Autoxidation Core@Anti-Oxidation Shell Structure as a Catalyst Support for Oxygen Reduction Reaction in Proton Exchange Membrane Fuel Cell

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Proton exchange membrane fuel cells (PEMFCs) provide zero emission power sources for electric vehicles and portable electronic devices. Although significant progresses for the widespread application of electrochemical energy technology have been achieved, some drawbacks such as catalytic activity, durability, and high cost of catalysts still remain. Pt-based catalysts are regarded as the most efficient catalysts for sluggish kinetics of oxygen reduction reaction (ORR). However, their prohibitive cost limits the commercialization of PEMFCs. Therefore, we proposed a NiCo@Au core shell structure as Pt-free ORR electrocatalyst in PEMFCs. NiCo alloy was synthesized as core to introduce ionization tendency and autoxidation reaction. Au as a shell was synthesized to prevent oxidation of core NiCo and increase catalytic activity for ORR. Herein, we report the synthesis, characterization, electrochemical properties, and PEMFCs performance of the novel NiCo@Au core-shell as a catalyst for ORR in PEMFCs application. Based on results of this study, possible mechanism for catalytic of autoxidation core@anti-oxidation shell in PEMFCs is suggested.

Keywords: *Core shell structure, Autoxidation, Catalyst support, Oxygen reduction reaction, Proton exchange membrane fuel cell*

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) provide zero emission power sources for electric vehicles and portable electronic devices due to their high energy efficiency, power density and low clean utilization [1,2]. However, there are some challenges for the large scale application of PEMFCs such performance, durability, and cost of anode and cathode catalysts. One of them is the prohibitive cost of Pt-based catalyst for oxygen reduction reaction (ORR) at cathode which shows sluggish kinetics than hydrogen oxidation reaction at anode, therefore Pt loading at the cathode exceeds the anode loading [3]. To reduce the cost and improve the ORR activity, many ongoing research efforts have been devoted to search Pt-free catalyst such as transitional metal alloys, metal oxides, and heterogeneous carbon. Also, the degradation of cathode catalysts plays a critical role in decreasing the operation time of PEMFCs [4-6]. However, searching for more active ORR activity and less expensive catalysts with reliable durability than Pt still remains a significant challenge.

Recently, core-shell structures also have been reported as catalysts in PEMFCs. Core-shell structures usually consist of a thin layer of pure noble metal in the shell and a core alloy made of a combination of metal elements that are targeted to meet two main objectives: reducing the cost and enhancing the catalytic. Even though both objectives have been shown to be met, a huge challenge remains that is related to the long-term durability of the core shell structure. This is because the less noble metal which is only Pt and Au is prone to relatively easy dissolution in the harsh acid conditions [7,8]. Particularly, Au shows excellent durability, but it presents lower ORR activity than Pt and transitional metals [9]. On the other hands, the most of transition metals are easily able to react with oxygen molecule as it was named autoxidation [10]. Therefore, the most of developed transition metal catalyst

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is being activated in only alkali condition. The transitional metal as catalysts for cathode in PEMFCs have problem that oxidation reaction is proceed in advance of ORR process which include absorption and desorption of oxygen molecule, because autoxidation reaction of transition metals is stronger than oxidation reaction of hydrogen ion.

Thus, we proposed NiCo@Au core shell structure as Pt-free ORR electrocatalyst in PEMFCs. NiCo alloy was synthesized as core to introduce the ionization tendency and the autoxiation reaction, and Au as shell was synthesized to prevent oxidation of core NiCo as well as catalytic for ORR. Herein, we report the synthesis, characterization, electrochemical properties, and PEMFCs performance of novel NiCo@Au core-shell as catalyst for ORR in PEMFCs application. Based on these results, possible mechanism for catalytic of autoxidation core@anti-oxidation shell in PEMFCs is suggested.

2. Experimental Methods

NiCo alloy nanoparticles were synthesized as core material. Nickel chloride (NiCl$_2$·6H$_2$O, 98%, Kanto Chemical) and cobalt chloride (CoCl$_2$·6H$_2$O, 99%, Kanto Chemical) of each 1.15 g were solved in 5 °C chilled Di water of 400 mL. In addition, ammonium hydroxide (NH$_4$OH 28% aqueous solution, Alfa Aesar) of 10mL and potassium hydroxide (KOH, 86%, Kanto Chemical) of 0.5 g were added in the stock solution. And then, metallic salts were reduced by sodium borohydride (NaBH$_4$, 98%, Sigma Aldrich) of 2 g keeping 5 °C and string. Precipitated particles were filtrated using 100 nm membrane filter with 4 L Di water for cleaning. The NiCo alloy was synthesized and re-crystallized by heat treatment of 800 °C during 6 hr under argon purged furnace. Next step, the NiCo alloy nanoparticles of 0.5 g and gold chloride (HAuCl$_4$·6H$_2$O, 99%, Kanto Chemical) of 0.5 g were mixed using hand milling. Au layer was deposited on the NiCo alloy particles by heat treatment of 800 °C during 6 hr on argon purged furnace. Flow chart of the experimental procedure for synthesizing of NiCo@Au core-shell is shown in Fig. 1. The characteristics of synthesized samples were investigated using X-ray Diffraction (XRD, Rigaku Smart lab woth Cu Kα radiation), transmission electron microscopy and energy
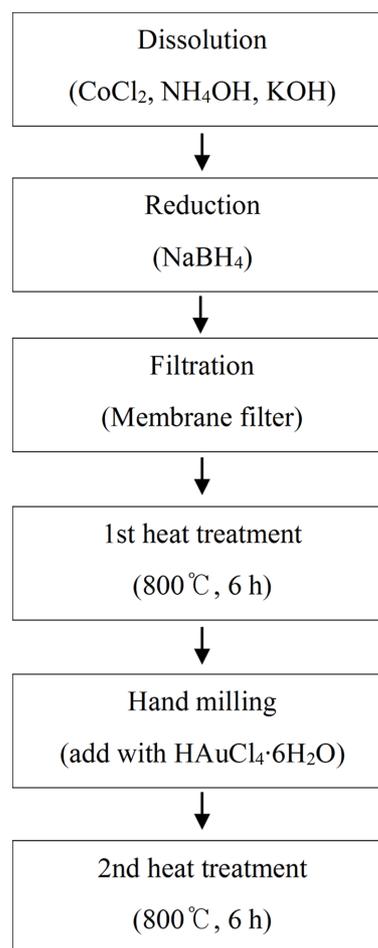
Fig. 1. Experimental procedure conducted to synthesize NiCo@Au core-shell

dispersive X-ray spectroscopy (TEM and EDS, JEOL JEM 2500SE).

The electrochemical measurements were carried out on an HZ-5000 electrochemical analyzer (Hokudo Denko Inc.). The three electrode system was consisted of each sample on a glassy carbon (GC) electrode as working electrode, an Ag/AgCl (saturated KCl, 0.198 V vs SHE) as reference electrode, and a counter electrode using platinum wire. Synthesized samples were prepared by dispersing nanoparticles on ketjen black carbon (K.B., Lion EC-600JD) according to the weight ratio of nanoparticles = 20:80 and the mixture were stirred overnight. The catalyst ink was prepared by adding 5 mg of finely ground catalyst to a 50 mL of Nifion® solution (DE 521, 5 wt% in a mixture of lower aliphatic alcohols and water) and 0.5 mL ethanol (C$_2$H$_5$OH, ≥ 99.5% Kanto Chemical). The ink was sonicated by at least 30 mins.

Then a volume of 5 μL form the suspension was loaded onto the glassy carbon (GC) electrode and dried at room temperature. Cyclic voltammetery (CV) was conducted at s scan rate of 50 mVs^{-1} in 1 M sulfuric acid solution (1 M H$_2$SO$_4$, ≥ 99.5% Kanto Chemical), and all measurements were observed at both argon and oxygen saturated conditions.

PEMFC performance was performed using a specific membrane electrode assembly (MEA) according to decal method. Decal ink was prepared to mix with 5 mg of catalyst (cathode: sample/carbon), 66 μL of Nafion® 5 wt% dispersion solution, and 234 μL of ethanol. The anode was a 20 wt% Pt on Vulkan XC-72 (20 wt% of Pt/C, Sigma-Aldrich). 180 μL of each suspension was dropped on the 3.16 cm^2 of Teflon® sheet, and dried at room temperature for 60 mins. Unit cell was assembled with 3.16 cm^2 of cathode sheet and 4.3 cm^2 of Nafion® sheet, and 3.16 cm^2 of anode sheet, which was pressed at 140 ℃, 12 MPa for 180 secs. Unit PEMFC was evaluated 450 SCCM of flow rate under 1.3 atm. All unit cell parts including gas pipe, cell and water tank were kept at 90 ℃.

3. Results

All samples were synthesized a facile method based on electrochemical reduction using reducing agent and heat treatment. The morphological and phase structure were confirmed by XRD and TEM and EDS mapping. The X-ray diffraction of NiCo alloy as core and NiCo@Au as core@shell were shown in Fig. 2a. Firstly, The NiCo alloy nanoparticles were synthesized using reducing agent at low temperature to prevent the increasing of particle size. The prepared NiCo as core materials indicate to peak at 2θ of 44.8°, 51.7°, and 76.12° corresponds to diffraction from (111), (200) and (220) planes, respectively of the fine NiCo alloy structure. The diffraction peak positions of NiCo@Au are the same as Au of standard, and diffraction peaks at 38.1°, 44.4°, 64.5°, 77.5°, and 81.7° have agreed with a metallic Au structure assigned to the shell structure. No diffraction peak of NiCo was detected in XRD pattern, suggesting that Au layer successfully covers the NiCo nanoparticles. Fig. 2b exhibit representative high resolution TEM images of NiCo@Au, indicating that the nanoparticles show spherical shape. From TEM images, the outlayer of the nanoparticles show different contrast,

(a)

(b)
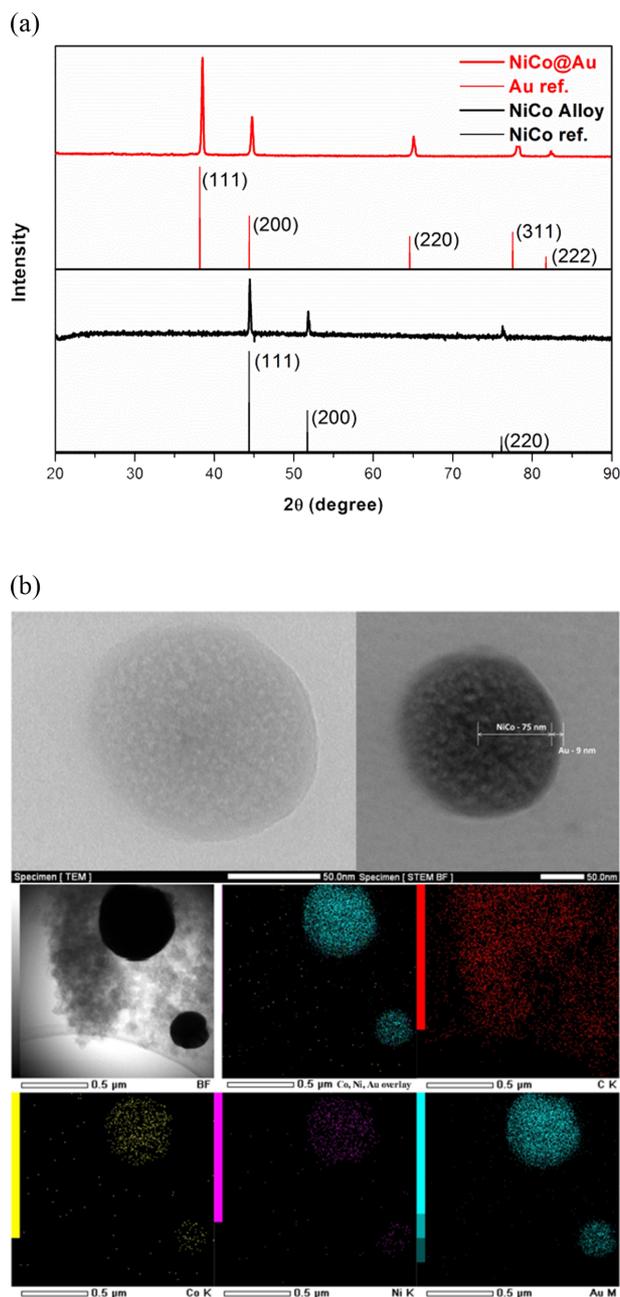
Fig. 2. (a) XRD pattern of NiCo and NiCo@Au synthesized powder, (b) TEM images and dark-field TEM images NiCo@Au, and the corresponding Co, Ni, and Au element mapping images

which is attributed to be a thin Au layer deposited on NiCo core to form the core-shell structure. The diameter of NiCo@Au revealed approximately 84 nm, each diameter of core and shell was about 75 nm and 9 nm, respectively. The average diameter is approximately 198 ± 88 nm. EDS mapping images of NiCo@Au correspond to the elemental composition as shown in Fig. 2b. The
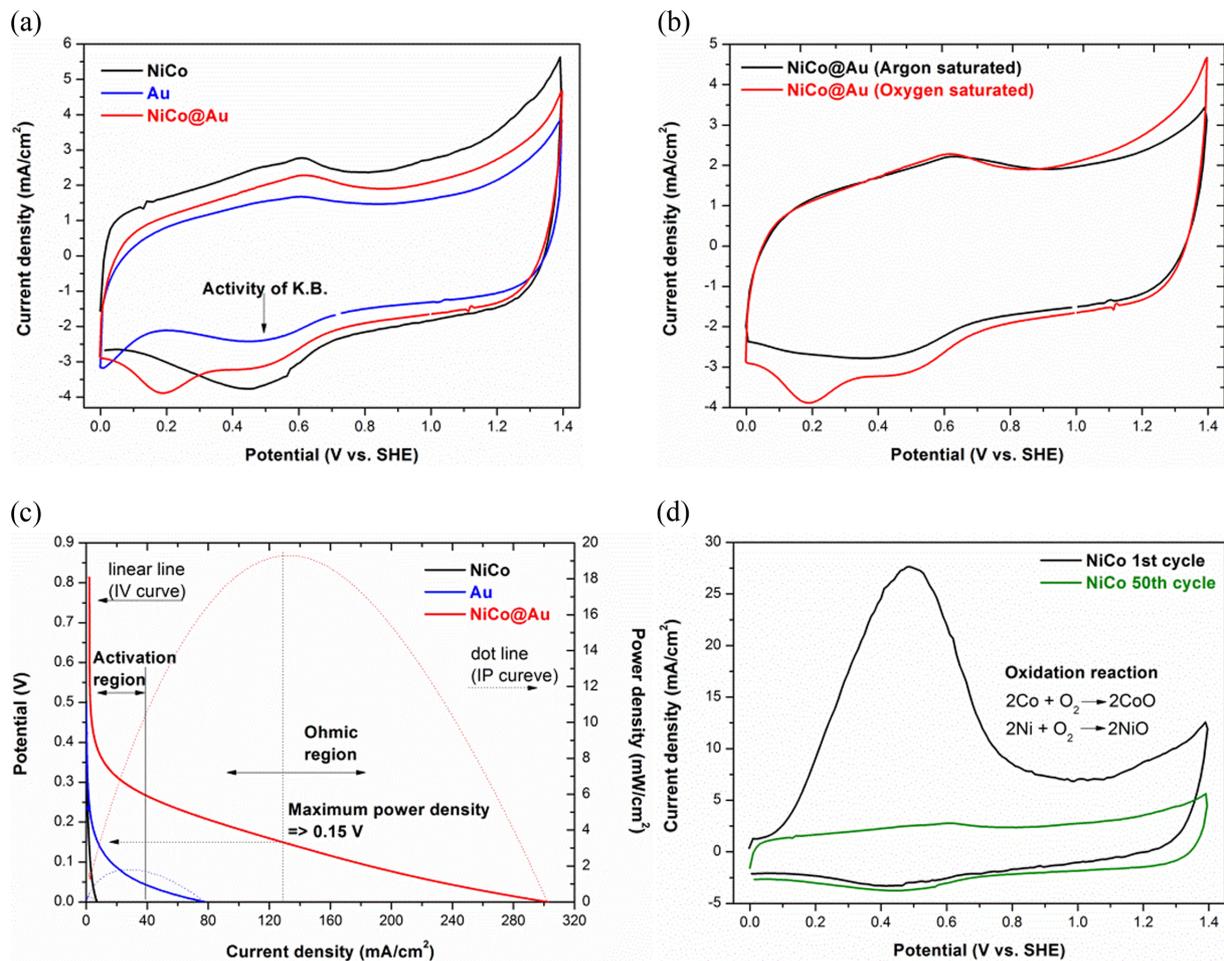
Fig. 3. CV curves ; (a) NiCo alloy, Au and NiCo@Au catalyst in O$_2$-saturated 0.5 M H$_2$SO$_4$ solution, (b) oxidation activity of NiCo alloy, (c) in order to confirm ORR of NiCo@Au and (d) IV curve of PEMFC using each cathodic catalyst

low intensity of Co and Ni and high intensity of Au suggestes that core@shell is covered with gold layer on the nickel and cobalt alloy.

To investigate the catalytic activates toward ORR of as-prepared NiCo alloy nanoparticle, Au nanoparticles, and NiCo@Au were evaluated by the CV as shown in Fig. 3a. All hysteric curves showed broad peak at around 0.45 V (vs. SHE) due to the carbon redox reaction from K.B support. However, NiCo@Au indicates a well-defined characteristics redox peak at around 0.2 V, suggesting oxygen reduction reaction. Also, Fig. 3b exhibits the CV curves of NiCo@Au. It was measured in the 1 M H$_2$SO$_4$ electrolyte under O$_2$ and Ar$_2$ saturated condition. No obvious reduction peak revealed under Ar$_2$-saturated condition. In contrast, the CV curve under O$_2$-saturated condition shows a prominent cathodic peak at 0.2 V, corresponding to the occurrence of ORR of the

electrode in O$_2$ electrolyte as shown in Fig 3a. From the CV results, it is confirmed that the voltage for maximum current of NiCo@Au can be generated 0.2 V (vs. SHE) from ORR process. Consequently, this is well related with maximum power density of the laboratory scale handmade PEMFCs system using NiCo@Au catalyst with 20 mW/cm^2 at 0.15 V (vs. SHE). The deviation of 0.05 V was expected to voltage drop caused by cell activation and ohmic resistance as shown in Fig. 3c.

4. Discussion

Structural analysis using XRD and TEM confirmed the core@shell structure; NiCo as core, Au as shell. Additionally, synthesized NiCo@Au shows catalytic activity in ORR and PEMFCs. When the single phase of each materials has no ORR activity but, core@shell

structure provides the electocatalytic performance. We could assume the reason that NiCo@Au has ORR activity as follows; Firstly, we focused on the 1st cycle of NiCo alloy as shown in Fig. 3d. The intensive oxidation reaction was occurred at 0.5 V, and no reduction reaction of NiCo after 50th cycle, suggesting that NiCo alloy was oxidized at 0.5 V in acid condition. The reduction and oxidation reaction should occur at the same voltage, but absence of reduction reaction means oxidation reaction is dominant in this condition. Generally, oxygen molecules are physically adsorbed on the surface due to the polarity of the material. Subsequently, the oxygen adsorbed on the surface is chemically bonded with material, resulting produce an oxide. Based on these two aspects, we choose the oxidative transitional metal for physical adsorbing of oxygen as core and deposit the Au as shell structure for anti-oxidation layer as well as for conductivity.

To describe the autoxiation core@anti-oxidation shell structure as catalyst for ORR, it is necessary to confirm adsorption of oxygen with core@shell structure which synthesized by suggested above assumption. The oxygen adsorption of NiCo alloy originated from oxidation should maintain the adsorption with oxygen continuously in the presence of Au outlayer. Also, Au as metallic bonded material has free electron, so it is assumed that Au has electron flexibility by delocalized electron of NiCo alloy. Consequently, the 1st step of reaction concept of synthetic mechanism as follows; autoxiation core@anti-oxidation shell catalyst should be inhibit the chemical reaction with oxygen and only provide physical adsorption with oxygen by encapsulating autoxidative NiCo with anti-oxidative Au.

The ORR in the PEMFCs includes the reaction with two hydrogen atoms and one oxygen atom, regarding that the activity of ORR might be increased by extending the oxygen molecules bond distance. XRD result indicates that the planes distance of 111 planes for NiCo alloy is calculated 0.204 nm, which is FCC structure. Oxides of nickel and cobalt are known two species as a monoxide or a trioxide, suggesting that oxygen molecules should be stretched in order to react with NiCo alloy for oxidation. In this regard, it can be assumed that the stretched oxygen molecules are physically absorbed by inhibiting oxidation on Au shell layer. Subsequently, hose stretched oxygen molecules might react with hydrogen feed from anode.
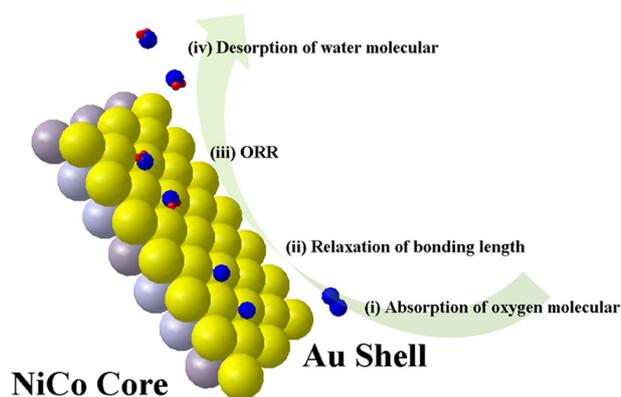
Fig. 4. Schematic of catalytic reaction at NiCo@Au electrocatalyst

5. Conclusions

Consequently, we proposed that the catalyst activity is facilitated by autoxidation core@anti-oxidation shell structure, as shown Fig. 4.

(i) Oxygen molecules were absorbed by autoxidation of core.

(ii) Bond distance of absorbed oxygen molecules was stretched by core materials without oxidation due to inert shell material.

(iii) The stretched oxygen molecules were reacted with hydrogen ion.

(iv) Water as production was detached from catalyst surface.

We expected to novel concept for electrocatalyst as autoxiation core@anti-oxidation shell structure, and may be a promising low cost catalyst in PEMFCs.

Acknowledgement

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