

Environmental impacts of the Vanadium redox-flow batteries

Material's Engineering Bachelor's thesis

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Abstract

Vanadium redox-flow batteries (VRFB) is one of the most promising large-scale energy storage technologies for integrating renewable energy in electrical grids. They help to resolve global energy and environmental issues. In recent years, scientists are studying the degree of sustainability of this technology and its effects on the environment. In this bachelor's thesis the environmental impacts of VRFB are discussed. Resources, recycling and reuse processes, disposal and emissions are taken into consideration and two electrolyte rebalancing methods are presented to extend the lifetime of the electroactive material. The entire lifecycle of the VRFB, from manufacturing to end-of-life phase, shows that VRFB have a great potential to reduce environmental impacts with efficient recycling and reuse of its materials. Also, a comparative analysis to lithium-ion batteries is done and the role of VRFB in the energy industry is discussed. LIBs are more suitable for portable electronic applications, and VRFBs are better for stationary energy storage. Finally, a homemade analytical system is introduced to in operando measure the gases (by gas chromatography) evolved from laboratory scale VRFBs operated under accelerated stress testing conditions.

Tiivistelmä

Vanadium virtausakut ovat yksi lupaavimmista suuren mittakaavan energian varastointi teknologioista, jonka avulla uusiutuvaa energiaa voidaan integroida sähköverkkoon. Ne auttavat ratkomaan maailmanlaajuisia energia- ja ympäristöongelmia. Teknologiaa ja sen ympäristövaikutuksia on tutkittu paljon viime vuosina. Tässä kandidaatin tutkielmassa keskustellaan vanadium virtausakkujen ympäristövaikutuksista. Resurssit, kierrätys- ja uudelleenkäyttöprosessit, loppusijoitus sekä päästöt ovat huomioitu. Kaksi elektrolyytin tasapainotus metodia esitetään, joiden avulla elektroaktiivisen materiaalin elinikää voidaan pidentää. Koko vanadium virtausakun elinkaari, valmistuksesta elinkaaren loppuvaiheeseen osoittaa, että sillä on hyvä potentiaali vähentää ympäristövaikutuksia kiinnittämällä huomio tehokkaaseen kierrätykseen ja materiaalien uusiokäyttöön. Vanadium virtausakkujen ominaisuuksia sekä ympäristövaikutuksia verrataan litiumioni akkuihin ja keskustellaan virtausakkujen roolista energiasektorilla. Litiumakut soveltuvat paremmin monipuolisiin elektroniikan sovellutuksiin ja vanadium virtausakut sopivat paremmin pysyvään energian varastointiin. Lopuksi esitetään kokeellinen menetelmä, jossa laboratoriotason vanadium virtausakkuja testataan nopeutettujen olosuhteiden alaisuudessa ja mitataan syntyviä kaasuja kaasukromatografian avulla.

Key words: vanadium redox-flow battery, VRFB, flow battery, environment, energy storage

Avainsanat: vanadium virtausakku, virtausakku, ympäristö, energian varastointi

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Introduction

The future of energy consumption is based on renewable and sustainable energy solutions. They form a rapidly growing and constantly developing industry. In theory it's easy and possible to increase the amount of renewable energy but it must be same time environmentally and economically efficient. Substitutes for fossil fuels are constantly being searched to curb the effects of climate change. The growing field of renewable energy also needs a supportive, environmentally friendly way to storage it. The intermittency of renewable energy can be solved with flow batteries. This thesis is focused on Vanadium redox-flow batteries (VRFB) which are intended for a large-scale energy storage. Spare energy from renewables is charged to the electrolyte tanks of the VRFB through reduction and oxidation reactions. Electrons flows through ion exchange membrane from positive to negative half-cell. Opposite reactions occurs when the battery is discharged, and the energy is released to the grid [1]. Grid-scale storage enables sufficient renewable energy even in those times when the energy sources are not stable because the sun is not shining, or the wind is not blowing [2].

VRFB has many promising features which make it a competitive product on the market scale. It has for example high energy efficiency, long life cycle, low maintenance cost and almost unlimited capacity [3]. These types of features are not enough to make a breakthrough in battery industry. The environmental effects of batteries must also be considered, and the commissioning requires a broad understanding of those. These topics have not yet been researched much. Environmental effects of the VRFB are examined based on LCA-analyses and other literature. This thesis will go through each part of the life cycle and consider the environmental impacts of different areas. We also compare the results with the more studied lithium-ion batteries (LIB) and examine the contribution of VRFB in the realization of global energy and environmental goals.

Possible future research focuses, which can be used to make the battery as efficient, safe and environmentally friendly as possible, are looked in the end. Because of the long-life cycle of the VRFB, accelerated stress testing conditions are needed. These conditions enable an illustrative situation where the battery is cycled over its limits, and it starts to evolve gases. Illustrative and experimental approach to detect VRFB degradation gases is presented.

1 VRFB life cycle

1.1 Resources

Resources of the VRRB are mainly focused on the materials needed to manufacture the system. The system is built from stacks, periphery, and electrolyte tanks. Stacks are made from steel and can be composed of multiple individual cells. Each individual cell is assembled with end plates, gaskets, two carbon felt-based electrodes, carbon foam and membrane. End plates are usually made from polyvinyl chloride (PVC) and gaskets from fluoroelastomer (FKM) or Teflon. Carbon foam is placed in the middle of the gasket to improve the active surface area of the electrode materials [4]. The standard material for the membrane is Nafion. In an energy capacity of 8.3 MWh and power output of 1 MW within the VRFB system, the stacks account for 3.1 % of the total weight (wt%). Wt% of the periphery is 1.6%. The periphery includes all the remaining components of the system, except electrolyte tanks. Remaining components are membrane pumps, heat exchanger, piping, inverter, copper cables and battery management system [5].

Electrolyte tanks are the most space-consuming components. The minimum amount of tanks are two, one for the positive electrolyte and one for the negative electrolyte, but it is easy to increase the number according to how big system is wanted. Tanks are usually made of glass fiber. Wt% of tanks is 10.2 %. [5] Tanks contain the vanadium electrolyte. Vanadium electrolyte is a mixture of 1.6 M Vanadium electrolyte, 2M sulphuric acid and water as diluter. Wt% of the vanadium electrolyte is 85.1% [5].

The vanadium pentoxide (V₂O₅) is the most used raw material for the electrolyte. It is a side product of titanomagnetite ores which are mostly mined in South Africa. Titanomagnetite ores can be processed several ways to get ammonium polyvanadate (APV). The ore is used for steel production and as a by-product, a slag containing 25 % of vanadium is obtained. The slag is grinded, roasted and leached with ammonium sulphate or sulphuric acid to get APV [5]. Titanomagnetite can also be processed by roasting it with sodium sulphate or sodium carbonate and then leached with water. APV is going through a calcination or roasting process to be converted into V₂O₅. Finally, the vanadium electrolyte is prepared from V₂O₅ and can be done by chemical reduction, electrolysis, solvent extraction, or ion exchange. The former is the most widely used method in which V₂O₅ is first dissolved into sulphuric acid and then reduced to vanadium electrolyte, using oxalic acid as reducing agent [6]. A simplified process to produce vanadium electrolyte from titanomagnetite is represented in Figure 1.



Figure 1. Vanadium electrolyte preparation

In the VRFB system the most space consuming parts are the tanks, but they only take up about 3 % of the overall manufacturing costs of the VRFB system [7]. Those tanks hold the vanadium electrolyte which is by far having the largest mass percentage of the whole VRFB system. Approximately 30 % of the overall manufacturing costs are attributed to the vanadium electrolyte [7]. Therefore, the sustainable use of vanadium resources is particularly important.

1.2 Recycling and reuse

The VRFB system can reach up to 95 % recycling efficiency if the recycling process is done correctly [8]. Plastic from stacks, periphery and electrolyte tanks can be recycled or incinerated. Metals (steel, copper) from stacks and periphery are fully recyclable. Cables and electronic waste from periphery have working recycling processes as well.

Since the life cycle of the electrolyte is about 20 years and no system has yet reached that age, there is not much information about the condition of the electrolyte in its end-of-life phase. The electrolyte does not degrade significantly, but it may experience some capacity losses during charge and discharge. Capacity loss is a result of oxidation of the V^{2+} -ions in the negative half-cell and therefore it's important to operate the system under inert atmosphere. Capacity loss may also be related to ionic imbalance because the ion-exchange membrane can't separate the cells 100 percent certainty. It is said that the electrolyte could be recycled and reused if it goes through re-processing and purification to restore its capacity [9].

There are a few possible methods to rebalance the electrolytes. As a first strategy, rebalancing can be done by mixing the negative and positive electrolytes. This process is represented in figure 2, where the different oxidation stages of the electrolyte V^{+2} , V^{+3} , V^{+4} and V^{+5} give the system the colours violet, green, blue and yellow, respectively. Electrolyte imbalance occurs when oxygen enters the system. Mixing the positive and negative solutions will not fix the whole imbalance but it will longer the lifetime of the electrolytes. [9]



Figure 2: Rebalancing the electrolyte by mixing.

Another way to rebalance the electrolyte is done with a regeneration cell. This cell is connected in flow to the positive tank of the VRFB. Regeneration cell is reducing V⁺⁵-ions to V⁺⁴-ions and pumping them back to positive tank to fix the imbalance. With this system, it is possible to regulate the ion balance while the battery is in use [9]. The imbalance in the latter device and its regeneration process is represented in Figure 3.



Figure 3: Rebalancing the electrolyte with regeneration cell.

Recycled and rebalanced vanadium electrolyte can also be used as feedstock in vanadium production. It is a more efficient way to produce vanadium and the process uses less energy compared to mining [10]. The presented electrolyte rebalancing methods help to reduce the amount of waste that ends up being disposed of.

1.3 Disposal

Waste going to disposal consist of all the residue from manufacturing, use and end-of life phases. Most of the manufacturing waste is from the electrolyte preparation, which consist of various work phases and lot of residues from the mining processes. Figure 4 shows how much waste is generated when manufacturing 1 kilogram of vanadium electrolyte. Largest part of the waste consists of titan slag and hard coal. Treatment waste and waste from pre-reduction kiln is the second largest part of the waste share. Small amounts of oxygen furnace waste, aluminium, water, vanadium, ammonia, and inert waste are also generated during electrolyte manufacturing. Hard coal, titan slag and waste from pre-reduction kiln are from ore treatment. Treatment waste is also from the ore treatment, but it is placed to inert material landfill. Vanadium-containing slag is a side-product of steelmaking and the oxygen furnace waste is a by-product of that. All the other inert waste is also by-product of steelmaking. Loss vanadium is caused by leaching process. Waste water and ammonia is mostly from the calcination process. Waste aluminium is due to APV precipitation, and it is going to sanitary landfill. [11]



Figure 4. Waste from manufacturing 1 kg of vanadium electrolyte

Battery components manufacturing also generates waste. They are coming from Nafion membrane, electrodes, and gaskets manufacturing. Producing 1 kilogram of Nafion membrane generates 15.2 kilograms of waste. Most of it is a treatment waste which is hazardous and goes to incineration. The share of hazardous waste is around 8 kilograms. The remaining part consists of solvents, sodium chloride and sodium hydroxide. Producing 1 kilogram of carbon felt electrodes produces 3 kilogram of waste plastic, which is due to the acrylonitrile, methyl methacrylate and oil used in the raw felt manufacturing. To produce 1 kilogram of FKM gaskets produces 0.175 kilograms of hazardous treatment waste, which is due to the only environmental impact generated by different manufacturing processes. Emissions are also an important part of the overall environmental impact.

1.4 Emissions

Emissions can be distributed to manufacturing, use, and end-of-life phases. They can be measured with different kind of indicators, which are global warming potential (GWP), human toxicity potential (HTP), acidification potential (AP) and abiotic depletion potential (ADP). GWP expresses the amount of greenhouse gases absorbed and it is measured in kilograms of CO₂ equivalent in MWh. HTP expresses the amount of absorbed gases that are harmful to humans and is measured in kilograms of 1,4-dichlrobenzene equivalent in MWh.

AP refers to acid rain and is measured in kilograms of SO₂ equivalent in MWh. ADP refers the number of abiotic resources removed from earth and is measured in grams of antimony (Sb) equivalent in MWh [12].

In manufacturing phase, emissions come from transportation, component production and ore mining. The mining process of vanadium titanomagnetite requires fuels and electricity and it emits dust and gas. Most of the mining processes takes place in South Africa where the main electricity source is coal, which further increases emissions [13]. In component production, electrolyte is again the main contributor of emissions. Figures 5 and 6 demonstrate the share of gas emissions when producing 1 kilogram of vanadium electrolyte, where carbon dioxide is the biggest emission source. Vanadium electrolyte contains around 10 wt % of vanadium pentoxide with purity of 97.5 %. To produce 1 kilogram of vanadium pentoxide releases 0.812 kilogram of carbon dioxide equivalent. Other main sources of emissions are sulphur dioxide, nitrogen oxides, water, hydrogen chloride, small particulates, and carbon monoxide. There can also be small amounts of other compounds e.g., lead, copper, chromium, methane, and bromine. [11]



Figure 5. Share of gas emissions in electrolyte manufacturing



Figure 6. Enlarged plot from gas emissions in electrolyte manufacturing

Transportation is another source of emissions. Components are manufactured and needed globally and ships, freights, trucks etc., are used to transport them. Transportation releases greenhouse gases but is impossible to say how much because the transportation type and time may change depending on the case. Use phase of the VRFB takes electricity to charge and discharge the batteries. Use phase emissions depend on the type of electricity source used. The best scenario is to use renewable energy, so the emissions are lower.

End-of-life phase consist of disassembling the battery and recycling its different components. To recycle the parts properly transportation is needed. Parts are carried to incinerators or other waste handling facilities. In bigger picture the end-of-life phase is a small part of different indicators in the battery's whole life cycle [11].

Treatment of the components needs electricity, and in this case, the best scenario is to use renewable energy to minimize the emissions. Some of the components are incinerated, what is releasing greenhouse gases and air pollutants.

When considering battery systems made from recycled and virgin materials, there is a difference between emissions and indicators. In all indicators, GWP, HTP, AP and ADP, the results are lower when using recycled materials. Differences also occur when comparing the source of electricity used in the battery systems. Most common electricity sources are wind,

photovoltaic and grid energy. Lowest CO₂ emissions are in a system which uses wind energy and recycled materials. HTP and AP emissions have the same result. Highest CO₂ emissions occur in a system which uses virgin materials and is connected to average German grid mix. Grid emissions are from fossil sources used in power plants. Again, HTP and AP has the same result. In ADP consideration, lowest emissions are in recycled system connected to grid. Highest emissions are in the not recycled photovoltaic system. Renewable energy sources like photovoltaic systems usually needs major sources of metals and minerals which increases the ADP value [12].

2 Comparative analysis

In the comparative analysis VRFB is compared with the widely used lithium-ion battery (LIB). Both batteries are built from small cells, which consists of anode, cathode, electrolyte, positive and negative current collector [14]. During charging LIBs, lithium ions are flowing from cathode to anode through the separator. During discharging opposite reaction occurs [15].

The main difference in the design of the batteries is that VRFB store energy in electrolyte solutions and LIB store it in solid cells [10]. Increasing the capacity of the batteries needs to be done either by increasing the volume of electrolyte tanks or the amount of battery cells [16]. Increasing the capacity is easier in the VRFB because there is no need to connect dozens of cells together. Building large-scale LIBs is not cost-effective and has the risk of explosion. On the other hand, large and heavy vanadium electrolyte tanks cannot be used in applications like cars or phones, for which LIBs are better. VRFBs suits better for stationary energy storage in industrial and grid scale. The differences in both designs also impact costs. Capacity increase is much cheaper in VRFB than in LIB and a bigger electrolyte tank can reduce the energy costs in the use phase.

In both battery types, degradation and aging processes are not so well known. To study these degradation processes researchers have used e.g. gas chromatography, mass spectrometry or NMR techniques [17]. There is more data about the LIB aging processes. Lithium ions interaction with graphite electrodes is causing degradation in cells [16]. Degradation reduces the lifetime of the battery and leads to capacity losses. Extreme conditions like hot weather may also decrease the life cycle and cause damage to the battery. These environmental conditions mainly concern LIB and don't have a big defence to VRFB [10]. Some studies have shown that electrolyte aging in LIB creates for example different complex phosphates. Gas evolution in LIB is huge safety risk which make them flammable. When degradation gases react with oxygen, the battery can explode and catch fire [18]. VRFB liquid electrolyte is non-flammable and much safer to use. Still, more data is needed on the degradation processes of both battery types. LIB cannot be fully discharged because it can cause damage and speed up the degradation. VRFB is fully dischargeable.

A big difference occurs in the recyclability. VRFB can be almost fully recycled when LIB ends up easily to landfill [10]. VRFB recyclability is also improved by a financial incentive. While earth's crust seals more vanadium in it, the extraction process is expensive, which is why it is more profitable to use recycled vanadium [16]. Carbon dioxide emissions are also much greater in the VRFB than in LIB [19]. Manufacturing a LIB of same capacity from virgin minerals is cheaper than VRFB due to mineral extraction processes. Cost efficiency is comparative to life cycle. It is more efficient to users to invest in a longer life cycle VRFB than a shorter life cycle LIB. VRFB longer life cycle is due to its four oxidation levels which enable it unlimited cycles.

3 Mitigating actions

3.1 Energy storage goals and strategies

European Association for Storage of Energy (EASE) has estimated that the annual energy storage capacity must increase 14 GW per year to reach its targets. The 2030 target is to have 200 GW energy storage capacity and in 2050, 600 GW. These targets are important part of the European Commission energy transition strategy and EU climate targets. [20]

VRFB and flow batteries in general belongs to bi-directional, power-to-X-to-power technologies. This means that the electricity is stored before it is transferred back into the system. These technologies are the main contributors to reach EU: s 2030 energy storage targets. A smaller part, around a quarter belongs to one-directional, power-to-X technologies. These include e.g. electrolysers or thermal storage. Around a third of the energy storage needs are targeted to pumped-storage hydroelectricity (PHS). Remaining solutions used to reach the storage targets consist of flow batteries, gravity storage, flywheels, magnetic energy storage, supercapacitors, compressed/liquid air storage, etc. When moving from 2030 to 2050, the PHS share is the smallest part of the installed power capacity. In the future the share of other technologies such as flow batteries increases [21].

3.2 VRFB role

When looking more closely at the energy storage needs, it can be stated that the share of flow batteries is relatively small. It is clear that these types of systems are still needed. Energy storage solutions can be modified based on different needs, environments, and resources. Not all places can use the same solution, which is why there are alternatives. According to European Commissions Clean Energy Technology Observatory, VRFB has reached a level 9 in a technology readiness level (TRL). Definition to TRL level 9 is "actual system proven in operational environment (competitive manufacturing in the case of key enabling technologies; or in space)" [22]. This achievement in itself is not enough, which is why VRFB systems still need more development and research to reduce their costs and be more competitive in the markets. Drastic changes in the price of electricity are common these days. To equalize this situation, it is important to invest into new renewable and bi-directional technologies. VRFB provides much needed flexibility to the energy industry and is in a key position to back-up energy fluctuation.

VRFBs have a lot of benefits and unique features which make them a competitive solution in the energy storage industry. According to a global leading vanadium company Vanitec's commissioned report, Western Europe is reaching the VRFB capacity of 9.3 GW by 2031. It is around 5 % of the 200 GW target capacity [10].

4 Future research

In order to improve the efficiency of VRFB in the energy sector, further research is crucial, especially in battery aging processes. Due to limited operational history, understanding degradation mechanisms is vital. For this purpose, batteries will be operated under accelerated stress testing conditions, including cycling the systems at high current densities, -temperatures and fast flow rates to generate pressure. Gas evolution during accelerated stress testing conditions will be monitored using low-cost sensors. Laboratory-scale batteries will degrade in a gas-tight chamber, allowing gas measurement in-operando using chemical and electrochemical sensors. A portable micro-GC will also be adapted to the system (in gas flow) to analyse the evolved gases by gas chromatography, focusing on CO and CO₂ release from the positive side of the battery and H₂ from the negative side. Gas evolution data helps predict aging and diagnose the VRFB condition.

To produce this experimental research, first step is to build the battery. For the battery assembly is needed two end plates, four gasket rings, two carbon plates, carbon foam, Nafion membrane in DI water, small plastic tubes to hold battery together while assembling, four screws, eight flat disks, four butterflies, two short and two long plastic tubes and four cable ties or special adapters to connect tubes. The system assembly procedure is described below:

- Cut two pieces of carbon foam with a special cutter. Sonicate pieces for 10min in DI water.
- 2. Put gasket rings on end plate.
- 3. Add plastic tubes to the smaller holes.
- 4. Add carbon plate.
- 5. Add Teflon gasket.
- 6. Add carbon foam to the center of Teflon.
- 7. Cut membrane ($\approx 3.5 cm x 3.5 cm$) and place it on top of the carbon foam.
- 8. Add Teflon gasket.
- 9. Add carbon foam to the center of Teflon.

10. Add carbon plate.

11. Add end plate.

12. Add screws and flat disks to bigger holes and remove plastic tubes.

13. Tighten the screws evenly. First with 100 N x m and then with 150 N x m.

14. Add plastic tubes and tighten them with cable ties.



Figure 7. Assembly of an experimental VRFB.

After assembling the battery, it needs to be run first to check for electrolyte leakages. If it doesn't leak, empty the water tubes and add vanadium electrolytes. To prove the concept in this thesis, 0.16 M of the latter electrolyte was considered. The setup included two tubes of 20 ml and 2 M H₂SO₄ as a solvent: mix 4 ml of 1.6 M Vanadium and 36 ml of 2M H₂SO₄ solution and separate to 20 ml tubes. Tubes were covered with lids. It is important to make proper holes to the lids because the tubes need to be inert.

Preliminary results (Figures 8 and 9) obtained with voltage limits of 1.7 V and 0.9 V exhibited a significant loss of capacity when cycling the VRFB with 150 mA. Since the solutions were fed with nitrogen during the experiment, it was assumed that the loss of capacity was the product of a material degradation process.



Figure 8. Experimental data of the VRFB test



Figure 9. Experimental data of the VRFB test

To investigate the degradation gases produced by the VRFB, the system was connected in gas flow (through container outlet holes) to a micro-GC. Figure 10 represents the system

proposed in this thesis to analyze the decomposition gases of VRFBs under accelerated stress testing conditions, where a battery is connected to a pump which regulates the flow rate, and to a battery cycler which regulates the charge-discharge cycling process. The cycler is connected to a computer with a proper battery cycling program. The column connects a gas chromatograph and a battery chamber. Nitrogen is used as a carrier gas. A Flow controller is assembled between the nitrogen gas and gas chromatograph to follow and ensure the right gas flow rate.



Figure 10. Experimental setup for detecting degradation gases.

Finally, an experimental setup is proposed to investigate the degradation and cycling stability of VRFBs under accelerated stress testing conditions. Its implementation in real systems will provide valuable data for battery improvements and innovations. For a future work it is proposed to work on the optimization of this electroanalytical analysis strategy to develop a powerful tool for the study of degradation processes in batteries.

5 Conclusions

It is clear that renewable energy storage will be a trendsetter in the energy industry. Searching new technologies to substitute fossil fuels is crucial part to reach global climate and energy targets. Grid-scale energy storage systems should be updated and improved to face the problem of intermittency presented by renewable energies.

As a promising technology, VRFB is a compatible solution with large scale energy storage. Its unique properties such as long life cycle and high volumetric capacity are due to its electrolyte composition which consist of vanadium in four different oxidation stages. Despite these outstanding characteristics, research on the environmental impacts of VRFBs has not presented significant advances. Some LCA-analyses have been reported and the most important results were discussed in this thesis. Most of the environmental impacts are from the manufacturing phase of the VRFB. Vanadium electrolyte preparation causes the largest emissions which is due to the mining and multiple manufacturing processes.

VRFBs have a great advantage in terms of recyclability. Its recycling efficiency can reach up to 95 % and still there is ongoing research to improve the recycling processes. This high recyclability is a major advantage over LIB. The key position in the recycling phase is in the vanadium electrolyte which accounts for 85 % mass of the entire system. Various methods for rebalancing and reusing the vanadium electrolyte have been discussed. An analysis based on the comparison between VRFB and LIB technologies is presented. LIBs are more suitable for portable electronic applications, and VRBSs are better for stationary energy storage.

For boosting the development of VRFB technology, more information on its degradation mechanism is needed. In this thesis, a homemade analytical system was introduced to in operando measure the degradation gases (by gas chromatography) evolved from laboratory scale VRFBs operated under accelerated stress testing conditions and experimental preliminary results of the system were discussed. The development of these type of gas sensing systems will be crucial for improving the development of VRFBs. Continued development and research are crucial to enhance the competitiveness of VRFBs and contribute to the realization of global energy and environmental goals.

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