



# Oxygen reduction reaction on nickel-based Prussian blue analog frameworks synthesized *via* electrochemical anodization route

Hoa Thi Bui<sup>a</sup>, Nabeen K. Shrestha<sup>b,\*</sup>, Keumnam Cho<sup>a</sup>, Chinna Bathula<sup>b</sup>, Henry Opoku<sup>b</sup>, Yong-Young Noh<sup>b,\*</sup>, Sung-Hwan Han<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Institute of Materials Design, Hanyang University, Seoul 04763, Republic of Korea

<sup>b</sup> Department of Energy and Materials Engineering, Dongguk University, Seoul 04620, Republic of Korea

## ARTICLE INFO

### Keywords:

Prussian blue analogue  
Nickel hexacyanoferrate  
Frameworks  
Morphology  
Electrocatalysis  
ORR

## ABSTRACT

The present work reports on the morphological influence of catalyst on oxygen reduction reaction (ORR). As a catalyst, Prussian blue analog structured nickel hexacyanoferrate (Ni-HCF) with two distinct morphologically controlled frameworks, *viz.* granular crystalline bulk film and rose-petal like structured thin film having smooth surface, are synthesized *via* controlled anodization route, and their morphological influence on the ORR is investigated. In addition, the influence of addition of carbon black, which is commonly used as catalytic dispersing support, is also studied on the catalytic mechanism for the ORR. Based on the hydrodynamic voltammetry of the electrocatalytic films on rotating disk electrode, the number of electrons involved in the reduction of an O<sub>2</sub> molecule, and the kinetic current density of the reaction are estimated. While the pristine Ni-HCF frameworks based catalyst, regardless of their morphology, demonstrates the direct reduction of O<sub>2</sub> with participation of 4 electrons, the frameworks when mixed with carbon black as support diverts the reduction *via* two steps with participation of 2 electrons at each step. A larger kinetic current density is, however, obtained in the case of granular crystalline bulk film of the Ni-HCF frameworks.

## 1. Introduction

In recent years, great attentions have been focused on the development of economically and environmentally sustainable energy sources that can address the future energy crisis and environmental issue due to green-house effect [1,2]. Among the various zero emission based energy conversation technologies, fuel cells are considered as one of the highly desirable high-capacity energy systems that could address the urgent requirement for zero emission fuel in electric vehicles [3–6]. However, sluggish cathodic kinetic on the O<sub>2</sub> reduction reaction (ORR) is the key hurdle for commercialization of the fuel cell technology. Practically, platinum demonstrates as a reliable ORR electrocatalyst, and carbon supported platinum nanoparticles are traditionally employed as cathode based material to reduce O<sub>2</sub> efficiently [7]. However, platinum, being one of the most precious rare metals, and the high loading of platinum that requires to overcome the sluggish kinetics of the ORR, unfavorably rises the cost of energy conversion. In addition, methanol crossover and carbon monoxide poisoning effects on the platinum catalysts block the active catalytic sites, thereby hindering the ORR [8]. These are the two common issues in

fuel cells that are forcing scientists to search for substitution of platinum with cost-effective precious metal-free based catalytic materials. In attempts to address these issues, various materials such as non-noble metal-based oxides, nitrides, chalcogenides [7], pristine and N-doped carbon-materials, catalyst based on Cu-metal [9], transition metal-nitrogen-carbon materials [10], and so on have been explored extensively.

Prussian blue and its analog compounds are metal-organic frameworks consisting of highly porous crystalline feature with high stability against air and water. These materials have demonstrated as promising candidates for electrocatalysis [11–15]. To the best of our knowledge, so far only the prototypical Prussian blue hexacyanometalate framework (*i.e.*, ferric hexacyanoferrate, Fe<sub>4</sub>[Fe(CN)<sub>6</sub>]<sub>3</sub>) has been investigated on ORR, particularly by compositing with second catalytic materials as catalytic dispersing matrix [16–21]. Moreover, the Prussian blue is usually synthesized by a general procedure of mixing the aqueous solution of Fe<sup>3+</sup> and [Fe(CN)<sub>6</sub>]<sup>4-</sup>. This procedure randomly produces large granular crystals of Prussian blue, which can lead to a poor contact intimacy with the carbon black support, thereby engendering poor electron transfer. Electrochemical anodization is a well-

\* Corresponding authors.

E-mail addresses: [nabeenkshrestha@hotmail.com](mailto:nabeenkshrestha@hotmail.com) (N.K. Shrestha), [yynoh@dongguk.edu](mailto:yynoh@dongguk.edu) (Y.-Y. Noh), [shhan@hanyang.ac.kr](mailto:shhan@hanyang.ac.kr) (S.-H. Han).

<https://doi.org/10.1016/j.jelechem.2018.09.033>

Received 19 July 2018; Received in revised form 15 September 2018; Accepted 16 September 2018

Available online 18 September 2018

1572-6657/ © 2018 Elsevier B.V. All rights reserved.

established technology to deposit porous metal oxide film on the anodized surface. However, this technology has been rarely extended to deposit metal-organic frameworks. Herein, two morphologically distinct granular bulk film, and uniform thin film forms of Ni-HCF frameworks are deposited in the present work *via* controlled electrochemical anodization of nickel substrate in  $[\text{Fe}(\text{CN})_6]^{3-}$  electrolyte. The electrocatalytic performance and the reaction mechanism on ORR of these anodically synthesized morphologically distinct Ni-HCF frameworks were studied. As alkaline media are less aggressive against corrosion of the catalysts, and the ORR kinetics are faster in alkaline media, great interests have been paid by researchers on alkaline based energy conversion technology such as metal-air battery [22–24], and alkaline based fuel cells [25–30]. Hence, we have studied the catalytic behaviors of the Ni-HCF frameworks on ORR, particularly in alkaline medium. Note that the goal of this work is, however, not to develop and present Prussian blue framework based excellent ORR catalyst, but to investigate the influence of the morphology of the Ni-HCF frameworks on their catalytic performance. On the other hand, carbon black is the common choice of dispersing matrix for the ORR electrocatalysts. Most of the previous studies dealing on the influence of the catalytic dispersing matrix on ORR are limited to the issue on durability of carbon supported Pt (Pt/C) catalysts [31–34]. The influence of the carbon support on mechanistic aspect of the ORR has, however, been hardly studied [35]. Hence, in addition to the morphological influence of the catalysts, it is scientifically highly significant to study the influence of the carbon black support on the catalytic performance to provide new insights particularly on ORR mechanism.

## 2. Experimental details

### 2.1. Chemicals and materials

All chemicals were of reagent grade and were used without further purification. Nickel sheet ( $\phi = 0.3$  mm thick, Nilaco, Japan) was cut into  $2 \times 2$  cm pieces and were cleaned sequentially in acetone, ethanol and deionized water for 10 min each in an ultrasonic bath followed by dried in a stream of argon. Deionized water was used throughout the experiment.

### 2.2. Deposition of Ni-HCF

Ni-HCF film was deposited *via* anodization of a nickel substrate. For the anodization, an electrochemical cell consisting of two-electrode system with a nickel substrate anode and a Pt plate cathode was employed. The clean nickel substrate was exposed to the electrolyte by pressing against a rubber O-ring ( $\phi = 10$  mm) in the cell using a copper back-contact electrode plate. The substrate was anodized at 2 V for 18 h against a Pt cathode in 0.1 M  $\text{K}_3[\text{Fe}(\text{CN})_6]$  electrolyte (99% purity, Sigma-Aldrich) prepared in 80 vol% of glycerol ( $\geq 99.5\%$ , Sigma-Aldrich). In this case, a thin smooth film was obtained on the anodized surface. On the other hand, to obtain the granular crystalline bulk film, anodization of the substrate was performed at 2 V for 5 h in an aqueous electrolyte containing 0.1 M  $\text{K}_3[\text{Fe}(\text{CN})_6]$ . In this case, a very rough and uneven deposit on the anodized surface was obtained. Meanwhile, some masses of the anodized product dislodged from the anode into the electrolyte were also obtained, turning the electrolyte turbid. After the anodization, the films were washed thoroughly in running water followed by immersing the film for 24 h in water, and changing the water frequently in every 4 h. Finally, the films were air-dried at room temperature. Note that the sample prepared in 100% aqueous based electrolyte cracked and crumbled into powder when became dry. The thin film and the loosely packed powdery mass of the Ni-HCF were collected simply by scraping the anodized surface carefully.

### 2.3. Characterization of anodic deposits

The surface topography of these materials are characterized using field emission electron microscopy (FE-SEM, HITACHI S-4800) and the chemical composition are studied using energy dispersive X-ray microanalyzer (EDX, EM912), and X-ray photoelectron spectroscopy (XPS, VG scientific ESCALAB MK II). The crystal structure of the materials is elucidated using X-ray diffractometry (XRD, Rigaku D/MAX 2600 V,  $\text{Cu K}\alpha = 0.15418$  nm), high resolution transmission electron microscopy (HRTEM, Omega EM), and selected area electron diffractometry (SAED). The distribution of constitutional elements in the materials was studied by elemental mapping using scanning transmission electron microscopy (STEM).

### 2.4. Electrochemical measurements

For the experiments, ink solution was prepared by mixing a composite catalyst (4 mg) and CB (16 mg) in an aliquot (4 mL) of the EtOH solution, which contains 0.45% v/v of Nafion® 117, with a vortex mixer and an ultrasonic homogenizer. The ink solution (3  $\mu\text{L}$ ) was dropped on a GC rotating disk electrode ( $S = 0.07065$  cm<sup>2</sup>), and dried at room temperature for 24 h. Electrocatalytic performance on ORR was studied using linear sweep voltammetry in O<sub>2</sub>-saturated 0.1 M KOH (measured pH = 13.4) electrolyte at room temperature. For the measurement, a three-electrode system with a Pt wire counter electrode and a Ag/AgCl (in 3 M NaCl) reference electrode was used, and the voltammograms were recorded using the Electrochemical Interface & Impedance Analyser (COMPACTSTAT, IVIUM Technologies) at various electrode rotating speeds of 200, 300, 400, 600, 800, 1000, 1200, 1400, and 1600 rpm. The intrinsic activity of the catalyst can be determined by the kinetic current density without mass transfer effect, which is derived from the Koutecky-Levich equation [36], given below.

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_l}, \quad c = \frac{1}{j_k} + \frac{1}{0.62nFAC_0^*D_0^{2/3}\nu^{-1/6}\omega^{1/2}}$$

Here,  $j$ ,  $j_k$ , and  $j_{l,c}$  are the measured, kinetic, and diffusion-limited current densities, respectively.  $j_{l,c}$  is determined by the number of electrons transferred ( $n$ ) per O<sub>2</sub> molecule, the Faraday constant ( $F = 96,485$  C mol<sup>-1</sup>), the geometrical area ( $A$ ) of the electrode, the concentration of the dissolved O<sub>2</sub> ( $C_0^* = 1.9 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup> in 0.1 M KOH), the diffusion coefficient of O<sub>2</sub> ( $D_0 = 1.2 \times 10^{-3}$  mol cm<sup>-3</sup> in 0.1 M KOH), the kinetic viscosity of the solution ( $\nu = (0.01$  cm<sup>2</sup> s<sup>-1</sup> in 0.1 M KOH)), and the rotational speed of the electrode ( $\omega$ ).  $j_k$  is generally extrapolated from the Koutecky-Levich plot ( $j^{-1}$  vs  $\omega^{-1/2}$ ) at various rotational speeds. Alternatively, it can also be derived by using the measured  $j_{l,c}$  at a single rotation speed, typically at 1600 rpm.

## 3. Results and discussion

Fig. 1a shows SEM view of the bulk film of the Ni-HCF crystal produced by anodization of nickel plate in 100% aqueous based  $[\text{Fe}(\text{CN})_6]^{4-}$  electrolyte. As a result of swift precipitation reaction between the Ni<sup>2+</sup> produced from oxidation of nickel plate and the  $[\text{Fe}(\text{CN})_6]^{4-}$  present in the electrolyte, the electrolyte became turbid and a loosely adhered precipitated mass on the anodized surface was obtained. The SEM topography of the precipitated Ni-HCF bulk film reveals that the product consists of small granular crystals. In contrast, when the anodization and precipitation reaction was decelerated significantly by adding viscous glycerol to the electrolyte, the precipitation reaction took a long time to deposit thin uniform film of Ni-HCF on the anodized surface. Fig. 1b shows SEM view of the Ni-HCF thin film deposited on the anodized surface when the nickel plate was anodized at 2 V vs Pt cathode for 18 h in aqueous  $[\text{Fe}(\text{CN})_6]^{4-}$  electrolyte containing 80 vol % glycerol. Owing to the slow growing rate of the Ni-HCF, film consisting of large rose-petal like structure with smooth surface (*i.e.* having

Download English Version:

<https://daneshyari.com/en/article/10225195>

Download Persian Version:

<https://daneshyari.com/article/10225195>

[Daneshyari.com](https://daneshyari.com)