

Review Article

Graphene Functionalized Carbon Felt/Graphite Felt Fabrication as Electrodes for Vanadium Redox Flow Batteries (VRBs): A Review

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ABSTRACT

The growth in the development of renewable energy sources has led to tremendous attention to the research in energy storage systems. One of the electrochemical energy storage systems that have shown great potential to be used on a large scale is vanadium redox flow batteries (VRBs), as they possess flexible designs, long life cycles, and high energy density. Carbon felts (CF), and graphite felts (GF) have commonly been used as electrodes in VRBs. To improve market penetration using VRB technology, researchers have focused on electrode modifications to increase the power density and rate capabilities of VRBs. One of the carbon-based modifications which have shown significant improvements in the performance of VRBs is the use of graphene, which has outstanding electrochemical and physical characteristics as an electrocatalyst. In this review, electrochemical, physical, and other methods which have been reported in the graphene functionalization of graphite felt/carbon felt are discussed. The working principle and limiting methods were elaborated on and discussed for each method. Finally, recommendations for future developments are also highlighted.

Keywords: Carbon felt, electrode fabrication, graphene, vanadium redox flow battery

ARTICLE INFO

Article history:

Received: 13 June 2022

Accepted: 16 August 2022

Published: 24 May 2023

DOI: <https://doi.org/10.47836/pjst.31.4.05>

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INTRODUCTION

The widespread use of fossil fuels has caused various environmental drawbacks. To avoid this, various renewable energy sources, such as solar and wind, are being

developed and implemented worldwide. However, their volatility and intermittent problems pose a barrier to the large-scale application of clean energy. Hence, a reliable energy storage system is required.

Electrical energy storage systems can be divided into geological energy storage technologies, flywheels and supercapacitors, and battery storage technologies. Geological energy storage technologies (compressed air and pumped hydro energy storage) are suited for large-scale energy storage but are costly. At the same time, flywheels and supercapacitors have high and low energy densities, which are more suitable for power management. Lead acid, lithium-ion, and redox flow batteries (RFBs) are examples of battery storage technologies that are potential candidates for large-scale energy storage. Compared to other commercial batteries, RFBs have the advantage of design flexibility as the energy and power density can be decoupled. It also merits high energy density, a long life cycle, and rapid response.

The vanadium redox flow battery (VRB) is an electrochemical energy storage system with the following components, electrolytes, a membrane, and electrodes. The electrolytes (both anolyte and catholyte) are stored in tanks and circulated through the cell using pumps. An example of the VRB setup is shown in Figure 1.

The VRB electrode reactions are as given in Equations 1 to 3:

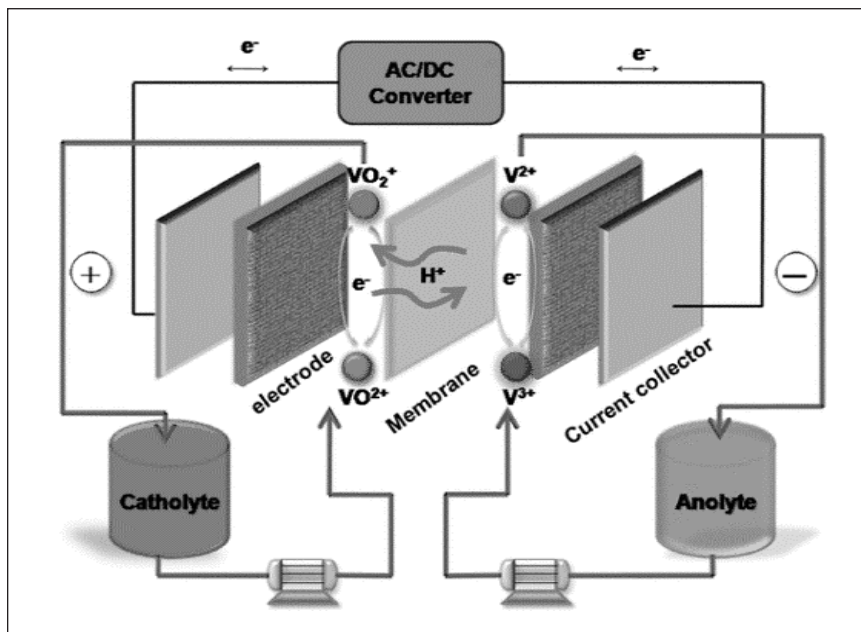
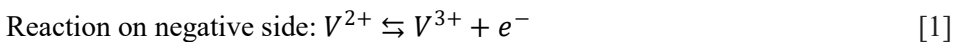
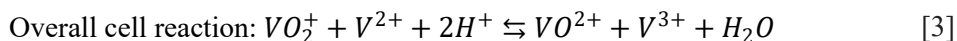
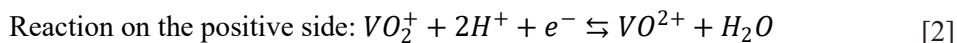


Figure 1. Schematic of vanadium redox flow battery setup (Ding et al., 2013). Reprinted (adapted) with permission from Ding et al., 2013. Copyright 2013 American Chemical Society



The reaction shows that as VRB is discharged, V^{2+} is oxidized to V^{3+} on the negative electrode while VO_2^+ is reduced to VO^{2+} on the positive electrode, and only one electron is involved in this process. Apart from the one-electron transfer, water and two protons are exchanged to maintain the charge balance. The analysis shows that the positive electrode reaction is the one that is limiting the performance of VRB. Hence, researchers are focused on developing materials with high electrochemical kinetics towards VO_2^+/VO^{2+} to enhance the overall performance of VRB.

Carbon felts (CF) and graphite felts (GF) have been commonly used as the electrodes in the VRBs due to their three-dimensional structure, their high conductivity as well as their chemical stability (González et al., 2017; Moghim et al., 2017). However, they are hydrophobic, resulting in poor wettability and low electrochemical activity. This results in severe polarization and low device efficiency which requires the development of catalyst materials to enhance its performance. (González et al., 2017; Moghim et al., 2017; Xia et al., 2019).

Among the carbonaceous electrocatalyst, graphene has attracted wide interest due to its outstanding properties, such as large specific surface area ($\sim 2600 \text{ m}^2/\text{g}$), high electrical conductivity ($\sim 200,000 \text{ cm}^2/\text{V s}$), chemical stability and high thermal conductivity ($\sim 5000 \text{ W/m K}$). These properties are crucial to enhance the active reaction sites and electron transportation. Due to the potentials demonstrated by graphene, researchers have worked extensively on the fabrication process of graphene-modified carbon felt/graphite felt with the aim of further enhancing the electrochemical activity of the electrode towards the vanadium ion couples via two key aspects, which are (1) to maximize the effective surface area of the electrodes by reducing the stacking of graphene layers and (2) by improving the bond between the graphene coating and the carbon felt which will promote the electrode's stability. This article reviewed and summarized the literature on the fabrication of graphene-functionalized graphite felt/carbon felt for vanadium redox flow batteries (VRBs).

Physical Method

One of the general methods in preparing graphene-coated carbon felt is the dipping-drying process. In this process, carbon felt (CF) is dipped into a suspension of graphene or graphene oxide and allowed to dry before it is ready for use. This process is based on the inherent solid-liquid interaction between the surface tension of the graphene oxide solution and carbon felt/graphite felt substrate (Tang & Yan, 2017). Li et al. (2013) dipped CF into a suspension of GO and dried it. Subsequently, the GO-coated CF was reduced

electrochemically at different potentials in phosphate buffer solution (PBS) before using it as the electrodes in the VRB (Li et al., 2013). It was found that the prepared graphene-coated CF demonstrated lower electrochemical polarization, and its energy efficiency was approximately 82%. Moghim et al. (2017) and Opar et al. (2020) prepared graphene-coated carbon felt using this dipping-drying process using graphene ink and three-dimensional graphene, respectively. By dipping CF into different concentrations of graphene ink (1–5 mg/mL) to load different amounts of graphene on the CF, Moghim et al. (2017) found that 2 mg/mL was the optimum concentration. Loading beyond 2 mg/mL did not significantly improve peak current (Moghim et al., 2017). Meanwhile, Opar et al. (2020) coated CF with three-dimensional graphene to reduce the restacking and agglomeration of graphene layers due to the strong π - π interactions. The graphene layers were covalently bonded to CF as the triblock polymer (P123) was used. After the dip and dry process, the CFs were weighed to determine the amount of graphene loaded.

Meanwhile, Xia et al. (2019) dipped CF into graphene by adding a Nafion binder to obtain graphene-coated CF. The study by Xia et al. (2019) focused on the correlation between the number of dipping times and the electrochemical performance of the VRB. As the dipping times increased, the amount of Nafion deposited also increased. The Nafion has no contribution to the electrochemical activity; therefore, a higher amount deposited is detrimental to the electrochemical performance. (Xia et al., 2019).

Preparing graphene-coated CF by dipping is relatively simple and requires no special equipment. However, the authors did not report whether the graphene layers suffer from peeling from the CF over long cycles. It is slightly trickier to determine the amount of graphene loaded when a binder such as Nafion is used. The use of binders in this process also increases the fabrication cost and reduces the surface area and conductivity of the electrodes (Opar et al., 2020; Zhang et al., 2016).

Sankar et al. (2018) prepared graphene-coated CF using electrostatic assembly. In the layer-by-layer assembly, a cationic polyelectrolyte is used as a binder between the two graphene layers (Sankar et al., 2018). As the porosity and thickness can be obtained for each layer, the total deposited layers can be tailored to the specific peak currents required. Compared to the physical dipping method, electrostatic layer-by-layer assembly provided better control over the electrode surface morphology and electrocatalytic activity. This technique also demonstrated scale-up potential as the number of reaction active sites can be systematically calculated.

With the aim of preparing an electrode that is suitable for practical implementation, Bellani et al. (2021) incorporated graphene prepared from wet jet milling of graphite onto CF, which was plasma treated using an infiltration method with the assistance of polyvinylidene fluoride (PVDF) binder (Bellani et al., 2021). Electrodes prepared without the PVDF binder were also tested, and the graphene flakes peeled off easily, resulting in fast deterioration of the VRFB performance (Bellani et al., 2021).

Electrochemical Method

Besides the physical methods of fabricating graphene-coated carbon felts discussed earlier, researchers have also explored electrochemical methods as they are economical, controllable, and scalable. Gonzalez et al. (2017) and Nia et al. (2018) demonstrated the use of electrophoretic deposition (EPD) and electrodeposition to simultaneously deposit and reduce graphene oxide (GO) produced by the Hummers' method.

The EPD process is usually conducted in a two-electrode system where the electric potential (direct or modulated mode) is applied to the graphene oxide solution. GO produced by the Hummers' method contained various oxygen functional groups (hydroxyl and epoxide on the basal planes, carboxylate, and carbonyl on the edges). When the electric field is applied, negatively charged GO moves to the oppositely charged electrode, transferring it from the suspension and depositing it on the electrodes (Diba et al., 2016) (Ma et al., 2018).

Using the EPD method at 10 V for 3 hours, Gonzalez et al. (2017) prepared reduced graphene oxide (rGO) coated CF, while the study by Nia et al. (2018) used the cyclic voltammetry method in the potential range of 0 to -1.5 V. A schematic diagram of the EPD process is illustrated in Figure 2. Besides physical adsorption, chemical bonds formed also helped the graphene layers formed to adhere to CF surfaces. Simultaneously, during the EPD and electrodeposition process, the GO was reduced, which enabled the recovery of π - π bonds (An et al., 2010; González et al., 2017; Nia et al., 2018). The stability of the graphene-coated CF prepared through the EPD process was tested over 20 cycles, and a high energy efficiency of 95.8% remained, showing no graphene peeling was evident. Like the electrodeposited graphene-coated CF, the energy efficiency remained unchanged after 20 cycles. When the cycles were increased to 80, the energy efficiency decreased slightly.

Apart from using GO from Hummers' method as the source to deposit graphene on CF, Gürsu et al. (2018) have also demonstrated a one-step procedure to coat CF using cyclic voltammetry (CV) from pencil graphite in sulfuric acid solution (Gürsu et al., 2018). In this one-step procedure, the pencil graphite was oxidized through electrochemical in-situ oxidation, and it was then electrochemically reduced to rGO, which can be observed through the cyclic voltammograms. The intensities of the anodic and cathodic peaks were found to have increased proportionally with the number of cycles. The stability of the electrodes was studied using cyclic voltammetry for 500 cycles, and it did not show any significant changes in the cyclic voltammogram.

As the studies show, electrochemical procedures are simple, controllable, and scalable to fabricate graphene-coated carbon felt. Despite the significant advantages, literature on forming graphene-coated carbon felt/graphite felt through electrochemical procedures is limited.

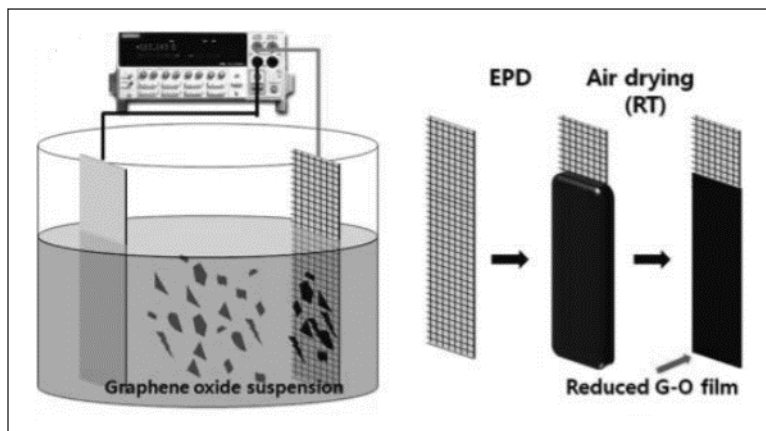


Figure 2. A schematic diagram of the EPD process (An et al., 2010). Reprinted (adapted) with permission from An et al., 2010. Copyright 2010 American Chemical Society

Other Methods

Besides the physical and electrochemical methods elaborated above, other methods such as electrospinning, chemical vapor deposition (CVD), and microwave plasma-enhanced CVD have been reported. Jing et al. (2019) proposed an electrospinning method to fabricate graphene-coated CF. The electrospinning technique relies on the electrostatic repulsion between the surface charges to continuously synthesize various scalable assemblies (Al-Dhahebi et al., 2022). It is also known as a cost-effective, simple, and versatile technique. The partially reduced GO-coated CF was successfully prepared by introducing GO into the electrospinning solution, followed by a carbonization process (Jing et al., 2019). The oxygen content in the partially reduced GO formed has significantly enhanced the hydrophilicity of the CF and the electrochemical performance of the VRB (increased by 9.0% in energy efficiency).

An in-situ microwave plasma-enhanced chemical vapor deposition method synthesized 3D graphene nanowell decorated carbon felts (Li et al., 2016). The graphene sheets were vertically grown and wrapped in the fibers in CF. It increases the electrode's surface area, promoting the vanadium ions' electrocatalytic activity. The prepared electrodes showed no morphological changes after 100 charge and discharge cycles.

Meanwhile, Long et al. (2021) studied the large-scale (20 cm x 20 cm) preparation of graphene-modified carbon felt using the chemical vapor deposition method (CVD). The electrodes enhanced electrical conductivity and redox catalytic performance. The prepared electrodes endured over 500 cycles of charge-discharge with only slight decay observed (Long et al., 2021). Both the microwave plasma-enhanced chemical vapor deposition and chemical vapor deposition (CVD) methods have successfully demonstrated the preparation of graphene-modified carbon felt. Long et al. (2021) was the first study on the large-scale

preparation of graphene-modified carbon felt and is another step toward the practical use of graphene-modified carbon felts as electrodes in VRBs. However, using CVD requires a highly expensive instrument, and the reaction process emits by-products in the form of toxic gases.

OUTLOOK

A suitable electrode for VRBs requires high electrical conductivity, specific surface area, and inertness to strong acids. Carbon felt/graphite felt met all the requirements, which makes it, thus far, the best material to be used. However, its low chemical activity towards the vanadium ion couple results in severe polarization and low device efficiency. Modifications with noble metals (Ru, Pt & Au) are not cost-effective at a large scale. Intrinsic control of morphologies is required when low-cost metals are used to guarantee high VRB performance and metal oxides (PbO_2 , NiO & CeO_2) decompose in strong acids, which are used as VRBs electrolytes. As graphene-based materials have a high specific surface area, high conductivity, and abundant active groups, graphene-modified CF/GF has shown superior performance to pristine CF/GF. However, several interesting challenges need to be overcome for the large-scale application of graphene-coated CF/GF in VRBs. Firstly, control over the graphene loading is crucial as it provides the electroactive sites which enhance the electrochemical performance of the VRB. Controlling the graphene loaded on CF/GF, the amount required can be tailored to the desired VRB performance. Secondly, the cycling life of the graphene coating is also key to applying graphene-modified CF practically. Peeling of the graphene layers is detrimental to the energy efficiency of the VRB. The number of cycles tested in the literature is limited and is insufficient to conclude the performance of graphene-modified CF/GF over long cycles. Thirdly, large-scale preparation of the graphene-modified CF is important as it is necessary to ensure that the procedure can be applied at the industrial scale. To our knowledge, limited large-scale preparation of graphene-modified CF was reported. We are convinced that with more research, graphene-modified carbon felt can be applied in a large-scale use of vanadium redox flow battery.

CONCLUSION

This study has reviewed various methods to prepare graphene-modified carbon felt/graphite felt (CF/GF) as the electrode material for vanadium redox flow batteries and discussed the advantageous and disadvantageous of each method reported. The methods have successfully prepared graphene-modified CF/GF, which performed superiorly compared to pristine CF/GF, demonstrating its potential to be integrated into large-scale vanadium redox flow battery deployment. The challenges which need to be overcome are also discussed. Further research conducted can overcome these barriers and realize the full potential of graphene-coated CF/GF in large-scale VRBs applications.

ACKNOWLEDGEMENTS

The authors thank the Ministry of Higher Education for Fundamental Research Grant Scheme (FRGS) (FRGS/1/2020/STG05/UPM/02/3), Universiti Putra Malaysia for Geran Inisiatif Putra Muda (GP-IPM) (9683600) and UPM-Kyutech International Symposium on Applied Engineering and Sciences 2021 (SAES 2021) and Universiti Putra Malaysia for supporting the publication fee.

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