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Graphite felt with vapor grown carbon fibers as electrodes for vanadium redox flow batteries

YANG Hsiharn^a, HUNG Chein-Hsin^a, WANG Shuo-Ping^a, and CHIANG I-Long^b^a Graduate Institute of Precision Engineering, National Chung Hsing University, Taichung 40227, Taiwan, China^b CeTech Cooperation, Ltd., Taichung 41456, Taiwan, China

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Abstract

Several methods to produce vapor grown carbon fibers (VGCFs) on graphite felt as electrodes for vanadium redox flow batteries (VRB) were described. The experiments include graphite felt preparation and VGCF production onto graphite fiber in the felt. Several attempts were made using nickel and cobalt catalyst coatings on the graphite felt. The nickel catalyst came from nickel nitride solution. It was prepared by dipping graphite felt into the solution and decomposed using heat treatment. Cobalt nanoparticles were sprayed onto graphite felt. Both experiments resulted in carbon nanotubes and VGCFs growth onto graphite fiber in the felt. The experimental results show that VGCFs and carbon nanotubes with the range of 20 to 70 nm in diameter are grown in the graphite felt using different catalysts. The encouraged results show the single VRB cell test with new electrodes can increase the charge/discharge efficiency by more than 12% compared to conventional graphite felt.

Keywords: graphite felt; vapor grown carbon fibers; carbon nanotube; vanadium redox flow battery

1. Introduction

Numerous renewable energies are available in the world such as solar energy, wind power, and geothermal. As expected, fossil fuel may be exhausted within few decades, making new energy or storage technologies with clean and high efficiency desired. It can be anticipated that renewable energy sources will have increased contribution to the electricity supply within several decades. Wind power is an impressive renewable energy for its clean generation process. However, the energy storage issue from wind power must be improved.

Among all new energy storage technologies currently under development around the world, the vanadium redox flow battery (VRB) appears to offer great promise as a low cost, high efficiency large-scale energy storage system [1-4]. Thaller proposed the vanadium redox flow battery in 1975. It is an electrochemical device for energy storage. It has received attention because of its long life, fast response time, deep-discharge capability, and low pollution emitting for energy storage [5]. The structure of a VRB single cell includes an electrolyte tank, magnetic pump, cation exchange membrane, graphite felt, electrode and bipolar plate. The electrochemical cell stores or releases power by shifting the

ratio of the two vanadium species present at each electrode. The system power is determined by the rate of reaction in the vanadium species at each electrode and the total surface area of the electrodes. The amount of energy stored in the system is determined by the vanadium species concentration and the volume of the reservoirs [6].

Carbon fibers have a very wide range of characteristics because of the various fabrication methods. Commercial vanadium redox flow battery electrodes typically use graphite felt. Graphite felt is made through polymer pyrolysis. It can be treated to increase the number of surface oxide sites or heated to increase its crystallinity and conductivity. Polyacrylonitrile (PAN) based carbon felt has a wide potential operational range and stability for use as both anode and cathode. It is available with high surface area at reasonable cost. It has been used as electrode materials in many applications [7-13]. Because VGCF has excellent electrical conductivity and high surface area to volume ratio, it is suitable for electrodes in many batteries. VGCF is used in lithium ion batteries (LIB) to improve high power ability and prolong the life cycle.

Conventional VRB uses graphite felt as electrodes, requiring low electrical resistivity and high surface to volume

ratio to store electrical carriers. In this study, the proposed idea is to catalyze a coating onto the graphite felt and grow carbon nano-fibers onto the felt using a vapor deposition process. VGCFs grown onto the carbon fiber surface will enhance the charge and discharge efficiency for vanadium redox flow batteries.

2. Experimental

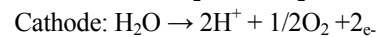
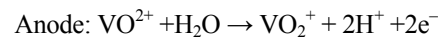
Several methods for growing VGCFs onto carbon fibers are examined in this study. The carbon fiber precursor is PAN-based oxidization fiber. The oxidized fibers were fabricated using the needle punch technique using felt based on a desired weight basis. PAN based oxidized fibers were spun using needle punch in 7 mm thick felt. Heat treatment and graphitization were then proceeded to result in 6 mm thick graphite felt for conventional VRBs' electrodes. The oxidized fiber felt was placed into a high temperature oven with nitrogen inert environment. The felt was heated up to 900 °C with the temperature maintained for 50 min. The power was then turned off and cooling the oven to room temperature for obtaining carbon fiber felt. The following step spray coated or soaked the carbon catalyst (e.g. iron, nickel or cobalt) onto the carbon fiber surface. The vapor deposition hydrocarbon to carbon process adhered to the catalyst surface under high temperature. The graphite-structure carbon is then precipitated using catalysts through diffusion, over-saturation, aging, continuously repeated absorption, carbon over-saturation and precipitation eventually forming a slender carbon tube a few microns/tens nanometers in diameter. The carbon electrode produced by VGCFs process exhibits very fine thermal and electrical conductivity as well as excellent mechanical properties which enable the battery module to increase battery efficiency and service life. The production process gives VGCF great potential.

Transition metals (e.g. iron, nickel, cobalt or their alloys, etc.) are mostly chosen as the source materials. This study used two metals, nickel from nickel nitrate and cobalt nanoparticles as catalysts. Carbon fiber felt was dipped into the 2 M (mole) solution of nickel nitrate mixed with DI water. A magnetic stirring plate was used to blend the nickel nitrate to evenly adhere onto the carbon fibers. The soaked carbon fiber felt was placed on a hot plate to dry at 100 °C for 60 min. The felt was then moved into a vacuum high temperature oven filled with nitrogen to sinter at 900 °C for 60 min. Then the carbon felt was taken out after cooling the oven to room temperature. The second experiment mixed cobalt nanoparticles with DI water blended into a 2 M solution. A spray gun was used to spray the carbon felt evenly. A similar process was used to dry the carbon felt on the hot

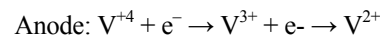
plate at 100 °C for 60 min. After the two catalysts were deposited onto the carbon felt surface, the VGCF growth process was initiated. The samples were placed into a graphite vacuum furnace filled with argon and sintered at 1000 °C for 10 min. During the cooling process, VGCF can grow onto the carbon fibers in the felt while cooling the furnace for 8 hours. The graphite felt with VGCFs was completed for VRB characteristic application.

A single VRB cell was used for the electrode test as shown in Fig. 1. The battery electrolyte is composed of 0.2 M VOSO_4 and 0.4 M H_2SO_4 solution. At the beginning of the battery charge, both the positive and negative electrolytes are a blue solution with V^{4+} valence. The volumes of both electrolytes are different due to the difference in valence charge. The positive electrolyte volume is twice that of the negative. The responses of the positive and negative electrolytes during charge are shown as follows:

Anode reaction:



Cathode reaction:



Because the battery uses $\text{VOSO}_4(\text{V}^{4+})$ as the initial electrolyte, the positive electrolyte will be oxidized from +4 valence to +5 valence during charge and the negative electrolyte reduced from +4 to +3 to +2, i.e. the amount of electricity charged and discharged is different for the positive and negative electrolyte. After completion of the initial charge, during the subsequent charge and discharge, the positive electrolyte valence change will only be +4 and +5. The valence change of the negative electrolyte will be +2 and +3. Therefore, the charge/discharge efficiency will not be the same for the initial and subsequent charge/discharge. The

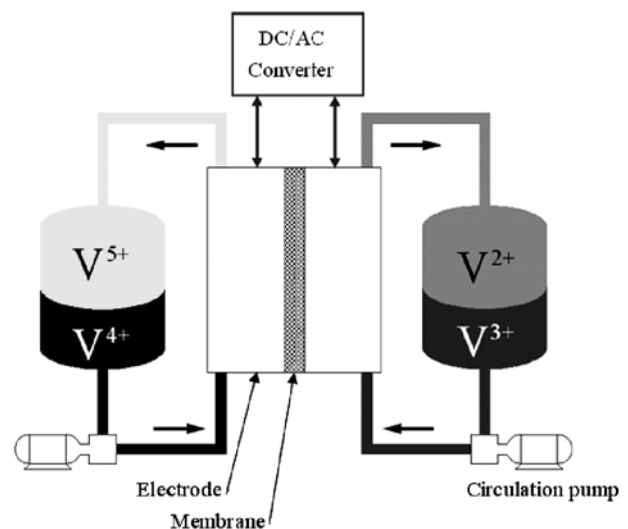


Fig. 1. Structure diagram of a VRB single cell.

volume of the initial positive side electrolyte was 200 ml in this study during initialization and that of the initial negative side was 100 ml. For the charge and discharge efficiency measured in the initial reaction, the initial positive electrolyte must be twice that of the negative. For the charge and discharge efficiency measured in the subsequent reactions, the positive side and the negative side must adjust back to the 1:1 ratio.

Graphite felt with VGCFs was used as the electrodes on both the positive and negative sides. The sample size was 10 cm² with the thickness 6 mm. The current density for the charge/discharge was 40 mA per unit with a Nafion® 117 membrane used as the separator between the two sides. Any electrolyte leakage will mix and cause an efficiency drop. Circulation pumps with a 4 L/h flow rate were used in the electrolyte on both sides to circulate the electrolyte.

3. Results and discussion

Graphite felt is the product of carbon felt. The precursor of carbon felt is the oxidized fiber felt. The combined process reduces the fiber mass by around 55 – 60 wt.% during heat treatment, called graphitization. Most of the non-carbon elements within the fibers are volatilized in the form of methane, hydrogen, water and various other gases. The resulting graphite fiber has a diameter of 7 ~ 8 μm as shown in Fig. 2. The aforementioned graphite felt is treated by soaking it in or spraying it with transition metals to grow VGCFs. Graphite felt soaked in nickel nitrate solution, followed by high temperature treatment, will produce carbon nanotubes roughly in the 40 to 70 nm range, as shown in Fig. 3. Graphite felt sprayed with cobalt nanoparticles after undergoing high temperature treatment, will produce carbon nanotubes were in the 20 to 50 nm range, as shown in Fig. 4.

The charge/discharge efficiency test of a single cell, is completed when the charging voltage reaches 2.2 V. The color of both sides will change completely. The positive

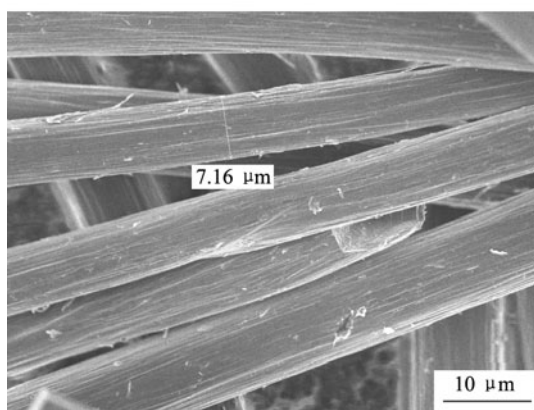


Fig. 2. SEM micrograph of the graphite fiber in the felt.

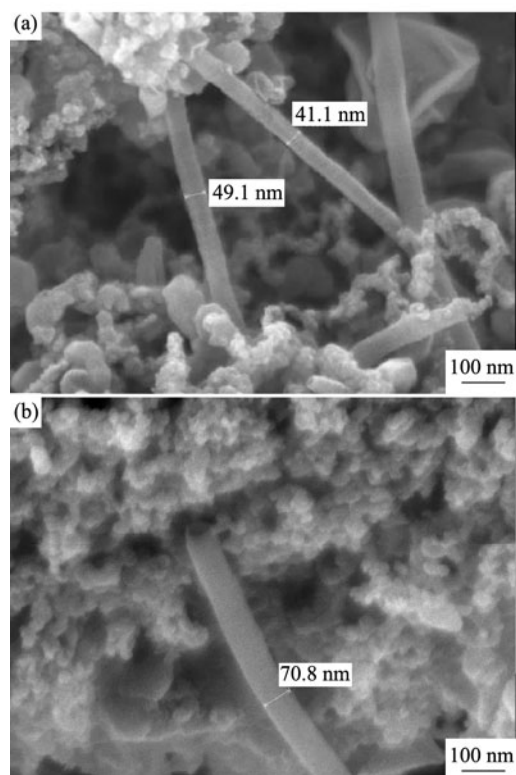


Fig. 3. SEM micrograph of the VGCF and carbon nanotubes in the graphite felt by using nickel nitrate; (a) carbon nanotubes with 40~50 nm in diameter, (b) carbon nanotubes with 70 nm in diameter.

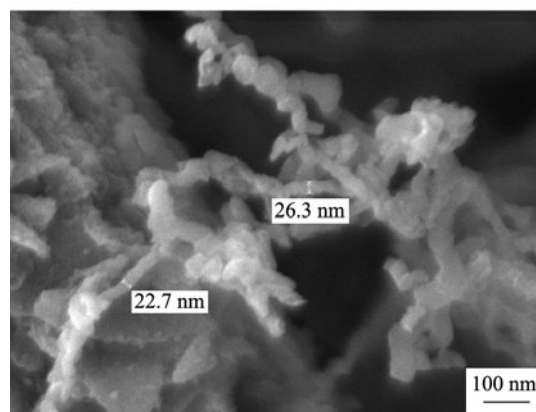


Fig. 4. SEM micrograph of the VGCF in the graphite felt by using cobalt nanoparticles; VCFG with 23 nm in diameter.

electrolyte will change from blue (V^{4+}) → yellow (V^{5+}) and the negative electrolyte will change from blue (V^{4+}) → purple (V^{2+}). When the cell voltage reaches 0.0V in the discharging process, the battery is completely discharged. The charge/discharge efficiency is calculated by charging W.hr/ discharging W.hr. Three types of electrodes were used for the measurement test including conventional graphite felt, graphite felt soaked in nickel nitrate, and graphite felt sprayed with cobalt nanoparticles. Fig. 5 shows the charge/

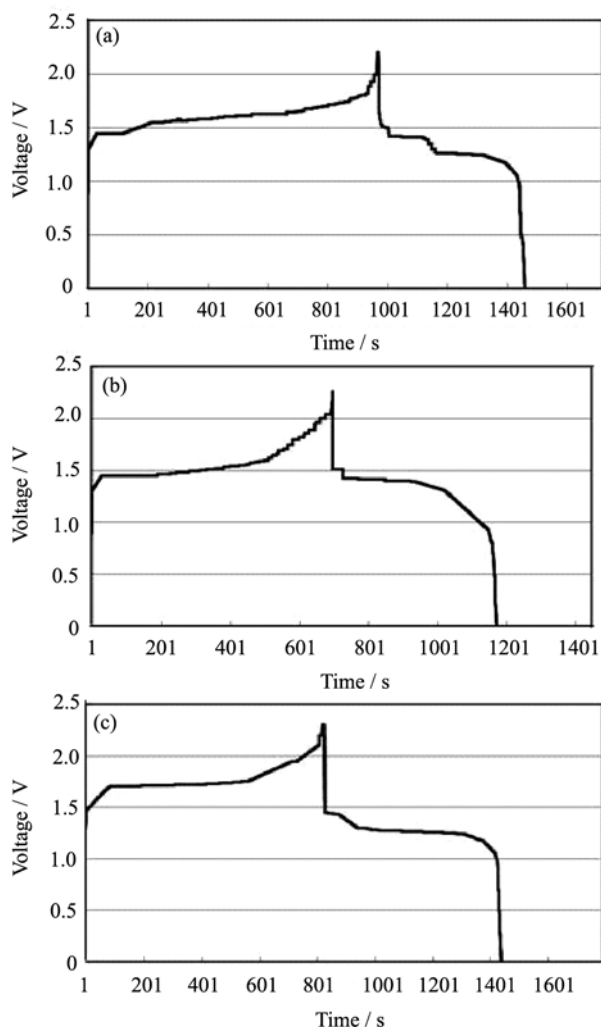


Fig. 5. Charge/discharge performance chart of conventional graphite felts: (a) conventional graphite felt; (b) graphite felt with carbon nanotubes; (c) graphite felt with VGCFs.

discharge performance using different electrodes. The charge/discharge efficiency using conventional graphite felt at the second charge was 37%. The charge/discharge efficiency using graphite felt soaked in nickel nitrate at the second charge was 46%. The charge/discharge efficiency using graphite felt sprayed with cobalt nanoparticles at the second charge was 49%. The graphite felts with VGCFs produced higher performance than conventional graphite felt.

4. Conclusion

This study successfully produced VGCFs and nanotubes 20 ~ 80 nm in diameter in graphite felt. However, these methods required catalysts adhered to the graphite fiber surface. VGCFs and carbon nanotubes in the graphite felt can enhance the VRB charge/discharge efficiency, but the fab-

rication cost is also increased.

Acknowledgement

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