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## Short Communication

# Electrocatalytic activity of nitrogen-doped CNT graphite felt hybrid for all-vanadium redox flow batteries

Dae-Soo Yang, Jang Yong Lee, Sang-Woo Jo, Sang Jun Yoon, Tae-Ho Kim<sup>\*</sup>, Young Taik Hong<sup>\*\*</sup>

Center for Membranes, Korea Research Institute of Chemical Technology (KRICT), 141 Gajeong-ro, Yuseong-gu, Daejeon 305-600, Republic of Korea

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## ABSTRACT

Novel nitrogen-doped CNT-containing graphite felt (N-CNT/GF) hybrid electrodes with high electrocatalytic activity were developed for all-vanadium redox flow batteries (VRFBs). A simple, effective preparation method for N-CNT/GFs using metal (Fe, Co, and Ni) phthalocyanines as the carbon and nitrogen precursor is presented. We found that different metal precursors generated different densities of N-CNTs on the surface of the GFs due to the various interactions of the metals (Fe, Co, Ni) with the carbon precursor during carbonization. Higher density and longer N-CNTs were obtained for N-CNT/GF (Fe), which gave rise to a higher N-doping concentration, enhanced wettability and conductivity, and improved electrochemical reactivity. When used as an electrode in a VRFB single cell, this material showed outstanding performance with an increase in energy efficiency of more than 20% compared to pure GF at a high current density (150 mA/cm<sup>2</sup>).

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## Introduction

All-vanadium redox flow batteries (VRFBs) have found widespread application as rechargeable grid-scale energy storage systems (EES) for renewable energy sources, because of their multi-megawatt load leveling capacity [1–5]. VRFBs also have advantages, such as decoupling of energy and power, environmental friendliness, high round-trip efficiency, and long cycle life [6–8]. Despite their great promise for various

applications, the commercialization of VRFBs has suffered a huge setback due to their low rate capability and efficiency [9].

It is a prerequisite to improve the power density of VRFBs to increase their market feasibility. VRFBs should be able to operate at high voltage during discharge at high current density, which implies that polarization losses (activation, Ohmic, and concentration polarization) need to be reduced [10]. As the overpotentials due to activation and concentration polarization remain the same for a certain cell configuration, Ohmic polarization is generally considered the major factor

<sup>\*</sup> Corresponding author.

<sup>\*\*</sup> Corresponding author.

E-mail addresses: [thkim@kRICT.re.kr](mailto:thkim@kRICT.re.kr) (T.-H. Kim), [ythong@kRICT.re.kr](mailto:ythong@kRICT.re.kr) (Y.T. Hong).

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determining the polarization losses [9,11,12]. Since the redox reactions involving vanadium ions take place on the electrode surface, the development of electrochemically active electrodes is very important to reduce Ohmic polarization, as it is strongly dependent on the electrocatalytic activity of the electrodes. Given their high conductivity and excellent stability in acid electrolytes, carbon electrodes, such as graphite felt (GF), carbon felt, and carbon paper, are being widely researched for use in VRFBs [13–15]. Among these electrodes, GFs have been most widely used due to their high porosity, allowing easy penetration of electrolytes, and low production costs. However, the inherent low specific surface area and poor catalytic activity of GFs result in poor electrochemical reactivity with vanadium electrolytes in VRFBs.

Heteroatom-doped carbons are emerging as an excellent alternative to the widely used carbon electrodes [16–18]. In particular, N-doping of carbon materials, including carbon nanotubes (CNTs), graphene, and mesoporous carbon, has been extensively studied for the fabrication of next-generation VRFB electrodes [19–21]. Furthermore, unlike metal/carbon composites, N-doped carbon materials have been found to show much-improved conductivity and thermal and chemical stability [22–28]. However, the complexity of the synthesis method and harmful effects of the nitrogen precursors, such as ammonia and ethylene diamine, hinder the large-scale synthesis of N-doped carbon electrodes [29–31].

The modification of GF with CNTs has been reported recently [32]. Yan et al. demonstrated the first application of CNTs grafted with carboxyl moieties for VRFBs [13,33]. They proposed that CNTs grafted with oxygen-containing groups can catalyze  $\text{VO}^{2+}/\text{VO}_2^+$  redox reactions with much greater efficiency. However, the preparation of high-quality CNTs involves the use of highly sophisticated techniques, such as laser ablation, arc discharge, and chemical vapor deposition (CVD), which limits scale-up of the technology and increases the cost of production. Thus, the difficulty in producing doped CNTs is the biggest challenge in their large-scale use for VRFBs. Therefore, it is necessary to develop an easy synthesis method that facilitates the application of doped CNTs for this application.

In this study, we developed N-doped CNT/GF hybrid electrodes (N-CNT/GFs) with a high density of CNTs on the surface of GFs. A simple and effective method for fabricating N-CNT/GFs using metal (Fe, Co, and Ni) phthalocyanine (Pc) as a carbon and nitrogen precursor is presented. The synthesized N-CNT/GF(X) (where X is the metal Fe, Co, or Ni) electrode was then investigated as a catalyst for the vanadium redox reaction. The higher density of the N-CNTs obtained for N-CNT/GF(Fe) sample resulted in an increased concentration of N-doping and improved electrochemical reactivity, resulting in outstanding performance of the VRFB single cell.

## Material and methods

### Synthesis of CNT hybrid/N-doped GF

FePc, CoPc, and NiPc were purchased from Alfa Aesar (Korea) and commercial GF was purchased from PAN-based carbon,

Standard Energy Co. Ltd., Korea. All chemicals were analytical grade and used without further purification. Firstly, the pure GF was washed with acetone to clean the outer surface. Then, the washed GF was put in  $1.0 \text{ mol L}^{-1}$  NaOH aqueous solution and stirred for 6 h to make the GF surface more hydrophilic. The obtained GF was then washed with deionized water and then dried at  $60^\circ\text{C}$  overnight. For the preparation of the N-CNT/GF hybrid, typically, 0.1 g of the metal phthalocyanine (M-Pc; M = Fe, Co, or Ni) was firstly dispersed in 4 mL of EtOH solution and stirred for 1 h at  $25^\circ\text{C}$ , to achieve a homogeneous solution. The homogeneously mixed M-Pc solution was then infiltrated into 0.1 g ( $9 \text{ cm}^2$ ) of GF and then dried at  $40^\circ\text{C}$  overnight. The GF which had adsorbed the M-Pc was then pyrolyzed in two steps at a constant  $\text{Ar}/\text{H}_2$  flow rate of 120/30 sccm, respectively; firstly at  $350^\circ\text{C}$  for 1 h, then at  $900^\circ\text{C}$  for 2 h. The first aging step at  $350^\circ\text{C}$  was necessary for efficient infiltration and polymerization of iron phthalocyanine in the pores of the GF before high-temperature calcination at  $900^\circ\text{C}$ . The resultant N-CNT/GF(X) materials were obtained by removing the residual metal species by etching with 1 M HCl aqueous solution followed by repeated washing with deionized water. The synthesized materials were labeled as N-CNT/GF(Fe), N-CNT/GF(Co), and N-CNT/GF(Ni) according to the M-Pc precursor for the N-doped CNT.

### Sample characterization

The morphology and microstructure of the obtained samples were investigated by scanning electron microscopy (SEM) using a Hitachi S-4700 microscope (Japan) operated at an acceleration voltage of 10 kV. High-resolution transmission electron microscopy (HRTEM) images were obtained using a JEOL FE-2010 microscope operated at 200 kV. The metal residues in the materials were examined by X-ray diffraction (XRD) analysis with a Rigaku Smart Lab X-ray diffractometer with  $\text{Cu-K}\alpha$  radiation operating at 40 kV and 30 mA. X-ray photoelectron spectroscopy (XPS) analyses were performed with a KRATOS AXIS NOVA XPS system with a monochromated  $\text{Al-K}\alpha$  (150 W) source. The nitrogen adsorption–desorption isotherms were measured at  $-196^\circ\text{C}$  using a Micromeritics ASAP 2020 accelerated surface area and porosimetry system. The specific surface area was determined using the Brunauer–Emmett–Teller (BET) method.

### Electrochemical measurements

To investigate the electrochemical properties of the GF electrodes, cyclic voltammetry (GAMRY Reference 600) was performed using a three-electrode cell; platinum wire and the modified GF samples were used as the counter and working electrodes, respectively, with a Ag/AgCl reference electrode. The CV test was performed over the voltage range from 0 to 1.6 V vs. Ag/AgCl and at scan rates ranging from  $5 \text{ mV s}^{-1}$ . The electrolyte contained 0.1 M  $\text{VOSO}_4$  in a 3.0 M  $\text{H}_2\text{SO}_4$  solution. Further, electrochemical impedance spectroscopy (EIS) was performed by applying an AC voltage of 5 mV amplitude over the frequency range from  $10^5$  to  $1^{-1}$  Hz at 0.75 mV. All electrochemical measurements were conducted using a Bio-Logic SP-300 potentiostat/galvanostat controller.

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