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Prussian Blue-Carbon Hybrid as a Non-Precious Electrocatalyst for the Oxygen Reduction Reaction in Alkaline Medium

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ABSTRACT

We describe a simple approach for the Prussian blue nanocubes dispersed on carbon composite (PBC/C) as a non-precious catalyst for the electrochemical oxygen reduction reaction (ORR) in alkaline medium. The interaction between Prussian blue (PB) and the carbon support was confirmed by using FT-IR, and XPS spectroscopy. PBC/C catalyst exhibits 100 mV more positive onset potential than Prussian blue supported on carbon (PB/VXC-72) for ORR. Rotating disk electrode measurements showed that PBC/C had about 17 times higher oxygen reduction mass activity compared to the PB/VXC-72 physical mixture. PBC/C hybrid catalyst exhibited superior durability in aqueous alkaline medium compared with Pt/C and also provided low H_2O_2 production confirmed by rotating ring-disk electrode measurement. The PBC/C catalyst showed better activity and selectivity, which can be attributed to the synergistic coupling effects between the PB nanocubes and carbon support.

1. Introduction

The oxygen reduction reaction (ORR) is received great attention in the past decades owing to its importance in energy applications including fuel cells [1]. Platinum (Pt) particles dispersed on carbon (Pt/C) or Pt based alloy nanoparticles is usually used as major catalyst for proton exchange membrane fuel cell (PEMFCs) and so many other applications in electrochemical catalyst fields. However, Pt/C based catalysts during fuel cell operation have a serious problem such as carbon oxidation from Pt/C and agglomeration of Pt/C lead to performance loss of PEMFCs. Additionally, high cost of Pt-used and durability of Pt during fuel cell operation are the most technical limitations in the commercialization of fuel cell technology [2–4]. Hence, considerable efforts have been devoted to develop alternative catalysts based on non-precious materials to decrease the cost of fuel cell catalyst by adopting the innovative approaches. Recently, there has been considerable progress in the development of non-precious metal catalyst for oxygen reduction reaction. Especially in the last decade, transition metal-nitrogen doped on carbon in the form of M-N-C seems to be an alternative catalyst for the ORR [5–8]. Metal (Fe, Co), phthalocyanines and other M-N_4-macrocycles supported on various carbon materials have received much attention in last few decades as possible alternative ORR catalysts in alkaline medium [9]. The metal coordinated nitrogen-doped carbon based catalysts have been studied as a promising efficient non-precious metal electrocatalysts for oxygen reduction reaction [10]. A series of non-precious metal electrocatalysts were introduced by Dodelet and co-workers from pyrolyzing iron or cobalt precursors on carbon in the presence of a nitrogen precursor [11–13]. These studies have provided an attractive ways to prepare oxygen reduction electrocatalysts. Recently, Dai et al. prepared vertically aligned nitrogen-doped carbon nanotube arrays showed better activity than conventional Pt/C catalysts and additionally exhibited good ORR selectivity in an alkaline medium [14]. Peng et al. [15] fabricated the Fe-N doped on carbon with a graphene structure, which showed high ORR onset potential and the half wave potential is 60 mV lower than Pt/C catalyst. However, the ORR activities of non-precious metal catalysts are still on less competitive compared to Pt [16–21]. Therefore, it remains a challenge to develop an efficient, cost-effective ORR non-precious catalyst.

Conventional methods for preparing non-precious catalysts involve the pyrolysis of carbon-supported metal N_4-macrocycles. All these methods primarily involve an impregnation procedure and heat treatment at temperatures ranging from 600 to 900 °C in an inert atmosphere such as Ar or N_2, depending on the heat-treatment temperatures, the M-N_4 moiety can be partially or completely decomposed, forming new catalytic sites, which are no longer N_4-macrocycles. However, the used sources of nitrogen-containing precursors are poisonous and very expensive, and the preparation methods are also complicated. So, the development of

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simple, easy to handle, and efficient method to fabricate electroactive based catalyst is required.

Recently, Prussian blue or Ferric hexacyanoferrate ($Fe_4[Fe(CN)_6]_3$) has received considerable attention due to varied morphologies, unique properties and potential applications in molecular magnet devices [22,23], energy storage [24], electrochromic device [25], electrochemistry and H_2O_2 sensors [26,27]. Generally, the conventional synthesis of PB nanomaterials with controllable size and shape made by direct reaction of the $[M'(CN)_6]^{n-}$ anions with M^{m+} cations in a neutral aqueous solution to made the composition of $M_i^{m+}[M'(CN)_6]^{n-}$. The synthesis technique developed by Vaucher et al. prepared PB nanoparticles which had cube size about 39 nm by slow photoreduction of $[Fe(C_2O_4)_3]^{3-}$ to produce Fe^{2+} in the presence of $[Fe(CN)_6]^{3-}$ ions [28]. Wu et al. prepared PB nanocube by sonochemical reaction synthesis of $K_4Fe(CN)$ with hydrochloric acid result in Prussian blue nanocube which had a mean size about 250 nm [29]. The ORR activity and selectivity of transition metal hexacyanometalate precursors on carbon pyrolyzed at 800 °C have been studied in a neutral buffer solution [30]. Recently, ferric ferrocyanide was used as cathode catalyst for membraneless hydrogen peroxide fuel cell and a maximum power density of 1.55 mW cm^{-2} was observed [31]. However, to our knowledge, no report on the synthesis of PB using a single iron-source precursor by solid state pyrolysis has been published to date.

In the current study, Prussian blue nanocubes carbon composite which consists of Fe-N-C is introduced as an ORR electrocatalyst, prepared by a simple method. The synthesis was accomplished by a single-step route pyrolysis, using a readily available single iron precursor; followed by acid treatment resulted in the formation of Prussian blue cubes. The method is facile and easy to handle. The novelty of the current approach relies on the synthesis of PBC/C and we further demonstrate the use of this composite as an electrocatalyst for the ORR and we found that PBC/C hybrid catalyst exhibits good activity compared to a physical mixture and moreover PBC/C showed better durability than Pt/C catalyst.

2. Experimental

2.1. Materials

Iron (III) ethylenediaminetetraacetic acid sodium (Fe-EDTA), Hydrochloric acid, Ethanol was purchased from Sigma-Aldrich, and Pt/C (10 wt% Pt) was procured from Alfa Aesar (Johnson Matthey Ltd.). All other chemicals were used as received. De-ionized (DI) water (18.4 MΩ cm) used for the experiments was produced by a Millipore system.

2.2. Synthesis of Prussian blue nanocubes on carbon (PBC/C)

Solid-state pyrolysis was conducted using commercial Swagelok union cells. Five hundred milligrams of precursor (Fe-EDTA) was filled into the cell at room temperature under the atmospheric condition. The precursor filled cell was closed tightly with the other plug and then placed in the center of a tubular furnace. The temperature was raised at a heating rate of 10 °C min^{-1} up to 700 °C, and the temperature was maintained for 1, and 3 h. The pyrolysis temperature (700 °C) was fixed based on the thermogravimetric analysis of precursor; no further weight loss up to 900 °C was observed (Fig. S2). After pyrolysis of the precursor, the cell was cooled to room temperature. The entire process was conducted under autogenic conditions with no gas flow. The products prepared at 700 °C for 1, and 3 h were denoted as E-71, and E-73, respectively. One hundred milligrams of as-synthesized product was stirred in 5 mL of concentrated HCl for 24 h to dissolve oxide. The product was recovered by using centrifuging at 10,000 rpm for 10 min. The compound was washed with copious water and ethanol, formation of dark blue product was observed, and dried overnight in a vacuum oven at 60 °C. The products prepared at 700 °C for 1, and 3 h followed by acid treatment are denoted as EW-71, and PBC/C, respectively.

2.3. Synthesis of physical mixture of Prussian blue on carbon (PB/VXC-72)

Iron cyanide (Sigma-Aldrich, commercial grade) and Vulcan XC-72 (VXC-72) carbon was mixed by sonication for 30 min. The carbon dispersion consists of 100 mg of carbon in 10 mL of ethanol; the iron cyanide (100 mg) was dissolved in 10 mL of ethanol. The iron cyanide solution was added slowly into the carbon dispersion with magnetic stirring and heating at a temperature of 60 °C. Once the addition of iron cyanide solution was completed, the temperature was kept for 6 h with continuous stirring. After 6 h stirring, ethanol was removed by centrifuging at 10,000 rpm for 10 min, and dried at 60 °C under vacuum for overnight. Afterwards, the sample was obtained in the form of black powder, denoted as PB/VXC-72.

2.4. Physico-chemical characterizations

The morphology of the samples was observed using a field-emission scanning electron microscope (FE-SEM, Hitachi, S-4800II) with an accelerating voltage of 3 kV. Before the observations, the samples were coated with Osmium. The crystal structure of calcined samples was investigated by powder X-ray diffraction (XRD, Panalytical, and Empyrean) using Cu Kα radiation at a generator voltage of 40 kV and a tube current of 30 mA. Elemental analysis was performed by X-ray photoelectron spectroscope (XPS, Thermo Fisher Scientific, ESCALAB250 XPS system, Theta Probe XPS system) using monochromatic Al Kα source at 15 kV and 150 W. Binding energy values at x-axis were calibrated by using C1s from a carbon value taken as 284.6 eV. The UV-vis spectroscopy data were performed by use of a Cary 5000 UV-VIS-NIR at room temperature.

2.5. Electrochemical oxygen reduction

Electrochemical tests were carried out by using cyclic voltammetry (CV), rotating-disc-electrode (RDE) and rotating ring-disk electrode (RRDE) with 3-electrode system configuration using a potentiostat (Biologic, VSP). A 3-electrode cell consisting of the glassy carbon (0.07 cm^2), Pt wire and Ag/AgCl electrodes act as working electrode, counter and reference electrodes, respectively. The catalyst ink for electrochemical measurements was fabricated by dispersing 5 mg of the catalyst in 250 μL isopropyl alcohol and 2 μL of Nafion (5%) by ultrasonication for 30 min to form a homogenous dispersion ink. From this dispersion, the catalyst ink was dropped onto a glassy carbon electrode surface. Then the solvent was naturally evaporated at room temperature. The oxygen reduction activities were measured by hydrodynamic voltammetry in an O_2-saturated 0.1 M KOH at room temperature. For RDE and RRDE, 1 mg cm^{-2} and 1.2 mg cm^{-2} of the catalyst was loaded onto GC electrodes using 3 and 4 mm-diameter glassy carbon disks, respectively. The electrolyte solution was purged with nitrogen gas for 30 min before the electrochemical measurement. A flow of O_2 was maintained over the electrolyte during the measurement to ensure O_2 atmosphere inside the cell. The formation of $H_2O_2$and the electron transfer number were determined by follow equation;

$$H_2O_2(\%) = 200 \times \frac{I_R/N}{I_D(I_R/N)}$$