Review

Flow batteries with solid energy boosters

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Abstract

Adding solid electroactive materials as energy boosters to flow battery tanks provides, in principle, a path to electrical energy storing systems with simultaneously high specific energy and specific power that can solve the needs of both automotive and stationary energy storage markets. This work reviews the physical and chemical principles behind this new class of flow batteries, the history of this technology, and the reasons why it failed to reach the markets.

Keywords

Redox batteries, redox mediators, redox-targeted solids, redox-assisted flow batteries, redox-mediating fluid, solid electroactive materials

Introduction

Flow batteries are unique electric power sources that are rechargeable and allow for independent scaling (decoupling) of energy and power [1-9]. The latter feature allows for optimizing (runtime, cost, size, weight, etc.) of the system for a particular application, whereas most other energy storing systems (e.g. batteries with solid electroactive materials (SEAM), supercapacitors, flywheels) have a narrow range of the energy-to-power ratio (i.e., the characteristic runtime).

Figures 1A and 1B illustrate the difference between the two aforementioned battery types. On the top (Figure 1A) is the most common type of battery that uses only solid electroactive materials (SEAMs). For the sake of illustration, let’s assume that the discharged negative SEAM is lithium titanium phosphate and the discharged positive SEAM is lithium iron phosphate. Then, the discharge reactions are (1)-(3):

\begin{align}
\text{in the posode:} & \quad \text{FePO}_4 + \text{Li}^+ + e^- = \text{LiFePO}_4 \\
\text{in the negode:} & \quad \frac{1}{2}\text{Li}_3\text{Ti}_2(\text{PO}_4)_3 - \text{Li}^+ - e^- = \frac{1}{2}\text{LiTi}_2(\text{PO}_4)_3 \\
\text{in full cell:} & \quad \text{FePO}_4 + \frac{1}{2}\text{Li}_3\text{Ti}_2(\text{PO}_4)_3 = \frac{1}{2}\text{LiTi}_2(\text{PO}_4)_3 + \text{LiFePO}_4
\end{align}
Figure 1. Schematic diagram of A - a conventional battery (only one cell is shown) with solid electroactive materials (SEAMs): green-dielectrics, yellow-electrolyte, blue- negode, red-posode. Electronically conducting particles and binders are not shown; B - a traditional redox flow battery (tRFB) with one cell in a stack: negolyte fluids are blue, posolyte fluids are red, charged fluids are darker colors, discharged are lighter color; C - a slurry-flow (semisold) redox flow battery (sRFB); D - a flow battery with solid energy boosters (SEB).
In Figure 1A, the iron phosphate is shown in red, the lithium titanate is in blue, and a dielectric porous membrane and a cell casing are in green. Both electrode reactions (1) and (2) are electrochemically reversible, and they are coupled via exchange of the same species (Li\textsuperscript{+}), thus their combination can produce a rechargeable battery. Indeed, such a system has been demonstrated [10]. A full cell reaction in the discharge direction for such a SEAM battery is shown in eq. (3).

Let’s jump to the opposite situation, where all electroactive species are present only in liquid phases. Figure 1B shows a redox flow battery, where all electroactive species are dissolved in water and the discharge reactions are [10]:

\begin{align*}
\text{in a flow battery} \\
\text{on the posode:} & \quad [\text{Fe(CN)}_6]^{3-} + e^- = [\text{Fe(CN)}_6]^{4-} \quad (4) \\
\text{on the negode:} & \quad S^{2-} - e^- = \frac{1}{2}S_2^{2-} \quad (5) \\
\text{in full cell:} & \quad [\text{Fe(CN)}_6]^{3-} + S^{2-} = [\text{Fe(CN)}_6]^{4-} + \frac{1}{2}S_2^{2-} \quad (6)
\end{align*}

A counter-cations, such as Li\textsuperscript{+}, Na\textsuperscript{+} or K\textsuperscript{+}, can be used for charge balance in half-reactions (4) and (5), and they are transferred through a cation-selective membrane (Figure 1B).

**Disadvantages of RFBs**

RFBs usually present five main disadvantages (D1-D5 below) compared to SEAM batteries, which explains why the former have not been able to capture even a single market niche.

**D1 Heavier weight**

Due to the presence of a large amount of non-electroactive solvent(s), the specific energy of flow batteries is usually lower than that of SEAM batteries. There are, however, several important exceptions, where highly soluble (or fluid in a pure state) multi-electron species are involved, such as Zn-Cl\textsubscript{2} [11-17] and H\textsubscript{2}-LiBrO\textsubscript{3} [18,19] flow batteries. The weight problem is further aggravated by the use of mixed reagents, as described in D3 below.

**D2 Chemical crossover**

Since at least one electroactive species in flow batteries is present in a fluid state, and the separator is usually not perfectly selective, a chemical crossover between the posode and negode is normally expected in RFBs. In the example shown Figure 1B, we intentionally selected a chemistry where electroactive species are anions because a durable cation-selective membrane such as Nafion can slow down the internal self-discharge reactions (7)-(8) inside this battery:

\begin{align*}
\text{in solution:} & \quad [\text{Fe(CN)}_6]^{3-} + \frac{1}{2}S_2^{2-} = [\text{Fe(CN)}_6]^{4-} + S_\downarrow \quad (7) \\
\text{in solution:} & \quad [\text{Fe(CN)}_6]^{3-} + \frac{1}{2}S^{2-} = [\text{Fe(CN)}_6]^{4-} + \frac{1}{2}S_\downarrow \quad (8)
\end{align*}

Nevertheless, even ion-selective membranes have Donnan’s exclusion limit on how much charge selectivity they can sustain. For example, Nafion with an equivalent weight of 1200 g/mol H\textsuperscript{+} becomes noticeably permeable to chloride ions in contact with HCl solutions above 1 M concentration [20]. With respect to other anions, Nafion and its analogues typically maintain charge selectivity also up to ca. 1 M [21-25] and they can slow down the parasitic (i.e., without generating the electric current on through the cell) reaction (6) in solution as well as other potential side-reactions. At higher concentrations of electroactive anions, however, the cross-over becomes noticeable. In the particular example of sulfide-ferricyanide redox battery (4) and (5), with the total dissolved sulfur concentration of 2.0 M (in 0.1 M LiOH) and the total dissolved iron cyanide complex concentration of 0.3 M (also in 0.1 M LiOH), sulfur deposits form on the positive (ferricyanide) side of a Nafion 117 membrane [10].
The solvent cross-over in the flow batteries is usually even more significant than the cross-over of the electroactive species. As Nafion has no selectivity with respect to water permeation, even trivial pressure differences between the posolyte and negolyte during pumping result in water transfer from one flow circuit to another [26]. The cross-over of liquid-phase species is a common drawback of redox batteries.

D3 Energy and power dilution

In flow batteries undergoing long-term cycling, the crossover is mitigated by starting with a premixed solution of discharged reagents and by occasional mixing and splitting the discharged posolyte and discharged negolyte during cycling. Although, this approach does not work for the example in eq. (6) because this particular system suffers from the precipitation of sulfur in reactions (6) and (7), the use of premixed reagents is the standard practise for many flow battery chemistries, e.g., Cr-Fe [27]. The main drawback of premixing is the reduced concentrations of the electroactive species in the redox fluids. For example, while the aqueous solubilities of both CrCl$_3$ and FeCl$_2$ are both ca. 2.0 M at room temperature, the mixed solution has half of these concentrations, i.e., 1.0 M of CrCl$_3$ + 1.0 M of FeCl$_2$ [27]. Of course, the iron species in the negolyte and chromium species in the posolyte do not participate in the energy storage cycle and serve as ballasts adding to the cost of energy since twice the amount of chemicals, solvent and storage tanks volume per Ah is needed. Halving the concentration of the electroactive species also results in ca. two-fold increase in the capital cost of power: since both electrode kinetics- and mass-transport limited currents typically have a first-order dependence on the reagent concentrations, lowering the concentrations requires a compensatory increase in the cell area (i.e., a large power stack), if the same power rating and energy efficiency is required.

A clever way to overcome the mixing problem in an RFB is by employing electroactive species with three or more oxidation states. We shall refer to such chemistries as ambipolar [28,29], i.e., capable of a redox process on both negode and posode. Although numerous ambipolar RFB chemistries have been demonstrated in laboratories [30,31] (e.g. uranium [32], neptunium [33], all-chromium-EDTA [34], polyoxometallates [35,36], fullerene [37], borane clusters [38], and nitronyl nitroxide [39]), all-vanadium redox flow battery (VRFB) invented in 1986 by Maria Skyllas-Kazacos at the University of New South Wales, Australia [40,41] is the only ambipolar flow battery chemistry, that has been commercialized [42-51].

D4 Incomplete utilization of reagents

Since it is not feasible to fully electrolyze the flowing reagent in a finite time, flow batteries are not cycled between 100 and 0 % state of charge (SoC) but rather between 85 and 15 % (or even more narrow ranges) [52], which contributes to an increased cost of energy and a heavier weight.

D5 Inferior energy efficiency of RFBs

The most significant and rarely discussed drawback of redox flow batteries is their lower energy efficiency compared to SEAM batteries [53]. For example, whereas lithium-ion batteries typically operate at better than 90 % cycle energy efficiency [54-56], the corresponding value for VRFBs is usually around 65 % [57,58].

For sufficiently thick electrodes commonly used in both LIBs and VRFBs, and when the electronic conductivity of the porous electrode is much larger than its ionic conductivity (a goal we try to attain), the electrode area-specific resistance (ASR) is approximately equal to the product of the electrode thickness $L$ and of its ionic conductivity $\sigma$ [59].
In order to understand the reasons for the inferior energy efficiency of VRFBs compared to LIBs we need to look at the following factors:

1. VRFBs use acidic aqueous redox fluids with ca. 30-50 S/m ionic conductivity [60], whereas LIBs electrolytes have LiPF₆ in alkyl carbonate and ca. 0.25 S/m conductivity [61]. The electrolyte conductivity favors VRFBs in terms of better energy efficiency, but the useful figure of merit here is the cell area-specific resistance rather than the ionic conductivities of the electrolytes.

In practice, the higher ionic conductivity of VRFB cannot overcome the drawbacks of the other two factors;

2. lithium-ion batteries have a higher (3.20 V at 50 % SoC for lithium iron phosphate batteries) [62] open circuit voltage than VRFBs (1.35 V at 50 % SoC) [63]. This, however, is a minor effect in practice because of the small parameter ratio (3.20 V / 1.35 V = 2.37);

3. the most important reason for the superior energy efficiency of LIBs is their low operating current density (ca. 1 mA/cm²) compared to VRFBs, which are usually operated 100 to 500 mA/cm² in order to reduce the capital cost of power (i.e., the size of the power stack) [53].

For details about the structure and manufacturing of modern LIBs and VRFBs, we refer the readers to the refs. [64] and [65], respectively. As a result of their design and operation differences, and despite their significantly lower area-specific resistance, VRFBs are inferior to LIBs in terms of their energy efficiency. In general, redox flow batteries have a lower energy efficiency than SEAM batteries. In fact, a 2016 German study concluded that for household-sized solar panel systems, the use of a LIB for electric energy storage is a "better choice for all cases economically" than VRFB, primarily because of the better energy efficiency of LIBs [66].

**Advantages of RFBs**

So far, we have discussed the disadvantages of RFBs compared to SEAM batteries. These disadvantages explain why SEAM batteries dominate all energy storage markets currently. This brings the question: *"why does the interest in flow batteries persist?"* There are two market niches where flow batteries may be competitive:

**A1 Electric vehicles**

Some flow batteries are attractive for use in electric vehicles [67] because the transfer of charged reagents (two hoses) and discharged products (third hose) between the charging station and the vehicle may be accomplished quickly and similarly to gasoline transfer in a case of cars with internal combustion engines. Unfortunately, not many RFB chemistries have high enough specific energy to assure a 300+ km driving range on a single charge. Only if the mass fraction of non-electroactive solvent(s) in an RFB is reduced and multi-electron reagents are employed RFBs can achieve specific energies competitive with (or better than) lithium-ion batteries.

Besides cars, submarines and air electric vehicles are examples of such high-specific energy markets. In fact, the very first widely publicized flow battery was used to power an airship: on August 9, 1884, French inventor and military engineer Charles Renard flew the dirigible *La France*, powered by a Zn-Cl₂ RFB [68,69]. Zinc-chlorine [70,71] and zinc-bromine [70-93] flow batteries were investigated for use in fully electric vehicles (FEVs) in the 1970s and 1980s, and so were, at different times, Li-Cl₂ [87,94-97] and H₂-LiBrO₃ [18,19,98-101] flow batteries. Another type of high-specific energy flow battery is shown in Figure 1C. It uses slurries instead of true liquids to store and transport energy within a flow battery. In the case of lithium-ion battery materials, the equivalent concentration of redox-electrons in a slurry can reach 24 M, and this is where the name of an MIT
startup, which attempts to commercialize such technology, comes from [102-104]. 24 M is specifically interested in using slurry flow batteries for fully electric vehicles (FEVs) [105]. In general, the equivalent electron concentration in lithium-ion battery intercalation materials varies between 20 and 24 M [106,107], whereas in all-liquid RFBs it is 1-2 M.

A2 Stationary energy storage

The second market niche for RFBs is stationary energy storage (SES), where flow batteries may allow for a lower total cost of ownership in applications requiring long (e.g., > 4 h) charge-discharge cycles [108]. Let’s illustrate this with an example.

The magenta line in Figure 2 shows the cost of lithium-iron phosphate batteries approximated and extrapolated from the wholesale price data in ref. [109]. In our model, the cost of this SEAM battery scales proportionally with its nominal energy. The nominal power for SEAM batteries is also directly proportional to their energy, thus, one curve (magenta in Figure 2) can represent batteries with a variable power-energy rating. This is not the case for redox flow batteries (RFBs), where energy (the tanks) and power (the stack) ratings (as well as their costs) can be scaled independently from each other, as shown in Figure 1B. For this reason, we use four cost-energy plots to illustrate the economics of VRFBs in Figure 2: for 1 kW (red), 10 kW (green), 100 kW (blue) and 1 MW (violet) systems. In practice, the RFB’s cost advantage shows up only in systems with a design half-cycle runtime longer than 3-6 h. For example, in Figure 2, the cost of VRFBs becomes lower than that of LIBs for the energy/power ratios over 7 h. We shall emphasize here that the cost and weight advantages of RFBs originate from their ability to scale their energy (tanks) and power (stack) independently, thus allowing for a cost, weight, runtime, etc. optimization depending on the application.

For the sake of full disclosure, we shall note that:
1. we were able to demonstrate in Figure 2 the capital cost advantage of VRFB over LiBs, only when we assumed the VRFB’s capital cost of energy (350 $/kWh) on the lower end of the literature data [110];
2. more sophisticated cost analysis methods (such as levelized cost of energy and net present value) yield more favorable outcomes for VRFBs, due to the longer cycle life of this technology [112-117], but the calculated profit margin is nevertheless too low to justify investments into this technology, especially when risks and alternative investments are taken into account [118-124];
3. our analysis does not take into account the effects of energy efficiency, which favors SEAM batteries due to their low operating current density, as discussed in our previous publication [53]. In order to properly account for energy efficiency, the cost of the energy storage system should be considered together with the cost of the input energy.

**Solid energy boosters for redox flow batteries**

Finally, let’s take a look at Figure 1D. It shows the same stack as Figure 1B and the same dissolved redox couples. What is different is the solid electroactive materials (SEAMs) added to the energy tanks. These SEAMs can exchange electrons with liquid phase redox-mediators, as shown in Eqs. (10) and (11), as well as in Figure 3. Thus, the solid electroactive materials (SEAMs), added to tanks with redox flow battery (RFB) fluid, serve as solid energy boosters (SEBs). Such systems are the subject of this review. Another example of a redox flow battery with solid energy boosters (SEB-RFB) is shown in Figure 11.

\[
\begin{align*}
\text{in positive SEAM:} & \quad \text{FePO}_4 + \text{Li}^+ + [\text{Fe(CN)}_6]^{4^-} = \text{LiFePO}_4 + [\text{Fe(CN)}_6]^{3^-} \\
\text{on the posode:} & \quad [\text{Fe(CN)}_6]^{3^-} + e^- = [\text{Fe(CN)}_6]^{4^-} \\
\text{on the negode:} & \quad S^2^- + e^- = \frac{1}{2}S_2^{2^-} \\
\text{in negative SEAM:} & \quad \frac{1}{2}\text{Li}_3\text{Ti}_2(\text{PO}_4)_3 + \frac{1}{2}S_2^{2^-} = \frac{1}{2}\text{LiTi}_2(\text{PO}_4)_3 + S^2^- + \text{Li}^+ \\
\text{full cell:} & \quad \text{FePO}_4 + \frac{1}{2}\text{Li}_3\text{Ti}_2(\text{PO}_4)_3 = \frac{1}{2}\text{LiTi}_2(\text{PO}_4)_3 + \text{LiFePO}_4
\end{align*}
\]

**Figure 3.** Cyclic voltammograms of (black) carbon electrode in 0.1 M LiOH aq.; (blue) same as black with LiTi2(PO4)3 on the carbon electrode; (green) same as black with Li2S4 added; (red) same as black with LiFePO4 on the carbon electrode; (magenta) same as black with K4Fe(CN)6 added. Digitized and replotted from data in ref. [10]
Redox flow batteries with solid energy boosters (SEB-RFBS) offer several potential advantages over non-flow batteries with solid electroactive materials (see items 1-7 below) and over other redox flow batteries (see items 8-11 below) [7,125,126]:

1. SEAMs that have too poor electric conductivity to be used in regular SEAM batteries can be used to store energy as solid energy boosters (SEBs), as long as redox-fast soluble mediators are used to deliver this energy to the power stack [127]. Even conventional SEAMs with good electric conductivity can benefit from redox-targeting as their charge utilization improves [125,128,129].

2. SEB - RFBs may allow for higher specific energy (lower weight and volume) than the SEAM batteries based on the same chemistry since the relative mass- and volume- fractions of solvent(s), binders, conductors, current collectors, etc. in a SEB battery are small or zero. For instance, the pure C6 - LiCoO2 chemicals contain 157.7 Ah/kg of reversible Li+ charge, but an actual cylindrical (i.e., most densely packed) 18650 battery in 2017 had only 57.8 Ah/kg or 37% of the theoretical [130], apparently leaving room for an up to 2.7 times (= 1 / 0.37) improvement. In most commercial lithium-ion batteries, the mass dilution factor was between 4 and 5 (compare the theoretical values for ROTS-LIB and actual values for SEAM Li-ion in Figure 4) [131]. The 3 to 5-fold gains in specific energy were considered significantly larger than any potential concurrent losses in the energy efficiency (see double voltage loss below), thus possibly justifying the preference of lithium-ion batteries of the SEB-RFB type in electric vehicles. However, history took a somewhat different trajectory, and the specific energy of LIBs increased as well, reaching by 2022 ca. 70% of the theoretical specific energy (see Conclusions and outlook below).

3. For the same reason of eliminating/reducing coating/supporting materials and processes, the energy cost can be lower.

4. More uniform rates of solid-state reactions that reduce the stress and improve the durability of individual SEAM particles and of SEAM assemblies [125].

5. The specific power of the system can be significantly increased [125].

6. Redox targeting assures better tolerance to overcharging and overdischarging [125].

7. Recycling used batteries is much easier [125].

8. The specific energy and energy density of SEB-RFBs are larger (3-15 times improvements have been demonstrated) [132] than those of no-boosters RFBs based on the same liquid-phase chemistry.

9. The SEAM layer on the electrode may inhibit undesirable reactions displayed by a bare current collector [133].

10. Soluble redox-couples and solvents that are prohibitively expensive for traditional RFBs can be used as mediators in SEB-RFBs, because of the smaller amounts of the liquid electrolyte(s) that are required in the latter case.

11. Due to their chemical decoupling of energy and power, SEB-RFBs routinely achieve much larger area-specific power (ASP) than other high-specific energy flow batteries, i.e., slurry [103, 104] and microemulsions [134,135] RFBs.

12. The main disadvantage of the SEB-RFBs is the double voltage loss: for both negode and posode there is an overvoltage on the electrode as well as a voltage mismatch between the mediator and booster [132], while SEAM and traditional flow batteries have only one of these two types of overvoltages, as explained in Supplementary Material (Thermodynamics of redox targeting).
Figure 4. Volumetric energy density versus specific energy for different flow battery systems. Redrawn from the data in ref. [136]

Figure 5. Fraction of the booster's charge accessible during 20-80 % SOC cycling of a single redox mediator couple as a function of the standard redox potential mismatch ($E_0^*-E_B^*$) between the mediator (D) and the booster (B) for different values of the booster’s “interaction parameter” $\beta$ shown in the inset as different colors. In all cases $n = 1$

It is worth examining the voltage loss/mismatch between a solid booster and a dissolved mediator in more details, since such a phenomenon exists neither in SEAM batteries nor in traditional flow batteries, and is unfamiliar to most readers. When one mediator couple per solid energy booster is used, this booster/mediator energy mismatch manifests itself not as voltage loss...
but as an incomplete charge utilization of the booster or the mediators or both. This is illustrated in Figure 5, where the X axis shows the mismatch between the standard redox potential of booster B and of the dissolved D mediator. The Y-axis shows the fraction of the booster’s Ah capacity, which can exchange charge with the dissolved mediator. For the latter, we assumed a fast 1-electron reaction with a Nernstian slope of RT/F, i.e., a thermal Boltzman distribution of electronic density of states. For the booster, however, we assumed a broader distribution, defined by an “interaction parameter” $\beta$, as described in Supplementary Material (Thermodynamics of redox targeting). As evident from Figure 5, narrow boosters (with $\beta \geq 1.5$) can achieve over 85% charge utilization, but only if a dissolved mediator with a perfect match with the standard redox potential of the booster is used. Even a 50 mV potential mismatch would result in poor utilization of the booster capacity. On the other hand, a broad booster (see the curve with $\beta = 5$ in Figure 5) can tolerate a larger mismatch in standard potentials, but the booster’s charge utilization is low even under the best conditions. Poor charge utilization of the booster’s capacity defeats the whole purpose of using a SEB to increase the specific energy of a flow battery system.

In most demonstrated systems, the problem of poor booster utilization is solved by using two dissolved mediating couples for each electrode: one has a redox potential more positive than the booster’s, and the other – more negative. The couples on the outer end of the boosters’ voltage window are used to charge the boosters, and the couples inside the boosters’ voltage window are used to discharge the boosters, as shown in Figure 9 below. The use of two mediating couples for one booster solves the problem of poor utilization of the booster’s charge capacity, but it creates an additional source of voltage loss and thus reduces the charge-discharge energy efficiency. Usually, this double voltage loss is mitigated using solid energy boosters (SEBs) with a large voltage difference between them. However, the larger voltage difference requires using a solvent with a large voltage window, which are either non-aqueous solvents or water-in-salt systems. Both suffer from poor ionic conductivity, which manifests itself in lower area-specific power. The inferior energy efficiency of SEB-RFBs is a major factor against their use for stationary energy storage.

However, ROTS-RFBs have been considered not only for stationary energy storage (where efficiency and cost are the decisive factors) but also for high specific-energy applications (such as the military), and thus we shall examine such applications in more details below.

What are the appropriate figures of merit to compare SEB-RFBs with SEAM-Bs and regular RFBs? For electric vehicles, specific energy (Wh/kg), i.e., the system weight, is the most important. For flow batteries, a great challenge has been lowering the cost of power. Thus, in these cases, comparing area-specific power (ASP) is apposite. However, peak ASP is usually observed near a 50% energy efficiency, which is too low for practical applications. For this reason, we chose to compare the ASP at $0.75^{0.5} = 86.6$% one-way efficiency, and only for discharge, since such data are usually more readily available than the data for charge.

There are at least two ways to look at the energy storage system in Figure 1D. One can start with an RFB shown in Figure 1B and treat the SEAMs added in Figure 1D as solid energy boosters for the flow battery. In this view, the system in Figure 1D increases the specific energy of the system in Figure 1B (since the SEAMs normally have a high Ah/kg content than liquids with dissolved redox species) and reduces the cost of energy (if the $$/Ah cost of the boosters (SEAMs) is lower than that of the dissolved mediators (DEAMs). Alternatively, one can start with a picture of a SEAM battery in Figure 1A, remove non-electroactive solids from the electrode layers, move current collectors to a power stack, and add dissolved mediators to transfer the charge from the SEAMs to the current
collector. In this case, one would refer to the SEAMs as redox-targeted solids (ROTS). Such different views partially explain the different terminology discussed below in relation to Table 1.

For the sake of completeness, we shall mention that redox-targeting has been applied to some non-flow batteries (i.e., where the liquid phase with soluble mediator(s) does not circulate), e.g., to lithium-sulfur batteries [137,138] and non-solid energy boosters, such as to O2 oxidant from the air in redox-mediated fuel cells [139,140]. This review focuses, nevertheless, on systems that employ both flowing reagents and solid energy boosters.

Qi and Koenig proposed in 2017 a classification of redox flow batteries with solid-electroactive materials [7]. In addition to three kinds of slurry RFBs, they mention Type IV:

Type I: flowing carbon as electrochemical reaction electrodes;
Type II: flowing solid active materials with flowing carbon conducting network;
Type III: flowing active material particles colliding on current collectors without carbon;
Type IV: targeted redox mediators as the power carriers with static solid active materials providing energy storage.

The focus of this review would be classified as Type IV. Our search and data analysis methodologies are described in Supplementary Material (Patent Search and Non-Patent Search).

**Terminology**

Table 1 shows what terminology was used to describe the subject of this review in different years. The overall breakdown is: 107 redox mediator; 73 redox-targeted solid (ROTS); 32 solid energy booster (SEB); 11 chemical redox; 7 redox-assisted; 5 redox relay; 2 insoluble redox-active material.

However, it is more instructive to analyse the change in the terminology usage shown in Table 1.

**Table 1. The number of different terms used to described ROTS/SEB-RFBs in different years (the earliest priority year is used for patent families and the publication year for all other documents)**

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<th>Redox mediator</th>
<th>Redox targeted solid</th>
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<th>Solid energy booster</th>
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*the data for 2022 are incomplete at the time of writing.
One can see that the terms redox relay and chemical redox flow batteries are the oldest, but they never gained popularity. The term flow batteries with redox mediator(s) came second, and it was displaced by the term flow batteries with redox-targeted solids. Currently, the term flow batteries with solid energy boosters is gaining popularity. The terms chemical redox flow batteries, redox-assisted flow batteries and flow batteries with insoluble active materials were used only a few times and quickly fell out of use because these terms are neither descriptive nor accurate. We believe the terms solid energy boosters and redox-targeted solids are the most appropriate, and we will use them preferably throughout this review.

**History of redox flow batteries with solid energy boosters**

A summary of patenting and publication activities in SEB-RFB area is shown in Table 2. It is worth noting that these trends follow the classical TRIZ cycle of innovation, which alternates between fast growth and plateau stages [141], with the very first TRIZ innovation cycle being completed nowadays. As a result, despite the short (ca. 15 years) history of SEB-RFBs, it can be split into four time periods, as shown in Figure 6 and Tables 2 and 3: 2006-2010 Proof of concept; 2011-2015 Independent verifications; 2016-2018 Explosive growth; 2019-2022 Steady growth.

We shall discuss each of these periods separately below.

*Figure 6. Publications (patent families, journal articles and other) related to SEB-RFBs vs priority or publication year*
### Table 2. Publications about SEB-RFBs sorted by reference type

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### Table 3. Counts of patent families (in red) and non-patent publications (in blue) about SEB-RFBs sorted by inventors’/authors’ country*

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*The “year” column for patents refers to the earliest priority date, and for all other documents to the publication date. The data for 2021 and after are incomplete due to patent publication delays (usually 18 months between priority and publication dates) [142]; A bubble plot version of this table, sorted by applicant, is provided in Supplementary material (2022 Patent thickets)
2006–2010: Proof of concept

The earliest documented evidence of the idea of flow batteries with solid energy boosters can be traced to patent application IB2006/053832 (publication number WO2007/116363)[143] filed on 2006-04-07 by High Power Lithium SA [143,144], a venture capital-funded start-up company in Lausanne, Switzerland. The goal of this work was to improve the utilization of lithium-ion posode materials (with an example of LiFePO₄) in lithium-ion batteries and to reduce the amount of conductive carbon additives at the same time. The idea of dissolved redox mediators came about as an extension of the inventors’ earlier work on adsorbed redox mediators (“molecular wires”) for a poor electronic conductor LiFePO₄ [145].

The inventors prepared an electrode layer consisting of 95 wt.% LiFePO₄ and 5 wt.% of PVDF without carbon additives (see Figure 7). This electrode did not show noticeable electrochemical intercalation of lithium ions, as was expected from a poorly electronically conducting LiFePO₄. Upon addition of dissolved 10-methylphenothiazine (or 2,2’-bipyridine derivative complexes of Os or Ru) to the posolyte, a significant increase (not shown) in the accessible charge was observed, suggesting the occurrence of reactions similar to (10) and (11). The inventors concluded that the addition of a dissolved mediator allowed for electrochemical polarization of the whole particle network by the current collector even though the lithium insertion material is electronically insulating and no carbon additive is used to promote conduction [146]. The inventors also reported an unexpected beneficial role of carbon nanotubes added to such a system with solid electroactive material and a dissolved redox mediator. Indeed, if one looks at equations (10) and (11), one may conclude that these are purely chemical processes that proceed via a direct transfer between a solid booster and a dissolved mediator. In this scenario, there is no room for catalysis by carbon nanotubes. However, if one adds reactions (4) and (5), which are electrochemical and allow for a spatial decoupling of the electron donor and the electron acceptor sites, the “catalytic effect” of the carbon nanotubes becomes understandable.

The patent application IB2006/053832 [146] was filed by High Power Lithium (without naming EPFL) directly with WIPO as the first receiving office. Although the practice of patent filing directly at WIPO bypassing a national office is allowed by the Patent Cooperation Treaty of 1970 per Rule 19.1(a)(iii), it is rather rare in general. However, it is a common practice in Switzerland because this country typically issues patents without substantial examination and leaves it up to the courts to decide the patent’s validity. Using WIPO’s headquarters as a filing office allows Swiss inventors to get their patents examined by the Swiss Federal Institute of Intellectual property before issuance, thus affording such patents presumption of validity in Swiss courts [148].
The application eventually entered the national phase in Austria (via the EPO), India, PR China, USA, S. Korea and Japan, as shown in Figure 2. The unusually large (for a small company and compared to the other patent applications from HPL) geographic scale implied that the company considered this invention as highly valuable commercially. Nevertheless, while the applications were still pending, High Power Lithium (HPL) was acquired by New York Stock Exchange-listed Dow Inc., headquartered in Midland, MI, USA. Soon after, Dow abandoned all three patent families that it acquired with HPL, including IB2006/053832 (Figure 4), despite favorable reports from the patent examiners.

During this period, the Lausanne group published two journal communications [147,149] based on the results disclosed in the aforementioned [146] patent application. The Angewandte Chemie communication was focused on charge-discharge cycling of a poorly electronically conducting LiFePO$_4$ using either two dissolved mediators (both were Os$^{+2/+3}$ complexes with substituted 2,2'-bipyridine ligands) or one (10-methylphenothiazine, MPTZ) [149]. The Journal of Power Sources communication added triphenylamine, phenoxazines and phenothiazines, known as overcharge protectors in lithium-ion batteries [147].

After EPFL, Qing Wang took a postdoctoral position at National Renewable Energy Laboratory in Colorado, USA, where he worked on different topics. The EPFL team also did not immediately follow this work. Thus, after the first proof-of-concept, the development of flow batteries with solid energy boosters came hiatus.

2011-2015: Independent verifications

In 2008, Prof. Qing Wang started a tenure-track position at the Department of Materials Science and Engineering at the National University of Singapore (NUS). While most of his work at that time was related to dye-sensitized solar cells, his group published a few studies of SEB-RFBs [106,136,150-155]. They demonstrated redox-targeting of LiFePO$_4$ (using ferrocene couple on the low-potential side and 1,1'-dibromoferrocene couple on the high-potential side) [106] and of Li$_{0.5}$TiO$_2$ (using cobaltocene and decamethylcobaltocene couples) [151]. The two-flanking couple's approach [156,157] differed from the original approach, with one mediator introduced in the earlier work [126]. The difference between the two redox-targeting methods is discussed in Supplementary Material (Thermodynamics of redox targeting). The NUS team found that the slow electron transport inside poorly-conducting LiFePO$_4$ particles often limits the rate of (de)lithiation and that addition of carbon accelerates the process.

During this period, some new research groups became interested in redox-targeting lithium battery materials. Collaborators from Bar-Ilan University (Israel) and Technical University of Munich (Germany) demonstrated redox-targeting of sulfur using ferrocene derivatives [158,159]. A team from Panasonic (Japan) demonstrated redox targeting of LiFePO$_4$ with tetrathiafulvalene and of V$_2$O$_5$ with 9,10 – phenanthrenequinone [160]. Collaborators from the Massachusetts Institute of Technology (MIT) and the University of California-Oakland (UCO) patented a battery where sulfur was reversibly redox-targeted using soluble benzoperyleneimide derivatives [161]. A team from Sandia National Lab (SNL) filed a US patent application, where redox targeting polynoxometalates with soluble organic mediators was proposed along with prophetic-only examples [162]. Neither the MIT-UCO [161], nor the SNL [162] patents have been transferred to a manufacturer as of 2022-04. First review articles about flow batteries with solid energy boosters (redox-targeted solids) were also published during this period [136,155,163].
2016-2018: Explosive growth

The most distinct feature of this period was aggressive patenting by Panasonic (Japan), shown as the red squares in Figure 6 and data for Japan in Table 3. Although it was limited only to Japan, PR China and the USA, the number of filed patent families (21) was significant [164-184]. However, only one [182] of these applications had experimental data from a full cell and only two [178,179] from half-cells. All three of these applications were filed in 2018. In all previous years, Panasonic reported prophetic examples only.

During this period, Prof. Qing Wang’s team at the National University of Singapore (NUS) was more active in journal publishing [10,127,128,185-200] (see Table 3) than in patenting [201,202] (see the green line in Figure 9), while their contribution to the development of the technology was much more substantial than that of Panasonic’s. Figure 8 shows a clever approach to redox-targeting LiFePO$_4$ ($E^\circ$=3.45 V vs. Li/Li$^+$) using the coexisting I$_3^-$/I$^-$ (3.15 V) and 2I$_3^-$/3I$_2$ (3.70 V) solution-phase redox couples. More recently, a Swedish group used the same booster-mediator (iodine-triiodide-iron phosphate) combination paired with sodium $\beta'$-alumina membrane and metallic Na negode to demonstrate a 3 V battery [203]. Regrettably, the high ohmic resistance of the ceramic membrane limited the cycling rate to 0.13 mA/cm$^2$.

![Figure 8. Schematic diagram of redox-targeting of LiFePO$_4$ electrode using the triiodide/iodine/iodine triplet according to ref. [185]](image)

![Figure 9. Cyclic voltammograms of F-dopped SnO$_2$-Al$_2$O$_3$ electrode in 1 M LiTFSI in TEGDME (blue) with LiFePO$_4$ coating on the electrode; (green) bare electrode with lithium iodide added to the electrolyte. The two waves correspond to the reactions of triiodide in Fig. 15; (red) coated with LiFePO$_4$ and with LiI in the electrolyte. Digitized and redrawn from ref. [185]](image)

Another group from the National University of Singapore demonstrated redox targeting of LiFePO$_4$ using ferrocene and sym-dibromoferrocene [192]. They also reported that pre-lithiation of the membrane in such an anhydrous battery significantly improves its conductivity and reduces cross-over.

Prof. Girault’s group at EPFL, where Qing Wang performed the very first studies of SEBs for RFBs [146,147,149], also became interested in SEB-RFBs. They demonstrated the use of polyaniline (PANI) as a solid energy booster (SEB) coupled with Fe$^{3+/2+}$ dissolved mediator for the emeraldine-pernigraniline transition [204]. Not surprisingly, the V$^{4+}$/V$^{3+}$ couple was not effective as a redox-mediator for the leucoemeraldine-emeraldine transitions due to its well-known slow kinetics [205-207].
addition of electronically conducting carbon black was found to increase the accessible charge of PANI 3-fold, similar to what was reported earlier for other SEBs [146,151].

A group from the Nanjing University of Information Science and Technology (PR China) demonstrated the use of Ni and Cr cyclopentadienes as well as of ethylviologen as redox-mediators for sulfur in Li-S batteries [208,209]. Several reviews touching SEB-RFBs were published by Qing Wang’s group [10,187,193,195,199] and others [210].

2019-2022: Decline from the main players and increase from newcomers

The most notable change during this period was a decline in the number of patent applications from Panasonic (see the data for Japan in Table 3). Since this decline started in 2018 (i.e., earlier than the 18-month publication delay prior to our patent search in 2022-03), it is caused by an actual decrease in the SEB-RFB patenting activity by Panasonic and not by a data availability artefact. Neither Panasonic’s own patent disclosures nor other publications explain the rationale behind the apparent withdrawal of the firm from the SEB-RFB area.

The number of non-patent publications from the National University of Singapore (NUS) and PR China also went somewhat during this period (see Table 3). At the same time, there was a continuous growth of publications from the USA (see Table 3) and the entrance of new research groups from multiple countries (Germany, Estonia, Finland, France, S. Korea, Malaysia, Spain, Sweden, UK) albeit with only 1 or 2 publications.

During this period, Qing Wang’s group at NUS reported the use of redox-targeting in recycling spent lithium-ion batteries [211], and demonstrated nearly-quantitative utilization of SEB in a non-aqueous sodium-ion battery (see Figures 11 and 12). This group was also interested in developing RFBs with single molecule redox-targeting (SMRT) [212] on both negode and posode: e.g., for LiFePO4 in water using water-soluble ferrocene derivatives [213], for polyimide-nickel hexacyanoferrate [214], for alkaline nickel-metal hydride battery [215], and for two redox-transitions in Prussian Blue [216] for the more negative (3e^- at 0.5 V vs. SHE) using ferri/ferrocyanide dissolved mediator (DM) and for the more positive (2e^- at 1.2 V vs. SHE) using Br2/Br^- DM (see Figure 10) [217,218].

One of the most important works from NUS during this period was the development of solid energy boosters for VRFBs [220]. The currently most popular version of VRFB chemistry, developed around 2012 at Pacific Northwest National Laboratory in the USA [221,222], uses solutions comprising 2.5 M of dissolved vanadium species, 2.5 M of sulfate and 6 M of chloride. Although this mixed sulfate-chloride chemistry allowed for a ca. 3-fold increase in the vanadium concentration compared to the older sulfate-only chemistry, it still suffers from the precipitation of V3+ species at -5 °C and V2O5 at +50 °C [223]. The NUS group wanted to add solid energy boosters (SEBs) to the vanadium tanks so that the size, weight and, potentially, the operating cost of the battery would be reduced while allowing the use of the dissolved mediators at lower concentrations so that the precipitateon/clogging problems can be avoided. (VO)6[Fe(CN)6]3 Prussian Blue Analogue (PBA) was discharged form of the posolyte’s SEB. Since it has a redox transition at the same potential as the VO2+/VO3 transition, no other dissolved mediator was used. RDE measurement found that the booster also served as an excellent electrocatalyst for the V3+/4+ redox couple in the solution (see Figure 13).

Galvanostatic cycling solution (see Figure 14) of a positive half-cell showed that the utilization of the PBA booster was ca. 70 % [220]. Although these results are encouraging, the durability of Prussian Blue Analogues (PBAs) in acidic solutions still needs to be demonstrated.
**Figure 11.** Schematic illustration of a redox targeting-based redox flow sodium-ion battery. The tanks are filled with Na$_3$V$_2$(PO$_4$)$_3$ granules. The equivalent SEBs’ concentrations correspond to 14.7 m (molal, i.e. mol/kg of solvent) in the negolyte tank and to 7.4 m in the posolyte tank. 9-fluorenone in TEGDME+DMSO was used as a mediator in the posolyte and MPTZ in PC was used as a mediator in the negolyte. Nafion+PVDF membrane. Redrawn from ref. [219]

**Figure 12.** Cyclic voltammograms of N-methylphenothiazine (MPTZ, in propylene carbonate) and 9-fluorenone (in glyme 4 + dimethylsulfoxide mixture) and those of the solid material Na$_4$V$_2$(PO$_4$)$_3$. The scan rate is 0.1 V/s for redox molecules and 0.001 V/s for solid material. Digitized and redrawn from ref. [219]

**Figure 13.** 5 mV/s cyclic voltammograms of a bare (black and green) and PBA-modified (blue and red) glassy carbon disk electrode rotating 1600 rpm in 2 M H$_2$SO$_4$ (black and blue lines) and in 2 M H$_2$SO$_4$ + 5 mM VO$_2^+$ + 5 mM VO$^{2+}$ (green and red lines). Digitized and redrawn from ref. [220]

**Figure 14.** (right) Galvanostatic cycling at 30 mA·cm$^{-2}$ of 0.60 M VO$_2^+$/VO$^{2+}$ sulfate solution without (black) and with vanadium PBA solid. Negolyte is present in an excess. Digitized and redrawn from ref. [220]
Also notable during this period was a demonstration by a Spanish group of redox targeting a well-known SEAM material NiOOH/Ni(OH)$_2$ using a single ferri/ferrocyanide mediator couple in combination with several different negolytes (see Fig. 15) [224]. Fig. 16 shows experimental data [107] equivalent to our calculations in Supplementary Material (Thermodynamics of redox targeting). Using that terminology, we conclude from Fig. 16 that NiOOH/Ni(OH)$_2$ is a super-Nernstian material, as expected for a two-phase electrochemical transition. In Fig. 16, cycling ferri/ferrocyanide mediator in solution between 15 and 85 % state of charge (SoC) results in a favorable cycling of a narrow NiOOH booster between 0 and 78 % SoC, despite a ca. 80 mV mismatch (the exact value depends on the solution composition) in the standard redox potentials of the mediator and the booster.

*Figure 15. Operating principle of a solid NiOOH electrode coupled with ferrocyanide as a dissolved redox mediator. Redrawn from a figure in ref. [224]*

*Figure 16. Equilibrium potentials of the NiOOH booster and ferri/ferrocyanide mediator couple as functions of their state of charge. This figure is equivalent to Fig. S-4-in the Supplementary Material (Thermodynamics of redox targeting). Replotted from the experimental data in ref. [107]*
In 2021-2022, several research groups undertook detailed studies of redox-targeting of LiFePO$_4$ booster with aqueous ferricyanide. The group of Prof. Emmanuel Baudrin from Université de Picardie Jules Verne in France studied single-molecule redox targeting (SMRT) of LiFePO$_4$ using ferri-/ferrocyanide couple, with $E^\ddagger$ - tuned by the addition of DMSO and LiCl [225]. The authors demonstrated that the total capacity of the posolyte can be doubled upon the addition of only 1 % of solid LFP by volume. It’s worth noting that to be able to achieve high flow rates and high SEB utilization with a stable flow, they used porous LFP pellets prepared by spark plasma sintering rather than an LFP powder. To the best of our knowledge, the solid energy boosters in RFBs have not been used in a fluidized bed reactor.

Some interesting results came from fundamental studies as well. It was found that during chemical redox-targeting, the oxidation (delithiation) of LiFePO$_4$ was generally faster than the reduction (lithiation) of FePO$_4$ [226]. Also, the activation energy for the chemical pathways was higher than for electrochemical [226]. Further studies are needed to find out if this effect is real, or an artefact of experiment/data analysis. What was clear, nevertheless, is that the redox-targeting reactions can be fast enough to experience mass-transport limitations in porous solids. In their following study, the University of Virginia group improved their packed-bed reactor for the delithiation of ca. 60 nm LiFePO$_4$ particles, which eliminated mass-transport restrictions with just 0.3 M concentration of [Fe(CN)$_6$]$_3^-$ [226]. Increasing the delithiation temperature from 22 to 40 °C did not have a significant effect on the reaction rate, suggesting that transport inside the booster may be rate-limiting. However, decreasing the delithiation temperature from 22 to 13 and 4 °C resulted in a reduced reaction rate, which could be due to reaction (10) becoming rate-limiting because of the slow diffusion of Li$^+$ in the solid phase.

Sanford, McNeil and their coworkers from the University of Michigan demonstrated a general route to ROTS-RFBs based on the use of a dissolved redox-active monomer in solution (and of its corresponding polymer as a solid energy booster [227]. They found that ca. 50 % of the booster is utilized in their first non-optimized cell. Among the most significant recent developments from PR China was a demonstration of Zn-MnO$_2$ battery with a positive Br$_2$ posolyte mediator [228] and lithium-sulfur ROTS-RFB [209,229]. Several reviews about SEB-RFBs were also published during this period [230-233].

Conclusions and outlook

In the preceding discussion, we showed that flow batteries with solid energy boosters (SEBs) had a turbulent history with peak activity in 2016-2018 and apparent abandonment of this technology by the main contributors thereafter. Neither we nor the publications cited in this review discuss the reasons for the decline in the interest in this technology. We shall attempt to answer this question now.

In disadvantage D5 we showed that redox flow batteries (RFBs) are inferior in the stationary energy storage (SES) market to batteries with solid electroactive materials (SEAM) in general (and to LIBs in particular) in terms of energy efficiency. We used LFP chemistry for this analysis because it is the lowest cost LIB chemistry and because by 2022, it has been selected for both small and large stationary installations by most developers. The conclusions that we made for RFBs, in general, apply to SEB-RFBs as well, because the energy efficiency of the latter is worse than the energy efficiency of the former. Thus, based on the energy efficiency considerations alone, one should reject the use of flow batteries (with or without solid energy boosters) in the stationary energy storage markets in favor of non-flow batteries with solid electroactive materials. One possible exception to this conclusion is market, where the cost of the input energy (and thus the energy efficiency) is less important than the
system’s durability and self-discharge. Reserve power is an example of such a market, and it can be served well by traditional (without solid energy boosters) RFBs [53].

The question now is whether SEB-LIBs are better than traditional (non-flow) LIBs for cars (and other types of vehicles), since longer driving range (i.e., battery’s system-level specific energy) is more important in this market, that battery’s energy efficiency [234,235]. Figure 17 shows the historical progress of the specific energy of lithium-ion batteries.

![Figure 17. Specific energy of lithium-ion batteries (various formats and chemistries) vs. production year. References: 2015-Crabtree [237], 2020-Dominko [238] 2020-Tesla [239]](image)

The red and blue triangles in Figure 17 refer to the data from recent review articles, where neither the battery chemistry nor battery formats were differentiated. It is worth noting that in thirty years since their first commercial introduction LIBs specific energy increased by a factor of 3.75. In 2020 Tesla, Inc. reported [236] that the specific energy of Panasonic’s 2170 format cylindrical cells used in Model 3 is 260 Wh/kg, i.e., 57 % of the value for pure chemicals (459 Wh/kg), as shown in Figure 17. If this chemistry is used in a SEB-RFB, such system-level energy dilution (57 %) will be achieved only if the booster tank and the stack have over 75 % (i.e., 0.570.5) energy efficiency each, even if we do not account for the stack weight of the stack, redox fluids and pumps. This simple estimation shows that the contemporary traditional SEAM-LIBs surpassed the SEB-LIBs in terms of specific energy at the system level. Regarding the electric vehicles market, we conclude that any weight reduction gained due to the elimination of binders and current collectors when going from SEAM batteries to SEB-RFBs, is likely to be negated by the reduced energy efficiency and by the addition of a power stack and related components.

With both stationary and vehicle markets lost to traditional LIBs, redox flow batteries with solid energy boosters do not have a competitive market niche that can revive interest in this technology.
Abbreviations:

ASP  Area-specific power
CV   Cyclic voltammogram or cyclic voltammetry
DEAM Dissolved electroactive material
DM   Dissolved mediator
DMSO Dimethylsulfoxide
E°   Standard electrode potential
EPO European Patent Office
EU   European Union
FEV  Fully electric vehicle
GC   Glassy carbon
HPL  High Power Lithium, a Swiss startup company
IB   International Bureau of WIPO
ICE  Internal combustion engine
LES  Liquid energy storage, i.e., traditional RFBs without solid energy boosters (SEBs)
LFP  Lithium iron phosphate
LFPB Lithium-iron phosphate SEAM battery (LFPB)
LNCMB Lithium ion-nickel-cobalt-manganese oxide SEAM battery
MIT  Massachusetts Institute of Technology
MPTZ 10-methylphenothiazine
NoSS No stoichiometric solutes
NUS  National University of Singapore
OCV  Open-circuit voltage
PBA  Prussian Blue analogue
PC   Propylene carbonate
PCT  Patent Cooperation Treaty of 1970
RFB  Redox flow battery
RMF  Redox-mediating fluid
ROTS Redox-targeted solid, same as SEB
SEAM Solid electroactive material
SEB  Solid energy booster, same as ROTS
SMRT Single-molecule redox-targeting
SNL  Sandia National Laboratories, New Mexico, USA
SoC  State of charge
SQL  Structured Query Language
RFB  Redox flow battery
RMF  Redox-mediating fluid
ROTS Redox-targeted solid(s), same as SEB
TRIZ Theory of solving inventive problems
VRFB Vanadium redox flow battery
WIPO World’s Intellectual Property Organization
UCO  University of California-Oakland
UK   United Kingdom of Great Britain and Northern Ireland
USA United States of America

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