Modifying Electrodes to Enhance the Energy Density of Vanadium Redox Flow Batteries

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Abstract: Redox flow battery (RFB) as a promised way of large-scale energy storage has been getting more attention recently, due to the gradually growth demand for electricity. Vanadium flow battery (VFB), an RFB containing vanadium ions, has been proven to be a candidate of interest for industrial applications. They have the advantages of relatively high safety, low costs and high durability against other RFBs. However, the high costs and low energy density prohibit the application of VFBs. Promoting energy efficiency is crucial to address those concerns since higher energy efficiency will lead to a decreased consumption of raw materials and low energy dissipation. Electrodes, where the redox reactions occur, play a key role in improving energy efficiency. There have existed a bunch of approaches to modify the performance of electrodes. In this paper, recent research achievements on electrode modifications including surface modification, structural and configuration modification, introducing electrocatalyst and electrode material modification will be discussed.

1 INTRODUCTION

To achieve the ambitious goals of reaching "peak carbon" and attaining carbon neutrality, industries are increasingly turning to alternative sources of sustainable resources, including photovoltaics (PV) and wind power, within the new energy sector (IEA, 2023). According to projections by the International Energy Agency (IEA), onshore wind and PV are anticipated to contribute up to one-third of global electricity generation this year (IEA, 2023). Despite their growing adoption, these sources of electricity often encounter challenges related to intermittency and instability, which can jeopardise the security and reliability of the power grid.

Traditional batteries have several drawbacks in these application scenarios. Firstly, they typically rely on non-renewable energy sources such as fossil fuels for charging, thus failing to achieve carbon neutrality goals. Secondly, traditional batteries have relatively low energy density, which is unable to support the requirements of extensive energy repository. Additionally, the lifespan of traditional batteries is limited, requiring frequent replacement and maintenance, thereby increasing costs and resource consumption.

Redox flow batteries (RFBs), composed of two electrodes, two current collectors, and a separator (Emmett and Roberts, 2021), offer numerous advantages including the ability to separate capacity and power, deep charge and discharge capabilities, rapid response times, long cycle life, high safety standards, and adaptable designs. Consequently, they hold immense potential for large-scale energy storage solutions aimed at addressing the aforementioned challenges. However, the widespread implementation of existing RFB technology is impeded by various drawbacks, including high operational and capital costs, low energy density, and stability concerns (Emmett and Roberts, 2021). Vanadium flow battery (VFB) as a king of RFB has been obtaining more interest recently. As the electrolytes in VFB only contains vanadium compounds, the penetration phenomena which is another common concern in RFB, can be minimized.

Among these limitations, energy density and cost efficiency are particularly crucial (Emmett and Roberts, 2021). Obtaining a high energy efficiency is an effective approach to address those problems mentioned before (Emmett and Roberts, 2021). With higher energy efficiency, the capital cost and operation cost can be reduced by lower amount of reactants and materials usage. Higher energy capacity

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is achieved by the reduced energy dissipation (Wu et al., 2023). Electrode, as a major part of the VFB system, provides the place for redox reaction to happen and charge to transfer as well. By optimizing electrode materials and selecting designs with high activity and stability, the ohmic potential will be reduced while the conductivity and redox reaction rate can be enhanced. This can be achieved through the use of novel nanomaterials or surface modifications such as coatings or functionalization to improve electrode catalytic activity, thereby enhancing battery performance and energy efficiency. Currently, the mainstream approach for electrode modification involves improving electrode materials and structures. However, this requires high electrode stability, as high potential differences may cause corrosion or oxidation of electrode materials.

This study provides a synthesized review of recent improvements in electrode modifications for VFBs, including modifications to electrocatalysts and electrode materials and surfaces, aiming to address challenges like scant energy concentration and vanadium flow batteries' intrinsic high-expense through improving power efficiency.

2 REACTION PRINCIPLES AND STRUCTURES

A typical flow battery consists of a catholyte, an anolyte, carbon felt electrodes, graphite flow fields, a membrane, and current collectors, shown as Figure 1. The catholyte and anolyte are injected into their separate half-cells. The electrolyte flow is directed over the carbon-felt electrodes by the graphite flow fields (Emmett and Roberts, 2021). These electrodes provide surface area for redox reactions (Emmett and Roberts, 2021). The separator ensures zero species crossover and uninterrupted transport of hydrated hydrogen ions. In the course of the redox reactions, the anolyte is oxidized by losing electrons. These electrons flow to the cathode fluid through the external circuit, where they are accepted and restored the cathode solution. The figure below shows the charging and discharge cycle of the pillar oxidation and reduction fluid battery. Whenever a electron (hydrogenated ion) moves from anode fluid to cathode fluid, H^+ cross the membrane to keep the charge neutral.

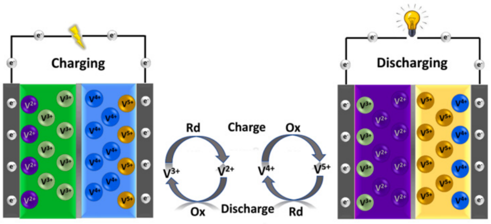

Figure 1: Charging and discharging process for a typical Vanadium flow battery (Sankaralingam et al., 2021)

Electrode materials mainly affect the energy density of the battery through these aspects: Conductivity, Surface area, Electrochemical activity and Corrosion resistance.

Highly conductive electrode materials can reduce the ohmic loss inside the battery, thereby improving the efficiency of the battery. The specific area of the electrode material surface significantly influences the electrochemical reaction rate. Therefore, as long as the specific surface area becomes larger, the more active sites used in electrochemical reactions, which can accelerate the charge transfer process and increase the battery's power density and energy density. The rate and reversibility of electrochemical reactions are determined by the electrochemical activity exhibited by electrode materials. Highly electroactive materials more efficiently catalyse vanadium ion redox reactions, reduce overpotential, and improve battery energy efficiency. The electrolyte used in vanadium flow batteries is usually highly acidic (such as sulfuric acid), which requires the electrode material to have good corrosion resistance to ensure long-term stable operation. Otherwise, the electrode will corrode and react, and the battery's energy density will be reduced.

3 IMPROVEMENT METHODS

As stated before, the modification of VFBs focuses on electrodes and electrolytes. Meanwhile, the electrode regulates the electrochemical activity of oxidation and reduced coupling and provides active sites for the oxidation reaction, this is of great significance for improving battery performance, making a critical contribution. Modifications on the electrode itself and configuration can manipulate the electrochemical polarizations, concentration and ohmic which are key factors for VFB performance evaluation (Wu et al., 2023).

3.1 Surface Modification

There are three important parameters for the performance evaluation of VFBs. Wettability indicates the distribution of electrolyte on electrode. Voltage efficiency (VE) indicates the ratio of input voltage (charging) and output voltage (discharging). Energy efficiency (EE) refers to the energy dissipation during the charging and discharging process. It is defined as the ratio between the actual energy output and the theoretical energy output. These factors determine the performance of VFB. EE and VE are key to the improvement of VFB’ s performance. Higher EE will lead to a lower energy reduction, in other words, the output energy can be promoted. Similar effect can be expected with an increased VE. The goal of surface modification is to maximize all three parameters - wettability, voltage efficiency, and energy efficiency, in order to achieve an increase in energy density. Carbon felt (CF) and graphite felt (GF) are commonly used electrodes in VFBs due to they are highly conductive and stable under acidic conditions. However, modifications are essential for CF and GF to overcome their drawbacks on low catalytic activity and specific surface area. Increasing the surface functional groups by thermal treatment and doping is one of the most common ways to address those shortcomings. Thermal treatment and doping can introduce more oxygen-containing functional groups (OCFs) to the electrode surface resulting in enhancement on wettability and electrochemical activity. Coating is another alternative for surface modification. By introducing electrocatalyst to the electrode surface, the performance of electrode becomes highly tuneable (Wu et al., 2023).

3.2 Structural and Configure Modification

The modification of electrode structure can effectively increase the active surface area, enhancing the power and energy density of the flow battery by supplying additional active sites for reactions. In addition to the optimization of electrode structure and configuration, the optimization of flow field design can also contribute to improving the performance of redox flow batteries, such as energy density. A recent study (Yaji et al., 2018) employed topology optimization to refine the flow field configuration in vanadium redox flow batteries. The study formulated the optimization problem with the objective of maximizing the generation rate of vanadium species, considering the porous nature of the carbon fibre electrode and the mass transfer coefficient dependent on local velocity. The results indicated that the interdigitated flow field pattern is an effective design for VRFBs, which can help improve the charge-discharge efficiency of VRFBs (Yaji et al., 2018). Therefore, the energy density of flow batteries can be improved to a certain extent by optimizing the flow field design.

3.3 Introducing Electrocatalyst

Electrocatalysts are typically heterogenous catalysts promoting electrochemical reactions and are widely used in electrode modification (Raveendran et al., 2023). The catalytic mechanism of electrocatalysts is sophisticated and varies among different materials. Overall speaking, electrocatalysts function at the surface of electrode altering the reaction pathway and reducing the activation energy of electrochemical reactions (Raveendran et al., 2023). They play crucial roles in VFBs offering enhancement on the reactivity of the system and more active sites for ion exchange to take place. Adding an electrocatalyst into the VFB system can increase energy efficiency and lowering costs.

3.3.1 Carbon-Based Electrocatalyst

Carbon-based electrocatalysts are responsible for increasing the surface area of electrodes (Liu et al., 2018) represented by carbon nanotube (CNT), carbon felt, carbon nanosheet, graphite oxide, etc. Compared to the other two electrocatalysts, carbon-based electrocatalysts are stable in acidic solutions with high conductivity, cheap and easy to manufacture. However, they experience limitations on low specific surface area and low catalytic activity (Wu et al., 2023).

Modifications on carbon-based electrocatalysts are essential for their further application. Increasing the number of OCFs is an applicable way of reinforcing the catalytic activity and gathering more attention recently (Molina-Serrano et al., 2024). Although higher numbers of OCFs introduced to the electrocatalyst by thermal treatment as mentioned in 3.1 can increase the catalytic activity in carbon-based electrocatalysts by enhancing the wettability, mass transfer rate and number of active sites, there exists a trade-off between the activity and conductivity (Molina-Serrano et al., 2024). Heteroatom doping is another strategy to raise the conductivity and catalytic activity (Wu et al., 2023 & Liu et al., 2018). The active sites on carbon electrode are regulated by the defects introduced by the doped heteroatom on lattice resulting in a higher electron affinity. There exists varies types of doping dominated by nitrogen, oxygen and phosphorate, offering doped electrodes a high tunability on properties including reversibility, EE, power and durability to fit varies working conditions.

3.3.2 Metal-Based Electrocatalyst

Metal-based electrocatalyst are typically metal oxides and metal halides. They are highly promised materials with low cost and high conductivity. Metal-based electrocatalysts are mainly in deposited form and able to decrease the energy barrier of redox reactions happens at the electrode which is one of the major limitations of CF and GF electrodes restricting the reactivity.

Bi deposition is an important method of modification where the Bi ions reduced on the carbon electrode by deposition can largely enhance the redox reaction rate, VE and EE of VFB by implying a greater charge exchange rate under high current density (Liu et al., 2018). However, this reinforcement is bounded by the amount of Bi loaded onto the electrode, and this boundary value has not been studied thoroughly for VFBs yet. In parallel with ion deposition, transition metal oxide is also used for meta-based electrocatalyst with lowest cost among different improvement methods (Liu et al., 2018). Due to the transition metals have various valency states and are able to act as active sites for receiving reactive species. Those evenly dispersed metal oxide particles generate more surface-active OCFs and active sites, making the electrode more hydrophilic and permeable for electrolyte. They are also stable at working conditions and easy to be prepared. Besides of metal oxide, metal boride, carbide and nitride which are covalent bonded electro-deficient compounds, are materials of interest at present. They can promote the electron transfer by accepting unpaired electrons from the metal ions resulting in a significantly higher electric conductivity than metal oxides (Wu et al., 2023). Such high electric conductivity enables a much higher electron transfer rate in VFBs.

3.3.3 Composite-Based Electrocatalyst

Composite, by definition, includes a wide range of different materials. Composite-based electrocatalysts have a significantly higher electrocatalytic activity than individual composition, due to the interactions between the electrocatalyst and support. For instance, Bi metal and carbon-based materials composite is one of the composite-based electrocatalysts of interest recently (Wu et al., 2023). By introducing Bi metals into the complex and regulated carbon structure, the diffusion pathways of electrochemical reactants can be manipulated. With this, composite materials are able to provide a better electrode performance than each single materials included. As discussed in previous, transition metal compounds act as active sites for redox reaction to happens and carbon-based materials acts as support being responsible for electric conduction. Besides of metal-carbon composites, polymer composite and metal-organic-frameworks (MOFs) are other types of composites with huge prospect on electrode modification (Liu et al., 2018). MOFs are highly tuneable materials with high porosity and specific surface area, in other words, they are able to provide a significant number of active sites for redox reactions and their tunability enables them suitable for various type of operation requirements incorporating with various type of composited materials.

3.4 Electrode Material Modification

As discussed before, traditional electrode materials such as GF and CF experience various of limitations and electrode material modification is necessary to VFBs. Similar to electrocatalysts, doping, coating, surface functionalization and application of composite materials are methodologies widely used at present (Liu et al., 2018). Some examples can be found in Table 1.

Qiao et al. (Qiao et al., 2022) successfully prepared nitrogen-doped carbon felt using an ammonium sulphate hydrothermal synthesis strategy, significantly promoting the electrochemical property of vanadium redox flow battery electrodes. This paper indicates the importance of nitrogen doping in strengthening the hydrophilicity and electrochemical reactivity of electrode materials, achieving a 3.91% increase in efficiency in energy use contrasted to the original pure carbon felt under a charge flow density of $80\ \mathrm{mA \cdot cm^{-2}}$. This innovative perspective promotes progress in the field of flow batteries, particularly in the realm of vanadium.

Deng et al. (Deng et al., 2022) fabricated a multi-dimensional framework electrode material by the composite of three different-dimensional carbon materials structures (0D, 2D, and 3D), which offers high electrocatalytic activity, rapid charge transfer, and a large area for redox reactions. This MFC-GF electrode, owing to the high electrocatalytic activity of its edge carbon, exhibits excellent electrochemical performance towards the redox pairs and suppresses the hydrogen evolution reaction in the negative electrolyte.

Table 1. Modification of electrode material.

Electrode material	Increase in EE	Reference electrode material	Reference
N doped CF	7.2%	CF	Qiao et al. (Qiao et al., 2022)
MnO@C/CF	8.5 %	CF	Chen et al. (Chen et al., 2023)
MFC-GF	18.3%	GF	Deng et al. (Deng et al., 2022)

4 CONCLUSION

The activity of carbon-based electrocatalysts can be enhanced by increasing the number of oxygen-containing functional groups. Additionally, introducing dopant atoms at active sites can significantly increase electron affinity. The deposition of Bi can effectively increase the charge transfer rate of carbon electrodes, and covalently bonded electro-deficient compounds combined with unpaired electrons from metal ions can achieve higher electrical conductivity. Composite-based electrocatalysts incorporating metal-organic frameworks (MOFs) can supply a wealth of active centers for reactions, thereby significantly enhancing the performance of batteries. The modified graphite felt, MFC, significantly increases current density and lifespan due to its high electrocatalytic activity and hindrance of hydrogen evolution.

In the future, modifications in electrode materials, such as thermal treatment, doping, and coating, will become increasingly prevalent and play a more significant role due to their significant enhancement on vanadium redox flow battery performance. We look forward to the development and application of even better electrode materials to further enhance flow battery performance.

AUTHORS CONTRIBUTION

All the authors contributed equally and their names were listed in alphabetical order.

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