

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.

Table of Content:

1. Introduction and zinc-halogen batteries.
 2. Vanadium RFBs- the technology frontrunners.
 3. The misfortunes of polysulfide-polybromide flow batteries : 1980-2010.
 4. The benefits of submicron electrode fiber diameter and RFB efficiency.
 5. The “lithium or vanadium” quandary.
 - 5.1. Capital cost.
 - 5.2. Durability.
 - 5.3. Energy efficiency.
 6. What is ahead for RFBs?
 7. Further reading.
- Appendix A. Relationships between structural micro- and macro- parameters of a porous electrode.
- Appendix B. Relationships between permeability and porosity for selected structures.
- Appendix C. Ohmic losses in a porous electrode.
- Appendix D. Pressure loss in the porous electrode.

Appendix E.	Patent searches.
Appendix F.	Non-patent searches.
Appendix H.	Historic publications about zinc-halogen and related batteries.
Appendix I.	Patent-journal correlation for other batteries.
Appendix J.	Crossover in flow batteries.
Appendix K.	Comparison of Scientific Bibliographic Databases.

Notations and abbreviations

a	m^{-1}	inner surface area to volume ratio for a porous media, $a = 0.5(1 - \epsilon) d^{-1}$
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 $\delta = [(1 - \epsilon)(4/\pi)]^{0.5}$
ϵ		porosity $\epsilon = 1 - (\pi/4) \delta^2$
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.

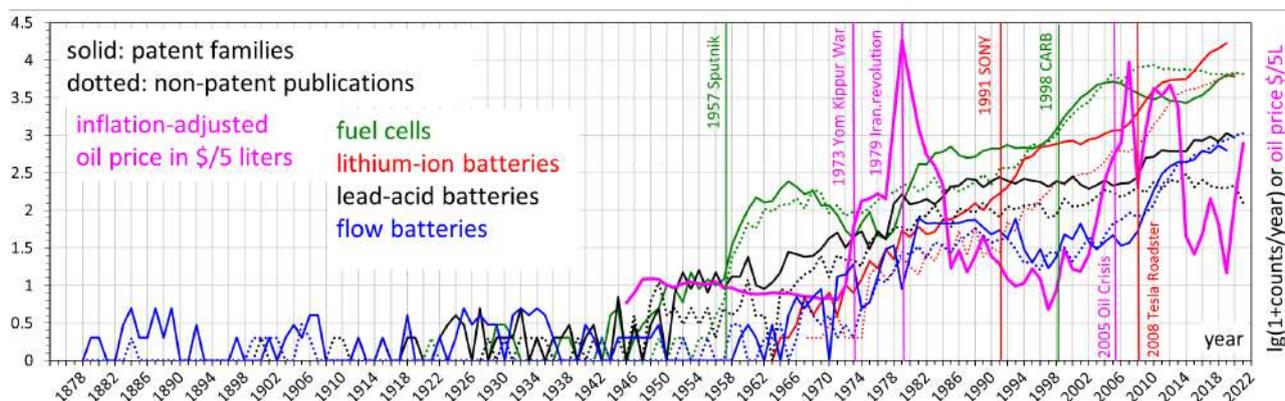


Fig. 1. The number of patent families (solid lines) and of journal articles (dotted lines) related to fuel cells (all types, green), to flow batteries (blue), to lithium (metal and ion) batteries (red) and to lead-acid batteries (black) vs the earliest priority (for patents) or publication (for journals) 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)

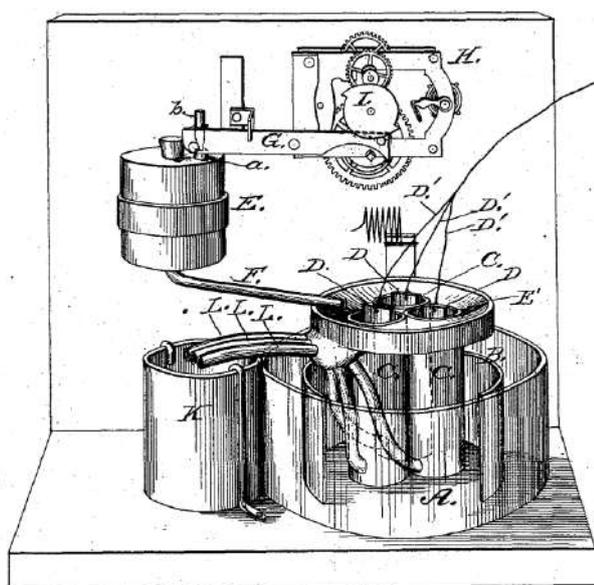


Fig. 2. Zn-Br₂ flow battery from John Doyle's patent US224404(70) filed on September 29, 1879:
 A-spill enclosure (dielectric container),
 B-cylindrical zinc negode,
 C-porous dielectric jars/separators (3 are shown),
 D-porous electron-conducting (e.g. carbon) posodes coated on the inner surfaces of 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).

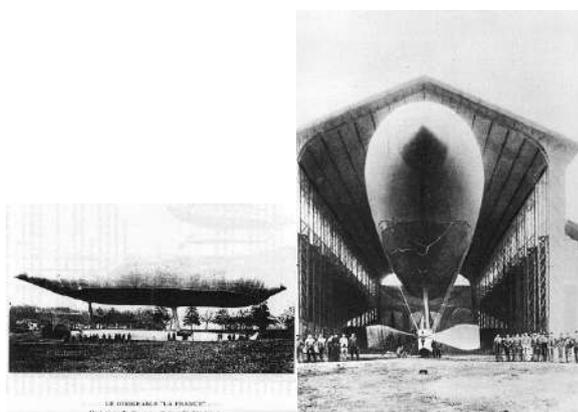


Fig.3. 1884 photograph of the airship La France. © expired.(78)

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)

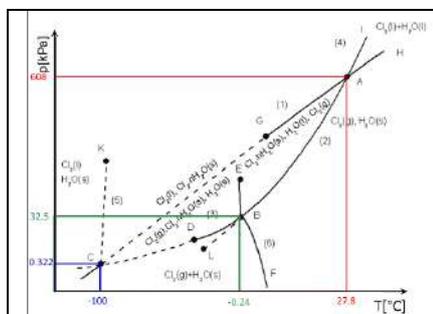


Fig.4. Partial phase diagram for Cl₂-H₂O mixture. Redrawn from data in ref. (110)

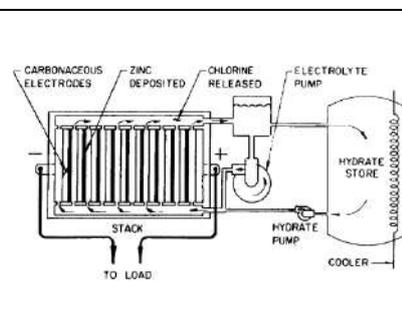


Fig.5. Schematic diagram of zinc-chlorine hydrate battery during charging.(82) © expired

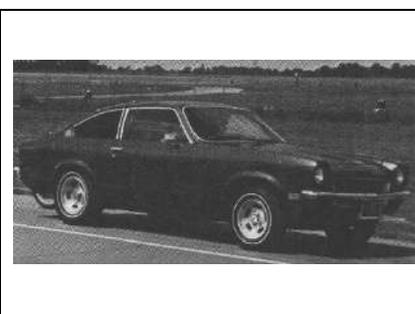


Fig.6. Modified 1971 Vega hatchback powered by 24 40Vx8A Zn-Cl₂ batteries like in Fig.5. (82) © expired.

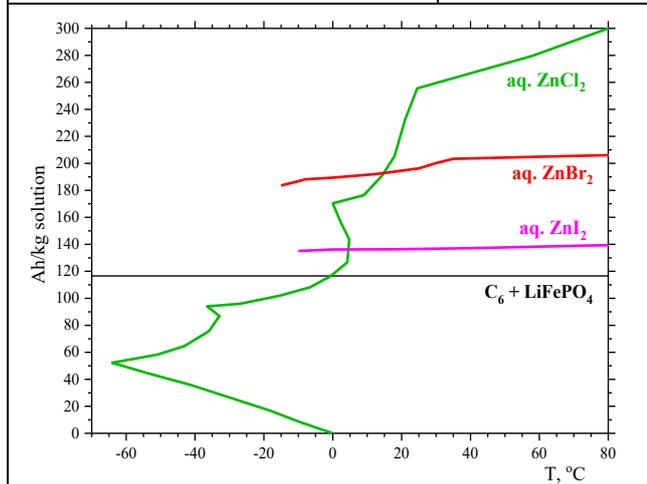


Fig.7. Solubilities of zinc halides in water shown as the number of Ah per kg of *solution*, assuming 2 e⁻ per ZnX₂. Data credits: ZnCl₂, (111, 112) ZnBr₂,(113) ZnI₂,(113) Also shown as the black line is the specific charge of a lithium-ion battery reagents.

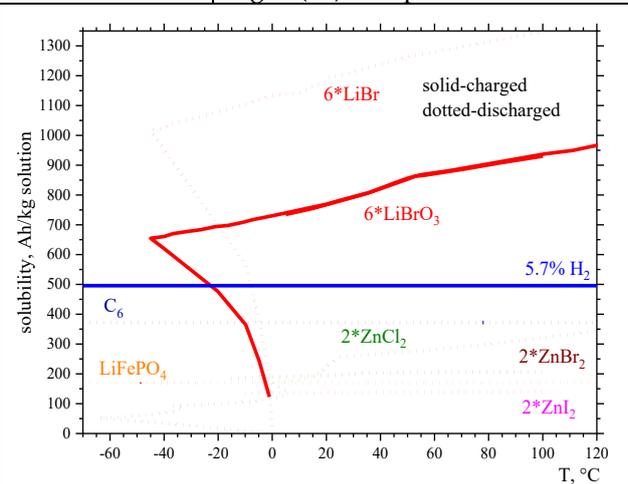


Fig.8. Solubilities of LiBrO₃(114) and LiBr (115-117) in water shown as the number of Ah per kg of *solution*, assuming 6 e⁻ per LiXO₃. The data for 2e⁻ zinc halides from Fig. 7, as well as lithium-ion batteries and H₂ fuel cells are also shown for comparison.

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 S_n²⁻ - 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 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)

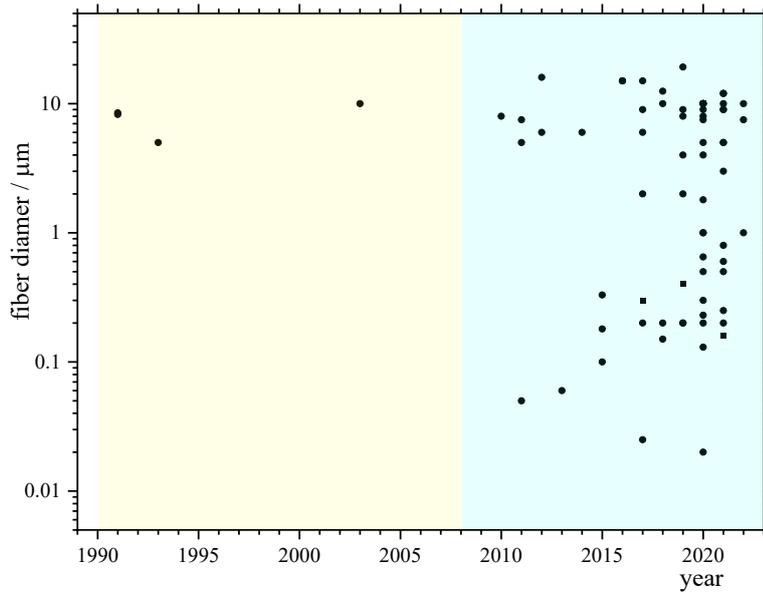


Fig.9. The fiber diameter reported in publications about VRFBs vs priority (for patents) or publication (for all other documents) year.

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:

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

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_-).

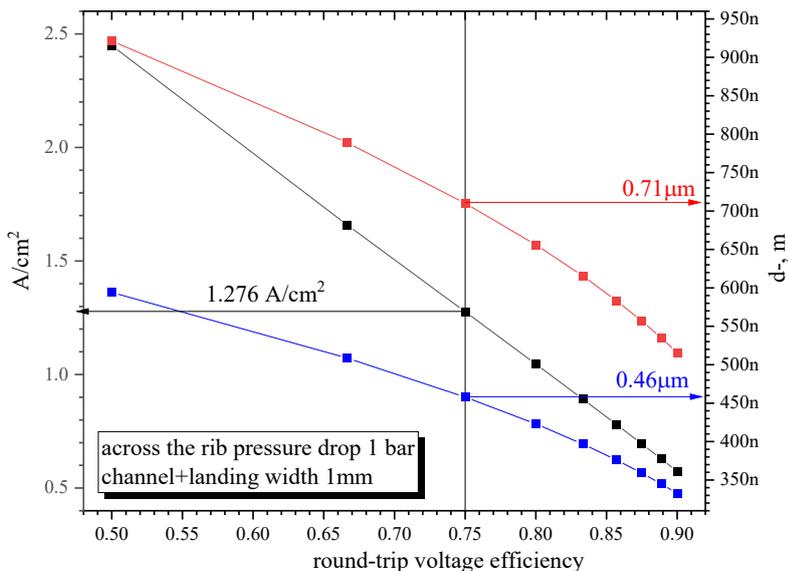


Fig.10. The calculated negode's (blue) and posode's (red) fiber diameters and the round-trip voltage efficiency (black) required to maintain the 1 bar pressure drop across 1 mm width in a VRFB for the current density shown on the Y-axis.

The results of combing (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 A/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 A/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/cm^2 and with 0.7 W/cm^2 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 \times 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/cm^2). We would like to mention here in passing, that the electrocatalytic effects in VRFB reactions is comparatively (to H_2 and O_2 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/cm^2 , 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/cm^2 (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/cm^2 . In this case the peak *one-way* energy efficiency of 89% is observed at 120 mA/cm^2 . 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.

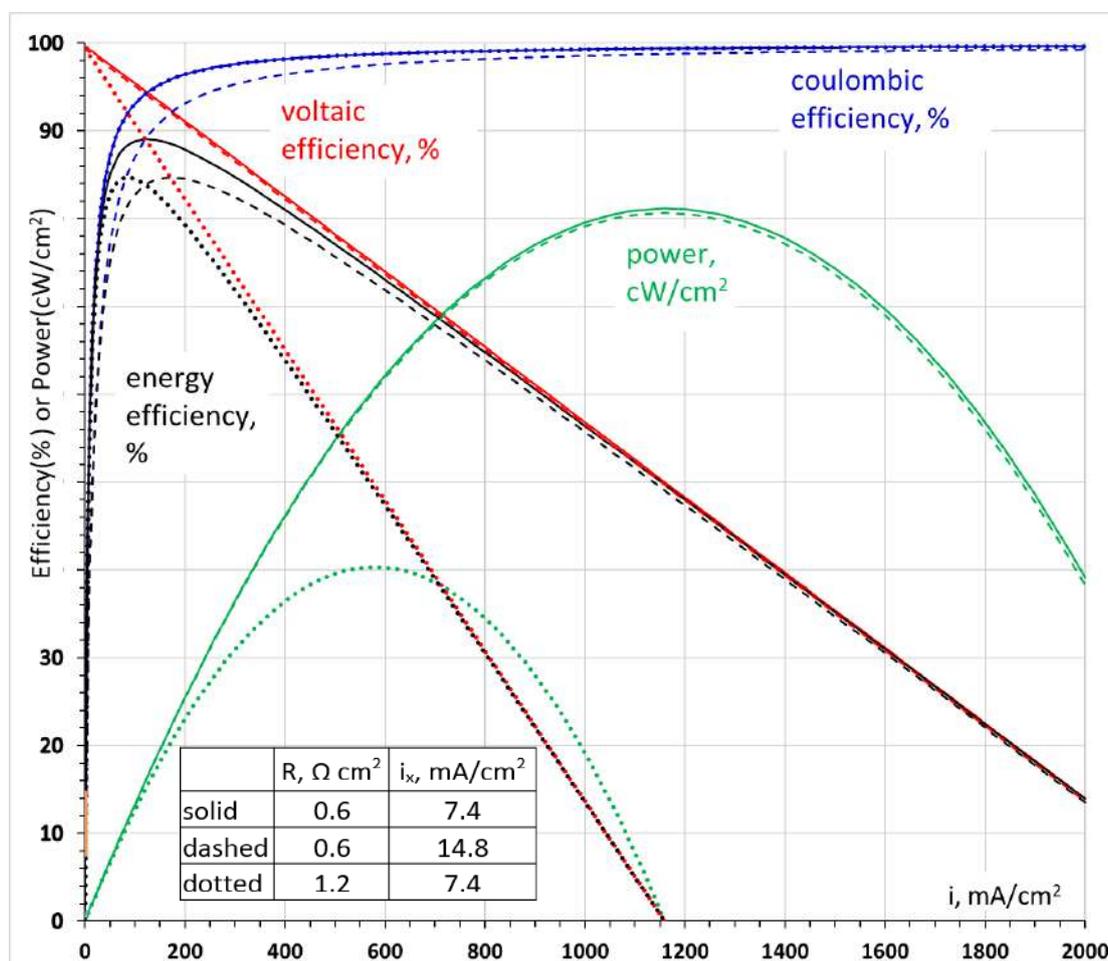


Fig. 11. Simulated area-specific power (green line, right axis) as well as voltaic (red line), coulombic (blue line) and total energy (black line) *one-way* efficiencies for a VRFB prototype. Solid lines refer to the base case (cell’s area-specific resistance is 0.6 Ω/cm² according to Ref.(344) and the 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 the 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.

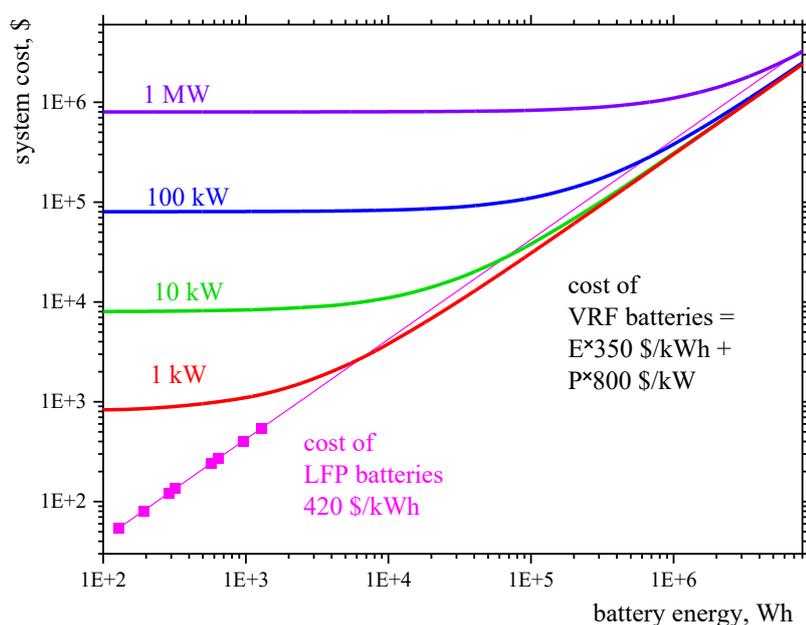
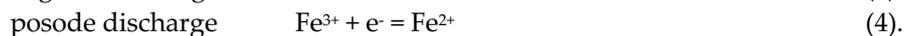
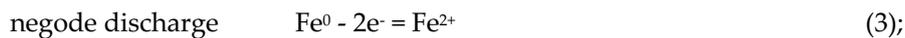


Fig.12. The capital costs of lithium iron phosphate (LFP) batteries (magenta) (384) and of vanadium redox flow (VRF) batteries (red, green, blue and violet)(385, 386) for different energy and power ratings.

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 H₂ evolution on the negative during charge (20, 402-404, 415, 416) and the precipitation of Fe³⁺ 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 negative'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 positive (e.g. LiFePO₄) 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 LiMn₂O₄ and Li⁺ for Ni²⁺ lattice site exchange in LiNiO₂. 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 V₂O₅ 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 H₂ 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. $> 0.5 A/cm^2$) current densities results in a poor voltaic efficiency (e.g. $<75%$ one-way), while operating at low current densities (e.g. $< 10 mA/cm^2$) 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 viazine 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 ≥ 900 °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/cm² 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 ≤ 1 cm² 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/cm²) 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.

Acknowledgements: The author thanks Dr. Adam Whitehead (Invinity Energy Systems, Scotland), Dr. Gael Mourouga (ETH Zurich, Switzerland), Dr. Robert Gloukhovski (Technion, Israel), Prof. Kan-Lin Hsueh (National United University, Taiwan), Prof. Djamila Rekioua (Université de Béjaïa, Algeria), Prof. Shrihari Sankarasubramanian (University of Texas at San Antonio, USA), Dr. Ruediger Schweiss (SGL Carbon GmbH, Germany), Prof. Kevian Huang (University of South Carolina, USA) and two anonymous reviewers for providing comments about a pre-print of this article via qeios.com and researchgate.net. We are also grateful to Prof. Takeshi Sugahara of Osaka University (Japan) for sharing a preprint of ref.(582) This work was supported in part by the Russian Science Foundation (project no. 15-13-20038).

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)

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

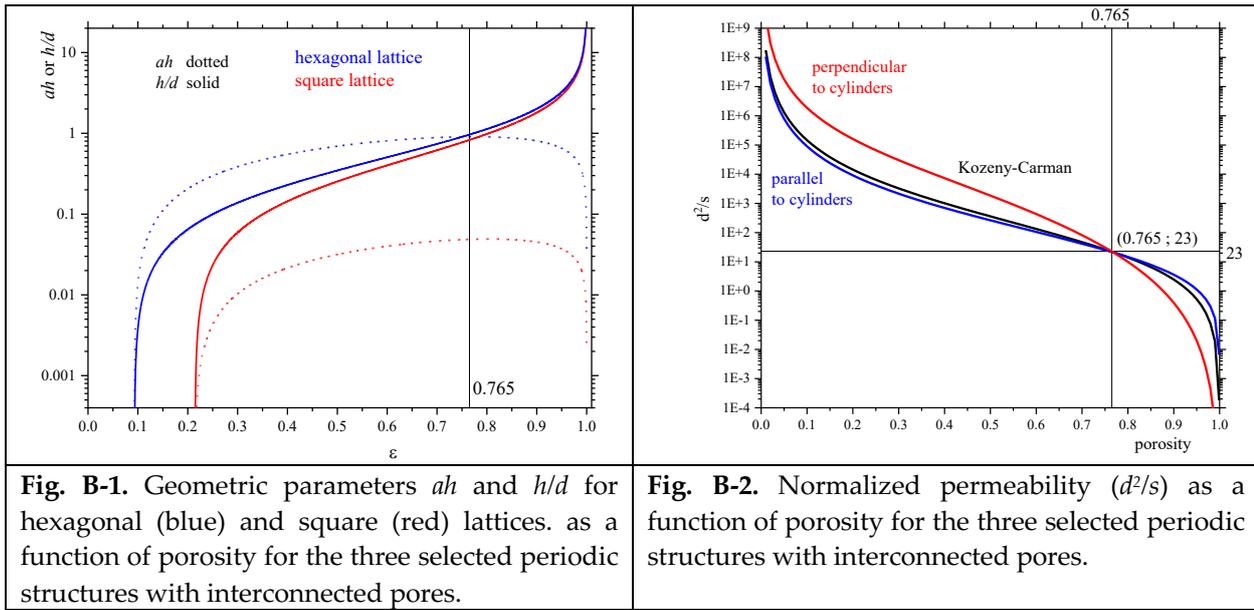


Fig. B-1. Geometric parameters ah and h/d for hexagonal (blue) and square (red) lattices. as a function of porosity for the three selected periodic structures with interconnected pores.

Fig. B-2. Normalized permeability (d^2/s) as a function of porosity for the three selected periodic structures with interconnected pores.

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.

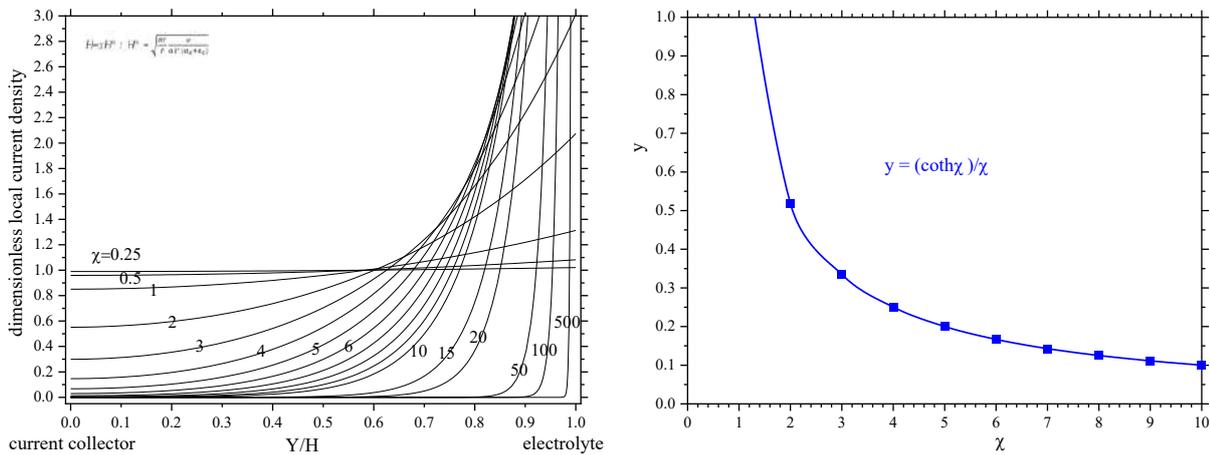


Fig. C-1. (right) Dimensionless local current density in a porous electrode with infinitely large electronic conductivity. See ref. (546) for the details of notations and derivation.

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

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

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 $\kappa \gg \sigma$

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

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

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

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

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

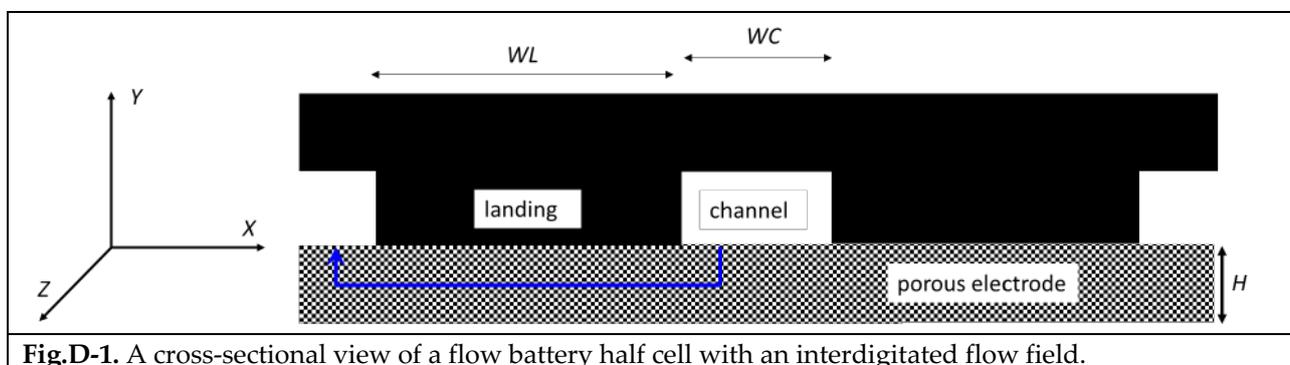


Fig.D-1. A cross-sectional view of a flow battery half cell with an interdigitated flow field.

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

$$u = v/(HWZ) \quad HWZ u = v \quad (D-8).$$

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

$$v = HWZ u = \frac{I}{nF C_0 \phi} \quad (D-9).$$

$$u = \frac{I}{nF C_0 \phi HWZ} \quad (D-10).$$

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 ν) 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):

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

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 $\psi = 23$:

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

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

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

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

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

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

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

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

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.

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

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

$$H = \chi H^0 = \chi \sqrt{\frac{RT}{F} \frac{\sigma}{a i^2 (\alpha_a + \alpha_c)}} \quad (\text{D-19}),$$

and

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

from (A1-14) we arrive at

$$H = \chi H^0 = \chi \sqrt{\frac{RT}{F} \frac{\sigma d}{(\alpha_a + \alpha_c) \beta(1-\varepsilon) i^2}} [m] \quad (\text{D-21}).$$

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

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

Then we arrive at

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

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.

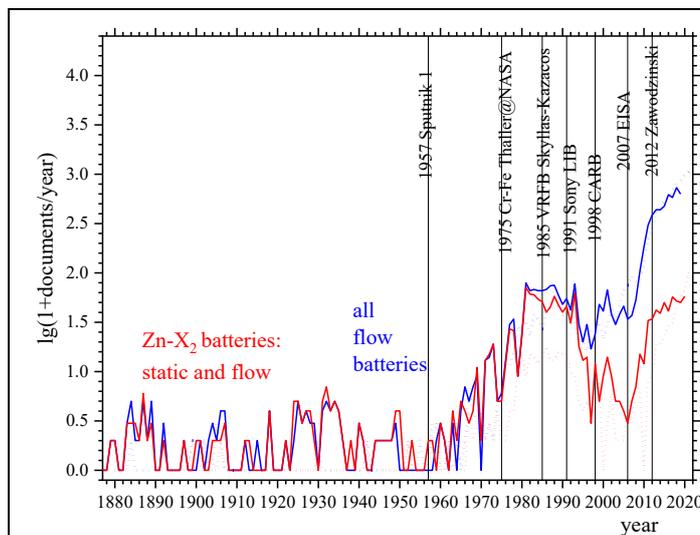


Fig. H1. The numbers of patent families vs priority year and of journal articles vs publication year for all flow batteries (blue lines), and for zinc-halogen batteries (red lines). In some years the red line lies above the blue line due to non-flow (static) zinc-halogen batteries. The vertical lines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

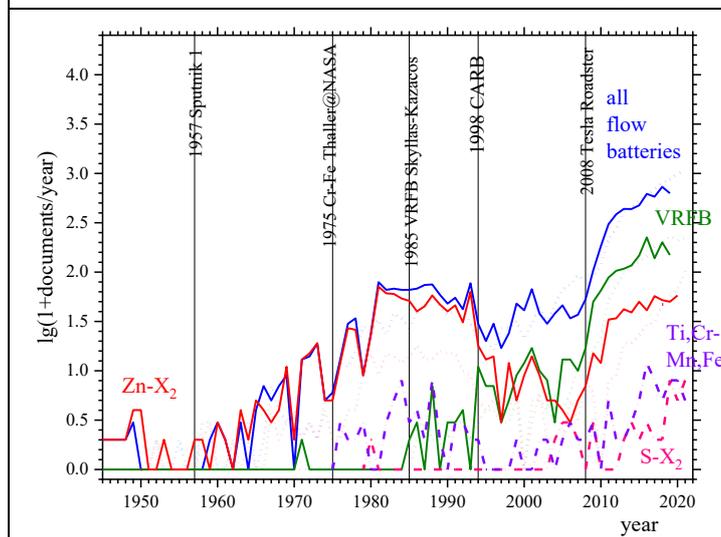


Fig. H2. The numbers of patent families (solid lines) vs priority year and of journal articles (dotted lines) vs publication year for all flow batteries (blue lines), VRFBs (green lines), zinc-halogen batteries (red lines), Ti,Cr-Mn,Fe flow batteries (violet line), polysulfide-halogen batteries (pink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

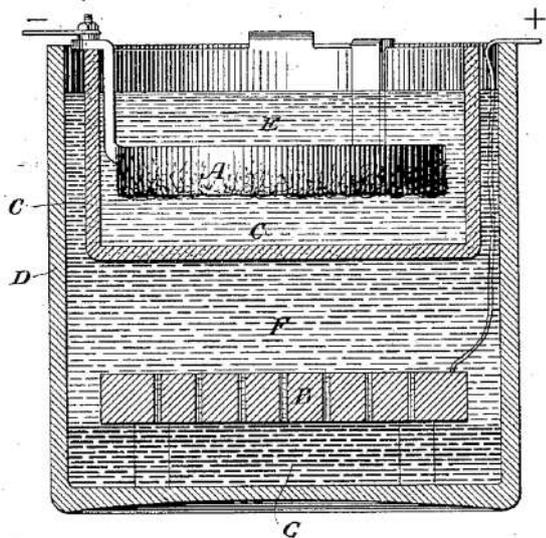


Fig. H4. A rechargeable *static* Zn-Br₂ battery from the 1884 Bradley's patent: A-negative Zn electrode, B-positive carbon plate electrode, C-porous dielectric cell/diaphragm, D-outer casing, E, F - ZnBr₂ solutions, G-a layer of liquid bromine.(71, 72)

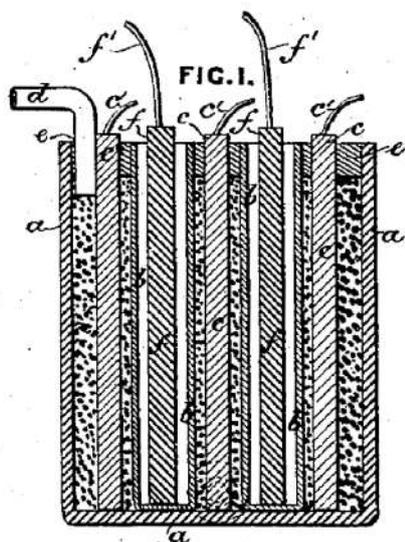


Fig. H5. A non-rechargeable *flow* Zn-Cl₂ battery from the 1884 patent by Upward and Pridham.(614)

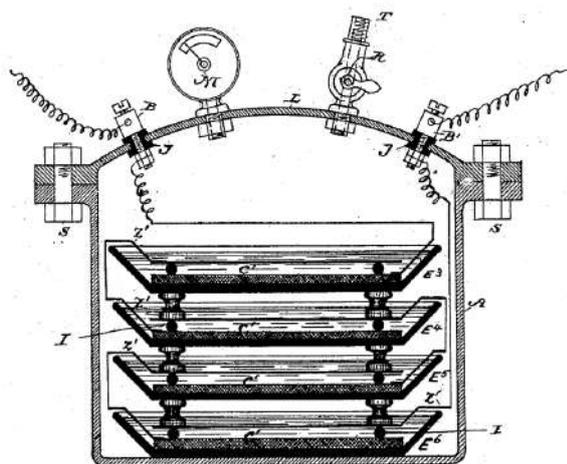


Fig. H6. A rechargeable *static* pressurized Zn-Cl₂ battery from the 1888 patent by Pieper.(615)

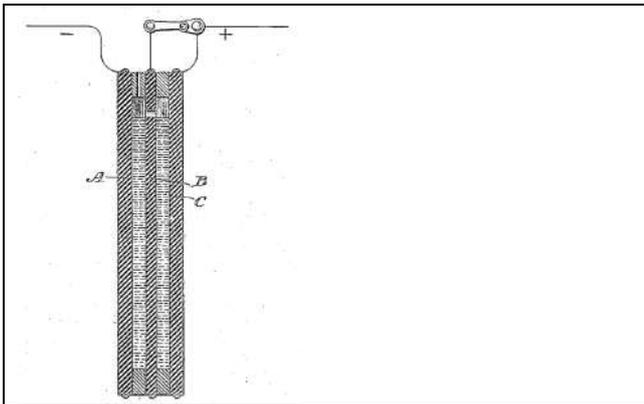


Fig. H7. A rechargeable static Zn-Br₂ battery from the 1889 patent by Bradley.(73) A similar design was proposed in 1901 by Lyons and Broadwell.(616)

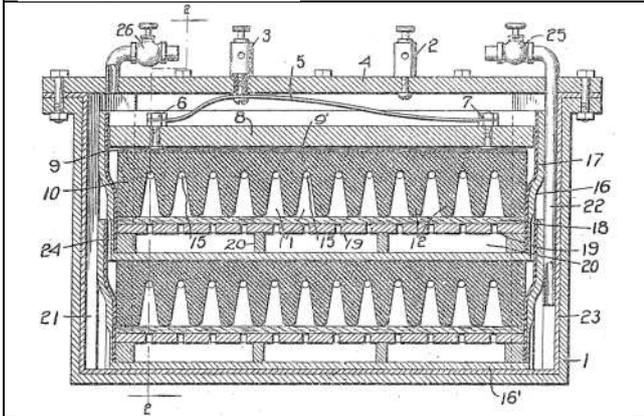


Fig. H8. A zinc-halogen flow battery from the 1912 patent by H.E.R.Little.(617)
 10-carbon posodes,
 11-groves for posolyte supply,
 12-ridges of carbon posodes,
 15-posolyte inlets,
 18-asbestos diaphragm,
 19-Zn negodes,
 20-frame,
 25-posolyte inlet valve,
 26-posolyte outlet valve.

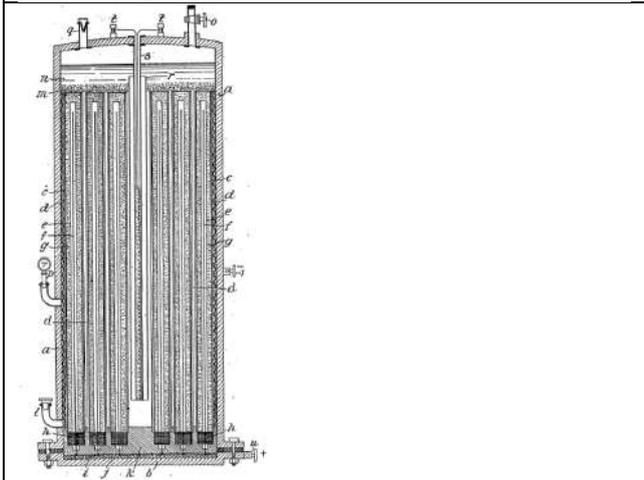


Fig. H9. A rechargeable non-flow pressurized Zn-Cl₂ battery from the 1917 patent by Guglielmo Marconi.(610, 618)

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.

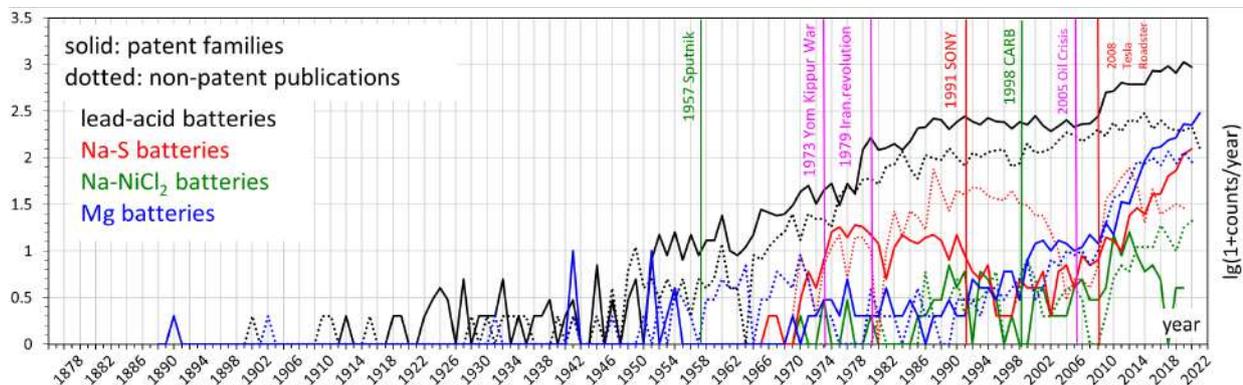


Fig. I1. The numbers of patent families (solid lines) vs priority year and of journal articles (dotted lines) vs publication year for lead-acid (black), sodium-sulfur (red), sodium-nickel chloride (green) and magnesium metal (primary and rechargeable) batteries.

The search methodology is explained in Apps E and F.

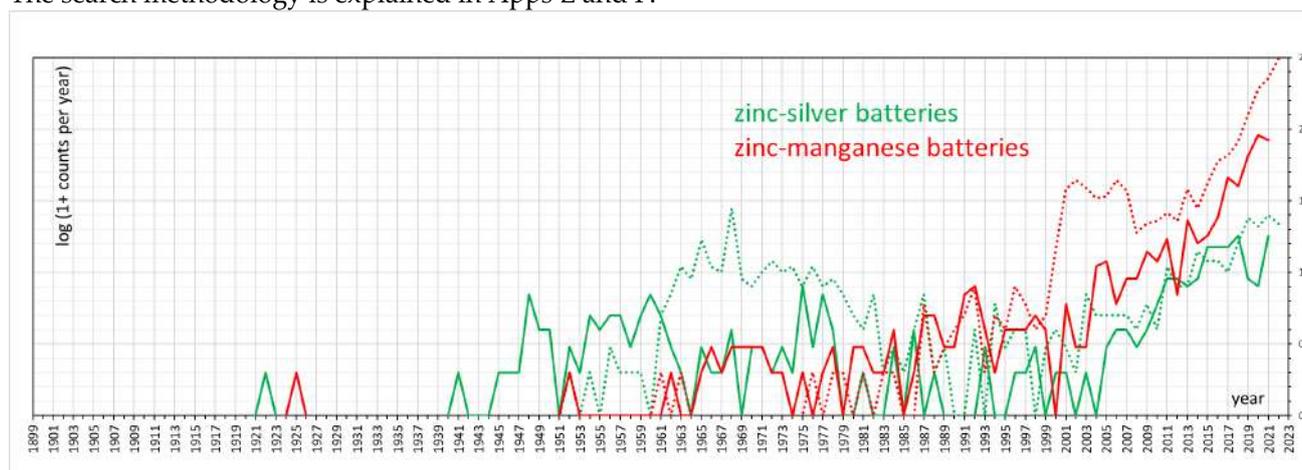


Fig. I1. The numbers of patent families (solid lines) vs priority year and of journal articles (dotted lines) vs publication year for zinc-manganese (red) and zinc-silver (green) batteries. The search methodology is explained in Apps E and G.

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 $20 \text{ }^\circ\text{C}$.

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.

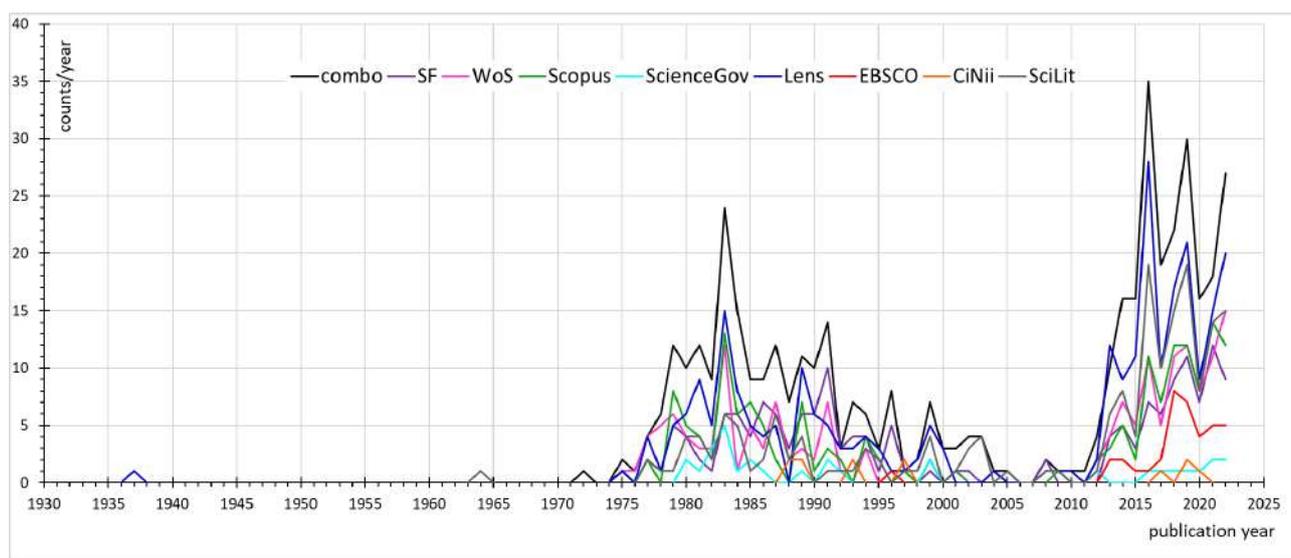


Fig. K1. The numbers of journal articles, referring to zinc-bromine batteries in their *titles*, va the publication year. The colored lines show the data from the eight databases as indicated in the inset. The black line refers to the combined result with duplicates removed.

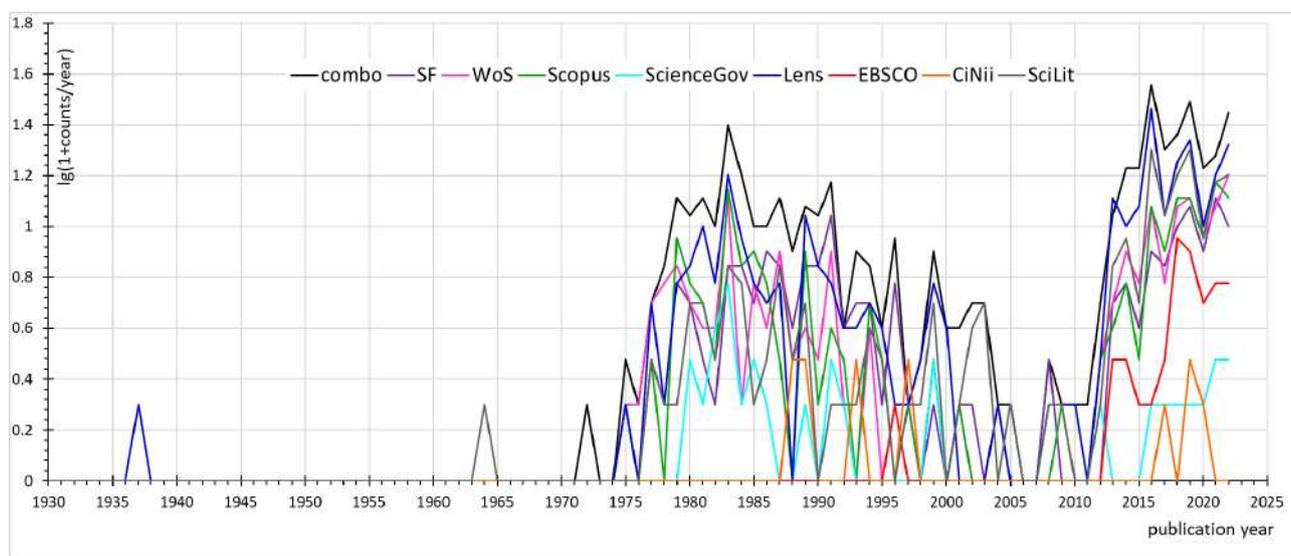


Fig. K2. The same data as in Fig. I1 but in semi-log coordinates.

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.

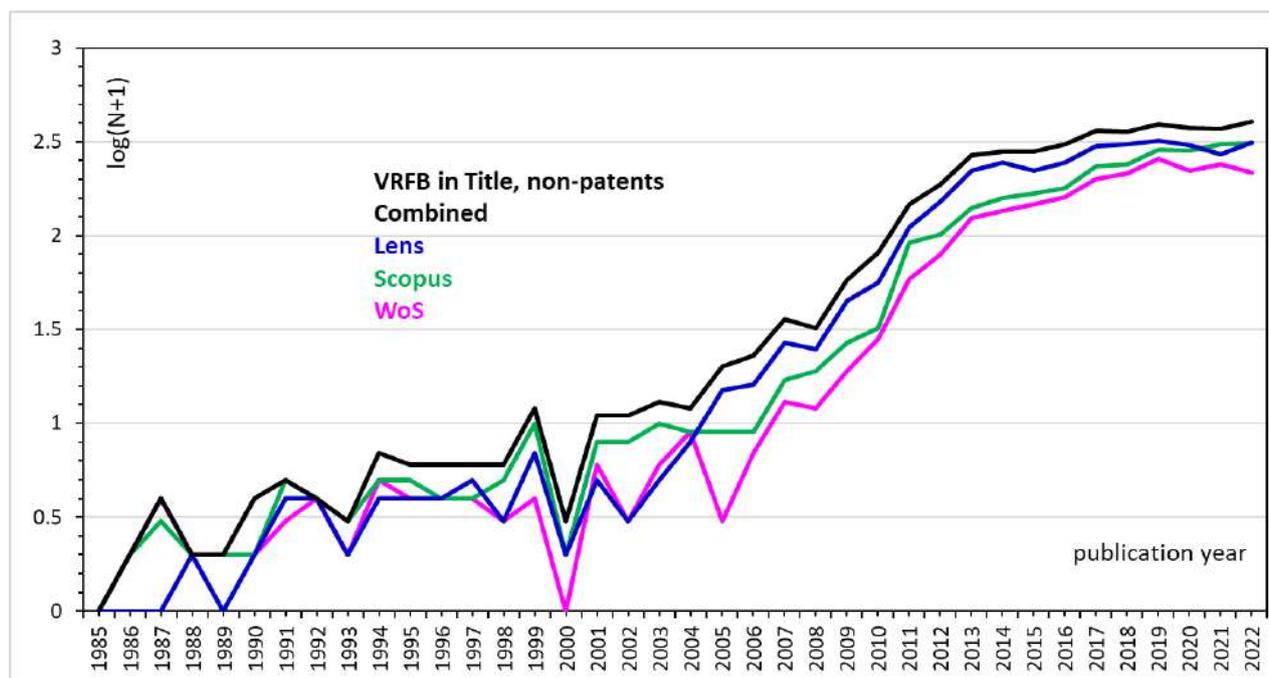


Fig. K3. The number of publications mentioning vanadium redox flow batteries in their titles (i.e. TI=(vanadium) AND TI=(redox OR flow) AND TI=(battery OR batteries OR cell OR cells OR accumulator OR accumulators)) by year for three popular non-patent Scientific Bibliographic Databases.

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.

CITED REFERENCES:

1. Y. V. Tolmachev, A. Piatkivskiy, V. V. Ryzhov, D. V. Konev and M. A. Vorotyntsev, "Energy cycle based on a high specific energy aqueous flow battery and its potential use for fully electric vehicles and for direct solar-to-chemical energy conversion." *J. Solid State Electrochem.*, **19**, 2711 (2015) 10.1007/s10008-015-2805-z.
2. Y. V. Tolmachev and S. V. Starodubceva, "Flow batteries with solid energy boosters." *J. Electrochem. Sci. Eng.*, **12**, 731 (2022) 10.5599/jese.1363.
3. Y. V. Tolmachev, "Hydrogen-halogen electrochemical cells: A review of applications and technologies." *Russ. J. Electrochem.*, **50**, 301 (2014) 10.1134/S1023193513120069.
4. R. F. Savinell, "Development of a titanium/iron redox couple flow battery system." Thesis (1977)
5. R. F. L. Savinell, C. C. ; Chiang, S. H. ; Coetzee, J. F. ; Galasco, R. T., Investigation of a parallel plate fe-ti redox electrochemical cell, in *Journal of the Electrochemical Society*, INVESTIGATIONOFAPARALLELPLATEFETIREDOXELECTROCHEMICALCELL1978 Editor, p. C336 (1978)
6. R. F. L. Savinell, C. C. ; Galasco, R. T. ; Chiang, S. H. ; Coetzee, J. F., "Discharge characteristics of a soluble iron-titanium battery system." *Journal of the Electrochemical Society*, **126**, 357 (1979) 10.1149/1.2129043.
7. C. C. G. Liu, R. T. ; Savinell, R. F., "Enhancing performance of the titanium(iii)/titanium(iv) couple for redox battery applications." *Journal of the Electrochemical Society*, **128**, 1755 (1981) 10.1149/1.2127725.
8. C. C. Liu, R. T. Galasco and R. F. Savinell, "Operating performance of an fe-ti stationary redox battery in the presence of lead." *J Electrochem Soc*, **129**, 2502 (1982) 10.1149/1.2123592.
9. R. F. Savinell, Transition metal oxide-coated titanium electrodes for redox batteries, in, TRANSITIONMETALOXIDECOATEDTITANIUMELECTRODESFORREDOXBATTERIES1982 Editor, p. 56 pp., Lawrence Berkeley Lab. (1982)
10. S. D. S. Fritts, R. F., Modeling of the platinum-membrane interface of a hydrogen-bromine fuel-cell, in *Journal of the Electrochemical Society*, MODELINGOF THE PLATINUM MEMBRANE INTERFACE OF A HYDROGEN BROMINE FUEL CELL 1987 Editor, p. C413 (1987)
11. R. F. Savinelli and S. D. Fritts, "Theoretical performance of a hydrogen bromine rechargeable spe fuel-cell." *J Power Sources*, **22**, 423 (1988) 10.1016/0378-7753(88)80035-1.
12. S. D. Fritts and R. F. Savinell, "Simulation studies on the performance of the hydrogen electrode bonded to proton-exchange membranes in the hydrogen-bromine fuel-cell." *J Power Sources*, **28**, 301 (1989) 10.1016/0378-7753(89)80058-8.
13. S. D. Fritts and R. F. Savinell, "Simulation studies on the performance of the hydrogen electrode bonded to proton exchange membranes in the hydrogenbromine fuel cell." *J Power Sources*, **28**, 301 (1989) 10.1016/0378-7753(89)80058-8.
14. X. P. Ke, Joseph M. ; Alexander, J. Iwan D. ; Wainright, Jesse S. ; Zawodzinski, Thomas A. ; Savinell, Robert F., "Rechargeable redox flow batteries: Flow fields, stacks and design considerations." *Chemical Society Reviews*, **47**, 8721 (2018) 10.1039/c8cs00072g.
15. F. Savinell Robert and S. Wainright Jesse, "Iron flow batteries." 2012DK-0792876 2012-06-012012US-14122885 2012-06-012014JP-0513737 2012-06-012013KR-7034154 2012-06-012012CN-80027075 2012-06-012012EP-0792876 2012-06-012012WO-US40429 2012-06-01 (2001-06-01).
16. T. J. Petek, J. S. Wainright and R. F. Savinell, "Slurry electrode for an all-iron flow battery for low cost large-scale energy storage." in *Fuels and Petrochemicals Division 2013 - Core Programming Area at the 2013 AIChE Annual Meeting: Global Challenges for Engineering a Sustainable Future*, p. 11 (2013)
17. K. L. Hawthorne, J. S. Wainright and R. F. Savinell, "Maximizing plating density and efficiency for a negative deposition reaction in a flow battery." *J Power Sources*, **269**, 216 (2014) 10.1016/j.jpowsour.2014.06.125.
18. K. L. Hawthorne, J. S. Wainright and R. F. Savinell, "Studies of iron-ligand complexes for an all-iron flow battery application." *J Electrochem Soc*, **161**, A1662 (2014) 10.1149/2.0761410jes.
19. M. A. Miller, J. S. Wainright and R. F. Savinell, "Communication - iron ionic liquid electrolytes for redox flow battery applications." *J Electrochem Soc*, **163**, A578 (2016) 10.1149/2.0061605jes.

20. S. Selverston, R. F. Savinell and J. S. Wainright, "In-tank hydrogen-ferric ion recombination." *J Power Sources*, **324**, 674 (2016) 10.1016/j.jpowsour.2016.05.126.
21. M. A. Miller, J. S. Wainright and R. F. Savinell, "Iron electrodeposition in a deep eutectic solvent for flow batteries." *J Electrochem Soc*, **164**, A796 (2017) 10.1149/2.1141704jes.
22. S. Selverston, S. Wainright Jesse and R. Savinell, "Sealed aqueous flow battery systems with in-tank electrolyte rebalancing." 2016WO-US56230 2016-10-102016DK-0854529 2016-10-102018JP-0517725 2016-10-102016US-15766121 2016-10-102016EP-0854529 2016-10-102016CN-80070054 2016-10-102018KR-7012989 2016-10-102016AU-0334392 2016-10-102021US-17363269 2021-06-302021JP-0100129 2021-06-16 (2016WO-US56230 2016-10-102016DK-0854529 2016-10-102018JP-0517725 2016-10-102016US-15766121 2016-10-102016EP-0854529 2016-10-102016CN-80070054 2016-10-102018KR-7012989 2016-10-102016AU-0334392 2016-10-102021US-17363269 2021-06-302021JP-0100129 2021-06-16).
23. N. S. Sinclair, R. F. Savinell and J. S. Wainright, "A perspective on the design and scale up of a novel redox flow battery." *MRS Energy Sustain.*, **9**, 387 (2022) 10.1557/s43581-022-00046-8.
24. N. S. Sinclair, R. F. Savinell and J. S. Wainright, "A perspective on the design and scale up of a novel redox flow battery." *MRS. Energy. Sustain.*, **9**, 387 (2022) 10.1557/s43581-022-00046-8.
25. E. A. Stricker, K. W. Krueger, R. F. Savinell and J. S. Wainright, "Investigating a bromide supported electrolyte for an all-copper flow battery." *J Electrochem Soc*, **165**, A1797 (2018) 10.1149/2.1031809jes.
26. E. Stricker, Z. Adler, J. Wainright and R. Savinell, "Diffusion coefficients of cuprous and cupric ions in electrolytes with high concentrations of bromide ions." *J Chem Eng Data*, **64**, 1095 (2019) 10.1021/acs.jced.8b00990.
27. S. Selverston, R. F. Savinell and J. S. Wainright, "Zinc-iron flow batteries with common electrolyte." *J Electrochem Soc*, **164**, A1069 (2017) 10.1149/2.0591706jes.
28. A. Bourke, M. A. Miller, R. P. Lynch, J. S. Wainright, R. F. Savinell and D. N. Buckley, "Electrode kinetics in all-vanadium flow batteries: Effects of electrochemical treatments." in *Symposium on Joint General Session: Batteries and Energy Storage -and- Fuel Cells, Electrolytes, and Energy Conversion - 227th ECS Meeting*, A. Manivannan, T. R. Jow, K. Edstrom, V. Kalra and B. Y. Liaw Editors, p. 181 (2015) 10.1149/06608.0181ecst.
29. I. L. Escalante-Garcia, J. S. Wainright, L. T. Thompson and R. F. Savinell, "Performance of a non-aqueous vanadium acetylacetonate prototype redox flow battery: Examination of separators and capacity decay." *J Electrochem Soc*, **162**, A363 (2015) 10.1149/2.0471503jes.
30. A. Bourke, M. A. Miller, R. P. Lynch, X. Gao, J. Landon, J. S. Wainright, R. F. Savinell, et al., "Electrode kinetics of vanadium flow batteries: Contrasting responses of v-ii-v-iii and v-iv-v-v to electrochemical pretreatment of carbon." *J Electrochem Soc*, **163**, A5097 (2016) 10.1149/2.0131601jes.
31. M. A. Miller, A. Bourke, N. Quill, J. S. Wainright, R. P. Lynch, D. N. Buckley and R. F. Savinell, "Kinetic study of electrochemical treatment of carbon fiber microelectrodes leading to in situ enhancement of vanadium flow battery efficiency." *J Electrochem Soc*, **163**, A2095 (2016) 10.1149/2.1091609jes.
32. X. Ke, J. M. Prah, J. I. D. Alexander and R. F. Savinell, "Mathematical modeling of electrolyte flow in a segment of flow channel over porous electrode layered system in vanadium flow battery with flow field design." *Electrochim Acta*, **223**, 124 (2017) 10.1016/j.electacta.2016.12.017.
33. N. S. Sinclair, D. Poe, R. F. Savinell, E. J. Maginn and J. S. Wainright, "A nitroxide containing organic molecule in a deep eutectic solvent for flow battery applications." *J Electrochem Soc*, **168** (2021) 10.1149/1945-7111/abe28a.
34. X. Shen, N. Sinclair, J. Wainright, A. Imel, B. Barth, T. Zawodzinski and R. F. Savinell, "A study of ferrocene diffusion in toluene/tween 20/1-butanol/water microemulsions for redox flow battery applications." *J Electrochem Soc*, **168** (2021) 10.1149/1945-7111/ac0b26.
35. W. M. Wang, J. Wang and D. Ton, "Prospects for renewable energy. Meeting the challenges of integration with storage." in *Smart grid*, p. 103, Elsevier Inc. (2012) 10.1016/B978-0-12-386452-9.00005-X.
36. M. Beaudin, H. Zareipour, A. Schellenberg and W. Rosehart, "Energy storage for mitigating the variability of renewable electricity sources." in *Energy storage for smart grids: Planning and operation for renewable and variable energy resources (vers)*, p. 1, Elsevier Inc. (2015) 10.1016/B978-0-12-410491-4.00001-4.
37. B. Droste-Franke, "Review of the need for storage capacity depending on the share of renewable energies." in *Electrochemical energy storage for renewable sources and grid balancing*, p. 61, Elsevier Inc. (2015) 10.1016/B978-0-444-62616-5.00006-1.

38. J. Kim, Y. Suharto and T. U. Daim, "Evaluation of electrical energy storage (ees) technologies for renewable energy: A case from the us pacific northwest." *J. Energy Storage*, **11**, 25 (2017) 10.1016/j.est.2017.01.003.
39. Y. Yang, S. Bremner, C. Menictas and M. Kay, "Battery energy storage system size determination in renewable energy systems: A review." *Renewable Sustainable Energy Rev*, **91**, 109 (2018) 10.1016/j.rser.2018.03.047.
40. J. Koskela, S. L. Penttinen, T. Vesterinen, H. Holttinen, J. Konttinen, P. Järventausta, J. Kiviluoma, et al., "The role of energy storage and backup solutions for management of a system with a high amount of variable renewable power." in *Electrification: Accelerating the energy transition*, p. 105, Elsevier (2021) 10.1016/B978-0-12-822143-3.00001-9.
41. J. Loacuteppez Prol and W. P. Schill, "The economics of variable renewable energy and electricity storage." *Annu. Rev. Resour. Econ.*, **13**, 443 (2021) 10.1146/annurev-resource-101620-081246.
42. N. Mcilwaine, A. M. Foley, D. J. Morrow, D. Al Kez, C. Zhang, X. Lu and R. J. Best, "A state-of-the-art techno-economic review of distributed and embedded energy storage for energy systems." *Energy*, **229** (2021) 10.1016/j.energy.2021.120461.
43. T. McMahon, "Annual average domestic crude oil prices 1946-present." in *Inflation Data* (2022)<https://inflationdata.com/articles/inflation-adjusted-prices/historical-crude-oil-prices-table/>.
44. J. Allen and C. Oppenheim, "The overlap of u.S. And canadian patent literature with journal literature literature with journal literature." *World Patent Information*, **1**, 77 (1979) 10.1016/S0172-2190(79)90038-3.
45. T. S. Eisenschitz, A. M. Lazard and C. J. Willey, "Patent groups and their relationship with journal literature." *Journal of Information Science*, **12**, 53 (1986) 10.1177/016555158601200109.
46. J. H. Schwartz, "What has been published - more patents than journal literature." *Journal of Chemical Education*, **53**, 57 (1976) 10.1021/ed053p57.
47. S. Bhattacharya and M. Meyer, "Large firms and the science-technology interface - patents, patent citations, and scientific output of multinational corporations in thin films." *Scientometrics*, **58**, 265 (2003) 10.1023/a:1026284510104.
48. R. C. Shair, S. R. Lerner, P. A. Joyner and G. E. Evans, "A review of batteries and fuel cells for space power systems." *J Spacecr Rockets*, **4**, 833 (1967) 10.2514/3.28974.
49. M. Warshay and P. R. Prokopius, "The fuel cell in space: Yesterday, today and tomorrow." *J Power Sources*, **29**, 193 (1990) 10.1016/0378-7753(90)80019-A.
50. P. Costamagna and S. Srinivasan, "Quantum jumps in the pemfc science and technology from the 1960s to the year 2000: Part i. Fundamental scientific aspects." *J Power Sources*, **102**, 242 (2001) 10.1016/S0378-7753(01)00807-2.
51. M. L. Perry and T. F. Fuller, "A historical perspective of fuel cell technology in the 20th century." *J Electrochem Soc*, **149**, S59 (2002) 10.1149/1.1488651.
52. J. H. Scott, "Fuel cell development for nasa's human exploration program: Benchmarking with "the hydrogen economy." *J. Fuel Cell Sci. Technol.*, **6**, 0210111 (2009) 10.1115/1.2972170.
53. S. Gottesfeld, "Fuel cell techno-personal milestones 1984-2006." *J Power Sources*, **171**, 37 (2007) 10.1016/j.jpowsour.2006.11.081.
54. Y. Wang, D. F. Ruiz Diaz, K. S. Chen, Z. Wang and X. C. Adroher, "Materials, technological status, and fundamentals of pem fuel cells – a review." *Mater. Today*, **32**, 178 (2020) 10.1016/j.mattod.2019.06.005.
55. W. M. D. Van Vorst and R. S. George, "Impact of the california clean air act." *Int. J. Hydrog. Energy*, **22**, 31 (1997) 10.1016/s0360-3199(96)00081-x.
56. D. L. Greene, S. Park and C. Liu, "Public policy and the transition to electric drive vehicles in the u.S.: The role of the zero emission vehicles mandates." *Energy Strateg. Rev.*, **5**, 66 (2014) 10.1016/j.esr.2014.10.005.
57. S. Aberoumand, P. Woodfield, B. Shabani and D. V. Dao, "Advances in electrode and electrolyte improvements in vanadium redox flow batteries with a focus on the nanofluidic electrolyte approach." *Physics Reports-Review Section of Physics Letters*, **881**, 1 (2020) 10.1016/j.physrep.2020.08.001.
58. F. Razi and I. Dincer, "Challenges, opportunities and future directions in hydrogen sector development in canada." *Int. J. Hydrog. Energy*, **47**, 9083 (2022) 10.1016/j.ijhydene.2022.01.014.

59. F. Zhao, Z. Mu, H. Hao, Z. Liu, X. He, S. Victor Przesmitzki and A. Ahmad Amer, "Hydrogen fuel cell vehicle development in china: An industry chain perspective." *Energy Technol.*, **8** (2020) 10.1002/ente.202000179.
60. "A future for hydrogen in european transportation." *Nat. Catal.*, **3**, 91 (2020) 10.1038/s41929-020-0438-9.
61. U. Khan, T. Yamamoto and H. Sato, "Understanding the discontinuance trend of hydrogen fuel cell vehicles in japan." *Int. J. Hydrog. Energy*, **47**, 31949 (2022) 10.1016/j.ijhydene.2022.07.141.
62. M. A. Azni and R. M. Khalid, "Hydrogen fuel cell legal framework in the united states, germany, and south korea—a model for a regulation in malaysia." *Sustainability*, **13**, 1 (2021) 10.3390/su13042214.
63. U. Bossel, "Does a hydrogen economy make sense?" *Proc. IEEE*, **94**, 1826 (2006) 10.1109/JPROC.2006.883715.
64. A. M. Oliveira, R. R. Beswick and Y. S. Yan, "A green hydrogen economy for a renewable energy society." *Curr. Opin. Chem. Eng.*, **33**, 7 (2021) 10.1016/j.coche.2021.100701.
65. M. J. Haugen, L. Paoli, J. Cullen, D. Cebon and A. M. Boies, "A fork in the road: Which energy pathway offers the greatest energy efficiency and co2 reduction potential for low-carbon vehicles?" *Appl. Energy*, **283**, 10 (2021) 10.1016/j.apenergy.2020.116295.
66. D. Biello, R.I.P. Hydrogen economy? Obama cuts hydrogen car funding, in *Scientific American* (2009)
67. J. Voelcker, "Top 10 tech cars 2007." *IEEE Spectrum*, **44**, 34 (2007) 10.1109/MSPEC.2007.339648.
68. C. Edwards, "Power vacuum." *Eng. Technol.*, **5**, 25 (2010) 10.1049/et.2010.0905.
69. L. Ulrich, "The greening of the supercar." *IEEE Spectrum*, **47**, 36 (2010) 10.1109/MSPEC.2010.5583461.
70. J. Doyle, "Galvanic battery." 1880US-224404D 0 (1880US-224404D 0).
71. C. S. Bradley, "Electric accumulator." DE34454D 0 (1885).
72. C. S. Bradley, 1885US-312802D 0 (1885US-312802D 0).
73. , 1889US-409448D 0 (1889US-409448D 0).
74. H. H. Dow, "A zinc-bromide storage battery." *Trans. Am. Electrochem. Soc.*, **1**, 127 (1902)
75. S. F. Barnartt, David A., "Bromine-zinc secondary cells." *Journal of the Electrochemical Society*, **111**, 1201 (1964) 10.1149/1.2425960.
76. Up in a balloon, boys: French scientists solve the problem of aerial flight. Bound to the north pole possibilities of the balloon in warfare, science, and discovery made reasonable probabilities by recent developments in air ships under the auspices of the french government--five miles the limit in altitude to man's flight, in *The Washington Post (1877-1922)*, p. 21, Washington, D.C. (1894)
77. P. L. Howard, "The chlorine-zinc primary cell." *Journal of the Electrochemical Society*, **99**, C206 (1952) 10.1149/1.2779739.
78. Krebs photo albums: Chalais-meudon: N° 9 - france in profile august 9, 1884, in (2000)
79. J. Mcbreen, "Rechargeable zinc batteries." *Journal of Electroanalytical Chemistry*, **168**, 415 (1984) 10.1016/0368-1874(84)87113-0.
80. H. E. H. Cairns E.J., "Electrochemical power for transportation." in *Comprehensive treatise of electrochemistry* (1981) 10.1007/978-1-4615-6687-8_15
81. S. Gross, "Review of candidate batteries for electric vehicles." *Energy Conversion*, **15**, 95 (1972) 10.1016/0013-7480(76)90021-8.
82. C. J. Amato, A zinc-chloride battery - the missing link to a practical electric car in 1973 *International Automotive Engineering Congress and Exposition*, p. 11 (1973-02-01) 10.4271/730248.
83. V. K. Mcelheny, Utilities backing a \$7.6 million effort to develop new batteries for use in electric autos, in *New York Times (1923-)*, p. 47 (1977)
84. Development of the zinc-chlorine battery for utility applications, in *Interim Report, EM-1051, Parts 4-Appendixes Research Project 226-3*, ENERGY DEVELOPMENT ASSOCIATES A Gulf + Western Company (1979)
85. C. H. C. Chi, P. ; Symons, P. C., Modeling of zinc-chloride batteries for electric vehicles, in *Proc. Intersoc. Energy Convers. Eng. Conf.*, MODELINGOFZINCCHLORIDEBATTERIESFORELECTRICVEHICLES1979 Editor, p. 692 (1979)
86. R. G. B. Zalosh, S. N. ; Short, T. P. ; Tsui, R. K., Chlorine hazard evaluation for the zinc-chlorine electric vehicle battery, in,

- CHLORINEHAZARDEVALUATIONFORTHEZINCCHLORINEELECTRICVEHICLEBATTERY1980 Editor, p. 167 pp., Fac. Mutual Res. Corp. (1980)
87. T. R. Crompton, "Zinc – chlorine batteries." in *Small batteries: Volume 1 secondary cells*, p. 198, Macmillan Education UK. Palgrave, London, London (1982) 10.1007/978-1-349-04633-1_8.
 88. F. G. S. Will, H. S., "Performance analysis of zinc-bromine batteries in vehicle and utility applications." *Journal of Power Sources*, **5**, 173 (1980) 10.1016/0378-7753(80)80105-4.
 89. G. D. R. Clerici, M. ; Marchetto, M., Zinc-bromine storage battery for electric vehicles, in, ZINCBROMINESTORAGEBATTERYFORELECTRICVEHICLES1975 Editor, p. 167, Academic (1975)
 90. F. G. Will, "Zinc-bromine battery: Possible candidate for electric vehicles and load leveling." *Proc Intersoc Energy Convers Eng Conf 12th*, 250 (1977)
 91. M. J. O. Montgomery, J. E. ; Putt, R. A., Gould zinc-bromine battery-applicability for vehicle propulsion, in *Journal of the Electrochemical Society*, GOULDZINCBROMINEBATTERYAPPLICABILITYFORVEHICLEPROPULSION1978 Editor, p. C343 (1978)
 92. P. a. B. Malachesky, R. J. ; Einstein, H. ; Grimes, P. ; Kantner, E. ; Newby, K. ; Young, A., Design and performance of bipolar, flowing electrolye zinc-bromine batteries for electric vehicles, in *SAE Techni. Paper.*, DESIGNANDPERFORMANCEOFBIPOLARFLOWINGELECTROLYEZINCBROMINEBATTERIESFORELECTRICVEHICLES1982 Editor, SAE International (1982) 10.4271/820177.
 93. M. T. Futamata, Sachio, "Current status of battery developments for vehicular application. 5. Zinc-bromine battery." *Osaka Kogyo Gijutsu Shikensho Kiho*, **37**, 240 (1986)
 94. D. Scott, High-energy (zinc-bromine) battery, in *Popular Science*, HIGHENERGYZINCBROMINEBATTERY1987 Editor, p. 60, Bonnier Corporation, New York (1987)
 95. R. Oki, "Auxiliary battery charge control unit at complete discharge of zinc-bromine battery for electric car." 1990JP-0011566 1990-01-19 (1990JP-0011566 1990-01-19).
 96. J. E. Bolsted, P. ; Miles, R. ; Petersen, R. ; Yaccarino, K. ; Lott, S., Proof-of-concept zinc/bromine electric vehicle battery, in, PROOFOFCONCEPTZINCBROMINEELECTRICVEHICLEBATTERY1991 Editor, p. 98 pp., Johnson Controls, Inc. (1991)
 97. G. Tomazic, Zinc-bromine systems for ev-batteries-advances and future outlook, in *Proc.-Electrochem. Soc.*, ZINCBROMINESYSTEMSFORVVBATTERIESADVANCESANDFUTUREOUTLOOK1996 Editor, p. 212, Electrochemical Society (1996)
 98. C. W. Ponce De León, F. C., "Secondary batteries – zinc systems | zinc–bromine." in *Encyclopedia of electrochemical power sources*. Pp. , C. G. Dyer, Juergen; Moseley, Patrick; Ogumi, Zempachi; Rand, David ; Scrosati, Bruno Editor, p. 487, Elsevier, Amsterdam, NL (2009) 10.1016/B978-044452745-5.00856-X.
 99. D. H. Swan, B. Dickinson, M. Arikara and G. S. Tomazic, "Demonstration of a zinc bromine battery in an electric vehicle." *IEEE Aerosp Electron Syst Mag*, **9**, 20 (1994) 10.1109/62.282513.
 100. D. H. Swan, B. Dickinson, M. Arikara and M. Prabhu, "Construction and performance of a high voltage zinc bromine battery in an electric vehicle." in *Proceedings of the 10th Annual Battery Conference on Applications and Advances*, Anon Editor, p. 135, Piscataway, NJ, United States Long Beach, CA, USA (1995)
 101. K. Shin, J. H. Lee, J. Heo and H. T. Kim, "Current status and challenges for practical flowless zn–br batteries." *Curr. Opin. Electrochem.*, **32** (2022) 10.1016/j.coelec.2021.100898.
 102. R. Kim, H. G. Kim, G. Doo, C. Choi, S. Kim, J.-H. Lee, J. Heo, et al., "Ultrathin nafion-filled porous membrane for zinc/bromine redox flow batteries." *Scientific Reports (Nature Publisher Group)*, **7**, 1 (2017) 10.1038/s41598-017-10850-9.
 103. J. E. Wu, Q. Dai, H. M. Zhang and X. F. Li, "Recent development in composite membranes for flow batteries." *ChemSusChem*, **13**, 3805 (2020) 10.1002/cssc.202000633.
 104. R. Zito and H. Ardebili, *Energy storage: A new approach* (2019) 10.1002/9781119083979.
 105. Zbb energy raises usd 13m in public offering, in *SeeNews North America*, Sofia, Bulgaria (2014)
 106. Y. Yin, Z. Yuan and X. Li, "Rechargeable aqueous zinc-bromine batteries: An overview and future perspectives." *Phys. Chem. Chem. Phys.*, **23**, 26070 (2021) 10.1039/d1cp03987c.
 107. Segen Ltd.: 120kwh redflow zinc-bromine flow battery goes into operation at swansea university, in *News Bites - Private Companies*, Melbourne (2020)
 108. M. C. Wu, T. S. Zhao, L. Wei, H. R. Jiang and R. H. Zhang, "Improved electrolyte for zinc-bromine flow batteries." *J Power Sources*, **384**, 232 (2018) 10.1016/j.jpowsour.2018.03.006.

109. C. Ponce De León and F. C. Walsh, "Secondary batteries - zinc systems | zinc-bromine." in *Encyclopedia of electrochemical power sources*, p. 487, Elsevier (2009) 10.1016/B978-044452745-5.00856-X.
110. L. Kótai, I. Gács, S. Bálint, G. Lakatos, A. Angyal and R. N. Mehrotra, "A review on the oldest known gas-hydrate-the chemistry of chlorine hydrate." *Trends Inorg. Chem*, **13** (2012)
111. F. Mylius and R. Dietz, "Zinc chloride. Solubility of salts. Xiv." *Ber. Dtsch. chem. Ges.*, **38**, 921 (1905)
112. S. B. Pillai, R. J. Wilcox, B. G. Hillis, B. P. Losey and J. D. Martin, "Understanding the water-in-salt to salt-in-water characteristics across the zinc chloride: Water phase diagram." *J Phys Chem B*, **126**, 2265 (2022) 10.1021/acs.jpcc.1c10530.
113. R. Dietz, "Die löslichkeit der halogensalze des zinks und cadmiums. Studien über die löslichkeit der salze. Ii." *Berichte der deutschen chemischen Gesellschaft*, **32**, 90 (1899) 10.1002/cber.18990320118.
114. J. P. Simmons and W. F. Waldeck, "The system: Lithium bromate-water." *J. Am. Chem. Soc.*, **53**, 1725 (1931) 10.1021/ja01356a013.
115. J. J. Kessis, "The water-lithium bromide systems." *Bull. Soc. Chim. Fr.*, 48 (1965)
116. D. A. Boryta, "Solubility of lithium bromide in water between -5/ degrees and +100 degrees c (45 percent to 70 percent lithum bromide)." *J Chem Eng Data*, **15**, 142 (1970) 10.1021/je60044a030.
117. J. Patek and J. Klomfar, "Solid-liquid phase equilibrium in the systems of libr-h2o and licl-h2o." *Fluid Phase Equilibria*, **250**, 138 (2006) 10.1016/j.fluid.2006.09.005.
118. F. Nodon, "Making a constant electric battery or differential battery. Herstellung einer konstanten elektrischen batterie oder difflerential-batterie. ." DE44177D 0 (DE44177D 0).
119. F. Boisier and A. Lizarralde, "Accumulator to halogenated salt." NL34896D 01931FR-0735714D 1931-07-20 (NL34896D 01931FR-0735714D 1931-07-20).
120. F. Boisier and À. Lizarralde, "Accumulaæur à l'iode." BE389876D 0 (BE389876D 0).
121. F. Boisier and A. Lizarralde, "Halogenated salt storage battery." 1932FR-0043201D 1932-07-20 (1932FR-0043201D 1932-07-20).
122. "Improvements relating to electric accumulators." 1932GB-0001805 1932-01-20 (1932GB-0001805 1932-01-20).
123. G. Meunier, "Zinc-iodine accumulator." BE399499D 0 (BE399499D 0).
124. "Accumulator." 1931DE-B153736 1931-12-31 (1931DE-B153736 1931-12-31).
125. F. Maertens, "Iodine accumulator." BE406663D 0 (BE406663D 0).
126. J. Meunier, "Accumulateur électrique a l'iode." BE408021D 0 (BE408021D 0).
127. F. Hochwald, "Improvements in or relating to secondary cells." 1935GB-0000037 1935-01-01 (1935GB-0000037 1935-01-01).
128. Y. Yoda, H. Sugawa and K. Sugimoto, "Zinc-iodine storage battery." 1984JP-0192474 1984-09-17 (1984JP-0192474 1984-09-17).
129. H. Sugawa, K. Sugimoto and Y. Yoda, "Zinc-iodine secondary battery." 1985JP-0181659 1985-08-21 (1985JP-0181659 1985-08-21).
130. K. Sugimoto, Y. Yoda, S. Yoshida and H. Sugawa, "Dendrite preventing method for zinc-iodine secondary battery." 1986JP-0030642 1986-02-17 (1986JP-0030642 1986-02-17).
131. T. Y. Kanbara, T. ; Ikawa, H. ; Tagawa, T. ; Imai, H., "Porous, chemically stable, electrically conducting composites prepared by sintering mixtures of carbon and clay." *Journal of Materials Science Letters*, **6**, 1195 (1987) 10.1007/bf01729180.
132. J. Schmidt, "The zinc-iodine cell-an accumulator without metal electrodes." *Prax. Naturwiss., Chem.*, **38**, 32 (1989)
133. L. J. Yan, T. F. Liu, X. M. Zeng, L. Sun, X. H. Meng, M. Ling, M. Q. Fan, et al., "Multifunctional porous carbon strategy assisting high-performance aqueous zinc-iodine battery." *Carbon*, **187**, 145 (2022) 10.1016/j.carbon.2021.11.007.
134. W. Shang, Q. Li, F. Jiang, B. Huang, J. Song, S. Yun, X. Liu, et al., "Boosting zn||li2 battery's performance by coating a zeolite-based cation-exchange protecting layer." *Nano-Micro Lett.*, **14** (2022) 10.1007/s40820-022-00825-5.
135. D. Lin and Y. Li, "Recent advances of aqueous rechargeable zinc-iodine batteries: Challenges, solutions, and prospects." *Adv Mater*, **34**, 28 (2022) 10.1002/adma.202108856.

136. Z. Li, X. Wu, X. Yu, S. Zhou, Y. Qiao, H. Zhou and S. G. Sun, "Long-life aqueous zn-i₂ battery enabled by a low-cost multifunctional zeolite membrane separator." *Nano Lett.*, **22**, 2538 (2022) 10.1021/acs.nanolett.2c00460.
137. X. Jin, L. Song, C. Dai, Y. Xiao, Y. Han, X. Li, Y. Wang, et al., "A flexible aqueous zinc-iodine microbattery with unprecedented energy density." *Adv Mater* (2022) 10.1002/adma.202109450.
138. Y. P. Zou, T. T. Liu, Q. J. Du, Y. Y. Li, H. B. Yi, X. Zhou, Z. X. Li, et al., "A four-electron zn-i₂ aqueous battery enabled by reversible i⁻/i²⁺ conversion." *Nat. Commun.*, **12**, 11 (2021) 10.1038/s41467-020-20331-9.
139. F. Zhang, Q. Wang and Y. B. Tang, "Extended iodine chemistry: Toward high-energy-density aqueous zinc-ion batteries." *Matter*, **4**, 2637 (2021) 10.1016/j.matt.2021.06.030.
140. Y. Q. Yang, S. Q. Liang and J. Zhou, "Progress and prospect of the zinc-iodine battery." *Curr. Opin. Electrochem.*, **30**, 6 (2021) 10.1016/j.coelec.2021.100761.
141. J. Yang, Y. X. Song, Q. H. Liu and A. Tang, "High-capacity zinc-iodine flow batteries enabled by a polymer-polyiodide complex cathode." *J. Mater. Chem. A*, **9**, 16093 (2021) 10.1039/d1ta03905a.
142. F. Shakerihosseini, S. R. Daemi, D. Momodu, D. J. L. Brett, P. R. Shearing and E. P. L. Roberts, "Influence of flow field design on zinc deposition and performance in a zinc-iodide flow battery." *ACS Appl. Mater. Interfaces*, **13**, 41563 (2021) 10.1021/acsami.1c09770.
143. L. T. Ma, Y. R. Ying, S. M. Chen, Z. D. Huang, X. L. Li, H. T. Huang and C. Y. Zhi, "Electrocatalytic iodine reduction reaction enabled by aqueous zinc-iodine battery with improved power and energy densities." *Angew. Chem.-Int. Edit.*, **60**, 3791 (2021) 10.1002/anie.202014447.
144. Q. P. Jian, M. C. Wu, H. R. Jiang, Y. K. Lin and T. S. Zhao, "A trifunctional electrolyte for high-performance zinc-iodine flow batteries." *J Power Sources*, **484**, 229238 (2021) 10.1016/j.jpowsour.2020.229238.
145. C. J. Chen, Z. W. Li, Y. H. Xu, Y. F. An, L. Y. Wu, Y. Sun, H. J. Liao, et al., "High-energy density aqueous zinc-iodine batteries with ultra-long cycle life enabled by the zn₂ additive." *ACS Sustain. Chem. Eng.*, **9**, 13268 (2021) 10.1021/acssuschemeng.1c04481.
146. W. Li, K. Wang and K. Jiang, "A high energy efficiency and long life aqueous zn-i₂ battery." *J. Mater. Chem. A*, **8**, 3785 (2020) 10.1039/c9ta13081k.
147. Y. L. He, M. M. Liu and J. T. Zhang, "Rational modulation of carbon fibers for high-performance zinc-iodine batteries." *Adv. Sustain. Syst.*, **4**, 15 (2020) 10.1002/adsu.202000138.
148. C. X. Xie, H. M. Zhang, W. B. Xu, W. Wang and X. F. Li, "A long cycle life, self-healing zinc-iodine flow battery with high power density." *Angew. Chem.-Int. Edit.*, **57**, 11171 (2018) 10.1002/anie.201803122.
149. Y. Li, L. Liu, H. Li, F. Cheng and J. Chen, "Rechargeable aqueous zinc-iodine batteries: Pore confining mechanism and flexible device application." *Chem. Commun.*, **54**, 6792 (2018) 10.1039/c8cc02616e.
150. H. Zhang, Y. Cheng, Q. Lai, X. Li, X. Xi and C. Wang, "Zinc-iodine flow battery." 2014CN-0776231 2014-12-11 (2014CN-0776231 2014-12-11).
151. "Neutral zinc-iodine redox flow battery." 2017CN-1091359 2017-11-08 (2017CN-1091359 2017-11-08).
152. "Gel electrolyte and zinc-bromine or zinc-iodine single flow battery." 2019CN-1250755 2019-12-09 (2019CN-1250755 2019-12-09).
153. Y. Zhao, Y. Li, J. Mao, Z. Yi, N. Mubarak, Y. Zheng, J. K. Kim, et al., "Accelerating the dissolution kinetics of iodine with a cosolvent for a high-current zinc-iodine flow battery." *J. Mater. Chem. A* (2022) 10.1039/d2ta03195g.
154. L. Q. Zhang, M. J. Zhang, H. L. Guo, Z. H. Tian, L. F. Ge, G. J. He, J. J. Huang, et al., "A universal polyiodide regulation using quaternization engineering toward high value-added and ultra-stable zinc-iodine batteries." *Adv. Sci.*, **9**, 10 (2022) 10.1002/advs.202105598.
155. F. X. Wang, J. C. Tseng, Z. C. Liu, P. P. Zhang, G. Wang, G. B. Chen, W. X. Wu, et al., "A stimulus-responsive zinc-iodine battery with smart overcharge self-protection function." *Adv Mater*, **32**, 7 (2020) 10.1002/adma.202000287.
156. S. Kheawhom and W. Kao-Ian, "Rechargeable aqueous zinc-iodine cell." 2019WO-TH00070 2019-12-23 (2019WO-TH00070 2019-12-23).
157. X. L. Li, M. Li, Z. D. Huang, G. J. Liang, Z. Chen, Q. Yang, Q. Huang, et al., "Activating the i⁰/i⁻ redox couple in an aqueous i₂-zn battery to achieve a high voltage plateau." *Energy Environ. Sci.*, **14**, 407 (2021) 10.1039/d0ee03086d.

158. L. F. Arenas Martinez, "An electrochemical engineering approach to improvements in the zinc-cerium redox flow battery." Thesis, Ann Arbor (2017)
159. F. C. P. D. L. Walsh, Carlos ; Berlouis, Len ; Nikiforidis, George ; Arenas-Martinez, Luis F. ; Hodgson, David ; Hall, David, "The development of zn-ce hybrid redox flow batteries for energy storage and their continuing challenges." *Chempluschem*, **80**, 288 (2015) 10.1002/cplu.201402103.
160. Z. L. Xie, Qingchao ; Chang, Zhiwen ; Zhang, Xinbo, "The developments and challenges of cerium half-cell in zinc-cerium redox flow battery for energy storage." *Electrochimica Acta*, **90**, 695 (2013) 10.1016/j.electacta.2012.12.066.
161. L. Clarke Robert, B. Dougherty, S. Harrison, J. Millington Peter and S. Mohanta, "Cerium batteries." 2001WO-US41678 2001-08-102001US-10483951 2001-08-102002US-10483941 2002-02-122002US-10483953 2002-02-122002US-10483942 2002-02-122002US-10483952 2002-02-122002US-10484581 2002-02-122002AT-0719005T 2002-02-122002WO-US04748 2002-02-122002WO-US05145 2002-02-122002WO-US04740 2002-02-122002WO-US04749 2002-02-122002WO-US04738 2002-02-122002PT-0719005T 2002-02-122002ES-0717450T 2002-02-122002ES-0719005T 2002-02-122002EP-0719005 2002-02-122002EP-0709571 2002-02-122002EP-0717450 2002-02-122002DK-0719005 2002-02-122002DE-6038988 2002-02-122002DE-6026147 2002-02-122002AT-0717450T 2002-02-122003US-10418678 2003-04-172005US-11248638 2005-10-11 (2001).
162. X. Xie, F. Mushtaq, Q. Wang and W. A. Daoud, "The renaissance of the zn-ce flow battery: Dual-membrane configuration enables unprecedentedly high efficiency." *ACS Energy Lett.*, **7**, 3484 (2022) 10.1021/acsenerylett.2c01646.
163. O. K. Bingah and M. D. Pritzker, "Graphite felt modified with wo3, sno2, and binary wo3/sno2-mixtures as novel positive electrodes for cerium-based redox flow batteries." *Int. J. Energy Res.*, **46**, 4680 (2022) 10.1002/er.7463.
164. L. H. Thaller, Redox flow batteries, in *Journal of the Electrochemical Society*, REDOXFLOWBATTERIES1977 Editor, p. C278 (1977)
165. R. P. Hollandsworth and G. B. Adams, "Role of microcomputers in secondary battery development and testing." *Electrochem Soc, Inc, Fall Meet, Extended Abstr*, **79-2**, 254 (1979)
166. J. Remick Robert and G. P. Ang Peter, "Electrically rechargeable anionically active reduction-oxidation electrical storage-supply system." 1981US-06299977 1981-09-08 (1981US-06299977 1981-09-08).
167. R. Remick and E. Camara, Electrochemistry of the sulfide/polysulfide couple, in, Institute of Gas Technology, Chicago, IL (United States) (1983-07-01) 10.2172/5443566.
168. S. Licht, "An energetic medium for electrochemical storage utilizing the high aqueous solubility of potassium polysulfide." *J. Electrochem. Soc.*, **134**, 2137 (1987) 10.1149/1.2100838.
169. R. Zito, "Electrochemical energy storage and/or power delivery cell with ph control." 1993US-08128126 1993-09-291993ZA-0007283 1993-09-301993MY-0002065 1993-10-081995UA-0038276 1993-10-131993PH-0047005 1993-10-041996SG-0043831 1993-10-131993WO-GB02107 1993-10-131995SK-0000481 1993-10-131995RU-0109922 1993-10-131993PL-0308266 1993-10-131993NZ-0256709 1993-10-131994JP-0509757 1993-10-131995HU-0000843 1993-10-131993ES-0922593T 1993-10-131993EP-0922593 1993-10-131993EG-0000655 1993-10-131993DZ-0000113 1993-10-131993DK-0922593 1993-10-131993DE-6003179 1993-10-131995CZ-0000954 1993-10-131993CN-0119108 1993-10-131993CA-2145883 1993-10-131993BR-0007234 1993-10-131993AU-0051535 1993-10-131993AT-0922593T 1993-10-131993IL-0107236 1993-10-111995VN-1001083 1995-04-111995FI-0001815 1995-04-131995BG-0099562 1995-04-111995NO-0001377 1995-04-071995KR-7001483 1995-04-141996GR-0402078 1996-08-021998HK-0100168 1998-01-09 (1992).
170. R. Zito, "Electrochemical apparatus for energy storage and/or power delivery comprising multi-compartment cells." 1993US-08128117 1993-09-291993ZA-0007284 1993-09-301993MY-0002066 1993-10-081993TW-0108472 1993-10-171993IL-0107237 1993-10-111993WO-GB02110 1993-10-131994JP-0509760 1993-10-131993ES-0922596T 1993-10-131993EP-0922596 1993-10-131993EG-0000656 1993-10-131993DZ-0000112 1993-10-131993DK-0922596 1993-10-131993DE-6016387 1993-10-131993CN-0119107 1993-10-131993AU-0051538 1993-10-131993AT-0922596T 1993-10-131998GR-0400219 1998-02-041998HK-0106600 1998-06-25 (1993).
171. R. Zito Jr, "Storage battery having bromine positive active material." 1963US-04317507 1963-10-21 (1963US-04317507 1963-10-21).
172. R. Zito Jr, "Zinc-bromine secondary cell." 1965US-04484556 1965-09-02 (1965US-04484556 1965-09-02).

173. R. Zito, "Zinc-bromine battery with long term stability." 1982US-06441491 1982-11-151983AU-0021313 1983-11-141983JP-0212638 1983-11-141983GB-0030036 1983-11-101983EP-0306866 1983-11-101983CA-0440932 1983-11-101983ZA-0008458 1983-11-14 (1982US-06441491 1982-11-151983AU-0021313 1983-11-141983JP-0212638 1983-11-141983GB-0030036 1983-11-101983EP-0306866 1983-11-101983CA-0440932 1983-11-101983ZA-0008458 1983-11-14).
174. Regenesys utility scale energy storage, in (2004)
175. J. Morrissey Patrick, J. Mitchell Philip and E. Male Stewart, "Electrolyte rebalancing system." 1998GB-0015173 1998-07-132000SG-0074690 1999-07-022001CZ-0000106 1999-07-021999US-09743639 1999-07-021999AT-0929536T 1999-07-021999TW-0111869 1999-07-131999MY-0002929 1999-07-121999WO-GB02103 1999-07-022001SK-0000043 1999-07-021999PT-0929536T 1999-07-021999PL-0345548 1999-07-021999NZ-0509674 1999-07-022000JP-0559607 1999-07-021999IL-0140615 1999-07-022001HU-0004189 1999-07-021999GB-0015591 1999-07-021999ES-0929536T 1999-07-021999EP-0929536 1999-07-021999DK-0929536 1999-07-021999DE-6002922 1999-07-021999CN-0810393 1999-07-021999CA-2337038 1999-07-021999BR-0012065 1999-07-021999AU-0046326 1999-07-021999GB-0028344 1999-11-302000MY-0003012 2000-06-302002HU-0001565 2000-06-302000ES-0942239T 2000-06-302000EP-0942239 2000-06-302000DK-0942239 2000-06-302000DE-6006816 2000-06-302001CZ-0004611 2000-06-302000CN-0809866 2000-06-302000CA-2377927 2000-06-302000BR-0012126 2000-06-302000AU-0056943 2000-06-302000AT-0942239T 2000-06-302000IL-0146997 2000-06-302001SG-0081371 2000-06-302001JP-0508530 2000-06-302000US-10018531 2000-06-302000NZ-0516113 2000-06-302001RU-0134619 2000-06-302000WO-GB02536 2000-06-302001SK-0001932 2000-06-302000PT-0942239T 2000-06-302000PL-0363053 2000-06-302000GB-0016332 2000-07-032001IN-MN00021 2001-01-042001KR-7000521 2001-01-122001NO-0000182 2001-01-112001VN-1000136 2001-02-132001BG-0105245 2001-02-132001ZA-0010371 2001-12-182001VN-1001268 2001-12-272001BG-0106253 2001-12-202001IN-MN01586 2001-12-132001NO-0006388 2001-12-272002KR-7000017 2002-01-02 (1999-06-02).
176. J. Morrissey Patrick and E. Cooley Graham, "Methods of detecting the onset of colloid formation in particular sulfur precipitation." 1999GB-0013185 1999-06-072001SG-0074004 2000-06-072000AT-0937067T 2000-06-072000AU-0052358 2000-06-072000US-09980313 2000-06-072000BR-0011390 2000-06-072000WO-GB02206 2000-06-072001SK-0001750 2000-06-072000PT-0937067T 2000-06-072000PL-0351870 2000-06-072000NZ-0515862 2000-06-072001JP-0501363 2000-06-072000IL-0146763 2000-06-072002HU-0001563 2000-06-072000GB-0013869 2000-06-072000ES-0937067T 2000-06-072000EP-0937067 2000-06-072000DK-0937067 2000-06-072000DE-6001655 2000-06-072001CZ-0004336 2000-06-072000CN-0811278 2000-06-072000CA-2371067 2000-06-072001IN-MN01515 2001-11-292001ZA-0009795 2001-11-282001BG-0106166 2001-12-032001KR-7015715 2001-12-062001NO-0005905 2001-12-032001VN-1001188 2001-12-04 (1999-06-07).
177. E. Cooley Graham, E. Male Stewart, J. Mitchell Philip and I. a. N. Whyte, "Method of carrying out electrochemical reactions with an electrocatalyst." 1999GB-0001235 1999-01-202000WO-GB00128 2000-01-192000JP-0595393 2000-01-192000EP-0900702 2000-01-192000DK-0900702 2000-01-192000DE-6002036 2000-01-192000CA-2360969 2000-01-192000AU-0030630 2000-01-192000AT-0900702T 2000-01-192001NO-0003461 2001-07-12 (1999).
178. E. Cooley Graham, E. Male Stewart, J. Mitchell Philip and I. a. N. Whyte, "Method of carrying out electrochemical reactions with an electrocatalyst." 1999GB-0001235 1999-01-202000WO-GB00128 2000-01-192000JP-0595393 2000-01-192000EP-0900702 2000-01-192000DK-0900702 2000-01-192000DE-6002036 2000-01-192000CA-2360969 2000-01-192000AU-0030630 2000-01-192000AT-0900702T 2000-01-192001NO-0003461 2001-07-12 (1999-01-20).
179. S. Fletcher and J. Van Dijk Nicholas, "An electrode for the reduction of polysulfide species." 2002GB-0007214 2002-03-272004SG-0053849 2003-03-262003US-10508614 2003-03-262003MY-0001053 2003-03-252003WO-GB01316 2003-03-262003TW-0106813 2003-03-262003NZ-0535454 2003-03-262003JP-0581280 2003-03-262003EP-0708363 2003-03-262003CN-0807015 2003-03-262003CA-2480089 2003-03-262003AU-0212543 2003-03-262004ZA-0007663 2004-09-222004KR-7015350 2004-09-242004NO-0004521 2004-10-21 (2002).
180. B. Davidson, T. Calver, A. Price and D. Simchock, "Large-scale storage solution? Regenesys regenerative fuel cell." *Renewable energy world*, 3, 84 (2000)
181. I. N. D. Provided by Federal, Inc, Requesting proposals for completing tva's regenesys plant in columbus, mississippi, in, REQUESTINGPROPOSALSFORCOMPLETINGTVASREGENESYSPLANTINCOLUMBUSMISSISSIPPI2004 Editor, p. 1, Federal Information & News Dispatch, LLC, Washington (2004)

182. I. H. Grant, J. , Tva's regenesys energy storage project, in *IEEE Power-Engineering-Society Summer Meeting*, TVASREGENESYSENERGYSTORAGEPROJECT2002 Editor, p. 321, Ieee, Chicago, Il (2002) 10.1109/PESS.2002.1043242.
183. A. Ray, "Tva's public power institute (ppi): Tva board listening session on renewable energy." in (2008)https://tva.maripo.com/tva_ppi.htm.
184. P. Morrissey, "Regenesys: A new energy storage technology." *International Journal of Ambient Energy*, **21**, 213 (2000) 10.1080/01430750.2000.9675376.
185. Regenesys charges "giant battery", in *Tce*, REGENESYSCHARGESGIANTBATTERY2002 Editor, p. 16 (2002)
186. D. P. R. Scamman, G. W. ; Roberts, E. P. L., "Numerical modelling of a bromide-polysulphide redox flow battery part 1: Modelling approach and validation for a pilot-scale system." *Journal of Power Sources*, **189**, 1220 (2009) 10.1016/j.jpowsour.2009.01.071.
187. D. P. R. Scamman, Gavin W. ; Roberts, Edward P. L., "Numerical modelling of a bromide-polysulphide redox flow battery. Part 2: Evaluation of a utility-scale system." *Journal of Power Sources*, **189**, 1231 (2009) 10.1016/j.jpowsour.2009.01.076.
188. Rwe abandons regenesys project, in *The Guardian*, RWEABANDONSREGENESYSPROJECT2004 Editor, p. 9 (2004)
189. Z. H. Z. H. Z. P. Y. Baolian, Research on electrode materials and systems for sodium polysulfide/bromine flow energy storage batteries, in *2004 China Materials Research Conference*, RESEARCHONELECTRODEMATERIALSANDSYSTEMSFORSODIUMPOLYSULFIDEBROMINEFLOWENERGYSTORAGEBATTERIES2004 Editor, p. 7, Beijing, China (2004)
190. P. Z. Zhao, Huamin ; Zhou, Hantao ; Yi, Baolian, "Nickel foam and carbon felt applications for sodium poly sulfide/bromine redox flow battery electrodes." *Electrochimica Acta*, **51**, 1091 (2005) 10.1016/j.electacta.2005.06.008.
191. H. Z. Zhou, Huamin ; Zhao, Ping ; Yi, Baolian, "Novel cobalt coated carbon felt as high performance negative electrode in sodium polysulfide/bromine redox flow battery." *Electrochemistry (Tokyo, Jpn.)*, **74**, 296 (2006) 10.5796/electrochemistry.74.296.
192. H. Z. Zhou, Huamin ; Zhao, Ping ; Yi, Baolian, "A comparative study of carbon felt and activated carbon based electrodes for sodium polysulfide/bromine redox flow battery." *Electrochimica Acta*, **51**, 6304 (2006) 10.1016/j.electacta.2006.03.106.
193. Z. Hantao, "Study of sodium polysulfide/bromine flow energy storage batteries." Thesis (2006)
194. I. E. L. Stephens, C. Ducati and D. J. Fray, "Correlating microstructure and activity for polysulfide reduction and oxidation at ws2 electrocatalysts." *Journal of the Electrochemical Society*, **160**, A757 (2013) 10.1149/2.027306jes.
195. C. B. Bruneau, Yu-Jia ; Goenaga, Gabriel ; Zawodzinski, Tom, Catalyst study and characterization for a polysulfide bromine redox flow battery, in *Abstracts, 66th Southeast Regional Meeting of the American Chemical Society, Nashville, TN, United States, October 16-19*, CATALYSTSTUDYANDCHARACTERIZATIONFORAPOLYSULFIDEBROMINEREDOXFLOWBATTERY2014 Editor, p. SERMACS, American Chemical Society (2014)
196. L. N. W. Wang, X. F. ; Liu, J. Y. ; Yang, H. ; Fu, C. M. ; Xia, Y. Y. ; Liu, T. X., "A rechargeable metal-free full-liquid sulfur-bromine battery for sustainable energy storage." *Journal of Materials Chemistry A*, **6**, 20737 (2018) 10.1039/c8ta07951j.
197. M. M. Gross and A. Manthiram, "Long-life polysulfide-polyhalide batteries with a mediator-ion solid electrolyte." *Acs Applied Energy Materials*, **2**, 3445 (2019) 10.1021/acsaem.9b00253.
198. W. Kangro Dr, "Method for storing electrical energy." 1949DE-P047135 1949-06-28 (1949).
199. W. Kangro Dr, "Method for storing electrical energy in liquids." 1954DE-K022841 1954-07-14 (1954).
200. W. Kangro and H. Pieper, "Zur frage der speicherung von elektrischer energie in flüssigkeiten." *Electrochim Acta*, **7**, 435 (1962) 10.1016/0013-4686(62)80032-2.
201. R. F. Savinell, C. C. Liu, S. H. Chiang, J. F. Coetzee and R. T. Galasco, "Investigation of a parallel plate iron-titanium redox electrochemical cell." *Proc Electrochem Soc*, **79-1**, 468 (1979)
202. R. F. Gahn, N. H. Hagedorn and J. S. Ling, "Single cell performance studies on the fe/cr redox energy storage system using mixed reactant solutions at elevated temperature." *NASA Technical Memorandum* (1983)

203. P. S. Fedkiw and R. W. Watts, "A mathematical-model for the iron chromium redox battery." *J Electrochem Soc*, **131**, 701 (1984) 10.1149/1.2115676.
204. K. Sawai, I. Tari, T. Ohzuku and T. Hirai, "On the polarization characteristics of the fe/cr redox flow cell." *Mem Fac Eng Osaka City Univ*, **29**, 139 (1988)
205. K. Sawai, I. Tari, T. Ohzuku and T. Hirai, "Characterization of fe/cr redox flow cell having a 2-tank and a 4-tank system." *Denki Kagaku*, **57**, 511 (1989)
206. M. Lopezatalaya, G. Codina, J. R. Perez, J. L. Vazquez, A. Aldaz and M. A. Climent, "Behavior of the cr(iii)/cr(ii) reaction on gold graphite-electrodes - application to redox flow storage cell." *Journal of Power Sources*, **35**, 225 (1991) 10.1016/0378-7753(91)80108-a.
207. G. Codina and A. Aldaz, "Scale-up studies of an fe/cr redox flow battery based on shunt current analysis." *Journal of Applied Electrochemistry*, **22**, 668 (1992) 10.1007/bf01092617.
208. M. Lopezatalaya, G. Codina, J. R. Perez, J. L. Vazquez and A. Aldaz, "Optimization studies on a fe/cr redox flow battery." *Journal of Power Sources*, **39**, 147 (1992) 10.1016/0378-7753(92)80133-v.
209. A. Negishi, H. Kaneko and K. Nozaki, "Characterization of carbon electrode materials for flow-type batteries." *Denki Kagaku*, **61**, 1442 (1993) 10.5796/electrochemistry.61.1442.
210. G. Codina, J. R. Perez, M. Lopezatalaya, J. L. Vazquez and A. Aldaz, "Development of a 0.1 kw power accumulation pilot-plant based on an fe/cr redox flow battery .1. Considerations on flow-distribution design." *Journal of Power Sources*, **48**, 293 (1994) 10.1016/0378-7753(94)80026-x.
211. C. Y. Sun and H. Zhang, "Review of the development of first-generation redox flow batteries: Iron-chromium system." *ChemSusChem*, **15**, 15 (2022) 10.1002/cssc.202101798.
212. J. P. Du Toit, H. M. Krieg, N. Mans and D. J. Van Der Westhuizen, "Uv-vis spectrophotometric analytical technique for monitoring fe²⁺ in the positive electrolyte of an icrfb." *Journal of Power Sources*, **553**, 11 (2023) 10.1016/j.jpowsour.2022.232178.
213. Y. X. Wang, K. Geng, Q. Tan, T. G. Guo, X. Hu, H. Y. Tang, L. Liu, et al., "Highly ion selective proton exchange membrane based on sulfonated polybenzimidazoles for iron-chromium redox flow battery." *ACS Appl. Ener. Mat.*, **10** (2022) 10.1021/acsaem.2c03471.
214. Y. K. Zeng, T. S. Zhao, L. An, X. L. Zhou and L. Wei, "A comparative study of all-vanadium and iron-chromium redox flow batteries for large-scale energy storage." *J Power Sources*, **300**, 438 (2015) 10.1016/j.jpowsour.2015.09.100.
215. Y. K. Zeng, X. L. Zhou, L. An, L. Wei and T. S. Zhao, "A high-performance flow-field structured iron-chromium redox flow battery." *J Power Sources*, **324**, 738 (2016) 10.1016/j.jpowsour.2016.05.138.
216. S. Lacey, "Enervault nears completion of its first commercial-scale flow battery: The company says it's prepared to beat doe's cost targets for redox flow batteries." in (2014-01-09)<https://www.greentechmedia.com/articles/read/enervault-nears-completion-of-its-first-commercial-scale-flow-battery>.
217. K. E. Rodby, M. L. Perry and F. R. Brushett, "Assessing capacity loss remediation methods for asymmetric redox flow battery chemistries using leveled cost of storage." *J Power Sources*, **506** (2021) 10.1016/j.jpowsour.2021.230085.
218. Q. Xu, X. Y. Chen, S. Y. Wang, C. Guo, Y. C. Niu, R. G. Zuo, Z. J. Yang, et al., "The recycling of waste per-fluorinated sulfonic acid for reformulation and membrane application in iron-chromium redox flow batteries." *Energies*, **15**, 10 (2022) 10.3390/en15228717.
219. C. S. Sun, Chuanyu ; Zhang, Huan ; Zhang, Huan, "Review of the development of first-generation redox flow batteries: Iron-chromium system." *Chemsuschem*, **15**, e202101798 (2022) 10.1002/cssc.202101798.
220. L. Qiao, S. M. Liu, M. L. Fang, M. J. Yang and X. K. Ma, "A composite membrane with high stability and low cost specifically for iron-chromium flow battery." *Polymers*, **14**, 14 (2022) 10.3390/polym14112245.
221. N. Mans, H. Krieg and D. Van Der Westhuizen, "The effect of electrolyte composition on single-cell iron-chromium flow battery performance." *SSRN Electronic Journal* (2022) 10.2139/ssrn.4246727.
222. C. T. C. Wan, K. E. Rodby, M. L. Perry, Y. M. Chiang and F. R. Brushett, "Hydrogen evolution mitigation in iron-chromium redox flow batteries via electrochemical purification of the electrolyte." *Journal of Power Sources*, **554**, 10 (2023) 10.1016/j.jpowsour.2022.232248.
223. Y. Su, H. L. Ren, S. Zhao, N. Chen, X. M. Wang, Y. X. Zhao, Y. Bai, et al., "Improved performance of iron-chromium flow batteries using sno₂-coated graphite felt electrodes." *Ceramics International* (2022) 10.1016/j.ceramint.2022.10.274.

224. Y. Su, N. Chen, H. L. Ren, L. L. Guo, Z. Li and X. M. Wang, "Preparation and properties of indium ion modified graphite felt composite electrode." *Front. Chem.*, **10** (2022) 10.3389/fchem.2022.899287.
225. B. H. Robb, S. E. Waters, J. D. Saraidaridis and M. P. Marshak, "Realized potential as neutral pH flow batteries achieve high power densities." *Cell Reports Physical Science*, **3**, 101118 (2022) 10.1016/j.xcrp.2022.101118.
226. "List of Enervault's 4 funding rounds totaling \$26.3m." in (2012)https://www.crunchbase.com/search/funding_rounds/field/organizations/funding_total/enervault.
227. C. Horne, LinkedIn profile, in (2008-2015)
228. J. Shepard, "Enervault looking for new ownership." in (2015-04-14)<https://eepower.com/news/enervault-looking-for-new-ownership/#>.
229. E. Wesoff, "Flow battery startup Enervault is 'restructuring' after failure to gain needed funding." in (2015-04-13)<https://www.greentechmedia.com/articles/read/flow-battery-startup-enervault-is-restructuring-after-failure-to-gain-nee>.
230. E. Wesoff, "Flow battery startup Enervault files for assignment before creditors: It's over for the VC-funded energy storage company." in (2015-06-15)<https://www.greentechmedia.com/articles/read/flow-battery-startup-enervault-files-for-assignment-before-creditors>.
231. C. H. R. Bae, E. P. L. ; Dryfe, R. A. W., "Chromium redox couples for application to redox flow batteries." *Electrochimica Acta*, **48**, 279 (2002) 10.1016/s0013-4686(02)00649-7.
232. X. Bin, "Electrochemical property of chromium battery." *Chinese Journal of Power Sources* (2007)
233. L. Dan, "Study on the electrical property of all-chromium flow battery." *Chinese Battery Industry* (2007)
234. W.-Z. Huang, D. Li, S.-T. Zhang, L.-J. Li, J.-L. Lei and B. Xiang, "Electrochemical property of chromium battery." *Dianyuan Jishu*, **31**, 906 (2007)
235. S.-T. Zhang, R. Zhang and D. Li, "Study on the electrical property of all-chromium flow battery." *Dianchi Gongye*, **12**, 225 (2007)
236. Q. Liu, A. A. Shinkle, Y. Li, C. W. Monroe, L. T. Thompson and A. E. S. Sleightholme, "Non-aqueous chromium acetylacetonate electrolyte for redox flow batteries." *Electrochem. Commun.*, **12**, 1634 (2010) 10.1016/j.elecom.2010.09.013.
237. C. Bae, E. P. L. Roberts, M. H. Chakrabarti and M. Saleem, "All-chromium redox flow battery for renewable energy storage." *Int. J. Green Energy*, **8**, 248 (2011) 10.1080/15435075.2010.549598.
238. E. R. Sum, M. ; Skyllas-Kazacos, M., "Investigation of the vanadium(v)/vanadium(iv) system for use in the positive half-cell of a redox battery." *Journal of Power Sources*, **16**, 85 (1985) 10.1016/0378-7753(85)80082-3.
239. E. S.-K. Sum, M., "A study of the vanadium(ii)/vanadium(iii) redox couple for redox flow cell applications." *Journal of Power Sources*, **15**, 179 (1985) 10.1016/0378-7753(85)80071-9.
240. M. Rychcik and M. Skyllas-Kazacos, "Evaluation of electrode materials for vanadium redox cell." *J Power Sources*, **19**, 45 (1987) 10.1016/0378-7753(87)80006-X.
241. M. Rychcik and M. Skyllas-Kazacos, "Characteristics of a new all-vanadium redox flow battery." *J Power Sources*, **22**, 59 (1988) 10.1016/0378-7753(88)80005-3.
242. M. Skyllas-Kazacos, M. Rychcik and G. Robins Robert, "All vanadium redox battery." 1986AU-0055562 1986-04-02.
243. M. Skyllas-Kazacos, "All-vanadium redox battery and additives." 1988WO-AU00472 1988-12-09 1989AU-0028153 1989-12-09.
244. M. Skyllas-Kazacos, M. Kazacos and C. Mcdermott Rodney John, "Vanadium charging cell and vanadium dual battery system." 1989AU-0028152 1989-12-09.
245. M. Kazacos and S. Kazacos Maria, "High energy density vanadium electrolyte solutions, methods of preparation thereof and all-vanadium redox cells and batteries containing high energy vanadium electrolyte solutions." 1996AT-0911853T 1996-05-03 1996AU-0054914 1996-05-03 1996US-08945869 1996-05-03 1996WO-AU00268 1996-05-03 1996NZ-0306364 1996-05-03 1996ES-0911853T 1996-05-03 1996EP-0911853 1996-05-03 1996DE-6030298 1996-05-03 1996CA-2220075 1996-05-03 1998HK-0110321 1998-08-31 2002US-10226751 2002-08-22.

246. G. Kear, A. A. Shah and F. C. Walsh, "Development of the all-vanadium redox flow battery for energy storage: A review of technological, financial and policy aspects." *International Journal of Energy Research*, **36**, 1105 (2012) 10.1002/er.1863.
247. P. Costamagna and S. Srinivasan, "Quantum jumps in the pemfc science and technology from the 1960s to the year 2000 part i. Fundamental scientific aspects." *J. Power Sources*, **102**, 242 (2001) 10.1016/s0378-7753(01)00807-2.
248. P. Costamagna and S. Srinivasan, "Quantum jumps in the pemfc science and technology from the 1960s to the year 2000 part ii. Engineering, technology development and application aspects." *J. Power Sources*, **102**, 253 (2001) 10.1016/s0378-7753(01)00808-4.
249. E. Antolini, "Recent developments in polymer electrolyte fuel cell electrodes." *J. Appl. Electrochem.*, **34**, 563 (2004) 10.1023/B:JACH.0000021923.67264.bb.
250. B. Scrosati and J. Garche, "Lithium batteries: Status, prospects and future." *J Power Sources*, **195**, 2419 (2010) 10.1016/j.jpowsour.2009.11.048.
251. F. Schipper and D. Aurbach, "A brief review: Past, present and future of lithium ion batteries." *Russ J Electrochem*, **52**, 1095 (2016) 10.1134/s1023193516120120.
252. M. Winter, B. Barnett and K. Xu, "Before li ion batteries." *Chem. Rev.*, **118**, 11433 (2018) 10.1021/acs.chemrev.8b00422.
253. M. V. Reddy, A. Mauger, C. M. Julien, A. Paoletta and K. Zaghib, "Brief history of early lithium-battery development." *Materials*, **13**, 9 (2020) 10.3390/ma13081884.
254. M. Skyllas-Kazacos, G. Kazacos, G. Poon and H. Verseema, "Recent advances with unsw vanadium-based redox flow batteries." *Int. J. Energy Res.*, **34**, 182 (2010) 10.1002/er.1658.
255. P. Alotto, M. Guarnieri and F. Moro, "Redox flow batteries for the storage of renewable energy: A review." *Renewable Sustainable Energy Rev*, **29**, 325 (2014) 10.1016/j.rser.2013.08.001.
256. Z. B. Huang, A. L. Mu, L. X. Wu and H. Wang, "Vanadium redox flow batteries: Flow field design and flow rate optimization." *J. Energy Storage*, **45**, 14 (2022) 10.1016/j.est.2021.103526.
257. M. Kazacos and M. Skyllas-Kazacos, "Performance-characteristics of carbon plastic electrodes in the all-vanadium redox cell." *Journal of the Electrochemical Society*, **136**, 2759 (1989) 10.1149/1.2097588.
258. M. Skyllas-Kazacos, D. Kasherman, D. R. Hong and M. Kazacos, "Characteristics and performance of 1 kw unsw vanadium redox battery." *J Power Sources*, **35**, 399 (1991) 10.1016/0378-7753(91)80058-6.
259. F. Xing, T. Liu, Y. B. Yin, R. Bi, Q. Zhang, L. K. Yin and X. F. Li, "Highly active hollow porous carbon spheres@graphite felt composite electrode for high power density vanadium flow batteries." *Adv. Funct. Mater.*, **32**, 9 (2022) 10.1002/adfm.202111267.
260. J. Egerer, P. Y. Oei and C. Lorenz, "Renewable energy sources as the cornerstone of the german energiewende." in *Energiewende "made in germany": Low carbon electricity sector reform in the european context*, p. 141, Springer International Publishing (2018) 10.1007/978-3-319-95126-3_6.
261. L. Perry Michael, "Flow battery with interdigitated flow field." US9166243 (2009-12-18).
262. D. S. Aaron, Q. Liu, Z. Tang, G. M. Grim, A. B. Papandrew, A. Turhan, T. A. Zawodzinski, et al., "Dramatic performance gains in vanadium redox flow batteries through modified cell architecture." *J Power Sources*, **206**, 450 (2012) 10.1016/j.jpowsour.2011.12.026.
263. M. Kapoor and A. Verma, "Technical benchmarking and challenges of kilowatt scale vanadium redox flow battery." *Wiley Interdiscip. Rev. Energy Environ.*, **17** (2022) 10.1002/wene.439.
264. G. Aparicio-Mauricio, F. A. Rodriguez, J. J. H. Pijpers, M. R. Cruz-Diaz and E. P. Rivero, "Cfd modeling of residence time distribution and experimental validation in a redox flow battery using free and porous flow." *J. Energy Storage*, **29**, 12 (2020) 10.1016/j.est.2020.101337.
265. A. A. Wong, S. M. Rubinstein and M. J. Aziz, "Direct visualization of electrochemical reactions and heterogeneous transport within porous electrodes in operando by fluorescence microscopy." *Cell Rep. Phys. Sci.*, **2**, 13 (2021) 10.1016/j.xcrp.2021.100388.
266. M. Van Der Heijden, R. Van Gorp, M. A. Sadeghi, J. Gostick and A. Forner-Cuenca, "Assessing the versatility and robustness of pore network modeling to simulate redox flow battery electrode performance." *Journal of the Electrochemical Society*, **169**, 18 (2022) 10.1149/1945-7111/ac5e46.
267. M. D. R. Kok, A. Khalifa and J. T. Gostick, "Multiphysics simulation of the flow battery cathode: Cell architecture and electrode optimization." *J Electrochem Soc*, **163**, A1408 (2016) 10.1149/2.1281607jes.

268. L. Li, S. Kim, W. Wang, M. Vijayakumar, Z. Nie, B. Chen, J. Zhang, et al., "A stable vanadium redox-flow battery with high energy density for large-scale energy storage." *Adv. Energy Mater.*, **1**, 394 (2011) 10.1002/aenm.201100008.
269. Y. Yang, Y. Zhang, L. Tang, T. Liu, J. Huang, S. Peng and X. Yang, "Investigations on physicochemical properties and electrochemical performance of sulfate-chloride mixed acid electrolyte for vanadium redox flow battery." *J Power Sources*, **434** (2019) 10.1016/j.jpowsour.2019.226719.
270. N. Roznyatovskaya, J. Noack, H. Mild, M. Fühl, P. Fischer, K. Pinkwart, J. Tübke, et al., "Vanadium electrolyte for all-vanadium redox-flow batteries: The effect of the counter ion." *Batteries*, **5** (2019) 10.3390/batteries5010013.
271. S. H. Saravi, S. Honarparvar and C. C. Chen, "Thermodynamic modeling of hcl-h₂o binary system with symmetric electrolyte nrtl model." *J. Chem. Thermodyn.*, **125**, 159 (2018) 10.1016/j.jct.2018.05.024.
272. A. H. Whitehead, in (2022)
273. A. Ishihara, I. Satoshi, M. Takeuchi, D. Naohiro and K. Ueno, "Carbon electrode material for vanadium redox flow battery." 2004JP-0342527 2004-11-26 (2004JP-0342527 2004-11-26).
274. S. Liu, K. Huang, Q. Zhang, R. Chen, X. Shi, H. Li, B. I. N. Huang, et al., "Electrode materials and all-vanadium redox flow battery containing electrode materials." 2009CN-0162904 2009-08-19 (2009CN-0162904 2009-08-19).
275. J. Zhang, R. An, X. Wang, J. I. E. Ma, S. Liu, F. An and X. Yi, "Composite carbon electrode for all-vanadium flow battery and preparation method thereof." 2013CN-0671295 2013-12-12 (2013CN-0671295 2013-12-12).
276. H. Yang, C. H. Hung, S. P. Wang and I. L. Chiang, "Graphite felt with vapor grown carbon fibers as electrodes for vanadium redox flow batteries." *Rare Met.*, **30**, 1 (2011) 10.1007/s12598-011-0226-4.
277. G. J. Wei, J. G. Liu, H. Zhao and C. W. Yan, "Electrospun carbon nanofibres as electrode materials toward vo²⁺/vo²⁺ redox couple for vanadium flow battery." *J Power Sources*, **241**, 709 (2013) 10.1016/j.jpowsour.2013.05.008.
278. A. Fetyan, I. Derr, M. K. Kayarkatte, J. Langner, D. Bernsmeier, R. Kraehnert and C. Roth, "Electrospun carbon nanofibers as alternative electrode materials for vanadium redox flow batteries." *ChemElectroChem*, **2**, 2055 (2015) 10.1002/celec.201500284.
279. K. J. Kim, M. S. Park, Y. J. Kim, J. H. Kim, S. X. Dou and M. Skyllas-Kazacos, "A technology review of electrodes and reaction mechanisms in vanadium redox flow batteries." *Journal of Materials Chemistry A*, **3**, 16913 (2015) 10.1039/c5ta02613j.
280. C. Busacca, O. Di Blasi, G. Giacoppo, N. Briguglio, V. Antonucci and A. Di Blasi, "High performance electrospun nickel manganite on carbon nanofibers electrode for vanadium redox flow battery." *Electrochim Acta*, **355**, 9 (2020) 10.1016/j.electacta.2020.136755.
281. A. Di Blasi, C. Busacca, O. Di Blasia, N. Briguglio, G. Squadrito and V. Antonucci, "Synthesis of flexible electrodes based on electrospun carbon nanofibers with mn₃o₄ nanoparticles for vanadium redox flow battery application." *Appl. Energy*, **190**, 165 (2017) 10.1016/j.apenergy.2016.12.129.
282. C. Xu, X. F. Li, T. Liu and H. M. Zhang, "Design and synthesis of a free-standing carbon nano-fibrous web electrode with ultra large pores for high-performance vanadium flow batteries." *RSC Adv.*, **7**, 45932 (2017) 10.1039/c7ra07365h.
283. C. Xu, X. F. Yang, X. F. Li, T. Liu and H. M. Zhang, "Ultrathin free-standing electrospun carbon nanofibers web as the electrode of the vanadium flow batteries." *J. Energy Chem.*, **26**, 730 (2017) 10.1016/j.jechem.2017.03.005.
284. G. H. He, Y. H. Song, S. L. Chen and L. Wang, "Porous carbon nanofiber mats from electrospun polyacrylonitrile/polymethylmethacrylate composite nanofibers for supercapacitor electrode materials." *J Mater Sci*, **53**, 9721 (2018) 10.1007/s10853-018-2277-5.
285. J. Sun, L. Zeng, H. R. Jiang, C. Y. H. Chao and T. S. Zhao, "Formation of electrodes by self-assembling porous carbon fibers into bundles for vanadium redox flow batteries." *J Power Sources*, **405**, 106 (2018) 10.1016/j.jpowsour.2018.10.035.
286. A. Fetyan, J. Schneider, M. Schnucklake, G. A. El-Nagar, R. Banerjee, N. Bevilacqua, R. Zeis, et al., "Comparison of electrospun carbon-carbon composite and commercial felt for their activity and electrolyte utilization in vanadium redox flow batteries." *ChemElectroChem*, **6**, 6 (2019) 10.1002/celec.201801706.

287. Z. X. He, M. M. Li, Y. H. Li, L. Wang, J. Zhu, W. Meng, C. C. Li, et al., "Electrospun nitrogen-doped carbon nanofiber as negative electrode for vanadium redox flow battery." *Appl Surf Sci*, **469**, 423 (2019) 10.1016/j.apsusc.2018.10.220.
288. Z. X. He, M. M. Li, Y. H. Li, C. C. Li, Z. Yi, J. Zhu, L. Dai, et al., "ZrO₂ nanoparticle embedded carbon nanofibers by electrospinning technique as advanced negative electrode materials for vanadium redox flow battery." *Electrochim Acta*, **309**, 166 (2019) 10.1016/j.electacta.2019.04.100.
289. M. H. Jing, Z. Y. Xu, D. W. Fang, X. Z. Fan, J. G. Liu and C. W. Yan, "Anchoring effect of the partially reduced graphene oxide doped electrospun carbon nanofibers on their electrochemical performances in vanadium flow battery." *J Power Sources*, **425**, 94 (2019) 10.1016/j.jpowsour.2019.04.003.
290. M. D. R. Kok, R. Jervis, P. R. Shearing and J. T. Gostick, Fluid transport properties from 3d tomographic images of electrospun carbon electrodes for flow batteries, in *Symposium on Plasma Nano Science and Technology held during the 231st Meeting of the Electrochemical-Society (ECS)*, p. 129, Electrochemical Soc Inc, New Orleans, LA (2017) 10.1149/07711.0129ecst.
291. M. Schnucklake, M. Cheng, M. Maleki and C. Roth, "A mini-review on decorating, templating of commercial and electrospinning of new porous carbon electrodes for vanadium redox flow batteries." *J. Phys-Mater.*, **4**, 18 (2021) 10.1088/2515-7639/abf1a9.
292. Z. H. Zhang, B. F. Bai, L. Zeng, L. Wei and T. S. Zhao, "Aligned electrospun carbon nanofibers as electrodes for vanadium redox flow batteries." *Energy Technol.*, **7**, 8 (2019) 10.1002/ente.201900488.
293. L. Zeng, J. Sun, T. S. Zhao, Y. X. Ren and L. Wei, "Balancing the specific surface area and mass diffusion property of electrospun carbon fibers to enhance the cell performance of vanadium redox flow battery." *Int. J. Hydrog. Energy*, **45**, 12565 (2020) 10.1016/j.ijhydene.2020.02.177.
294. V. S. Daniel'-Bek, "On the question of the polarization of porous electrodes. 1. On the current distribution inside the electrode (in russ.)." *Zh. Fiz. Khim.*, **22**, 697 (1948)
295. J. J. Coleman, "Distribution of current in porous electrodes." *J Electrochem Soc*, **98**, 26 (1951) 10.1149/1.2778099.
296. O. S. Ksenzhek and V. V. Stender, *Doklady Akad. Nauk S.S.S.R.*, **106**, 487 (1956)
297. O. S. Ksenzhek and V. V. Stender, *Doklady Akad. Nauk S.S.S.R.*, **107**, 280 (1956)
298. O. S. Ksenzhek and V. V. Stender, *Zhur. Priklad. Khim.*, **32**, 110 (1959)
299. J. Euler and W. Nonnenmacher, "Stromverteilung in porösen elektroden." *Electrochim Acta*, **2**, 268 (1960) 10.1016/0013-4686(60)80025-4.
300. J. S. Newman and C. W. Tobias, "Theoretical analysis of current distribution in porous electrodes." *J Electrochem Soc*, **109**, 1183 (1962) 10.1149/1.2425269.
301. J. Newman and K. E. Thomas-Alyea, *Electrochemical systems. 3rd edition.*, John Wiley & Sons (2012)
302. T. Zou, L. J. Luo, Y. W. Liao, P. Y. Wang, J. Zhang and L. H. Yu, "Study on operating conditions of household vanadium redox flow battery energy storage system." *J. Energy Storage*, **46**, 8 (2022) 10.1016/j.est.2021.103859.
303. B. M. Sivakumar, V. Prabhakaran, K. Duanmu, E. Thomsen, B. Berland, N. Gomez, D. Reed, et al., "Long-term structural and chemical stability of carbon electrodes in vanadium redox flow battery." *ACS Appl. Ener. Mat.*, **4**, 6074 (2021) 10.1021/acsaem.1c00912.
304. S. Tsushima and T. Suzuki, "Modeling and simulation of vanadium redox flow battery with interdigitated flow field for optimizing electrode architecture." *J Electrochem Soc*, **167**, 11 (2020) 10.1149/1945-7111/ab6dd0.
305. J. M. Jeong, K. I. Jeong, J. H. Oh, Y. S. Chung and S. S. Kim, "Stacked carbon paper electrodes with pseudo-channel effect to improve flow characteristics of electrolyte in vanadium redox flow batteries." *Appl. Mater. Today*, **24**, 9 (2021) 10.1016/j.apmt.2021.101139.
306. S. Yadav, M. D. R. Kok, A. Forner-Cuenca, K. M. Tenny, Y. M. Chiang, F. R. Brushett, R. Jervis, et al., "Fabrication of high surface area ribbon electrodes for use in redox flow batteries via coaxial electrospinning." *J. Energy Storage*, **33**, 7 (2021) 10.1016/j.est.2020.102079.
307. R. Van Gorp, M. Van Der Heijden, M. A. Sadeghi, J. Gostick and A. F. Cuenca, "Starting from the bottom: Coupling a genetic algorithm and pore network model for porous electrode design." *Chemrxiv* (2022)
308. J. Sun, M. C. Wu, X. Z. Fan, Y. H. Wan, C. Y. H. Chao and T. S. Zhao, "Aligned microfibers interweaved with highly porous carbon nanofibers: A novel electrode for high-power vanadium redox flow batteries." *Energy Storage Mater.*, **43**, 30 (2021) 10.1016/j.ensm.2021.08.034.

309. M. Cecchetti, M. Messaggi, A. Donazzi, A. Facibeni, V. Russo, C. S. Casari, A. Li Bassi, et al., "A combined morphological and electrochemical characterization of carbon electrodes in vanadium redox flow batteries: Insights into positive and negative electrode performance." *Electrochim Acta*, **329**, 10 (2020) 10.1016/j.electacta.2019.135143.
310. J. Sun, H. R. Jiang, M. C. Wu, X. Z. Fan, C. Y. H. Chao and T. S. Zhao, "Aligned hierarchical electrodes for high-performance aqueous redox flow battery." *Appl. Energy*, **271**, 10 (2020) 10.1016/j.apenergy.2020.115235.
311. J. Sun, H. R. Jiang, M. C. Wu, X. Z. Fan, C. Y. H. Chao and T. S. Zhao, "A novel electrode formed with electrospun nano- and micro-scale carbon fibers for aqueous redox flow batteries." *J Power Sources*, **470**, 9 (2020) 10.1016/j.jpowsour.2020.228441.
312. B. K. Chakrabarti, E. Kalamaras, M. Ouyang, X. Liu, G. Remy, P. F. Wilson, M. A. Williams, et al., "Trichome-like carbon-metal fabrics made of carbon microfibers, carbon nanotubes, and Fe-based nanoparticles as electrodes for regenerative hydrogen/vanadium flow cells." *ACS Appl. Nano Mat.*, **4**, 10754 (2021) 10.1021/acsanm.1c02195.
313. Q. X. Wu, Y. H. Lv, L. Y. Lin, X. Y. Zhang, Y. Liu and X. L. Zhou, "An improved thin-film electrode for vanadium redox flow batteries enabled by a dual layered structure." *J Power Sources*, **410**, 152 (2019) 10.1016/j.jpowsour.2018.11.020.
314. C. T. C. Wan, R. R. Jacquemond, Y. M. Chiang, K. Nijmeijer, F. R. Brushett and A. Forner-Cuenca, "Non-solvent induced phase separation enables designer redox flow battery electrodes." *Adv Mater*, **33** (2021) 10.1002/adma.202006716.
315. Y. H. Zhao, Y. Li, M. Ihsan-Ul-Haq, N. Mubarak, M. Y. Xu, X. Y. Qin, T. S. Zhao, et al., "Highly porous carbon nanofiber electrodes for vanadium redox flow batteries." *Nanoscale*, **14**, 5804 (2022) 10.1039/d1nr08376g.
316. D. W. Fang, X. Y. An, A. Zhang, X. Li, N. Liu, X. X. Ma and M. H. Jing, "Green and affordable manufacturing method for multi-scale porous carbon nanofibers and its application in vanadium redox flow battery." *Journal of the Electrochemical Society*, **169**, 7 (2022) 10.1149/1945-7111/ac4b20.
317. J. Su, Z. Y. Li, L. L. Hao and L. L. Qin, "Preparation and electrocatalytic activity of a cobalt mixed nitrogen 3d carbon nanostructure @ carbon felt toward an all-vanadium redox flow battery." *Applied Sciences-Basel*, **12**, 10 (2022) 10.3390/app12052304.
318. Q. Li, Q. Dong, T. Zhang, Z. Xue, J. Li, Z. Wang and H. Sun, "Performance of room-temperature activated tubular polypyrrole modified graphite felt composite electrode in vanadium redox flow battery." *Electrochim Acta*, **409** (2022) 10.1016/j.electacta.2022.139970.
319. Z. X. Tai, D. Y. Ju, S. Sato and K. Hanawa, "Discrete coating of CNT on carbon fiber surfaces and the effect on improving the electrochemical performance of VRFB systems." *Coatings*, **11**, 11 (2021) 10.3390/coatings11060736.
320. I. Kroner, M. Becker and T. Turek, "Determination of rate constants and reaction orders of vanadium-ion kinetics on carbon fiber electrodes." *ChemElectroChem*, **7**, 4314 (2020) 10.1002/celec.202001033.
321. S. Mcardle, L. Landon-Lane and A. T. Marshall, "Using single fibre electrodes to determine the spatial variability of rate constants across carbon felt electrodes." *Electrochem. Commun.*, **131** (2021) 10.1016/j.elecom.2021.107122.
322. J. Gao, Y. Yang, Y. Ren, W. Zhu, J. Li, Y. Liu, L. Dai, et al., "A novel hafnium boride catalyst for vanadium redox flow battery." *Ionics*, **28**, 4273 (2022) 10.1007/s11581-022-04656-7.
323. R. J. Huang, S. Q. Liu, Z. He, W. W. Zhu, G. Y. Ye, Y. K. Su, W. W. Deng, et al., "Electron-deficient sites for improving V^{2+}/V^{3+} redox kinetics in vanadium redox flow batteries." *Adv. Funct. Mater.*, **32**, 10 (2022) 10.1002/adfm.202111661.
324. Y. Ren, Y. Yang, J. Li, W. Zhu, J. Gao, Y. Liu, L. Dai, et al., "Synergistic catalysis of carbon/bismuth composite for V^{3+}/V^{2+} reaction in vanadium redox flow battery." *Ionics*, **28**, 4261 (2022) 10.1007/s11581-022-04663-8.
325. A. K. Tripathi, D. Priyadarshani, M. E. Joy, R. Maurya and M. Neergat, "The impact of overpotential on the enthalpy of activation and pre-exponential factor of electrochemical redox reactions." *Physical Chemistry Chemical Physics*, **24**, 16031 (2022) 10.1039/d2cp00404f.

326. A. Lindner, H. Radinger, F. Scheiba and H. Ehrenberg, "Structure-activity correlation of thermally activated graphite electrodes for vanadium flow batteries." *Rsc Advances*, **12**, 14119 (2022) 10.1039/d2ra02368g.
327. Q. Li, X. D. Zhang and H. Sun, "Dimethyl sulfoxide treated $\text{Ti}_3\text{C}_2\text{Tx}$ as a catalyst for $\text{V}^{3+}/\text{V}^{2+}$ reaction in vanadium redox flow batteries." *Journal of the Electrochemical Society*, **169**, 7 (2022) 10.1149/1945-7111/ac71d5.
328. S. C. Kim, J. Paick, J. S. Yi and D. Lee, "Marked importance of surface defects rather than oxygen functionalities of carbon electrodes for the intrinsic vanadium redox kinetics in flow batteries." *J Power Sources*, **520**, 11 (2022) 10.1016/j.jpowsour.2021.230813.
329. Z. L. He, Yanrong|Zhang, Tianao|Zhu, Ye|Dai, Lei|Yao, Shuo|Zhu, Wenjie|Wang, Ling, "Electrode materials for vanadium redox flow batteries: Intrinsic treatment and introducing catalyst." *Chemical Engineering Journal*, **427**, N.PAG (2022) 10.1016/j.cej.2021.131680.
330. M. G. Ersozoglul, H. Gursu, M. Gencten, A. S. Sarac and Y. Sahin, "A new approach to prepare n-/s-doped free-standing graphene oxides for vanadium redox flow battery." *International Journal of Energy Research* (2022) 10.1002/er.8091.
331. Q. Deng, X. Y. Huangyang, X. Zhang, Z. H. Xiao, W. B. Zhou, H. R. Wang, H. Y. Liu, et al., "Edge-rich multidimensional frame carbon as high-performance electrode material for vanadium redox flow batteries." *Adv. Energy Mater.*, **12**, 9 (2022) 10.1002/aenm.202103186.
332. T. X. Zhang, Y. Q. Jiang, Z. X. Zhang, J. Xue, Y. H. Li, Y. G. Liu, Z. S. Chen, et al., "Zirconium boride as a novel negative catalyst for vanadium redox flow battery." *Ceram Int*, **47**, 20276 (2021) 10.1016/j.ceramint.2021.04.036.
333. Q. Zhang, T. Liu, H. M. Zhang and X. F. Li, "Highly active ag nanoparticle electrocatalysts toward $\text{V}^{2+}/\text{V}^{3+}$ redox reaction." *ACS Appl. Ener. Mat.*, **4**, 3913 (2021) 10.1021/acsaem.1c00297.
334. D. J. You, J. Y. Lou, X. Q. Li, Y. L. Zhou, X. Q. Sun and X. L. Wang, "Investigation of advanced catalytic effect of Co_3O_4 nanosheets modified carbon felts as vanadium flow battery electrodes." *J Power Sources*, **494**, 9 (2021) 10.1016/j.jpowsour.2021.229775.
335. Z. F. Yang, Y. G. Wei, Y. K. Zeng and Y. P. Yuan, "Effects of in-situ bismuth catalyst electrodeposition on performance of vanadium redox flow batteries." *J Power Sources*, **506**, 9 (2021) 10.1016/j.jpowsour.2021.230238.
336. J. Xue, Y. Q. Jiang, Z. X. Zhang, T. X. Zhang, C. Han, Y. G. Liu, Z. S. Chen, et al., "A novel catalyst of titanium boride toward $\text{V}^{3+}/\text{V}^{2+}$ redox reaction for vanadium redox flow battery." *J Alloys Compd*, **875**, 10 (2021) 10.1016/j.jallcom.2021.159915.
337. J. Xu, Y. Q. Zhang, Z. F. Huang, C. K. Jia and S. Y. Wang, "Surface modification of carbon-based electrodes for vanadium redox flow batteries." *Energy & Fuels*, **35**, 8617 (2021) 10.1021/acs.energyfuels.1c00722.
338. M. K. K. Singh, Manshu|Verma, Anil, "Recent progress on carbon and metal based electrocatalysts for vanadium redox flow battery." *Wiley Interdisciplinary Reviews-Energy and Environment*, **10**, e393 (2021) 10.1002/wene.393.
339. C. Y. Sun, E. Negro, A. Nale, G. Pagot, K. Vezzu, T. A. Zawodzinski, L. Meda, et al., "An efficient barrier toward vanadium crossover in redox flow batteries: The bilayer nafion/(WO_3)_x hybrid inorganic-organic membrane." *Electrochim Acta*, **378**, 11 (2021) 10.1016/j.electacta.2021.138133.
340. T. Wang, J. Han, K. Kim, A. Münchinger, Y. Gao, A. Farchi, Y. K. Choe, et al., "Suppressing vanadium crossover using sulfonated aromatic ion exchange membranes for high performance flow batteries." *Mater. Adv.*, **1**, 2206 (2020) 10.1039/d0ma00508h.
341. A. H. Whitehead, A. Robertson, B. Martin, E. Martin and E. Wilson, "Experimental benchmarking of redox flow cells." *Batteries-Basel*, **8**, 13 (2022) 10.3390/batteries8110207.
342. M. Kapoor and A. Verma, "Technical benchmarking and challenges of kilowatt scale vanadium redox flow battery." *Wiley Interdiscip. Rev. Energy Environ.*, **11** (2022) 10.1002/wene.439.
343. Y. S. Chou, N. Devi, S. C. Yen, P. Singh and Y. S. Chen, "Study on the self-discharge of an all-vanadium redox flow battery through monitoring individual cell voltages." *ACS Sustainable Chem. Eng.*, **10**, 12245 (2022) 10.1021/acssuschemeng.2c03148.

344. T. S. Wang, J. Lee, X. F. Wang, K. Wang, C. Bae and S. Kim, "Surface-engineered nafion/cnts nanocomposite membrane with improved voltage efficiency for vanadium redox flow battery." *J. Appl. Polym. Sci.*, **139**, 10 (2022) 10.1002/app.51628.
345. N. Omar, M. A. Monem, Y. Firouz, J. Salminen, J. Smekens, O. Hegazy, H. Gaulous, et al., "Lithium iron phosphate based battery - assessment of the aging parameters and development of cycle life model." *Appl. Energy*, **113**, 1575 (2014) 10.1016/j.apenergy.2013.09.003.
346. W. Vermeer, G. R. Chandra Mouli and P. Bauer, "A comprehensive review on the characteristics and modeling of lithium-ion battery aging." *IEEE Trans. Transp. Electrification*, **8**, 2205 (2022) 10.1109/TTE.2021.3138357.
347. M. C. Yagci, T. Feldmann, E. Bollin, M. Schmidt and W. G. Bessler, "Aging characteristics of stationary lithium-ion battery systems with serial and parallel cell configurations." *Energies*, **15** (2022) 10.3390/en15113922.
348. Y. Lv, W. Luo, Y. Mo and G. Zhang, "Investigation on the thermo-electric-electrochemical characteristics of retired lfp batteries for echelon applications." *RSC Adv.*, **12**, 14127 (2022) 10.1039/d2ra02278h.
349. T. B. Reddy, *Linden's handbook of batteries*, McGraw-Hill Education (2011)
350. Y. Dai, S. Cheng, Q. J. Gan, T. J. Yu, X. Wu and F. L. Bi, "Life prediction of ni-cd battery based on linear wiener process." *Journal of Central South University*, **28**, 2919 (2021) 10.1007/s11771-021-4816-5.
351. T. M. Kulin, "Life cycle testing of a sealed 24-v, 42-ah nickel-cadmium aircraft battery." *IEEE Aerosp Electron Syst Mag*, **12**, 17 (1997) 10.1109/62.624323.
352. A. A. Kebede, T. Kalogiannis, J. Van Mierlo and M. Berecibar, "A comprehensive review of stationary energy storage devices for large scale renewable energy sources grid integration." *Renewable Sustainable Energy Rev*, **159** (2022) 10.1016/j.rser.2022.112213.
353. "Lockheed martin buys sun catalytix." *Chem. Eng. News*, **92**, 22 (2014) 10.1021/cen-09235-buscon.
354. E. L. Littauer and W. R. Momyer, "Reactive metal battery cathode - of porous, pref. Reducible, material having supply of cathode reactant to surface." WO8403802-A WOUS00228 16 Feb 1984 US4481266-A US478695 25 Mar 1983 EP140906-A EP901156 16 Feb 1984 JP60500789-W JP501088 16 Feb 1984 (WO8403802-A WOUS00228 16 Feb 1984 US4481266-A US478695 25 Mar 1983 EP140906-A EP901156 16 Feb 1984 JP60500789-W JP501088 16 Feb 1984).
355. R. I. Klootwyk, "Electrochemical battery pressure contact - exerts uniform pressure on stacked anodes and cathodes under all operating stages of battery." US4189528-A US955565 30 Oct 1978 DE2942745-A DE2942745 23 Oct 1979 DE2942745-C DE2942745 23 Oct 1979 (US4189528-A US955565 30 Oct 1978 DE2942745-A DE2942745 23 Oct 1979 DE2942745-C DE2942745 23 Oct 1979).
356. R. I. Klootwyk, "Electrochemical battery - with thrust device for consumable anode and control grooves for electrolyte flow." DE2943046-A DE2943046 25 Oct 1979 DE2943046-C DE2943046 25 Oct 1979 (DE2943046-A DE2943046 25 Oct 1979 DE2943046-C DE2943046 25 Oct 1979).
357. G. B. Adams, "Hybrid redox secondary battery - using ferricyanide-ferrocyanide couple in alkaline catholyte and zinc anode." DE2854097-A DE2854097 14 Dec 1978 US4180623-A US928785 28 Jul 1978 (DE2854097-A DE2854097 14 Dec 1978 US4180623-A US928785 28 Jul 1978).
358. R. M. Darling, "Techno-economic analyses of several redox flow batteries using leveled cost of energy storage." *Current Opinion in Chemical Engineering*, **37** (2022) 10.1016/j.coche.2022.100855.
359. I. Ameresco, Ameresco begins second phase of department of defense funded flow battery investigation, in *Business Wire (English)* (2022)
360. E. Virguez, X. Wang and D. Patino-Echeverri, "Utility-scale photovoltaics and storage: Decarbonizing and reducing greenhouse gases abatement costs." *Appl. Energy*, **282** (2021) 10.1016/j.apenergy.2020.116120.
361. M. J. Lain, J. Brandon and E. Kendrick, "Design strategies for high power vs. High energy lithium ion cells." *Batteries*, **5** (2019) 10.3390/batteries5040064.
362. M. J. Lain and E. Kendrick, "Understanding the limitations of lithium ion batteries at high rates." *J Power Sources*, **493** (2021) 10.1016/j.jpowsour.2021.229690.
363. K. G. Gallagher, S. E. Trask, C. Bauer, T. Woehle, S. F. Lux, M. Tschech, P. Lamp, et al., "Optimizing areal capacities through understanding the limitations of lithium-ion electrodes." *J Electrochem Soc*, **163**, A138 (2016) 10.1149/2.0321602jes.

364. J. Leadbetter and L. G. Swan, "Selection of battery technology to support grid-integrated renewable electricity." *J Power Sources*, **216**, 376 (2012) 10.1016/j.jpowsour.2012.05.081.
365. M. Singh, J. Kaiser and H. Hahn, "Thick electrodes for high energy lithium ion batteries." *J Electrochem Soc*, **162**, A1196 (2015) 10.1149/2.0401507jes.
366. M. Singh, J. Kaiser and H. Hahn, "Effect of porosity on the thick electrodes for high energy density lithium ion batteries for stationary applications." *Batteries*, **2** (2016) 10.3390/batteries2040035.
367. M. Singh, J. Kaiser and H. Hahn, "A systematic study of thick electrodes for high energy lithium ion batteries." *J Electroanal Chem*, **782**, 245 (2016) 10.1016/j.jelechem.2016.10.040.
368. K. Kisu, S. Aoyagi, H. Nagatomo, E. Iwama, M. T. H. Reid, W. Naoi and K. Naoi, "Internal resistance mapping preparation to optimize electrode thickness and density using symmetric cell for high-performance lithium-ion batteries and capacitors." *J Power Sources*, **396**, 207 (2018) 10.1016/j.jpowsour.2018.05.083.
369. W. Mei, H. Chen, J. Sun and Q. Wang, "The effect of electrode design parameters on battery performance and optimization of electrode thickness based on the electrochemical-thermal coupling model." *Sustain. Energy Fuels*, **3**, 148 (2019) 10.1039/c8se00503f.
370. B. Boz, T. Dev, A. Salvadori and J. L. Schaefer, "Review - electrolyte and electrode designs for enhanced ion transport properties to enable high performance lithium batteries." *J Electrochem Soc*, **168** (2021) 10.1149/1945-7111/ac1cc3.
371. J. Park, C. Jeon, W. Kim, S. J. Bong, S. Jeong and H. J. Kim, "Challenges, laser processing and electrochemical characteristics on application of ultra-thick electrode for high-energy lithium-ion battery." *J Power Sources*, **482** (2021) 10.1016/j.jpowsour.2020.228948.
372. S. Lee, J. Jang, D. Lee, J. Kim and J. Mun, "Synergetic effect of aqueous electrolyte and ultra-thick millimeter-scale lifepo4 cathode in aqueous lithium-ion batteries." *Int. J. Energy Res.*, **46**, 6480 (2022) 10.1002/er.7584.
373. C. C. Zhou, Z. Su, X. L. Gao, R. Cao, S. C. Yang and X. H. Liu, "Ultra-high-energy lithium-ion batteries enabled by aligned structured thick electrode design." *Rare Met.*, **41**, 14 (2022) 10.1007/s12598-021-01785-2.
374. K. G. Gallagher, P. A. Nelson and D. W. Dees, "Simplified calculation of the area specific impedance for battery design." *J Power Sources*, **196**, 2289 (2011) 10.1016/j.jpowsour.2010.10.020.
375. O. Schmidt, S. Melchior, A. Hawkes and I. Staffell, "Projecting the future levelized cost of electricity storage technologies." *Joule*, **3**, 81 (2019) 10.1016/j.joule.2018.12.008.
376. M. J. Li, W. Zhao, X. Chen and W. Q. Tao, "Economic analysis of a new class of vanadium redox-flow battery for medium- and large-scale energy storage in commercial applications with renewable energy." *Appl Therm Eng*, **114**, 802 (2017) 10.1016/j.applthermaleng.2016.11.156.
377. Valuewalk: Vanadium redox flow batteries: The next big wave after lithium batteries, in, Newstex, Chatham (2016)
378. C. A. Hunter, M. M. Penev, E. P. Reznicek, J. Eichman, N. Rustagi and S. F. Baldwin, "Techno-economic analysis of long-duration energy storage and flexible power generation technologies to support high-variable renewable energy grids." *Joule*, **5**, 2077 (2021) 10.1016/j.joule.2021.06.018.
379. M. M. Rahman, A. O. Oni, E. Gemechu and A. Kumar, "The development of techno-economic models for the assessment of utility-scale electro-chemical battery storage systems." *Appl. Energy*, **283**, 15 (2021) 10.1016/j.apenergy.2020.116343.
380. J. Spector, "Tesla fulfilled its 100-day australia battery bet. What's that mean for the industry? ." in *GreenTech Media* (2017)<https://www.greentechmedia.com/articles/read/tesla-fulfills-australia-battery-bet-whats-that-mean-industry>.
381. C. Minke and M. a. D. Ledesma, "Impact of cell design and maintenance strategy on life cycle costs of vanadium redox flow batteries." *J. Energy Storage*, **21**, 571 (2019) 10.1016/j.est.2018.12.019.
382. F. P. Rivera, J. Zalamea, J. L. Espinoza and L. G. Gonzalez, "Sustainable use of spilled turbinable energy in ecuador: Three different energy storage systems." *Renewable & Sustainable Energy Reviews*, **156**, 15 (2022) 10.1016/j.rser.2021.112005.
383. S. Weber, J. F. Peters, M. Baumann and M. Weil, "Life cycle assessment of a vanadium redox flow battery." *Environmental Science & Technology*, **52**, 10864 (2018) 10.1021/acs.est.8b02073.
384. L:Fp battery prices from sinopoly, in (2020)

385. C. Minke and T. Turek, "Materials, system designs and modelling approaches in techno-economic assessment of all-vanadium redox flow batteries – a review." *Journal of Power Sources*, **376**, 66 (2018) 10.1016/j.jpowsour.2017.11.058.
386. C. Minke and M. A. Dorantes Ledesma, "Impact of cell design and maintenance strategy on life cycle costs of vanadium redox flow batteries." *J. Energy Storage*, **21**, 571 (2019) 10.1016/j.est.2018.12.019.
387. S. Weber, J. F. Peters, M. Baumann and M. Weil, "Life cycle assessment of a vanadium redox flow battery." *Environ. Sci. Technol.*, **52**, 10864 (2018) 10.1021/acs.est.8b02073.
388. J. Gouveia, A. Mendes, R. Monteiro, T. M. Mata, N. S. Caetano and A. A. Martins, "Life cycle assessment of a vanadium flow battery." *Energy Rep.*, **6**, 95 (2020) 10.1016/j.egyr.2019.08.025.
389. F. Rossi, M. L. Parisi, S. Greven, R. Basosi and A. Sinicropi, "Life cycle assessment of classic and innovative batteries for solar home systems in europe." *Energies*, **13** (2020) 10.3390/en13133454.
390. K. E. Rodby, T. J. Carney, Y. Ashraf Gandomi, J. L. Barton, R. M. Darling and F. R. Brushett, "Assessing the leveled cost of vanadium redox flow batteries with capacity fade and rebalancing." *Journal of Power Sources*, **460** (2020) 10.1016/j.jpowsour.2020.227958.
391. J. H. Vinco, A. E. E. D. C. Domingos, D. C. R. Espinosa, J. a. S. Tenório and M. D. P. G. Baltazar, "Unfolding the vanadium redox flow batteries: An indeep perspective on its components and current operation challenges." *J. Energy Storage*, **43** (2021) 10.1016/j.est.2021.103180.
392. B. E. Gaddy, V. Sivaram, T. B. Jones and L. Wayman, "Venture capital and cleantech: The wrong model for energy innovation." *Energy Policy*, **102**, 385 (2017) 10.1016/j.enpol.2016.12.035.
393. S. Bose, G. Dong, A. Simpson, S. Bose, G. Dong and A. Simpson, *Financing clean technology innovation and the transition to renewable energy*, p. 339, Palgrave, Basingstoke (2019) 10.1007/978-3-030-05624-7_14.
394. A. Goldstein, C. Doblinger, E. Baker and L. D. Anadón, "Patenting and business outcomes for cleantech startups funded by the advanced research projects agency-energy." *Nat. Energy*, **5**, 803 (2020) 10.1038/s41560-020-00683-8.
395. C. C. Niemann, P. Dickel and G. Eckardt, "The interplay of corporate entrepreneurship, environmental orientation, and performance in clean-tech firms-a doubled-edged sword." *Bus. Strategy Environ.*, **29**, 180 (2020) 10.1002/bse.2357.
396. P. D. Hegeman and R. Sørheim, "Why do they do it? Corporate venture capital investments in cleantech startups." *J. Clean. Prod.*, **294** (2021) 10.1016/j.jclepro.2021.126315.
397. R. Owen, G. Brennan, F. Lyon and T. Harrer, "Financing cleantech sme innovation: Setting an agenda." *IEEE Trans Eng Manage*, **68**, 1168 (2021) 10.1109/TEM.2020.3005702.
398. J. Cailou and L. Dehai, "Does venture capital stimulate the innovation of china's new energy enterprises?" *Energy*, **244** (2022) 10.1016/j.energy.2021.122704.
399. H. Zhang and C. Sun, "Cost-effective iron-based aqueous redox flow batteries for large-scale energy storage application: A review." *J Power Sources*, **493** (2021) 10.1016/j.jpowsour.2020.229445.
400. J. Escudero-González and P. Amparo López-Jiménez, "Iron redox battery as electrical energy storage system in the spanish energetic framework." *Int J Electr Power Energy Syst*, **61**, 421 (2014) 10.1016/j.ijepes.2014.03.067.
401. M. C. Tucker, A. Phillips and A. Z. Weber, "All-iron redox flow battery tailored for off-grid portable applications." *ChemSusChem*, **8**, 3996 (2015) 10.1002/cssc.201500845.
402. L. W. S. Hruska, R. F., "Investigation of factors affecting performance of the iron-redox battery." *Journal of the Electrochemical Society*, **128**, 18 (1981) 10.1149/1.2127366.
403. S. Selverston, E. Nagelli, J. S. Wainright and R. F. Savinell, "All-iron hybrid flow batteries with in-tank rebalancing." *J Electrochem Soc*, **166**, A1725 (2019) 10.1149/2.0281910jes.
404. B. S. Jayathilake, E. J. Plichta, M. A. Hendrickson and S. R. Narayanan, "Improvements to the coulombic efficiency of the iron electrode for an all-iron redox-flow battery." *J Electrochem Soc*, **165**, A1630 (2018) 10.1149/2.0451809jes.
405. S. Yu, X. Yue, J. Holoubek, X. Xing, E. Pan, T. Pascal and P. Liu, "A low-cost sulfate-based all iron redox flow battery." *J Power Sources*, **513** (2021) 10.1016/j.jpowsour.2021.230457.
406. T. Kender William, "Reverse polarity refresh method and redox flow battery system." 2021WO-US73079 2021-12-222021US-17643466 2021-12-09 (2020-12-22).

407. D. Anarghya, M. S. Anantha, K. Venkatesh, M. S. Santosh, M. G. Priya and H. B. Muralidhara, "Bermuda grass derived nitrogen-doped carbon as electrocatalyst in graphite felt electrode to increase the efficiency of all-iron redox flow batteries." *J Electroanal Chem*, **878** (2020) 10.1016/j.jelechem.2020.114577.
408. M. S. Anantha, D. Anarghya, C. Hu, N. Reddy, K. Venkatesh and H. B. Muralidhara, "Enhancing the electrochemical and cyclic performance of irfbs through electrode modification using novel mno₂@ceo₂ composite." *J Mater Sci Mater Electron*, **31**, 15286 (2020) 10.1007/s10854-020-04093-0.
409. M. S. Anantha, D. Anarghya, C. Hu, N. Reddy, K. Venkatesh and H. B. Muralidhara, "Electrochemical performance of graphene oxide modified graphite felt as a positive electrode in all-iron redox flow batteries." *J Appl Electrochem*, **51**, 331 (2021) 10.1007/s10800-020-01490-5.
410. A. Dinesh, M. S. Anantha, M. S. Santosh, M. N. Kumar, K. Venkatesh and H. B. Muralidhara, "Nitrogen-doped carbon spheres-decorated graphite felt as a high-performance electrode for fe based redox flow batteries." *Diamond Relat. Mat.*, **116** (2021) 10.1016/j.diamond.2021.108413.
411. A. Dinesh, M. S. Anantha, M. S. Santosh, M. G. Priya, K. Venkatesh, K. S. Yogesh Kumar, M. S. Raghu, et al., "Improved performance of iron-based redox flow batteries using wo₃ nanoparticles decorated graphite felt electrode." *Ceram Int*, **47**, 10250 (2021) 10.1016/j.ceramint.2020.09.225.
412. J. Chullipparambil Balakrishnan, M. Pulikkotti Peter, D. Davis Kombarakaran, J. Ambadan Kunjilona and J. Vadakkan Thomas, "Improvement in the performance of an fe/feii electrode in an all-iron redox flow battery by the addition of znii ions." *ChemistrySelect*, **7** (2022) 10.1002/slct.202201222.
413. L. Wei, M. C. Wu, T. S. Zhao, Y. K. Zeng and Y. X. Ren, "An aqueous alkaline battery consisting of inexpensive all-iron redox chemistries for large-scale energy storage." *Appl. Energy*, **215**, 98 (2018) 10.1016/j.apenergy.2018.01.080.
414. Y. Song, K. Zhang, X. Li, C. Yan, Q. Liu and A. Tang, "Tuning the ferrous coordination structure enables a highly reversible fe anode for long-life all-iron flow batteries." *J. Mater. Chem. A*, **9**, 26354 (2021) 10.1039/d1ta07295a.
415. J. Noack, M. Wernado, N. Roznyatovskaya, J. Ortner and K. Pinkwart, "Studies on fe/fe redox flow batteries with recombination cell." *J Electrochem Soc*, **167** (2020) 10.1149/1945-7111/abc50.
416. M. Peither, J. Buddhinie and N. Trogisch, "Rebalancing system of a fe/fe redox flow battery." 2020EP-0214269 (2020-12-15).
417. J. Noack, M. Berkers, J. Ortner and K. Pinkwart, "The influence of some electrolyte additives on the electrochemical performance of fe/fe²⁺-redox reactions for iron/iron redox flow batteries." *J Electrochem Soc*, **168** (2021) 10.1149/1945-7111/abf5a3.
418. E. Evans Craig and Y. Song, "Electrolytes for iron flow battery." 2014US-14201244 2014-03-07 2017US-15436593 2017-02-172017US-15711879 2017-09-212019JP-0545360 2018-02-142018AU-0221581 2018-02-142018DE-11000011 2018-02-142018WO-US18251 2018-02-142018EP-0753985 2018-02-142018CN-80012389 2018-02-142019IN-47037160 2019-09-16 PPN - (EP3583648) WO2018/152256 A1 2018-08-23 [WO2018152256] PPN - (DE112018000011) WO2018/152256 A1 2018-08-23 [WO2018152256] PPN - (JP7060607) WO2018/152256 A1 2018-08-23 [WO2018152256] PPN - (IN-393334) WO2018/152256 A1 2018-08-23 [WO2018152256] PPN - (AU2018221581) WO2018/152256 A1 2018-08-23 [WO2018152256] PPN - (CN110301060) WO2018/152256 A1 2018-08-23 [WO2018152256] (2013-03-12).
419. E. Evans Craig, S. Casey and Y. Song, "Alternative low cost electrodes for hybrid flow batteries." 2015US-14984416 2015-12-302017US-15601560 2017-05-222019JP-0564531 2018-05-152018EP-0805497 2018-05-152018CN-80034271 2018-05-152018WO-US32820 2018-05-152018AU-0271764 2018-05-152019IN-47042634 2019-10-212021US-17235810 2021-04-202022US-17653620 2022-03-04 PPN - (EP3602663) WO2018/217502 A1 2018-11-29 [WO2018217502] PPN - (JP7108640) WO2018/217502 A1 2018-11-29 [WO2018217502] PPN - (IN201947042634) WO2018/217502 A1 2018-11-29 [WO2018217502] PPN - (AU2018271764) WO2018/217502 A1 2018-11-29 [WO2018217502] PPN - (CN110679022) WO2018/217502 A1 2018-11-29 [WO2018217502] (2014-12-30).
420. P. Danko, "As ess rises in nyse debut, ceo focuses on \$308m opportunity to scale up." in *Portland Business Journal* (2021-10-11)<https://www.bizjournals.com/portland/news/2021/10/11/ess-dresselhuys-308m-opportunity.html>.
421. A. Colthorpe, "Ess inc becomes 'us' first publicly-traded long-duration energy storage company'." in (2021-10-12)

422. J. Young, "Special purpose acquisition company (spac) explained: Examples and risks." in *Investopedia* (2022-06-30) [https://www.investopedia.com/terms/s/spac.asp#:~:text=A%20special%20purpose%20acquisition%20company%20\(SPAC\)%20is%20a%20company%20without,merging%20with%20an%20existing%20company.](https://www.investopedia.com/terms/s/spac.asp#:~:text=A%20special%20purpose%20acquisition%20company%20(SPAC)%20is%20a%20company%20without,merging%20with%20an%20existing%20company.)
423. B. V. Reddy, "Warning the uk on special purpose acquisition companies (spacs): Great for wall street but a nightmare on main street." *J. Corp. Law Stud.* (2022) 10.1080/14735970.2022.2036413.
424. F. Kiesel, N. Klingelhöfer, D. Schiereck and S. Vismara, "Spac merger announcement returns and subsequent performance." *Eur. Financ. Manage.* (2022) 10.1111/eufm.12366.
425. E. Blankespoor, B. E. Hendricks, G. S. Miller and D. R. Stockbridge, Jr., "A hard look at spac projections." *Manage Sci*, **68**, 4742 (2022) 10.1287/mnsc.2022.4385.
426. Will vanadium push lithium aside as better choice for increasing demand of redox batteries, in *PR Newswire Europe Including UK Disclose*, New York (2018)
427. H. Sharifi, B. Mosallanejad, M. Mohammadzad, S. M. Hosseini-Hosseinabad and S. Ramakrishna, "Cycling performance of lifepo₄/graphite batteries and their degradation mechanism analysis via electrochemical and microscopic techniques." *Ionics*, **28**, 213 (2022) 10.1007/s11581-021-04258-9.
428. C. Doetsch and J. Burfeind, "Vanadium redox flow batteries." in *Storing energy: With special reference to renewable energy sources. 2nd edition.*, p. 363, Elsevier (2022) 10.1016/B978-0-12-824510-1.00030-1.
429. S. Xie, Y. Gong, X. Ping, J. Sun, X. Chen and Y. He, "Effect of overcharge on the electrochemical and thermal safety behaviors of lini_{0.5}mn_{0.3}co_{0.2}o₂/graphite lithium-ion batteries." *J. Energy Storage*, **46** (2022) 10.1016/j.est.2021.103829.
430. T. Li, X. Z. Yuan, L. Zhang, D. Song, K. Shi and C. Bock, "Degradation mechanisms and mitigation strategies of nickel-rich nmc-based lithium-ion batteries." *Electrochem. Energy Rev.*, **3**, 43 (2020) 10.1007/s41918-019-00053-3.
431. D. Graf, J. Marschewski, L. Ibing, D. Huckebrink, M. Fiebrandt, G. Hanau and V. Bertsch, "What drives capacity degradation in utility-scale battery energy storage systems? The impact of operating strategy and temperature in different grid applications." *J. Energy Storage*, **47**, 10 (2022) 10.1016/j.est.2021.103533.
432. X. Sui, M. Świerczyński, R. Teodorescu and D. I. Stroe, "The degradation behavior of lifepo₄/c batteries during long-term calendar aging." *Energies*, **14** (2021) 10.3390/en14061732.
433. M. Schimpe, J. V. Barreras, B. Wu and G. J. Offer, "Battery degradation-aware current derating: An effective method to prolong lifetime and ease thermal management." *J. Electrochem. Soc.*, **168** (2021) 10.1149/1945-7111/ac0553.
434. M. Azkue, M. Lucu, E. Martinez-Laserna and I. Aizpuru, "Calendar ageing model for li-ion batteries using transfer learning methods." *World Electr. Vehicle J.*, **12** (2021) 10.3390/wevj12030145.
435. M. Simolka, J. F. Heger, H. Kaess, I. Biswas and K. A. Friedrich, "Influence of cycling profile, depth of discharge and temperature on commercial lfp/c cell ageing: Post-mortem material analysis of structure, morphology and chemical composition." *J. Appl. Electrochem.*, **50**, 1101 (2020) 10.1007/s10800-020-01465-6.
436. J. S. Edge, S. O'kane, R. Prosser, N. D. Kirkaldy, A. N. Patel, A. Hales, A. Ghosh, et al., "Lithium ion battery degradation: What you need to know." *Phys. Chem. Chem. Phys.*, **23**, 8200 (2021) 10.1039/d1cp00359c.
437. S. Sankarasubramanian and B. Krishnamurthy, "A capacity fade model for lithium-ion batteries including diffusion and kinetics." *Electrochim Acta*, **70**, 248 (2012) 10.1016/j.electacta.2012.03.063.
438. M. Shabani, F. Wallin, E. Dahlquist and J. Yan, "Techno-economic assessment of battery storage integrated into a grid-connected and solar-powered residential building under different battery ageing models." *Appl. Energy*, **318** (2022) 10.1016/j.apenergy.2022.119166.
439. N. I. Shchurov, S. I. Dedov, B. V. Malozyomov, A. A. Shtang, N. V. Martyushev, R. V. Klyuev and S. N. Andriashin, "Degradation of lithium-ion batteries in an electric transport complex." *Energies*, **14** (2021) 10.3390/en14238072.
440. M. Philippot, D. Costa, M. S. Hosen, A. Senécat, E. Brouwers, E. Nanini-Maury, J. Van Mierlo, et al., "Environmental impact of the second life of an automotive battery: Reuse and repurpose based on ageing tests." *J. Clean. Prod.*, **366** (2022) 10.1016/j.jclepro.2022.132872.
441. X. Li, F. Jiang, K. Qu, Y. Wang, Y. Pan, M. Wang, Y. Liu, et al., "First atomic-scale insight into degradation in lithium iron phosphate cathodes by transmission electron microscopy." *J. Phys. Chem. Lett.*, **11**, 4608 (2020) 10.1021/acs.jpcclett.0c00317.

442. C. Yuan, H. Wang, D. Huang, C. Wu, D. Zhou and A. Mei, "The abrupt degradation of lifepo4/graphite battery induced by electrode inhomogeneity." *Solid State Ionics*, **374** (2022) 10.1016/j.ssi.2021.115832.
443. M. Haris, M. N. Hasan and S. Qin, "Degradation curve prediction of lithium-ion batteries based on knee point detection algorithm and convolutional neural network." *IEEE Trans. Instrum. Meas.*, **71** (2022) 10.1109/TIM.2022.3181307.
444. P. M. Attia, A. Bills, F. Brosa Planella, P. Dechent, G. Dos Reis, M. Dubarry, P. Gasper, et al., "Review - "knees" in lithium-ion battery aging trajectories." *J Electrochem Soc*, **169** (2022) 10.1149/1945-7111/ac6d13.
445. J. F. Weaver, "World's largest battery: 200mw/800mwh vanadium flow battery – site work ongoing." in (2017)<https://electrek.co/2017/12/21/worlds-largest-battery-200mw-800mwh-vanadium-flow-battery-rongke-power/>.
446. N. Blume, M. Becker, T. Turek and C. Minke, "Life cycle assessment of an industrial-scale vanadium flow battery." *J. Ind. Ecol.*, **26**, 1796 (2022) 10.1111/jiec.13328.
447. M. Jafari, A. Sakti and A. Botterud, "Optimization of electrolyte rebalancing in vanadium redox flow batteries." *IEEE Trans Energy Convers*, **37**, 748 (2022) 10.1109/TEC.2021.3136769.
448. G. Mourouga, R. P. Schaerer, X. Yang, T. Janoschka, T. J. Schmidt and J. O. Schumacher, "Physics-based 0d-u-i-soc cell performance model for aqueous organic redox flow batteries." *Electrochim Acta*, **415** (2022) 10.1016/j.electacta.2022.140185.
449. Y. H. Huang, Y. Su and A. Garg, "Measurement and prediction of decomposed energy efficiencies of lithium ion batteries with two charge models." *J. Electrochem. En. Conver. Stor.*, **18**, 9 (2021) 10.1115/1.4049576.
450. V. Bobanac, H. Basic and H. Pandzic, "Determining lithium-ion battery one-way energy efficiencies: Influence of c-rate and coulombic losses." in *19th International Conference on Smart Technologies (IEEE EUROCON)*, p. 385, Lviv, UKRAINE (2021) 10.1109/eurocon52738.2021.9535542.
451. D. S. L. Aaron, Q. ; Tang, Z. ; Grim, G. M. ; Papandrew, A. B. ; Turhan, A. ; Zawodzinski, T. A. ; Mench, M. M., "Dramatic performance gains in vanadium redox flow batteries through modified cell architecture." *Journal of Power Sources*, **206**, 450 (2012) 10.1016/j.jpowsour.2011.12.026.
452. M. Skyllas-Kazacos, "Vanadium flow batteries: Principles, characteristics, structure, evaluation." in *Redox flow batteries: Fundamentals and applications*, 1 ed., VANADIUMFLOWBATTERIESPRINCIPLESCHARACTERISTICSSTRUCTUREEVALUATION2017 Editor, p. 327, Taylor & Francis Group, Milton (2017) 10.1201/9781315152684.
453. R. Haas, C. Kemfert, H. Auer, A. Ajanovic, M. Sayer and A. Hiesl, "On the economics of storage for electricity: Current state and future market design prospects." *Wiley Interdiscip. Rev. Energy Environ.*, **11**, 27 (2022) 10.1002/wene.431.
454. M. Skyllas-Kazacos, "Performance improvements and cost considerations of the vanadium redox flow battery." in *Symposia on Large Scale Energy Storage 10 and Battery Safety and Failure Modes - 235th ECS Meeting*, T. V. Nguyen, T. P. Barrera, J. Nanda, B. Li, J. Xu, W. Wang, P. J. Kulesza, S. D. Minteer, G. Zhang and B. Liaw Editors, p. 29 (2019) 10.1149/08901.0029ecst.
455. M. Skyllas-Kazacos, L. Y. Cao, M. Kazacos, N. Kausar and A. Mousa, "Vanadium electrolyte studies for the vanadium redox battery a review." *ChemSusChem*, **9**, 1521 (2016) 10.1002/cssc.201600102.
456. A. R. Septiana, W. Honggowiranto, S. Sudaryanto, E. Kartini and R. Hidayat, "Comparative study on the ionic conductivities and redox properties of lipf6 and litfsi electrolytes and the characteristics of their rechargeable lithium ion batteries." in *1st Materials Research Society-Indonesia Conference and Congress 2017, MRS-INA C and C 2017*, E. Kartini Editor (2018) 10.1088/1757-899X/432/1/012061.
457. T. Elwert, Q. Hua and K. Schneider, Recycling of lithium iron phosphate batteries: Future prospects and research needs, in *International Workshop E-Mobility and Circular Economy, 2018*, U. A. Peuker, M. Reuter, D. Goldmann and R. Kratzsch Editors, p. 49, Trans Tech Publications Ltd (2019) 10.4028/www.scientific.net/MSF.959.49.
458. Z. B. Huang and A. L. Mu, "Research and analysis of performance improvement of vanadium redox flow battery in microgrid: A technology review." *Int. J. Energy Res.*, **45**, 14170 (2021) 10.1002/er.6716.
459. M. L. Perry, K. E. Rodby and F. R. Brushett, "Untapped potential: The need and opportunity for high-voltage aqueous redox flow batteries." *ACS Energy Letters*, **7**, 659 (2022) 10.1021/acsenenergylett.1c02225.

460. T. Waldmann, S. Rossler, M. Blessing, R. Schafer, R. G. Scurtu, W. Braunwarth and M. Wohlfahrt-Mehrens, "A direct comparison of pilot-scale li-ion cells in the formats phev1, pouch, and 21700." *J. Electrochem. Soc.*, **168**, 10 (2021) 10.1149/1945-7111/ac208c.
461. X. Y. Shi, O. C. Esan, X. Y. Huo, Y. N. Ma, Z. F. Pan, L. An and T. S. Zhao, "Polymer electrolyte membranes for vanadium redox flow batteries: Fundamentals and applications." *Progress in Energy and Combustion Science*, **85**, 39 (2021) 10.1016/j.pecs.2021.100926.
462. M. J. Lain, J. Brandon and E. Kendrick, "Design strategies for high power vs. High energy lithium ion cells." *Batteries-Basel*, **5**, 11 (2019) 10.3390/batteries5040064.
463. L. Wei, T. S. Zhao, Q. Xu, X. L. Zhou and Z. H. Zhang, "In-situ investigation of hydrogen evolution behavior in vanadium redox flow batteries." *Appl. Energy*, **190**, 1112 (2017) 10.1016/j.apenergy.2017.01.039.
464. A. Tang, J. Bao and M. Skyllas-Kazacos, "Dynamic modelling of the effects of ion diffusion and side reactions on the capacity loss for vanadium redox flow battery." *J Power Sources*, **196**, 10737 (2011) 10.1016/j.jpowsour.2011.09.003.
465. Q. T. Luo, L. Y. Li, W. Wang, Z. M. Nie, X. L. Wei, B. Li, B. W. Chen, et al., "Capacity decay and remediation of nafion-based all-vanadium redox flow batteries." *ChemSusChem*, **6**, 268 (2013) 10.1002/cssc.201200730.
466. K. E. Rodby, T. J. Carney, Y. A. Gandomi, J. L. Barton, R. M. Darling and F. R. Brushett, "Assessing the levelized cost of vanadium redox flow batteries with capacity fade and rebalancing." *J Power Sources*, **460**, 11 (2020) 10.1016/j.jpowsour.2020.227958.
467. I. Miller, E. Gencer and F. M. O'sullivan, "A general model for estimating emissions from integrated power generation and energy storage. Case study: Integration of solar photovoltaic power and wind power with batteries." *Processes*, **6**, 24 (2018) 10.3390/pr6120267.
468. M. Uhrig, S. Koenig, M. R. Suriyah and T. Leibfried, "Lithium-based vs. Vanadium redox flow batteries - a comparison for home storage systems." in *10th International Renewable Energy Storage Conference (IRES)*, P. Droege Editor, p. 35, Energy Procedia, Dusseldorf, GERMANY (2016) 10.1016/j.egypro.2016.10.095.
469. H. He, S. Tian, C. Glaubenskleee, B. Tarroja, S. Samuelson, O. A. Ogunseitani and J. M. Schoenung, Potential health impact assessment of large-scale production of batteries for the electric grid, in *7th Installment of the REWAS conference series held at the TMS Annual Meeting and Exhibition focuses on developing tomorrow's technical cycles, 2022*, A. Lazou, K. Daehn, C. Fleuriault, M. Gokelma, E. Olivetti and C. Meskers Editors, p. 417, Springer Science and Business Media Deutschland GmbH (2022) 10.1007/978-3-030-92563-5_43.
470. M. C. Argyrou, P. Christodoulides and S. A. Kalogirou, "Energy storage for electricity generation and related processes: Technologies appraisal and grid scale applications." *Renewable & Sustainable Energy Reviews*, **94**, 804 (2018) 10.1016/j.rser.2018.06.044.
471. T. Placke, R. Kloepsch, S. Dühnen and M. Winter, "Lithium ion, lithium metal, and alternative rechargeable battery technologies: The odyssey for high energy density." *J. Solid State Electrochem.*, **21**, 1939 (2017) 10.1007/s10008-017-3610-7.
472. M. S. Ziegler and J. E. Trancik, "Re-examining rates of lithium-ion battery technology improvement and cost decline." *Energy Environ. Sci.*, **14**, 1635 (2021) 10.1039/d0ee02681f.
473. T. Y. Li, F. Xing, T. Liu, J. W. Sun, D. Q. Shi, H. M. Zhang and X. F. Li, "Cost, performance prediction and optimization of a vanadium flow battery by machine-learning." *Energy Environ. Sci.*, **13**, 4353 (2020) 10.1039/d0ee02543g.
474. C. Minke and T. Turek, "Materials, system designs and modelling approaches in techno-economic assessment of all-vanadium redox flow batteries - a review." *Journal of Power Sources*, **376**, 66 (2018) 10.1016/j.jpowsour.2017.11.058.
475. C. Minke, U. Kunz and T. Turek, "Techno-economic assessment of novel vanadium redox flow batteries with large-area cells." *J Power Sources*, **361**, 105 (2017) 10.1016/j.jpowsour.2017.06.066.
476. F. Lambert, "Tesla megapack project with 730 mwh of capacity is now up and running on pg&e's network." in *Electrek* (2022) <https://electrek.co/2022/04/18/tesla-megapack-project-730-mwh-pge/>.
477. "All-vanadium redox flow battery star enterprise dalian rongke power scientific research report." in *InfNews* (2022) <https://inf.news/ne/auto/45a02c9749cb4f5c5cf5633e93345ee3.html>.

478. D. Roberts and S. Brown, "The economics of firm solar power from li-ion and vanadium flow batteries in california." *MRS. Energy. Sustain.*, **9**, 129 (2022) 10.1557/s43581-022-00028-w.
479. V. Di Noto, K. Vezzù, G. Crivellaro, G. Pagot, C. Sun, L. Meda, I. A. Rutkowska, et al., "A general electrochemical formalism for vanadium redox flow batteries." *Electrochim Acta*, **408** (2022) 10.1016/j.electacta.2022.139937.
480. J. Lee, J. T. Muya, H. Chung and J. Chang, "Unraveling v(v)-v(iv)-v(iii)-v(ii) redox electrochemistry in highly concentrated mixed acidic media for a vanadium redox flow battery: Origin of the parasitic hydrogen evolution reaction." *ACS Applied Materials and Interfaces*, **11**, 42066 (2019) 10.1021/acsami.9b12676.
481. W. Wang, X. Wang, M. Guo and J. Li, "Different treatments for positive and negative electrode materials of an all-vanadium redox flow battery." *Beijing Keji Daxue Xuebao*, **29**, 1141 (2007)
482. A. K. Singh, M. Pahlevaninezhad, N. Yasri and E. P. L. Roberts, "Degradation of carbon electrodes in the all-vanadium redox flow battery." *ChemSusChem*, **14**, 2100 (2021) 10.1002/cssc.202100082.
483. M. S. Ziegler, J. Y. Song and J. E. Trancik, "Determinants of lithium-ion battery technology cost decline." *Energy Environ. Sci.*, **14**, 6074 (2021) 10.1039/d1ee01313k.
484. T. Luth, S. Konig, M. Suriyah and T. Leibfried, "Passive components limit the cost reduction of conventionally designed vanadium redox flow batteries." in *12th International Renewable Energy Storage Conference (IRES)*, p. 379, Energy Procedia, Dusseldorf, GERMANY (2018) 10.1016/j.egypro.2018.11.040.
485. M. Resch, J. Buhler, B. Schachler, R. Kunert, A. Meier and A. Sumper, "Technical and economic comparison of grid supportive vanadium redox flow batteries for primary control reserve and community electricity storage in germany." *Int. J. Energy Res.*, **43**, 337 (2019) 10.1002/er.4269.
486. T. Steckel, A. Kendall and H. Ambrose, "Applying levelized cost of storage methodology to utility-scale second-life lithium-ion battery energy storage systems." *Appl. Energy*, **300**, 11 (2021) 10.1016/j.apenergy.2021.117309.
487. J. Geng, S. Gao, X. Sun, Z. Liu, F. Zhao and H. Hao, "Potential of electric vehicle batteries second use in energy storage systems: The case of china." *Energy*, **253** (2022) 10.1016/j.energy.2022.124159.
488. P. Selinis and F. Farmakis, "Review - a review on the anode and cathode materials for lithium-ion batteries with improved subzero temperature performance." *J Electrochem Soc*, **169** (2022) 10.1149/1945-7111/ac49cc.
489. P. Rao and S. Jayanti, "Influence of electrode design parameters on the performance of vanadium redox flow battery cells at low temperatures." *J Power Sources*, **482**, 9 (2021) 10.1016/j.jpowsour.2020.228988.
490. V. Petrov, *Triz. Theory of inventive problem solving: Level 1*, p. 1, Springer International Publishing (2019) 10.1007/978-3-030-04254-7.
491. D. Zhou, "Cerium ion electrolyte using silver ion as anode catalyst and preparation method thereof." 2010CN-0255106 2010-08-17 (2010CN-0255106 2010-08-17).
492. P. Leung, "Development of a zinc-cerium redox flow battery." Thesis (2011)
493. Z. P. Xie, "Study of positive electrolyte for zinc-cerium redox flow battery application." Thesis, Ann Arbor (2011)
494. R. Jin, L. Wang, D. Yin, C. Li, Y. Wu, Y. Cheng, J. Lin, et al., "Composite negative plate of cerium and zinc redox flow cell and preparation method of plate." 2013CN-0179939 2013-05-16 (2013CN-0179939 2013-05-16).
495. L. F. Arenas, C. P. D. León and F. C. Walsh, "Mass transport and active area of porous pt/ti electrodes for the zn-ce redox flow battery determined from limiting current measurements." *Electrochim Acta*, **221**, 154 (2016) 10.1016/j.electacta.2016.10.097.
496. L. F. Arenas, F. C. Walsh and C. Ponce De León, "The importance of cell geometry and electrolyte properties to the cell potential of zn-ce hybrid flow batteries." *J Electrochem Soc*, **163**, A5170 (2016) 10.1149/2.0261601jes.
497. Z. Xie, B. I. N. Yang, H. Yuan and A. Shi, "Cerium-based ionic liquid electrolyte for positive electrode of flow battery and preparation method of cerium-based ionic liquid electrolyte." 2016CN-0177723 2016-03-26 (2016CN-0177723 2016-03-26).
498. Z. Xie, B. I. N. Yang, H. Yuan and H. Liu, "Zinc-cerium-based ionic liquid flow battery." 2016CN-0178691 2016-03-26 (2016CN-0178691 2016-03-26).
499. K. Amini and M. D. Pritzker, "Life-cycle analysis of zinc-cerium redox flow batteries." *Electrochim Acta*, **356** (2020) 10.1016/j.electacta.2020.136785.

500. K. Amini and M. D. Pritzker, "A two-dimensional transient model for a zinc-cerium redox flow battery validated by extensive experimental data." *J Power Sources*, **506** (2021) 10.1016/j.jpowsour.2021.230237.
501. S. H. Ge, B. L. Yi and H. M. Zhang, "Study of a high power density sodium polysulfide/bromine energy storage cell." *J Appl Electrochem*, **34**, 181 (2004) 10.1023/B:JACH.0000009936.82613.ad.
502. P. Zhao, H. M. Zhang, H. Gao, B. L. Yi and H. T. Zhou, "Research progress in sodium polysulfide/bromine redox flow battery." *Huagong Xiandai*, **27**, 18 (2007)
503. D. P. Scamman, G. W. Reade and E. P. L. Roberts, "Numerical modelling of a bromide-polysulphide redox flow battery. Part 2: Evaluation of a utility-scale system." *J Power Sources*, **189**, 1231 (2009) 10.1016/j.jpowsour.2009.01.076.
504. D. P. Scamman, G. W. Reade and E. P. L. Roberts, "Numerical modelling of a bromide-polysulphide redox flow battery part 1: Modelling approach and validation for a pilot-scale system." *J Power Sources*, **189**, 1220 (2009) 10.1016/j.jpowsour.2009.01.071.
505. H. Zhang, "Polysulfide-bromine flow batteries (pbbs) for medium- and large-scale energy storage." in *Advances in batteries for medium and large-scale energy storage: Types and applications*, POLYSULFIDEBROMINEFLOWBATTERIESPBBIFORMEDIUMANDLARGESCALEENERGYSTORAGE2015 Editor, p. 317, Elsevier (2015) 10.1016/b978-1-78242-013-2.00009-1.
506. L. N. Wang, X. F. Wang, J. Y. Liu, H. Yang, C. M. Fu, Y. Y. Xia and T. X. Liu, "A rechargeable metal-free full-liquid sulfur-bromine battery for sustainable energy storage." *J. Mater. Chem. A*, **6**, 20737 (2018) 10.1039/c8ta07951j.
507. M. M. Gross and A. Manthiram, "Long-life polysulfide-polyhalide batteries with a mediator-ion solid electrolyte." *ACS Appl. Ener. Mat.*, **2**, 3445 (2019) 10.1021/acsaem.9b00253.
508. S. Zhang, W. Guo, F. Yang, P. Zheng, R. Qiao and Z. Li, "Recent progress in polysulfide redox-flow batteries." *Batteries and Supercaps*, **2**, 627 (2019) 10.1002/batt.201900056.
509. L. Su, A. F. Badel, C. Cao, J. J. Hinricher and F. R. Brushett, "Toward an inexpensive aqueous polysulfide-polyiodide redox flow battery." *Ind. Eng. Chem. Res.*, **56**, 9783 (2017) 10.1021/acs.iecr.7b01476.
510. W. Huang, Q. L. Zou and Y. C. Lu, "Ion-selective membrane-free dual sulfur-iodine catholyte for low-cost and high-power flow battery applications." *Batteries Supercaps*, **2**, 941 (2019) 10.1002/batt.201900107.
511. J. Zai, Y. Zhu, K. He, A. Iqbal, S. Huang, Z. Chen and X. Qian, "Sandwiched cu₇s₄@graphite felt electrode for high performance aqueous polysulfide/iodide redox flow batteries: Enhanced cycling stability and electrocatalytic dynamics of polysulfides." *Mater. Chem. Phys.*, **250** (2020) 10.1016/j.matchemphys.2020.123143.
512. Y. Zhu, K. He, T. T. Tsega, N. Ali, J. T. Zai, S. S. Huang, X. F. Qian, et al., "Cu₂cog₄ nanocrystals for high performance aqueous polysulfide/iodide redox flow batteries: Enhanced selectively towards the electrocatalytic conversion of polysulfides." *Sustain. Energ. Fuels*, **4**, 2892 (2020) 10.1039/c9se01201j.
513. Y. Qin, X. Li, W. Liu and X. Lei, "High-performance aqueous polysulfide-iodide flow battery realized by an efficient bifunctional catalyst based on copper sulfide." *Mater. Today Energy*, **21**, 8 (2021) 10.1016/j.mtener.2021.100746.
514. M. Rahimi, A. Molaei Dehkordi and E. P. L. Roberts, "Magnetic nanofluidic electrolyte for enhancing the performance of polysulfide/iodide redox flow batteries." *Electrochim Acta*, **369** (2021) 10.1016/j.electacta.2020.137687.
515. W. Glass and G. H. Boyle, "Performance of hydrogen-bromine fuel cells." in *Fuel cell systems*, p. 203 (1969) 10.1021/ba-1965-0047.ch015.
516. V. Jalan and J. A. Kosek, "Electrodes for a hydrogen bromine battery." *Journal of the Electrochemical Society*, **133**, C121 (1986)
517. K. L. C. Hsueh, D. T., Optimization of h₂/br₂ secondary battery for energy-storage, in *Journal of the Electrochemical Society*, OPTIMIZATIONOFH₂BR₂SECONDARYBATTERYFORENERGYSTORAGE1986 Editor, p. C121 (1986)
518. J. a. L. Kosek, A. B., "Advanced hydrogen electrode for a hydrogen bromine battery." *Journal of Power Sources*, **22**, 293 (1988) 10.1016/0378-7753(88)80024-7.
519. M. Kuttinger, R. Riasse, J. Wlodarczyk, P. Fischer and J. Tubke, "Improvement of safe bromine electrolytes and their cell performance in h₂/ br₂ flow batteries caused by tuning the bromine complexation equilibrium." *J Power Sources*, **520**, 12 (2022) 10.1016/j.jpowsour.2021.230804.

520. Y. Papat, D. P. Trudgeon, X. Li, P. Connor, A. Asokan and M. E. Suss, "Electrochemical testing of carbon materials as bromine electrodes for the hydrogen-bromine redox flow battery." *Batteries*, **8**, 166 (2022)
521. K. K. Saadi, Michael Fischer, Peter Zitoun, David, "Hydrogen-bromine redox-flow battery cycling with bromine complexing agent: On the benefits of nanoporous separator versus proton exchange membrane." *Energy Technol. (Weinheim, Ger.)*, **9**, 2000978 (2021) 10.1002/ente.202000978.
522. M. B. Kuettinger, Ruben Wlodarczyk, Jakub K. Fischer, Peter Tuebke, Jens, "Cycle behaviour of hydrogen bromine redox flow battery cells with bromine complexing agents." *Journal of Power Sources*, **495**, N.PAG (2021) 10.1016/j.jpowsour.2021.229820.
523. Y. a. K. Hugo, W. ; Dalessi, G. ; Forner-Cuenca, A. ; Borneman, Z. ; Nijmeijer, K., "Techno-economic analysis of a kilo-watt scale hydrogen-bromine flow battery system for sustainable energy storage." *Processes*, **8**, 1492 (2020) 10.3390/pr8111492.
524. K. Saadi, P. Nanikashvili, Z. Tatus-Portnoy, S. Hardisty, V. Shokhen, M. Zysler and D. Zitoun, "Crossover-tolerant coated platinum catalysts in hydrogen/bromine redox flow battery." *J Power Sources*, **422**, 84 (2019) 10.1016/j.jpowsour.2019.03.043.
525. Y. Li and T. V. Nguyen, "Core-shell rhodium sulfide catalyst for hydrogen evolution reaction / hydrogen oxidation reaction in hydrogen-bromine reversible fuel cell." *Journal of Power Sources*, **382**, 152 (2018) 10.1016/j.jpowsour.2018.02.005.
526. Y. a. K. Hugo, Wiebrand ; Sikkema, Friso ; Borneman, Zandrie ; Nijmeijer, Kitty, "Performance mapping of cation exchange membranes for hydrogen-bromine flow batteries for energy storage." *J. Membr. Sci.*, **566**, 406 (2018) 10.1016/j.memsci.2018.09.006.
527. K. K. Oh, Tae June ; Park, Sungjin ; Tucker, Michael C. ; Weber, Adam Z. ; Ju, Hyunchul, "Effect of flow-field structure on discharging and charging behavior of hydrogen/bromine redox flow batteries." *Electrochimica Acta*, **230**, 160 (2017) 10.1016/j.electacta.2017.01.125.
528. K. Oh, A. Z. Weber and H. Ju, "Study of bromine species crossover in h₂/br₂ redox flow batteries." *Int. J. Hydrog. Energy*, **42**, 3753 (2017) 10.1016/j.ijhydene.2016.12.063.
529. G. Lin, P. Y. Chong, V. Yarlagadda, T. V. Nguyen, R. J. Wycisk, P. N. Pintauro, M. Bates, et al., "Advanced hydrogen-bromine flow batteries with improved efficiency, durability and cost." *J Electrochem Soc*, **163**, A5049 (2016) 10.1149/2.0071601jes.
530. N. M. Singh, E. W., "Levelized cost of energy and sensitivity analysis for the hydrogen-bromine flow battery." *Journal of Power Sources*, **288**, 187 (2015) 10.1016/j.jpowsour.2015.04.114.
531. K. T. Cho, P. Ridgway, A. Z. Weber, S. Haussener, V. Battaglia and V. Srinivasan, "High performance hydrogen/bromine redox flow battery for grid-scale energy storage (vol 159, pg a1806, 2012)." *Journal of the Electrochemical Society*, **160**, X9 (2013) 10.1149/2.006308jes.
532. H. Y. Kreutzer, Venkata ; Van Nguyen, Trung, "Performance evaluation of a regenerative hydrogen-bromine fuel cell." *Journal of the Electrochemical Society*, **159**, F331 (2012) 10.1149/2.086207jes.
533. K. T. Cho, P. Ridgway, A. Z. Weber, S. Haussener, V. Battaglia and V. Srinivasan, "High performance hydrogen/bromine redox flow battery for grid-scale energy storage." *J Electrochem Soc*, **159**, A1806 (2012) 10.1149/2.018211jes.
534. M. Yang, Z. Xu, W. Xiang, H. Xu, M. Ding, L. Li, A. Tang, et al., "High performance and long cycle life neutral zinc-iron flow batteries enabled by zinc-bromide complexation." *Energy Storage Mater.*, **44**, 433 (2022) 10.1016/j.ensm.2021.10.043.
535. H. Kaku, Y. Kawagoe, Y. R. Dong, R. Tatsumi, K. Moriuchi and T. Shigematsu, "Enhanced performance of ti/mn redox flow battery." in *Symposium on Plasma Nano Science and Technology held during the 231st Meeting of the Electrochemical-Society (ECS)*, p. 173, ECS Transactions, New Orleans, LA (2017) 10.1149/07711.0173ecst.
536. H. Kaku, Y. R. Dong, K. Hanafusa, K. Moriuchi and T. Shigematsu, "Effect of ti(iv) ion on mn(iii) stability in ti/mn electrolyte for redox flow battery." in *Symposium on Large-Scale Energy Storage 7 - 229th ECS Meeting*, S. Narayanan, S. Mukerjee, C. Johnson and J. St-Pierre Editors, p. 1 (2016) 10.1149/07210.0001ecst.
537. A. O. O. Bahdad, Y. C. Li and T. Van Nguyen, "Characterization of the electrochemical behavior of mnso₄ with and without tioso₄ in h₂so₄ solution." *J Electrochem Soc*, **168**, 15 (2021) 10.1149/1945-7111/ac0e4e.
538. M. J. Nan, L. Qiao, Y. Q. Liu, H. M. Zhang and X. K. Ma, "Improved titanium-manganese flow battery with high capacity and high stability." *J Power Sources*, **522** (2022) 10.1016/j.jpowsour.2022.230995.

539. L. Qiao, C. X. Xie, M. J. Nan, H. M. Zhang, X. K. Ma and X. F. Li, "Highly stable titanium-manganese single flow batteries for stationary energy storage." *J. Mater. Chem. A*, **9**, 12606 (2021) 10.1039/d1ta01147b.
540. L. Qiao, M. L. Fang, S. M. Liu, H. M. Zhang and X. K. Ma, "New-generation iron-titanium flow batteries with low cost and ultrahigh stability for stationary energy storage." *Chem. Eng. J.*, **434**, 9 (2022) 10.1016/j.cej.2022.134588.
541. W. Wang, S. Kim, B. W. Chen, Z. M. Nie, J. L. Zhang, G. G. Xia, L. Y. Li, et al., "A new redox flow battery using fe/v redox couples in chloride supporting electrolyte." *Energy Environ. Sci.*, **4**, 4068 (2011) 10.1039/c0ee00765j.
542. Y. Liu and X. Xia, "Electrochemical behavior of the ce⁴⁺ / ce³⁺ couple in the novel ce - v redox flow cell." in *2008 MRS Fall Meeting*, p. 44, Boston, MA (2008) 10.1557/proc-1127-t01-03.
543. G. Rasmussen Paul, "Electrical storage device utilizing pyrazine-based cyanoazacarbons and polymers derived therefrom." 2011US-13169300 2011-06-27.
544. P. Rasmussen, A single substance organic redox flow battery, in, Vinazene Inc., 2853 Daleview Dr., Ann Arbor, MI 48105-9684 United States (2012-2013)
545. Vanadium redox flow battery companies, in (2022)
546. T. F. Fuller and J. N. Harb, *Electrochemical engineering*, John Wiley & Sons (2018)
547. S. B. Wan, X. W. Liang, H. R. Jiang, J. Sun, N. Djilali and T. S. Zhao, "A coupled machine learning and genetic algorithm approach to the design of porous electrodes for redox flow batteries." *Appl. Energy*, **298** (2021) 10.1016/j.apenergy.2021.117177.
548. S. Sadeghi and E. J. Javaran, "Comparison of combining redox flow and lead-acid batteries with on-grid and stand-alone photovoltaic systems." *Environ Prog Sustainable Energy*, **38** (2019) 10.1002/ep.13182.
549. M. Shahjalal, P. K. Roy, T. Shams, A. Fly, J. I. Chowdhury, M. R. Ahmed and K. Liu, "A review on second-life of li-ion batteries: Prospects, challenges, and issues." *Energy*, **241** (2022) 10.1016/j.energy.2021.122881.
550. T. Montes, M. Etxandi-Santolaya, J. Eichman, V. J. Ferreira, L. Trilla and C. Corchero, "Procedure for assessing the suitability of battery second life applications after ev first life." *Batteries*, **8** (2022) 10.3390/batteries8090122.
551. M. Bartolozzi, "Development of redox flow batteries-a historical bibliography." *Journal of Power Sources*, **27**, 219 (1989) 10.1016/0378-7753(89)80037-0.
552. M. Skyllas-Kazacos, "A historical preview of the vanadium redox flow battery development at school of chemical engineering and industrial chemistry." (2002)
553. C. F.-F. Ponce De Leon, A. ; Gonzalez-Garcia, J. ; Szanto, D. A. ; Walsh, F. C., "Redox flow cells for energy conversion." *Journal of Power Sources*, **160**, 716 (2006) 10.1016/j.jpowsour.2006.02.095.
554. A. Z. M. Weber, Matthew M. ; Meyers, Jeremy P. ; Ross, Philip N. ; Gostick, Jeffrey T. ; Liu, Qinghua, "Redox flow batteries: A review." *Journal of Applied Electrochemistry*, **41**, 1137 (2011) 10.1007/s10800-011-0348-2.
555. G. S. Kear, Akeel A. ; Walsh, Frank C., "Development of the all-vanadium redox flow battery for energy storage: A review of technological, financial and policy aspects." *International Journal of Energy Research*, **36**, 1105 (2012) 10.1002/er.1863.
556. H. Zhang, "Liquid redox rechargeable batteries." in *Electrochemical technologies for energy storage and conversion*, LIQUIDREDOXRECHARGEABLEBATTERIES2012 Editor, p. 279, Wiley-VCH (2012) 10.1002/9783527639496.ch7.
557. M. Skyllas-Kazacos, C. Menictas and T. Lim, "Redox flow batteries for medium-to large-scale energy storage." in *Electricity transmission, distribution and storage systems*, p. 398, Elsevier Ltd (2013) 10.1533/9780857097378.3.398.
558. A. L. Parasuraman, Tuti Mariana ; Menictas, Chris ; Skyllas-Kazacos, Maria, "Review of material research and development for vanadium redox flow battery applications." *Electrochimica Acta*, **101**, 27 (2013) 10.1016/j.electacta.2012.09.067.
559. C. Z. Ding, Huamin ; Li, Xianfeng ; Liu, Tao ; Xing, Feng, "Vanadium flow battery for energy storage: Prospects and challenges." *Journal of Physical Chemistry Letters*, **4**, 1281 (2013) 10.1021/jz4001032.
560. P. G. Alotto, M. ; Moro, F., "Redox flow batteries for the storage of renewable energy: A review." *Renewable Sustainable Energy Rev*, **29**, 325 (2014) 10.1016/j.rser.2013.08.001.

561. N. S. Hudak, "Practical thermodynamic quantities for aqueous vanadium- and iron-based flow batteries." *J Power Sources*, **269**, 962 (2014) 10.1016/j.jpowsour.2013.12.089.
562. M. M. Skyllas-Kazacos, J. F., "Vanadium redox flow batteries (vrbs) for medium- and large-scale energy storage." in *Advances in batteries for medium and large-scale energy storage: Types and applications*, VANADIUMREDOXFLOWBATTERIESVRBSFORMEDIUMANDLARGESCALEENERGYSTORAGE2015 Editor, p. 329, Elsevier (2015) 10.1016/b978-1-78242-013-2.00010-8.
563. K. J. P. Kim, Min-Sik ; Kim, Young-Jun ; Kim, Jung Ho ; Dou, Shi Xue ; Skyllas-Kazacos, M., "A technology review of electrodes and reaction mechanisms in vanadium redox flow batteries." *Journal of Materials Chemistry A*, **3**, 16913 (2015) 10.1039/c5ta02613j.
564. J. R. Noack, Nataliya ; Herr, Tatjana ; Fischer, Peter, "The chemistry of redox-flow batteries." *Angewandte Chemie-International Edition*, **54**, 9775 (2015) 10.1002/anie.201410823.
565. Q. Z. Huang and Q. Wang, "Next-generation, high-energy-density redox flow batteries." *Chempluschem*, **80**, 312 (2015) 10.1002/cplu.201402099.
566. L. Su, J. A. Kowalski, K. J. Carroll and F. R. Brushett, Recent developments and trends in redox flow batteries, in *Green Energy and Technology*, p. 673, Springer Verlag (2015) 10.1007/978-3-319-15458-9_24.
567. M. Skyllas-Kazacos, "Flow batteries: Vanadium and beyond." in *Redox flow batteries: Fundamentals and applications*, p. 327, CRC Press (2017) 10.1201/9781315152684.
568. R. Holze, *Kinetics of fast redox systems for energy storage*, p. 591, Springer International Publishing Ag, Cham (2017) 10.1007/978-3-662-46657-5_18.
569. C. K. Z. Zhang, L. Y. ; Ding, Y. ; Peng, S. S. ; Guo, X. L. ; Zhao, Y. ; He, G. H. ; Yu, G. H., "Progress and prospects of next-generation redox flow batteries." *Energy Storage Materials*, **15**, 324 (2018) 10.1016/j.ensm.2018.06.008.
570. L. F. D. L. Arenas, C. P. ; Walsh, F. C., "Redox flow batteries for energy storage: Their promise, achievements and challenges." *Current Opinion in Electrochemistry*, **16**, 117 (2019) 10.1016/j.coelec.2019.05.007.
571. A. B. Forner-Cuenca, F. R., "Engineering porous electrodes for next-generation redox flow batteries: Recent progress and opportunities." *Current Opinion in Electrochemistry*, **18**, 113 (2019) 10.1016/j.coelec.2019.11.002.
572. T. Shigematsu, "The development and demonstration status of practical flow battery systems." *Current Opinion in Electrochemistry*, **18**, 55 (2019) 10.1016/j.coelec.2019.10.001.
573. H. M. Zhang, "Progress and perspectives of flow battery technologies." *Current Opinion in Electrochemistry*, **18**, 123 (2019) 10.1016/j.coelec.2019.10.015.
574. E. Sánchez-Díez, E. Ventosa, M. Guarnieri, A. Trovò, C. Flox, R. Marcilla, F. Soavi, et al., "Redox flow batteries: Status and perspective towards sustainable stationary energy storage." *J Power Sources*, **481** (2021) 10.1016/j.jpowsour.2020.228804.
575. M. M. Petrov, A. D. Modestov, D. V. Konev, A. E. Antipov, P. A. Loktionov, R. D. Pichugov, N. V. Kartashova, et al., "Redox flow batteries: Role in modern electric power industry and comparative characteristics of the main types." *Russian Chemical Reviews*, **90**, 677 (2021) 10.1070/rcr4987.
576. H. M. Zhang, W. J. Lu and X. F. Li, "Progress and perspectives of flow battery technologies." *Electrochemical Energy Reviews*, **2**, 492 (2019) 10.1007/s41918-019-00047-1.
577. L. Zhang, R. Feng, W. Wang and G. Yu, "Emerging chemistries and molecular designs for flow batteries." *Nat. Rev. Chem.* (2022) 10.1038/s41570-022-00394-6.
578. G. Gupta, B. Satola, L. Komsijska, C. Harms, T. Hickmann and A. Dyck, "Electrochemical aging and characterization of graphite-polymer based composite bipolar plates for vanadium redox flow batteries." *J Electrochem Soc*, **169**, 080503 (2022) 10.1149/1945-7111/ac8240.
579. E. Ventosa, "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." *Curr. Opin. Chem. Eng.*, **37**, 100834 (2022) 10.1016/j.coche.2022.100834.
580. A. Antipov, R. Pichugov, L. Abunaeva, S. F. Tong, M. Petrov, A. Pustovalova, I. Speshilov, et al., "Halogen hybrid flow batteries advances for stationary chemical power sources technologies." *Energies*, **15**, 20 (2022) 10.3390/en15197397.
581. R. K. Gautam and A. Kumar, "A review of bipolar plate materials and flow field designs in the all-vanadium redox flow battery." *J. Energy Storage*, **48** (2022) 10.1016/j.est.2022.104003.

582. K. Maeda, M. Moritoki, S. Yae, K. Fukui, N. Fukumuro and T. Sugahara, "Pressure-induced evolution in the durability of nickel-metal hydride batteries under high-current charge." *Phys. Chem. Chem. Phys.*, **24**, 14085 (2022) 10.1039/d1cp05100h.
583. Z. Zhu, Q. Wang and Q. Wu, "On the examination of the darcy permeability of soft fibrous porous media; new correlations." *Chem. Eng. Sci.*, **173**, 525 (2017) 10.1016/j.ces.2017.08.021.
584. O. Rahli, L. Tadriss and M. Miscevic, "Experimental analysis of fibrous porous media permeability." *AIChE J.*, **42**, 3547 (1996) 10.1002/aic.690421224.
585. A. Tamayol, F. Mcgregor and M. Bahrami, "Single phase through-plane permeability of carbon paper gas diffusion layers." *J. Power Sources*, **204**, 94 (2012) 10.1016/j.jpowsour.2011.11.084.
586. M. Kaviani, *Principles of heat transfer in porous media*, Springer Science & Business Media (2012) 10.1007/978-1-4684-0412-8.
587. J. Happel, "Viscous flow relative to arrays of cylinders." *AIChE J.*, **5**, 174 (1959) 10.1002/aic.690050211.
588. T. Yang, L. Hu, D. Yu, X. Xiong, J. Chvojka, M. Venkataraman, M. Petru, et al., "Simple determination of key structural parameters for fibrous materials enabled by ergun-type and kozeny-type equations." *Polym Test*, **108** (2022) 10.1016/j.polymertesting.2022.107514.
589. P. Xu and B. Yu, "Developing a new form of permeability and kozeny-carman constant for homogeneous porous media by means of fractal geometry." *Adv. Water Resour.*, **31**, 74 (2008) 10.1016/j.advwatres.2007.06.003.
590. R. K. Jervis, M. D. R. ; Neville, T. P. ; Meyer, Q. ; Brown, L. D. ; Iacoviello, F. ; Gostick, J. T. ; Brett, D. J. L. ; Shearing, P. R., "In situ compression and x-ray computed tomography of flow battery electrodes." *J. Energy Chem.*, **27**, 1353 (2018) 10.1016/j.jechem.2018.03.022.
591. T. J. T. Davies, Joseph J., "High-performance vanadium redox flow batteries with graphite felt electrodes." *C-Journal of Carbon Research*, **4**, 8/1 (2018) 10.3390/c4010008.
592. H. T. Zhang, Yi ; Li, Jiayan ; Xue, Bing, "Studies on properties of rayon- and polyacrylonitrile-based graphite felt electrodes affecting fe/cr redox flow battery performance." *Electrochimica Acta*, **248**, 603 (2017) 10.1016/j.electacta.2017.08.016.
593. M. B. Becker, Niels ; Tenhumberg, Nils ; Turek, Thomas, "Kinetic studies at carbon felt electrodes for vanadium redox-flow batteries under controlled transfer current density conditions." *Electrochimica Acta*, **252**, 12 (2017) 10.1016/j.electacta.2017.07.062.
594. M. D. R. J. Kok, Rhodri ; Brett, Dan ; Shearing, Paul R. ; Gostick, Jeff T., "Insights into the effect of structural heterogeneity in carbonized electrospun fibrous mats for flow battery electrodes by x-ray tomography." *Small*, **14**, 15 (2018) 10.1002/smll.201703616.
595. S. K. Liu, M. ; Kim, Y. ; Barton, J. L. ; Brushett, F. R. ; Gostick, J., "Evaluation of electrospun fibrous mats targeted for use as flow battery electrodes." *Journal of the Electrochemical Society*, **164**, A2038 (2017) 10.1149/2.1301709jes.
596. A. Tang, J. Bao and M. Skyllas-Kazacos, "Studies on pressure losses and flow rate optimization in vanadium redox flow battery." *J Power Sources*, **248**, 154 (2014) 10.1016/j.jpowsour.2013.09.071.
597. F. F. Rivera, B. Miranda-Alcántara, G. Orozco, C. Ponce De León and L. F. Arenas, "Pressure drop analysis on the positive half-cell of a cerium redox flow battery using computational fluid dynamics: Mathematical and modelling aspects of porous media." *Front. Chem. Sci. Eng.*, **15**, 399 (2021) 10.1007/s11705-020-1934-9.
598. M. Kugel, "Kohle-zink-element. ." DE45468D 0 (1887-08-23).
599. E. Brousseau, "Halide-electrolyte secondary battery." 1904FR-0348605D 1904-12-06 (1904FR-0348605D 1904-12-06).
600. E. Brousseau, "Secondary cell and battery." 1905FR-0361058D 1905-11-30 (1905FR-0361058D 1905-11-30).
601. E. Almeida Salazar, "Secondary battery or accumulator." BE268047D 0NL18640D 01925US-01075432 1925-12-14 (BE268047D 0NL18640D 01925US-01075432 1925-12-14).
602. "Improvements in or relating to galvanic batteries." 1925GB-0032718 1925-12-28 (1925GB-0032718 1925-12-28).
603. E. M. Gardner, 1886US-342508D 0 (1886US-342508D 0).
604. , 1892US-468887D 0 (1892US-468887D 0).
605. S. W. Maquay, "Galvanic battery." 1890US-433738D 0 (1890US-433738D 0).

606. C. E. Eagan, 1887US-00249194 1887-09-08 (1887US-00249194 1887-09-08).
607. J. Reed Charles, "Galvanic battery." 1901US-00068024 1901-07-12 (1901US-00068024 1901-07-12).
608. "Improvements in and relating to double-fluid cells." 1924GB-0027275 1924-11-14 (1924GB-0027275 1924-11-14).
609. J. E. Pearce, 1887US-356261D 0 (1887US-356261D 0).
610. "Improvements in electric accumulators." 1918GB-0005867 1918-04-05 (1918GB-0005867 1918-04-05).
611. A. Emanuel Philip, "Electric battery." 1915US-01059838 1915-11-05 1915US-01065330 1915-12-06 1915US-01065329 1915-12-06 (1915US-01059838 1915-11-05 1915US-01065330 1915-12-06 1915US-01065329 1915-12-06).
612. , DE55193D 0 (DE55193D 0).
613. , GB2823 (GB2823).
614. A. R. Upward and C. W. Pridham, "Galvanic battery and apparatus connected therewith." 1887US-357646D 0 (1887US-357646D 0).
615. , 1888US-00288373 1888-10-17 (1888US-00288373 1888-10-17).
616. A. Lyons John and C. Broadwell Edward, "Electrical storage-cell." 1903US-00140664 1903-01-26 (1903US-00140664 1903-01-26).
617. E. R. Little Homer, "Primary battery." 1912US-00711693 1912-07-26 (1912US-00711693 1912-07-26).
618. G. Marconi, "Electric accumulator." 1918US-01221501 1918-03-09 (1918US-01221501 1918-03-09).
619. J. Newman and N. P. Balsara, *Electrochemical systems*, John Wiley & Sons (2021)
620. J. Shin, B. Jeong, M. F. Chinannai and H. Ju, "Mitigation of water and electrolyte imbalance in all-vanadium redox flow batteries." *Electrochim Acta*, **390** (2021) 10.1016/j.electacta.2021.138858.
621. K. Oh, M. Moazzam, G. Gwak and H. Ju, "Water crossover phenomena in all-vanadium redox flow batteries." *Electrochim Acta*, **297**, 101 (2019) 10.1016/j.electacta.2018.11.151.
622. R. Xiong, B. Xiong, Q. Zhang, S. Shi, Y. Su and D. Zhang, "Capacity fading model of vanadium redox flow battery considering water molecules migration." *Int. J. Green Energy* (2022) 10.1080/15435075.2021.2015599.
623. J. T. Vardner, A. A. Ye, D. A. Valdes and A. C. West, "Current-driven vanadium crossover as a function of soc and sod in the vanadium redox flow battery." *J Electrochem Soc*, **167** (2020) 10.1149/1945-7111/ab88bc.
624. L. Y. Li, S. Kim, W. Wang, M. Vijayakumar, Z. M. Nie, B. W. Chen, J. L. Zhang, et al., "A stable vanadium redox-flow battery with high energy density for large-scale energy storage." *Advanced Energy Materials*, **1**, 394 (2011) 10.1002/aenm.201100008.
625. E. Lallo, A. Khataee and R. W. Lindström, "Vanadium redox flow battery using aemion™ anion exchange membranes." *Process.*, **10** (2022) 10.3390/pr10020270.
626. L. A.V. and L. E.E., "The choice of russian researchers between scopus and web of science: Results of questionnaire by the russian foundation for fundamental research." in (2020-11-30) https://podpiska.rfbr.ru/storage/rfbr_survey1.html.
627. S. Jeong, S.-K. Chun, J. Lee and Y. Kwon, "Application of porous carbon catalyst activating reaction of positive electrode in vanadium redox flow battery." *Journal of Energy Engineering*, **23**, 150 (2014) 10.5855/energy.2014.23.3.150.
628. B. K. Chakrabarti, D. Nir, V. Yufit, P. V. Aravind and N. P. Brandon, "Enhanced performance of an all-vanadium redox flow battery employing graphene modified carbon paper electrodes." *World Academy of Science, Engineering and Technology, International Journal of Chemical and Molecular Engineering*, **11**, 622 (2017) 10.5281/zenodo.1131954.
629. H. Peng, Z. Liu and C. Tao, "Chaotic phenomenon in vanadium redox flow battery." *International Journal Of Petrochemical Science & Engineering*, **2** (2017) 10.15406/ipcse.2017.02.00031.
630. A. Habekost, "Vanadium redox flow batteries with different electrodes and membranes." *World Journal of Chemical Education*, **6**, 8 (2018) 10.12691/wjce-6-1-2.
631. K. K. P. D. K. K. Pathak and N. Tjprc, "Feasibility of using vanadium redox flow battery as energy storage in solar chimney power plants." *International Journal of Mechanical and Production Engineering Research and Development*, **10**, 9303 (2020) 10.24247/ijmperdjun2020882.
632. H. T, "Test of surface roughness for bipolar plates for vanadium redox flow batteries and biological fuel cells." *Research & Development in Material Science*, **14**, 1502 (2020) 10.31031/rdms.2020.14.000829.

633. B.-Y. Jung, C.-H. Ryu and G.-J. Hwang, "A study on the effect gasket thickness and electrolyte flow rate in the all-vanadium redox flow battery." *Journal of the Korean Battery Society*, **1**, 152 (2021) 10.53619/kobs.2021.12.1.2.152.
634. İ. Kayalı and G. Elden, "A study on different flow channel shapes in a vanadium redox flow battery with serpentine flow field." *Int. J. Sust. Aviat.*, **7**, 334 (2021) 10.1504/ijsa.2021.119692.
635. K. Ngamsai and A. Arpornwichanop, Electrochemical model development and overcharging investigation of the vanadium redox flow battery, in, p. 117, University of Maribor Press (2017) 10.18690/978-961-286-052-3.12.
636. A. N. M. A. Siddiquee and K. Jeong, Conjugated dynamic modeling on vanadium redox flow battery with non-constant variance for renewable power plant applications, in, American Society of Mechanical Engineers (2016) 10.1115/imece2016-67462.
637. C. Stegner, An open circuit voltage and overpotential model for an all vanadium redox flow battery derived from several years of operating data, in, Atlantis Press (2022) 10.2991/ah.k.220301.012.
638. R. Wittman, Gas evolution from mixed-acid vanadium redox flow battery, in, US DOE (2021) 10.2172/1870092.
639. B. Zhang, Y. G. Lei, B. Bai and T. Zhao, Numerical investigation of thermal management for kilowatt vanadium redox flow batteries, in, Begellhouse (2014) 10.1615/ihtc15.tmg.008913.
640. Y. Okita, Y. Nagasaka and Y. Taguchi, "Experimental study on measurement of diffusion coefficient of electrolyte solutions using infrared solet forced rayleigh scattering method: Application to anode active material for vanadium redox flow battery." *The Proceedings of the Thermal Engineering Conference*, **2020**, 0175 (2020) 10.1299/jsmeted.2020.0175.
641. H. Jiang, "Towards high-performance vanadium redox flow batteries by cost-effectively enhancing the transport and electrochemical properties of electrodes." Thesis (2019) 10.14711/thesis-991012638164003412.
642. F. J. Oldenburg, "Membrane design towards improved vanadium redox flow batteries." Thesis (2019) 10.3929/ethz-b-000371207.
643. L. Eifert, "Characterization and modification of carbon electrodes for vanadium redox flow batteries." Thesis (2020) 10.18725/oparu-34975.
644. C. P. Munoz, "Mathematical modelling of vanadium-based redox flow batteries." Thesis (2020) 10.25560/87188.
645. S. J. Yoon, "Development of modified graphite felt electrodes for the vanadium redox flow battery." Thesis (2020) 10.22028/d291-31337.
646. G. Qiu, "Pore-scale modeling of transport phenomena in vanadium redox flow batteries." Thesis (2021) 10.17918/etd-3906.
647. P. C. Ghimire, "Electrode modification and in-situ studies to enhance the performance of vanadium redox flow batteries." Thesis (2022) 10.32657/10356/88800.
648. Y. Zou, "Vanadium flow batteries : Principles, characteristics, structure, evaluation." in, p. 77, CRC Press (2017) 10.1201/9781315152684-3.
649. M. Dassisti, P. Mastroilli, A. Rizzuti, G. Cozzolino, M. Chimienti, A. G. Olabi, F. Matera, et al., "Vanadium: A transition metal for sustainable energy storing in redox flow batteries." in, Elsevier (2016) 10.1016/b978-0-12-803581-8.04007-8.
650. S. Kim, "Vanadium redox flow batteries: Electrochemical engineering." in, IntechOpen (2019) 10.5772/intechopen.85166.
651. S. Jayanti, R. Gundlapalli, R. Chetty, C. R. Jeevandoss, K. Ramanujam, D. S. Monder, R. Rengaswamy, et al., "Characteristics of an indigenously developed 1 kw vanadium redox flow battery stack." in, p. 923, Springer Singapore (2020) 10.1007/978-981-15-5955-6_88.
652. R. Chen, Z. Huang, R. Hempelmann, D. Henkensmeier and S. Kim, *Encyclopedia of electrochemistry - vanadium redox flow batteries*, p. 1, Wiley (2020) 10.1002/9783527610426.bard110010.
653. Lead-acid batteries for propulsion power of lightweight vehicles - general requirements and methods of test, in, BSI British Standards (2021) 10.3403/30376543u.
654. M. Gu Kang, W. Ahn, J. Kang, S. Ae Song, K. Kim, J. Young Woo, Y.-C. Jeong, et al., "Superior electrocatalytic negative electrode with tailored nitrogen functional group for vanadium redox flow battery." *J. Energy Chem.* (2022) 10.1016/j.jchem.2022.11.022.

655. B. Khaki, R. S. Sawant and P. Das, "Parameter estimation of vanadium redox battery electrochemical model by reduced number of sensors." *SSRN Electronic Journal* (2022) 10.2139/ssrn.4163033.
656. S. Sreenath, C. M. Pawar, P. Bavdane, D. Y. Nikumbe and R. K. Nagarale, "A sulfonated polyethylene–styrene cation exchange membrane: A potential separator material in vanadium redox flow battery applications." *Energy Advances*, **1**, 87 (2022) 10.1039/d1ya00059d.