

The Amazing Potential of Redox Flow Batteries for Renewable Energy Storage

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1. Abstract

A promising, renewable energy storing technology is the reduction-oxidation (redox flow) battery, which has been successfully applied to commercial applications. Redox flow batteries offer an easily scaled-up solution for storing energy, with minimal self-discharge and capacity loss after many charge-discharge cycles. Here, we review the literature on redox flow batteries, identify current research trends in the literature using a new software tool for identifying keywords, and suggest future directions for continuing redox flow battery research.

2. Introduction

The disastrous impacts of climate change are well recognized by the global scientific community.¹⁻¹⁰ Replacing fossil fuel energy systems with renewable energy systems are also recognized as a solution for combat this pressing issue.¹¹⁻¹⁴ Less often addressed is the need for safe, efficient storage of the energy produced by these renewable energy systems.¹⁵ Large scale battery infrastructure provides stability to the renewable grid during times of low production (e.g. low energy capture by solar systems on rainy days) while avoiding energy waste during periods of high production. Currently, lithium ion batteries are the standard for energy storage, however they have several major drawbacks: their maximum capacity degrades quickly, dropping slightly after each charge/discharge cycle; damage to the battery can result in fires or explosion; they rely on rare materials leading to their production having a high carbon footprint. An alternative to lithium-ion batteries are redox flow batteries, a promising energy storage technology that is posed to mitigate many of the drawbacks of lithium-ion batteries.

Redox flow batteries work on the principles of electrochemistry, generating a current of electrons by reducing and oxidizing electrolyte solutions in contact through a semipermeable membrane. **Fig. 1** shows a redox flow cell and its various components, including the semipermeable membrane and flow fields. The charge capacity of redox flow batteries is easily increased by increasing the amount of electrolyte solutions available (which require larger solution tanks). These batteries are easily recharged by reversing the voltage across the cell, and renewable energy sources such as solar power could be harnessed for this purpose. Redox flow batteries do not undergo the same functional degradations over time that have been observed in lithium-ion batteries.¹⁶ In this paper, we review the redox flow battery literature and identify current research trends, and conclude by suggesting future directions for research on redox flow batteries.

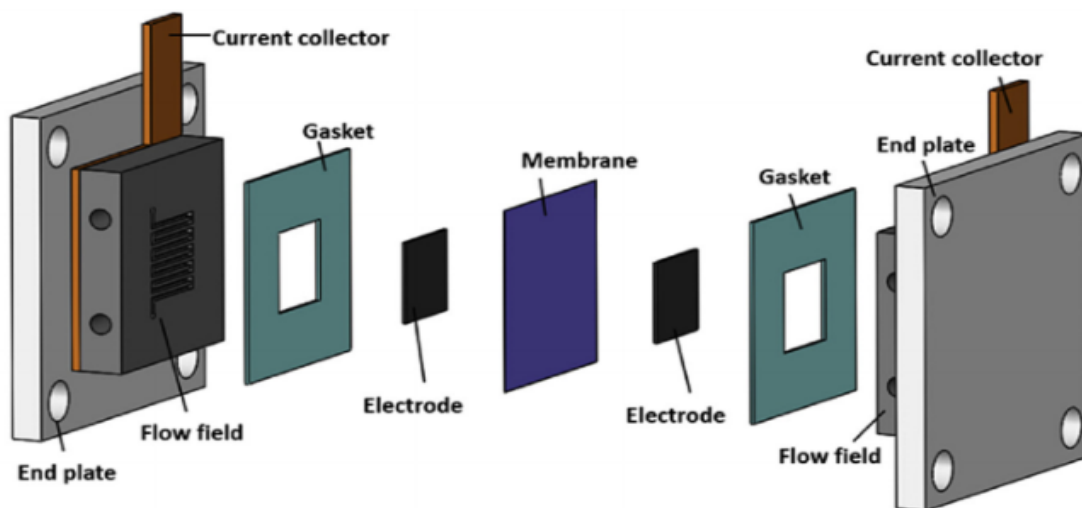


Fig. 1: Diagram of a redox flow cell¹⁷

3. Methodology

All papers included in the review were located using the Clarivate Analytics Web of Science database. An asterisk (*) was included in place of the last several letters of search terms, which allows the database search engine to compile all results that begin with the specified letters and end with any letter(s). For example, searching “batter*” will return results that contain the words: batter, battery, batteries, battering, etc. (see **Table 1** for the full list of search terms used in the study).

Table 1. Complete list of search terms used in the study.

Search Terms

redox flow batter*
 vanadium redox flow
 vanadium redox flow batter*
 microfluidic redox flow
 laminar flow microfluidic chip
 microfluidic chip
 novel redox flow
 novel redox flow batter*
 iron chromium redox flow
 iron chromium redox flow batter*
 three-dimensional print* redox flow batter*
 3D print* redox flow batter*

Note. The search terms in each row represent a single Web of Science search. Results gathered from all of these searches, once downloaded, were sorted into folders by topic.

To narrow the initial results of each search, the Web of Science Search Within tool and filters were used. With the search tools, experimental or review articles available in English were retained, and results with unrelated topics were omitted (e.g. biology). Remaining results from each search were downloaded as PDF files into separate folders by topic. Results were then narrowed further by deleting papers where the title, keywords, or abstract indicated that the paper topic was beyond the scope of our purpose. This process was initially conducted for identifying literature relevant to constructing and optimizing iron-chromium redox flow batteries, but was repurposed for this review. Papers were sorted into four general categories: 3D printing redox flow batteries, iron chromium redox flow batteries, microfluidic redox flow batteries, and redox flow batteries in general. In total, 97 papers were retained for the prior research on construction and optimization. These 97 papers were searched with data extraction software (below) to better identify what trends might be present in the literature. Of these 97 papers, only 19 suggested major trends in redox flow battery research. These 19 papers are included in the analysis section below.

In order to extract data from as many papers as possible, a program was written to extract data from all 97 papers, Data were compiled in one summary document. This was accomplished through a .NET console application called "PaperMole." The program is written in the C# programming language and utilizes the NuGet package "iTextSharp" to stream and edit PDF documents. Upon launching, the console prompts the user to input a keyword for the program to hunt for within the papers (**Fig. 2**). Once entered, the program then parses through each PDF document in the directory line by line. If the document cannot be read by the program, the console logs the error and prints the title of the paper that it could not process. Using regular expressions, the program tests whether a given line contains the keyword. If it does, the line is copied and entered into the summary document along with the given page number and line number where the keyword was located. The program loops through each paper in the directory and then terminates when it reaches the directory's end. In the console, it logs how many papers it attempted to process, how many papers it was able to process, and how many papers were not able to be processed. The console then tells the user how many of the papers contained the desired keyword and then the program terminates.

The results are exported in a text file located at the specified summary file path. Within the summary file, the number of papers processed, the number of papers with the keyword, and the keyword itself are written at the top. The body of the file consists of the title of each paper, the number of times that the keyword is found within the paper, and a copy of the line from the paper in which the keyword was found. The purpose of copying the entire line of text in which the keyword was found is to allow the reader of the text file to gain some context for which the keyword arises. In doing so, if the copied line appears to give a data point that fits within the scope of the literature review, the user can quickly consult the whole paper, find the data point at the given page and line number, and determine if the data point can be used.

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PaperMole
Version 2.0

*****

Keyword? :
pressure

*****

Checking for errors...
Unable to process Wang_et_al
Error code: No data is available for encoding 10000. For information on defining
a custom encoding, see the documentation for the Encoding.RegisterProvider meth
od.

*****

Successfully scanned 19 papers for the phrase "pressure".
Unable to process 1 papers.
13 papers contained the keyword.
6 papers did not contain the keyword.
*****

Press any key to exit
```

Fig. 2: The keyword search tool main screen

After the text search results were reviewed, papers were read and examined for trends in the literature. Of the 97 total papers analyzed, it was concluded that the 19 papers cited in this paper best illuminated trends in the redox flow battery literature. Based on these trends, possible future research directions were suggested. Four primary research trends were found, all of which are discussed below.

4. Analysis

Four major trends in 19 papers on redox flow battery research were identified from the literature review. These trends were: material and chemical membrane modifications, membraneless batteries, material and chemical electrode modifications, and electrode compression. Investigations of these trends, published in the literature, are summarized below.

Membranes + Membraneless

Nafion membranes are commonly used in redox flow batteries, but developments in redox flow battery technology have led to sulfonated poly(ether ether ketone) (SPEEK) membranes, which promise better performance for a lower cost. SPEEK membranes have demonstrated stable performance with less discharge capacity decline and a lower self-discharge rate than cells using Nafion membranes.¹⁸ Combined with lower capital costs, SPEEK membranes are a direction of interest for further improvement of redox flow batteries and are evidence of the maturation of the technology.

Furthermore, not only have physical modifications improved redox flow batteries, but increased performance through chemical modifications have also been demonstrated. In biofuel and in zinc-vanadium fuel cells, membranes have been successfully replaced by microfluidic chips^{19,20} and Whatmann #2 filter paper,²¹ respectively. These various research directions

suggest promise for an eventual substitution from common Nafion membranes to cheaper, equally or performance improving alternatives in redox flow battery membranes.

On top of the research being done to find cheaper alternatives to Nafion membranes, there is a movement toward removing the membrane from redox flow batteries altogether, thus eliminating this cost completely. These designs are comparable to microfluidic fuel cells. Microfluidic fuel cells use microfluidic chips as solution flow-through structures, and are designed to procure laminar flow within the battery cell. In microfluidic systems, reaction sites and electrode structures are confined to channels in the microfluidic chips.²² This design is inherently different from traditional redox flow batteries because microfluidic fuel cells are much smaller and compact, in comparison to the large and separated storage tanks typically used in the design of a redox flow battery. In one study, researchers examined five major designs of microfluidic batteries from studies published between 2004 and 2016, in order to suggest how these designs can be modified to fit the needs of a potentially membraneless redox flow battery. The performance metrics for investigating potential wider use and future commercialization of membraneless redox flow batteries were established. The biggest potential improvement in this new design is suggested to be optimized stackability of a unit membraneless redox flow battery.²³

Electrodes + Electrode Compression

New advances in electrode materials and optimization studies are also becoming more commonly studied in experimental research on redox flow batteries. One such new material technology is the graphite felt electrode. Graphite felt electrodes have been tested as a replacement for other, standard carbon felt electrode materials. Graphite felt has been shown to exhibit greater efficiency and stability than carbon felt electrodes and additional future research on graphite felt is recommended.²⁴ More specifically, two types of graphite felt materials have been compared for redox flow battery electrodes: rayon and polyacrylonitrile (R-GF and PAN-GF respectively). Both graphite felt technologies are promising for use as electrodes. PAN-GF proved easier and cheaper to manufacture and had better electrocatalytic properties, proving to have a faster charge transfer rate. R-GF is larger, however, which allows for better electrolytic solution diffusion and mass transfer.²⁵ Both technologies should be investigated further.

Aside from switching materials, existing electrodes can also be improved to increase performance. Some studies have focused on the use of high-performance porous carbon electrode configurations as a way to balance the cost and performance of this system.²⁶⁻²⁹ These electrode configurations are designed to increase the power output of the cell by either increasing reaction rates and kinetic rates,^{26, 28} mass transportation rate,³¹ or through increasing both the kinetic rates and active electrochemical surface area.²²

Moreover, redox flow batteries have been shown to improve their performance when the pressure drop between the tubing of the pumps and the cell is minimized. In order to keep a potential across the two solutions, pumps must constantly provide a current, which has an energy cost. This cost has a direct relationship with the presence of a pressure drop.^{16,30-34} One technique that has been shown to reduce this pressure drop is a reduction in felt electrode pad compression.^{16,30-31} Redox cells with decompressed pads demonstrated greater peak power

densities and performed more efficiently than cells with uncompressed felt³⁰. Cells with compressed felt exhibited a 45-70% increase in their pressure drop compared to when they had decompressed pads.³⁰ Decompressing the felt has also been shown to have no significant effect on the overall felt electrode pad surface area and in turn has little to no negative effect on the charge capturing capacity of the felt.³⁰

5. Conclusion

Redox flow batteries, as evidenced by an abundance of literature, are a very active field, with research being conducted to improve many aspects of these batteries, from membranes to electrodes and more. Continued investigation and innovation in the field of redox flow batteries will allow the technology to improve, growing cheaper and more efficient as time goes on. Combined with the modularity of many redox flow setups, the continued development of these technologies will be easy to implement into existing systems.

Redox flow battery technology is well positioned to service the energy storage needs of a renewable energy grid. Redox flow batteries are comparable to lithium ion batteries, and are similar if not better in terms of cost and material abundance.¹⁶ For these reasons, redox flow batteries are an important technology and their implementation in new energy storage systems may prove beneficial over the current standard of lithium ion batteries.

Going forward, redox flow batteries should be investigated further. There is still room for innovation in the technology, as evidenced by many recent papers pushing the field forward. Membrane technology could be improved by further investigation into SPEEK membranes, including investigating chemical composition and treatment. There is also the alternative route of removing the membrane entirely and reconfiguring the redox flow battery to emulate a fuel cell. Future work into the capability of microfluidics can be done to further explore this possibility. The identification of graphite felt as the superior choice for electrode material, as well as investigation of specific graphite felt materials to determine the ideal candidate is evidence of growth in the field and maturation of the technology of redox flow batteries. Moreover, if the felt is allowed to decompress, battery performance could be further optimized to minimize power loss. In sum, continued chemical and physical modifications to existing and novel battery component materials are the most promising directions for future redox flow battery research, based on trends identified in the literature.

6. Works Cited

1. Patz, J. A., Campbell-Lendrum, D., Holloway, T., & Foley, J. A. (2005). Impact of regional climate change on human health. *Nature*, *438*(7066), 310-317.
2. Wheeler, T., & Von Braun, J. (2013). Climate change impacts on global food security. *Science*, *341*(6145), 508-513.
3. Olesen, J. E., & Bindi, M. (2002). Consequences of climate change for European agricultural productivity, land use and policy. *European journal of agronomy*, *16*(4), 239-262.
4. Jacob, D. J., & Winner, D. A. (2009). Effect of climate change on air quality. *Atmospheric environment*, *43*(1), 51-63.
5. Baker, A. C., Glynn, P. W., & Riegl, B. (2008). Climate change and coral reef bleaching: An ecological assessment of long-term impacts, recovery trends and future outlook. *Estuarine, coastal and shelf science*, *80*(4), 435-471.
6. Paerl, H. W., & Huisman, J. (2009). Climate change: a catalyst for global expansion of harmful cyanobacterial blooms. *Environmental microbiology reports*, *1*(1), 27-37.
7. Foster, P. (2001). The potential negative impacts of global climate change on tropical montane cloud forests. *Earth-Science Reviews*, *55*(1-2), 73-106.
8. Doney, S. C., Ruckelshaus, M., Duffy, J. E., Barry, J. P., Chan, F., English, C. A., et al., (2012). Climate change impacts on marine ecosystems. *Annual Review of Marine Science*, *4*, 11-37.
9. Post, E., Forchhammer, M. C., Bret-Harte, M. S., Callaghan, T. V., Christensen, T. R., Elberling, B., et al., (2009). Ecological dynamics across the Arctic associated with recent climate change. *Science*, *325*(5946), 1355-1358.
10. Duarte, C. M. (2002). The future of seagrass meadows. *Environmental conservation*, *29*(2), 192-206.
11. Panwar, N. L., Kaushik, S. C., & Kothari, S. (2011). Role of renewable energy sources in environmental protection: A review. *Renewable and sustainable energy reviews*, *15*(3), 1513-1524.
12. Hadjipaschalis, I., Poullikkas, A., & Efthimiou, V. (2009). Overview of current and future energy storage technologies for electric power applications. *Renewable and sustainable energy reviews*, *13*(6-7), 1513-1522.
13. De Vries, B. J., Van Vuuren, D. P., & Hoogwijk, M. M. (2007). Renewable energy sources: Their global potential for the first-half of the 21st century at a global level: An integrated approach. *Energy policy*, *35*(4), 2590-2610.
14. Haines, A., Kovats, R. S., Campbell-Lendrum, D., & Corvalán, C. (2006). Climate change and human health: impacts, vulnerability, and mitigation. *The Lancet*, *367*(9528), 2101-2109.
15. Poizot, P., & Dolhem, F. (2011). Clean energy new deal for a sustainable world: from non-CO₂ generating energy sources to greener electrochemical storage devices. *Energy & Environmental Science*, *4*(6), 2003-2019.

16. Moro, F., Trovò, A., Bortolin, S., Del Col, D., & Guarnieri, M. (2017). An alternative low-loss stack topology for vanadium redox flow battery: Comparative assessment. *Journal of Power Sources*, 340, 229-241.
17. Zeng, Y. K., Zhou, X. L., An, L., Wei, L., & Zhao, T. S. (2016). A high-performance flow-field structured iron-chromium redox flow battery. *Journal of Power Sources*, 324, 738-744.
18. Sun, C. Y., Zhang, H., Luo, X. D., & Chen, N. (2019). A comparative study of Nafion and sulfonated poly (ether ether ketone) membrane performance for iron-chromium redox flow battery. *Ionics*, 25(9), 4219-4229.
19. Liu, C., Liu, L., Wang, X., Xu, B., & Lan, W. (2018). Enhancing the Performance of Microfluidic Fuel Cells by Modifying the Carbon-Fiber Paper Cathode by Air Annealing and Acid Oxidation. *Industrial & Engineering Chemistry Research*, 57(40), 13557-13565.
20. Pasala, V., & Ramanujam, K. (2019). Paper-Based Disposable Zinc-Vanadium Fuel Cell for Micropower Applications. *ChemistrySelect*, 4(29), 8398-8403.
21. Rewatkar, P., & Goel, S. (2018). Paper based membraneless co-laminar microfluidic glucose biofuel cell with MWCNT-fed bucky paper bioelectrodes. *IEEE transactions on nanobioscience*, 17(4), 374-379.
22. Kjeang E., Djilali N., Sinton D. (2008) Microfluidic Fuel Cells. In: Li D. (eds) Encyclopedia of Microfluidics and Nanofluidics.
23. Bamgbopa, M. O., Almheiri, S., & Sun, H. (2017). Prospects of recently developed membraneless cell designs for redox flow batteries. *Renewable and Sustainable Energy Reviews*, 70, 506-518.
24. Zhang, H., Chen, N., Sun, C., & Luo, X. (2020). Investigations on physicochemical properties and electrochemical performance of graphite felt and carbon felt for iron-chromium redox flow battery. *International Journal of Energy Research*.
25. Zhang, H., Tan, Y., Luo, X. D., Sun, C. Y., & Chen, N. (2019). Polarization Effects of a Rayon and Polyacrylonitrile Based Graphite Felt for Iron-Chromium Redox Flow Batteries. *ChemElectroChem*, 6(12), 3175-3188.
26. Li, L., Nikiforidis, G., Leung, M. K., & Daoud, W. A. (2016). Vanadium microfluidic fuel cell with novel multi-layer flow-through porous electrodes: Model, simulations and experiments. *Applied Energy*, 177, 729-739.
27. Lisboa, K. M., & Cotta, R. M. (2018). On the mass transport in membraneless flow batteries with flow-by configuration. *International Journal of Heat and Mass Transfer*, 122, 954-966.
28. Lee, J. W., Hong, J. K., & Kjeang, E. (2012). Electrochemical characteristics of vanadium redox reactions on porous carbon electrodes for microfluidic fuel cell applications. *Electrochimica Acta*, 83, 430-438.
29. Goulet, M. A., Habisch, A., & Kjeang, E. (2016). In situ enhancement of flow-through porous electrodes with carbon nanotubes via flowing deposition. *Electrochimica Acta*, 206, 36-44.
30. Brown, L. D., Neville, T. P., Jervis, R., Mason, T. J., Shearing, P. R., & Brett, D. J. (2016). The effect of felt compression on the performance and pressure drop of all-vanadium redox flow batteries. *Journal of Energy Storage*, 8, 91-98.

31. Messaggi, M., Canzi, P., Mereu, R., Baricci, A., Inzoli, F., Casalegno, A., & Zago, M. (2018). Analysis of flow field design on vanadium redox flow battery performance: development of 3D computational fluid dynamic model and experimental validation. *Applied energy*, 228, 1057-1070.
32. Qiu, G., Dennison, C. R., Knehr, K. W., Kumbur, E. C., & Sun, Y. (2012). Pore-scale analysis of effects of electrode morphology and electrolyte flow conditions on performance of vanadium redox flow batteries. *Journal of power sources*, 219, 223-234.
33. Yin, C., Gao, Y., Xie, G., Li, T., & Tang, H. (2019). Three dimensional multi-physical modeling study of interdigitated flow field in porous electrode for vanadium redox flow battery. *Journal of Power Sources*, 438, 227023.
34. Yin, C., Guo, S., Fang, H., Liu, J., Li, Y., & Tang, H. (2015). Numerical and experimental studies of stack shunt current for vanadium redox flow battery. *Applied energy*, 151, 237-248.