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Current Opinion in
Chemical Engineering

Semi-solid flow battery and redox-mediated flow battery: two strategies to implement the use of solid electroactive materials in high-energy redox-flow batteries

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Implementing the use of solid electroactive materials in redox-flow battery (RFB) configuration is an appealing challenge since the resulting battery technologies benefit from the high energy density of solid materials and the independent scalability of energy and power of RFB configuration. In recent years, two different strategies have emerged to achieve this goal: i) the *semi-solid flow batteries* and ii) the *redox-mediated flow batteries*, also referred to as redox targeting or solid booster, each battery type having intrinsic advantages and disadvantages. In this perspective review, recent progress addressing critical factors for each technology is revised. In particular, chemical engineering aspects are of vital importance for further improvement and practical deployment of these two technologies.

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Current Opinion in Chemical Engineering 2022, **37**:100834

This review comes from a themed issue on **Redox Flow Batteries**

Edited by **Yondan Li**, **Cristina Flox** and **Cuijuan Zhang**

For complete overview of the section, please refer to the article collection, “Redox Flow Batteries”

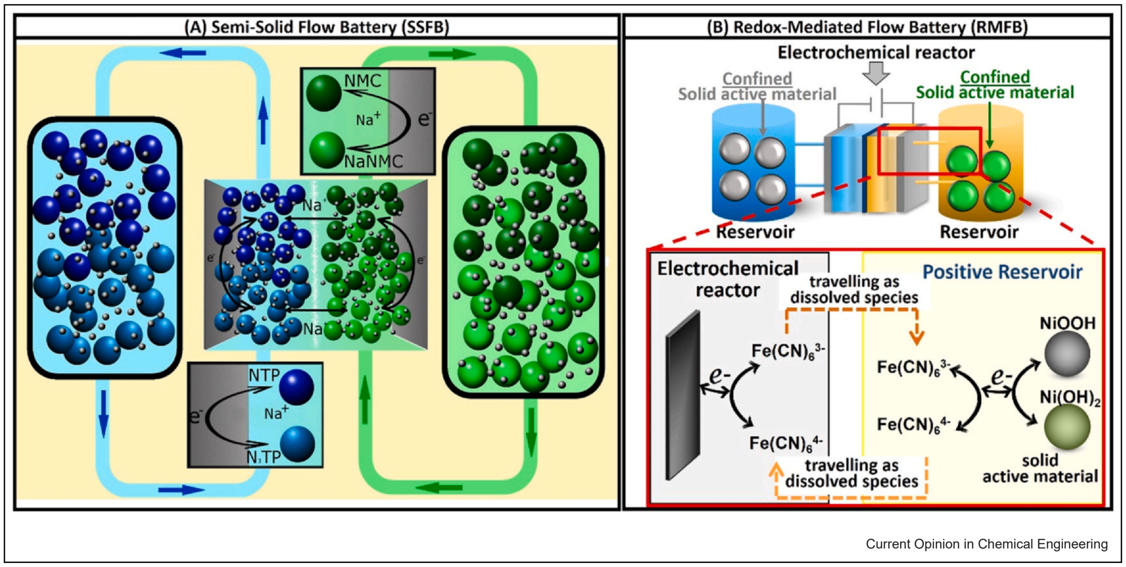
Available online 2th June 2022

https://doi.org/10.1016/j.coche.2022.100834

Introduction

The increasing need for energy storage has driven growth in the field of batteries, as they are nowadays used in multiple applications. Li-ion batteries (LiBs) dominate the market due to their energy density, energy efficiency, cycle life, and moderate cost. The irruption of electric vehicles has triggered an already-growing interest in this battery technology. The sharp increase in LiB production is driving a steady decrease in cost, but it has also raised concerns related to the availability of necessary elements, such as Co and Li, and environmental cycle life. These concerns together with the demanding requirements of emerging battery applications have brought much interest to alternative battery technologies. The redox-flow batteries (RFBs) are a family of battery technologies that are featured by the fact that energy-storing materials are stored outside the battery cells offering distinct characteristics [1]. The electroactive species are typically dissolved in an electrolyte that is stored in external reservoirs and pumped into an electrochemical reactor for energy conversion (electrical energy–chemical energy). Compared with LiBs, two intrinsic features are driving interest for RFBs: independent scalability of energy and power, and simple recyclability. On the other hand, practical energy density of RFBs is still far from the values achieved for LiBs. This disadvantage is due to the lower concentration of redox-active centers for dissolved species in an electrolyte, compared with that of solid particles. Despite incremental improvements in energy density have been achieved for RFBs, disruptive approaches were explored to boost it. The use of high-energy solid electroactive particles in RFB configuration is conceptually a simple idea. However, its implementation is not straightforward at all. Solid particles need to be electrically connected with the current collectors (electrochemical reactor) for charge transfer to occur, but at the same time, active materials should be stored in the external reservoirs for power and energy to remain decoupled. Note that we do not include hybrid-flow batteries such as Zn-flow batteries since solid electroactive species are stored inside the reactor. Generally, two major strategies are being followed to implement the use of solid materials in RFBs: i) the *semisolid flow batteries* (SSFBs) and ii) the *redox-mediated flow batteries* (RMFBs), also referred to as redox targeting or solid booster. The main difference between them relies on the fact that solid electroactive materials flow through the entire system in the form of slurries for SSFB (Figure 1a), while they are confined in the external reservoirs and dissolved species act as charge carriers (redox mediators) between reactor and reservoir for the case of RMFBs (Figure 1b). This short review article revises, from a personal perspective, recent progress on both types of RFBs addressing the remaining challenges.

Figure 1



Schematic representation of (**a**) the SSFBs and (**b**) the RMFBs.
Adapted with permission from Refs. [2,3].

Semisolid flow batteries

In the SSFB, solid electroactive particles are mixed with conducting additive and electrolyte forming an electrically and ionically conducting slurry that is referred to as semisolid electrode and used as an energy-storing fluid (Figure 1a). The pioneering work led by Chiang at MIT demonstrated the proof-of-concept for a Li-ion SSFB. Several studies extended the concept to different battery chemistries such as Na-ion [2], Li–S [4], and organic–redox materials [5], as well as aqueous-based electrolyte [6]. Besides the higher energy density, semisolid electrodes also enable the use of low-cost microporous separators, since solid electroactive particle are confined in their corresponding compartment by size exclusion. It should be noted that, in case of nonaqueous electrolyte, ion-selective membranes are not just more expensive, but their performances are poorer. Thus, the use of semisolid electrodes in nonaqueous electrolytes overcomes the challenges of the membrane for nonaqueous RFBs. Regardless the nature of the electrolyte, all SSFB chemistries share common challenges. The most important engineering aspects for SSFBs are related to the electrochemical reactor. Nevertheless, recent progress addressing the main challenges discussed below is sorted by battery key performance indicators to be improved.

Minimize energy consumption for continuous pumping of slurries

Continuous pumping of dense slurries consumes energy-reducing energy efficiency of the system. Thus, improving this aspect is a key aspect for practical development of SSFBs. In this sense, different strategies have been proposed in the literature. I) Intermittent-flow operation, in which the pump is switched on intermittently reducing the pumping consumption [7]. II) The gravity-induced flow-battery architecture represents a family of approaches to simpler, passively driven, low-dissipation flow for semisolid electrodes [8]. III) Improving rheological properties by adding chemical stabilizers in the formulation of semisolid electrodes [9,10]. IV) Addition of redox mediators that contribute to charge transport [11••,12•], which may enable reduction of carbon content improving flowability and ionic conductivity. An alternative to avoid continuous pumping is the use of semisolid electrode in static batteries. While the company 24 M employs nonflowable semisolid electrode to increase the areal capacity of the battery cells (24M Technologies, https://24-m.com/), and our group has exploited the use of semiflowable semisolid electrode to facilitate the recycling of static batteries [13].

One important practical point for SSFBs that remains unaddressed is the shunt currents when multiple cells in a cell stack are used. It is expected that this effect for SSFB is stronger than that experienced for conventional RFBs, which may lead to a significant decrease in energy efficiency. Intensive attention to this point is required.

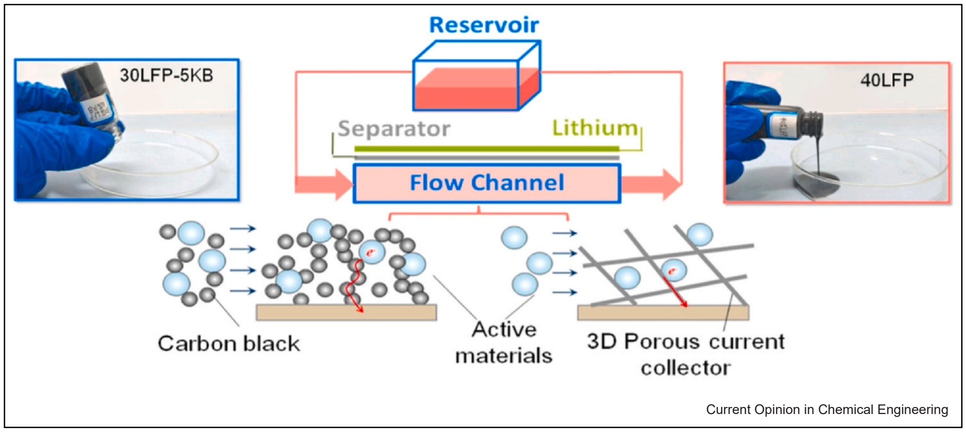
Increase specific power to decrease upfront cost of the system

Despite that the use of low-cost microporous separator reduces the upfront cost of the reactor per unit of area, the operating current density (mA cm^{-2}) and the specific power (W cm^{-2}) will determine whether the final power cost for SSFBs is lower than that of conventional RFBs. That is, power capacities directly determine the size of the electrochemical reactor to reach a target power, for example, 1 kW. Thus, the power cost (contribution of the electrochemical reactor) is strongly dependent on power capability. On the other hand, ion-selective membrane is the most expensive electrode of the electrochemical reactor. Thus, exchanging ion-selective membrane for microporous separators will lead to a significant decrease in power cost. This decrease will enable systems using microporous separators to operate at lower current density (large reactor). If the power cost is estimated as a function of the current density for systems based on ion-selective membrane and microporous separators, one can determine which is the minimum current density for a microporous separator-based system to have a lower power cost than an ion-selective membrane-based system operating at a given current density. To give a general idea, it was estimated that a minimum current density of 10 mA cm^{-2} is necessary for the power cost of SSFBs (1.2 V) to be lower than conventional all-vanadium RFBs operating at 100 mA cm^{-2} [14•]. In other words, the lower cost of microporous separator allows the use of 10 times more area (more separator, current collectors) to deliver the same power. Several studies have focused on tackling this issue. I) Exploring different types of electrically conducting networks, for example, nanotubes [15] and superconcentrated electrolytes [16]. Rheological properties should be investigated in the latter case. II) The addition of redox mediators proposed in refs. [11••] and [12•] could result in a reduction of carbon content and thus increase the ionic conductivity without compromising electron transport. III) Reactor geometry, for example, including 3D-printed conductive static mixers [17] and the use of tubular geometries [18], have been shown to play an important role. IV) Removal of carbon additive in the formulation of semisolid electrodes combined with the use of 3D current collectors [19••] (Figure 2). It should be noted that decrease in viscosity due to the lower carbon content can outweigh the increase in pressure drop due to the 3D current collector. Improvements of engineering aspects of the cell architecture are of vital importance, requiring much effort to be devoted, since many parameters can be optimized, even for conventional SSFB configuration, for example, reducing thickness while avoiding an increase in pressure.

Prevent electrolyte decomposition to increase cycle life and energy efficiency

The most widely used carbon additive is Ketjen black EC-600, in which the specific surface area is 1.200 m^2 g^{-1}. As a result, the electrochemical surface area is larger than that of conventional RFBs. In addition, electrodes are ‘mobile’, so that the total ‘fresh’ surface area of the entire electrode is huge compared with conventional RFBs. The former point leads to promoted water splitting in aqueous media, while the latter results in enhanced SEI formation in nonaqueous electrolytes. Removal of carbon additive from semisolid electrode combined with the use of 3D current collectors explored in Ref. [19••] is a promising approach to address the issues. Development of new materials that operate within the stability window of the electrolyte is a suitable approach [20], as demonstrated by Chen et al. by implementing the use of high-energy-density $CuSi_2P_3$ [10], as well as implementation of new electrolytes having large stability window such as superconcentrated electrolytes [21•]. And changing the nature of the carbon additive has also shown that hardly accessible materials for SSFBs such as SiO_x can be

Figure 2



Schematic representations of conventional SSFB configuration in which the slurries contain carbon additive and proposed concept in which slurries do not contain carbon additive and 3D current collector is required.
Adapted with permission from Ref. [19].

successfully lithiated using the appropriate network of carbon additive [15].

Search for new suitable chemistries for semisolid flow batteries

Much efforts are focused on developing new chemistries that are more suitable in SSFB configuration. For example, aqueous Zn–MnO_2 is an extremely cheap chemistry [22]. The implementation of these chemistries in RFB configuration that enables reducing the cost of power for long storage applications would result in a very suitable and cheap technology for storing energy for long periods of times. On the other hand, Si-based [15] and phosphorus-based [10] SSFBs pave the way toward high-energy-density nonaqueous SSFB. Last but not least, an important example is the implementation of sustainable organic-based solid materials bearing in mind the importance of abundance and accessibility of raw materials [5,11••].

Redox-mediated flow batteries

Also referred to as redox-targeting and solid-boosted flow batteries, solid electroactive particles in RMFBs are *confined* in the external reservoirs (Figure 1b). Electroactive species dissolved in the electrolyte carry charges between solid electroactive particles confirmed in the external reservoir and electrodes in the battery cells. Despite the pioneering works were conducted using nonaqueous electrolytes [23–25], this short review focuses on recent progress achieved in aqueous media since the need for ion-selective membranes that perform poorly in nonaqueous media is the main challenges in nonaqueous RMFBs. It should be noted that implementation of redox-mediated concept RFB architecture using microporous separators is possible through the use of colloidal redox polymer dissolved in electrolyte [26]. Thus, the emphasis of RMFB on aqueous systems is a personal perspective.

Since RMFBs employ the conventional configuration of RFBs, the most important engineering aspects for RMFBs are related to the external reservoirs. The key processes related to external reservoirs are here sorted into three categories as follows.

Spontaneous and reversible charge transfer between dissolved species and solid electroactive materials

Intrinsic thermodynamics and kinetics aspects of charge-transfer reaction between dissolved species and solid electroactive particles confined in the reservoirs are critical for this technology. Understanding these aspects is fundamental to achieve progress for RMFBs. Examples include the following studies. Wang et al. demonstrated that the thermodynamics shift of equilibrium potential of the redox electrolyte enables the use of one single redox mediator for both the charge and discharge process, enhancing voltage efficiency [27••]. Our group showed that opposite shift in redox potential of redox electrolyte and solid electroactive materials with the concentration of the salt makes certain pairs of redox mediator/solid booster very sensitive to parameters [3•]. Peljo et al. [28] investigated the influence of adding carbon additive in charge-transfer kinetics for the solid booster package. The addition of less than 10% CNT to the solid booster material promoted the charge transfer and improved the utilization rate of the solid booster. Importantly, research methodologies need to be standardized for the study of intrinsic properties. Recommendations are i) the use of techniques that provide redox potentials at equilibrium for evaluating thermodynamics aspects, instead of cyclic voltammetry [3], and ii) the use of scanning electrochemical microscopy to extract intrinsic kinetics properties [29].

Engineering aspects of the external reservoir

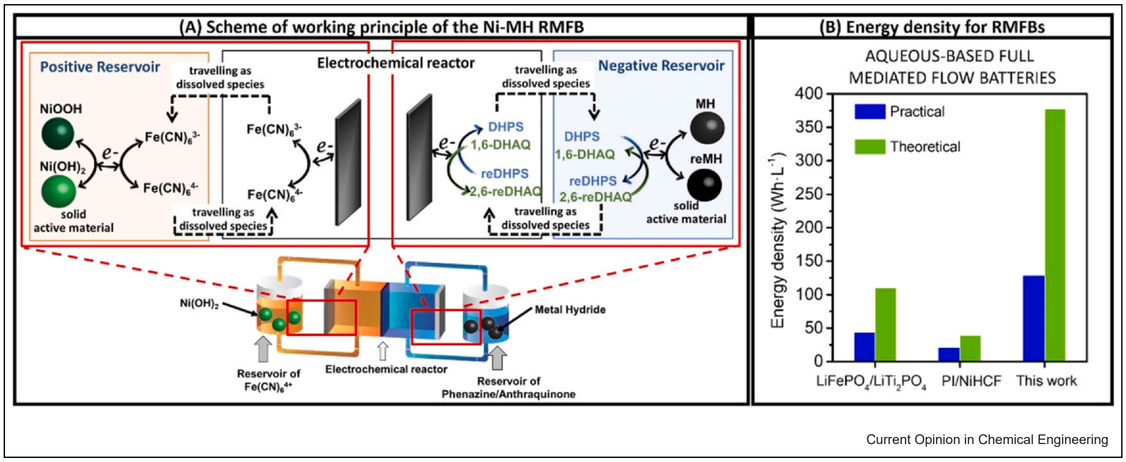
While these aspects may not be so critical at lab bench scale for proof-of-concept studies, efficient packaging of solid electroactive materials in the reservoirs is of great importance, especially when upscaling is aimed. Particles should be densely packed to maximize energy density, while facile and homogeneous flow of redox electrolyte should be maintained. In this regard, there are two relevant works. On the one hand, dense pellets of $LiFePO_4$ with controlled total porosity, obtained by spark plasma sintering using NaCl microcrystals as hard template, were used to investigate the influence of booster porosity in the kinetics [30•]. On the other hand, the influence of several experimental conditions for a packed-bed flow of solid electroactive materials was studied [31•]. Intensive efforts should be devoted for the engineering of the solid-containing reactor for this battery technology to move toward commercialization.

New chemistries suitable for redox-mediated flow batteries

Since the performance of a RMFB is dependent on the thermodynamics and kinetics of charge-transfer reaction between redox electrolytes and solid electroactive materials, exploring new chemistries (different redox mediators and solid boosters) is necessary to push the boundaries of RFB [32–34]. The generated knowledge should enable the demonstration of full cell having solid electroactive materials in both compartments, since at the moment, there are only few examples in aqueous media [35•,36•]. Our groups demonstrated a RMFB using $Ni(OH)_2$ and metal hydride as solid electroactive materials (Figure 3a) achieving energy-density values of 128 Wh L^{-1} and having the theoretical values of 378 Wh L^{-1} (Figure 3b) [37••]. These promising values of energy density for aqueous systems could open the door for RFB to application currently.

As for SSFBs, implementation of sustainable organic-based solid electroactive materials bearing in mind the

Figure 3



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(**a**) Illustration of the working principle of a Ni-MH RMFB and (**b**) comparison of energy densities for RMFB using solid electroactive material in both reservoirs from Refs. [35–37].
Adapted with permission from Ref. [37].

importance of abundance and accessibility of raw materials should be pursued when developing emerging technologies [36•,38,39]. In addition, it is worth noticing efforts for extending the working principle of RMFB to other aqueous-flow concepts such as thermal-to-electrical energy conversion [40], hydrogen [41–44], and ammonia production [45].

Conclusions and outlook

Despite that the ultimate goal of achieving high-energy flow batteries is common, the radically different strategies followed by SSFBs and RMFBs for implementing the use of solid electroactive materials lead to intrinsic advantages and challenges. At the moment, SSFBs and RMFBs appear to be more appealing for nonaqueous and aqueous electrolytes, respectively, due to the types of membranes required for each case. Confinement of electroactive species by size exclusion using microporous separator is of great interest for nonaqueous flow batteries. On the other hand, deployment of conventional RFB-cell architecture enabled by confinement of solid particles makes upscaling of RMFB more feasible for aqueous electrolytes. Thus, SSFBs and RMFBs are likely not competitors, but they are meant to cover different applications in future. Nevertheless, both families of batteries are still at their infancy, and much work, especially at chemical engineering aspects, is required to achieve further progress and the true practical potential of these technology. These key aspects to be addressed are grouped as follows:

SSFBs:

- *To minimize energy consumption for continuous pumping of slurries.*
- *To increase specific power to decrease upfront cost of the system.*
- *To prevent electrolyte decomposition to increase cycle life and energy efficiency.*

RMFBs:

- *To improve the intrinsic kinetics of charge-transfer reaction between redox mediator and solid booster.*
- *To address engineering aspects of the external reservoir* (e.g. *increase the density of the booster package, the flowability through the booster package, the mechanical stability of the booster package, and the charge-transfer rate*).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The author acknowledges the financial support from “la Caixa” Foundation, under Agreement LCF/PR/PR18/51130007” and the Spanish Government through the Research Challenges Programme (Grant RTI2018-099228-A-I00). E.V. thanks the Ministry of Science, Innovation and Universities (MINECO) for the financial support (RYC2018-026086-I).

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- •• of outstanding interest

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