

Flow Batteries From 1879 To 2022 And Beyond.

Yuriy V. Tolmachev

¹ Department of Civil and Environmental Engineering, University of Massachusetts, 01002 USA ;

*Corresponding Author: E-mail: ruthenium2008@yahoo.com .

Dedicated to Professor Robert Savinell on the occasion of his 70th birthday.

Abstract

We present a quantitative bibliometric study of flow battery technology from the first zinc-bromine cells in the 1870's to megawatt vanadium RFB installations in the 2020's. We emphasize, that the cost advantage of RFBs in multi-hour charge-discharge cycles is compromised by the inferior energy efficiency of these systems, and that there are limits on the efficiency improvement due to internal cross-over and the cost of power (at low current densities) and due to acceptable pressure drop (at high current densities). Differences between lithium-ion and vanadium redox flow batteries (VRFBs) are discussed from the end-user perspective. We conclude, that the area-specific resistance, cross-over current and durability of contemporaneous VRFBs are appropriate for commercialization in multi-hour stationary energy storage markets, and the most import direction in the VRFB development today is the reduction of stack materials and manufacturing costs. Chromium-iron RFBs should be given a renewed attention, since it seems to be the most promising durable low-energy-cost chemistry.

Keywords

Energy efficiency; voltaic efficiency; energy-to-power ratio; area-specific power; long-duration energy storage; secondary current distribution; carbon nanofibers; carbon microfibers, electrospinning; quantum jumps; porous electrode theory; porous media; pressure drop in porous electrode; patents-to-journal articles ratio; patent-journal correlation; bibliometrics; patentometrics; scientometrics; fuel cells; lithium-ion batteries; vanadium redox flow batteries; zinc-halogen batteries; zinc-bromine batteries; zinc-chlorine batteries; zinc-iodine batteries; all-iron hybrid flow batteries; bromine-sulfur batteries; polysulfide-polybromide batteries; academic databases, academic search engines, scholarly metadata search, comparison of scientific bibliographic databases, Web of Science; Scopus; SciLit; SciFinder; CiNii; CNKI; The Lens; lens.org; Questel-Orbit; Kozeny – Carman equation; Daniel'-Bek – Newman – Tobias porous electrode model, PostgreSQL, TRIZ, Special Purpose Acquisition Company, scientific bibliographic databases.

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Notations and abbreviations

a	m^{-1}	inner surface area to volume ratio for a porous media, $a = 0.5(1 - \varepsilon) d^{-1}$
A	m^2	membrane-projected cell area
AIHFB		all-iron hybrid flow battery
ASR	$Ohm\ m^{-2}$	area-specific resistance
C	mol/m^3	total conc. of Red and Ox forms of a redox couple
C_0	mol/m^3	inlet concentration, $C(1 + \phi)/2$
C_1	mol/m^3	outlet, concentration, $C(1 - \phi)/2$
CARB		California Air Resources Board
CNF		carbon nanofiber
d	m	effective particle or fiber diameter in a porous electrode
DNT		Daniel'-Bek-Newman-Tobias
h	m	interfiber distance in a porous electrode
H	m	electrode thickness
H°	m	effective electrode thickness, $H^\circ = [a i_0 (\alpha_a + \alpha_c) F / (RT\sigma)]^{-1/2}$
i°	A/m^2	exchange current density
I	A	cell current $I [A] = nF C_0 \phi v$
LAB		lead-acid battery
p	kg/ms^2	pressure
R	$Ohm\ m^2$	area-specific resistances of an negode, posode or membrane
s	m^2	hydraulic permeability of a porous media
SBB		polysulfide-polybromide (sulfur-bromine) battery
SEAM		solid electroactive material
SEI		solid electrolyte interface
SES		stationary energy storage
u	m/s	linear flow velocity
v	m^3/s	volumetric flow velocity
UNSW		University of New South Wales, Sidney, Australia.
W	m	WC+ WL
WC	m	channel width
WL	m	landing width
WZ	m	cell width
X	m	direction between the ribs in the interdigitated flow field
Y	m	direction normal to the membrane
Z	m	direction of the fluid flow in the flow field channels
$\alpha_a + \alpha_c$		the sum of anodic and cathodic transfer coefficients in linearized Buttler-Volmer equation.
β		dimensionless constant, 0.5 for a hexagonal lattice of circles and 1 for a square lattice
δ		$\equiv d/h$ ($0 < \delta < 1$), thus $\delta = [(1 - \varepsilon)(4/\pi)]^{0.5}$
ε		porosity $\varepsilon = 1 - (\pi/4) \delta^2$
η	H/H°	dimensionless electrode thickness, preferably set to $\eta = 2$.
ϕ		single -pass reagent utilization in a flow battery cell= $\Delta SoC \Delta \phi = 0.75 - 0.25 = 0.5$
κ	$A^2\ s^3\ m^{-3}\ kg^{-1}$	electronic conductivity of the porous electrode $S/m = A/(V\ m)$

λ	ratio of the interdigitated flow field period to the electrode thickness $(WC+WL)/H$
μ	landing to channel width ratio for the interdigitated flow field WL/WC
ν	$kg/(m\ s)$ dynamic viscosity,
σ	$A^2\ s^3\ m^{-3}\ kg^{-1}$ ionic conductivity of the porous electrode $S/m = A/(V\ m)$
χ	electrode thickness normalized to H^o . $\chi=2$ in this work.
ψ	d^2/s dimensionless normalized permeability of a porous media
Ξ	$d-/d+$ ratio of the fiber diameters in the negode and in the posode

1. Introduction and zinc-halogen batteries.

While a PhD student at Case Western Reserve University in the 1990's, I was honored to have Prof. Savinell on my dissertation committee. Although I was unaware at that time of his prior work on flow batteries, as I became involved with RFBs in 2015,(1-3) I learned, that flow battery topics have always played a prominent role throughout Robert Savinell's career. As a graduate student at the University of Pittsburg in the 1970's, Robert studied Ti-Fe chemistry.(4-6) He continued this work on RFBs as an assistant professor at the University of Akron in the early 1980's.(7-9) As a faculty member at CWRU in the 1980's, Prof. Savinell was involved in the development of H₂-Br₂ flow batteries.(10-13) In more recent years his work expanded(14) to all-iron (Fe-Fe³⁺),(15-24) all -copper(25, 26) and zinc-iron(27) hybrid flow batteries, as well as to all-vanadium,(28-32) organic ambipolar(33) and microemulsion(34) RFBs.

Although flow batteries is a *very* old technology (as discussed below), it experiences a renewed interest in the recent years, which has been prompted by the transition of the human civilization away from fossil fuels and toward renewable energy,(35-42) and by the corresponding shift in the electrochemistry community from fuel cells to rechargeable batteries. Among the latter, two battery types emerged as the main contenders in the stationary energy storage markets: batteries with solid electroactive materials (SEAM), represented mainly by lithium-ion batteries (LIBs), and redox flow batteries (RFBs), led by vanadium (VRFBs) and zinc-halogen (ZXBs) RFBs.

Fig.1 shows in semi-log coordinates the numbers of patent families (solid lines) and of journal articles (dotted lines), related to lithium batteries (Li-ion and Li-metal combined, shown in red), lead-acid batteries (LABs, shown in black), redox flow batteries (RFBs, shown in blue) and fuel cells (FCs, shown in green) by year. Several interesting conclusions can be drawn from this figure.

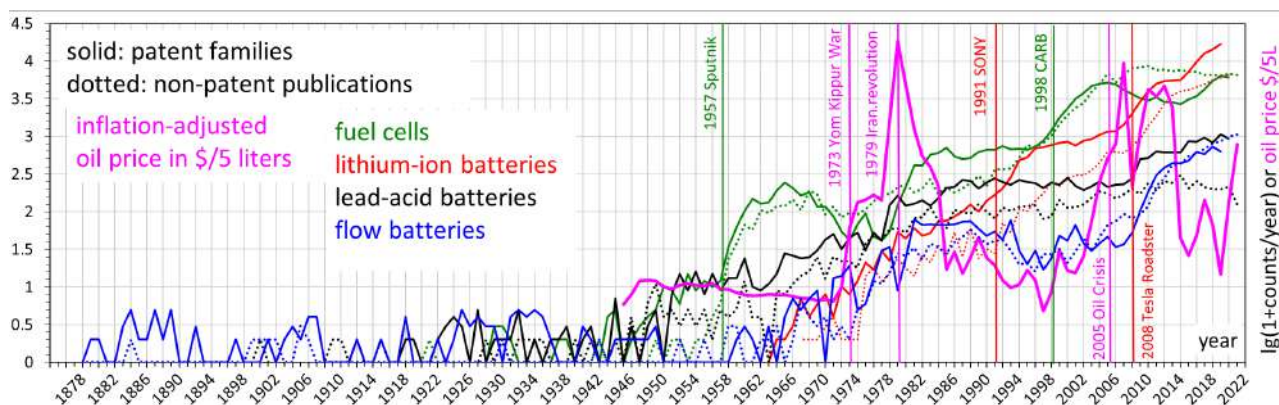


Fig. 1. The number of patent families (solid lines) and of journal articles (dotted lines) related to fuel cells (all types, green), to flow batteries (blue), to lithium (metal and ion) batteries (red) and to lead-acid batteries (black) vs the earliest priority (for patents) or publication (for journals) year. Also shown as the magenta line is the inflation-adjusted oil price in US\$/liter.(43) Variations of this plot for other battery chemistries are provided in Apps. H and I. The search methodology is explained in Apps. E and G.

Firstly, we would like to bring the readers' attention to a *striking correlation* between the number of *patent families* and *journal* articles related to each technology. Their ups, downs and plateaus follow similar time patterns, and, although the exact ratio of the number of patent families to non-patent publications for the same technology depends *to some extent* on the databases used and on the search strategy, we can generalize an observation that for commercially successful technologies (e.g. for lithium-ion batteries after 1991 or lead-acid batteries since 1950) the number of patent families is larger than the number of non-patent publications. On the other hand, for fuel cells patents – to – non-patents ratio has been less than one since ca. 2005.

The aforementioned strong patent / non-patent correlation prompted us to investigate pairwise match between journal authors and patent inventors, but we did not find a meaningful relationship (not shown).

Similar patent-journal studies in the past found rather weak (ca. 5-20 % overlap)(44, 45) pairwise correlations between journal article authors and patent inventors in general, which makes our finding of a *high non-pairwise correlation* even more surprising. We were unable to find prior observations of non-pairwise patent-journal correlations, except for four very small and outdated studies.(44-47) It would be interesting to explore patent-journal correlations in other areas of technology (see App.I for more examples).

Secondly, as Fig.1 shows, the increase in the research activity for the three electrochemical powersources can be correlated with political events and with technological breakthroughs. For example:

1957 the launch of Sputnik 1 by the USSR that year (see Fig.1) triggered an interest in developing fuel cells for space and military applications;(48-52)

1973 the rise on oil prices, following the Yom Kippur War of 1973 resulted in an increased activity in all three technologies;

1991 the market introduction of lithium-ion battery by Sony in 1991 was followed by an instant rise of patent applications and journal articles related to lithium (-ion) batteries;

1998 the rise in fuel cell activities after 1998 was caused by the combination of the following events:

- groundbreaking improvements in PEMFC design and performance made in Los Alamos National Laboratory in the early 1990's;(50, 53, 54)

- the zero-emission vehicle mandate by California Air Resources Board (CARB), which required "*2% of new cars sold in California in the 1998 model year...be absolutely non-polluting...vehicles, and that the percentage increases to 10 for the model year 2003*";(55, 56)

- the commitment to fund the development hydrogen fuel cell vehicles announced by the US President G.W.Bush in his 2003 State of the Union speech;(57) followed by similar initiatives in other countries.(58-62)

It is noteworthy, that the rise in fuel cell patenting between 1998 and 2008 (i.e. after the CARB mandate in Fig.1) was paralleled by a slow-down of lithium-ion battery patenting activities, suggesting energy-inefficient "Hydrogen Economy" had a more significant indirect negative impact on the technological progress and on the market adoption of energy efficient Battery Electric Vehicles, that was thought previously.(63-65)

In 2004-2006 the fuel cell activities slowed down (more pronounced for patents and less for journal articles), although the cut in the fuel cell funding by the Obama's administration was announced only in 2009.(66) It is possible, that the industry leaders started the "hydrogen-to-lithium" transition before it was officially declared, and we encourage the readers of this article to share their opinions regarding this time discrepancy.

2008 the launch of Tesla Roadster (the World's first serially-produced fully electric battery car with an over 320 km driving range) in 2008 (67-69) was a revolutionary event, that immediately boosted the research activity in lithium-ion batteries (see the two red lines in Fig.1).

Thirdly, we would like to note, that the flow battery technology, particularly its zinc-bromine version, is very old. As shown in Appendix H, it traces its origin back to the late 1800's, initially as static (non-flow) batteries. The very first description of a Zn-Br₂ *flow* battery (see Fig.2), that we able to find, is from an 1879 US patent by John Doyle,(70) who was a lesser-known contemporary of T. A. Edison. Albeit quite different from the later zinc-bromine battery designs (and from the modern cell stack, see Figs.H3, H4 and H5 in the Supplemental Information), it was a true refillable *flow* battery with multiple cells. Although Doyle did not claim its recharge, it would have been possible with an addition of pumps. Besides Doyle, many other inventors/corporations experimented with zinc-bromine batteries prior to the 1970's Oil Crises, including Charles S. Bradley,(71-73) Herbert H. Dow,(74) and Westinghouse Electric Corp.(75)

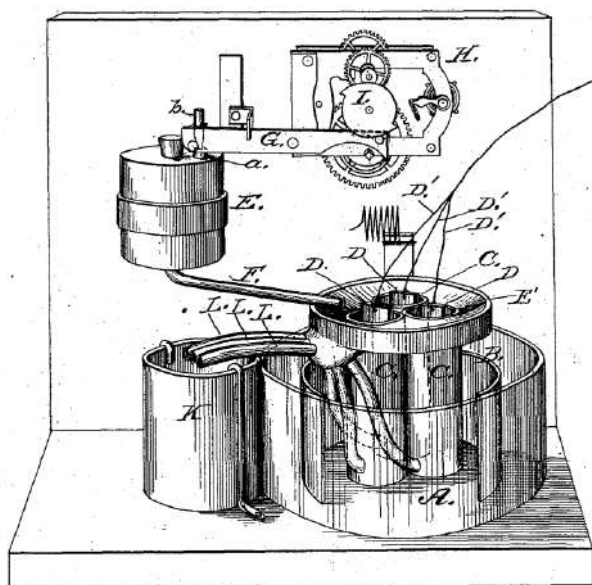


Fig. 2. Zn-Br₂ flow battery from John Doyle's patent US224404(70) filed on September 29, 1879:
 A-spill enclosure (dielectric container),
 B-cylindrical zinc negode,
 C-porous dielectric jars/separators (3 are shown),
 D-porous electron-conducting (e.g. carbon) posodes coated on the inner surfaces of the separators C's,
 D'-electric wires to the posodes,
 E- container with a posolyte liquid,
 E'- a funnel for the posolyte fluid,
 F-posolyte delivery tube,
 L-overflow tubes,
 K-container for discharged fluid.
 US government document -no ©.

The red curves in Figs. 1 and H1 (see Appendix H) show, that the interest in zinc-halogen flow batteries has had historical ups and downs. Although we do not display the separate trends for each of the three halogen versions, we can say briefly, that the zinc-chlorine batteries enjoyed the earliest publicity, when two French aeronautics pioneers Charles Renard and Arthur Krebs demonstrated the first fully controlled flight on August 9, 1884 using airship La France (see Fig.3), which was powered by a Zn-Cl₂ battery.(76) Electric cars powered by Zn-Cl₂ batteries were also demonstrated in the 1890's.(77) However, as combustion engines improved, the interest in electric vehicles in general, and in zinc-halogen batteries in particular, waned by 1910, albeit sporadic activity continued till the 1970's (see Fig. H1).

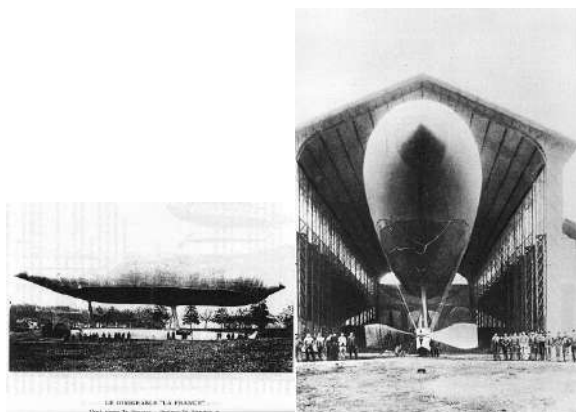


Fig.3. 1884 photograph of the airship La France. © expired.(78)

The interest in Zn-Cl₂ batteries, as plausible powersources for electric vehicles, was revived during the Oil Crises of 1970's-1980's.(79, 80) Energy Development Associates in Michigan (USA) was particularly prolific in developing this technology.(81-87) Their unique approach was based on using solid chlorine hydrates, which allowed for a compact Cl₂ storage at near ambient pressure and temperature (see Figs.4-5). Numerous battery prototypes (see Fig.5) and even several electric cars (see Fig.6) powered by Zn-Cl₂ batteries were built during that time. The reality of zinc-chlorine batteries is that the ZnCl₂ solubility (in moles per kg of solution) in water near room temperature is not significantly different from the ZnBr₂ solubility, but it has a stronger temperature dependence (see Fig.7), and the chlorine electrochemistry is much less reversible than that of bromine. Thus, in rechargeable applications, where an aqueous ZnCl₂ solution is stored within the system, there are no *practical* advantages of using Zn-Cl₂ over Zn-Br₂ RFBs.(79) It is likely that for these reasons, the interest in zinc-chlorine batteries came to an end by the 1990's.

On the other hand, zinc-bromine batteries research and development activities never stopped, as can be seen from Fig. H1 (in Appendix H). Indeed, with their > 150 Ah/kg specific charge down to freezing temperatures

(see Fig.7) and a 1.83 V open circuit voltage,(79) (i.e. with the *practical* system-level specific energy, which *may* rival that of lithium-ion batteries, see Fig.7), Zn-Br₂ batteries were considered for both stationary and transportation applications.(88-100) Another attractive feature of ZBBs is their low cost of energy (i.e. chemicals in \$/Wh): it is ca. 16 times lower than that of VRFBs and ca. 6 times lower than that of LiBs.(101) Bromine in the charged ZBB posolyte is usually stored as a water-immiscible liquid made of polybromide complexes of quaternary ammonium salts (such as asymmetric morpholiniums and pyridiniums). Most ZBBs use low-cost non-ionic porous hydrocarbon polymer membranes.(102, 103) This period culminated with the installation of a 20 kW - 150 kWh for Duke Power Company in Charlotte, NC (USA) in 1978, which was operated for about two years.(104)

A substantial amount of work on Zn-Br₂ batteries has been carried out since 1986 by ZBB Energy Corporation (renamed EnSync Energy Systems in 2015)(105) in Wisconsin (USA) in partnership (in the more recent years) with Meineng Energy in China and with Holu Energy in Hawaii,(106) as well as by RedFlow in Brisbane (Australia).(107) Modern Zn-Br₂ flow batteries typically operate at low current densities around 20-100 mA/cm² (cycle energy efficiency < 75%) to avoid the formation of Zn dendrites.(108) Under usual conditions, the overpotential on the zinc electrode is larger than the overpotential on the bromine electrode.(109)

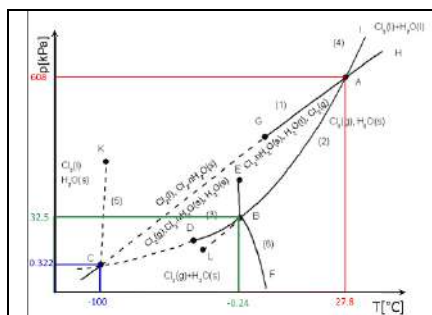


Fig.4. Partial phase diagram for Cl₂-H₂O mixture. Redrawn from data in ref. (110)

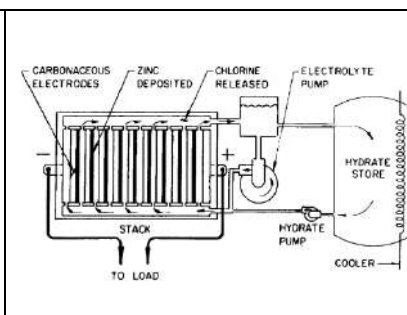


Fig.5. Schematic diagram of zinc-chlorine hydrate battery during charging.(82) © expired



Fig.6. Modified 1971 Vega hatchback powered by 24 40Vx8A Zn-Cl₂ batteries like in Fig.5. (82) © expired.

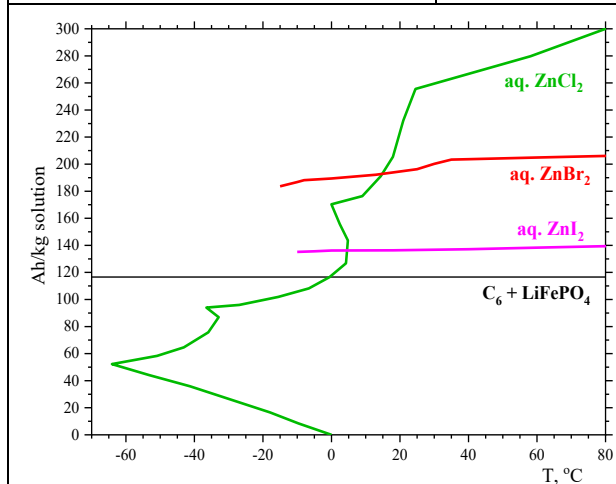


Fig.7. Solubilities of zinc halides in water shown as the number of Ah per kg of *solution*, assuming 2 e⁻ per ZnX₂. Data credits: ZnCl₂, (111, 112) ZnBr₂,(113) ZnI₂,(113) Also shown as the black line is the specific charge of a lithium-ion battery reagents.

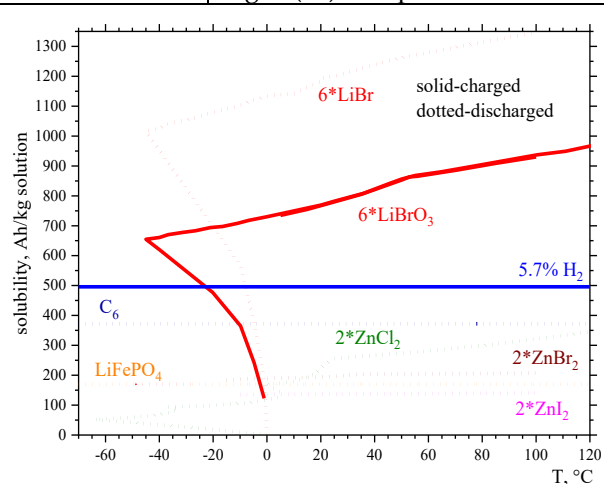


Fig.8. Solubilities of LiBrO₃(114) and LiBr (115-117) in water shown as the number of Ah per kg of *solution*, assuming 6 e⁻ per LiXO₃. The data for 2e⁻ zinc halides from Fig. 7, as well as lithium-ion batteries and H₂ fuel cells are also shown for comparison.

Zinc-iodine batteries also trace their origin to the 1800's.(118) Their development was quite active in the 1930's in France and Belgium (119-127) and in the 1980's in Japan(128-131) and elsewhere,(132) albeit not all

these prototypes were designed for the flow operation. Due to their superior safety, compared to the other metal-halogen batteries, Zn-I₂ batteries (both static and flow) have enjoyed a renewed interest since 2014,(132-149) particularly in Hong Kong/China(134, 140, 150-155) and Thailand.(156) Negatively charged polyiodides have a higher formation constants than other polyhalides, and for this reason cation-conducting membranes are effective in preventing I₂ crossover in Zn-I₂ batteries. Unlike Cl₂ and Br₂, I₂ is a solid at room temperature, and the precipitation of this intermediate is a common problem during Zn-I₂ batteries operation, albeit it is largely alleviated at low states of charge (SoCs) due to the formation of soluble polyiodides. The precipitation of I₂ can also be mitigated by using a mixed water- acetonitrile solvent.(153) An important recent development in iodine batteries is the use of the I(+1)/I(0) redox couple, which is about 0.54 V positive of the I(0)/I(-1) couple.(138, 157)

Since we are on the topic of zinc hybrid flow batteries, it is appropriate to mention Zn-Ce RFB, which has the largest (2.37 V) open-circuit voltage among commercially explored aqueous RFBs.(158-160) The most significant development and commercialization efforts in the field of Zn-Ce RFBs were undertaken by a Scottish start-up Plurion Ltd. and its predecessors between 2001(161) and 2009.(159) Since Ce(4+) corrodes carbon electrodes, platinized titanium was used in Zn-Ce RFB prototypes. The high cost and limited durability of platinum, as well as problems with remixing and rebalancing the electrolytes during cycling, were probably the main reasons for Plurion's eventual liquidation. Although there has been some interest in revising Zn-Ce RFBs recently,(162, 163) this technology is considered as a "no-go" by most RFB developers.

As far as the terminology is concerned, the terms "redox battery" and "flow battery" are much younger than zinc-halogen batteries. The terms "flow battery" and "redox flow battery" seemed to be used first by Thaller ca. 1977.(164) The term "redox battery" appears in 1979 in a conference paper by Lockheed Martin researchers in regard to a zinc-ferricyanide flow battery.(165)

2. The misfortunes of polysulfide-polybromide flow batteries : 1980-2010.

Although possibilities of using polysulfide and bromine redox couples in flow and static batteries, have been mentioned before, it was Robert Remick and Peter Ang of the Institute of Gas Technology (Chicago), who were the first to demonstrate (and claim in a patent) a rechargeable (cycled) polysulfide-polybromide battery (SBB) in 1981.(166) They quickly secured a DOE grant for detailed studies, that revealed MoS₂ as a preferred (yet less than ideal) electrocatalysis for the negode reaction.(167)

In 1987 Stuart Licht, while at Northeastern University (Boston, Massachusetts), demonstrated extraordinary aqueous solubility of potassium sulfides, for example 3:1 water:salt molar ratio for K₂S and K₂S₄ solutions, albeit this work showed only half-cell electrochemistry.(168) Nevertheless, sodium chemistry remained the mainstream among polysulfide-polybromide RFB developers, perhaps because of the higher solubility of NaBr (8.82 molal at 20 °C) compared to KBr (5.49 molal at 20 °C).

In 1992 National Power PLC (which was formed in 1990 as a result of privatization of the UK's electricity market) acquired from the Institute of Gas Technology the original US patent by Remick and Ang,(166) and started a research and development program in the field of polysulfide-polybromide RFB. Initial work at National Power was done by Ralph Zito,(169, 170) who was famously known for his prior work on Zn-Br₂ RFBs.(171-173) During the reorganization of the UK electricity market in the 1990's, the National Power patents were transferred to Innogy Technology Ventures Ltd, which became in 2002 a subsidiary of the German multi-utility RWE group of companies. Regenesys Technologies Limited was spanned off RWE-Innogy with a task of *expedient* demonstration and commercialization of polysulfide-polybromide RFBs, which were branded as Regenesys® batteries. By year 2001 Regenesys employed over 70 people and demonstrated 5 and 10 kW stacks.(174)

The Regenesys' SBB development program was much more vigorous than those of its predecessors. Ca. in 1999 the Regenesys team discovered, that sulfur is irreversibly oxidized to sulfate in a side-reaction. As their

attempts to develop a system with a mixed polysulfide-bromide negolyte and sulfide-free posolyte using a Nafion membrane turned out unsuccessful, they suggested adding more solid sulfur or polysulfides to the negolyte as part of normal battery cycling-rebalancing.(175) They also developed an ingenuine method to detect the onset of colloidal sulfur formation using electrokinetic sonic effect.(176) Although the early design of the Regenesys SBB was rather ineffective by modern standards (e.g. the membrane was not coated by catalytic layers, but rather was brought into a direct contact with 1.5 mm thick reticulated carbon electrodes on each side), it showed initial promise.(177) Notably, during charge at 34 mA/cm² the overvoltage at the negative electrode (0.65 V) was significantly larger than the overvoltage on the positive electrode (0.075 V).(177) Transition metal sulfides (178) and other complexes (179) were suggested as electrocatalysts for the negode reaction. In a later design, the operating current density was increased to 80 mA/cm².(175)

In 2001, the UK's Department of Trade and Industry funded ca. 50% of the total ca. £2 mln. cost (apparently with an expected cost-share from RWE-Innogy) of building a 100 kW Regenesys® battery at Little Barford in central England next to an existing gas-peaker plant and a proposed windmill site.(174, 180) A similar plant was also considered in Columbus, Mississippi in the USA,(181, 182) as a part of the ill-fated Tennessee Valley Authority.(183) A hypothetical 15 MW-120 MWh in the UK was also proposed for years 2000-2002.(184, 185) However, jumping from 10 to 100 kW stack proved to be more difficult, than it was expected for a modular system like an RFB. Stack leakage was allegedly addressed by improving the seal design and manufacturing tolerances.(174) After these improvements, fractures of endplates, of electrodes and of PVDF-lined tanks were reported as predominant failure modes throughout the testing. These problems (as well as chemical rebalancing) were not addressed during the time available for this demonstration project. In addition to this, Regenesys' own studies published in 2009 questioned the technical feasibility of long-term operation and the profitability of the SBB.(186, 187)

In 2003, after the Little Barford fiasco, RWE decided to abandon its Regenesys® technology (which was not invented at RWE, but rather inherited as a part of the Innogy acquisition). Apparently, RWE was unable to find a buyer for this divestiture, as its patents on this technology expired for non-paying maintenance fees in various countries between 2004 and 2013. The cost of developing the polysulfide-polybromide RFBs between 1990 and 2004, according to the company's reports, amounted to over 140 mln. £.(188)

Others also explored the feasibility of polysulfide-polybromide battery (SBB). Ca. in 2002 Dalian Institute of Chemical Physics (PR China), which became by then the World's leading flow battery developer, launched its own SBB program. In 2004-2006 they reported 1kW systems operating at 40mA/cm² with the cycle energy efficiency improving from 67 to 82 % mostly due to the development of new electrode materials.(189-192) Nevertheless, the SBB patenting and publication activity significantly decreased after 2006. It is likely, that the problem of sulfur deposition in the porous negode during long-term cycling,(193) as well as the concomitant success of vanadium redox flow batteries, were the main reasons for scaling down SBB activities. Since ca. 2010 SBB development has been confined mostly to academic laboratories and to development of new electrocatalysts, which nevertheless fall short of the required activity and durability targets.(194, 195)

In more recent years, polysulfide-polybromide batteries (SBBs) with Li⁺- (196) and Na⁺- (197) conducting ceramic separators have been demonstrated. Although these cells showed good cycle life (over 100 cycles without noticeable degradation), they were operated at ca. 1 mA/cm² because of the high ohmic resistance of the separators.

Despite all these developments, the interest in the aforementioned Zn - Br₂ and Sn²⁺ - Br₂ flow batteries started to decrease in the 1990's (see Fig. H2), because a new less-volatile, less-corrosive and less dangerous RFB chemistry has emerged: all-vanadium.

3. Vanadium RFBs- the technology frontrunners: 1985-now

The low current density, the dendrite formation and incomplete decoupling of energy and power in zinc hybrid flow batteries prompted interest in all-flow batteries, employing only fluid-phase (e.g. dissolved)

reagents. Walther Kangro, an Estonian chemist working Germany, seems to be the first to demonstrate in the 1950's flow batteries based fully on dissolved transition metal ions: Ti-Fe and Cr-Fe.(198-200) After some initial experimentations with Ti-Fe RFB (8, 201), NASA and some other groups in Japan and elsewhere(202-210) selected Cr-Fe chemistry for further development. In order to reduce the effect of time-varying concentration during RFB cycling, mixed solutions (i.e. comprising both chromium and iron species in the negolyte and in the posolyte) were used. Among disadvantages of the Cr-Fe chemistry are: hydrate isomerism (i.e. the equilibrium between electrochemically active Cr^{3+} chloro-complexes and inactive hexa-aqua complex, which is can be alleviated by adding chelating amino-ligands) and hydrogen evolution on the negode (which is mitigated by adding Pb salts for increasing the H_2 overpotential and Au salts for catalyzing the chromium electrode reaction).(211)

Although the interest in Cr-Fe RFB waned in the late 1980's (see Fig. H2), as vanadium RFBs were gaining popularity (see below), the *11 times lower cost of energy*(212-215) at 250 \$/kWh and 0.20 \$/(kWh×cycle)(216) of chromium-iron compared to vanadium chemistry was a sufficient reason to pursue revival of Cr-Fe RFB around 2010.(213, 217-221) While some promising developments have been reported for Cr-Fe RFBs during this period, such as amelioration of the parasitic HER by pre-electrolyzing impurities,(222) by adding electrocatalysts,(223, 224) as well as increase in the open-circuit voltage by adding complexing ligands,(225) apparently, these did not improve the technical and commercial viability of Cr-Fe RFBs. For example, a Silicon Valley startup EnerVault received \$26.3M in funding between 2010 and 2012 alone,(226) (and over \$35M in total between 2008-2013),(227) and had a ribbon-cutting ceremony for a 250 kW × 1 MWh energy storage facility at an almond farm in central California on 2014-05-22, before getting liquidated in 2015.(228-230) It is also worth noting all-chromium RFBs (typically, with organic ligands) have been demonstrated,(231-237) but this chemistry has not seen much development in the last 10 years, despite its potential cost advantages over the VRFB chemistry.

In the late 1980's Sum, Rychcik and Skyllas-Kazacos (238-241) at the University of New South Wales (UNSW) in Australia demonstrated the advantages of all-vanadium RFB chemistry, such as the existence of four oxidation states within the electrochemical voltage window of the graphite-aqueous acid interface, and thus the elimination of the mixing dilution, detrimental in Cr-Fe RFBs. UNSW filed several patents related to VRFBs,(242-245) that were later licensed to Japanese, Thai and Canadian corporations, which tried to commercialize this technology with variable success.(246)

During its ca. 40-year long history, vanadium redox flow battery development experienced several “quantum jumps”, somewhat similar to the progress of hydrogen polymer electrolyte fuel cells(247-249) and of lithium-ion batteries.(250-253) In the first period (1985-2008) VRFBs made at the University of New South Wales (UNSW) and by others(254) employed as the electrodes ca. 3-5 mm thick carbon felts with >90% porosity comprising 10-100 μm thick fibers.(255, 256) There were no channels in the bipolar plates, and the electrolyte (e.g. 1.7 M of vanadium ions in sulfuric acid) was forced to go through ca. 10 cm of the felt length. Such electrodes had a very high area-specific resistance (ASR) of ca. 5 $\Omega \text{ cm}^{-2}$.(257) and the pumping losses were ca. 10%–12% of RFB power. Surprisingly, the overall performance of VRFBs from UNSW (and from its patent licensee, V-Fuel Pty Ltd) at that time was not terrible: 80% round-trip stack energy (i.e. accounting for both voltaic and faradaic losses, but not for pumping losses) efficiency at 40 mA/cm² in a 1 kW stack.(254, 258)

The second period in the VRFB development (2009-now, see Fig.H2 in App.H(259)) started after the end of G.W. Bush's second presidential term in the USA and the following policy shift away from Hydrogen Economy(260), when numerous talented scientists and engineers from the fuel cell field switched to flow batteries. The first significant improvement during this period was the “zero-gap” design of the RFB's membrane-electrode assembly (MEA) proposed at United Technology Corporation,(261) the University of Tennessee and Oak Ridge National Laboratory,(262) where the carbon felts of the first period were replaced with carbon papers and whole assembly of the membrane, two electrodes and two bipolar plates was compressed (or mechanically bonded in later designs) similarly to the MEA design of the polymer electrolyte fuel cells of that time. Also, flow fields with serpentine channels were used in this new design in contrast to

“flat” or “equal path length” (i.e. without channels) bipolar plates employed by earlier VRFB developers.(263) The channels provided by the bipolar plates alleviated the problem of flow channeling(264-266) within the porous electrodes, that plagued the “equal path length” flow fields. The area-specific resistance of VRFB was reduced from 3.5 to 0.5 $\Omega \text{ cm}^2$, and the cell’s peak power was increased from 150 to 550 mW/cm^2 .(262) A further innovation was the realization,(267) that in single-phase flow systems (e.g. VRFB) it is possible to use dead-end channel flow fields (such as interdigitated), which are not suitable for PEM fuel cells due to clogging of gas channels by liquid water. The operating current density (for the same round trip voltage efficiency of 75% and ca. 1 atm pressure drop) of kW-sized stacks increased from ca. 40 mA/cm^2 in the 1990’s to over 100 mA/cm^2 in the 2010’s.(263)

The second major improvement (it came from Pacific Northwest National Laboratory)(268) was based on the discovery, that chloride ion stabilizes V^{4+} and V^{5+} species from precipitating, whereas sulfate stabilizes V^{3+} . The mixed sulfate-chloride electrolyte allowed for the use in VRFB solutions with the total vanadium concentration of 2.5 M over a whole temperature range between -20 and $+50$ $^{\circ}\text{C}$.(269) It is worth noting, that the based on the standard equilibrium potential of the $\text{V}(+5)/\text{V}(+4)$ couple it is expected to oxidize chloride, and for this reason chloride solutions were avoided in earlier VRFB studies. The surprising oxidative stability (albeit only at the state of charge below ca. 80%) of $\text{V}(+5)$ solutions in the presence of chloride was explained on the basis of activity coefficients.(270) Nevertheless, because of a high vapor pressure of HCl solutions,(271) such mixed electrolytes have not been widely adopted by the VRFB industry.(272)

The third major improvement was the switch in VRFBs and other flow batteries from multi-micron to submicron diameter fibers in the porous electrodes. The earliest experimental report of using submicron (0.05, 0.1 and 0.3 μm) carbon fibers (grown from the vapor phase and characterized by cyclic voltammetry in vanadium solutions) in a VRFB setting can be found in a 2004 Japanese patent application.(273) Similar methods were soon reported by others.(274-276) This process, however, has a low throughput and the durability of such carbon nanofibers weakly attached to carbon microfibers is questionable.

Wei et al. from the Institute of Metal Research, Chinese Academy of Sciences, claimed in 2013 to be the first group to employ as VRFB electrodes carbon nanofibers (CNFs), produced by pyrolysis of nanofibers from electrospun polymer solutions.(277) This work, however, went largely unnoticed, and it was not till 2015, when a German collaboration(278) reported the use of *free-standing* carbon nanofiber mats in VRFBs, the interest in the use of electrospun CNFs for RFB electrodes took off.(267, 279-290) This is illustrated in Fig.9, which shows the evolution of the carbon fiber diameter based on selected journal articles and patent applications related to VRFBs over the last 30 years. By 2018 porous electrodes made of electrospun carbon nanofibers became a popular choice for lab-scale RFB prototypes.(291) The resulting carbon nanofelts typically consist of fibers with diameter ranging from 20 nm to 2 μm and have porosity higher than 80%. (292, 293) However, in order to reduce the pressure drop within such fine porous structures, flow channels were required in the bipolar plates, resulting in further increase of the RFB’s manufacturing cost per unit area.(292)

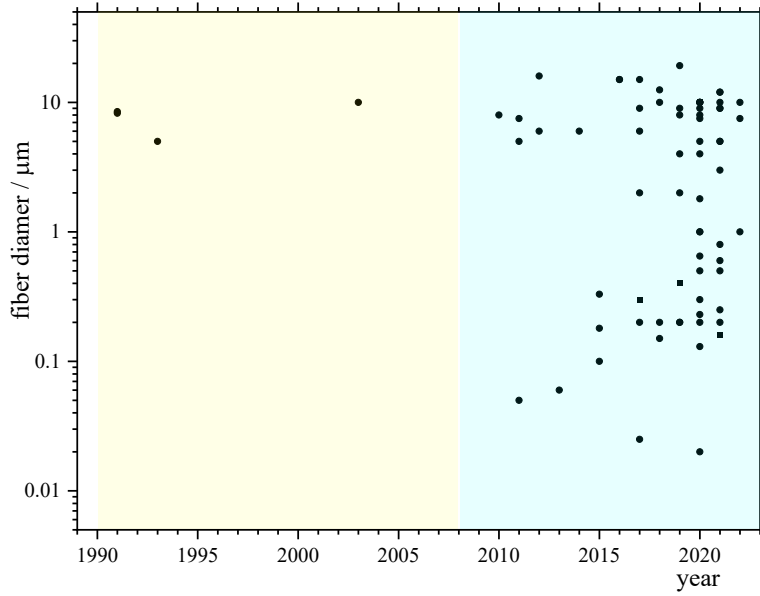


Fig.9. The fiber diameter reported in publications about VRFBs vs priority (for patents) or publication (for all other documents) year.

4. The benefits of submicron electrode fiber diameter and RFB efficiency.

A theoretical justification of using (sub)micron-diameter fibers in RFB electrodes was put forward in 2016 by a Canadian group.(267) They used a structureless model for the secondary current distribution in a porous electrode, that was originally published by Daniel'-Bek in 1948(294) and soon thereafter expanded and applied to model numerous practical electrochemical systems by Coleman,(295) by Ksenžek and Stender,(296-298) by Euler and Nonnenmacher,(299), and by Newman and Tobias.(300, 301) The Canadian group(267) predicted that (for a fixed pressure drop in the electrode using an example of the bromine/bromide reaction) there is an optimal fiber diameter between 1 and 3 μm and an optimal electrode porosity above 0.85, which results in a maximum area-specific power at a fixed voltage efficiency.

As shown in Appendix D, the pressure drop Δp across landing with the length L in an interdigitated flow field, required to assure the flow of reagent with a total concentration of C_0 and single-pass utilization ϕ (set to 0.5 below) sufficient to maintain current density i on the electrode (under secondary current distribution with linearized Butler-Volmer kinetics), is given by (D-23), labeled as (1) in the main text here:

$$\frac{\Delta p C_0}{i L^2} = \frac{\nu \psi}{n F \phi \chi} \frac{1}{d^{2.5}} \sqrt{\frac{F (\alpha_a + \alpha_c) \beta (1 - \epsilon) i^0}{RT \sigma}} \quad (1),$$

where ψ is the dimensionless permeability (set to 23 as explained in Appendix B), d is the electrode fiber diameter, χ is the dimensionless electrode thickness set to 2 according to Appendix C, the α 's are the transfer coefficients for the anodic and cathodic half-reactions, σ is the electrolyte conductivity, β is a dimensionless geometry coefficient (1 for square lattice and 0.5 for hexagonal), ϵ is the electrode's porosity, σ is the electrolyte's conductivity and i^0 is the exchange current density. The area specific electric resistance R_{int} of each electrode is given by (C-5) in Appendix C, which is labeled as (2) below:

$$R_{int} = \frac{\coth \chi}{\chi} \sqrt{\frac{RT d}{F \sigma i^0 (\alpha_a + \alpha_c) \beta (1 - \epsilon)}} \quad (2).$$

Now we know the ohmic (2) and pressure (1) losses in a porous electrode upon variation of the fiber diameter d at a fixed porosity ϵ . From these we can see, that the pressure drop in the electrode increases as $d^{-2.5}$, but the electrode's area-specific resistance (ASR) increases as $d^{0.5}$. Thus, there is an optimal diameter of fibers in a porous electrode. *A suitable criterion for optimizing the fiber diameters is the maximum system's area-specific power at a selected system's energy efficiency.* We shall clarify now, that we do not account for pumping energy losses in our analysis for two reasons:

- 1) the system pressure in commercial RFB installations is usually limited to 1 bar based on the costs of the pumps and of the stack sealing, and not on the pumping energy losses;
- 2) such losses comprise only 3%–5% of the VRFB power in 2020 state-of-the-art commercial systems,(263) although as much as 10% pumping energy losses have been reported for some VRFB systems.(302)

In order to minimize the pressure difference across the membrane (and the resulting hydrodynamic flow), we should keep both Δp and L the same for posode and negode. Since the kinetic parameters (i° and $\alpha_a + \alpha_c$) in Eq.(1) for the two electrodes are different, and since we decided to keep L , β , ε , χ and ψ the same (see App. C) for both electrodes and assumed v and σ to be similar, the most appropriate means to keep the same Δp on both sides of the membrane (see App.D) is by using different values of fiber diameter d for the posode (d_+) and for the negode (d_-).

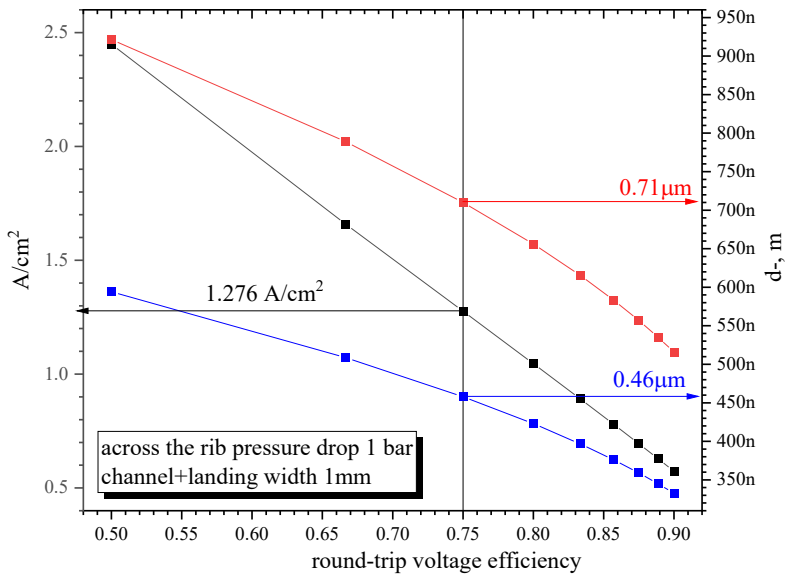


Fig.10. The calculated negode's (blue) and posode's (red) fiber diameters and the round-trip voltage efficiency (black) required to maintain the 1 bar pressure drop across 1 mm width in a VRFB for the current density shown on the Y-axis.

The results of combining (1) and (2) for the negode, posode and the membrane in a VRFB cell are shown in Fig. 10. The selected cell current density i is shown on the Y-axis. Starting with i , we calculated from (1) the fiber diameter d_+ required to assure 1 bar pressure drop for the posode, when the channel + landing width is fixed at 1 mm and the electrode's thickness is $2L^\circ$, and its porosity is 0.765 (see Appendix B), while maintaining the selected current density under the assumed single pass utilization of 0.5. Once we knew the required posode's fiber diameter d_+ , we calculated the negode's fiber diameter d_- from eq. (1), keeping in mind that its left-hand side is the same for both electrodes, thus *the required negode/posode fiber diameter ratio is constant* and equal to 0.645. After this, we calculated the voltage losses in each electrode and in the membrane (assuming the membrane's area-specific resistance of $0.1 \Omega \text{ cm}^2$) for the selected i , and came up with the one-way discharge voltage efficiency, *the square of which* is shown on the X-axis in Fig. 10.

Let's examine the predictions of Fig. 10. If we want to have for a VRFB battery's voltage round trip efficiency of 0.75 (see App. L), we can find, that it can be obtained with the $0.46 \mu\text{m}$ diameter fibers in the negode and $0.71 \mu\text{m}$ diameter fibers in the posode, and the suitable discharge current density is $1.276 \text{ A}/\text{cm}^2$. If we want to increase the voltage efficiency to 0.85, we need to reduce fiber diameters to 0.38 and $0.58 \mu\text{m}$ for the negode and posode, respectively. Also, the operating current density would need to be lowered to $0.857 \text{ A}/\text{cm}^2$ (unless we are willing to increase pressure drop in the electrodes). This example shows, that decreasing fiber diameter in the porous electrodes of flow batteries can improve *simultaneously* two contradictory performance metrics: the area-specific power and the electric energy efficiency. And this has been demonstrated in the works cited above, when the transition from carbon microfibers to carbon nanofiber was reviewed. The need for decreasing the fiber diameters has also been suggested, directly or indirectly, earlier in refs. (303-306)

Our results show, that further improvements in RFB's area-specific power at constant electric energy efficiency would require increasing the pressure drop in the porous electrodes above 1 bar. Since such transition would entail a substantial increase in the capital cost of the RFB systems (e.g. new pumps and seals), we should look at alternative solutions. One way to overcome the aforementioned TRIZ contradiction between the pressure drop and the electric energy efficiency is to use a wider porosity distribution instead of the uniform porosity assumed in the foregoing discussion. Indeed, such approaches have been reported recently.(307)

A Hong Kong group discussed the benefits of broad porosity distribution in 2018.(285) This was soon verified in details in their study,(308) that reported the use of porous carbon fibers with multimodal pore distribution in the 3 – 60 μm range as VRFB electrodes with a record-high peak power of 1.9 W/cm² and with 0.7 W/cm² at 87% (0.75^{0.5}) one-way energy efficiency. Advantages of broad pore size (or fiber diameter) distribution in RFB electrodes were reported recently by others as well.(309-312) Benefits of spatial porosity distribution within RFB porous electrodes (i.e. smaller pores near the membrane and larger pores near the flow fields) have also been demonstrated.(313, 314)

On the other hand, high-area electrodes with submicron pores, such as those comprising
ca. 20 nm pores in ca. 1.1 μm fibers with ca. 15 μm voids in between,(315) or
20 nm wide pits etched on the surface of 200 nm wide carbon fibers,(316) or
carbon nanoribbons with 0.4×0.8 μm cross-section,(306) or
carbon nanotubes grown on microfibers in commercial carbon felt (317-319)

were less successful in improving the power-efficiency performance of a VRFB on the complete cell level at practically relevant current densities (i.e. over 0.2 A/cm²). We would like to mention here in passing, that the electrocatalytic effects in VRFB reactions is comparatively (to H₂ and O₂ electrocatalysis) weak, often poorly reproducible and time-dependent.(320-338)

We shall note now, that some of the aforementioned “quantum jumps” *refer principally to academic innovations, as they have proven hard to scale-up and have not been universally-adopted by the flow-battery industry.*(272)

In conclusion of this section we shall ask ourselves the question: why do we want to increase the area-specific power of RFB stack? Would it be possible to run a RFB at a low current density (e.g. 1-10 mA/cm², as it is in the case of lead-acid and lithium-ion SEAM batteries) and have a larger stack with a lower area-specific cost? The answer to this question is negative for two reasons. Firstly, RFB suffer from a continuous cross-over of redox species through the membrane placed between the negolyte and posolyte. Even in the case of cation-selective membrane (such as Nafion 117) and anionic reagents the Donnan exclusion limit breaks down at concentrations above 1 M, (see Ref.(2) and citations therein). In the case of Nafion and cationic reagents (such as those in VRFBs) the cross-over (i.e. internal short-circuiting) current is about 4-10 mA/cm² (see App. J).(339-341) The second reason to operate flow batteries at larger current densities than SEAM batteries is due to the higher cost per area of an RFB stack compared to a SEAM battery. This is because the contemporary RFB stack design requires the use of costly bipolar plates with channels, while SEAM batteries avoid them.

The effects of cross-over and cell resistance on the battery's efficiency are exemplary illustrated in Fig. 11, where the blue lines show, that the faradaic efficiency decreases (due to the reagents' cross-over through the membrane) at low operating current densities, whereas the voltaic efficiency (the red line) decreases at high operating current densities (due to the cell's ohmic resistance). The black line is a total one-way energy efficiency, which is a product of faradaic and voltaic efficiencies. The solid lines in Fig. 11 refer to the base case: cell resistance 0.6 $\Omega\text{ cm}^2$, cross-over current 7.4 mA/cm². In this case the peak *one-way* energy efficiency of 89% is observed at 120 mA/cm². Doubling either the cell resistance or the cross-over current reduces the peak efficiency to 85%, which is not a tremendous loss. The round-trip efficiencies in the case can be approximated as squares of the one-way efficiencies, i.e. as 79 % and 72%, which is in the range reported for 1-10 kW stacks.(14, 342, 343) Although, these round-trip efficiencies are not as high as those of most SEAM

batteries (see section “3.3. Energy efficiency” below), they are acceptable for reserve power and, perhaps, in some other stationary energy storage markets.

It is worth noting, that in all three aforementioned cases, the energy efficiency goes through a maximum at a current density of about 50-150 mA/cm². At such current densities, the area-specific power (green lines in Fig. 11) does not depend much on either the cells resistance or the cross-over current. This is the desirable operating current range from the energy-efficiency viewpoint.

For better or worse, RFBs are not always operated at the peak energy efficiency.(14) In order to reduce the capital cost of power (the size of the stack), the operating current density is often set at a higher number. If we compare the data in Fig. 11 at 100 and 400 mA/cm², we will see a substantial decrease in power and efficiency only for the most resistive cell (dotted lines, 1.2 Ω/cm²). The two less resistive cells would be suitable for applications, that require occasional two-fold increases in power. Also, although 72-79% cycle energy efficiency is low compared to lithium-ion batteries (see below), it still may be acceptable to some customers, who need a system with unfrequent charge-discharge cycles, with a half-cycle duration longer than ca. 2h, and with a durability of over 5 years. This is discussed in details in the following section.

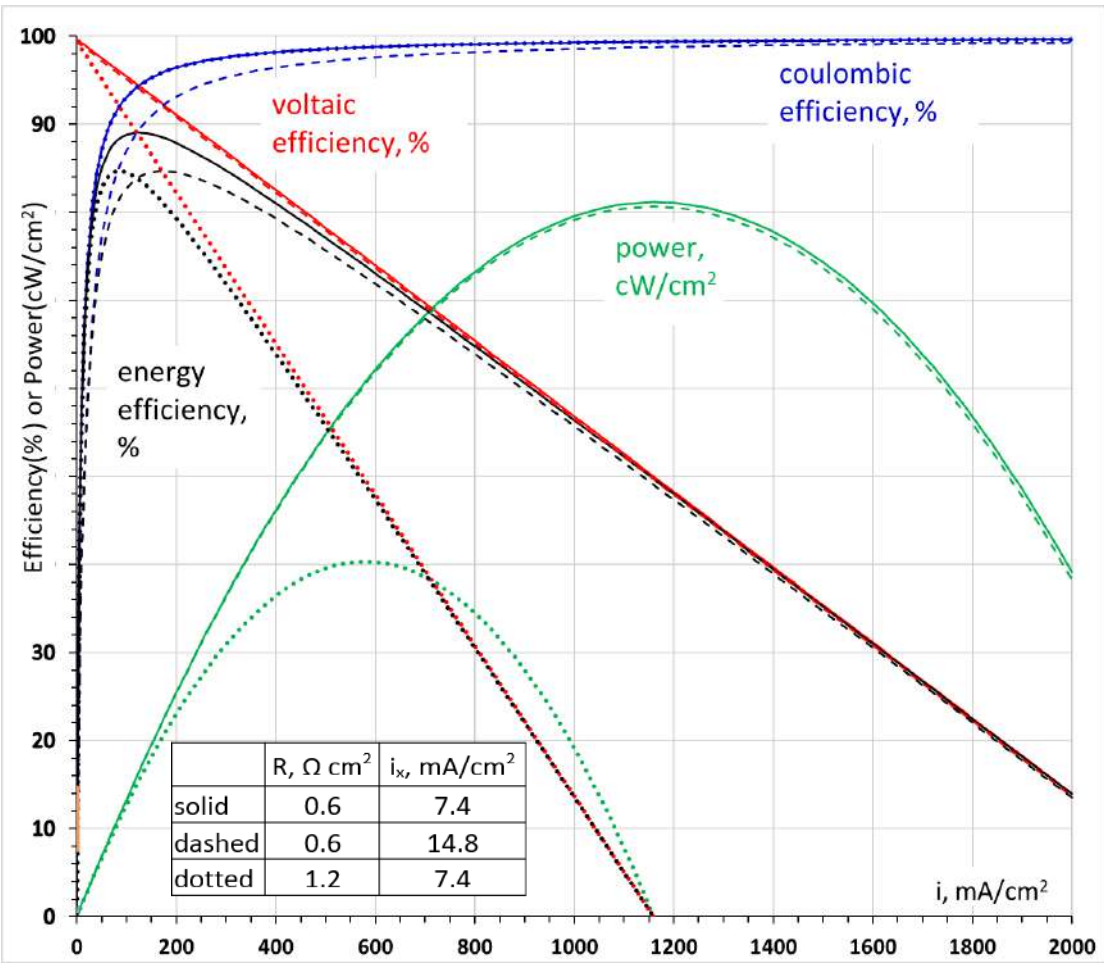


Fig. 11. Simulated area-specific power (green line, right axis) as well as voltaic (red line), coulombic (blue line) and total energy (black line) *one-way* efficiencies for a VRFB prototype. Solid lines refer to the base case (cell's area-specific resistance is 0.6 Ω/cm² according to Ref.(344) and the cross-over current is 7.4 mA/cm², as explained in App. J). Dashed lines- cross-over current is doubled. Dotted lines – ohmic resistance is doubled.

5. The “lithium or vanadium” quandary.

In this section we want to compare the suitability of flow batteries and SEAM batteries for different segments of the stationary energy storage market. Since VRFB is the most commercially successful flow battery chemistry (see Section 2. *Vanadium RFBs- the technology front-runners* above), it makes sense to use it as an example in our comparison. As an example of a SEAM battery, we shall use lithium-iron phosphate chemistry, because it currently dominates the SES market due to its superior combination of a low capital cost per kWh and a long cycle life (2,000-3,000 cycles).(345-348) The latter factor is especially pronounced, when LIBs (which are based on insertion reactions) are compared to batteries employing conversion reactions, such as lead-acid (with 200-1,000 cycles)(349) or cadmium-nickel (with 500-2,000 cycles).(349-351)

Although both LIBs and VRFBs can trace their origin to the Oil Crises Period of 1975-1989, their subsequent history was quite different: LIBs took off as soon as they were invented (see the red lines after 1991 in Fig.1, prior data points in these two plots mostly refer to unsuccessful LIBs prototypes with non-graphite negodes), while VRFBs (the blue lines) had to wait for the second Oil Crisis around 2008 to get to the first inflection point in their publication and patenting activities. Also, the number of LIB patents is ca. 25 times larger than the number of VRFB patents, and the number of LIB journal articles is ca. 20 times larger than the number of VRFB articles, illustrating, the fact that the market adoption (and profitability) of VRFBs has been much less successful than that of LIBs.(352) To a great extent this is because unlike LIBs, which benefited from the military and portable electronics markets in the 1990's, VRFBs do not have a *large* market niche with a high profit margin and a low market penetration barrier, where they are clearly superior to existing alternatives from the customer viewpoint. (We are aware of the purchase of a flow battery startup SunCatalytix by Lockheed-Martin (NYSE: LMT) in 2014,(353) and of Lockheed's own attempts to develop RFBs for nuclear missile silos in the 1980's,(354-357) and of on-going US Department of Defense- funded work at Raytheon Technologies (NYSE: RTX)(358) and at Ameresco, Inc. (NYSE: AMRC) with Invinity Energy Systems (LSE:IES),(359) but these are exceptional events in a niche market rather than a real market trend).

We shall compare LIBs and VRFBs using the following criteria:

1. capital cost for various energy-to-power ratios.
2. durability, such as cycle and calendar lives.
3. energy efficiency in a charge-discharge cycle.

5.1. Capital cost. The rise in the RFB activity after 2008 is related to the new demand from the long-duration niche of the stationary energy storage (SES) market. Under the presently low (<10%) power fraction of intermittent renewables in the grid generation capacity in most countries, SES systems with half-cycle duration of 2 h can meet most of the market demand.(360) However, as the share of solar panels and wind mills in the electric power generation rises above ca. 10 % , longer duration (e.g. 6h) SES systems are required.(360)

Batteries with solid electroactive materials (SEAMs) in general, and lithium-ion batteries (LIBs) specifically, normally have a the ratio of limiting energy (at low current density) to peak power of less than ca. 2 h,(361) (and usually around 0.2-0.6 h)(362-364) because of the increased area-specific resistance and reduced capacity utilization of electrode layers with the thickness over ca. 50-200 μm (or SEAM loadings over ca. 50-100 mAh/cm²). (363, 365-373) Due to finite ionic and electronic conductivities of the layers, thick layers would be underutilized during charge-discharge cycles.(374) For this reason, *SEAM batteries are not cost-effective in applications with multi-hour half-cycle duration.*

On the other hand, VRFBs allow for truly independent scaling of energy (tanks) and power(stacks). As a result, due to decoupling of their energy and power scale VRFBs have a cost advantage over LIBs in systems with half-cycle durations over 4-6 h (375) or over 8h (376, 377) or over 18 h (378) but not for shorter times.(379) The exact value of half-cycle duration break-even point is very sensitive to input parameters.(378) In commercial practice, the nominal energy-to-power ratio of the most LIBs for SES installations is about two hours,(380) while VRFBs installations have been designed typically for charge-discharge cycles over 4 h long.(378, 381-383)

This is further illustrated in Fig.12, where the magenta line shows the capital cost of lithium-iron phosphate batteries approximated and extrapolated from the wholesale price data in Ref.(384). 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 Fig.12) can represent batteries with a variable power - energy rating. This is not the case for vanadium redox flow batteries (VRFBs), where energy (the tanks) and power (the stack) ratings (as well as their costs) can be scaled independently from each other. For this reason, we use four cost-energy plots to illustrate the economics of VRFBs in Fig.12: 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 design half-cycle runtime longer than ca. 4-6 h. For example, in Fig.12 the cost of VRFBs becomes lower than the cost of LIBs for the energy/power ratios over 7h. 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* from each other, thus allowing for a cost/weight/runtime/etc. optimization depending on the application.

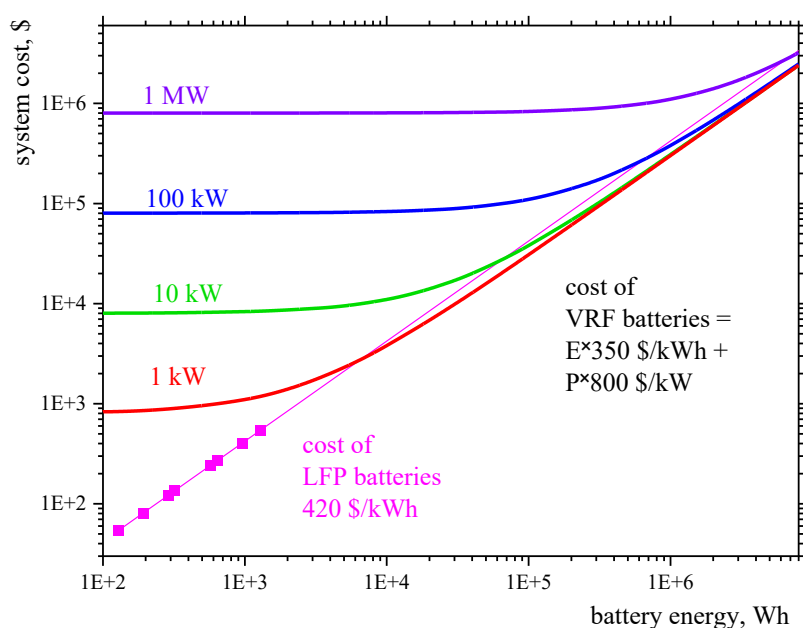
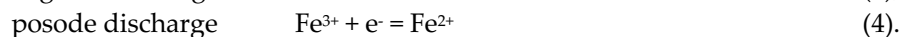
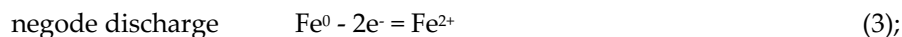


Fig.12. The capital costs of lithium iron phosphate (LFP) batteries (magenta) (384) and of vanadium redox flow (VRF) batteries (red, green, blue and violet)(385, 386) for different energy and power ratings.

For the sake of full disclosure we shall note, that

- 1) we were able to demonstrate in Fig. 12 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;(385)
- 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.(387-391) Nevertheless, the general problems of high risk and low profit margin in the clean energy business (392-398) have a negative effect on VRFB development and adoption.

We shall mention in passing all-iron hybrid flow batteries (AIHFBs), based on the chemistry shown in eqs. (3)-(4):(399)



This chemistry has a record-low capital cost of energy,(400, 401) and not surprisingly it attracted attention of some developers, such as those in the USA (CWRU,(15, 20, 402, 403), LBNL,(401) USC,(404) UCSD,(405) Honeywell,(406)), in India,(407-412) in China,(409, 413, 414) and in Germany.(415-417) Typically, carbon felts are used as insoluble posodes and negodes in such batteries, and the operating current densities are 10,(418) 20,(405) 25,(412) 50,(402, 408, 410) 100 (403, 404, 407) mA/cm² during charge and 10,(416) 20,(405) 50(402, 408, 415, 419) - 100(401, 403, 407, 410, 415) mA/cm² during discharge. The solubility of Fe species in such batteries can reach 2.2 M in a mixed water-ionic liquid solvent.(405) Among the technical challenges facing AIHFBs

are: the H_2 evolution on the negode during charge (20, 402-404, 415, 416) and the precipitation of Fe^{3+} species.(20, 403, 410)

Despite the aforementioned technical issues, all-iron hybrid flow batteries are being commercialized by a Portland, OR (USA)-based startup ESS Inc. ESS's patents are focused on stack design and assembly, rather than on developing new chemistries. Instead, previously reported iron plating solutions comprising iron chloride and/or sulfate salts, carboxylic acids and other additives are used. ESS Inc. is one of only a few flow battery start-ups that became listed on a stock exchange (NYSE: GWH on 2021-10-11)(420, 421) albeit not via a traditional Initial Public Offering, but rather via a more controversial practice of Special Purpose Acquisition Company,(422-425) which allows startups to publicly trade their stock before they become profitable. Undoubtedly, such "exit strategy" was possible due to the expertise of such as ESS's investors as Bill Gates' Breakthrough Energy Ventures, Softbank's SB Energy, BASF Venture Capital, Fidelity Management and Research, Koch Industries, Tortoise Capital Advisors and SB Energy Global Holdings.(421)

5.2. Durability. The second, and lesser known, advantage of RFBs compared to SEAM batteries is the longer useful (cycle and calendar) life of the former. Although there is a shortage of 5+ year-long studies in the operational environments in both cases, VRFBs are believed to have a substantially longer cycle and calendar life (13-25 years) than LIBs (<8 years).(375, 377, 426-428)

The main degradation mechanism for LIBs is the growth the solid electrolyte interface (SEI) on the negative electrode, which results in the increase in the negode's electric resistance and in the decrease of the amount of cyclable Li^+ ions. (429, 430) The SEI thickness grows as a square root of time in the charged state, as expected for a process limited by the diffusion of Li^+ through the SEI. This degradation pathway gets faster at higher temperatures, when storing at higher state-of-charge, and at higher charging rates.(431-435) This process results in ca. 10% loss in the cyclable charge capacity within ca. 7 months at 25 °C(436, 437) and in larger losses at harsher conditions.(432, 437-439) It is worth noting that the durability of titanate anodes is longer than that of graphite (which has a more negative with a more negative standard electrode potential), because the SEI growth on the former is not as fast.(440)

Detachment of electroactive particles from electronically conducting networks on both electrodes is a secondary degradation pathway for LIBs.(427) Amorphization of the surface layer on the posode (e.g. $LiFePO_4$) particles(441) usually occurs in a slower timescale, than the two aforementioned processes, but it can be a problem in fast cycling applications. There are also cathode-specific chemical degradation pathways: disproportionation/dissolution of $Mn(3+)$ species in the case of $LiMn_2O_4$ and Li^+ for Ni^{2+} lattice site exchange in $LiNiO_2$. These show up as both charge and power fade (increased resistance). Both positive and negative electrode materials are subject to fracturing due to the volumetric strain of repeated lithiation cycles.

However, in addition to the aforementioned gradual degradation, non-uniformity in the battery manufacturing (and in the current distribution during the battery operation) can result in a catastrophic LIB failure (due to Li plating) within a much smaller number of cycles.(442-444) Such catastrophic failures are more likely to occur in a larger format batteries, simply because of a larger electrode area per stack.

Although the degradation of VRFBs is much less understood, they are generally perceived as more durable than LIBs. The electroactive inorganic vanadium ions have infinite durability (provided that V_2O_5 precipitates are recovered and reused during the battery life), and they are easily recycled at the end of a stack's life. Vanadium batteries have an *expected* lifetime of at least 15,000 cycles, with negligible degradation during the first 20 years.(445, 446) Cross-over effects in VRFBs are readily mitigated by remixing,(303) and charge disbalance due to parasitic H_2 evolution is addressed by occasional rebalancing.(447) Thus, we consider these issues not as degradation phenomena, but as essential features of the normal VRFB operation.

5.3. Energy efficiency. The *most significant and rarely discussed drawback of redox flow batteries* is their lower energy efficiency compared to SEAM batteries. In general, round-trip energy efficiency of an energy storage

system can be defined as (energy recovered during discharge) / (energy spent during charge). This accounts for all losses, including pumping and battery management system for RFBs.(448)

In case of lithium-ion batteries after the initial formation of a solid electrolyte interface (SEI) on the negode (which is an example of faradaic losses), the cycle energy efficiency is typically 90-98 %.(377, 449, 450) On the other hand, the cycle energy efficiency of VRFBs is usually 60-75 %.(302, 377, 383, 449-454) The best cycle electric energy efficiency for ≥ 1 kW VRFB systems at 0.1 A/cm^2 is no better than 80%.(263) Three factors should be considered in order to understand the inferior voltaic efficiency of VRFBs:

- a) VRFBs use better conducting acidic aqueous redox fluids with ca. 30-50 S/m ionic conductivity,(455) than LIBs electrolytes, which employ LiPF_6 solutions in alkyl carbonate with ca. 0.25 S/m conductivity.(456) This factor, however, is insufficient in practice to overcome the other two, which favor LIBs;
- b) Lithium-ion batteries have a higher (3.20 V at 50% SoC for LiFePO_4 batteries)(457) open circuit voltage (OCV) than VRFBs (1.35 V at 50% SoC).(458, 459) However, this OCV ratio is only ca. 2.4 and it is of minor importance compared to the third factor;
- c) While LIBs in SES applications operate at low current densities (ca. 1 mA/cm^2),(460) there is a need to operate VRFBs at higher current densities ($150\text{-}500 \text{ mA/cm}^2$) (461) in order to lower the capital cost of power (i.e. the size of the power stack) and to reduce the impact of self-discharge due to the cross-over of charged species through the membrane (see Fig. 11). For the sake of complete disclosure, we shall note the A123's LiFePO_4 batteries can be discharged (but not charged) at 40 mA/cm^2 ,(462) which makes them particularly useful for application with < 1 h discharge durations.

The overall effect is that, despite their significantly lower area-specific resistance, VRFBs are inferior to LIBs in terms of their energy efficiency. And, *in general, redox flow batteries have a lower roundtrip energy efficiency than SEAM batteries*, simply because RFBs have to operate at higher current densities in order to reduce their cost of power and the impact of the cross-over through the membrane.

In addition to the three aforementioned sources of voltaic losses, flow batteries experience several types of faradaic inefficiencies, such as

- d) H_2 evolution on VRFB negodes during charge;(463)
- e) H_2 evolution in VRFB negolyte during standing;(463)
- f) CO_2 and/or O_2 evolution on VRFB posodes during charge;(463)
- g) oxidation of V^{2+} by O_2 from inadvertent air contamination.(464)

The faradaic inefficiencies (d)-(f) appear to the battery operator as a continuous loss of the available Ah capacity with cycling.(465) Since the predominant effect in the (d)-(f) list is the H_2 evolution, the the negolyte capacity looks limiting. The lost charge can be restored via *rebalancing*, such as chemical reduction of the excess V(+5) by oxalic acid(466) or (a less practically useful way) by the H_2 produced on the negode in (d).

h) Crossover of the solvent and the solutes through the membrane between the negolyte and the posolyte. The crossover of the solutes is ever-present because of the chemical potential differences for the solutes in the negolyte and the posolyte, and because the membrane lacks sufficient selectivity.(464) The solvent crossover can be caused by such trivial and unavoidable factors as temporary local pressure changes between the posolyte and the negolyte in one or more cells in a stack due to variations in viscosity or flow rate between the two fluids. The cross-over (h) is evidenced, for example, by the increase in the total concentration of vanadium species in (and of the volume of) the posolyte.(465) The cross-over problem(s) are remediated, for example, by an occasional transfer of the excess posolyte volume to the negolyte tank at the end of a discharge step.(465) Such operations are usually referred to as *remixing*.

In regard to VRFBs vs LIBs selection there is a general agreement on these questions:

- 1) when the cost of the input electric power is high, LIBs have an economic advantage over VRFBs due to their superior energy efficiency.(375, 383, 467, 468)

- 2) VRFBs have a higher recycling value,(383) lower recycling cost,(383) and a lower environmental impact than LIBs;(469)
- 3) the SES market share of LIBs in 2022 is ca. 50-100 of times larger than that of VRFBs regardless of whether energy or power metrics is used;(375, 470)
- 4) LIBs' current prices benefit from the economy of scale in the portable electronics and electric vehicles markets, which combined were ca. 300 times larger than the LIBs for SES sales in 2017;(375, 471)
- 5) LIBs experienced price per kWh reduction at the rate of -18%/year until ca. 2006 and at -5% thereafter,(472) whereas VRFBs have not experienced the economy-of-scale advantage;(381, 454, 473-475)
- 6) to the best of our knowledge, the World's largest operating LIB installation in July 2022 was Tesla's 182.5 MW / 730 MWh system in California,(476) whereas the largest VRFB (Dalian Rongke in PR China) was only a little smaller 100 MW / 400 MWh;(473, 477)
- 7) in the last 10 years the price of vanadium minerals has experienced a greater volatility than the price of lithium minerals;(454, 466, 475)
- 8) operational lifetime of VRFBs is longer than that of LIBs.(478)

At the same time a discord remains on the following questions:

- 9) which electrode reaction limits the power of VRFB: negode $V(+3)/(+2)$ or posode $V(+5)/V(+4)$,(326) how solution-phase equilibria (479) affect the electrode reactions, what is the role of adsorbed $V(II)$ species in blocking the electroreduction of solution-phase V^{3+} and in catalyzing the H_2 evolution,(480) and how the electrode kinetics changes with time;(326, 481, 482)
- 10) to what extent the aforementioned LIB's cost reduction was due to research and development (i.e. new materials and manufacturing methods) and due to the economy of scale;(472, 483)
- 11) how much further and at what rate the manufacturing cost of both technologies can go down due to innovations and due to the economy of scale; (375, 484)
- 12) which technology would be more expensive at the highest possible production levels, when the bottom-out cost is determined by the cost of materials; (473, 474, 484)
- 13) whether the longer useful life of VRFBs translates into their cost advantage over LIBs in some temporal-value-of-money metrics, such as Net Present Value or Total Cost of Ownership; (375, 381, 485)
- 14) whether the contemporary dominance of LIBs over VRFBs in the SES markets is due to an intrinsic techno-economic superiority of the former or due to a spill-over effect from the presently larger LIBs markets for portable electronics and electric vehicles;
- 15) which of the technologies is better suited for the following market niches: energy arbitrage, secondary response, tertiary response, peaker replacement, black start, congestion management, bill management, power reliability, deferral of the investments into transmission and distribution;(375)
- 16) whether repurposing of used automotive LIBs for SES markets has any economic or societal advantages over straightforward recycling of LIBs components;(348, 486, 487)
- 17) whether LIBs(488) and/or VRFBs(489) are suitable for operation below $0^\circ C$.
- 18) to what extent leasing (rather than buying) expensive vanadium solutions can alleviate the burden of a high-capital cost of energy for VRFB users.(466)

In the enumerated comparison list above, we deliberately emphasized energy efficiency, since *inefficient energy storage can undermine the whole idea of transition to renewable energy - based society*. As explained in Fig.11 above, Vanadium Redox Flow Batteries (and flow batteries in general) have a lower cycle energy efficiency than Lithium-Ion Batteries (or batteries with solid electroactive materials in general) due to the necessity to compromise the TRIZ (490) contradiction between the energy efficiency and the cost of power: operating flow batteries at high (e.g. $> 0.5 \text{ A/cm}^2$) current densities results in a poor voltaic efficiency (e.g. $< 75\%$ one-way), while operating at low current densities (e.g. $< 10 \text{ mA/cm}^2$) results in a poor faradaic (charge) efficiency, due the reagents' cross-over through membrane (in addition to the high capital cost of power).

6. What is ahead for RFBs?

As shown in the foregoing analysis, all-vanadium redox flow batteries emerged as unambiguous winners among RFBs in the race for the stationary energy storage markets. This is due to a fortuitous compromise between the aqueous solubility of their redox species, as well as between the thermodynamics and kinetics of their half-cell electrode reactions.

In addition to the aforementioned all-vanadium, zinc-halogen, zinc-cerium,(158, 491-500) and chromium-iron RFBs, several other combinations of inorganic redox couples have been seriously considered for use in redox flow batteries: polysulfide-polybromide,(501-508) polysulfide-polyiodide,(509-514) hydrogen-bromine,(3, 10-13, 515-533) zinc-iron,(534) titanium-manganese (535-539) and some other low cost combinations of metal-ion couples,(201, 540-542) but did not demonstrate substantial advantages over all-vanadium chemistry for the stationary energy storage markets, mostly because of problems with corrosion and with side reactions.

Among organic couples, ambipolar vinazene was considered as the most promising,(543) but the commercialization of this RFB chemistry was abandoned after the end of a Phase 2 ARPAE grant by a Michigan-based startup around 2015.(544) Durability is a common drawback of all known organic redox couples.

The inferior energy efficiency of vanadium (and of other) flow batteries is considered as the main argument against large-scale adoption of this technology for stationary energy storage, despite the superior cycle and calendar lives of VRFBs and the lower cost of their manufacturing compared to lithium-ion batteries.(468) *The most important finding of our study is the explanation, how porous electrodes made of carbon fibers with 0.1 - 2 μm diameter and broad pore size distribution can improve both the voltage energy efficiency and area-specific power while maintaining a tolerable the pressure drop in the porous electrodes.* We shall note, that despite the fact that there are ca. 40 (545) companies manufacturing VRFBs in late 2022, electrodes with submicron diameter fibers “remain at low Technology Readiness Level and have not been commercially applied”.(272)

One limitation of this work is a complete neglect of the finite electronic conductivity of the electrode fibers. Such effects are known to produce a current distribution with a minimum inside a porous electrode,(300, 546) and most of our conclusions will not be applicable to such cases. Fortunately, carbon nanofibers can usually be prepared (at carbonization temperature $\geq 900\text{ }^{\circ}\text{C}$) with a fairly large electronic conductivity, e.g. in the range from 650 to 900 S m^{-1} ,(277, 315) which is ca. ten times larger than the peak conductivity of aqueous sulfuric acid (77.2 S/m at 29.5%w and 21°C), thus making our conclusions relevant to many commercial systems. Another limitation is the neglect of anisotropy in the electrode properties. It has been demonstrated, that aligning electrode fibers in the redox-fluid flow direction can lower the pressure drop in the porous electrode without sacrifice in their area-specific power.(547) We also mentioned, that a broad porosity distribution in RFB electrode may resolve the TRIZ contradiction between the drop in the electrode’s area-specific electric resistance and the rise in its hydrodynamic resistance upon decreasing the fiber diameter, but this is a proper subject for a separate study.

We believe, that the recent race for the highest (over. 1 W/cm^2 have been demonstrated) (225, 259, 308) peak area-specific power (i.e. at 50% discharge energy efficiency, under low single-pass reagent utilization and in $\leq 1\text{ cm}^2$ cells) in RFBs pursues misguided priorities. While such peak ASP may be useful for tracking the progress of the cell design, what is really needed for the SES applications *today* is to *decrease the cost of stack per area*, while operating near the optimal energy efficiency. We shall note here, that the due to reagent cross-over, the optimal *energy* efficiency (i.e. the product of voltaic and faradaic efficiencies) of RFBs does not occur at the lowest current density (as it is for SEAM batteries), as shown in Fig. 11.

We must remember, that, in general, despite their longer cycle and calendar lives, flow batteries have a lower cycle energy efficiency than batteries with solid electroactive materials (SEAM), because there is a cross-over (i.e. internal short-circuiting) current (typically, 1-10 mA/cm^2) and because RFBs run at ca. 100 times higher current density to minimize the effect of the cross-over and to reduce the capital cost of power.

Therefore, the main RFB advantages (lower capital cost of energy in multi-hour cycles *and* longer life) *must be carefully weighed against their inferior energy efficiency*. Surprisingly, the main factor in deciding whether to use a flow battery (e.g. VRFB) or a SEAM battery (e.g. LiB) may be not in the properties of the storage systems, but in the cost of the input energy itself: the lower the cost of the input energy, the more likely VRFB can be optimal in such application with a frequent (e.g. daily) cycling.

For VRFBs (and related durable metal-ion RFBs) in the SES market the most urgent need is to decrease the stack cost per area without sacrificing materials durability. This calls for developing lower-cost materials and manufacturing methods for membrane, porous electrodes and bipolar plates. Note, that because in the contemporary RFB design ionic resistance of the electrodes is larger than that of membrane, developing better-conducting membranes is less important, than developing lower-cost (yet durable) membranes. The use of electrodes with submicron diameter carbon fibers can have a significant impact on RFB performance, if such electrodes can be manufactured at a lower cost. It is worth noting, that in the absence of reliable accelerated durability tests, RFB manufacturers (as well as end-users and their financiers) must take the risk of deploying systems with unknown life expectancy and failure modes.

Another well-suited market for redox-flow batteries is reserve (emergency) power. Due to infrequent charge-discharge cycles, the energy efficiency is less critical in this application, than long (> 24 h) half cycle time, zero self-discharge, safety and resilience (e.g. resistance to earthquakes and hurricanes). In the reserve power and off-grid markets RFBs will be replacing diesel generators, which are costly, inefficient and unreliable. This market has some high profit margin niches, and it is an early adopter of RFB technology (see Lockheed-Martin, Raytheon and Ameresco stories above). Finally, off-grid (e.g. island) markets is another promising niche for VRFBs,(548) especially in combination with solar panels and wind turbines.

Going back to Fig. 12, we want to note, that for most grid-connected homes and grid-levelling applications with daily cycling and a *half-cycle duration less than ca. 2 h* lithium-ion (rather than less durable lead-acid) batteries *appear* to be a more appropriate solution than VRFBs, especially if these LIBs can be repurposed for second life after their use in cars.(440, 549, 550)

7. Further reading.

The main purpose of this work is to provide an overview of the flow battery history from the contemporary perspective and to identify the most promising research and commercialization directions. Because of this focus, we omitted many entertaining stories of successes, of failures and of dead-end explorations, which are important for planning the future works. To compensate for this deficiency, we refer the reader to several most informative works, that cover some of the neglected aspects:

- 1989 Development of redox flow batteries-a historical bibliography.(551)
- 2002 A Historical Preview of the Vanadium Redox Flow Battery Development at School of Chemical Engineering and Industrial Chemistry.(552)
- 2006 Redox flow cells for energy conversion.(553)
- 2011 Redox flow batteries: a review.(554)
- 2012 Development of the all-vanadium redox flow battery for energy storage: a review of technological, financial and policy aspects.(555)
- 2012 Liquid Redox Rechargeable Batteries.(556)
- 2013 Redox flow batteries for medium-to large-scale energy storage.(557)
- 2013 Review of material research and development for vanadium redox flow battery applications.(558)
- 2013 Vanadium Flow Battery for Energy Storage: Prospects and Challenges.(559)
- 2014 Hydrogen-halogen electrochemical cells: A review of applications and technologies.(3)
- 2014 Redox flow batteries for the storage of renewable energy: A review.(560)
- 2014 Practical thermodynamic quantities for aqueous vanadium- and iron-based flow batteries.(561)
- 2015 Vanadium redox flow batteries (VRBs) for medium- and large-scale energy storage.(562)
- 2015 A technology review of electrodes and reaction mechanisms in vanadium redox flow batteries.(563)
- 2015 The Chemistry of Redox-Flow Batteries.(564)

- 2015 The Development of Zn-Ce Hybrid Redox Flow Batteries for Energy Storage and Their Continuing Challenges.(159)
- 2015 Next-Generation, High-Energy-Density Redox Flow Batteries.(565)
- 2015 Recent Developments and Trends in Redox Flow Batteries.(566)
- 2017 Flow batteries: Vanadium and beyond.(567)
- 2017 Kinetics of Fast Redox Systems for Energy Storage.(568)
- 2018 Rechargeable redox flow batteries: flow fields, stacks and design considerations.(14)
- 2018 Progress and prospects of next-generation redox flow batteries.(569)
- 2019 Redox flow batteries for energy storage: their promise, achievements and challenges.(570)
- 2019 Engineering porous electrodes for next-generation redox flow batteries: recent progress and opportunities.(571)
- 2019 The development and demonstration status of practical flow battery systems.(572)
- 2019 Progress and perspectives of flow battery technologies.(573)
- 2021 Redox flow batteries: Status and perspective towards sustainable stationary energy storage.(574)
- 2021 Redox flow batteries: role in modern electric power industry and comparative characteristics of the main types.(575)
- 2022 Technical benchmarking and challenges of kilowatt scale vanadium redox flow battery.(342)
- 2022 Emerging chemistries and molecular designs for flow batteries.(576)
- 2022 Techno-economic analyses of several redox flow batteries using levelized cost of energy storage.(358)
- 2022 Progress and Perspectives of Flow Battery Technologies.(577)
- 2022 Chemical redox of lithium-ion solid electroactive material in a packed bed flow reactor.(578)
- 2022 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.(579)
- 2022 Halogen Hybrid Flow Batteries Advances for Stationary Chemical Power Sources Technologies.(580)
- 2022 A review of bipolar plate materials and flow field designs in the all-vanadium redox flow battery.(581)

Data availability: The data generated during this study are available from the corresponding author upon a reasonable request.

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Appendix A. Relationships between structural micro- and macro- parameters of a porous electrode.

Although the Daniel'-Bek-Newman-Tobias (294, 300) (DNT) electric model of the porous electrode uses only one distance-like parameter a (m^{-1}), which is the ratio of the inner surface area to the volume of the porous media, the Kozeny-Carman (and related) hydrodynamic model(s) of a porous medium use a different distance-like parameter d (m) (the fiber diameter). (583) In order to have a model, that can optimize both electric and hydrodynamic properties of a porous electrode, we need to find the relationship between a , d and h , which is the interfiber distance in a porous electrode.

The functions $a(d, \varepsilon)$ and $a(h, \varepsilon)$ (where ε is porosity) depend on the specific geometry of the porous media. For the sake of simplicity, we will model the porous electrode as a square or hexagonal grid of circular fibers oriented parallel to the membrane, as shown in Table A-1.

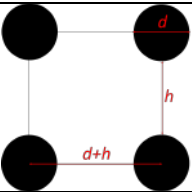
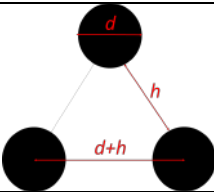
Apparently, this model is not applicable to real 3D electrodes with quasi-randomly oriented fibers, because it predicts zero permeability for porosities $\leq 1-\pi/4 \approx 0.214$ (for the square lattice), but since

(a) such lower porosity values are outside the range of the practical RFB electrodes with liquid-phase reagents, and

(b) the models, that we use below to estimate the permeability (pressure loss), show good agreement with experiment only for porosities in the range $[0.4 ; 0.95]$, (584)

this model suffices for our goal of relating micro- and macroscopic structural parameters of the porous electrode.

Table A1. Relationship between micro- and macro- structural parameters for 2D square and hexagonal lattices of circles. †

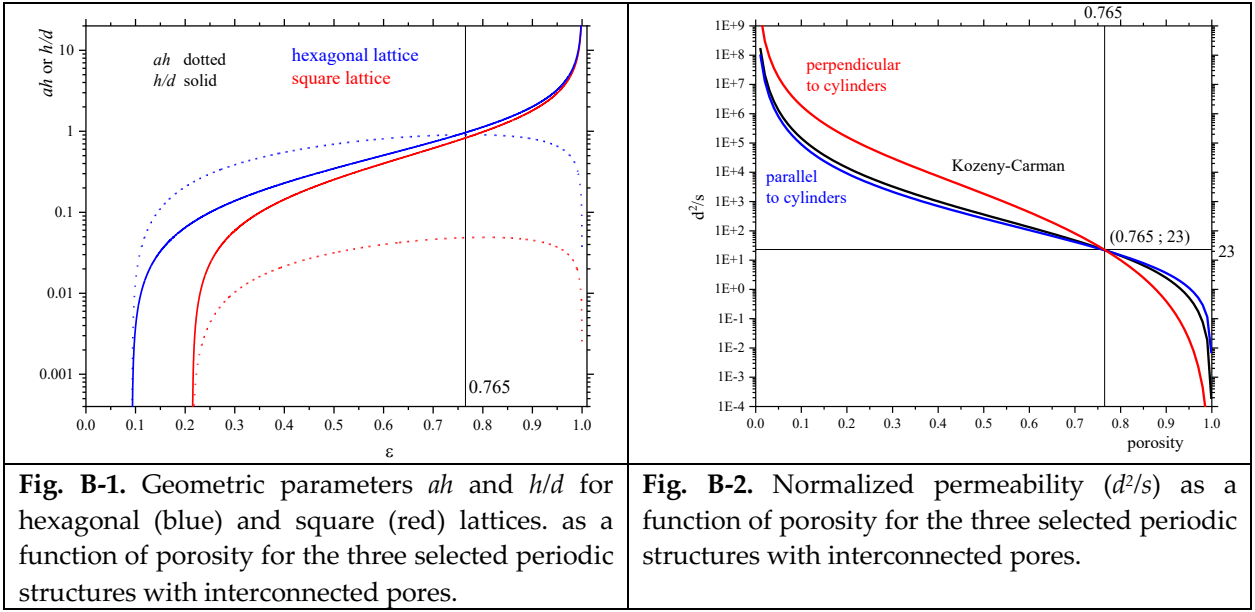
Parameter	Square lattice D_4	Hexagonal lattice D_6	row number
lattice structure			(A1-1)
total cell area, m^2	$(h+d)^2$	$(\sqrt{3}/4) (h+d)^2$	(A1-2)
filled cell area, m^2	$0.25 \pi d^2$	$0.125 \pi d^2$	(A1-3)
empty cell area, m^2	$(h+d)^2 - 0.25 \pi d^2$	$(\sqrt{3}/4) (h+d)^2 - 0.125 \pi d^2$	(A1-4)
porosity: (A1-4) over (A1-2)	$\varepsilon = 1 - \frac{\pi d^2}{4(h+d)^2}$	$\varepsilon = 1 - \frac{\pi d^2}{2\sqrt{3}(h+d)^2}$	(A1-5)
porosity vs a	$\varepsilon = 1 - ad$	$\varepsilon = 1 - 2ad$	(A1-6)
perimeter in one cell, m	πd	$0.5 \pi d$	(A1-7)
filled cross-area per cell, m^2	$S_f = \pi d^2$	$S_f = 0.5 \pi d^2$	(A1-8)
a , m^{-1} : (A1-6) over (A1-2)	$a = \frac{\pi d}{(h+d)^2}$	$a = \frac{2\pi d}{\sqrt{3}(h+d)^2}$	(A1-9)
(A1-8) and (A1-5): $(h+d)^2 =$	$(h+d)^2 = \frac{0.25\pi d^2}{1-\varepsilon} = \frac{\pi d}{a}$	$(h+d)^2 = \frac{1}{2\sqrt{3}} \frac{\pi d^2}{1-\varepsilon} = \frac{2\pi d}{a\sqrt{3}}$	(A1-10)
from (A1-9)	$ad = 0.25 (1 - \varepsilon)$	$ad = (4/\sqrt{3}) (1 - \varepsilon)$	(A1-11)
also from (A1-9)	$h/d = 0.5 \sqrt{\frac{\pi}{1-\varepsilon}} - 1$		(A1-12)
min porosity	$\varepsilon_{min} = 1 - \pi/4 \approx 0.215$	$\varepsilon_{min} = 1 - \pi/(2\sqrt{3}) \approx 0.0931$	(A1-13)
perimeter to area ratio via ε , m^{-1}	$a = (1 - \varepsilon) d^{-1}$	$a = 0.5(1 - \varepsilon) d^{-1}$	(A1-14)
fiber diameter, m	$d = (1 - \varepsilon) a^{-1}$	$d = 0.5(1 - \varepsilon) a^{-1}$	(A1-15)
perimeter to area ratio via h , m^{-1} (A1-6) / (A1-2)	$a = \pi d / (h+d)^2$	$a = (2\pi/\sqrt{3}) d / (h+d)^2$	(A1-16)
combining (A1-13) and (A1-15)	$(1 - \varepsilon) d^{-1} = \pi d / (h+d)^2$	$0.5(1 - \varepsilon) d^{-1} = (2\pi/\sqrt{3}) d / (h+d)^2$	(A1-17)
interfiber distance, m	$h = d \left(2 \sqrt{\frac{\pi}{1-\varepsilon}} - 1 \right)$	$h = d \left(2 \sqrt{\frac{\pi}{\sqrt{3}(1-\varepsilon)}} - 1 \right)$	(A1-18)
lattice period, m	$h+d = d \sqrt{\frac{\pi}{1-\varepsilon}}$	$h+d = d \sqrt{\frac{4\pi}{\sqrt{3}(1-\varepsilon)}}$	(A1-19)
dimensionless product ah	$ah = \frac{1-\varepsilon}{4} \left(\frac{1}{2} \sqrt{\frac{\pi}{(1-\varepsilon)}} - 1 \right)$	$ah = (1-\varepsilon) \left(\sqrt{\frac{\pi\sqrt{3}}{(1-\varepsilon)}} - 1 \right)$	(A1-20)

† We use two-dimensional terms in Table A1 rather than 3D to avoid confusion with the presented figures. The letter symbols, however, correspond to the 3D model according to the List of Notations and Abbreviations. For other formulas – see Ref. (585)

Appendix B. Relationships between permeability and porosity for selected structures.

Analytical expressions relating permeability s to the structural parameters (e.g. the fiber diameter d and the porosity ε) of the porous media are available for numerous geometries.(586, 587) Fig. B-1 (right) shows the relationships between the geometric parameters ah and h/d for hexagonal (blue) and square (red) lattices, based on the formulas in Appendix A. Fig. B-2 (left) shows the relationships between the normalized permeability d^2/s and porosity for semi-heuristic Kozeny-Carman (eq. B-1) model (black), (586, 588, 589) for a regular array of cylindrical fibers aligned parallel to the flow (blue) and perpendicular to the flow (red), based on the analytical expressions in formulas (2.20) , (2.29) and (2.33) in Ref. (586)

$$\frac{d^2}{s} = \frac{\varepsilon^3}{180(1-\varepsilon)^2} = KC(\varepsilon) \quad (B-1).$$



Thus, we have now a relationship between porosity ε , inner area to volume ratio a and interfiber distance (effective pore diameter) h . Eq. (A1-20) suggest, that decreasing the lattice constant h would be effective in increasing a and thus, the area-specific power. Although this is correct, there are practical limits on the minimum value of h related to the hydrodynamic resistance (i.e. pressure drop) in such electrodes. This is discussed in Appendix C.

The important conclusion from this analysis is that the three different models in Fig. B-2 predict a qualitatively similar d^2/s versus porosity behavior, and agree quantitatively at the point, where $\varepsilon = 0.765$ and $d^2/s = 23$. Incidentally or not, the porosity value of 0.765 falls within the typical range of *optimal* porosities in compressed carbon/graphite felts and of electrospun carbon nanofibers, that have been the most widely investigated type of RFB electrode materials since ca. 2017.(290, 304, 590-595) Thus, we can fix $\varepsilon = 0.765$ and $d^2/s = 23$ in our subsequent analysis.

Appendix C. Ohmic losses in a porous electrode.

In Appendix B we discussed *structured* models of a porous medium, characterized by its porosity ε and inner surface area-to-volume ratio a , in regard to its *hydrodynamic permeability*. Here we will use a similar approach to describe the *electric resistivity* of a porous electrode. This model was originally proposed by Daniel'-Bek in 1948,(294) developed in the modern form by Newman and Tobias in 1962,(300) and reviewed recently by Fuller and Harb.(546) A series of profiles of dimensionless current density under a primary current distribution in a porous electrode with an infinitely large electronic conductivity is shown in Fig. C-1.

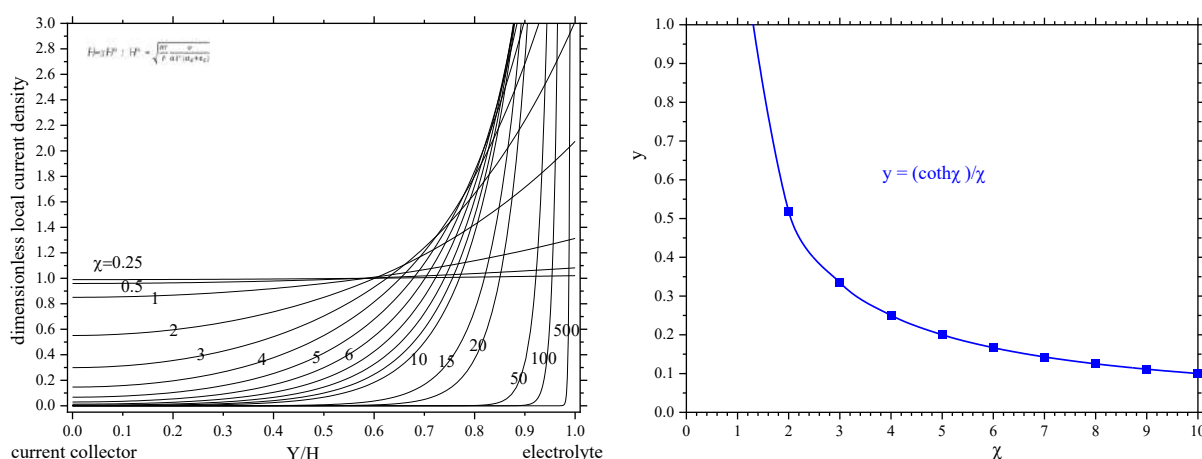


Fig. C-1. (right) Dimensionless local current density in a porous electrode with infinitely large electronic conductivity. See ref. (546) for the details of notations and derivation.

Fig. C-2. (left) The range of the dimensionless parameter $\coth \chi / \chi$.

By presenting this plot we want to show, that electrodes with a dimensional thickness

$$\chi = H/H^\circ > 2 \quad (\text{C-1}),$$

where

$$H^\circ = \sqrt{\frac{RT}{F a i^\circ (\alpha_a + \alpha_c)}} \quad (\text{C-2}),$$

are underutilized, since the electrode reaction takes place only in a thin layer of the porous electrode close to the bulk electrolyte. Therefore, such thick electrodes are wasteful: while the extra thickness does not generate more current it still contributes to ohmic losses. On the other hand, electrodes thinner than $1H^\circ$ do not generate a lot of current density per current collector, thus the cell's area-specific power is low. Fig. C-1 suggests, that

$$H = \chi H^\circ = 2 H^\circ \quad (\text{C-3}),$$

i.e. when the electrode is the thickest while still maintaining a reasonably uniform current distribution throughout, may be the optimal thickness. We shall proceed using the assumption $\chi=2$ ($0.5\coth 2=0.51866$, see Fig. C-2) Then, the area-specific resistance (ASR) of the porous electrode for $\kappa \gg \sigma$ is

$$R_{int} = (H^\circ / \sigma) \coth \chi / \chi \quad (\text{C-4}).$$

For $\kappa \gg \sigma$

$$R_{int} = \frac{H^2}{\sigma} \frac{\coth \chi}{\chi} = \frac{\coth \chi}{\chi} \sqrt{\frac{RT}{F a i^\circ (\alpha_a + \alpha_c)}} = \frac{\coth \chi}{\chi} \sqrt{\frac{RT d}{F a i^\circ (\alpha_a + \alpha_c) \beta (1-\varepsilon)}} \quad (\text{C-5}).$$

where we used $a = \frac{\beta(1-\varepsilon)}{d}$ from equation (A1-14). We shall note in passing, that H° is smaller for faster reactions (with larger i°), which means that for faster electrochemical reactions thinner electrodes can generate the same current density with a lower ohmic drop.

It also follows from (C-5), that R_{int} can be made smaller by decreasing fiber diameter d at constant porosity ε . However, the lower limit on the practically suitable d is determined by the resulting pressure drop in the porous electrode. This is discussed in Appendix D.

Appendix D. Pressure loss in the porous electrode.

The limit of the maximal acceptable pressure drop in an RFB stack is determined by the cost of high-pressure high-flow rate pumps and by the stack sealing requirements, long before it becomes affected by the energy losses due to pumping. In practice 1 bar (10^5 Pa) pressure drop in the porous electrodes is acceptable. (452, 474, 596, 597)

Let's find a relationship between current density per membrane area i , volumetric flow rate v and a single-pass reagent utilization φ in a flow battery cell with an interdigitated flow field, shown in Fig. D-1. The relationship between the cell total cell current I and volumetric flow velocity v is given by

$$I [A] = nF C_0 \varphi v \quad (D-6).$$

Then the required volumetric flow rate to sustain current I under single-pass utilization φ can be found from (D-7)

$$v = \frac{I}{nF C_0 \varphi} \dots \quad (D-7).$$

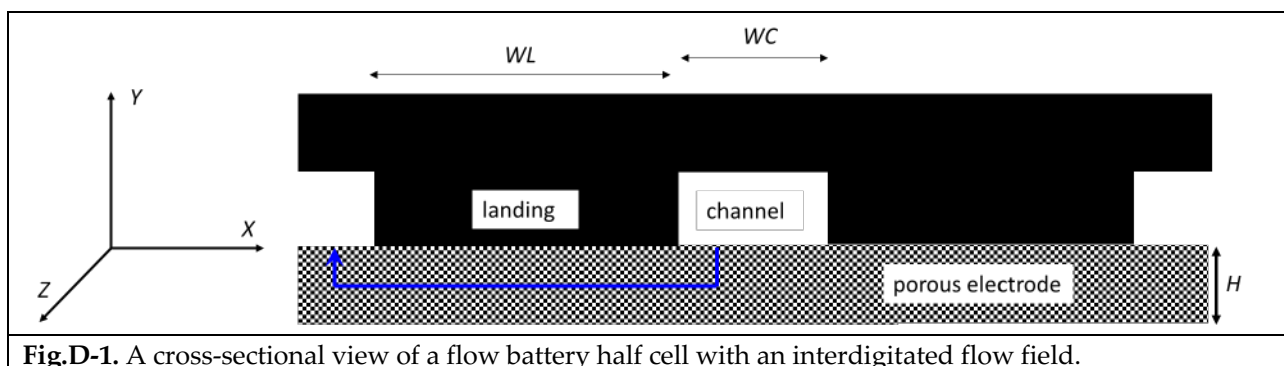


Fig.D-1. A cross-sectional view of a flow battery half cell with an interdigitated flow field.

We need to find a relationship between linear flow rate u , used to calculate the pressure in (D-12) below and volumetric flow rate v , determined by the required current in (D-7). The two values are connected via the cross-sectional area of the flow

$$u = v/(H W Z) \quad H W Z u = v \quad (D-8).$$

Plugging (D-7) into (D-8) yields

$$v = H W Z u = \frac{I}{nF C_0 \varphi} \quad (D-9).$$

$$u = \frac{I}{nF C_0 \varphi H W Z} \quad (D-10).$$

Since we assumed that the redox fluid's state of charge (SoC) changes between 0.75 and 0.25 in a single pass on discharge,

$$\Delta\phi = 0.75 - 0.25 = 0.5 \quad (D-11).$$

Now let's determine the energy loss associated with pumping a liquid (with dynamic viscosity η) through a porous electrode. For creeping (i.e. at low Reynolds numbers) flow with a volume-averaged linear velocity u through an isotropic porous media of length L , the pressure loss Δp is given by Darcy equation (4-7):

$$\frac{\Delta p}{L} = \frac{\eta u}{s} \dots \quad (D-12),$$

where the permeability s has a dimension of m^2 . (586) For the visualization purposes, it is instructive to look at the behavior of $1/s$, since this number is proportional to the pressure drop, as shown in eq. (D-12). Also, interesting is dimensionless normalized permeability, $\psi \equiv d^2/s$, which eliminates the dependence of permeability s on the fiber diameter d . As explained in Appendix B, we chose porosity $\varepsilon = 0.765$ and normalized permeability $\psi = 23$:

$$\frac{\Delta p}{L} = \psi \frac{\eta u}{d^2} \dots \quad (D-13)$$

Decreasing the fiber diameter results in an increased area-specific power of a battery simply due to an increase of electrode surface-to-volume ratio a for a fixed electrode layer thickness. For a fibrous porous electrode, assumed in our model, the contact resistances within the electrode can be neglected.

Then, from (D-12) and (D-13) we get

$$\Delta p = \frac{vu}{s} L = \psi \frac{vu}{d^2} L = \psi \frac{vL}{d^2} u \quad (D-14).$$

From the considerations of the reagent utilization in the electrode reaction, we can relate the electrode current I to reagent flow rate u :

$$u = \frac{I}{nF C_0 \phi H W Z} \quad (D-15).$$

Replacing u in (D-14) with (D-15) leads to

$$\Delta p = \psi \frac{vL}{d^2} u = \psi \frac{vL}{d^2} \frac{I}{nF C_0 \phi H W Z} \quad (D-16),$$

$$\text{and} \quad \Delta p = \psi \frac{vL}{d^2} u = \frac{\psi vL}{\chi d^2 nF C_0 \phi H^s W Z} \frac{I}{\chi} \quad (D-17).$$

Let's combine the terms, which are supposed to be the same on both side of the membrane in a cell, i.e. $\Delta p, I$ and C^0 . We shall note here, that such combination is an oversimplification of our 1D model. Even in a 2D model, the pressures cannot be same everywhere on both sides of the membrane.

$$\frac{\Delta p C_0}{I} = \frac{\psi vL}{\chi d^2 nF \phi H^s W Z} \frac{1}{\chi} = \frac{v}{nF} \frac{\psi}{\phi \chi} \frac{L}{d^2 H^s W Z} \quad (D-18).$$

Using the value of the electrode thickness from (C-3)

$$H = \chi H^0 = \chi \sqrt{\frac{RT}{F} \frac{\sigma}{a i^s (\alpha_a + \alpha_c)}} \quad (D-19),$$

and

$$a = \frac{\beta(1-\varepsilon)}{d} \quad (D-20)$$

from (A1-14) we arrive at

$$H = \chi H^0 = \chi \sqrt{\frac{RT}{F} \frac{\sigma d}{(\alpha_a + \alpha_c) \beta(1-\varepsilon) i^s}} [m] \quad (D-21).$$

Let's plug (D-21) into (D-18):

$$\frac{\Delta p C_0}{I} = \frac{v}{nF} \frac{\psi}{\phi \chi} \frac{L}{d^2 H^s W Z} \quad (D-22).$$

Then we arrive at

$$\frac{\Delta p C_0}{i L^2} = \frac{v \psi}{nF \phi \chi} \frac{1}{d^{2.5}} \sqrt{\frac{F (\alpha_a + \alpha_c) \beta(1-\varepsilon) i^s}{RT} \frac{L}{\sigma}} \quad (D-23).$$

The term $\Delta p C_0 / I$ in (D-23) combines parameters, that are *approximately* equal for the negode and posode, while the right-hand term in (D-23) contains the terms, which are different. This formula accounts for electrode thickness utilization by using $H = \chi H^0$ in (D-21).

Eq. (D-23) suggests, that the pressure rise due to decrease in the electrode fiber diameter can be compensated by making the landing width L smaller. However, once L gets smaller than the electrode thickness H , a non-uniform flow distribution in along the electrode thickness becomes a problem.

Appendix E. Patent searches.

Unlike journal articles, the content of patent documents is not subject to copyright, and thus there are no restrictions on accessibility and full - text mining of the latter. Questel-Orbit patent database (www.orbit.com) comprises 66 million patent families from 110 patent-issuing authorities, with 65 of the latter having searchable full-text high quality machine or human translations to English.

The biggest challenge, that we found with full text mining, was to filter out false positives, such as those, that mention the searched term incidentally, e.g. as a counter example. Since neither Questel-Orbit, nor any other patent database, known to us, can perform the required *user-controlled* relevancy search, we developed our own methodology, that allowed us to practically eliminate both false positives and false negatives. Below we illustrate a search for zinc-halogen batteries using FamPat subbase in Questel-Orbit. Similar search strategies were used for other flow batteries.

((zn OR zinc OR zink) S (I2 OR J2 OR +iodi+ OR +bromid+ OR +bromin+ OR Br OR Br2 OR chlorine OR Cl2 OR halogen OR polyhalid+) S (battery OR batteries OR cell OR cells OR accumulator OR accumulators OR pile OR piles OR liquid_stream OR liquid_flow OR redox_flow))/TI/ABS/DESX/CLMS/KEYW , where
TI/ABS/DESX Title, Abstract (for all patent families) and Examples (available only for US publications from 1976).

CLMS All claims from all jurisdictions and prosecution stages.

KEYW Concepts extracted from the full text of the patent publications using linguistic technology. They reflect the semantic content of the patent and are ranked by decreasing score.

The syntax operator, that we used to connect the related searched term was “S” , which means that the terms are in the same sentence. Neither CPC nor IPC codes were useful at this stage, because oftentimes they are incorrectly assigned by the receiving patent authorities, and such incorrect assignments are carried over to further prosecution stages. Also, the codes are often missing in the old patent families.

The full texts, abstracts and claims for all prosecution stages (original or machine-translated to English) of the selected patent families were exported into our patent database hosted on a PostgreSQL platform. There we calculated for each patent family how many times (NS) the searched string occurred in the exported text and the total count (NT) of all words in the exported text. The ratio of NS/NT was used to cut the relevant families from non-relevant. Typically, relevant families had SimpleRelevancyScore $NS/NT \geq 0.001$. In improved searches, actually used for this study, in calculating AdvancedRelevancyScore higher weights were given to the counts in Title, Abstract, Claims, Examples and Figure Captions. Patent Families with clearly erroneous Questel's Technology Domains (based on the IPC and CPC codes) were examined manually, and deleted, if needed.

Appendix F. Non-patent searches.

We performed non-patent searches using the following databases:

BASE	https://www.base-search.net/
EBSCO	https://www.ebsco.com/
CiNii	https://cir.nii.ac.jp/
CNKI	https://global.cnki.net/kns/brief/default_result.aspx
The Lens	lens.org
ProQuest	https://www.proquest.com/
science.gov	https://www.science.gov/
SciELO	https://scielo.org/ (also used as a part of Web of Science)
SciFinder	https://scifinder.cas.org/
SciLit	https://app.scilit.net/
Scopus	https://www.scopus.com/home.uri
Web of Science	https://access.clarivate.com/ (including Core, KJD and SciELO)

We would like to mention briefly, that no-cost BASE, The Lens and SciLit have substantial overlap in coverage with paid Scopus and Web of Science, and thus the former are recommended as potential replacements for the latter. No-cost CNKI, CiNii focus on Chinese and Japanese publications, respectively. They do not overlap much with either Scopus or Web of Science, and thus should be promoted by academic librarians as useful sources of unique scientific publications. EBSCO, ProQuest, science.gov and SciLit do not add much in terms of journal articles to Scopus or Web of Science, but they are good sources of “grey literature”, such as conferences, magazines, reports and theses. SciFinder stands out in terms of its superior coverage of scientific publications prior to ca. 1960, all the way back to 1800’s. Although we did not use chemical structure search, we shall note that this option is available in SciFinder, Scopus (Reaxys) and Questel-Orbit, but not in other databases.

We also considered the databases listed below, but decided against their use due to problems with precise searching or data exporting:

CORE	https://core.ac.uk/
Dimensions	dimensions.ai
Google Scholar	https://scholar.google.com/
Microsoft Academic	defunct as of 2022-01-01
Semantic Scholar	https://www.semanticscholar.org/

For flow battery searches, we used all available fields, and removed non-relevant references via a search-assisted inspection in EndNote. For non-RFB technologies (such as those shown in Figs.1 and App.I) our searches were less extensive than the aforementioned RFB searches. In order to focus only on highly-relevant publications, these searches were limited to document titles only. In Scopus’ our queries were:

for fuel cells: TITLE(fuel PRE/0 (cell OR cells)) OR TITLE(PEMFC OR PEMFCs OR PEFC OR PEFCs OR DMFC OR DMFCs OR AFC OR AFCs OR MCFC OR MCFCs OR SOFC OR SOFCs OR PAFC OR PAFCs) ;

for lithium-ion batteries: TITLE (lifepo4 OR li*mn*o* OR li*ni*o* OR li*co*o*) OR TITLE (lithium PRE/0 ion) OR TITLE (li PRE/0 ion)) AND TITLE (battery OR batteries OR accumulator OR accumulators) ;

for lead-acid batteries: TITLE(lead OR Pb) AND TITLE(acid) AND TITLE(battery OR batteries OR accumulator OR accumulators) ;

for zinc-manganese batteries: TITLE(zinc OR zn) AND TITLE (mangan* OR mn OR mn*o*) AND TITLE(battery OR batteries OR accumulator OR accumulators) ;

for zinc-silver batteries: TITLE(zinc OR Zn) AND TITLE(silver OR Ag OR Ag₂O OR AgO) AND TITLE(battery OR batteries OR accumulator OR accumulators).

Appendix H. Historic publications about zinc-halogen and related batteries.

Fig. H1 shows the number of patent families and journal articles about zinc-halogen batteries and about all types flow batteries vs priority or publication year, respectively, starting with year 1877.

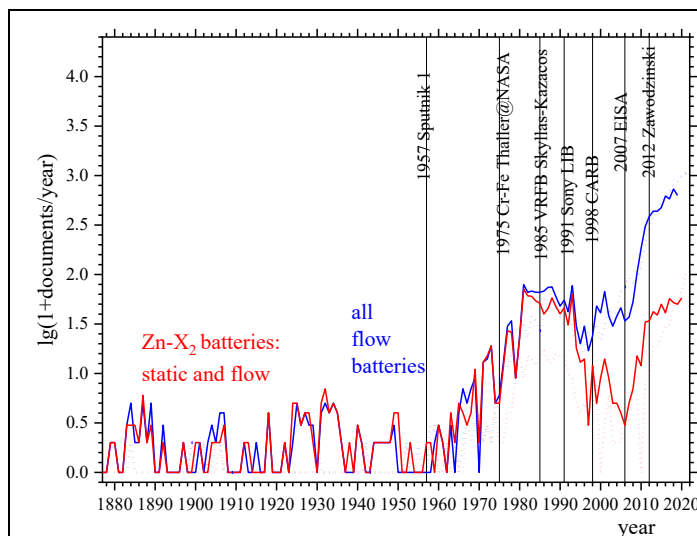


Fig. H1. The numbers of patent families vs priority year and of journal articles vs publication year for all flow batteries (blue lines), and for zinc-halogen batteries (red lines). In some years the red line lies above the blue line due to non-flow (static) zinc-halogen batteries. The vertical lines with years refer to events, that affected other electrochemical energy technologies.

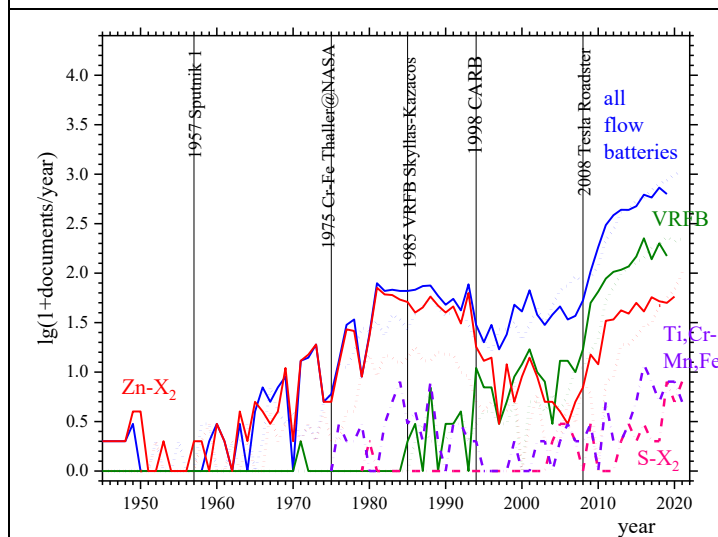


Fig. H2. The numbers of patent families (solid lines) vs priority year and of journal articles (dotted lines) vs publication year for all flow batteries (blue lines), VRFBs (green lines), zinc-halogen batteries (red lines), Ti,Cr-Mn,Fe flow batteries (violet line), polysulfide-halogen batteries (pink line). Dash-dotted lines are sums of patent families and journal articles.

The first thing, that we would like to notice in Fig.H1, is that zinc-bromine battery technology is very old. It seems, that the flow version of Zn-Br₂ battery (see Fig.1 in the main text) was demonstrated ca. 1879(70) before the non-flow versions. Static (i.e. non-flow) Zn-Br₂ batteries were patented nearly simultaneously by US, (71, 72, 74) British and German(598) inventors in the 1880's, as well as by later followers.(599-602)

For the sake of full disclosure, we shall mention, that at the turn of the last century there were also numerous reports of non-rechargeable batteries with Zn negode and liquid-phase oxidants, such as (bi)chromate,(603-605) ferric salts, (118, 606-608) Cl₂ gas,(609, 610) or HNO₃.(611) as well as of a small number batteries with all fluid electroactive materials, such as H₂-Fe³⁺.(612)

(This Invention received Provisional Protection only.)

PROVISIONAL SPECIFICATION left by Arthur Pillans Laurie at the Office of the Commissioners of Patents on the 28th June 1881.

ARTHUR PILLANS LAURIE, of Nairne Lodge, Duddingstone, Edinburgh, North Britain. "IMPROVEMENTS IN SECONDARY BATTERIES."

5 My Invention relating to improvements in secondary batteries has reference to the use for that purpose of a battery containing a single fluid, viz., a solution of iodide of zinc in water, the plates of the battery being zinc and carbon.

When a current is passed through the cell, zinc is deposited on the zinc plate, and iodine is set free at the carbon plate. The iodine is held in solution by the 10 iodide of zinc.

If the cell is now used to supply a current, the iodide of zinc attacks the zinc plate, the zinc set free at the carbon pole being dissolved by the free iodine.

Fig. H3. The front page of the oldest (1881) rechargeable Zn-I₂ flow battery patent. (613)

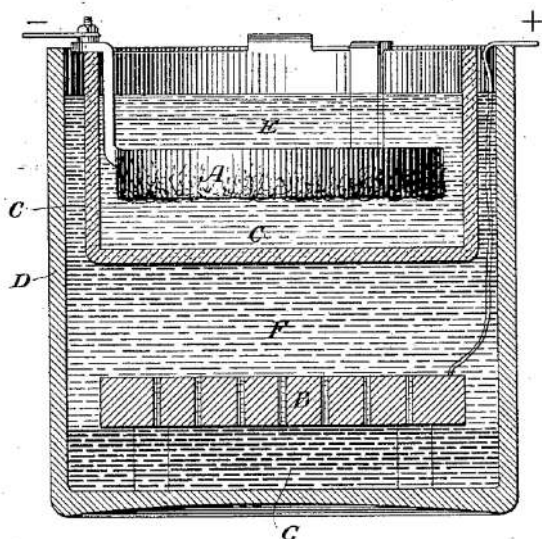


Fig. H4. A rechargeable *static* Zn-Br₂ battery from the 1884 Bradley's patent: A-negative Zn electrode, B-positive carbon plate electrode, C-porous dielectric cell/diaphragm, D-outer casing, E, F - ZnBr₂ solutions, G-a layer of liquid bromine.(71, 72)

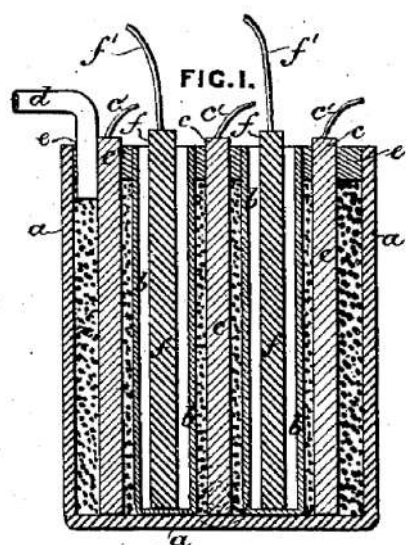


Fig. H5. A non-rechargeable *flow* Zn-Cl₂ battery from the 1884 patent by Upward and Pridham.(614)

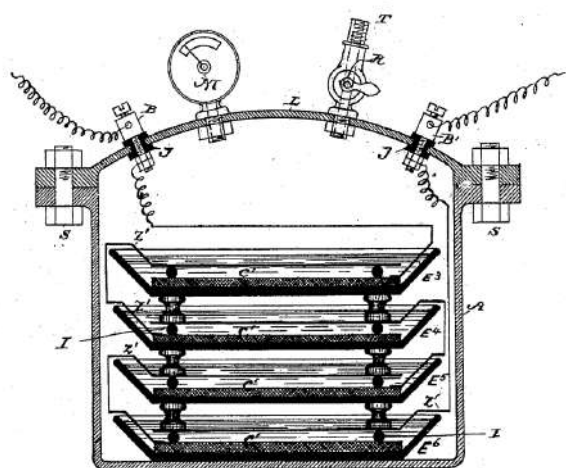


Fig. H6. A rechargeable *static* pressurized Zn-Cl₂ battery from the 1888 patent by Pieper.(615)

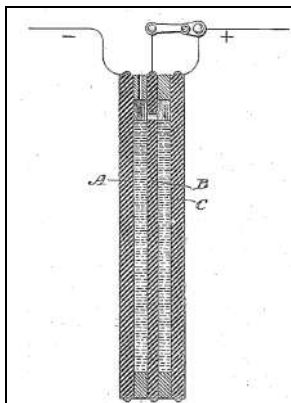


Fig. H7. A *rechargeable* static Zn-Br₂ battery from the 1889 patent by Bradley.(73) A similar design was proposed in 1901 by Lyons and Broadwell.(616)

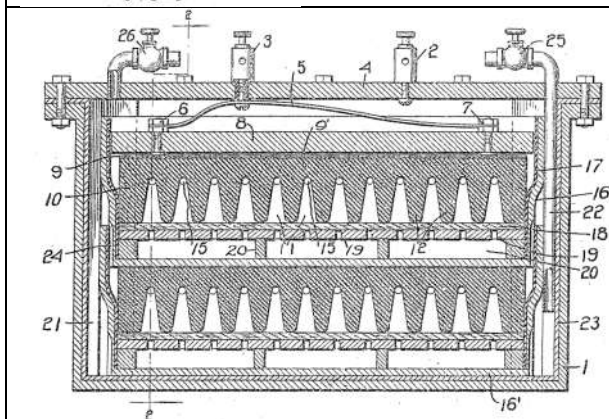


Fig. H8. A zinc-halogen *flow* battery from the 1912 patent by H.E.R.Little.(617)
10-carbon posodes,
11-groves for posolyte supply,
12-ridges of carbon posodes,
15-posolyte inlets,
18-asbestos diaphragm,
19-Zn negodes,
20-frame,
25-posolyte inlet valve,
26-posolyte outlet valve.

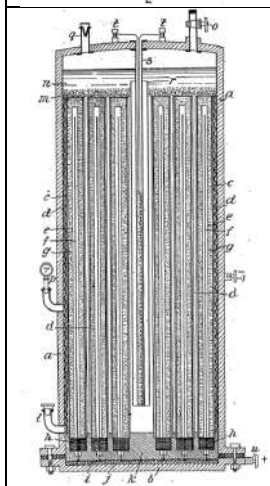


Fig. H9. A *rechargeable* non-flow pressurized Zn-Cl₂ battery from the 1917 patent by Guglielmo Marconi.(610, 618)

Appendix I. Patent-journal correlation for other batteries.

Fig. I1 shows the number of patent families (from Questel-Orbit) and journal articles (from Scopus) related to several electrochemical battery technologies. Although, the number of documents related to these battery types is smaller than the numbers in Fig.1, correlations between the patent and non-patent counts can be noticed visually.

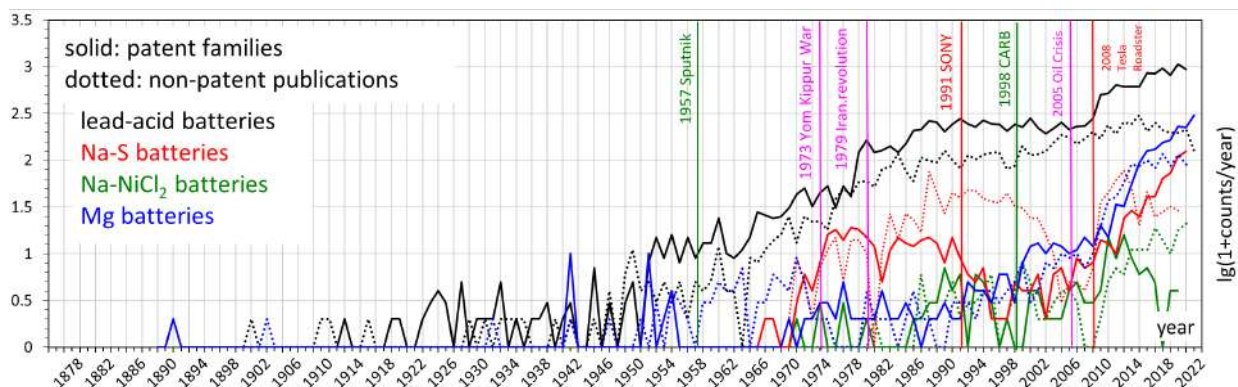


Fig. I1. The numbers of patent families (solid lines) vs priority year and of journal articles (dotted lines) vs publication year for lead-acid (black), sodium-sulfur (red), sodium-nickel chloride (green) and magnesium metal (primary and rechargeable) batteries.

The search methodology is explained in Apps E and F.

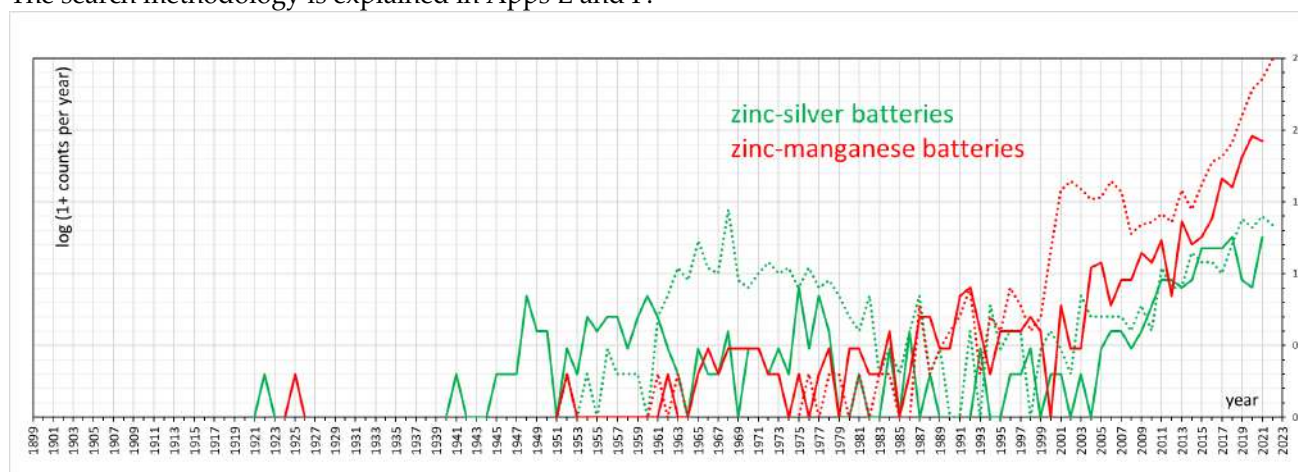


Fig. I1. The numbers of patent families (solid lines) vs priority year and of journal articles (dotted lines) vs publication year for zinc-manganese (red) and zinc-silver (green) batteries. The search methodology is explained in Apps E and G.

Appendix J. Crossover in flow batteries.

In electrochemical systems the flux of chemical species can be induced by gradients of pressure (hydrodynamic flow), concentration (diffusion or osmosis) or electric field (ion migration and electroosmotic drag).(619) Although osmosis(620) and pressure-induced flow(621) usually are the main mechanisms for solvent cross-over through the membrane,(622) these mechanisms are less important for ionic species. Instead, diffusion (at low current densities) and migration (at high current densities) are the main mechanisms for ion crossover in VRFBs.(623) The total (i.e. for all ions) migration current can be estimated from the membrane resistance (assumed as $0.6 \Omega/\text{cm}^2$ in Fig. 12).

The cross-over rate in the absence of an applied current (i.e. at the open circuit voltage of the cell) can be estimated from experimental data on ion permeabilities in Nafion. Permeability of Nafion 212 to VO^{2+} is reported in Ref.(344) as $4.69 \times 10^{-6} \text{ cm}^2/\text{min} = 7.82 \times 10^{-12} \text{ m}^2/\text{s}$. Taking $[\text{VO}^{2+}] = 2.5 \text{ M}$ (624) and Nafion 212 thickness as $51 \mu\text{m}$, we arrive to

$$i_x = 2 \times 7.82 \times 10^{-12} \text{ m}^2/\text{s} \times 9.648533 \text{ F/mol} \times 2.5 \text{ M} / 51 \mu\text{m} = 7.4 \text{ mA}/\text{cm}^2 \quad (\text{J-1}),$$

as an estimate for the VO^{2+} cross-over current density in a fully charged VRFB cell. The front factor “2” in (J-1) accounts for the flux of V^{2+} in the opposite direction. This value agrees well with $6 \text{ mA}/\text{cm}^2$ for Nafion 212 deduced from Fig. 11 in Ref. (339) and from Fig. 2A in Ref. (340), as well as with $4 \text{ mA}/\text{cm}^2$ reported in Ref. (341) It is worth noting here, that anion-exchange membranes assure a lower cross-over current for electroactive species in VRFBs,(625) e.g. $0.5 \text{ mA}/\text{cm}^2$ in Ref. (341) at 20°C .

Appendix K. Comparison of Scientific Bibliographic Databases.

In this section we compare the content of eight *scientific bibliographic databases* using the example of zinc-bromine battery. This technology has over 100-year history, yet it is not so popular as to run into export restrictions of SciFinder's user license. Since the purpose of this exercise is to compare the *content* (i.e. the covered documents) rather than the *search capabilities* of the databases, we searched only the primary (e.g. article) *titles*, rather than abstracts and keywords (in SciFinder abstracts and keywords cannot be searched separately, and keywords vary between different databases considerably). For the same reason, *stemming* was also turned off.

In Scopus' SQL our searches were as follows:

TITLE(zinc OR Zn) AND TITLE(bromine OR Br₂ OR Br OR polybromide) AND TITLE(battery OR batteries OR accumulator OR accumulators OR pile OR piles)

We intentionally excluded the word "cell" as a synonym for "battery", because such searches resulted in numerous irrelevant hits about biological cells. We shall also note, that, although the aforementioned "AND" searches did produce some false positive results (i.e. unrelated to electrochemical power sources), their number did not exceed 5%. In order to maintain a consistency of this *database content* comparison, such false positives were retained in this particular exercise.

The following eight databases were examined in this study:

EBSCO	https://www.ebsco.com/
CiNii	https://cir.nii.ac.jp/
CNKI	https://global.cnki.net/kns/brief/default_result.aspx
The Lens	lens.org
SciFinder	https://scifinder.cas.org/
science.gov	https://www.science.gov/
SciLit	https://app.scilit.net/
Scopus	https://www.scopus.com/home.uri
Web of Science	https://access.clarivate.com/ (including Core, KJD, SciELO and DCI))

In this and the following list, the names in **bold** font refer to free (as in *no-cost*) databases.

We also considered the nine *no-cost* (and subscription-access ProQuest) databases listed below, but decided against their use in the comparison exercise due to problems with precise searching or with data exporting:

BASE	https://www.base-search.net/ (limits: 1000 per search, 100 per export)
CiteSeerX	https://citeseerx.ist.psu.edu/
CORE	https://core.ac.uk/
Dimensions	dimensions.ai
Google Scholar	https://scholar.google.com/
Microsoft Academic	defunct as of 2022-01-01
NTRL	https://ntrl.ntis.gov/NTRL/ (most of its content is available through lens.org)
Our Research	https://gettheresearch.org/
ProQuest	https://www.proquest.com/
Semantic Scholar	https://www.semanticscholar.org/

We do not want to discourage other researchers from exploring these nine databases in the future, as their capabilities continue to improve.

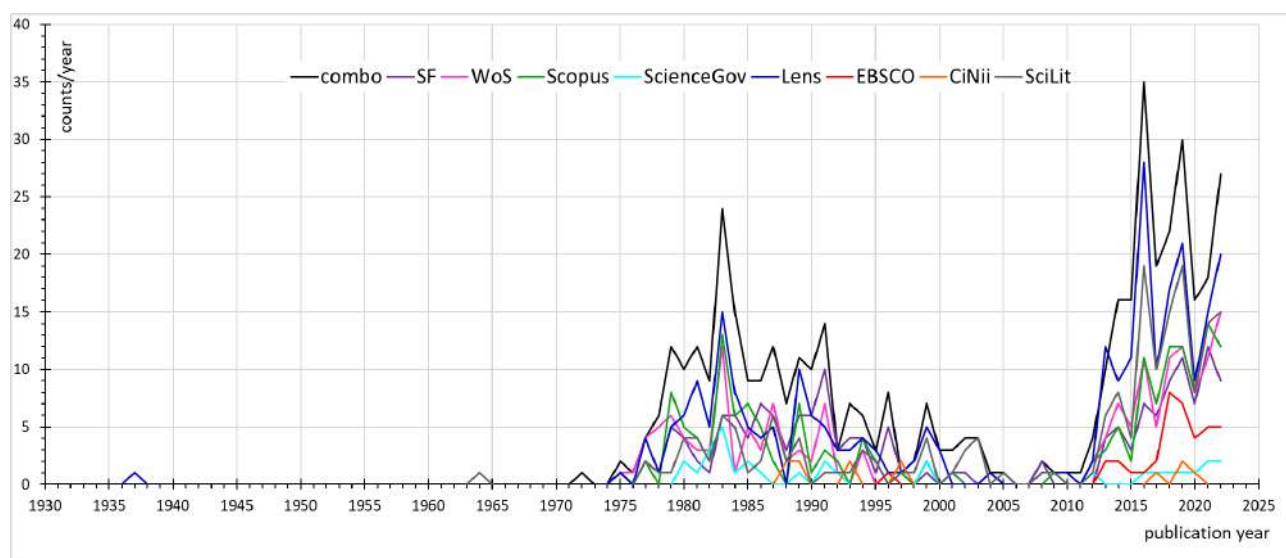


Fig. K1. The numbers of journal articles, referring to zinc-bromine batteries in their *titles*, va the publication year. The colored lines show the data from the eight databases as indicated in the inset. The black line refers to the combined result with duplicates removed.

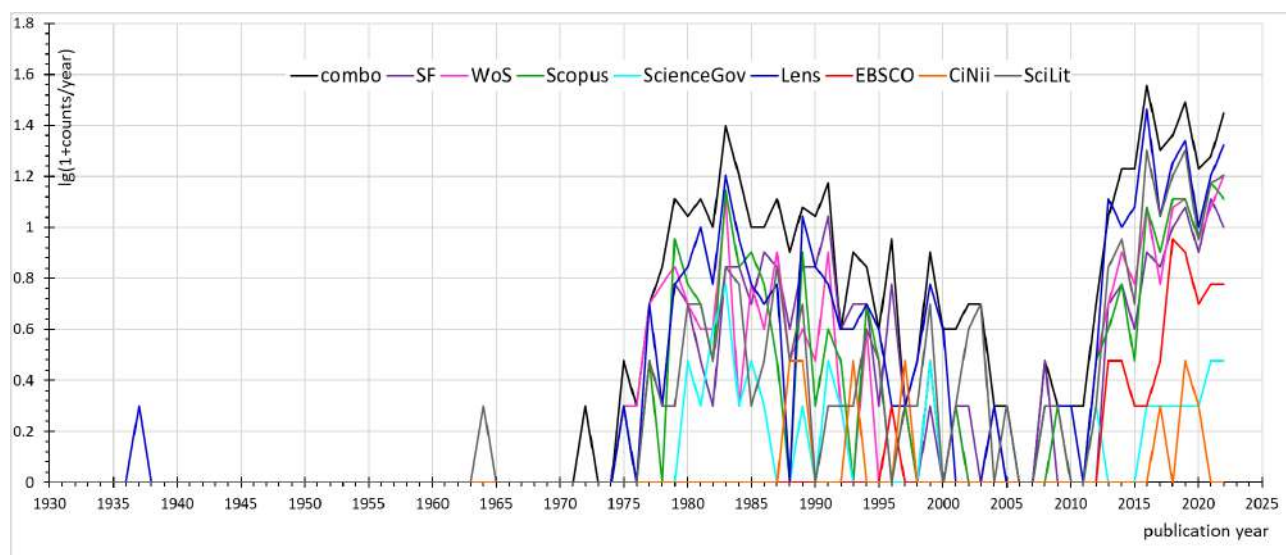


Fig. K2. The same data as in Fig. I1 but in semi-log coordinates.

The results of this exercise are shown in Figs. K1 and K2. Although this dataset is small (439 datapoints), we still can draw some interesting conclusions about the content of the nine databases:

- 1) no database is fully comprehensive, but no-cost The Lens (lens.org) has the best coverage in terms of the year span and the number of hits. Expensive Sci-Finder comes second, and free SciLit (operated by Open Access publisher MDPI) comes third.
- 2) Web of Science and Scopus provide similar number of hits with a ca. 90% overlap. Thus, they complement each other.(626) Both are inferior to The Lens in terms of coverage, although they provide more informative export options.
- 3) EBSCO, CiNii (Japan), science.gov (USA) include some sources not represented in the Big Three (Web of Science, Scopus and SciFinder).

We would like to mention briefly, that, based on our other studies not shown here, no-cost BASE, The Lens and SciLit have substantial overlap in coverage with paid Scopus and Web of Science, and thus the former are recommended as potential replacements for the latter. No-cost CNKI, CiNii focus on Chinese and Japanese publications, respectively. They do not overlap much with either Scopus or Web of Science, and thus should be promoted by academic librarians as useful sources of unique scientific publications. EBSCO,

ProQuest, science.gov and SciLit do not add much in terms of journal articles to Scopus or Web of Science, but they are good sources of “grey literature”, such as conferences, magazines, reports and theses. SciFinder stands out in terms of its superior coverage of scientific publications prior to ca. 1960, all the way back to 1800’s. Although we did not use chemical structure search, we shall note that this option is available in SciFinder, Scopus (Reaxys) and Questel-Orbit, but not in other databases.

Finally, The Lens (lens.org) stands out as the most comprehensive database in terms of the sources and the timespan, that it covers. The *no-cost* Lens is even better than extremely expensive SciFinder. Based on our conversations with several librarians at universities and national laboratories in the USA, Russia and Germany, we concluded that The Lens is largely unknown to the academic community, and we encourage the readers of this article to explore it, before it becomes a *for-a-fee* database.

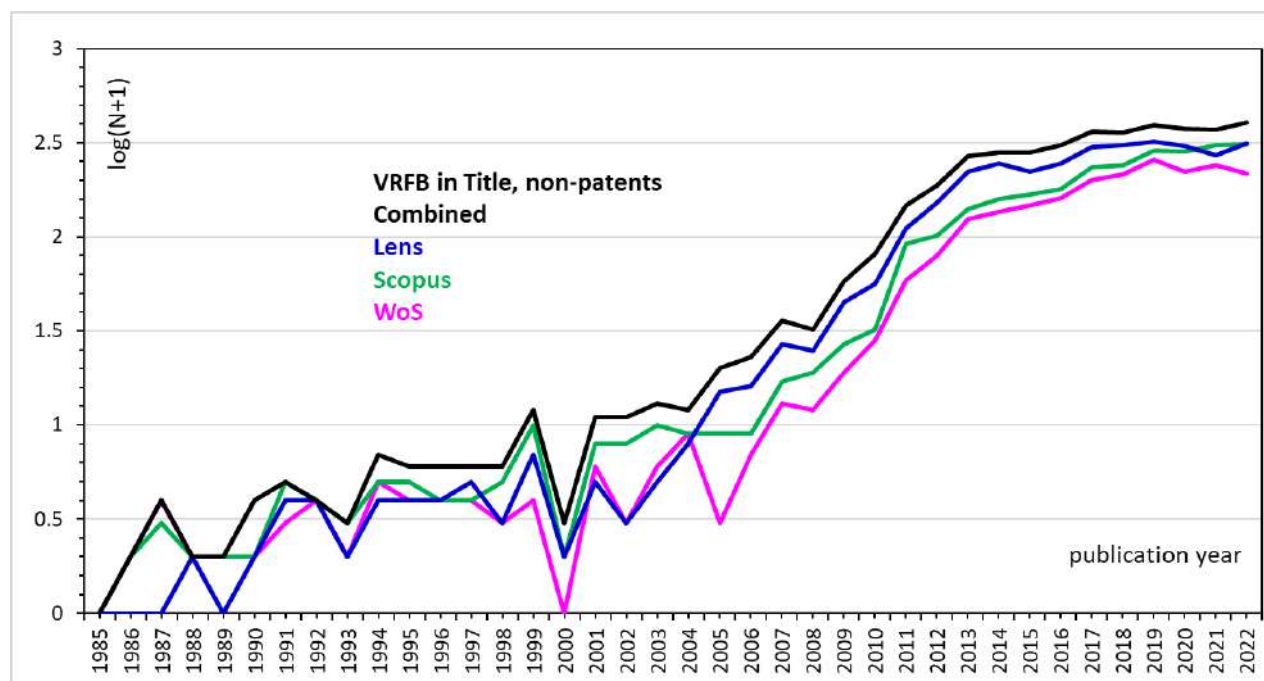


Fig. K3. The number of publications mentioning vanadium redox flow batteries in their titles (i.e. TI=(vanadium) AND TI=(redox OR flow) AND TI=(battery OR batteries OR cell OR cells OR accumulator OR accumulators)) by year for three popular non-patent Scientific Bibliographic Databases.

Fig. K3 shows analogous results for non-patent publications about vanadium redox flow batteries. The conclusions are similar to what we said about Fig.K3:

no database is fully comprehensive;

for years after 2005 the number of hits decreases in the sequence: The Lens > Scopus > Web of Science;

for the earlier years, Scopus often has the best coverage (note, that SciFinder was not included into this study).

It is worth noting, that the extra content in The Lens (which is not found in Scopus and Web of Science) comprises a diverse set of references, such as :

- 1) journals unindexed in WoS and Scopus,(627-634)
- 2) conferences unindexed in WoS and Scopus,(635-640)
- 3) theses,(641-647)
- 4) books and chapters,(648-652)
- 5) standards, (653)
- 6) publications, that have not been indexed by Scopus and WoS at the time of search (2022-12-07), but have been indexed by The Lens.(654-656)

However, despite this superior coverage of primary sources, The Lens, being an agglomeration database, suffers from duplicate references and from inconsistent citation content (e.g. some reference have Authors’

Address but most do not). For this reason, it would be premature in 2023 to cancel your subscriptions to both Scopus and Web of Science, but you should be able to replace the more expensive of the two with The Lens without regret.

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