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## Synergistic Enhancement of Vanadium Redox Flow Batteries via Carbon Nanotube-Decorated and Thermally-Acid Activated Carbon Felt Electrodes

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### Abstract


In recent years, Vanadium Redox Flow Batteries (VRFBs) have attracted significant attention as an important energy storage technology. These batteries are considered among the advanced energy storage systems that offer unique capabilities for power generation applications and other industrial uses. Today, the integration of this technology with solar power plants, wind farms, and thermal power stations has experienced substantial growth. Each vanadium redox flow battery cell consists of two half-cells separated by a proton exchange membrane. In addition, every single cell contains two electrodes that serve as the active sites for electrochemical reactions, through which chemical energy is converted into electrical energy. Carbon felt is one of the commonly used electrode materials in vanadium batteries. The objective of this study is to introduce an effective method for activating the surface of Carbon felt electrodes using Carbon Nanotubes (CNT), in such a way that electrochemical processes proceed at higher reaction rates, thereby enhancing the overall efficiency and performance of VRFBs.

**Keywords:** Renewable energy, Vanadium redox flow battery, Carbon nanotubes, Carbon felt.

## 1 | Introduction

Today, the utilization of renewable energy resources, particularly solar and wind energy, has received widespread attention. In such systems, due to seasonal and daily fluctuations in energy generation, the need for an energy storage source is consistently recognized.

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Among available technologies, redox flow batteries have emerged over the past decade as one of the most efficient energy storage systems worldwide, owing to their high efficiency, long service life, and environmentally benign operation [1], [2].

A schematic representation of a vanadium redox flow battery is presented in Fig. 1. Two electrolyte reservoirs, one connected to the positive electrode and the other to the negative electrode, enable the circulation of large volumes of electrolyte through the cell. An ion-exchange membrane prevents the mixing of the two electrolytes. During battery charging,  $V^{4+}$  at the positive electrode loses one electron through an external power supply and is oxidized to  $V^{5+}$ . The electron is transferred from the positive electrolyte to the negative terminal of the battery, where it reduces  $V^{3+}$  to  $V^{2+}$ . During discharge, the reverse process occurs spontaneously [3].

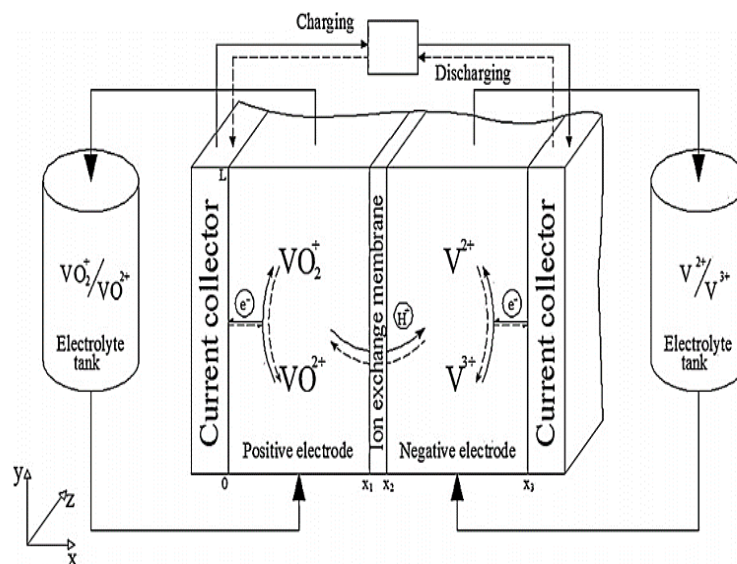


Fig. 1. General schematic of a vanadium redox flow battery.

As in other battery systems, electrodes play a critical role in Vanadium Redox Flow Batteries (VRFBs). Conventional materials used for vanadium battery electrodes include metals and carbon-based materials. Metallic materials, such as noble metals and their oxides, are used less frequently in vanadium batteries due to their high cost and low specific surface area. In contrast, carbon-based materials, including Carbon felt, carbon paper, and graphite powder, are widely employed in vanadium flow batteries because they offer significant advantages such as high specific surface area, a wide operational potential window, stability, and cost-effectiveness [4], [5].

However, the inherently sluggish kinetics and poor reversibility of carbon-based materials limit their application in VRFBs. Although extensive efforts have been devoted to modifying and enhancing their electrochemical properties [6], such modified electrodes have not yet been widely implemented in practical vanadium batteries or, in many cases, do not deliver satisfactory performance within full-cell configurations.

Due to their high specific surface area and excellent electrical conductivity, Carbon Nanotubes (CNTs) can be employed as electrocatalysts in a wide range of electrochemical processes. In this study, the surface activation of a carbon felt electrode using CNT is investigated with the aim of enhancing the performance of this electrode for application in a vanadium redox flow battery.

## 2 | Experimental Section

## 2.1 | Graphite Electrode Modification

Given that both graphite and Carbon felt are graphitic-based materials, and considering the low cost of graphite, preliminary experiments were conducted on graphite to verify the suitability of carbon nanotube catalysts for graphitic structures.

After polishing the graphite using fine-grit sandpaper and washing it with deionized water, a predetermined amount of chemically pretreated CNT was deposited onto its surface. The electrode was then dried at 70 °C.

## 2.2 | Modification of Carbon Felt Electrode

The loading of CNT onto the Carbon felt electrode was also performed by immersing the electrode in a carbon nanotube ink, followed by sonication (ultrasonic treatment) for 15 minutes using an ultrasonic device (ultrasonicator).

## 2.3 | Thermal–Acid Treatment of Carbon Felt

Initially, the Carbon felt was washed with ethanol and subsequently with distilled water, and then dried at 80 °C to remove any residual organic compounds from the system. Thereafter, it was immersed in 98% sulfuric acid for 5 hours, followed by thermal treatment at 450 °C for 2 hours.

## 2.4 | Electrochemical Studies

Cyclic Voltammetry (CV) measurements were performed using a Potentiostat–Galvanostat system (PGSTAT302) in an electrochemical cell containing an electrolyte composed of 0.2 M VOSO<sub>4</sub> in 1 M H<sub>2</sub>SO<sub>4</sub>.

The electrochemical cell consisted of a three-electrode configuration, including:

- I. Graphite or Carbon felt, either pristine or modified, is the working electrode.
- II. A platinum electrode is used as the counter (auxiliary) electrode.
- III. A silver/silver chloride (Ag/AgCl) electrode as the reference electrode.

## 3 | Discussion of Results

As shown in *Fig. 2*, which presents the cyclic voltammograms of the pristine graphite electrode and the Carbon nanotube-modified graphite electrode (C/CNT), it can be observed that the modified electrode exhibits an increased current response and a voltammogram that approaches more reversible behavior. Accordingly, the suitability of CNT for the modification of carbon-based electrodes for application in VRFBs is confirmed.

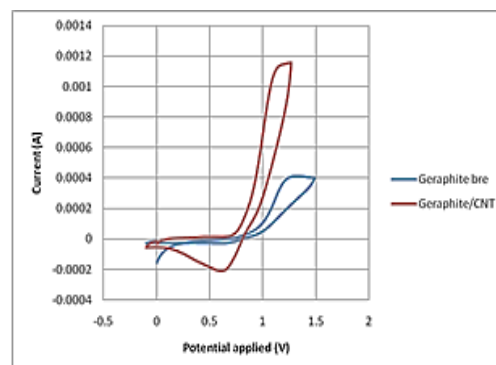


Fig.2. CV of bare graphite and graphite/CNT at a scan rate of 10 mV/s.

Fig. 3 presents the CV response of bare Carbon felt and CNT-modified Carbon felt. The incorporation of CNT was found to reduce the peak-to-peak separation ( $\Delta E_p$ ), indicating an improvement in the electrochemical reversibility of the system. Consequently, the CNT-modified electrode exhibited enhanced redox reversibility compared to the pristine Carbon felt.

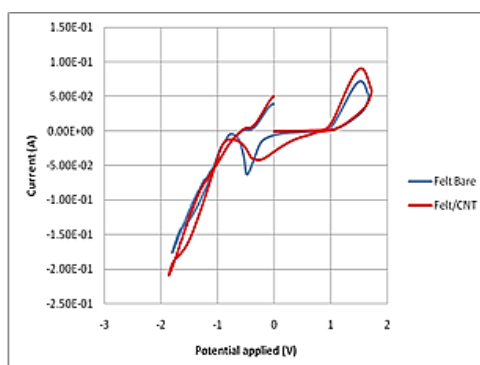


Fig. 3. CV of bare Carbon felt and Carbon felt/CNT at a scan rate of 10 mV/s.

Thermal treatment is a widely used method for activating carbon electrodes employed in VRFBs. Accordingly, a thermal–acid treatment was applied to complete the electrode modification process.

In the following, the CV responses of electrodes modified by thermal–acid treatment alone, as well as those modified by the combined use of CNT and thermal–acid treatment, are presented.

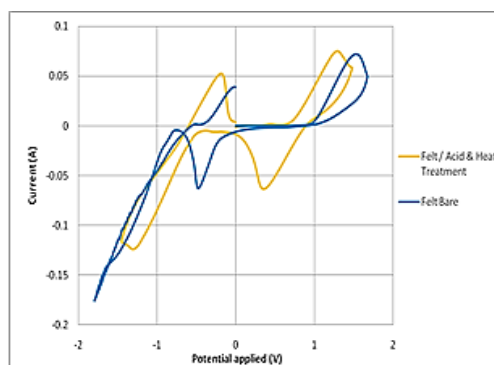
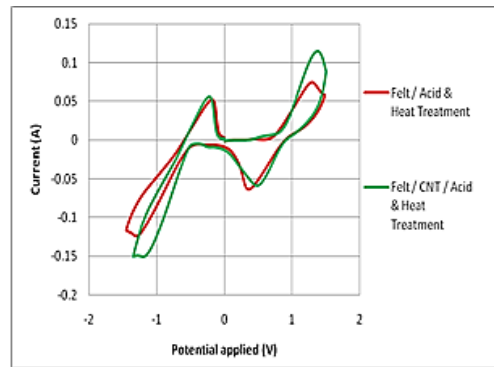


Fig. 4. CV of bare Carbon felt and acid and heat-treated carbon felt at a scan rate of 10 mV/s.

In Fig. 4, which corresponds to the thermal–acid treatment of the Carbon felt electrode, a decrease in  $\Delta E_p$  along with an increase in current is observed. This behavior indicates enhanced charge-transfer kinetics and faster electron transfer in the redox reactions occurring at the surface of the modified electrode [7].



**Fig. 5.** CV of acid & heat-treated Carbon felt and CNT/acid and heat-treated carbon felt at a scan rate of 10 mV/s.

When CNT was combined with the thermal–acid treatment for Carbon felt modification, a further increase in current was observed (*Fig. 5*). This result confirms the electrocatalytic effect of CNT on the electrochemical processes of VRFBs.

## 4 | Conclusion

In the present study, CNTs were employed as electrocatalysts to modify the surface of a Carbon felt electrode. A combination of thermal and chemical treatments was applied in order to enhance the quality and electrochemical performance of the Carbon felt electrode for application in VRFBs.

The results indicate that the performance of the electrode can be significantly improved through the deposition of CNT onto the Carbon felt surface, followed by thermal–acid treatment. This enhancement is attributed to the presence of oxygen-containing functional groups on the surface of the activated CNT, which are capable of facilitating the adsorption of vanadium species. Consequently, electrochemical reactions proceed more efficiently on the surface of the modified electrode.

## Conflict of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

## Data Availability

All data generated or analyzed during this study are included in this published article. No additional data are available.

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