devices that converts chemical energy into electrical energy through reversible oxidation and reduction of the working fluids. Redox flow batteries are considered by many to be a promising technology for the storage of energy for days or even weeks. Other advantages of RFBs are modularly and the ability to change the output power and energy capacity independently, by changing the size and number of cells in a stack and by adjusting the volume of electrolyte. Also, RFBs show a long lifecycle compared to lithium-ion batteries.

redox flow batteries | energy storage | batteries | stationary energy storage

1. Introduction

The use of electrical energy is growing globally, not only because of population growth but also due to the transversal use of electricity as an energy carrier in all sectors. According to the IRENA, by 2050, it is expected that electricity may represent 50% of total energy consumption, currently it only represents 20% of total consumption. This transition will be mostly achieved by the fast pace at which renewable energy sources, such as wind and solar, are being implemented in power production, replacing fossil fuels [1][2].

Although technologies to gather renewable energy sources and transform them into electricity need to evolve and be more efficient, these are not the only technologies required to accomplish this energetic transition. The intermittent nature of renewable energies makes it imperative to incorporate energy storage systems into the electrical grid to store the excesses of energy produced, allowing for it to be used when production is scarce. For such purpose, redox flow batteries (RFBs) are considered by many to be a promising technology for the storage of energy for days or even weeks [1][2][3]. RFBs show several advantages, such as the ability to be installed modularly and to change the output power and energy capacity independently, by changing the size and number of cells in a stack and by adjusting the volume of electrolyte, respectively. Moreover, RFB show a long lifecycle compared to lithium-ion batteries [2][3].

There are several types of RFB technologies, each having their strengths and weaknesses. Typical RFBs with aqueous electrolytes are the most well-known, however the electrochemical window of water limits the potentials that these batteries can achieve, which leads to low energy densities. On the other hand, non-aqueous electrolytes do not have this problem, however the active species show a low solubility in these solvents. Zinc–bromine flow batteries also have high energy densities at the cost of reduced system efficiency, mainly due to the auxiliary components required to operate these devices [2][3][4]. Slurry RFBs have a high energy density and are not limited by the low solubilities of active species. Nonetheless, this type of RFB increases the viscosity of the electrolyte and does not perform well at high currents [3][4][5].

Other emerging RFBs are also receiving significant attention due to their unique design and the advantages that come with it. Examples of these technologies are membraneless RFBs and metal–air RFBs, which may be promising energy storage devices since they could potentially exhibit higher energy densities and lower costs than first generation RFBs [3].

Among RFB technologies available, vanadium redox flow batteries (VRFB), commonly termed all-vanadium RFBs, have been the ones subject to the highest number of studies. Moreover, VRFBs have already been studied and installed for large scale applications. For instance, Barelli et al. [6] modeled the implementation of VRFB in the transport sector by combining this technology with $LiFePO_4$ batteries in an urban bus. In this study, it was shown that the hybrid system ensures a longer driving time and a higher lifespan when compared to a combination of $LiFePO_4$ batteries and fuel cells and/or $LiFePO_4$ batteries alone. Gouveia et al. [7] in 2020 showed the feasibility of the implementation of VRFBs with photovoltaic systems in a household. It was proven that the addition of VRFB resulted in lower environmental impact than using grid electricity.

RFB already has one of the biggest power capacities installed on commercial facilities when compared to other energy storage technologies, ca. 42% [8]. All these achievements lead us to believe that in the short–medium term this type of battery will exhibit a substantial reduction in its price, which will contribute to making it an even more interesting and low-cost technology for energy storage at different scales and in different sectors [1][2][3].

2. Redox Flow Batteries (RFB)

RFBs comprise three components: two tanks and a cell (*vide* **Figure 1**). The tanks are used to store electrolyte, the solution where the energy is stored, while the cell is where the redox reactions occur. This property of RFB is one of the main advantages of the technology since it is the reason why the quantity of energy stored is decoupled from the power output. By increasing the volume of electrolyte in the tanks, it is possible to store more energy; however, if the objective is to increase the power output, only the cell needs to be changed. Stacking cells in series increases the potential of the battery and amplifying the active area of the cell increases the current produced in the cell. The highly customizable nature of RFBs is generally rare in energy storage systems, but extremely versatile and interesting.

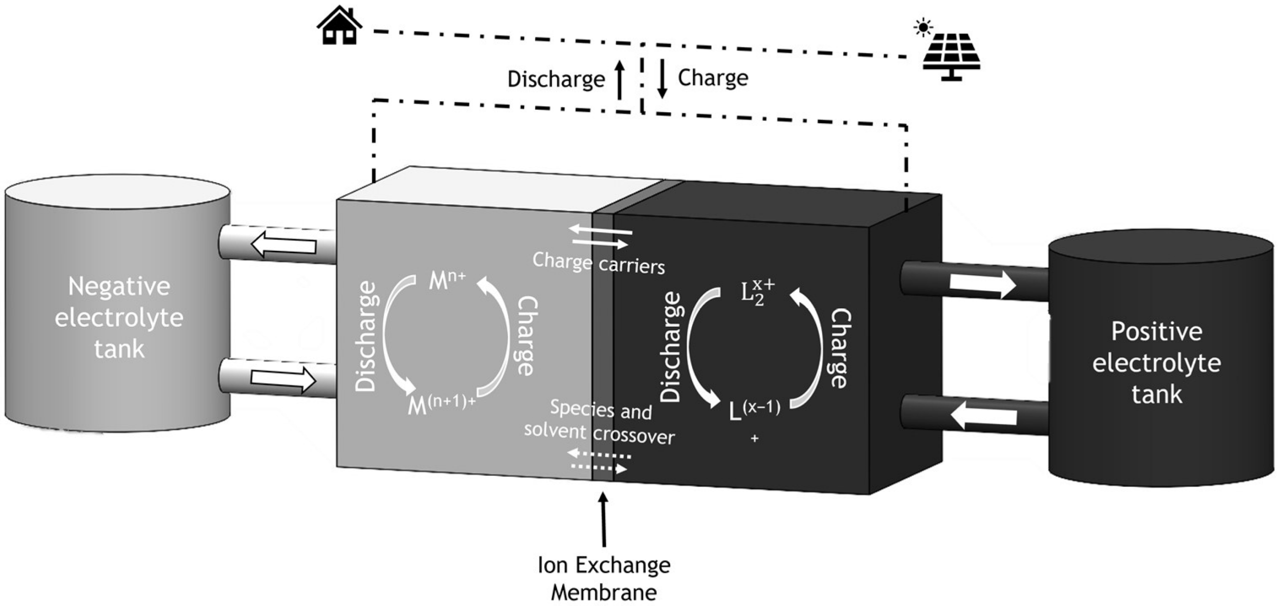

Figure 1. Schematic representation of an RFB.

Usually, the cell is composed of two current collectors, two bipolar plates, two electrodes, and one membrane as shown in **Figure 2**. When this is the case, the defining component of the battery is the electrolyte, e.g., a battery with vanadium electrolyte on both tanks is an all-vanadium redox flow battery (VRFB). Vanadium electrolytes have been widely studied and are well-known, having already been commercialized worldwide. Due to the huge development achieved by this type of RFB, being very close to its peak performance, further optimization of RFBs is a challenging task. The publications made in recent years have focused mainly on new electrolytes, active species, and solvents.

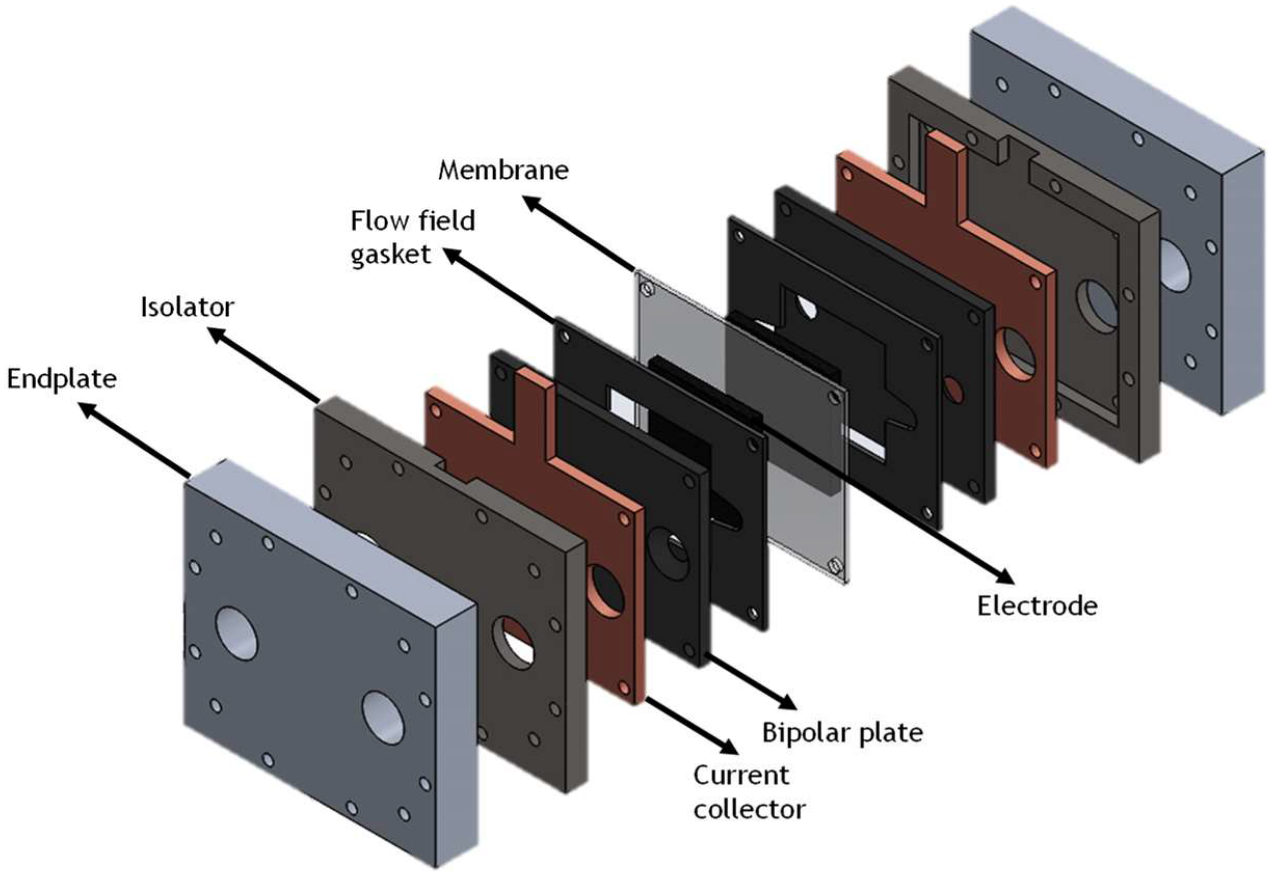

Figure 2. Components of an RFB's cell.

The field of RFB has reached an advanced level of development and the proof of that is the huge number of articles reported in the last few decades, i.e., 10,284 since 2000. The mentioned number resulted from using the search term ""RFB" or "Vanadium RFB" or "flow batteries"".

Figure 3 shows that the number of publications has been increasing over the years, however the development between 2000 and 2010 was not as significant as that which can be observed after 2010. Between 2000 and 2010, the number of publications tripled, i.e., from 54 to 180. The number of publications in 2020 is about twenty-nine times the number of those published in 2000. This increase in the number of publications is clearly related to the agendas designed for a cleaner environment. Moreover, considering the tendency found in the first semester of 2021, it is expected that the number of publications will keep increasing, suggesting that more research is being pursued in this field and also suggesting abundant funding availability.

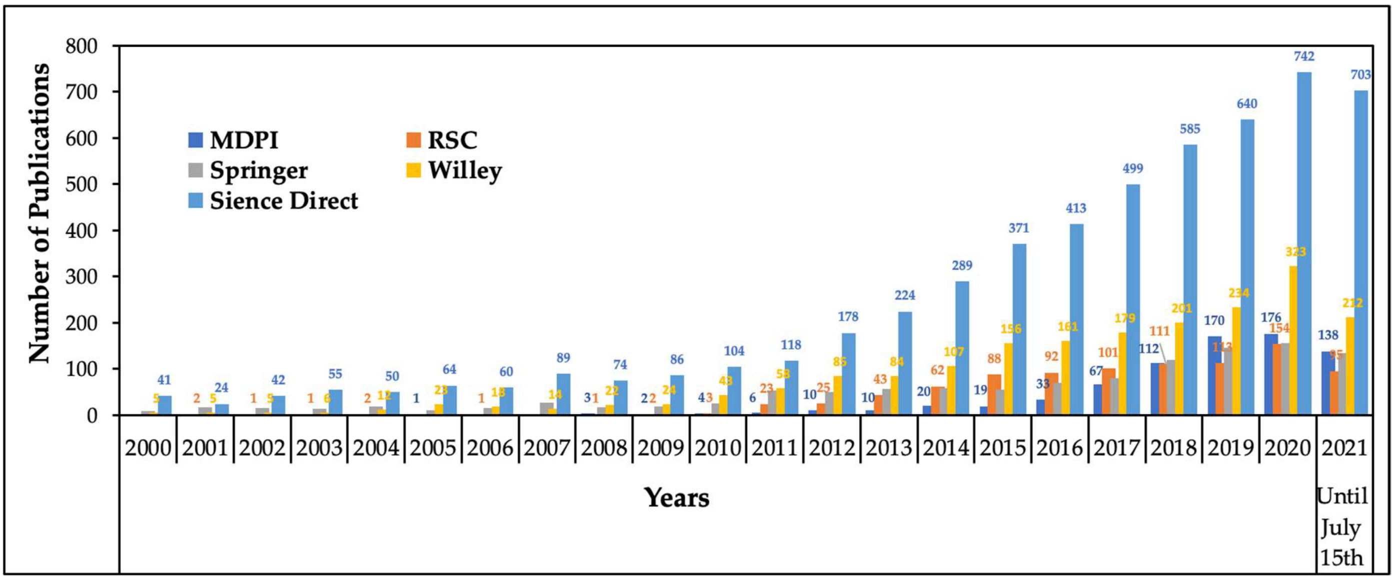

Figure 3. Bar chart of scientific publications published from 2000 until 15 July 2021 found in MDPI journals, Royal Society of Chemistry (RSC), *SpringerLink*, *Wiley Online Library*, and *Science Direct* publications using the search term "“RFB” or “Vanadium RFB” or “flow batteries”".

Table 1 shows the most representative review articles published since 2006 and it can be observed that the interest in the study of RFBs is increasing every year, reflecting the urgency to store energy from renewable energy sources and the constant concern for the environment. Generally, the first published reviews included the explanation of the technology and the phenomena associated with it. Over time, new reviews of more specific innovations appeared with the main objective of drawing attention to the problems detected, clearly showing the interest of the research community in optimizing this technology. With the growing interest and publication of new ideas, it has become increasingly difficult to synthesize and organize all the research fronts of RFBs, and so several review articles with different focuses have appeared. Additionally, new computer tools based on mathematical calculations have been included, allowing for the simulation of the behavior of new electroactive species, configurations, and materials for RFBs, either independently or in association with experimental work. The number of reviews in **Table 1** also shows a tendency for the adoption of VRFBs rather than other architectures and the need to compete with Li-ion batteries, which are currently considered by many to be the most promising batteries. The exponential growth in review papers published over the last few years is not only a consequence of this fact, but also because the RFB configuration involves the synergy of multiple fields of science and technology. The electrochemistry of the redox pair and its chemical solubility, the corrosion of bipolar plates, the fluid mechanics of the electrolyte, the treatment and selection of carbon-based materials such as electrodes, and the separation processes performed through a membrane are just some examples of the complexity and multidisciplinary aspects of this technology that, ultimately, will be used for electrotechnical purposes. Therefore, the published review papers are useful not only to organize and clarify the main aspects of the technology, but also to engage all necessary scientific fields in this complex but promising technology.

Table 1. The main review articles about RFBs published in the last few decades.

Year	Ref.	Authors	Discussed Subject Matter
2006	[9]	Ponce de Léon et al.	The different RFB systems were compared considering the OCP, power density, EE and charge–discharge behaviour.
2011	[10]	Weber et al.	RFB chemistries, kinetics and transport of RFBs were discussed. The electrode/cell modeling and designs were reviewed as well as future research needs.
	[11]	Li et al.	The requirements for ion exchange membranes for VRFBs were reviewed, as well as the development prospects for next-generation materials.
	[12]	Skyllas-Kazacos et al.	Discussion focused on the technology in general. An historical review was also considered as well as the latest commercial developments and large-scale field testing.
2012	[13]	Kear et al.	Development, commercialisation history, and current performance properties of intermediate- and large-scale VRFBs were reviewed. The potential for VRFB systems to meet the economic requirements was compared to the economic performance of thermal-based generators.
	[14]	Leung et al.	The development of RFB systems was reviewed. It was concluded that fundamental studies on chemistry and kinetics are necessary for many RFB technologies.
	[15]	Wang et al.	The chemistries and progresses of Li-ion and RFB were reviewed and compared. The authors discussed the research status of a Li–RFB hybrid system and concluded that it was still in its infancy.
2013	[16]	Wang et al.	Review of the main developments, particullarly new chemistries reported since 2010. The field of NA-RFBs was also included (i.e., redox chemistries, new RFB configurations) and was limited to R&D on cell-level components,

Year	Ref.	Authors	Discussed Subject Matter
			excluding stack system, e.g., flow-field simulations, shunt-current analysis, and bipolar plate development.
	[17]	Shin et al.	Non-aqueous RFB (NA-RFB) systems were compared to aqueous RFBs in terms of the current and power density through membranes.
2014	[18]	Chakrabarti et al.	The application of ionic liquids (ILs) and deep eutetic solvents (DESs) in different RFB configurations was reviewed. The prospect of applying DESs in RFBs was discussed using the results reported in the literature considering the electrochemical engineering aspects of these solvents.
	[19]	Alotto et al.	The state-of-the-art of the most important plants in service and programs development were discussed. The most relevant research issues were debated.
2015	[20]	Pan and Wang	The redox species of RFB were discussed. It was concluded that most of the non-aqueous electrolytes were focused on the catholyte, that the anodic species were limited, and that to fabricate a NA-RFB with high energy density, the development of anodic species was necessary.
	[21]	Soloveichik	A discussion on the different types of flow batteries was conducted. Technical and economical issues were also approached.
	[22]	Kim et al.	The technical trends in the selection, characterization, evaluation, and modification of electrodes for VRFBs were reviewed between 1985 and 2015.
	[23]	Xu and Zhao	The various issues associated with flow batteries were summarized and a critical review on the numerical investigations of each issue was performed.
	[24]	Huang et al.	NA-RFBs were compared with aqueous systems. The parameters included wider voltage windows, intrinsically faster electron-transfer kinetics, and more

Year	Ref.	Authors	Discussed Subject Matter
			extended working temperature ranges.
2016	[25]	Winsber et al.	Overview focused on different flow-battery systems ranging from the classical inorganic to organic/inorganic to RFBs with organic redox-active cathode and anode materials in terms of technical, economic, and environmental aspects.
	[26]	Kowalski et al.	Review focused on describing the main advances in the developments of redox active organic molecules for all-organic flow batteries.
	[27]	Park et al.	Review on the development of flow batteries focused on materials and chemistries, i.e., conventional aqueous RFBs and the next-generation flow batteries. Despite progress, next-generation battery systems based on organic, iodine, polysulfide or semi-solid materials are still uncertain.
2017	[28]	Arenas et al.	Review focused on the engineering aspects of RFBs. An approach to RFB design and scale-up was performed in order to reduce the gap in technological and research awareness between the academic literature and the industry.
	[29]	Leung et al.	Review of organic based RFB. Emphasis was given to electrode reactions in both aqueous and non-aqueous electrolytes. It was concluded that organic RFB containing materials of high solubilities and multi-electron-transfers meet the cost target for practical applications at the grid scale and in the automotive industry.
	[30]	Ye et al.	The impact on the voltage efficiency, CE, and EE of the types and properties of membranes on the VRFBs were reviewed. Material modification of carbon-based electrodes, catalyst application, and electrolytes using solid redox-active compounds in semi-solid RFB systems were also discussed.
	[31]	Choi et al.	Vanadium electrolyte technologies from the viewpoint of VRFB design was reviewed providing a logical understanding of how the electrolyte design influences battery performance.

Year	Ref.	Authors	Discussed Subject Matter
	[32]	Li and Liu	Review comparing the future of RFB technology with Li-ion batteries. The questions regarding breakthroughs needed to enable large-scale deployment of RFBs remain. It was concluded that finding a low-cost, highly soluble aqueous system was the most attractive approach.
	[33]	Musbaudeen et al.	Membraneless cell designs for RFBs were reviewed considering the evolutionary trend of membraneless flow cell design concepts.
	[34]	Zhou et al.	The progress in research on the transport phenomena of RFBs, as well as the critical transport issues, were reviewed.
2018	[35]	Chen et al.	The review focused on the advantages of organic materials for RFBs compared with inorganic-based RFBs and on the recent progress in organic RFBs in redox active materials. The properties of the electrolyte and the design of the membrane, including polymeric and ceramic membranes, were also debated.
	[36]	Zhang et al.	The performance metrics of RFBs and the progress on the key components of RFBs, including the membranes and new redox-active electrolytes, were reviewed.
	[37]	Liu et al.	The state-of-the-art of several modification methods on the electrode materials for VRFB were reviewed.
	[38]	Cao et al.	Review focused on vanadium electrolyte additives studied for VRFB regarding its function, including precipitation inhibitors, immobilizing agents, kinetic enhancers, electrolyte impurities, and chemical reductants.
	[39]	Xu et al.	Review focus on understanding the evaluation criteria of energy efficiency for RFBs.

Year	Ref.	Authors	Discussed Subject Matter
2019	[40]	Ke et al.	The first review focused on the influence on RFB cell performance linked with flow field designs, including their implementation in stacks. Several aspects were considered, e.g., flow field architecture types, flow distribution, cell performance, large-scale stack designs, stack performance, optimization of non-uniform flow distributions, shunt currents, and localized current distributions.
	[41]	Arenas et al.	Review focused on the four main types of RFB employing zinc electrodes, i.e., zinc–bromine, zinc–cerium, zinc–air and zinc–nickel. The main drawbacks linked with zinc deposition and dissolution, particularly in acid media, were also reviewed.
	[42]	Minke and Turek	The literature focused on the techno-economic assessment of VFB was reviewed. The data regarding materials, system designs, and modelling approaches were considred and critically analyzed.
	[43]	Lourenssen et al.	The current state of the art of VRFB technology was discussed, including the design and working principles. The critical research areas were highlighted along with future developments.
	[44]	Narayan et al.	The authors discussed the basic requirements to be satisfied by next-generation aqueous RFBs and concluded that a safe, affordable, sustainable, and robust long-duration energy storage system was promising with next-generation RFBs.
	[45]	Hogue and Toghill	A review of the metal coordination complexes studied as electrolytes for NA-RFBs that were reported in the previous decade.
	[46]	Gubler	The review focused on the key requirements and current development trends for membranes and separators for the VRFB.
	[47]	Arenas et al.	The research needs were reviewed. It was concluded that most academic studies focus on the development of catalysts tested in small electrochemical

Year	Ref.	Authors	Discussed Subject Matter
			cells was not realistic for advancing RFB technology; they are limited to short-term laboratory experiments.
2020	[48]	Rhodes et al.	A review on NA-RFBs was conducted. It was concluded that these are predicted to be sustainable systems as the components are mostly organic materials and that NA-RFBs represent the next generation of RFB for green energy storage.
	[49]	Clemente and Costa-Castelló	A review focused on the RFB models and the main control strategies of RFB systems, as well as the main techniques to estimate the state of charge.
	[50]	Gencten and Sahin	The electrode materials for VRFBs were reviewed. It was concluded that graphene coatings, heteroatom doping, and metal oxide modified carbon-based electrodes were mainly used. Most of the work regarding VRFBs is focused on novel stack design, electrode, membrane, and electrolyte components.
	[51]	Kwabi et al.	The review focused on the electrolyte lifetime in aqueous organic RFB. It was concluded that RFBs are promising alternatives for surpassing lithium ion batteries and aqueous organic RFBs have potentially lower cost than their vanadium-based counterparts.
	[52]	Zhong et al.	The state of the art of organic electroactive molecules for aqueous and non-aqueous RFBs were reviewed. It was concluded that this field was still in its initial stage since no RFB has been deemed suitable to replace VRFBs.
	[53]	Gentil et al.	The challenges in the past five years for the development of next-generation RFBs were discussed. NA-RFBs were not included. The review addressed aqueous organic RFBs (AO-RFBs) and the technologies developed to increase the energy density of RFBs.
	[54]	Ortiz-Martínez	This work reviewed the advances in the application of ILs in RFBs. The authors showed that most of the studies focused on the use of Ils as

Year	Ref.	Authors	Discussed Subject Matter
			supporting electrolytes and the latest studies showed their potential as electroactive species and electrolyte membranes.
	[55]	Ambrosi and Webster	The review focused on the most commonly used 3D printing fabrication methods as well as on the additive manufacturing technologies for the fabrication of RFB components that were classified according to the electrolyte nature used (i.e., aqueous and non-aqueous solvents).
	[56]	Aberoumand et al.	The review focused on VRFB technology methods developed to enhance the performance of the electrode and electrolyte as the main components.
	[57]	Esan et al.	The review focused on the modeling and simulation of RFB beyond the all-vanadium, including soluble lead–acid, semisolid, organic, zinc–nickel, zinc–bromine, hydrogen–bromine, sodium–air, and vanadium–cerium flow batteries.
	[58]	Tempelman et al.	A review on the most recent advancements in the structure design and optimization to improve the selectivity and conductivity of membranes.
2021	[5]	Wang et al.	The research progress of insoluble flow batteries was reviewed. The key challenges from the fundamental research point of view and practical application perspectives were compared.
	[3]	Sánchez-Díez et al.	A review of the aqueous system technologies that potentially fulfill cost requirements and enable large scale storage.
	[59]	Zhang and Sun	The review focused on iron-based aqueous RFBs. The main achievements were highlightned and it was concluded that there is no “perfect chemistry”.
	[60]	Emmet and Roberts	The review focused on the advances in aqueous RFBs with lesser known chemistries than vanadium. The authors expect that these chemistries will

7. Gouveia, J.R., Silva, E., Mata, T.M., Mendes, A., Caetano, N.S., Martins, A.A. Life Cycle Assessment of a Renewable Energy Generation System with a Vanadium Redox Flow Battery in a NZEB Household. Energy Rep. 2020, 6, 87–94.

Year	Ref.	Authors	Discussed Subject Matter
			become more viable than vanadium due to their lower material costs and less caustic nature.
	[61]	Symons	The review focused on the use of quinones for RFBs. It was concluded that most of the development on quinone-based RFBs is far from being commercially viable. The stability of quinones in high potential electrolytes is not enough and the attempts have led to very low overall cell voltages.
	[62]	Aramendia et al.	The studies and numerical models carried out by means of computational fluid dynamics (CFD) techniques were reviewed. Studies with stacks and approaches for VRFB optimization with CFD based models and different flow field designs to improve the electrochemical performance were discussed.
	[63]	Yuan et al.	The development of the membranes used in the three types of NA-RFBs were summarized and a comprehensive overview of the fundamentals, classification, and performance of the membranes applied in NA-RFBs was provided.

15. Wan […] ross Road between Li-Ion and Redox Flow Batteries. Adv. Energy Mater. 2012, 2, 770–779.

16. Wang, W.; Luo, Q.; Li, B.; Wei, X.; Li, L.; Yang, Z. Recent Progress in Redox Flow Battery Research and Development. Adv. Funct. Mater. 2013, 23, 970–986.

1?. Shin, S.-H.; Yun, S.-H.; Moon, S.-H. A Review of Current Developments in Non-Aqueous Redox Flow Batteries: Characterization of Their Membranes for Design Perspective. RSC Adv. 2013, 3, 9095–9116.

18. Chakrabarti, M.H.; Mjalli, F.S.; AlNashef, I.M.; Hashim, M.A.; Hussain, M.A.; Bahadori, L.; Low, C.T.J. Prospects of Applying Ionic Liquids and Deep Eutectic Solvents for Renewable Energy Storage by Means of Redox Flow Batteries. Renew. Sustain. Energy Rev. 2014, 30, 254–270.

19. Alotto, P.; Guarnieri, M.; Moro, F. Redox Flow Batteries for the Storage of Renewable Energy: A Review. Renew. Sustain. Energy Rev. 2014, 29, 325–335.

20. Pan, F.; Wang, Q. Redox Species of Redox Flow Batteries: A Review. Molecules 2015, 20, 20499–20517.

21. Soloveichik, G.L. Flow Batteries: Current Status and Trends. Available online: https://pubs.acs.org/doi/abs/10.1021/cr500720t (accessed on 19 August 2021).

2.1. Inorganic Aqueous

2.1.1. Vanadium Redox Flow Batteries (VRFB)

The first publication on all-vanadium or VRFB electrodes was performed in 1987 by Rychcik and Skyllas-Kazacos and was focused on the carbon–polymer composite electrode [64]. Since then, several studies on electrodes for the VRFB have been reported. Organic electroactive molecules in both non-aqueous and aqueous RFBs can be considered to be in their infancy since no RFBs has been reported to replace the VRFB. Therefore, several efforts to develop more advanced RFBs with organic electroactive materials toward practical applications are being pursued and put in practice [52].

The vanadium electrolytes are a key component for VRFB due to their performance and the cost–benefit ratio involved. The electrochemical activity and the concentration and stability of vanadium ions determine the energy density and the reliability of the VRFB. Therefore, these factors contribute to electrolyte technology improvement and are still under optimization towards a more reliable and cost-effective system [65][66][67][68]. The development of new electrode components for VRFB systems will certainly increase in the short–medium term for many industrial and residential applications.

Despite RFBs having been explored both with aqueous and non-aqueous electrolytes, to date aqueous electrolytes are the only commercially viable option [69]. Water is then used as solvent, mainly due to its high availability and therefore low cost. The cost involved is particularly relevant for a technology with relatively low energy density when compared to other battery technologies. Therefore, the electrolyte cost represents one of the major investment costs [69][70]. Moreover, aqueous electrolytes are highly conductive, have a lower viscosity, and can dissolve a wide range of transition metal salts, providing high ionic mobility [69].

The all-vanadium RFBs were proposed in 1988 by Skyllas-Kazacos to overcome problems related to crossover, low reversibility, and self-discharge of the earliest proposed RFBs by taking advantage of the four oxidation states of vanadium. This technology became known as generation 1 redox flow battery (G1 RFB) [71][72]. Later, it was proposed to replace the V(IV)/V(V) pair in the positive side of a V/HBr/HCl electrolyte to increase the operational temperature range of the battery leading to the development of the generation 2 redox flow battery (G2 RFB) [73][74][75]. Finally, in 2010, Pacific North-Northwest Laboratories proposed the use of an acidic mixture (H_2SO_4 and HCl) strategy to increase the solubility of vanadium ions in electrolyte and to achieve superior performance, which was referred to as the generation 3 RFB (G3 RFB). **Table 2** shows the main differences between the three generations of VRFB that will be discussed in the next sections. The information was collected from different references and organized to provide a quick picture of the main difference between the three generations of RFBs.

22. Kim, K.J.; Park, M.-S.; Kim, Y.-J.; Kim, J.H.; Dou, S.X.; Skyllas-Kazacos, M. A Technology Review of Electrodes and Reaction Mechanisms in Vanadium Redox Flow Batteries. J. Mater. Chem. A 2015, 3, 16913–16933.
23. Xu, Q.; Zhao, T.S. Fundamental Models for Flow Batteries. Prog. Energy Combust. Sci. 2015, 49, 40–58.
24. Huang, Y.; Gu, S.; Yan, Y.; Li, S.F.Y. Nonaqueous Redox-Flow Batteries: Features, Challenges, and Prospects. Curr. Opin. Chem. Eng. 2015, 8, 105–113.
25. Winsberg, J.; Hagemann, T.; Janoschka, T.; Hager, M.D.; Schubert, U.S. Redox-Flow Batteries: From Metals to Organic Redox-Active Materials. Angew. Chem. Int. Ed. 2017, 56, 686–711.
26. Kowalski, J.A.; Su, L.; Milshtein, J.D.; Brushett, F.R. Recent Advances in Molecular Engineering of Redox Active Organic Molecules for Nonaqueous Flow Batteries. Curr. Opin. Chem. Eng. 2016, 13, 45–52.
27. Park, M.; Ryu, J.; Wang, W.; Cho, J. Material Design and Engineering of Next-Generation Flow-Battery Technologies. Nat. Rev. Mater. 2016, 2, 1–18.
28. Arenas, L.F.; Ponce de León, C.; 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.

Table 2. Comparison between the three generations of RFBs (G1, G2, and G3).

	G1	G2	G3
Name	All-Vanadium	Vanadium-Polyhalide	Mixed Acid Vanadium
Positive Couple	V(III)/V(II)	V(III)/V(II)	V(III)/V(II)
Negative Couple	V(IV)/V(V)	$Cl^{-}/ClBr^{2-}$	V(IV)/V(V)
Supporting Electrolyte	H_2SO_4	HBr and HCl	H_2SO_4 and HCl
Vanadium Concentration (M)	1.5–2 [76]	2.0–3.0 [77]	2.5–3.0 [78]
Temperature Range (°C)	10–40 [76]	0–50 [79]	−5–50 [4][78][80]
Specific Energy (Wh/L)	20–33 [77]	35–70 [77]	22–40 [4][78][80]

2… e León, … J.
3… Redox … s.
3…
… 2017,
3… Energy
3… Cell
3… ne
35. Chen, H.; Cong, G.; Lu, Y.-C. Recent Progress in Organic Redox Flow Batteries: Active Materials, Electrolytes and Membranes. J. Energy Chem. 2018, 27, 1304–1325.

All-Vanadium Redox Flow Battery (G1 RFB)

All-vanadium RFBs are one of the most technologically advanced redox flow systems, and there are already several commercial systems installed [81]. The largest one so far announced has a rated output of 200 MW and a capacity of 800 MWh and is located in Dalian, Liaoning Province, China [4]. The all-vanadium chemistry has one of the highest redox potentials (1.26 V) that can be fully used with low risk of starting the hydrogen evolution reaction and no permanent consequences if the species from the positive side cross over to the negative side, or vice versa. However, species crossover is still challenging since it induces self-discharge. V^{2+} reacts easily with oxygen, which discharges the negative tank of the battery, and V^{5+} precipitates at temperatures of ca. 40 °C [43][82][83]. This technology has already proven its effectiveness and the main research looks to optimize its performance and efficiency and achieve higher power outputs at lower prices. This objective has been mostly tackled by targeting the ohmic resistances, one of the biggest causes of power loss in VRFBs [84]. The electrodes and bipolar plates are the main subjects of research to reduce the overall resistance.

In the last few years, several manuscripts have reported outstanding results accomplished in innovative and creative ways to produce, treat, or dope the electrodes. For instance, X. L. Zhou and his team, in 2016, showed a modification of carbon papers by KOH activation of the fibers, achieving 82% energy efficiency at 400 mA cm^{-2} in charge–discharge cycles [85]. In the same year, L. Wei et al. [86] reported a VRFB with an energy efficiency of 80.1% at 300 mA cm^{-2} by depositing copper nanoparticles on graphite felt. Two years later, Sun and coworkers proposed a new way to produce carbon-based materials with larger surface areas for VRFB, which consisted of electrospinning polyacrylonitrile and polystyrene binary solutions, forming fiber bundles. When these woven nanofibers were tested as prepared in a cell, the group achieved an energy efficiency of 80.1% at 200 mA cm^{-2} [87]. By using the electrospinning method, Busacca et al. [88] synthesized a composite material based on nickel manganite and carbon nanofibers that had ca. 80% EE at 200 mA cm^{-2}. The most remarkable VRFB performances reported to date belong to H. R. Jiang and Z. Xu and their coworkers. The former reached an EE of 80.8% at 600 mA cm^{-2}, and the battery was cycled for 20,000 cycles without substantial degradation at the same current density. This was accomplished with a simple treatment in a furnace under ambient air at 500 °C for 8 h, followed by electrodeposition of bismuth nanoparticles on the negative graphite felt and the addition of an interdigitated flow field in the battery [89]. Xu and coworkers reported 80.4% EE at 500 mA cm^{-2} with an average EE loss of 0.01% through 1000 cycles. In this work, they used a quenching–cracking strategy to change the morphology of the fibers in the production of carbon felt, followed by graphitization, and doping with sulfur [90]. An interesting production method for a new material to be used as electrode was reported by I. Mustafa and colleagues. They produced a macro-porous carbon nano-foam by implementing a freeze-drying step in their tape casting fabrication method. Using these electrodes, their cell achieved an EE of ca. 80% at 50 mA cm^{-2} for 100 cycles [91].

The bipolar plates also contribute to the ohmic resistances; however, it is not enough to use a more conductive material, the electrical contact resistance between the bipolar plate and the electrode also needs to be reduced. Taking this into account, publications that focus on bipolar plates aim to lessen the ohmic resistances by reducing the electrical resistance of the material, the contact resistance, or both. Han et al. [92] produced bipolar plates with TiO_2 nanotubes coated with IrO_x. By using this material, it was possible to reduce the thickness of the bipolar

36. Zhang, C.; Zhang, L.; Ding, Y.; Peng, S.; Guo, X.; Zhao, Y.; He, G.; Yu, G. Progress and Prospects of Next-Generation Redox Flow Batteries. Energy Storage Mater. 2018, 15, 324–350.
37. Liu, T.; Li, X.; Zhang, H.; Chen, J. Progress on the Electrode Materials towards Vanadium Flow Batteries (VFBs) with Improved Power Density. J. Energy Chem. 2018, 27, 1292–1303.
38. Cao, L.; Skyllas-Kazacos, M.; Menictas, C.; Noack, J. A Review of Electrolyte Additives and Impurities in Vanadium Redox Flow Batteries. J. Energy Chem. 2018, 27, 1269–1291.
39. Xu, Q.; Ji, Y.N.; Qin, L.Y.; Leung, P.K.; Qiao, F.; Li, Y.S.; Su, H.N. Evaluation of Redox Flow Batteries Goes beyond Round-Trip Efficiency: A Technical Review. J. Energy Storage 2018, 16, 108–116.
40. Ke, X.; Prahl, J.M.; Alexander, J.I.D.; Wainright, J.S.; Zawodzinski, T.A.; Savinell, R.F. Rechargeable Redox Flow Batteries: Flow Fields, Stacks and Design Considerations. Chem. Soc. Rev. 2018, 47, 8721–8743.
41. Arenas, L.F.; Loh, A.; Trudgeon, D.P.; Li, X.; Ponce de León, C.; Walsh, F.C. The Characteristics and Performance of Hybrid Redox Flow Batteries with Zinc Negative Electrodes for Energy Storage. Renew. Sustain. Energy Rev. 2018, 90, 992–1016.
42. Minke, C.; Turek, T. Materials, System Designs and Modelling Approaches in Techno-Economic Assessment of All-Vanadium Redox Flow Batteries—A Review. J. Power Sources 2018, 376, 66–81.
43. Lourenssen, K.; Williams, J.; Ahmadpour, F.; Clemmer, R.; Tasnim, S. Vanadium Redox Flow Batteries: A Comprehensive Review. J. Energy Storage 2019, 25, 100844.
44. Narayan, S.R.; Nirmalchandar, A.; Murali, A.; Yang, B.; Hoober-Burkhardt, L.; Krishnamoorthy, S.; Prakash, G.K.S. Next-Generation Aqueous Flow Battery Chemistries. Curr. Opin. Electrochem. 2019, 18, 72–80.
45. Hogue, R.W.; Toghill, K.E. Metal Coordination Complexes in Nonaqueous Redox Flow Batteries. Curr. Opin. Electrochem. 2019, 18, 37–45.
46. Gubler, L. Membranes and Separators for Redox Flow Batteries. Curr. Opin. Electrochem. 2019, 18, 31–36.
47. Arenas, L.F.; Ponce de León, C.; Walsh, F.C. Redox Flow Batteries for Energy Storage: Their Promise, Achievements and Challenges. Curr. Opin. Electrochem. 2019, 16, 117–126.
48. Rhodes, Z.; Cabrera-Pardo, J.R.; Li, M.; Minteer, S.D. Electrochemical Advances in Non-Aqueous Redox Flow Batteries. Isr. J. Chem. 2021, 61, 101–112.
49. Clemente, A.; Costa-Castelló, R. Redox Flow Batteries: A Literature Review Oriented to Automatic Control. Energies 2020, 13, 4514.

plates when compared to the commercial graphite typically used. Ca. 83% of EE at 40 mA cm^{-2} was reported and the battery was cycled for 100 cycles at the same current density without substantial degradation. A new low-carbon-content design based on the bridging effect of graphene for bipolar plates published by Liao and colleagues [93] achieved ca. 83% EE at 140 mA cm^{-2}. The same group proposed another low-carbon-content bipolar plate, composed of graphene, carbon fibers and graphite powders, having reached ca. 81% EE at 140 mA cm^{-2} with these bipolar plates [94]. Jiang et al. [95] proposed a way to exclude the layer of resin on the surface of composite bipolar plates by using a surface treatment that grows cactus-like carbon nanofibers from catalyst cores. This technique resulted in an EE of ca. 80% at 160 mA cm^{-2}.

Membranes have an important influence on two factors: the ionic conductivity and vanadium crossover. Reducing crossover prevents self-discharge, however this is normally accomplished by reducing the ionic conductivity. For this reason, there needs to be a tradeoff between these two parameters to assemble a battery that has a high ionic conductivity and low vanadium crossover. D. Zheng and colleagues studied a hybrid membrane using the solution casting method, where they embedded UiO-66-SO_3H in a Nafion matrix to enhance the ion selectivity of the membrane. With this strategy, a vanadium permeation of one-third was achieved compared to a recasting Nafion membrane, an EE of 81% at 160 mA cm^{-2}, and the cell could be cycled for 1000 cycles at 80 mA cm^{-2} without a noticeable performance change [96]. There was also an environmentally friendly method proposed to produce positively-charged membranes derived from pyridine-containing poly(aryl ether ketone ketone), where B. Zhang et al. [97] reduced the vanadium permeability to $3.4 \cdot 10^{-7}$ cm^2 min^{-1}, achieving 80.1% EE at 180 mA cm^{-2} and stable cycling for 1000 cycles (ca. 600 at 120 mA cm^{-2} and 400 at 140 mA cm^{-2}). Wan et al. [98] developed a composite membrane with a dense but thin polybenzimidazole layer and a thick but porous layer made with polybenzimidazole electrospun nanofibers. This novel technique of using polybenzimidazole demonstrated a vanadium permeability one order of magnitude lower than a Nafion 212 membrane, an EE of 82% at 150 mA cm^{-2}, and stable operation for 200 cycles at 80 mA cm^{-2}. In 2020, Kushner and colleagues studied the factors that impact the transport phenomena through the membrane in a VRFB. In this manuscript, it was found that there are few studies that analyze crossover at currents different from zero, which is a major flaw in these works, since migrating fluxes are increased at high current densities [99]. Shin et al. [100] suggest an innovative strategy to alleviate electrolyte imbalances, which are caused by crossover and water transport through the membrane. The proposed strategy is based on using different concentrations of sulfuric acid on the positive and negative electrolyte.

VRFBs are one of the few RFB technologies that are in a very advanced phase of development, mainly due to the large boost of technological improvement given in the last few years. VRFB have outstanding properties for stationary applications and have one of the best performances in this sector; however, they still have room to grow. Moreover, it is expected that this technology will have a gigantic impact on the energy production transition. It will also impact on the share of the energy storage market in the next few years, since at present there are no alternatives good enough to take its place.

Vanadium-Polyhalide Redox Flow Battery (G2 RFB)

RFBs are well known for their long working life and decoupled power and energy. However, one of their major drawbacks is their low energy density, which ultimately limits their commercial application for stationary storage. A

50. Gentten, M.; Sahin, Y. A Critical Review on Progress of the Electrode Materials of Vanadium Redox Flow Battery. Int. J. Energy Res. 2020, 44, 7903–7923.

51. Kwabi, D.G.; Ji, Y.; Aziz, M.J. Electrolyte Lifetime in Aqueous Organic Redox Flow Batteries: A Critical Review. Chem. Rev. 2020, 120, 6467–6489.

52. Zhong, F.; Yang, M.; Ding, M.; Jia, C. Organic Electroactive Molecule-Based Electrolytes for Redox Flow Batteries: Status and Challenges of Molecular Design. Front. Chem. 2020, 8, 451.

53. Gentil, S.; Reynard, D.; Girault, H.H. Aqueous Organic and Redox-Mediated Redox Flow Batteries: A Review. Curr. Opin. Electrochem. 2020, 21, 7–13.

54. Ortiz-Martínez, V.M.; Gómez-Coma, L.; Pérez, G.; Ortiz, A.; Ortiz, I. The Roles of Ionic Liquids as New Electrolytes in Redox Flow Batteries. Sep. Purif. Technol. 2020, 252, 117436.

55. Ambrosi, A.; Webster, R.D. 3D Printing for Aqueous and Non-Aqueous Redox Flow Batteries. Curr. Opin. Electrochem. 2020, 20, 28–35.

56. Aberoumand, S.; Woodfield, P.; Shabani, B.; Dao, D.V. Advances in Electrode and Electrolyte Improvements in Vanadium Redox Flow Batteries with a Focus on the Nanofluidic Electrolyte Approach. Phys. Rep. 2020, 881, 1–49.

57. Esan, O.C.; Shi, X.; Pan, Z.; Huo, X.; An, L.; Zhao, T.S. Modeling and Simulation of Flow Batteries. Adv. Energy Mater. 2020, 10, 2000758.

58. Tempelman, C.H.L.; Jacobs, J.F.; Balzer, R.M.; Degirmenci, V. Membranes for All Vanadium Redox Flow Batteries. J. Energy Storage 2020, 32, 101754.

59. Zhang, H.; Sun, C. Cost-Effective Iron-Based Aqueous Redox Flow Batteries for Large-Scale Energy Storage Application: A Review. J. Power Sources 2021, 493, 229445.

60. Emmett, R.K.; Roberts, M.E. Recent Developments in Alternative Aqueous Redox Flow Batteries for Grid-Scale Energy Storage. J. Power Sources 2021, 506, 230087.

61. Symons, P. Quinones for Redox Flow Batteries. Curr. Opin. Electrochem. 2021, 29, 100759.

62. Aramendia, I.; Fernandez-Gamiz, U.; Martinez-San-Vicente, A.; Zulueta, E.; Lopez-Guede, J.M. Vanadium Redox Flow Batteries: A Review Oriented to Fluid-Dynamic Optimization. Energies 2021, 14, 176.

63. Yuan, J.; Pan, Z.-Z.; Jin, Y.; Qiu, Q.; Zhang, C.; Zhao, Y.; Li, Y. Membranes in Non-Aqueous Redox Flow Battery: A Review. J. Power Sources 2021, 500, 229983.

64. Rychcik, M.; Skyllas-Kazacos, M. Evaluation of Electrode Materials for Vanadium Redox Cell. J. Power Sources 1987, 19, 45–54.

65. Roznyatovskaya, N.; Noack, J.; Mild, H.; Fühl, M.; Fischer, P.; Pinkwart, K.; Tübke, J.; Skyllas-Kazacos, M. Vanadium Electrolyte for All-Vanadium Redox-Flow Batteries: The Effect of the

possible strategy to increase this parameter is to increase the solubility of the redox species in the solvent and therefore to store more energy in the same volume of electrolyte. Accordingly, it was proposed that a vanadium–halide solution (HBr and HCl) electrolyte could achieve higher solubilities for vanadium ions, the reactions for which are indicated in Equations (1)–(3) [73][74][75].

Negative Side: $2\,VCl_3 + 2\,e^- \rightleftharpoons 2\,VCl_2 + 2\,Cl^-$ (1)

Positive Side: $2\,Br^- + Cl^- \rightleftharpoons ClBr_2^- + 2\,e^-$ (2)

Positive Side: $Br^- + 2\,Cl^- \rightleftharpoons BrCl_2^- + 2\,e^-$ (3)

A typical electrolyte is composed of 7–9 M HBr with 1.5–2 M HCl and 2–3 M vanadium. Due to the higher solubility of vanadium bromide, the volume of the positive half-cell electrolyte tank can be severely reduced, leading to an enhanced specific energy of 25–50 Wh kg^{-1} and an energy density in the range of 35–70 Wh L^{-1} [77]. Additionally, since a mixed solution of V/HBr/HCl is used in both half-cells, the long-term issues associated with cross-contamination through the membrane are mitigated [77][101][102]. Another interesting feature about this configuration is that since there is no V(IV)/V(V) pair on the positive side, this battery does not suffer from the limited solubility of V^{5+} at high temperatures, increasing the temperature range of operation to 0–50 °C [79]. However, the possibility of bromine vapor formation is one of the major drawbacks of this configuration. To minimize this, it is common to use complexing agents such as tetrabutylammonium bromide, polyethylene glycol, N-methyl-N-ethyl morpholinium bromide, and Nmethyl-N-ethyl pyrrolidinium. As consequence, a feature of G2 RFBs is the formation of a second phase composed of the bromine complexing agents during the cell charge step [101][102][103]. Despite the efforts to produce and screen more efficient compounds for this technology [77][104], these complexing agents are too expensive and still represent a significant economical barrier. The development of more cost-effective alternatives to prevent the bromine evolution are mandatory for the commercialization of the G2 RFB [101][102][103].

Mixed Acid Vanadium Redox Flow Battery (G3 RFB)

Another way to optimize the solubility of redox species is to use electrolyte additives to thermodynamically increase the solubility threshold and therefore to improve the kinetics, stability, and energy density of redox flow batteries. It is known that vanadium ions V^{2+}, V^{3+}, and VO^{2+}(i.e., V^{4+}) precipitate as its sulfate salts at low temperatures through the exothermal reactions represented by Equations (4)–(6) [4][38][105].

$$SO_4^{2-} + V^{2+} \rightarrow VSO_4 \quad (4)$$

$$3\,SO_4^{2-} + 2\,V^{3+} \rightarrow V_2(SO_4)_3 \quad (5)$$

$$SO_4^{2-} + VO^{2+} \rightarrow VO(SO_4) \quad (6)$$

However, VO_2^+ (i.e., V^{5+}) does not precipitate as a sulphate salt but it reacts with water in an endothermal reaction [4][38][105]:

$$2\,VO_2^+ + H_2O \rightarrow V_2O_5 + 2H^+ \quad (7)$$

Counter-Ion. Batteries 2019, 5, 13.

66. Heo, J.; Han, J.-Y.; Kim, S.; Yuk, S.; Choi, C.; Kim, R.; Lee, J.-H.; Klassen, A.; Ryi, S.-K.; Kim, H.-T. Catalytic Production of Impurity-Free V 3.5+ Electrolyte for Vanadium Redox Flow Batteries. Nat. Commun. 2019, 10, 4412.

67. Martin, J.; Schafner, K.; Turek, T. Preparation of Electrolyte for Vanadium Redox-Flow Batteries Based on Vanadium Pentoxide. Energy Technol. 2020, 8, 2000522.

68. Zhang, Z.H.; Wei, L.; Wu, M.C.; Bai, B.F.; Zhao, T.S. Chloride Ions as an Electrolyte Additive for High Performance Vanadium Redox Flow Batteries. Appl. Energy 2021, 289, 116690.

69. Endres, F. Ionic Liquids: Promising Solvents for Electrochemistry. Z. Für Phys. Chem. 2004, 218, 255–284.

70. Viswanathan, V.; Crawford, A.; Stephenson, D.; Kim, S.; Wang, W.; Li, B.; Coffey, G.; Thomsen, E.; Graff, G.; Balducci, P.; et al. Cost and Performance Model for Redox Flow Batteries. J. Power Sources 2014, 247, 1040–1051.

71. Lim, H.S.; Lackner, A.M.; Knechtli, R.C. Zinc-Bromine Secondary Battery. J. Electrochem. Soc. 1977, 124, 1154–1157.

72. Rychcik, M.; Skyllas-Kazacos, M. Characteristics of a New All-Vanadium Redox Flow Battery. J. Power Sources 1988, 22, 59–67.

73. Kazacos, M.; Skyllas-Kazacos, M. High Energy Density Vanadium Electrolyte Solutions, Methods of Preparation Thereof and All-Vanadium Redox Cells and Batteries Containing High Energy Vanadium Electrolyte Solutions. CA2220075C, 7 September 1996.

74. Skyllas-Kazacos, M. Vanadium/Polyhalide Redox Flow Battery. U.S. Patent US7320844B2, 22 January 2008.

75. Skyllas-Kazacos, M. Novel Vanadium Chloride/Polyhalide Redox Flow Battery. J. Power Sources 2003, 124, 299–302.

76. Wu, X.; Liu, J.; Xiang, X.; Zhang, J.; Hu, J.; Wu, Y. Electrolytes for Vanadium Redox Flow Batteries. Pure Appl. Chem. 2014, 86, 661–669.

77. Skyllas-Kazacos, M.; Kazacos, G.; Poon, G.; Verseema, H. Recent Advances with UNSW Vanadium-Based Redox Flow Batteries. Int. J. Energy Res. 2010, 34, 182–189.

78. Li, L.; Kim, S.; Wang, W.; Vijayakumar, M.; Nie, Z.; Chen, B.; Zhang, J.; Xia, G.; Hu, J.; Graff, G.; et al. A Stable Vanadium Redox-Flow Battery with High Energy Density for Large-Scale Energy Storage. Adv. Energy Mater. 2011, 1, 394–400.

79. Menictas, C.; Skyllas-Kazacos, M.; Lim, T.M. Advances in Batteries for Medium and Large-Scale Energy Storage; Elsevier: Amsterdam, The Netherlands, 2015; ISBN 978-1-78242-013-2.

Therefore, increasing temperature will increase the solubility of vanadium salts but will also shift Equation (7) to the right, reducing the amount of V^{5+} dissolved. This leads to a tradeoff situation where higher temperatures will favor the solubility of V^{2+}, V^{3+}, and V^{4+} but will disfavor the solubility of V^{5+}

If the operational SoC window is narrowed, the concentration of each vanadium species never reaches values high enough to precipitate and therefore it is possible to increase the temperature window. Additionally, operating at lower concentrations causes a similar effect; however, ultimately, both methods decrease the energy density since the former decreases the amount of energy stored per mol of vanadium and the latter decreases the amount of vanadium available in the electrolyte to store the energy [106]. The chemical equilibrium of these reactions needs to be shifted in order to increase the solubility of vanadium, or at least decrease the kinetics of the precipitation reactions [4].

The Pacific Northwest National Laboratory proposed a possible alternative to solve this problem by adding hydrochloric acid (HCl) to the electrolyte solution, resulting in the mixed-acid vanadium redox flow battery (G3 RFB). This way, it is possible to increase the concentration of H^+, shifting the chemical equilibrium of Equation (7) to decrease the precipitation of V_2O_5 without increasing the concentration of SO_4^{2-} ions [78]. In fact, by using the Mixed-Acid electrolyte it was possible not only to increase the energy density by 70%, but also to achieve wider temperature ranges, i.e., from 10 to 40 °C and from −5 to 50 °C and thus potentially removing the need of temperature control over the electrolyte [4][78][80].

In 2013, Kim et al. [107] reported a 1.1 kW stack operating at 80 mA cm^{-2} with 82% energy efficiency. The same group also reported that the mixed-acid electrolyte presented a lower pressure drop and therefore lower pumping losses due to an electrolyte with lower viscosity and no precipitation at temperatures higher than 45 °C.

In 2016, Reed et al. [108] also reported a kW class stack operating at 320 mA cm^{-2} with 75% energy efficiency due to improved electrode microstructure and flow field design, and also confirmed operations above 50 °C without detrimental effects. In 2019, the viscosity, conductivity, and electrochemical properties were investigated and optimized by Yang et al. [109], and it was concluded by their group that the optimal battery efficiency and capacity would be reached at 2.2 M vanadium concentration, 2.75 M sulfate concentration, and 5.8 M chloride ion concentration. However, the main drawback of this strategy is the presence of chloride ions, which can lead to chlorine evolution at the positive electrode, which implies not only safety hazards but also consequences such as thermal precipitation of V^{5+} and pump blocking [4][38][108][110]. Despite several efforts to improve and optimize the mixed-acid RFB [111][112][113][114], and studies showed that the mixed-acid electrolyte can operate until 1.7 V without gas evolution [115], it still remains one of the biggest threats to the commercialization of this technology [3]. There are also studies about using immobilizing agents, such as phosphoric acid (H_3PO_4) and ammonium phosphate ($(NH_4)_3PO_4$, but improving the vanadium solubility in RFBs involves complex and controversial chemical processes, and it still is an open topic of discussion [4][38][79][105][109][110].

2.1.2. Polyoxometalates

80. Rahman, F.; Skyllas-Kazacos, M. Vanadium Redox Battery: Positive Half-Cell Electrolyte Studies. J. Power Sources 2009, 189, 1212–1219.
81. Bryans, D.; Amstutz, V.; Girault, H.H.; Berlouis, L.E.A. Characterisation of a 200 KW/400 KWh Vanadium Redox Flow Battery. Batteries 2018, 4, 54.
82. Noack, J.; Roznyatovskaya, N.; Herr, T.; Fischer, P. The Chemistry of Redox-Flow Batteries. Angew. Chem. Int. Ed. 2015, 54, 9776–9809.
83. Cunha, A.; Martins, J.; Rodrigues, N.; Brito, F.P. Vanadium Redox Flow Batteries: A Technology Review. Int. J. Energy Res. 2015, 39, 889–918.
84. Aaron, D.; Tang, Z.; Papandrew, A.B.; Zawodzinski, T.A. Polarization Curve Analysis of All-Vanadium Redox Flow Batteries. J. Appl. Electrochem. 2011, 41, 1175.
85. Zhou, X.L.; Zeng, Y.K.; Zhu, X.B.; Wei, L.; Zhao, T.S. A High-Performance Dual-Scale Porous Electrode for Vanadium Redox Flow Batteries. J. Power Sources 2016, 325, 329–336.
86. Wei, L.; Zhao, T.S.; Zeng, L.; Zhou, X.L.; Zeng, Y.K. Copper Nanoparticle-Deposited Graphite Felt Electrodes for All Vanadium Redox Flow Batteries. Appl. Energy 2016, 180, 386–391.
87. Sun, J.; Zeng, L.; Jiang, H.; Chao, C.; Zhao, T. Formation of Electrodes by Self-Assembling Porous Carbon Fibers into Bundles for Vanadium Redox Flow Batteries. J. Power Sources 2018, 405, 106–113.
88. Busacca, C.; Blasi, O.D.; Giacoppo, G.; Briguglio, N.; Antonucci, V.; Blasi, A.D. High Performance Electrospun Nickel Manganite on Carbon Nanofibers Electrode for Vanadium Redox Flow Battery. Electrochim. Acta 2020, 355, 136755.
89. Jiang, H.R.; Sun, J.; Wei, L.; Wu, M.C.; Shyy, W.; Zhao, T.S. A High Power Density and Long Cycle Life Vanadium Redox Flow Battery. Energy Storage Mater. 2020, 24, 529–540.
90. Xu, Z.; Zhu, M.; Zhang, K.; Zhang, X.; Xu, L.; Liu, J.; Liu, T.; Yan, C. Inspired by "Quenching-Cracking" Strategy: Structure-Based Design of Sulfur-Doped Graphite Felts for Ultrahigh-Rate Vanadium Redox Flow Batteries. Energy Storage Mater. 2021, 39, 166–175.
91. Mustafa, I.; Susantyoko, R.; Wu, C.-H.; Ahmed, F.; Hashaikeh, R.; Almarzooqi, F.; Almheiri, S. Nanoscopic and Macro-Porous Carbon Nano-Foam Electrodes with Improved Mass Transport for Vanadium Redox Flow Batteries. Sci. Rep. 2019, 9, 17655.
92. Han, J.; Yoo, H.; Kim, M.; Lee, G.; Choi, J. High-Performance Bipolar Plate of Thin IrOx-Coated TiO2 Nanotubes in Vanadium Redox Flow Batteries. Catal. Today 2017, 295, 132–139.
93. Liao, W.; Zhang, Y.; Zhou, X.; Zhuang, M.; Guo, D.; Jiang, F.; Yu, Q. Low-Carbon-Content Composite Bipolar Plates: A Novel Design and Its Performance in Vanadium Redox Flow Batteries. ChemistrySelect 2019, 4, 2421–2427.

In the last few years, polyoxometalates (POMs) have been getting attention in the development of RFBs as an interesting electrolyte alternative for the next generation of RFBs. POMs are inorganic agglomerates composed of oxygen atoms and transition metals in their highest oxidation state to form metal-oxo units in which the metal ion acts as a polyhedral building block [116][117]. Among the various POMs structures, the most studied with application in RFB are the Keggin-type, $[XM_{12}O_{40}]^{n-}$ and Wells–Dawson-type structures, $[X_2M_{18}O_{62}]^{n-}$. Due to their vast structural diversity, POMs exhibit huge electrochemical versatility [118][119][120].

In 2018, Friedl et al. proposed POMs electrolytes for energy storage applications due to their relevant advantages [118]. The interaction of the redox centers of the POMs is generally reduced due to their large sizes [3] and the electrons added by reduction to the POMs are not allocated to a specific atom, therefore allowing for fast kinetics and high-power densities [121][122]. Moreover, the large size of the POMs, which range from 6 to 25 Å [123], along with the electrostatic repulsion, do not allow the permeation through the actual RFBs' commercial cation exchange membranes (CEM), preventing cross-over and mixing of the active species [124].

The interest in applying POMs to RFBs is vast and is still at an initial stage. The volumetric energy density of the VRFB is directly influenced by the number of reversible redox electrons, the difference in redox potentials between the catholyte and anolyte, and the solubility of the redox species in the electrolyte. The electrical storage capacity of VRFBs is limited to one electron per molecule. The structural diversity of POMs based on Keggin and Wells–Dawson-type structures exhibit the ability to exchange multiple electrons reversibly. The RFB energy density is frequently restricted by the solubility of the redox active species in the anolyte and catholyte. Therefore, it is easy to understand that one of the ways to increase the energy density is using energy-dense solid materials such as $LiFePO_4$ or Li_xTiO_2. The species are chosen based on the redox potentials to ensure that they intervene in the chemical reduction and oxidation of the solid components. This strategy allows for low viscosity, a high charging rate, and a high energy density [124].

Regarding solubility in the electrolyte, polyanions of POMs with small counterions are highly soluble in aqueous media. Some POMs have been reported as exhibiting high solubility, for instance using SiW_{12} a concentration of 0.875 mol L^{-1} was obtained [118]. With multiple redox-active centers per molecule, this enables a high energy density in the battery. Moreover, both SiW_{12} and PV_{14} are stable during the operation of the battery. Drops in capacity only seem to stem from a parasitic reaction with residual oxygen.

The solubility of POMs in non-aqueous solvents is generally low. For instance, VanGelder et al. [125] studied polyoxovanadate alkoxide clusters, $[V_6O_7(OR)_{12}]$ (R stands for OCH_3, OCH_2CH_3), as charge carriers in NA-RFBs [126]. These materials displayed four one-electron redox couples over a potential range of ~2 V. The result is that during the charging in a symmetric system, the polyalkoxovanadate undertakes a two-electron reduction at the negative electrode concurrently with a two-electron oxidation at the positive electrode. To further enhance energy density, the solubility of the polyalkoxovanadate may be increased by replacing several surface alkoxy groups with ethers. Clusters with mixed ether/alkoxy group surface functionalization displayed improved solubility (up to 1.2 M in 0.1 M [TBA][PF6] in ACN). While the increased solubility in organic solvent and multi-electron redox chemistry is promising for enhanced energy density, preliminary testing of the functionalized polyoxovanadate clusters in a RFB

94. Liao, W.; Jiang, F.; Zhang, Y.; Zhou, X.; He, Z. Highly-Conductive Composite Bipolar Plate Based on Ternary Carbon Materials and Its Performance in Redox Flow Batteries. Renew. Energy 2020, 152, 1310–1316.

95. Jiang, F.; Liao, W.; Ayukawa, T.; Yoon, S.-H.; Nakabayashi, K.; Miyawaki, J. Enhanced Performance and Durability of Composite Bipolar Plate with Surface Modification of Cactus-like Carbon Nanofibers. J. Power Sources 2021, 482, 228903.

96. Zhang, D.; Xin, L.; Xia, Y.; Dai, L.; Qu, K.; Huang, K.; Fan, Y.; Xu, Z. Advanced Nafion Hybrid Membranes with Fast Proton Transport Channels toward High-Performance Vanadium Redox Flow Battery. J. Membr. Sci. 2021, 624, 119047.

97. Zhang, B.; Zhao, M.; Liu, Q.; Zhang, X.; Fu, Y.; Zhang, E.; Wang, G.; Zhang, Z.; Yuan, X.; Zhang, S. High Performance Membranes Based on Pyridine Containing Poly (Aryl Ether Ketone Ketone) for Vanadium Redox Flow Battery Applications. J. Power Sources 2021, 506, 230128.

98. Wan, Y.H.; Sun, J.; Jiang, H.R.; Fan, X.Z.; Zhao, T.S. A Highly-Efficient Composite Polybenzimidazole Membrane for Vanadium Redox Flow Battery. J. Power Sources 2021, 489, 229502.

99. Kushner, D.I.; Crothers, A.R.; Kusoglu, A.; Weber, A.Z. Transport Phenomena in Flow Battery Ion-Conducting Membranes. Curr. Opin. Electrochem. 2020, 21, 132–139.

100. Shin, J.; Jeong, B.; Chinannai, M.F.; Ju, H. Mitigation of Water and Electrolyte Imbalance in All-Vanadium Redox Flow Batteries. Electrochim. Acta 2021, 390, 138858.

101. Skyllas-Kazacos, M.; Cao, L.; Kazacos, M.; Kausar, N.; Mousa, A. Vanadium Electrolyte Studies for the Vanadium Redox Battery-A Review. ChemSusChem 2016, 9, 1521–1543.

102. Kazacos, M.; Skyllas-Kazacos, M.; Kazacos, N. Vanadium Halide Redox Flow Battery. U.S. Patent US7976974B2, 12 July 2011.

103. Kim, D.; Kim, Y.; Lee, Y.; Jeon, J. 1,2-Dimethylimidazole Based Bromine Complexing Agents for Vanadium Bromine Redox Flow Batteries. Int. J. Hydrog. Energy 2019, 44, 12024–12032.

104. Vafiadis, H.; Skyllas-Kazacos, M. Evaluation of Membranes for the Novel Vanadium Bromine Redox Flow Cell. J. Membr. Sci. 2006, 279, 394–402.

105. Vijayakumar, M.; Li, L.; Graff, G.; Liu, J.; Zhang, H.; Yang, Z.; Hu, J.Z. Towards Understanding the Poor Thermal Stability of V5+ Electrolyte Solution in Vanadium Redox Flow Batteries. J. Power Sources 2011, 196, 3669–3672.

106. Roe, S.; Menictas, C.; Skyllas-Kazacos, M. A High Energy Density Vanadium Redox Flow Battery with 3 M Vanadium Electrolyte. J. Electrochem. Soc. 2015, 163, A5023.

107. Kim, S.; Thomsen, E.; Xia, G.; Nie, Z.; Bao, J.; Recknagle, K.; Wang, W.; Viswanathan, V.; Luo, Q.; Wei, X.; et al. 1 kW/1 kWh Advanced Vanadium Redox Flow Battery Utilizing Mixed Acid

showed steady capacity fade. The authors reported that cyclic voltammetry of electrolytes following 30 cycles in a RFB lead to partial degradation of the polyoxovanadate clusters [126].

Nevertheless, POMs also show the advantage that, when coupled with organic cations, they can be used in NA-RFBs [127][128] and thus overcome the barrier of the maximum voltage window of the current aqueous system, enabling the increase of the energy density of RFBs [129][130][131].

Regarding kinetics of these types of materials, this is influenced by the POMs' large size and by their reduced interaction between the redox centers and the molecules of solvent. The outer-sphere reorganization energy of the electron leads to a reduced interaction, which in turn leads to a low electron transfer energy and therefore high power density. Moreover, the reorganization energy of the inner sphere is low due to the extra electrons that are frequently delocalized. This causes a minimal variation in coordination upon reduction or oxidation [132].

Based on their versatility and properties, POMs have been studied for application in RFBs. To highlight the operation of an aqueous POM-based RFB, Liu et al. [133] developed the tungsten–cobalt symmetric redox flow battery, $H_6[CoW_{12}O_{40}]$ [133].

During the charging (or discharging) process, Co is reversibly oxidized (or reduced) on the positive side, the anode (or cathode); on the negative side, the cathode (or anode), W is reduced (or oxidized).

POM-based RFBs can be subdivided into symmetric or non-symmetric, depending whether the same electrolyte is used or not on the positive and negative side, and aqueous or non-aqueous (i.e., organic).

The application of POMs in NA-RFB is the main focus of research, mainly due to non-aqueous POM-based flow batteries, which have the potential to reach higher energy densities due to the abovementioned properties of POMs, e.g., solubility and existence of multi-electron redox pairs [123][129][130][133][134][135].

Others are also seeking to apply POMs to the remaining components of RFBs [119][121][128][136][137][138]. Among the described advantages for the use of POMs, it is worth mentioning the fact that they allow for the exchange of several electrons per reaction, have high kinetics, and their size prevents the existence of crossover. Since they have good solubility in non-aqueous solvents, they also have the advantage of being able to overcome the electrochemical window of water. However, currently they still face problems in reaching active areas higher than 5 cm^2 and current densities competitive with current technologies. Despite the investment required to synthesize the POM-based electrolyte, POMs may eventually overcome the current RFBs considering all the advantages they can add to current energy storage. Current studies are still at an early stage, but if we invested in their optimization, they could lead to high-performance RFBs.

2.2. Organic Aqueous

Aqueous organic redox flow batteries (A-ORFB) started to be studied as a solution for the aqueous inorganic RFB shortcomings. Organic molecules can be easily produced, and their precursors are abundant, which eliminates the

Electrolytes. J. Power Sources 2013, 237, 300–309.
108. Reed, D.; Thomsen, E.; Li, B.; Wang, W.; Nie, Z.; Koeppel, B.; Kizewski, J.; Sprenkle, V. Stack Developments in a KW Class All Vanadium Mixed Acid Redox Flow Battery at the Pacific Northwest National Laboratory. J. Electrochem. Soc. 2016, 163, A5211–A5219.
109. Yang, Y.; Zhang, Y.; Tang, L.; Liu, T.; Huang, J.; Peng, S.; Yang, X. Investigations on Physicochemical Properties and Electrochemical Performance of Sulfate-Chloride Mixed Acid Electrolyte for Vanadium Redox Flow Battery. J. Power Sources 2019, 434, 226719.
110. Kim, S.; Vijayakumar, M.; Wang, W.; Zhang, J.; Chen, B.; Nie, Z.; Chen, F.; Hu, J.; Li, L.; Yang, Z. Chloride Supporting Electrolytes for All-Vanadium Redox Flow Batteries. Phys. Chem. Chem. Phys. 2011, 13, 18186–18193.
111. Li, B.; Gu, M.; Nie, Z.; Shao, Y.; Luo, Q.; Wei, X.; Li, X.; Xiao, J.; Wang, C.; Sprenkle, V.; et al. Bismuth Nanoparticle Decorating Graphite Felt as a High-Performance Electrode for an All-Vanadium Redox Flow Battery. Nano Lett. 2013, 13, 1330–1335.
112. Schwenzer, B.; Zhang, J.; Kim, S.; Li, L.; Liu, J.; Yang, Z. Membrane Development for Vanadium Redox Flow Batteries. ChemSusChem 2011, 4, 1388–1406.
113. Vijayakumar, M.; Bhuvaneswari, M.S.; Nachimuthu, P.; Schwenzer, B.; Kim, S.; Yang, Z.; Liu, J.; Graff, G.L.; Thevuthasan, S.; Hu, J. Spectroscopic Investigations of the Fouling Process on Nafion Membranes in Vanadium Redox Flow Batteries. J. Membr. Sci. 2011, 366, 325–334.
114. Reed, D.; Thomsen, E.; Wang, W.; Nie, Z.; Li, B.; Wei, X.; Koeppel, B.; Sprenkle, V. Performance of Nafion® N115, Nafion® NR-212, and Nafion® NR-211 in a 1 KW Class All Vanadium Mixed Acid Redox Flow Battery. J. Power Sources 2015, 285, 425–430.
115. Yang, Y.; Zhang, Y.; Liu, T.; Huang, J. Improved Broad Temperature Adaptability and Energy Density of Vanadium Redox Flow Battery Based on Sulfate-Chloride Mixed Acid by Optimizing the Concentration of Electrolyte. J. Power Sources 2019, 415, 62–68.
116. Ueda, T. Electrochemistry of Polyoxometalates: From Fundamental Aspects to Applications. ChemElectroChem 2018, 5, 823–838.
117. Yang, L.; Lei, J.; Fan, J.; Yuan, R.; Zheng, M.; Chen, J.; Dong, Q. The Intrinsic Charge Carrier Behaviors and Applications of Polyoxometalate Clusters Based Materials. Adv. Mater. 2021, 2005019.
118. Friedl, J.; Holland-Cunz, M.V.; Cording, F.; Pfanschilling, F.L.; Wills, C.; McFarlane, W.; Schricker, B.; Fleck, R.; Wolfschmidt, H.; Stimming, U. Asymmetric Polyoxometalate Electrolytes for Advanced Redox Flow Batteries. Energy Environ. Sci. 2018, 11, 3010–3018.
119. Ji, Y.; Huang, L.; Hu, J.; Streb, C.; Song, Y.-F. Polyoxometalate-Functionalized Nanocarbon Materials for Energy Conversion, Energy Storage and Sensor Systems. Energy Environ. Sci.

problem of running out of raw materials to produce these active species and lowers their price. The organic active species are highly versatile and tunable, making personalization of active species for different applications a possibility, but, more importantly, the endless number of organic molecules that can be synthetized give the chance of finding a molecule that will fill all the requirements to reach commercialization with ease. The characteristics appealing properties for the active species to be used in RFB are high solubility, high standard redox potential, electrochemical stability, high number of electrons to transfer, fast kinetics, and good reversibility. In the past few years, great attention has been given to organic active species to find molecules that fulfill all these desirable characteristics and apply them in aqueous electrolytes. However, this goal has not been reached yet [25][139][140].

Currently, the focus of research into this technology has been on the active species. For this reason, the latest findings on A-ORFB have been divided in new negative electrolytes and new positive electrolytes.

In 2018, Hollas et al. [141] modified the phenazine molecular structure to reach a solubility of up to 1.8 M. The authors reported an electrolyte with a near-saturation concentration of the phenazine derivative (7,8-dihydroxyphenazine-2sulfonic acid) on the negative side and ferrocyanide (FeCN) as the active species on the positive electrolyte. An EE higher than 75% at 100 mA cm^{-2} with a capacity retention of 99.98% per cycle for 500 cycles was achieved. Two years later, W. Lee and colleagues reported that a solution of 1,2-naphthoquinone-4-sulfonic acid sodium salt (NQ-S) and 2-hydroxy-1,4-naphthoquinone (Lawsone) is a negative electrolyte. To test this electrolyte in a cell, ferrocyanide as the active species in the positive electrolyte was used, having reached 55% EE at 100 mA cm^{-2} with a capacity decay rate of 6 × 10−3 Ah L^{-1} for the duration of 200 cycles [142]. In 2021, two studies using viologens were published, where different strategies to reduce the dimerization of viologen radical cations and improve the active species performance in AORFB were used. L. Liu et al. [143] used α-cyclodextrin as a molecular spectator to weaken the intermolecular interactions of viologen radicals. When this solution was applied in a full cell, using a ferrocene derivative as the active species in the positive electrolyte, they achieved 59.8% EE at 40 mA cm^{-2}. Korshunov et al. [144] reported the employment of (2-hydroxypropyl)-β-cyclodextrin with 1-decyl-1′-ethyl-4,4′-bipyridinium dibromide as a host-guest complex to enhance the performance of the viologen negative electrolyte. When this new negative electrolyte was tested in a cell with (ferrocenylmethyl)trimethylammonium chloride (FcNCl) solution in the positive electrolyte, they reached an EE higher than 62% at 13.33 mA cm^{-2} for 500 cycles with a capacity fade rate of 3.7 × 10−2% per cycle. L. Xia and coworker found an anthraquinone with high solubility, 3-((9,10-dioxo-9,10-dihydroanthracen-1-yl)amino)-N,N,N-trimethylpropan-1-aminium chloride, that was able to reach a concentration as high as 1.44 M. When paired with FcNCl as the positive active species in a cell, it exhibited ca. 68% EE during 100 cycles at 60 mA cm^{-2} [145].

The development of organic active species for positive electrolytes is more challenging than for negative electrolytes, thanks to their lower stability. However, having a battery with all organic active species is still a great objective for RFBs. With that in mind, some publications have been made in the past few years where different organic active species have been reported to be implemented in positive electrolytes. Hoober-Burkhardt and coworkers synthesized and characterized 3,6-dihydroxy-2,4-dimethylbenzenesulfonic acid (DHDMBS), a novel active species to be used in the positive electrolyte. After that, they coupled the new active species with anthraquinone-2,7-disulfonic acid (AQDS) in a cell and reported a CE of almost 100% at 100 mA cm^{-2} for over 25

2015, 8, 776–780.

120. Friedl, J.; Al-Oweini, R.; Herpich, M.; Keita, B.; Kortz, U.; Stimming, U. Electrochemical Studies of Tri-Manganese Substituted Keggin Polyoxoanions. Electrochim. Acta 2014, 141, 357–366.

121. Chen, H.-Y.; Friedl, J.; Pan, C.-J.; Haider, A.; Al-Oweini, R.; Cheah, Y.L.; Lin, M.-H.; Kortz, U.; Hwang, B.-J.; Srinivasan, M.; et al. In Situ X-ray Absorption near Edge Structure Studies and Charge Transfer Kinetics of Na6 Electrodes. Phys. Chem. Chem. Phys. 2017, 19, 3358–3365.

122. Laborda, E.; Henstridge, M.C.; Batchelor-McAuley, C.; Compton, R.G. Asymmetric Marcus–Hush Theory for Voltammetry. Chem. Soc. Rev. 2013, 12.

123. Cao, Y.; Chen, J.-J.J.; Barteau, M.A. Systematic Approaches to Improving the Performance of Polyoxometalates in Non-Aqueous Redox Flow Batteries. J. Energy Chem. 2020, 50, 115–124.

124. Friedl, J.; Pfanschilling, F.L.; Holland-Cunz, M.V.; Fleck, R.; Schricker, B.; Wolfschmidt, H.; Stimming, U. A Polyoxometalate Redox Flow Battery: Functionality and Upscale. Clean Energy 2019, 3, 278–287.

125. VanGelder, L.E.; Pratt, H.D.; Anderson, T.M.; Matson, E.M. Surface Functionalization of Polyoxovanadium Clusters: Generation of Highly Soluble Charge Carriers for Nonaqueous Energy Storage. Chem. Commun. 2019, 55, 12247–12250.

126. Cameron, J.M.; Holc, C.; Kibler, A.J.; Peake, C.L.; Walsh, D.A.; Newton, G.N.; Johnson, L.R. Molecular Redox Species for Next-Generation Batteries. Chem. Soc. Rev. 2021, 50, 5863–5883.

127. Yang, D.; Liang, Y.; Ma, P.; Li, S.; Wang, J.; Niu, J. Self Assembly of Carboxylate/Alcoholate Functionalized Ring-Shape Phosphomolybdates. CrystEngComm 2014, 16, 8041–8046.

128. Proust, A.; Matt, B.; Villanneau, R.; Guillemot, G.; Gouzerh, P.; Izzet, G. Functionalization and Post-Functionalization: A Step towards Polyoxometalate-Based Materials. Chem. Soc. Rev. 2012, 41, 7605.

129. VanGelder, L.E.; Kosswattaarachchi, A.M.; Forrestel, P.L.; Cook, T.R.; Matson, E.M. Polyoxovanadate-Alkoxide Clusters as Multi-Electron Charge Carriers for Symmetric Non-Aqueous Redox Flow Batteries. Chem. Sci. 2018, 9, 1692–1699.

130. VanGelder, L.E.; Schreiber, E.; Matson, E.M. Physicochemical Implications of Alkoxide "Mixing" in Polyoxovanadium Clusters for Nonaqueous Energy Storage. J. Mater. Chem. A 2019, 7, 4893–4902.

131. Chakrabarti, M.H.; Dryfe, R.A.W.; Roberts, E.P.L. Evaluation of Electrolytes for Redox Flow Battery Applications. Electrochim. Acta 2007, 52, 2189–2195.

132. Bai, P.; Bazant, M.Z. Charge Transfer Kinetics at the Solid–Solid Interface in Porous Electrodes. Nat. Commun. 2014, 5, 3585.

cycles, however, DHDMBS crossover from the positive to the negative side of the cell through the membrane, which led to capacity loss [146]. Later, the same group studied this problem and found that DHDMBS crossed through the membrane because of its small size when compared to AQDS, and that DHDMBS does a protodesulfonation reaction when in strongly acidic conditions. They also experimented with a symmetric cell that had DHDMBS and AQDS in both electrolytes, and to reduce capacity fade they joined that strategy with a mix and split cycling protocol and with a "polarity-switching" protocol. These techniques showed reduced capacity fade [147]. Hu et al. [148] reported a new cyclic nitroxide radical class with five-membered ring pyrrolidine and pyrroline motifs. The molecule 3-carbamoyl-2,2,5,5-tetramethylpyrroline-1-oxyl was studied as an active species for the positive electrolyte paired with bis(3-trimethylammonio)propyl viologen in a cell, having reached ca. 64% EE at 50 mA cm^{-2} and good stability over 500 cycles at 40 mA cm^{-2}. X. Yang and colleagues published a work where they synthesized four new hydroquinone derivatives bearing morpholinomethylene and/or methyl groups in different positions on the benzene ring. 2,6-dimethyl-3,5-bis(morpholinomethylene)benzene-1,4-diol showed a capacity decay of 0.45% per day [149].

Some studies have the main objective of studying the performance of organic electrolytes in a cell configuration. T. Liu and colleagues reported an A-ORFB using methyl viologen (MV) and 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (4-HO-TEMPO), having achieved an EE of 62.5% at 60 mA cm^{-2} with stable cycling through 100 cycles [150]. B. Hu et al. [151] studied the effect of supporting electrolytes and ion exchange membranes on the performance of an A-ORFB cell with FcNCl and MV. In this manuscript, the authors achieved 79% EE at 60 mA cm^{-2} with great stability for 200 cycles. The same author also reported an A-ORFB using 1,1′-bis[3-(trimethylammonio)propyl]-4,4′-bipyridinium tetrachloride and 4-trimethylammonium-TEMPO chloride as active species. In this study, the authors demonstrated an EE that ranged from 87% at 20 mA cm^{-2} to 48% at 80 mA cm^{-2} with good cycling stability for 500 cycles [152]. Feng et al. [153] developed a ketone to be implemented as the active species in an A-ORFB by undergoing hydrogenation and dehydrogenation reactions. The fluorenone derivative that was produced showed efficient operation and stable long-term cycling. Some studies have the main objective of studying the performance of organic electrolytes in a cell configuration. T. Liu and colleagues reported an A-ORFB using methyl viologen (MV) and 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (4-HO-TEMPO), having achieved an EE of 62.5% at 60 mA cm^{-2} with stable cycling through 100 cycles [150]. B. Hu et al. [151] studied the effect of supporting electrolytes and ion exchange membranes on the performance of an A-ORFB cell with FcNCl and MV. In this manuscript, the authors achieved 79% EE at 60 mA cm^{-2} with great stability for 200 cycles. The same author also reported an A-ORFB using 1,1′-bis[3-(trimethylammonio)propyl]-4,4′-bipyridinium tetrachloride and 4-trimethylammonium-TEMPO chloride as active species. In this study, the authors demonstrated an EE that ranged from 87% at 20 mA cm^{-2} to 48% at 80 mA cm^{-2} with good cycling stability for 500 cycles [152]. Feng et al. [153] developed a ketone to be implemented as the active species in an A-ORFB by undergoing hydrogenation and dehydrogenation reactions. The fluorenone derivative that was produced showed efficient operation and stable long-term cycling.

Organometallic complexes have also received some attention from the scientific community for their tunable standard redox potential and the reduced crossover of active species through the membrane. C. Noh et al. [154] explored iron- and cobalt-triethanolamine as redox couples. With this redox couple the authors recorded a performance of 62% EE at 40 mA cm^{-2} for 20 cycles. Later, the same group improved upon this result by

133. Liu, Y.; Lu, S.; Wang, H.; Yang, C.; Su, X.; Xiang, Y. An Aqueous Redox Flow Battery with a Tungsten-Cobalt Heteropolyacid as the Electrolyte for Both the Anode and Cathode. Adv. Energy Mater. 2017, 7, 1601224.

134. Chen, J.-J.J.; Barteau, M.A. Molybdenum Polyoxometalates as Active Species for Energy Storage in Non-Aqueous Media. J. Energy Storage 2017, 13, 255–261.

135. Laramie, S.M.; Milshtein, J.D.; Breault, T.M.; Brushett, F.R.; Thompson, L.T. Performance and Cost Characteristics of Multi-Electron Transfer, Common Ion Exchange Non-Aqueous Redox Flow Batteries. J. Power Sources 2016, 327, 681–692.

136. Li, Q.; Zhang, L.; Dai, J.; Tang, H.; Li, Q.; Xue, H.; Pang, H. Polyoxometalate-Based Materials for Advanced Electrochemical Energy Conversion and Storage. Chem. Eng. J. 2018, 351, 441–461.

137. Wang, D.; Liu, L.; Jiang, J.; Chen, L.; Zhao, J. Polyoxometalate-Based Composite Materials in Electrochemistry: State-of-the-Art Progress and Future Outlook. Nanoscale 2020, 12, 5705–5718.

138. Chen, H.-Y.; Wee, G.; Al-Oweini, R.; Friedl, J.; Tan, K.S.; Wang, Y.; Wong, C.L.; Kortz, U.; Stimming, U.; Srinivasan, M. A Polyoxovanadate as an Advanced Electrode Material for Supercapacitors. ChemPhysChem 2014, 15, 2162–2169.

139. Luo, J.; Hu, B.; Hu, M.; Zhao, Y.; Liu, T.L. Status and Prospects of Organic Redox Flow Batteries toward Sustainable Energy Storage. ACS Energy Lett. 2019, 4, 2220–2240.

140. Singh, V.; Kim, S.; Kang, J.; Byon, H.R. Aqueous Organic Redox Flow Batteries. Nano Res. 2019, 12, 1988–2001.

141. Hollas, A.; Wei, X.; Murugesan, V.; Nie, Z.; Li, B.; Reed, D.; Liu, J.; Sprenkle, V.; Wang, W. A Biomimetic High-Capacity Phenazine-Based Anolyte for Aqueous Organic Redox Flow Batteries. Nat. Energy 2018, 3, 508–514.

142. Lee, W.; Park, G.; Kwon, Y. Alkaline Aqueous Organic Redox Flow Batteries of High Energy and Power Densities Using Mixed Naphthoquinone Derivatives. Chem. Eng. J. 2020, 386, 123985.

143. Liu, L.; Yao, Y.; Wang, Z.; Lu, Y.-C. Viologen Radical Stabilization by Molecular Spectators for Aqueous Organic Redox Flow Batteries. Nano Energy 2021, 84, 105897.

144. Korshunov, A.; Gibalova, A.; Grünebaum, M.; Ravoo, B.J.; Winter, M.; Cekic-Laskovic, I. Host-Guest Interactions Enhance the Performance of Viologen Electrolytes for Aqueous Organic Redox Flow Batteries. Batter. Supercaps 2021, 4, 923–928.

145. Xia, L.; Huo, W.; Gao, H.; Zhang, H.; Chu, F.; Liu, H.; Tan, Z. Intramolecular Hydrogen Bonds Induced High Solubility for Efficient and Stable Anthraquinone Based Neutral Aqueous Organic Redox Flow Batteries. J. Power Sources 2021, 498, 229896.

146. Hoober-Burkhardt, L.; Krishnamoorthy, S.; Yang, B.; Murali, A.; Nirmalchandar, A.; Prakash, G.K.S.; Narayanan, S.R. A New Michael-Reaction-Resistant Benzoquinone for Aqueous Organic

incorporating a new ligand, triisopropanolamine. Using the new ligand, the authors achieved 77% EE at 40 mA cm^{-2} for 100 cycles [155]. W. Ruan and colleagues studied a cell using FeCN and Cr with dipicolinic acid as a ligand. Their tests show EE values that begin at ca. 90% and drop to 85% through 120 cycles at 10 mA cm^{-2} [156]. M. Shin et al. [157] also used FeCN to couple with an organometallic complex composed of Fe and 3-[bis(2-hydroxyethyl)amino]-2-hydroxypropanesulfonic acid as a ligand. This redox couple could be cycled for 100 cycles at 80 mA cm^{-2} with an EE of 70%. Organometallic complexes have also received some attention from the scientific community for their tunable standard redox potential and the reduced crossover of active species through the membrane. C. Noh et al. [154] explored iron- and cobalt-triethanolamine as redox couples. With this redox couple the authors recorded a performance of 62% EE at 40 mA cm^{-2} for 20 cycles. Later, the same group improved upon this result by incorporating a new ligand, triisopropanolamine. Using the new ligand, the authors achieved 77% EE at 40 mA cm^{-2} for 100 cycles [155]. W. Ruan and colleagues studied a cell using FeCN and Cr with dipicolinic acid as a ligand. Their tests show EE that begin at ca. 90% and drop to 85% through 120 cycles at 10 mA cm^{-2} [156]. M. Shin et al. [157] also used FeCN to couple with an organometallic complex composed of Fe and 3-[bis(2-hydroxyethyl) amino]-2-hydroxypropanesulfonic acid as a ligand. This redox couple could be cycled for 100 cycles at 80 mA cm^{-2} with an EE of 70%.

A-ORFBs are an important branch of RFBs, and their commercial application would be a huge step for these technologies. Even though organic species are highly versatile and tunable, an organic redox pair that can compete with the performance achieved by VRFBs has not been discovered, which shows how far away A-ORFBs still are from being commercially available. However, the simulation tools that are now available to find new molecules that have the desired properties for this application make the search easier and may allow us to achieve this goal more quickly.

2.3. Non-Aqueous Solvents

Non-aqueous RFBs (NA-RFB) represent one of the emerging large-scale energy storage systems that promise to overcome the low energy density of aqueous redox flow batteries (ARFB). In these, the use of an aqueous electrolyte limits the cell potential in the electrochemical stability window of water [158][159]. Despite the great interest, NA-RFBs have not reached their full potential yet because the challenges of low electrolyte conductivities, stability, and cost limit their development [159]. Moreover, special attention needs to be paid to the end-of-life process of the materials [160]. Non-aqueous RFBs (NA-RFB) represent one of the emerging large-scale energy storage systems that promise to overcome the low energy density of aqueous redox flow batteries (ARFB). In these, the use of an aqueous electrolyte limits the cell potential in the electrochemical stability window of water [158][159]. Despite the great interest, NA-RFBs have not reached their full potential yet because the challenges of low electrolyte conductivities, stability, and cost limit their development [159]. Moreover, special attention needs to be paid to the end-of-life process of the materials [160].

The development of NA-RFB is limited by the lack of electroactive compounds (catholytes and anolytes) that also meet the conditions: (1) redox potential exceeding the potential limits of water; (2) high solubility in non-aqueous media; and (3) high stability during electrochemical cycles [161]. The development of NA-RFBs is limited by the lack

Redox Flow Batteries. J. Electrochem. Soc. 2017, 164, A600.

147. Murali, A.; Nirmalchandar, A.; Krishnamoorthy, S.; Hoober-Burkhardt, L.; Yang, B.; Soloveichik, G.; Prakash, G.K.S.; Narayanan, S.R. Understanding and Mitigating Capacity Fade in Aqueous Organic Redox Flow Batteries. J. Electrochem. Soc. 2018, 165, A1193.

148. Hu, B.; Fan, H.; Li, H.; Ravivarma, M.; Song, J. Five-Membered Ring Nitroxide Radical: A New Class of High-Potential, Stable Catholyte for Neutral Aqueous Organic Redox Flow Batteries. Adv. Funct. Mater. 2021, 31, 2102734.

149. Yang, X.; Garcia, S.N.; Janoschka, T.; Kónya, D.; Hager, M.D.; Schubert, U.S. Novel, Stable Catholyte for Aqueous Organic Redox Flow Batteries: Symmetric Cell Study of Hydroquinones with High Accessible Capacity. Molecules 2021, 26, 3823.

150. Liu, T.; Wei, X.; Nie, Z.; Sprenkle, V.; Wang, W. A Total Organic Aqueous Redox Flow Battery Employing a Low Cost and Sustainable Methyl Viologen Anolyte and 4-HO-TEMPO Catholyte. Adv. Energy Mater. 2016, 6, 1501449.

151. Hu, B.; Seefeldt, C.; DeBruler, C.; Liu, T.L. Boosting the Energy Efficiency and Power Performance of Neutral Aqueous Organic Redox Flow Batteries. J. Mater. Chem. A 2017, 5, 22137–22145.

152. Hu, B.; Tang, Y.; Luo, J.; Grove, G.; Guo, Y.; Liu, T.L. Improved Radical Stability of Viologen Anolytes in Aqueous Organic Redox Flow Batteries. Chem. Commun. 2018, 54, 6871–6874.

153. Feng, R.; Zhang, X.; Murugesan, V.; Hollas, A.; Chen, Y.; Shao, Y.; Walter, E.; Wellala, N.P.N.; Yan, L.; Rosso, K.M.; et al. Reversible Ketone Hydrogenation and Dehydrogenation for Aqueous Organic Redox Flow Batteries. Science 2021, 372, 836–840.

154. Noh, C.; Chung, Y.; Kwon, Y. Organometallic Redox Flow Batteries Using Iron Triethanolamine and Cobalt Triethanolamine Complexes. J. Power Sources 2020, 466, 228333.

155. Noh, C.; Chung, Y.; Kwon, Y. Highly Stable Aqueous Organometallic Redox Flow Batteries Using Cobalt Triisopropanolamine and Iron Triisopropanolamine Complexes. Chem. Eng. J. 2021, 405, 126966.

156. Ruan, W.; Mao, J.; Yang, S.; Shi, C.; Jia, G.; Chen, Q. Designing Cr Complexes for a Neutral Fe–Cr Redox Flow Battery. Chem. Commun. 2020, 56, 3171–3174.

157. Shin, M.; Noh, C.; Chung, Y.; Kwon, Y. All Iron Aqueous Redox Flow Batteries Using Organometallic Complexes Consisting of Iron and 3--2-Hydroxypropanesulfonic Acid Ligand and Ferrocyanide as Redox Couple. Chem. Eng. J. 2020, 398, 125631.

158. Shinkle, A.A.; Sleightholme, A.E.S.; Thompson, L.T.; Monroe, C.W. Electrode Kinetics in Non-Aqueous Vanadium Acetylacetonate Redox Flow Batteries. J. Appl. Electrochem. 2011, 41, 1191–1199.

of electroactive compounds (catholytes and anolytes) that also meet the conditions of (1) redox potential exceeding the potential limits of water, (2) high solubility in nonaqueous media, and (3) high stability during electrochemical cycles [161].

NA-RFBs can be classified through the reactive species of the redox pairs and through the non-aqueous solvent. **Figure 4** shows a schematic representation of the operation of a NA-RFBs. During the discharge of the battery, pumps circulate the solution from the anode to the system of the NA-RFBs, where it passes through the electrode, where oxidation occurs, i.e., releases electrons that are transported to the external circuit [162]. On the other hand, the charge-carrying species passes through the ion exchange membrane that is separating the compartments of the RFB [163]. A general redox reaction during the charge process is represented in Equations (8) and (9).

Cathode: $[ML_n]^{(z+x)+} \rightarrow [ML_n]^{z+} + xe^-$ (8)

Anode: $[ML_n]^{(z-y)+} + ye^- \rightarrow [ML_n]^{z+}$ (9)

where *M* is a transition metal, *L* is a ligand, and *n* is the number of ligands.

159. Ding, Y.; Zhang, C.; Zhang, L.; Zhou, Y.; Yu, G. Molecular Engineering of Organic Electroactive Materials for Redox Flow Batteries. Chem. Soc. Rev. 2018, 47, 69–103.

160. Sun, C.-N.; Mench, M.M.; Zawodzinski, T.A. High Performance Redox Flow Batteries: An Analysis of the Upper Performance Limits of Flow Batteries Using Non-Aqueous Solvents. Electrochim. Acta 2017, 237, 199–206.

161. Sevov, C.S.; Fisher, S.L.; Thompson, L.T.; Sanford, M.S. Mechanism-Based Development of a Low-Potential, Soluble, and Cyclable Multielectron Anolyte for Nonaqueous Redox Flow Batteries. J. Am. Chem. Soc. 2016, 138, 15378–15384.

162. Chalamala, B.R.; Soundappan, T.; Fisher, G.R.; Anstey, M.R.; Viswanathan, V.V.; Perry, M.L. Redox Flow Batteries: An Engineering Perspective. Proc. IEEE 2014, 102, 976–999.

163. Li, M.; Rhodes, Z.; Cabrera-Pardo, J.R.; Minteer, S.D. Recent Advancements in Rational Design of Non-Aqueous Organic Redox Flow Batteries. Sustain. Energy Fuels 2020, 4, 4370–4389.

164. Matsuda, Y.; Tanaka, K.; Okada, M.; Takasu, Y.; Morita, M. A Rechargeable Redox Battery Utilizing Ruthenium Complexes with Non-Aqueous Organic Electrolyte. J. Appl. Electrochem. 1988, 18, 909–914.

165. Milshtein, J.D.; Kaur, A.P.; Casselman, M.D.; Kowalski, J.A.; Modekrutti, S.; Zhang, P.L.; Harsha Attanayake, N.; Elliott, C.F.; Parkin, S.R.; Risko, C.; et al. High Current Density, Long Duration Cycling of Soluble Organic Active Species for Non-Aqueous Redox Flow Batteries. Energy Environ. Sci. 2016, 9, 3531–3543.

166. Yuan, J.; Zhang, C.; Liu, T.; Zhen, Y.; Pan, Z.-Z.; Li, Y. Two-Dimensional Metal-Organic Framework Nanosheets-Modified Porous Separator for Non-Aqueous Redox Flow Batteries. J. Membr. Sci. 2020, 612, 118463.

167. Armstrong, C.G.; Hogue, R.W.; Toghill, K.E. Characterisation of the Ferrocene/Ferrocenium Ion Redox Couple as a Model Chemistry for Non-Aqueous Redox Flow Battery Research. J. Electroanal. Chem. 2020, 872, 114241.

168. Li, Y.; Geysens, P.; Zhang, X.; Sniekers, J.; Fransaer, J.; Binnemans, K.; Vankelecom, I.F.J. Cerium-Containing Complexes for Low-Cost, Non-Aqueous Redox Flow Batteries (RFBs). J. Power Sources 2020, 450, 227634.

169. Kosswattaarachchi, A.M.; Cook, T.R. Concentration-Dependent Charge-Discharge Characteristics of Non-Aqueous Redox Flow Battery Electrolyte Combinations. Electrochim. Acta 2018, 261, 296–306.

170. Sleightholme, A.E.S.; Shinkle, A.A.; Liu, Q.; Li, Y.; Monroe, C.W.; Thompson, L.T. Non-Aqueous Manganese Acetylacetonate Electrolyte for Redox Flow Batteries. J. Power Sources 2011, 196, 5742–5745.

171. Liu, Q.; Shinkle, A.A.; Li, Y.; Monroe, C.W.; Thompson, L.T.; Sleightholme, A.E.S. Non-Aqueous Chromium Acetylacetonate Electrolyte for Redox Flow Batteries. Electrochem. Commun. 2010, 12, 1634–1637.

172. Liu, Q.; Sleightholme, A.E.S.; Shinkle, A.A.; Li, Y.; Thompson, L.T. Non-Aqueous Vanadium Acetylacetonate Electrolyte for Redox Flow Batteries. Electrochem. Commun. 2009, 11, 2312–2315.

173. Kaur, A.P.; Holubowitch, N.E.; Ergun, S.; Elliott, C.F.; Odom, S.A. A Highly Soluble Organic Catholyte for Non-Aqueous Redox Flow Batteries. Energy Technol. 2015, 3, 476–480.

174. Su, L.; Ferrandon, M.; Kowalski, J.A.; Vaughey, J.T.; Brushett, F.R. Electrolyte Development for Non-Aqueous Redox Flow Batteries Using a High-Throughput Screening Platform. J. Electrochem. Soc. 2014, 161, A1905–A1914.

175. Mun, J.; Lee, M.-J.; Park, J.-W.; Oh, D.-J.; Lee, D.-Y.; Doo, S.-G. Non-Aqueous Redox Flow Batteries with Nickel and Iron Tris(2,2′-Bipyridine) Complex Electrolyte. Electrochem. Solid-State Lett. 2012, 15, A80.

176. Hamelet, S.; Tzedakis, T.; Leriche, J.-B.; Sailler, S.; Larcher, D.; Taberna, P.-L.; Simon, P.; Tarascon, J.-M. Non-Aqueous Li-Based Redox Flow Batteries. J. Electrochem. Soc. 2012, 159, A1360–A1367.

177. Li, Z.; Li, S.; Liu, S.; Huang, K.; Fang, D.; Wang, F.; Peng, S. Electrochemical Properties of an All-Organic Redox Flow Battery Using 2,2,6,6-Tetramethyl-1-Piperidinyloxy and N-Methylphthalimide. Electrochem. Solid-State Lett. 2011, 14, A171.

178. Kwon, G.; Lee, K.; Lee, M.H.; Lee, B.; Lee, S.; Jung, S.-K.; Ku, K.; Kim, J.; Park, S.Y.; Kwon, J.E.; et al. Bio-Inspired Molecular Redesign of a Multi-Redox Catholyte for High-Energy Non-Aqueous Organic Redox Flow Batteries. Chem 2019, 5, 2642–2656.

179. Mirle, C.R.; Raja, M.; Vasudevarao, P.; Sankararaman, S.; Kothandaraman, R. Functionalized Carbazole as a Cathode for High Voltage Non-Aqueous Organic Redox Flow Batteries. New J. Chem. 2020, 44, 14401–14410.

180. Chai, J.; Lashgari, A.; Wang, X.; Williams, C.K.; Jiang, J. "Jimmy" All-PEGylated Redox-Active Metal-Free Organic Molecules in Non-Aqueous Redox Flow Battery. J. Mater. Chem. A 2020, 8, 15715–15724.

181. Baek, J.; Kwon, G.; Byeon, J.E.; Song, H.; Kang, K.; Lee, E. Tunable Redox-Active Triazenyl-Carbene Platforms: A New Class of Anolytes for Non-Aqueous Organic Redox Flow Batteries. ACS Appl. Mater. Interfaces 2020, 12, 37338–37345.

182. Silcox, B. Stability and Cyclability Predictions of Redox Active Organic Molecules for Non-Aqueous Redox Flow Batteries. Ph.D. Thesis, University of Michigan, Ann Arbor, MI, USA, 2021.

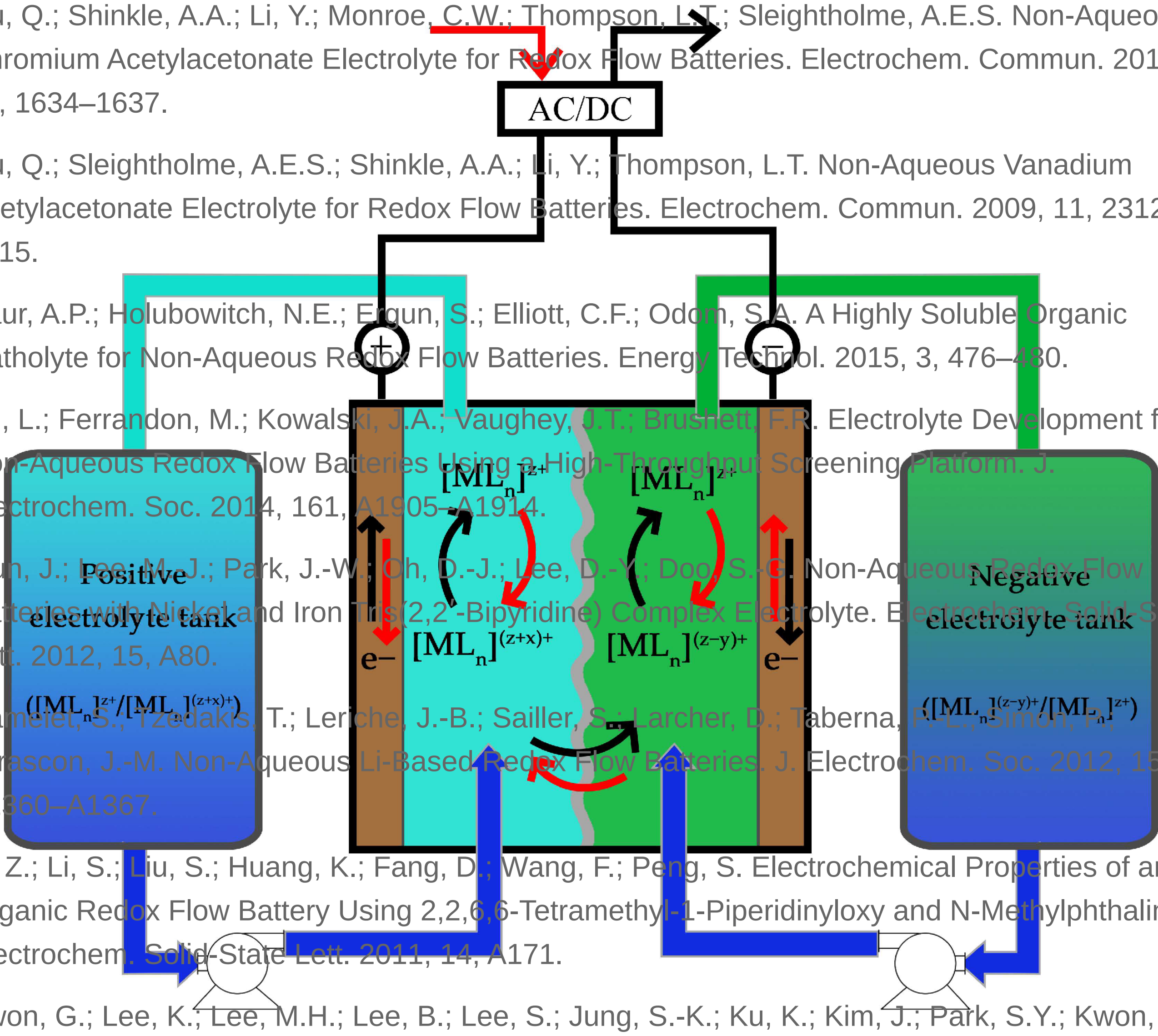

Figure 4. Schematic diagram of a NA-RFB.

The main difference between aqueous and NA-RFBs is in the electrolyte solvent and supporting. In NA-RFBs, organic solvents such as acetonitrile (ACN) [158][164][165][166][167][168][169][170][171][172], propylene carbonate (PC) [165][169][173][174][175], and ethylene carbonate (EC) [173][174][176], are used to dissolve metal–ligand complexes as reactive species. To improve conductivity, an ionic liquid is added as a supporting electrolyte such as tetraethylammonium tetrafluoroborate (TEABF4) due to its compatibility with organic solvents [82].

One of the major limitations of NA-RFBs is the low solubility of the metal ligands in organic electrolytes. Furthermore, the voltage losses due to ohmic effects are more significant than in RFBs because the conductivity of the non-aqueous organic solvent-based electrolyte is twice that of the aqueous acidic medium [160][163]. To overcome these limitations, all-organic redox flow batteries (AO-ORFBs) have been proposed to bring together the advantages of using a non-aqueous electrolyte and electroactive organic compounds [177]. This battery was composed of 2,2,6,6,-teramethyl-1-piperidinylxy (TEMPO) and N-methylphthalimide dissolved in acetronitrile and supported by $NaClO_4$. Tests performed indicate an equilibrium cell potential of 1.6 V, stability in charge–discharge cycles, and a coulombic efficiency of 90%, showing that all-organic RFBs show excellent potential for application in NA-RFBs [177].

Kwon et al. [178], in 2019, reported a multi-redox BMEPZ inspired by biosystems as a promising catholyte material with the highest energy density demonstrated for organic RFBs, but they also reported further engineering of redox active organic molecules (ROMs). Kosswattaarachchi and Cook studied different combinations of anolytes and catholytes, also reporting that these combinations and their concentrations influence cycling behavior and charge–discharge profiles [169]. Mirle et al. [179] proposed a carbazole-based catholyte, and a group of researchers from the University of Cincinnati proposed a NA-RFB based on all-PEGylated redox-active metal-free organic molecules [180]. Other than the mentioned groups, there have also been studies on ROM as a possible electroactive compound for NA-RFBs [181][182][183][184][185].

Another promising system in which higher cell voltages can be achieved are the thermally regenerative batteries. In such systems, thermal reactions induce a chemical reaction to charge the battery. Most of these types of batteries are generally based on silver or copper [186]. The main advantage of these systems is that in addition to heat-to-power conversion, they are also able to store energy. Recently, a power density of 30 W m^{-2} by a single cell was reported. The cell reported operated at a hydraulic retention time of 2 s (flow rate = 2 mL min^{-1}) and showed a stable power production over 100 successive cycles [186].

Despite recent efforts by researchers to develop NA-RFBs, one of the great challenges is to develop membranes that meet all the requirements for their proper functioning, which include several properties such as high ionic conductivity and selectivity, low swellability, low cost, and high stability, both mechanical and chemical [187][188][189]. To this end, Yuan et al. in 2021 presented a set of radar plots summarizing the performance, advantages, and shortcomings of current membranes [63]. The analysis of the plots in **Figure 5** allows us to observe why none of the current advances in membrane development are solving the problems of the technology. Nevertheless, it is possible to get an insight into which feature can be sacrificed to maximize another in each case. To use NA-RFBs on a large scale, membrane development is a problem that must be overcome.

183. Armstrong, C.G.; Hogue, R.W.; Toghill, K.E. Application of the Dianion Croconate Violet for Symmetric Organic Non-Aqueous Redox Flow Battery Electrolytes. J. Power Sources 2019, 440, 227037.

184. Sharma, S.; Andrade, G.A.; Maurya, S.; Popov, I.A.; Batista, E.R.; Davis, B.L.; Mukundan, R.; Smythe, N.C.; Tondreau, A.M.; Yang, P.; et al. Iron-Iminopyridine Complexes as Charge Carriers for Non-Aqueous Redox Flow Battery Applications. Energy Storage Mater. 2021, 37, 576–586.

185. Sharma, S.; Rathod, S.; Prakash Yadav, S.; Chakraborty, A.; Shukla, A.K.; Aetukuri, N.; Patil, S. Electrochemical Evaluation of Diketopyrrolopyrrole Derivatives for Nonaqueous Redox Flow Batteries. Chem. Eur. J. 2021.

186. Rahimi, M.; Kim, T.; Gorski, C.A.; Logan, B.E. A Thermally Regenerative Ammonia Battery with Carbon-Silver Electrodes for Converting Low-Grade Waste Heat to Electricity. J. Power Sources 2018, 373, 95–102.

187. Zhang, H.; Zhang, H.; Li, X.; Mai, Z.; Zhang, J. Nanofiltration (NF) Membranes: The Next Generation Separators for All Vanadium Redox Flow Batteries (VRBs)? Energy Environ. Sci. 2011, 4, 1676–1679.

188. Qiao, L.; Zhang, H.; Lu, W.; Dai, Q.; Li, X. Advanced Porous Membranes with Tunable Morphology Regulated by Ionic Strength of Nonsolvent for Flow Battery. ACS Appl. Mater. Interfaces 2019, 11, 24107–24113.

189. Su, L.; Zhang, D.; Peng, S.; Wu, X.; Luo, Y.; He, G. Orientated Graphene Oxide/Nafion Ultra-Thin Layer Coated Composite Membranes for Vanadium Redox Flow Battery. Int. J. Hydrog. Energy 2017, 42, 21806–21816.

190. Zhang, M.; Moore, M.; Watson, J.S.; Zawodzinski, T.A.; Counce, R.M. Capital Cost Sensitivity Analysis of an All-Vanadium Redox-Flow Battery. J. Electrochem. Soc. 2012, 159, A1183.

191. Navalpotro, P.; Neves, C.M.S.S.; Palma, J.; Freire, M.G.; Coutinho, J.A.P.; Marcilla, R. Pioneering Use of Ionic Liquid-Based Aqueous Biphasic Systems as Membrane-Free Batteries. Adv. Sci. 2018, 5, 1800576.

192. Park, H.B.; Lee, K.H.; Sung, H.J. Performance of H-Shaped Membraneless Micro Fuel Cells. J. Power Sources 2013, 226, 266–271.

193. López-Montesinos, P.O.; Yossakda, N.; Schmidt, A.; Brushett, F.R.; Pelton, W.E.; Kenis, P.J.A. Design, Fabrication, and Characterization of a Planar, Silicon-Based, Monolithically Integrated Micro Laminar Flow Fuel Cell with a Bridge-Shaped Microchannel Cross-Section. J. Power Sources 2011, 196, 4638–4645.

194. Marschewski, J.; Jung, S.; Ruch, P.; Prasad, N.; Mazzotti, S.; Michel, B.; Poulikakos, D. Mixing with Herringbone-Inspired Microstructures: Overcoming the Diffusion Limit in Co-Laminar Microfluidic Devices. Lab Chip 2015, 15, 1923–1933.

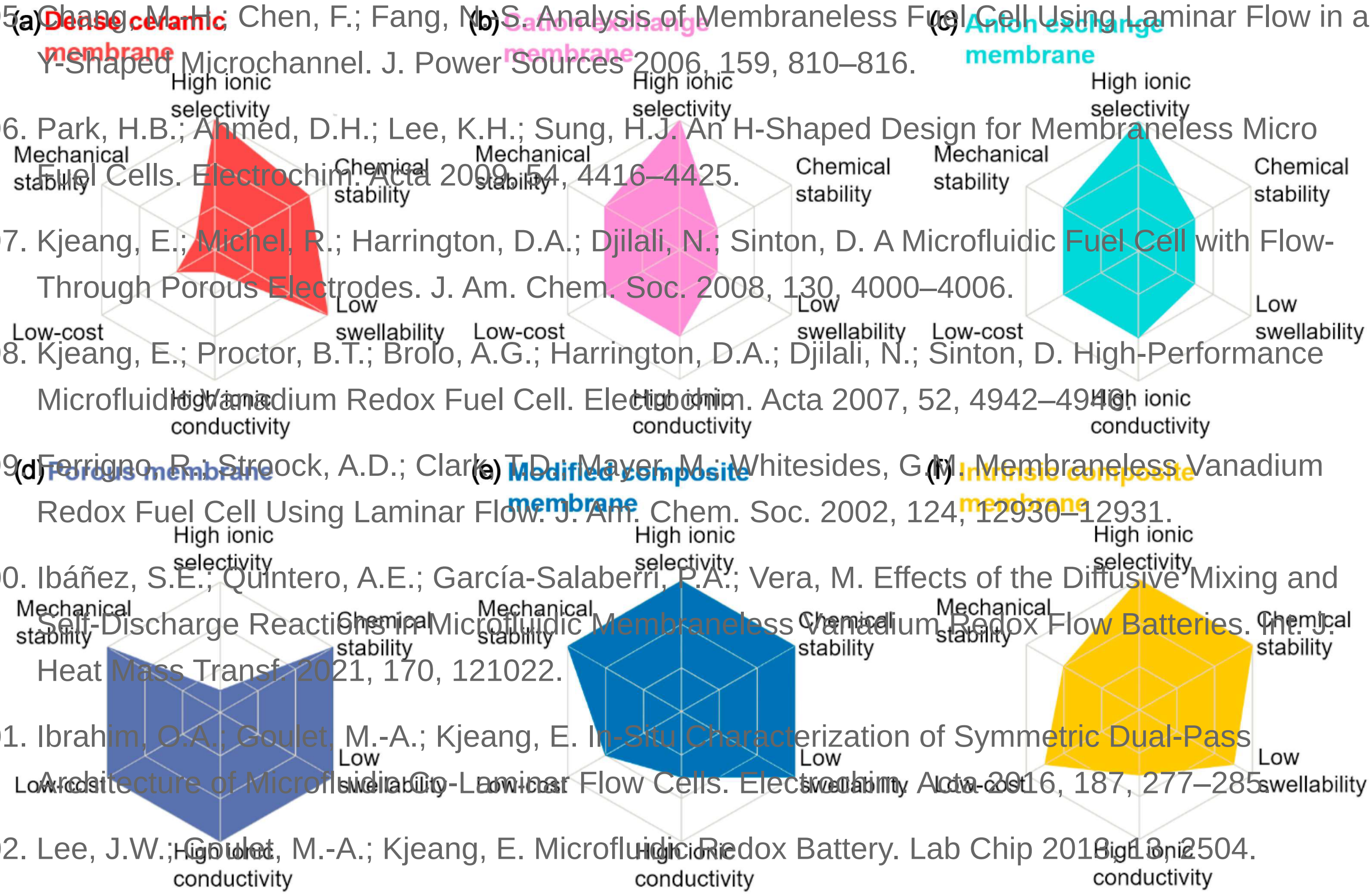

Figure 5. Radar plots of the performance properties of different membranes [68]. Copyright 2021, Elsevier.

The literature found shows that to move towards advanced NA-RFBs it will be necessary to develop and/or optimize the anolytes and catholytes currently available. In this context, improved anolytes and catholytes with enhanced electrochemical performance particularly stability and reversibility will be developed. The analysis of the current state of the art also indicates that the expansion of the redox-active molecules for NA-RFBs started showing promising results in reaching the potential to become interesting for commercialization in the last three years. Moreover, for practical applications, the lifetime of redox electrolytes need to be further improved, namely their stability and species crossover.

3. Other RFB Configurations

There have been attempts to improve RFBs by changing their configuration. These changes aim to increase the energy density of the devices and/or reduce costs in new and innovative ways. These configurations also make the redox flow battery technology more versatile and able to be implemented in a wider array of applications. In this section, these different configurations will be approached, namely membraneless flow batteries, metal–air flow batteries and metal–air fuel cells, solid targeted flow batteries, and semi-solid flow batteries.

3.1. Membraneless

195. Chang, M.-H.; Chen, F.; Fang, N.-S. Analysis of Membraneless Fuel Cell Using Laminar Flow in a Y-Shaped Microchannel. J. Power Sources 2006, 159, 810–816.

196. Park, H.B.; Ahmed, D.H.; Lee, K.H.; Sung, H.J. An H-Shaped Design for Membraneless Micro Fuel Cells. Electrochim. Acta 2009, 54, 4416–4425.

197. Kjeang, E.; Michel, R.; Harrington, D.A.; Djilali, N.; Sinton, D. A Microfluidic Fuel Cell with Flow-Through Porous Electrodes. J. Am. Chem. Soc. 2008, 130, 4000–4006.

198. Kjeang, E.; Proctor, B.T.; Brolo, A.G.; Harrington, D.A.; Djilali, N.; Sinton, D. High-Performance Microfluidic Vanadium Redox Fuel Cell. Electrochim. Acta 2007, 52, 4942–4946.

199. Ferrigno, R.; Stroock, A.D.; Clark, T.D.; Mayer, M.; Whitesides, G.M. Membraneless Vanadium Redox Fuel Cell Using Laminar Flow. J. Am. Chem. Soc. 2002, 124, 12930–12931.

200. Ibáñez, S.E.; Quintero, A.E.; García-Salaberri, P.A.; Vera, M. Effects of the Diffusive Mixing and Self-Discharge Reactions in Microfluidic Membraneless Vanadium Redox Flow Batteries. Int. J. Heat Mass Transf. 2021, 170, 121022.

201. Ibrahim, O.A.; Goulet, M.-A.; Kjeang, E. In-Situ Characterization of Symmetric Dual-Pass Architecture of Microfluidic Co-Laminar Flow Cells. Electrochim. Acta 2016, 187, 277–285.

202. Lee, J.W.; Goulet, M.-A.; Kjeang, E. Microfluidic Redox Battery. Lab Chip 2013, 13, 2504.

203. Marschewski, J.; Ruch, P.; Ebejer, N.; Huerta Kanan, O.; Lhermitte, G.; Cabrol, Q.; Michel, B.; Poulikakos, D. On the Mass Transfer Performance Enhancement of Membraneless Redox Flow Cells with Mixing Promoters. Int. J. Heat Mass Transf. 2017, 106, 884–894.

204. Navalpotro, P.; Palma, J.; Anderson, M.; Marcilla, R. A Membrane-Free Redox Flow Battery with Two Immiscible Redox Electrolytes. Angew. Chem. 2017, 129, 12634–12639.

205. Bamgbopa, M.O.; Shao-Horn, Y.; Hashaikeh, R.; Almheiri, S. Cyclable Membraneless Redox Flow Batteries Based on Immiscible Liquid Electrolytes: Demonstration with All-Iron Redox Chemistry. Electrochim. Acta 2018, 267, 41–50.

206. Navalpotro, P.; Trujillo, C.; Montes, I.; Neves, C.M.S.S.; Palma, J.; Freire, M.G.; Coutinho, J.A.P.; Marcilla, R. Critical Aspects of Membrane-Free Aqueous Battery Based on Two Immiscible Neutral Electrolytes. Energy Storage Mater. 2020, 26, 400–407.

207. Navalpotro, P.; Sierra, N.; Trujillo, C.; Montes, I.; Palma, J.; Marcilla, R. Exploring the Versatility of Membrane-Free Battery Concept Using Different Combinations of Immiscible Redox Electrolytes. ACS Appl. Mater. Interfaces 2018, 10, 41246–41256.

208. Molina-Osorio, A.F.; Gamero-Quijano, A.; Peljo, P.; Scanlon, M.D. Membraneless Energy Conversion and Storage Using Immiscible Electrolyte Solutions. Curr. Opin. Electrochem. 2020, 21, 100–108.

Cost analysis studies showed most of the capital cost is due to the expensive ion exchange membranes [190]. One ambitious attempt to circumvent this problem is to design a configuration that does not rely on any membrane at all. This implies not only lower capital costs but also a device with lower resistance due to the lack of membrane [191]. Currently, there are two main alternatives to accomplish that: the laminar membraneless and the immiscible membraneless.

The laminar membraneless relies on hydrodynamic principles to keep a parallel laminar flow between the two electrolytes, creating an interface between them that is responsible for the ionic exchange [33].

The major concern of this approach is the high crossover that leads to a coulombic efficiency of ca. 50% [33]. Despite several configurations being designed and tested to date in order to decrease the crossover effect, this has not been achieved [192][193][194][195][196]. Not only that, but in some cases, this effect is so high that it is not possible to operate the cell in regenerative mode, and therefore the device is called a laminar flow fuel cell [192][193][195][196][197][198][199].

Additionally, the diffusion layer between the two electrolytes thickens towards the channel, which increases the cell resistance [33]. An alternative to reduce this effect is to increase the flow rate; however, this also represents a limitation, since the flow must be kept laminar in order to avoid the mixture of electrolytes [33].

Finally, since one of the major concerns about laminar flow membraneless cells is the reactant flow control, most of works were performed in microfluidic fuel cells. Despite this having a positive impact on the efficiency and current density of the device, it also increases the challenge to upscale this technology [194][197][198][200][201][202][203].

The immiscible membraneless RFB relies on thermodynamical principles to keep a parallel flow between two or more immiscible electrolytes. Therefore, since the very chemical properties of electrolytes create an interface between the two phases, it is possible to design an electrochemical device without using a membrane [204].

The major advantage of this kind of configuration in comparison with the laminar flow strategy is the reduction of reactant cross-over effect since the electrolytes are spontaneously separated due to their partition coefficients [205][206]. Additionally, it is easier to recirculate the electrolytes to operate in regenerative mode (charge–discharge cycles) [204][205][206][207][208].

However, as long as the anolyte and catholyte molecules on the interface are constantly in contact, this strategy still leads to higher indexes of self-discharge, which currently is one of the major drawbacks to be surpassed [206][207][208]. Despite there being some more advanced strategies to use the immiscible membraneless configuration, e.g., two non-aqueous phases separated by an aqueous phase, these devices are still on the laboratory scale due to their low energy density, solvent evaporation (which leads to unstable CDC), high ohmic resistance, and reliance on flammable organic solvents [209].

Finally, since the separation of electrolytes is provided by the partition coefficient, it also means that in order to select a redox pair for this battery configuration, one must not only combine good electrochemical stability and

209. Peljo, P.; Bichon, M.; Girault, H.H. Ion Transfer Battery: Storing Energy by Transferring Ions across Liquid–Liquid Interfaces. Chem. Commun. 2016, 52, 9761–9764.

210. Han, X.; Li, X.; White, J.; Zhong, C.; Deng, Y.; Hu, W.; Ma, T. Metal–Air Batteries: From Static to Flow System. Adv. Energy Mater. 2018, 8, 1801396.

211. Yu, W.; Shang, W.; Tan, P.; Chen, B.; Wu, Z.; Xu, H.; Shao, Z.; Liu, M.; Ni, M. Toward a New Generation of Low Cost, Efficient, and Durable Metal–Air Flow Batteries. J. Mater. Chem. A 2019, 7, 26744–26768.

212. Risbud, M.; Menictas, C.; Skyllas-Kazacos, M.; Noack, J. Vanadium Oxygen Fuel Cell Utilising High Concentration Electrolyte. Batteries 2019, 5, 24.

213. Charvát, J.; Mazúr, P.; Paidar, M.; Pocedič, J.; Vrána, J.; Mrlík, J.; Kosek, J. The Role of Ion Exchange Membrane in Vanadium Oxygen Fuel Cell. J. Membr. Sci. 2021, 629, 119271.

214. Chen, P.-T.; Sangeetha, T.; Hsu, T.-W.; Yang, C.-J.; Yung, T.-Y.; Yan, W.-M.; Huang, K.D. Improved Performance of a Zn-Air Fuel Cell by Coupling Zn Particle Fuel and Flowing Electrolyte. Chem. Phys. Lett. 2019, 728, 160–166.

215. Pei, P.; Huang, S.; Chen, D.; Li, Y.; Wu, Z.; Ren, P.; Wang, K.; Jia, X. A High-Energy-Density and Long-Stable-Performance Zinc-Air Fuel Cell System. Appl. Energy 2019, 241, 124–129.

216. Sangeetha, T.; Chen, P.-T.; Yan, W.-M.; Huang, K.D. Enhancement of Air-Flow Management in Zn-Air Fuel Cells by the Optimization of Air-Flow Parameters. Energy 2020, 197, 117181.

217. Zhang, N.; Deng, C.; Tao, S.; Guo, L.; Cheng, Y. Bifunctional Oxygen Electrodes with Gradient Hydrophilic/Hydrophobic Reactive Interfaces for Metal Air Flow Batteries. Chem. Eng. Sci. 2020, 224, 115795.

218. Yang, T.-F.; Lu, J.-H.; Yan, W.-M.; Ghalambaz, M. Optimization of Pulse Current on Energy Storage of Zinc-Air Flow Batteries. J. Power Sources 2019, 442, 227253.

219. Yu, W.; Shang, W.; Xiao, X.; Ma, Y.; Chen, Z.; Chen, B.; Xu, H.; Ni, M.; Tan, P. Elucidating the Mechanism of Discharge Performance Improvement in Zinc-Air Flow Batteries: A Combination of Experimental and Modeling Investigations. J. Energy Storage 2021, 40, 102779.

220. Huang, J.; Faghri, A. Capacity Enhancement of a Lithium Oxygen Flow Battery. Electrochim. Acta 2015, 174, 908–918.

221. Guang Zhu, Y.; Jia, C.; Yang, J.; Pan, F.; Huang, Q.; Wang, Q. Dual Redox Catalysts for Oxygen Reduction and Evolution Reactions: Towards a Redox Flow $Li–O_2$ Battery. Chem. Commun. 2015, 51, 9451–9454.

222. Zhu, Y.G.; Wang, X.; Jia, C.; Yang, J.; Wang, Q. Redox-Mediated ORR and OER Reactions: Redox Flow Lithium Oxygen Batteries Enabled with a Pair of Soluble Redox Catalysts. ACS Catal. 2016, 6, 6191–6197.

reversibility with a high concentration in their carbon and also an appropriate particle coefficient to guarantee the main advantages of this strategy [191][204][206][207][208].

3.2. Metal–Air Flow Batteries (MAFB) and Metal–Air Fuel Cells (MAFC)

MAFB are one of the answers for the low energy density of classical RFB and, as an added advantage, this technology also reduces the cost of materials. By reacting a metal, on the anode side, and oxygen, on the cathode side, it is possible to reduce the volume of the batteries, while also increasing the standard redox potential of the cell. These technologies are still in an early stage of their development; however, they show great potential as an energy storage system [3][210][211]. The main difference between MAFB and MAFC is that the latter are not rechargeable. Nevertheless, both technologies have a lot of similarities with RFBs, and they will both be discussed in this review. To date, most works published focus on the combination of vanadium, zinc, or lithium with air. This subchapter will focus on these technologies.

Vanadium–air fuel cells (VAFC) are very interesting to achieve higher energy densities when compared to VRFB. In these batteries, V (II) reacts with oxygen to produce V (III) and water. The utilization of air as one of the electrolytes removes the need to use two tanks to store energy but also unlocks the potential to increase the concentration of vanadium in the electrolyte operating at higher temperatures, since the V (V) solubility problems do not influence this technology. In 2019, a VAFC was reported by Risbud et al. [212]. They achieved a power density of 22 mW cm^{-2} at 40 mA cm^{-2} with a vanadium concentration of 3.0 M. With this concentration of vanadium, the VAFC has a theoretical energy density of 143.8 Wh L^{-1}, almost 3.5 times greater than a VRFC with the same concentration of active species. The membrane is a very important component of this technology.

Similarly to VRFB, the membrane needs to have a low permeability of vanadium ions, be chemically stable, and have a high ionic conductivity. In addition to this, low oxygen permeability through the membrane is required, as well as good water permeability to achieve good performance of the VAFC. Charvát et al. [213] studied the use of different cation-exchange membranes in a VAFC. They found that thinner membranes show better performance and stability under current load. The best assembly recorded a peak power density of 57 mW cm^{-2} and 75% coulombic efficiency with a discharge current density of 50 mA cm^{-2} and a charge current density of 150 mA cm^{-2}.

Zinc–air fuel cells (ZAFC) have the advantage of having a bigger standard potential (1.65 V) than VAFC (1.49 V). This technology still has a lot of parameters to be optimized. In 2019, Chen et al. [214] studied how the electrolyte flowrate affected the performance of a ZAFC, with zinc particles suspended in the solution. They reported a current density of 518.6 mA cm^{-2} at a potential of 0.8 V, which corresponds to a maximum power density of 427.7 mW cm^{-2} when using an optimum electrolyte flowrate of 100 mL min^{-1}. The reaction of oxidation of zinc produces zincate, which can become zinc oxide if the solution becomes oversaturated. This factor hinders the discharge reaction in the ZAFC; however, Pei et al. [215] incorporated a filter on the hydraulic circuit of the electrolyte to remove the circulation of these particles and thus reduce the effects of this problem. They also optimized the flow field of the anode to reduce passivation of this component, achieving an electrolyte capacity of 1025 Ah L^{-1}. On the other hand, Sageetha et al. [216] focused on the cathode side of the cell, testing different inlet air velocities, different oxygen ratios and pressurization of the inlet gases. Introducing air flow to the cell improved the cell's performance,

223. Ruggeri, I.; Arbizzani, C.; Soavi, F. Carbonaceous Catholyte for High Energy Density Semi-Solid Li/O2 Flow Battery. Carbon 2018, 130, 749–757.

224. Guo, L.; Guo, H.; Huang, H.; Tao, S.; Cheng, Y. Inhibition of Zinc Dendrites in Zinc-Based Flow Batteries. Front. Chem. 2020, 8, 557.

225. Xu, Z.; Fan, Q.; Li, Y.; Wang, J.; Lund, P.D. Review of Zinc Dendrite Formation in Zinc Bromine Redox Flow Battery. Renew. Sustain. Energy Rev. 2020, 127, 109838.

226. 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.

227. 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.

228. Jiang, H.R.; Wu, M.C.; Ren, Y.X.; Shyy, W.; Zhao, T.S. Towards a Uniform Distribution of Zinc in the Negative Electrode for Zinc Bromine Flow Batteries. Appl. Energy 2018, 213, 366–374.

229. Archana, K.S.; Naresh, R.p.; Enale, H.; Rajendran, V.; Mohan, A.M.V.; Bhaskar, A.; Ragupathy, P.; Dixon, D. Effect of Positive Electrode Modification on the Performance of Zinc-Bromine Redox Flow Batteries. J. Energy Storage 2020, 29, 101462.

230. Lu, W.; Xu, P.; Shao, S.; Li, T.; Zhang, H.; Li, X. Multifunctional Carbon Felt Electrode with N-Rich Defects Enables a Long-Cycle Zinc-Bromine Flow Battery with Ultrahigh Power Density. Adv. Funct. Mater. 2021, 31, 2102913.

231. Mariyappan, K.; Velmurugan, R.; Subramanian, B.; Ragupathy, P.; Ulaganathan, M. Low Loading of Felt for Enhancing Multifunctional Activity towards Achieving High Energy Efficiency of Zn–Br2 Redox Flow Battery. J. Power Sources 2021, 482, 228912.

232. Lee, J.-N.; Do, E.; Kim, Y.; Yu, J.-S.; Kim, K.J. Development of Titanium 3D Mesh Interlayer for Enhancing the Electrochemical Performance of Zinc–Bromine Flow Battery. Sci. Rep. 2021, 11, 4508.

233. Yuan, X.; Mo, J.; Huang, J.; Liu, J.; Liu, C.; Zeng, X.; Zhou, W.; Yue, J.; Wu, X.; Wu, Y. An Aqueous Hybrid Zinc-Bromine Battery with High Voltage and Energy Density. ChemElectroChem 2020, 7, 1531–1536.

234. 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.

235. Adith, R.V.; Naresh, R.p.; Mariyappan, K.; Ulaganathan, M.; Ragupathy, P. An Optimistic Approach on Flow Rate and Supporting Electrolyte for Enhancing the Performance Characteristics of Zn-Br2 Redox Flow Battery. Electrochim. Acta 2021, 388, 138451.

when compared to a cell with no air flow. Pressurizing the air also had a beneficial effect, since the content of O_2 was larger, and pure oxygen showed even better results.

The main difficulty for MAFB is finding cheap electrocatalysts that are active in the oxygen reduction reaction and in the oxygen evolution reaction. Moreover, these reactions are very sluggish, making the development of these electrocatalysts imperative to assure batteries with high efficiencies [3][210][211]. Zhang et al. [217] reported a zinc–air flow battery (ZAFB) that ran for 100 h without significant performance degradation. They designed a gradient hydrophilic/hydrophobic reactive interface in bifunctional oxygen electrodes, which reduced the overpotential at 50 mA cm^{-2} by 190 mV, increasing energy efficiency.

ZAFBs have an additional problem: the change of phase on the anode. Zinc is in a solid state and starts oxidizing to Zn^{2+} during operation, transforming it into an aqueous state. When the battery is recharged, zinc ions are reduced back into solid state, which can lead to the formation of dendrites that can easily puncture the membrane. The reduction of zinc can be influenced by many parameters. Using pulse current instead of direct current to recharge ZAFB (at 40 °C, a current of 1.4 A, frequency 50 Hz and 25% duty) has been shown to be an effective way to diminish the particle size of reduced zinc, and also, increase the amount that is reduced [218]. On the other hand, Yu et al. [219] assessed the advantage of using a flowing electrolyte in a ZAFB compared to a static zinc–air battery. They found that flowing the electrolyte improves the transfer of hydroxide and zincate ions, which translates to a 10% greater peak power density and 23% better specific discharge capacity.

Lithium–air flow batteries (LAFBs) appeared as a solution to the problems that were noticed with lithium–air static batteries, e.g., pore clogs, high overpotentials, and low power density [210]. In 2015, Huang and Faghri developed a two-dimensional model for an aprotic LAFB, which was able to formulate two methods to increase the battery capacity; the dual layer cathode and alternating electrolyte flow, achieving 105% higher capacity and an increase of 3.7% of cathode capacity, respectively [220]. Y. G. Zhu et al. [221] showed a LAFB with soluble redox catalysts; however, the author's solution did not solve the voltage hysteresis, which is noticeable in this type of battery due to the overpotentials. Later, the same group reported another study using the same strategy, however the soluble redox catalysts were changed. This study also proved to be unsuccessful since the catalysts used degraded over long cycles [222]. Ruggeri, Arbizzani, and Soavi proposed a lithium–air slurry flow battery, studying different weight percentages of Super-P® and Pureblack® carbons on the positive electrolyte. This report showed that by using this method the battery could be cycled for 120 cycles, i.e., 60 at 1.0 mA cm^{-2} and 60 at 0.5 mA cm^{-2} [223].

Even though MAFCs and MAFBs are promising technologies as energy storage systems, they are still in a very early stage of development and far from being a commercial technology. MAFCs still have questions that have not been correctly and fully addressed, such as their implementation on a real system. How would the electrolyte be recharged in this situation? Would the addition of another system to recharge the electrolyte be a viable option? How would the second electrolyte used to recharge the main electrolyte be used? On the other hand, MAFBs are easier to implement than MAFCs. However, the challenge and the high cost to design electrodes that are active in the oxygen reduction reaction and in the oxygen evolution reaction must still be overcome.

236. Yu, F.; Zhang, C.; Wang, F.; Gu, Y.; Zhang, P.; Waclawik, E.R.; Du, A.; Ostrikov, K.; Wang, H. A Zinc Bromine "Supercapattery" System Combining Triple Functions of Capacitive, Pseudocapacitive and Battery-Type Charge Storage. Mater. Horiz. 2020, 7, 495–503.

237. Wang, Z.; Tam, L.-Y.S.; Lu, Y.-C. Flexible Solid Flow Electrodes for High-Energy Scalable Energy Storage. Joule 2019, 3, 1677–1688.

238. Qi, Z.; Koenig, G.M. Review Article: Flow Battery Systems with Solid Electroactive Materials. J. Vac. Sci. Technol. B Nanotechnol. Microelectron. Mater. Process. Meas. Phenom. 2017, 35, 040801.

239. Ventosa, E.; Buchholz, D.; Klink, S.; Flox, C.; Chagas, L.G.; Vaalma, C.; Schuhmann, W.; Passerini, S.; Morante, J.R. Non-Aqueous Semi-Solid Flow Battery Based on Na-Ion Chemistry. P2-Type NaxNi0.22Co0.11Mn0.66O2–NaTi2(PO4)3. Chem. Commun. 2015, 51, 7298–7301.

240. Liu, Y.; Hu, Q.; Zhong, J.; Wang, Z.; Guo, H.; Yan, G.; Li, X.; Peng, W.; Wang, J. A Renewable Sedimentary Slurry Battery: Preliminary Study in Zinc Electrodes. iScience 2020, 23, 101821.

241. Percin, K.; Rommerskirchen, A.; Sengpiel, R.; Gendel, Y.; Wessling, M. 3D-Printed Conductive Static Mixers Enable All-Vanadium Redox Flow Battery Using Slurry Electrodes. J. Power Sources 2018, 379, 228–233.

242. Petek, T.J.; Hoyt, N.C.; Savinell, R.F.; Wainright, J.S. Slurry Electrodes for Iron Plating in an All-Iron Flow Battery. J. Power Sources 2015, 294, 620–626.

243. Chen, H.; Liu, Y.; Zhang, X.; Lan, Q.; Chu, Y.; Li, Y.; Wu, Q. Single-Component Slurry Based Lithium-Ion Flow Battery with 3D Current Collectors. J. Power Sources 2021, 485, 229319.

244. Ye, J.; Xia, L.; Wu, C.; Ding, M.; Jia, C.; Wang, Q. Redox Targeting-Based Flow Batteries. J. Phys. D Appl. Phys. 2019, 52, 443001.

245. Chayambuka, K.; Fransaer, J.; Dominguez-Benetton, X. Modeling and Design of Semi-Solid Flow Batteries. J. Power Sources 2019, 434, 226740.

246. Li, Z.; Smith, K.C.; Dong, Y.; Baram, N.; Fan, F.Y.; Xie, J.; Limthongkul, P.; Carter, W.C.; Chiang, Y.-M. Aqueous Semi-Solid Flow Cell: Demonstration and Analysis. Phys. Chem. Chem. Phys. 2013, 15, 15833–15839.

247. Zhu, Y.G.; Narayanan, T.M.; Tulodziecki, M.; Sanchez-Casalongue, H.; Horn, Q.C.; Meda, L.; Yu, Y.; Sun, J.; Regier, T.; McKinley, G.H.; et al. High-Energy and High-Power Zn–Ni Flow Batteries with Semi-Solid Electrodes. Sustain. Energy Fuels 2020, 4, 4076–4085.

248. Mourshed, M.; Niya, S.M.R.; Ojha, R.; Rosengarten, G.; Andrews, J.; Shabani, B. Carbon-Based Slurry Electrodes for Energy Storage and Power Supply Systems. Energy Storage Mater. 2021, S2405829721002440.

3.3. Zinc–Bromine Flow Batteries

Zinc–bromine flow batteries (ZBFB) are inserted in the electroplated flow battery category. This section will focus on the ZBFB, since this is considered one of the most representative type of electroplated flow battery, with a lot of research conducted to improve its performance. Moreover, this technology is one of the few RFB that has been commercially available and has large scale applications. When ZBFBs are fully charged, zinc is in the solid state, which gives an advantage in energy density to this type of RFB in relation to others. Additionally, ZBFB have a redox standard potential of 1.58 V. Even though the theoretical ZBFB specific energy is 440 Wh kg^{-1}, commercial systems only reach 14–19% of this value. These batteries also suffer from other problems, e.g., zinc dendrite formation in the negative electrode, corrosion of the electrode, and the addition of expensive complexing agents to prevent the diffusion of bromine. The core materials used in ZBFB are cheaper than the ones used on other RFBs, however, the solutions to solve the problems previously explained make the commercial price of these batteries similar to other RFBs [3][10][224][225]. Zinc–bromine flow batteries (ZBFB) are inserted in the electroplated flow battery category. These batteries also suffer from other problems, such as zinc dendrites formation in the negative electrode, corrosion of the electrode and the addition of expensive complexing agents to prevent the diffusion of bromine. The core materials used in ZBFB are cheaper than the ones used on other RFBs; however, the solutions to solve the problems previously explained make the commercial price of these batteries similar to other RFBs [3][10][224][225].

The focus of research toward ZBFB has been the reduction of dendrite formation and improvement of the electrolyte conductivity. To attenuate these downsides, M. C. Wu et al. [226] added chloride-based salts to act as a supporting electrolyte and showed 74.3% EE at 40 mA cm^{-2}, which represented an improvement of 13.9% when compared to a ZBFB without this addition to the electrolyte. Furthermore, they did a thermal treatment to the graphite felt electrode, which improved the performance of the cell even more reaching a value of 81.8% EE at the same current density. The same group surpassed these results one year later by adding methanesulfonic acid to the electrolyte, which further increased the EE to 75% at the same current density. In this study, thermally treated electrodes were also added, which translated to an EE of 78% at 80 mA cm^{-2} (in the previous publication, they had achieved 70% EE at the same current density) [227].

H. R. Jiang and coworkers studied how to promote a uniform distribution of zinc throughout the electrode and found that it was possible to achieve this by increasing the number of single vacancies, having demonstrated this by comparing a graphite felt electrode with defects and an original graphite felt electrode in a ZBFB [228]. Archana et al. [229] opted to just modify the graphite felt electrode with a thermal treatment and a plasma treatment under oxygen and nitrogen atmospheres. The authors reported that electrodes with high surface areas and functional groups showed improved performance during cycling at low current densities. However, it was concluded that for higher current densities, electrodes covered with oxygen functional groups on the surface were preferred. W. Lu doped carbon felt electrodes with nitrogen, reaching an EE of 63.07% at 180 mA cm^{-2}, with a more uniform deposition of zinc on its surface [230]. Mariyappan and coworkers studied the effect of adding a low loading of platinum on graphite felt using a pulsed laser deposition. An 88% EE at 50 mA cm^{-2} was achieved using the mentioned strategy [231]. Lee et al. [232] implemented a titanium-based mesh interlayer with a carbon-based

249. Yan, W.; Wang, C.; Tian, J.; Zhu, G.; Ma, L.; Wang, Y.; Chen, R.; Hu, Y.; Wang, L.; Chen, T.; et al. All-Polymer Particulate Slurry Batteries. Nat. Commun. 2019, 10, 2513.
250. Yan, R.; Wang, Q. Redox-Targeting-Based Flow Batteries for Large-Scale Energy Storage. Adv. Mater. 2018, 30, 1802406.
251. Lohaus, J.; Rall, D.; Kruse, M.; Steinberger, V.; Wessling, M. On Charge Percolation in Slurry Electrodes Used in Vanadium Redox Flow Batteries. Electrochem. Commun. 2019, 101, 104–108.
252. Brunini, V.E.; Chiang, Y.-M.; Carter, W.C. Modeling the Hydrodynamic and Electrochemical Efficiency of Semi-Solid Flow Batteries. Electrochim. Acta 2012, 69, 301–307.
253. Páez, T.; Martínez-Cuezva, A.; Palma, J.; Ventosa, E. Mediated Alkaline Flow Batteries: From Fundamentals to Application. ACS Appl. Energy Mater. 2019, 2, 8328–8336.
254. Zanzola, E.; Dennison, C.R.; Battistel, A.; Peljo, P.; Vrubel, H.; Amstutz, V.; Girault, H.H. Redox Solid Energy Boosters for Flow Batteries: Polyaniline as a Case Study. Electrochim. Acta 2017, 235, 664–671.
255. Zhou, M.; Huang, Q.; Pham Truong, T.N.; Ghilane, J.; Zhu, Y.G.; Jia, C.; Yan, R.; Fan, L.; Randriamahazaka, H.; Wang, Q. Nernstian-Potential-Driven Redox-Targeting Reactions of Battery Materials. Chem 2017, 3, 1036–1049.
256. Moghaddam, M.; Sepp, S.; Wiberg, C.; Bertei, A.; Rucci, A.; Peljo, P. Thermodynamics, Charge Transfer and Practical Considerations of Solid Boosters in Redox Flow Batteries. Molecules 2021, 26, 2111.
257. Choi, N.H.; del Olmo, D.; Milian, D.; El Kissi, N.; Fischer, P.; Pinkwart, K.; Tübke, J. Use of Carbon Additives towards Rechargeable Zinc Slurry Air Flow Batteries. Energies 2020, 13, 4482.
258. Dmello, R.; Milshtein, J.D.; Brushett, F.R.; Smith, K.C. Cost-Driven Materials Selection Criteria for Redox Flow Battery Electrolytes. J. Power Sources 2016, 330, 261–272.

electrode to suppress the formation of dendrites, achieving 48.2% EE at 40 mA cm^{-2}. A cathode catalyst of carbon-manganite nanoflakes in combination with a K^{+}-conducting membrane were studied by X. Yuan and his team. An average output potential of 2.15 V and 276.7 Wh kg^{-1} energy density without capacity fade over 200 cycles was reported [233].

Even though changes in the electrode and on the electrolyte are the most reported strategies to improve the performance of ZBFB, there are also other strategies that should be considered. L. Hua et al. [234] proposed a porous composite membrane in addition to a bromine complexing agent and reached an EE of 85.31% at 40 mA cm^{-2} with a stable operation at 140 mA cm^{-2}. The influence of flow rate on the polarization effect and the addition of perchloric acid to the positive electrolyte were studied by Adith and coworkers, having achieved an EE of ca. 69% at 30 mA cm^{-2} [235]. F. Yu and coworkers aimed higher, and proposed a “supercapattery” by using soluble additives in the electrolyte combined with a S/P co-doped carbon-based positive electrode and a carbon cloth-based negative electrode. These changes culminated in a battery with 270 Wh kg^{-1} and a maximum power density of 9300 W kg^{-1} [236].

ZBFB are one of the RFBs with the most know-how. However, these batteries still exhibit disadvantages that cannot be ignored. Problems such as the formation of dendrites can only be mitigated and never fully solved. The premise of ZBFB is very enticing, i.e., higher redox standard potential, higher specific energy, and low-cost materials. Nonetheless, the extra care that must be taken with these types of batteries to ensure safe use and long life increase their price, making them lose the main advantages against batteries that use more expensive materials. Even though these batteries are commercially available, they do not seem a promising a long-term solution, and will be replaced as soon as an improved low-cost option becomes available.

3.4. Semi-Solid (Slurry Flow Batteries)

3.4.1. Without Redox Mediator

In order to overcome the solubility limitations of conventional electrolytes, one possible alternative is to use a semi-solid electrolyte [237][238]. This approach means that the active species are a suspension (instead of solution) and therefore can react without being dissolved in the electrolyte. The electrodes are usually carbon paper and/or suspended porous materials (conducting additive) since graphite felt would be clogged by the suspended species [237][238]. This configuration is represented in **Figure 6**.

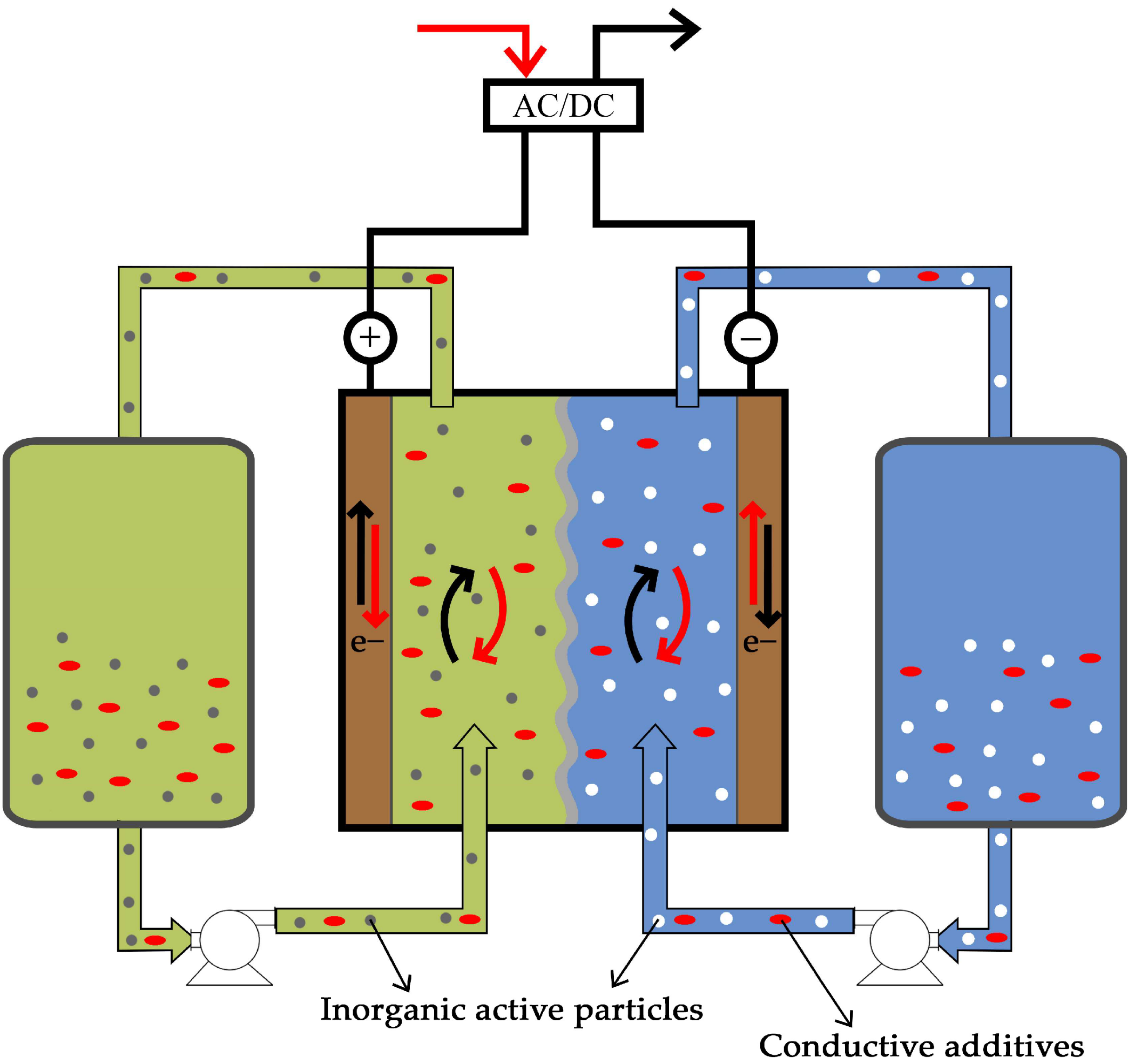

Figure 6. Representation of a semi-solid RFB without a redox mediator. Adapted from Ref. [239], Copyright 2015, Royal Society of Chemistry.

Since the concentration of these redox species is not limited by the solubility threshold, it is possible to achieve higher energy densities both with inorganic or organic redox species [59][237][238][240][241][242][243][244][245]. Additionally, the semi-solid RFB can be either aqueous [246][247] or non-aqueous, such as the one represented in **Figure 7**. Furthermore, decreasing the particle size will result in improved diffusion, enhanced charge transfer, and higher current densities [248]. However, despite these advantages, it is also true that decreasing the particle size will also contribute to the crossover effect and therefore will reduce the coulombic efficiency [248]. Beyond that, for higher concentrations the viscosity of the electrolyte will also increase, ultimately increasing the pressure drop, which is one of the biggest drawbacks of this strategy [3][207][210][213][214][216][217][218].

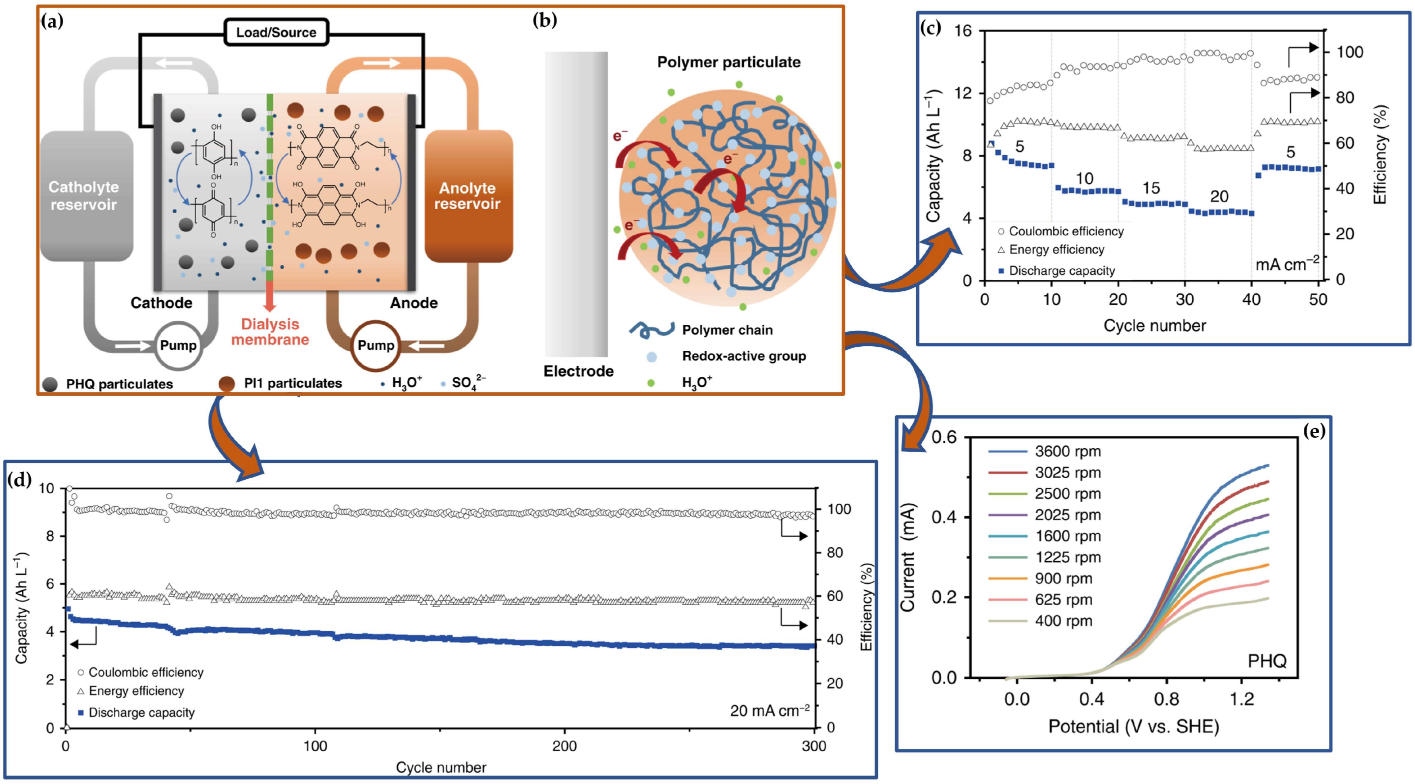

Figure 7. Organic slurry RFB based on all polymer particulate suspension reported by Yan et al. [249]. (**a**) Schematic representation of the mentioned organic slurry RFB. (**b**) Illustration of the proposed kinetic mechanism to elucidate the charge transfer particulates in the redox processes. (**c**) The capacity, coulombic efficiency, and voltage efficiency in a galvanostatic charge–discharge cycle for current densities from 5 mA cm^{-2} to 20 mA cm^{-2}. (**d**) Representation of the long-term stability during charge–discharge cycles at 20 mA cm^{-2}. (**e**) Representation of the polarization curves for different flowrates. Copyright 2019, Springer Nature.

Finally, there is also a trade off when choosing the concentration of carbon particles (conductive additives): increasing it enhances the solution’s electrical conductivity and therefore improves the electrochemical performance of the device; however, it will also increase the viscosity of the suspension and will reduce the energy density [238][250][251][252].

3.4.2. Redox Mediator

In order to circumvent the pressure drop issued due to higher concentrations of redox species, it is possible to use redox mediators, which means that the main redox species do not flow with the electrolyte, which is restricted to the reservoirs. Instead, a redox mediator (secondary redox species) flows into the cell, reacts when in contact with the bipolar plate, and then goes back to the tank and reacts with the main redox species [5][244][253]. This principle is schematized in **Figure 8**. In order to circumvent the pressure drop issues due to higher concentrations of redox species, it is possible to use redox mediators, which means that the main redox species do not flow with the electrolyte, being restricted on the reservoirs. Instead, a redox mediator (secondary redox species) flows into the cell, reacts when in contact with the bipolar plate, and then goes back to the tank and reacts with the main redox species [5][244][253]. This principle is schematized in **Figure 8**.

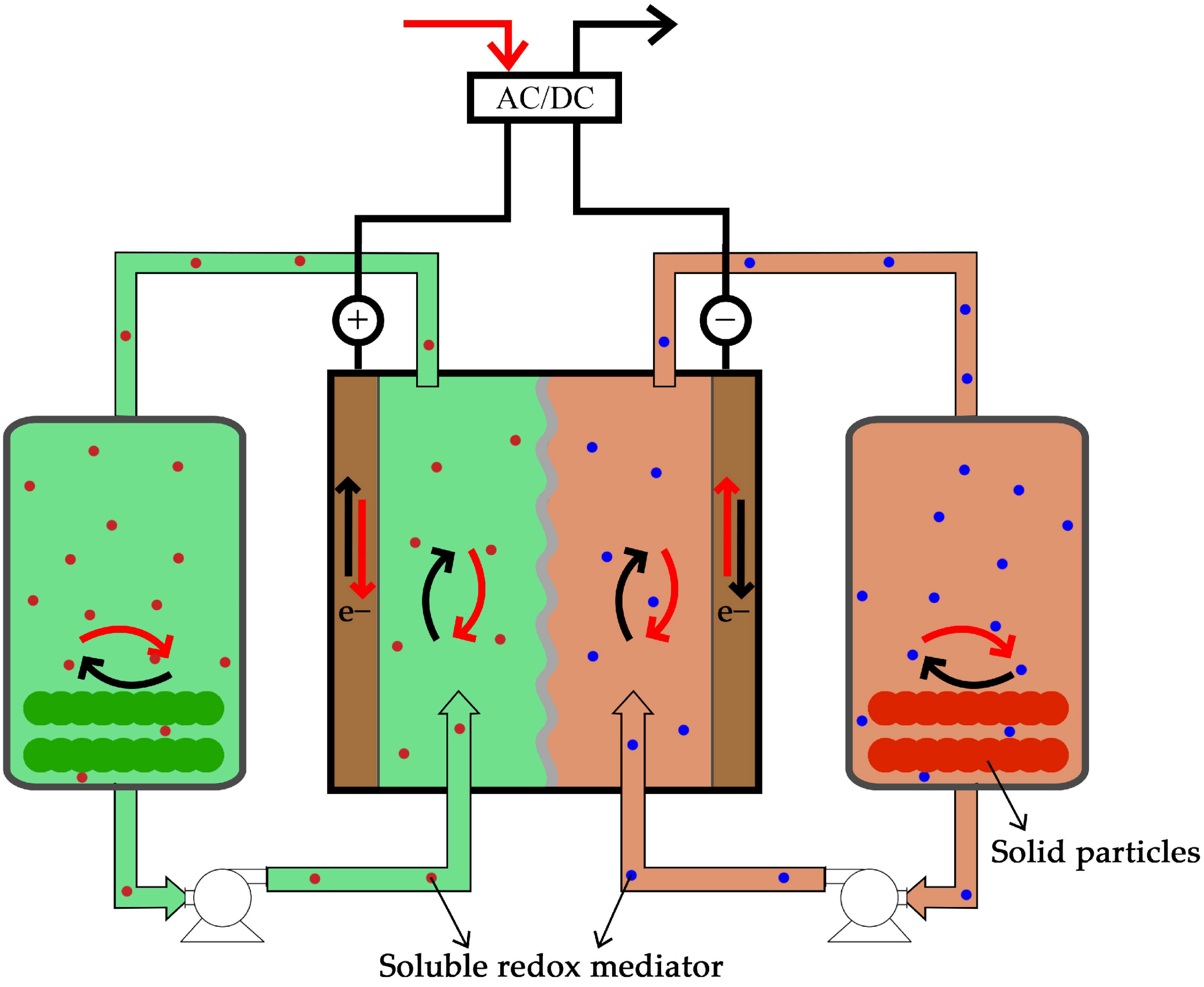

Figure 8. Representation of a semi-solid RFB with redox mediator. Adapted from Ref. [20], Copyright 2015, MDPI.

Therefore, it is possible to store energy on the main species while relying on the fluidity and viscosity of the redox mediator, not only decreasing the pressure drop but also enhancing the charge transport and thus the power output [244][250]. The major drawbacks of this approach is that since there are two kinetic processes involved (in cell and in tanks), the device electrochemical performance tends to decrease (coulombic and voltage efficiency, current/power density), despite there still being some divergence about this topic [53][254]. Additionally, this double kinetics system leads to a dependence between power and capacity [250][255] and the screening process of choosing mediator and active species gets even harder when compared to other electrolytes [250].

To conclude, semi-solid batteries are a promising strategy to achieve the main advantages of conventional RFBs for chemistries that otherwise would be electroplated on the graphite felt (therefore, power and energy are not decoupled). Semi-solid batteries can also increase the energy density since the latter is not limited by the solubility of the species. Furthermore, the charge storage capacity of the solid particles can be restrained in the tanks and ca. 80% of this capacity can be reached depending on the compatibility established between the redox electrolyte and redox solid [256]. Furthermore, it is also possible to combine the slurry redox flow battery with other configurations, e.g., slurry–air [257]. However, every approach until now severely undermines the electrolyte flow due to high viscosity, increasing the pressure drop and ultimately decreasing the round-trip efficiency. Despite some attempts to circumvent this, e.g., decreasing the conductivity additives or using mediator species, it ultimately undermines the reaction rate and therefore current density or even efficiencies are compromised. To make this technology commercially viable, it is essential to overcome these problems.

4. Challenges and Future Perspectives

The main challenges of most RFBs include establishing harmless and environmentally acceptable electrolytes that are sustainable and cost-effective. Developing suitable electrode materials and electrocatalyst coatings easy to produce at a large scale, particularly for organic RFBs, is a major barrier. Most challenges related to RFBs are linked to battery design, which has the potential to enhance energy density by lowering the high viscosity of electrolytes. The aspects for improvement include the control of the flow of the electrolyte, electron communication at the interface of electrode, and the electrode surface. On the other hand, although not relevant for stationary energy storage, the weight of these types of batteries is a barrier for the non-stationary transition. Soon, the research focus should be on decreasing the development cost of this type of battery to make them more attractive and allow for their massive utilization. Therefore, the future of RFBs must involve the optimization of new active species and new configurations to overcome the current difficulties. These studies should be complemented with life cycle assessment studies on new batteries to ensure that environmentally friendly technologies are employed.

According to the literature, to reach a wide market diffusion, the capital cost of RFBs should be less than USD$ 150 (kW h)$^{-1}$ by 2023 [29]. For aqueous systems, Dmello et al. [258] suggest a cost target of USD$ 100 (kW h)$^{-1}$. However, this cost was dependent on the active material cost, active material molar mass, specific resistance of the battery, and cell voltage. The value proposed was based on combining USD$ 2 kg^{-1} active material cost, 100 g mol^{-1} molar mass of active material, 0.5 Ω cm^2 area specific resistance of the battery, and 0.79 V cell voltage. Regarding non-aqueous systems, the cost is not so dependent on the active material cost since the cost of solvents used may range from USD$ 2 to 20 kg^{-1}, (e.g., nitriles, glymes, and carbonates, may go up to USD$ 20 kg^{-1}) and fluorinated salts (e.g., tetrafluoroborates, hexafluorophosphates and bis(tri-fluoromethylsulfonyl)imides, USD$ 2 kg^{-1}). Therefore, the most effective methodology to reduce the overall cost of NA-RFB is by increasing the cell voltage. Dmello et al. [258] proposed a cost target of USD$ 100 (kW h)$^{-1}$ by combining 100 g mol^{-1} molar mass of active material with area specific resistance of the battery of 2.5 Ω cm^2, a cell voltage of 3.0 V, a 0.2 salt ratio, and 3.3 mol kg^{-1} active molarity [258].

It will be necessary to establish the RFB parameters that are affected by degradation, such as corrosion, and their impact level on performance. It will be, likewise, important to define the state of health of a RFB system that, to the best of the authors' knowledge, has not been studied in detail (nor is there yet a plan to do so).

Another area that needs attention is the detection of failures, the characterization of such failures, their cause, and the damage level within the system. Nevertheless, it should be kept in mind that the variables to be measured and the instrumentation to be used should be balanced between the efficiency and costs involved. Another important tool is the automation that will have an extremely important role here since it will allow us to reduce costs and implement the detection mechanisms capitalizing RFB's performance and making it safer and more reliable. The development of suitable mathematical models to simulate and rationalize the cell performance as well as the development of consistent multi- and unsymmetrical cycle performance at a large-scale pilot in modular stacks, i.e., up to grid-level, will also be of extreme importance.

The use of computational tools and interdisciplinary knowledge created may be expressively improved to meet the criteria for commercialization and global applications. Understanding the fundamentals of such systems through modeling, design, synthesis, and wide-scale collaboration between research groups will allow us to address the energy storage needs of the future [48].