



ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

Synergistic improvement of oxygen reduction reaction on gold/cerium-phosphate catalysts

Joonhyeon Kang^{a,1}, Sujin Byun^{a,1}, Seunghoon Nam^a, Suji Kang^a,
Taeho Moon^{b,**}, Byungwoo Park^{a,*}

^aWCU Hybrid Materials Program, Department of Materials Science and Engineering,
Research Institute of Advanced Materials, Seoul National University, Seoul 151-744, Republic of Korea

^bDepartment of Materials Science and Engineering, Dankook University, Cheonan, Chungnam 330-714,
Republic of Korea

ARTICLE INFO

Article history:

Received 15 March 2014

Received in revised form

23 April 2014

Accepted 29 April 2014

Available online 10 June 2014

Keywords:

Fuel cell

Electrocatalyst

Oxygen reduction reaction

Nanocomposite

ABSTRACT

The main challenge in fuel cells lies in improving slow oxygen reduction reaction (ORR) kinetics causing low conversion efficiencies. Here, we introduce the Au/CePO₄-binary nanocomposites as effective oxygen reduction catalysts in alkaline media. The ORR activity comparable with Pt is achieved through the serial 4-electron reduction pathway. The bi-functionality of CePO₄ is suggested to explain the remarkably enhanced activity on the Au/CePO₄ nanocomposites. Significantly, the own catalytic activity of CePO₄ for hydrogen peroxide is demonstrated, validating synergistic effects with Au for complete ORR.

Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Fuel cells converting chemical energy to electrical energy have attracted a lot of interests as one of future-power-generation technologies for green economy. However, a low conversion efficiency caused by slow kinetics of oxygen reduction reaction (ORR) has been a major problem hindering practical application [1–6]. Among several types, alkaline fuel cells (AFCs) are a promising route for realizing the application of fuel cells, because of the advantages such as low anode-fuel

crossover, tolerance for CO poisoning, feasible activities for non-Pt metals (e.g., Au, Ag, etc.), and non-precious metal oxides (Fe-, Co-, Ni-based oxides) [7–14]. Though non-precious metal oxides generally cost much less than Pt, they have lower electronic conductivity, and the activity is relatively low. Furthermore, the understanding of the reaction mechanisms on the catalyst is still lacking.

Progress in the *d*-band model, which describes the relation between catalytic activity and electronic structure of transition metals, allows us to systematically design and predict a brand-new catalyst on the basis of transition metals [15–17].

* Corresponding author. Tel.: +82 2 880 8319; fax: +82 2 885 9671.

** Corresponding author. Tel.: +82 41 550 3534; fax: +82 41 559 7866.

E-mail addresses: taehom@dankook.ac.kr (T. Moon), byungwoo@snu.ac.kr (B. Park).

¹ Two authors contributed equally to this work.

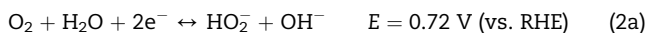
<http://dx.doi.org/10.1016/j.ijhydene.2014.04.211>

0360-3199/Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Of them, gold is known to be the most stable metal, which ensures long-term durability against dissolution.

The use of pure Au still brings up cost concerns, which is the major challenge for the application. The cost effectiveness can be adequately overcome by the introduction of Au-based composites taking advantage of the controlled electronic structure of Au. The ORR on Au surface does not occur via complete 4-electron reduction like on Pt, which encourages much effort to be made for Au to achieve comparable activity to that of Pt by alloying Au with other metals, or by combination with various metal oxides or metal phosphates [18–21].

In alkaline media, the ORR proceeds predominantly in three different pathways [22,23], as seen below, and the equilibrium potentials for each reaction at pH 13 are denoted in terms of a reversible hydrogen electrode (RHE), considering the dependence of the equilibrium potential on pH [24]:



The direct 4-electron reaction (Eq. (1)) reduces oxygen to water or hydroxyl ion as a reaction product. However, 2-electron (Eq. (2a)) or series 4-electron (Eq. (2a) → Eq. (2b)) reaction generates hydrogen peroxides as bi-products or intermediates. The pathways are sensitive to the type and crystallographic orientation of transition metals. In the case of Au, (100) planes exhibit the highest activity through the series 4-electron reduction pathway, whereas partial oxygen reduction to hydrogen peroxide (Eq. (2a)) occurs on (111) and (110) planes [25,26].

In the previous publications [20,21], we showed that the Au/AlPO₄ nanocomposite catalysts enabled 4-electron reduction in alkaline media with (111) and (110) Au orientations. The AlPO₄ in the binary nanocomposite played a role in enhancing the catalytic activity of Au by electronic interactions with Au, and did not participate in ORR. Therefore, ideas on finding other metal phosphate compound that may have its own catalytic activity remained a future work to achieve better ORR efficiency.

In this paper, the Au/CePO₄-binary nanocomposites are introduced as an effective oxygen reduction catalyst in alkaline media. The ORR activity comparable with Pt is demonstrated through the serial 4-electron reduction pathway. The bi-functionality of the CePO₄ in Au/CePO₄ is suggested to explain the remarkably enhanced activity. Significantly, the own catalytic activity of CePO₄ for HO₂⁻ intermediates is demonstrated, bringing synergistic effects with Au for more complete ORR.

Experimental procedure

The Au/CePO₄ nanocomposites were prepared by co-sputtering using Au and CePO₄ targets on ITO-coated glass

at room temperature. In order to control the Au/CePO₄ ratio, Au-sputtering power was fixed to 10 W, and CePO₄-sputtering power was changed between 20 W and 60 W. The as-deposited samples were annealed at 200 °C for better adhesion to the ITO electrodes. In order to distinguish the effect of metal phosphates, the Au/AlPO₄ nanocomposites were prepared in the same manner [20]. For the comparison of ORR activity, the pure Au, Pt, CePO₄, and AlPO₄ films were also prepared.

Electrochemical characterizations, cyclic voltammetry (CV) and chronoamperometry were performed by using a potentiostat (CHI 604A: CH Instrumental Inc.). Hg/HgO and Pt wires were used as reference and counter electrodes, respectively. Oxygen reduction was measured in an O₂-saturated 0.1 M NaOH solution under the oxygen flow of 30 sccm at a scan rate of 50 mV/s. H₂O₂-reduction measurements were carried out in a N₂-purged 0.1 M NaOH solution, by adding 1.2 mM hydrogen peroxide. The surface orientation of Au in the Au/CePO₄ nanocomposites was estimated by underpotential deposition (UPD) using 1 mM lead nitrate (Pb(NO₃)₂·3H₂O) dissolved in 0.1 M NaOH at a scan rate of 50 mV/s.

X-ray photoelectron spectroscopy (XPS, AXIS-HSI: KRATOS) was used to analyze the electronic states of the Au (with monochromatic Mg K α radiation), and the binding energy was calibrated by using the peak position of C 1s. The nanocomposite phase was identified by X-ray diffraction (XRD, D8 Advance: Bruker), and the grain size of Au was estimated using the Scherrer equation. The atomic ratios of Ce/Au in the Au/CePO₄ nanocomposites were confirmed to be 0.042, 0.053, and 0.086 with the CePO₄-sputtering powers of 20, 40, and 60 W, respectively, as measured by an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Optima-4300 DV: Perkin–Elmer).

Results and discussion

X-ray diffraction for the nanocomposites (Fig. 1) confirms polycrystalline Au phase with amorphous cerium phosphate.

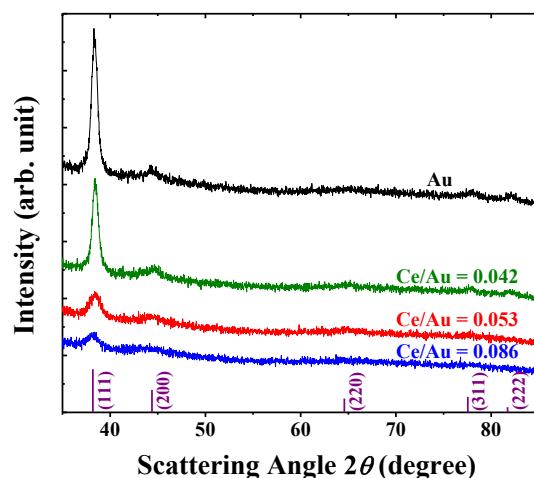


Fig. 1 – X-ray diffraction of the Au thin film and Au/CePO₄ nanocomposites. The ideal peak positions and intensities for Au (JCPDS 04-0784) are marked at the bottom.

Download English Version:

<https://daneshyari.com/en/article/1272234>

Download Persian Version:

<https://daneshyari.com/article/1272234>

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