



Electrocatalytic effect of NiO nanoparticles evenly distributed on a graphite felt electrode for vanadium redox flow batteries

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ABSTRACT

Vanadium redox flow batteries (VRFBs) have attracted considerable attention for potential use in the development of large-scale energy storage systems. However, the commercialization of VRFBs is still challenging because of their various overpotentials, which are due to the poor reversibility and electrochemical activity of graphite felt (GF) electrodes. In this study, we fabricated a NiO-decorated GF electrode that exhibited a clear electrocatalytic effect on the V^{2+}/V^{3+} and VO^{2+}/VO_2^+ redox reactions. Vanadium ions preferentially attached to each NiO site because of strong electrostatic affinity to the local negatively charged O^{2-} species. In particular, a significant amount of NiO bound to graphite by replacement of hydrogen from the hydroxyl groups with nickel ion, leading to an increase in the ratio of carboxyl groups to hydroxyl groups. The increase in the number of carboxyl groups also improved the VRFB performance, since the carboxyl functional group on GF surface acts as effective catalyst for the vanadium redox reactions. Furthermore, NiO nanoparticles enhanced the mass-transfer property of vanadium ions by the increased area and hydrophilicity of the electrode surface. To optimize the electrode structure for high electrochemical performance, the crystallinity and morphology of the NiO catalyst on GF were controlled via the operating temperature and precursor concentration. When optimized NiO/GF₃₀₀ was applied to VRFBs, it exhibited high energy efficiency (74.5%) at a high current rate (125 mA cm^{-2}), compared with GF without the catalyst (55.4%). Moreover, NiO-decorated GF exhibited durability and stability in acidic electrolyte during long-term operation for 300 cycles.

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1. Introduction

With the sharp increase in the global demand for green energy, renewable energy sources such as solar and wind energy have become significantly attractive. However, these energy sources cannot provide an immediate supply of electricity to remedy the energy imbalance because of the weather-dependent intermittent power production. Hence, there is growing interest in energy storage technology for efficient management of supply and demand of electricity from renewables [1–4]. Vanadium redox flow battery

(VRFB) is one of the most promising energy storage systems suitable for industrial and utility-scale applications because of its long-term cycling, low maintenance cost, and scalability [5–8]. Furthermore, VRFBs are free of crossover contamination because they use the same vanadium redox species in the positive and negative electrolytes [9–11]. The most outstanding feature of this system is that it allows independent modification of the power and energy capacity via regulation of the stack size and electrolyte volume [12].

Despite several advantages of VRFBs, their high polarization resistance at the electrolyte/electrode interface limits their commercial viability [13,14]. Although graphite felt (GF) has been typically employed as an electrode material because of its cost-effectiveness, high conductivity, acid resistance, and good stability [8,15,16], it has been found to have poor electrochemical activity in vanadium redox reactions (V^{2+}/V^{3+} and VO^{2+}/VO_2^+) [13,17–25].

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Several studies have focused on the surface modification of GF to enhance the electrochemical kinetics. Oxygen functional groups on the electrode surface have been widely reported to behave as electrocatalytic sites; they facilitate the adsorption and desorption of vanadium species. The functionalization of oxygen functional groups has been conducted by various approaches such as thermal treatment [14,15,26], acid treatment [14,27–29], plasma treatment [14,15], and electrochemical oxidation [14,28,29]. The electrochemical performance of VRFBs can be improved via deposition of metallic electrocatalysts, such as Pt [17], Bi [13,18], Cu [30], Ir [31], and CuPt₃ [32] on the electrode surface. However, the high cost and inferior mechanical stability of these metals limit their commercial applications. Moreover, decoration with metals can accelerate hydrogen evolution before the V²⁺/V³⁺ redox reaction at the negative electrode, leading to charge imbalance and undesirable low efficiency [31,32].

As alternative electrocatalysts, low-cost metal oxides such as WO₃ [19,20,33], MoO₂ [21], CeO₂ [22], ZrO₂ [23], PbO₂ [24], Mn₃O₄ [25], and Nb₂O₅ [34] have been reported to exhibit catalytic activity in vanadium redox reactions (Table S1). Activated-carbon-supported orthorhombic tungsten trioxide decreases the charge-transfer resistances for V²⁺/V³⁺ and VO²⁺/VO₂⁺ redox reactions [33]. Kabtamu et al. synthesized niobium-doped hexagonal tungsten trioxide nanowires on GF by a hydrothermal method [19]. They suggested that doping WO₃ nanowires with Nb expands the crystal lattice of WO₃, leading to the formation of some defects such as oxygen vacancies. These defects then act as active sites in heterogeneous catalysis, which in turn improve the energy efficiency (EE) of the VRFB. Molybdenum dioxide interconnected with mesoporous carbon foam has also been applied as an electrocatalyst [21]. MoO₂ intercalated by VO²⁺ and VO₂⁺ cations has been reported to play a significant conductor role in the promotion of the ion- and electron-transfer rates. The redox reaction for VO²⁺/VO₂⁺ has been reported to easily occur on CeO₂- or ZrO₂-decorated GF electrodes [22,23]. The electrocatalytic activity was ascribed to the abundance of the hydroxyl groups on the metal oxide surface and hydroxyl groups on the graphite fiber surface [21–23,34]. Similarly, GF electrode loaded with PbO₂ has been reported to enhance electrochemical activity in redox reactions involving positive vanadium species [24]. Pulse deposition was done to introduce a uniform coating of a mixture of orthorhombic and tetragonal PbO₂ on GF. Although Mn₃O₄ lowers the activation barrier for both V²⁺/V³⁺ and VO²⁺/VO₂⁺ redox reactions, its electrocatalytic effect is more pronounced in the VO²⁺/VO₂⁺ reaction [25]. In addition, monoclinic Nb₂O₅ nanorods are an efficient electrocatalyst for both V²⁺/V³⁺ and VO²⁺/VO₂⁺ redox couples [34]. Doping of tungsten into the lattice of Nb₂O₅ nanorods prevents the agglomeration of Nb₂O₅, thereby enhancing its electrocatalytic activity.

Although extensive studies have been reported on the metal oxides, details of the electrocatalytic effect of nickel oxide (NiO) for VRFBs have not been reported thus far to the best of our knowledge. NiO is an important semiconducting oxide with a wide band gap (~3.6 eV) [35]. Its main applications include batteries [36], supercapacitors [37], electrochromics [38], sensors [39], and water splitting [40]. In particular, the nanostructuring and compositing of NiO with carbon materials have led to superior performance in applications involving charge transfer, thus addressing their low electronic conductivity [41].

In this study, we synthesized NiO nanoparticles (NPs) that were evenly distributed on a GF electrode. We report their performance as a novel electrocatalyst for both positive and negative electrodes of VRFBs. The crystallinity and morphology of the NiO NPs on GF were simply controlled by stepwise thermal decomposition reactions of a precursor. The surface chemistry and electrochemical property of the modified electrode were characterized by various

physical and electrochemical methods.

2. Experimental

2.1. Formation of NiO NPs used as a catalyst on GF

All chemicals were used as received without purification. Commercial GF (PAN-based GF; GF-20-3F, Nippon Carbon, thickness: 3 mm) was employed as electrode substrate, and cleaned in acetone by ultrasonication for 10 min. To remove residual acetone, the bare GF was subsequently dried at 60 °C for 1 h in vacuum oven. This electrode was used as a reference sample in this study. To form a catalyst on bare GF surface, the NiO NPs on GF were synthesized by stepwise thermal decomposition. First, nickel nitrate hexahydrate (97%, Ni(NO₃)₂·6H₂O, Junsei) was dissolved in acetone, and the mixture was ultrasonicated for 5 min. The GF was immersed in a nickel nitrate hexahydrate solution (5 wt%) for 2 h and then dried at 60 °C in a vacuum oven for 1.5 h. The precursor layer was then evenly coated on the GF surface. Next, thermal treatment was carried out to convert the precursor into NiO NPs on GF. The temperature was increased from room temperature to 300 °C for 40 min and then maintained for 30 min under argon (Ar) at 20 Torr. The resultant NiO NP-decorated GF was used as electrodes for the test.

2.2. Characterization

Field-emission scanning electron microscopy (FE-SEM; Hitachi S-4800) was done to examine the surface morphologies of the electrodes. To analyze the distribution of the elements on the electrode surface, energy-dispersive X-ray spectroscopy (EDS, Nova Nano SEM 450) was carried out. X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (D/MAX-2500, Rigaku). X-ray photoelectron spectroscopy (XPS; Sigma Probe, Thermo VG Scientific) was performed to examine the surface chemistry of the electrodes. Thermogravimetric analysis (TGA) was carried out using a thermogravimetric analyzer (SDT Q600, TA Instruments). A gas adsorption analyzer (Belsorp-max, Micro-tracBEL) was utilized to evaluate the Brunauer–Emmett–Teller (BET) surface area. The samples for XRD, XPS, and BET analyses were prepared by compression of GF under constant pressure.

2.3. Electrochemical measurements

To investigate the electrochemical properties of the felt electrodes, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were carried out using a potentiostat/galvanostat/EIS system (EC-lab, BioLogic) and a cell built in-house. The cell was a three-electrode system consisting of a working electrode (test samples with 5 mm diameter and 0.196 cm² area), counter electrode (thermally treated carbon felt, 3 cm² area), and a reference electrode (Ag/AgCl). To avoid kinetic limitations for the working electrode, the area of the counter electrode was 15.3 times greater than those of the working electrodes [42]. The positive electrolyte (0.1 M VOSO₄/3.0 M H₂SO₄) and negative electrolyte (0.1 M V₂(SO₄)₃/3.0 M H₂SO₄) were prepared from VOSO₄·3.08H₂O (99.9%, Wako) and H₂SO₄ (98%, Merck). Before the samples were evaluated for the measurements, the electrolytes were purged with nitrogen for 20 min. CV test was performed at scan rates in the range of 5–100 mV s⁻¹, and EIS measurements were carried out by the application of an AC voltage with an amplitude of 15 mV over the frequency range of 10⁻¹ to 10⁶ Hz.

To perform charge/discharge tests, single-flow cells consisting of copper current collectors, graphite-based bipolar plates, felt electrodes, polytetrafluoroethylene flow frames, and Nafion 117

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