

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

# Electrocatalytic oxidation of water observed on a nano-gold/palladium electrode

Yosuke Nakayama and Munetaka Oyama\*

Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

A new and unknown electrocatalytic oxidation of water was found to occur on a nano-gold attached palladium electrode. Since the oxidation potential was negative enough to that of a well-known normal oxidation of water to form O<sub>2</sub>, the direct use of water as a fuel, instead of alcohols, might be possible using the nano-gold/palladium electrode.

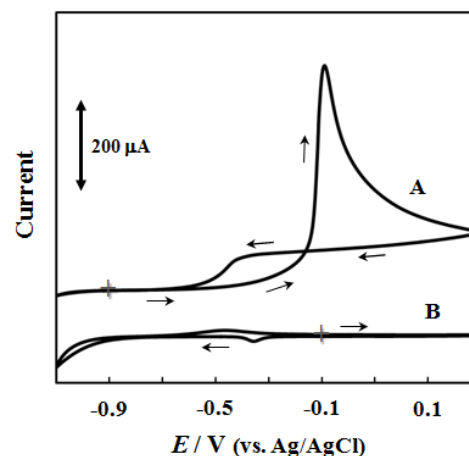
Direct alcohol fuel cells (DAFCs) have been attracting considerable interest in recent years as summarized in several reviews.<sup>1-6</sup> While direct methanol fuel cells (DMFCs) with platinum-related electrocatalysts have been extensively studied,<sup>1,2</sup> one of the recent concerns would be direct alkaline alcohol fuel cells (DAAFCs),<sup>3,4</sup> in particular, with palladium-based electrocatalysts.<sup>5</sup> In this case, ethanol can be used as an alternative fuel due to the less toxic and green characteristics, as direct ethanol fuel cells (DEFCs).

As for the fuels, while there is a tremendous number of reports using methanol, ethanol, ethylene glycol, etc., there is no report that water shows similar electrocatalytic oxidation reactions, to the best of our knowledge. This is quite natural because specific oxidation of water was not expected at the potential region where methanol or ethanol is oxidized in alkaline solutions, so that water has been used as the solvent in DAFCs. However, we have found that the electrocatalytic oxidation of water does occur with a gold-nanoparticle-attached palladium (nano-Au/Pd) electrode. Thus, in this communication, the phenomenon is shown for the first time.

The preparation of a nano-Au/Pd electrode is very simple. At first, an aqueous solution of gold nanoparticles (AuNPs), whose diameter was ca. 3.5 nm, was prepared according to the reported procedures.<sup>7</sup> Into the solution of 3.5-nm AuNPs, a commercially available Pd disk (diam. 1.6 mm) electrode (BAS Inc.) was immersed and suspended for 2 hours after polishing the surface. Since the small AuNPs can physi-sorb on surfaces just by immersion,<sup>8,9</sup> the AuNPs can be attached on the surface of the Pd disk electrode. After the modification, the surface of the nano-Au/Pd electrode was washed with water.

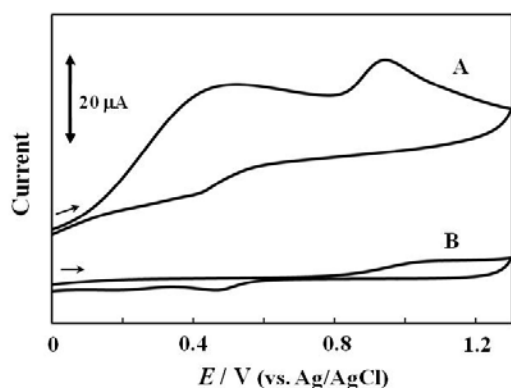
Cyclic voltammograms (CVs) were recorded in alkaline solutions with an unmodified Pd disk electrode and a AuNP-attached Pd disk (i.e., nanoAu/Pd) electrode without degassing. In an aqueous solution containing 1.0 M NaOH, interestingly the open circuit potential (OCP) was significantly different; it was ca. -0.10 V (vs. Ag/AgCl) with the Pd electrode and ca. -0.90 V with the nano-Au/Pd electrode. Hence, we recorded the CVs in Fig. 1

as the result of the positive going scans from the OCP to 0.2 V, followed by the negative going scan to -1.1 V and again to the OCP. As a remarkable characteristic of the results, a steep increase of the oxidation current was observed at -0.09 V (vs. Ag/AgCl) with the nano-Au/Pd electrode (Fig. 1A). The current increase was quite significant in comparison with the cyclic voltammogram recorded with the normal Pd electrode (Fig. 1B). This means the attached small AuNPs allowed a huge increase of the oxidation current in 1.0 M NaOH aqueous solution. While the electrochemical responses as in Fig. 1B have been reported with Pd bulk electrodes in alkaline media,<sup>10,11</sup> there is no report of the CV as in Fig. 1A, to the best of our knowledge.



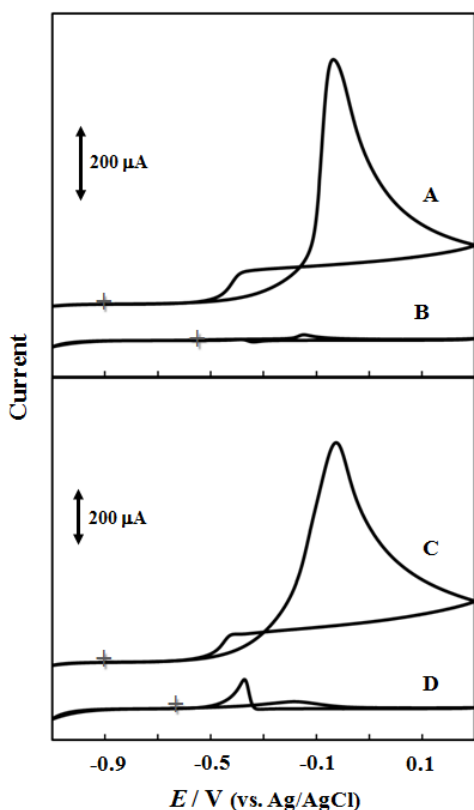
**Fig. 1** Cyclic voltammograms recorded in 1.0 M NaOH aqueous solution with (A) a nano-Au/Pd electrode and (B) a Pd electrode. Scan rate; 50 mVs<sup>-1</sup>. Each scan was started from the open circuit potential (+).

A similar unknown increase of the oxidation current was observed in acidic and neutral solutions. Fig. 2 shows the CVs recorded in 0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous solution. The significant current increase was observed overlapping with the oxidation of Pd and the reduction of Pd oxides, both of which appeared in Fig. 3A and B as a peak. In this case also, the onset potential of the increased current was negative enough to that of the oxidation of Pd. However, the response as shown in Fig. 1 was observed only in the alkaline solutions, and the current magnitude was smaller in the acidic H<sub>2</sub>SO<sub>4</sub> and the neutral KCl or phosphate buffer solutions.



**Fig. 2** Cyclic voltammograms recorded 0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous solution containing with (A) a nano-Au/Pd electrode or (B) a Pd electrode. Scan rate; 50 mV s<sup>-1</sup>.

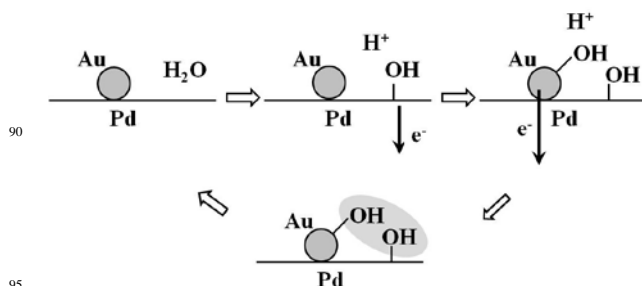
To make clear the source of oxidative response in Fig. 1A, we recorded CVs for (i) 1.0 M NaOH + 1.0 M methanol and (ii) 1.0 M NaOH + 1.0 M ethanol aqueous solutions with the Pd and nano-Au/Pd electrode (Fig. 3). As the result, while electrocatalytic responses were confirmed with the Pd electrode for both (i) and (ii), the results of the initial potential scan with the nano-Au/Pd electrode for (i) and (ii) were quite similar to the response in Fig. 1A having increased oxidation currents. Thus, the electrochemical response is expected to come from the solvent, i.e., water, not from the solutes.



**Fig. 3** Cyclic voltammograms recorded 1.0 M NaOH aqueous solution containing (A, B) 1.0 M methanol or (C, D) 1.0 M ethanol with (A, C) a nano-Au/Pd electrode or (B, D) a Pd electrode. Scan rate; 50 mV s<sup>-1</sup>. Each scan was started from the open circuit potential (+).

To know the exact mechanism for the electrochemical response with the increased oxidation current, more studies would be necessary. However, the key to bring about the oxidation current is the combination of AuNPs and bulk Pd, i.e., the nano-Au/Pd composite. We actually carried out the same modification of AuNPs on the surfaces of Au, Ag, Pt, Ni, Cu, Fe electrodes and indium tin oxides, but such a response as in Fig. 1A was never observed. Thus, it is inferred that the interfacial phenomena at the boundary areas between nano-Au and Pd bulk promote a new type of the oxidation of water. We confirmed that the response in Fig. 1 never obtained for the combination of nano-Pd and Au. So, some catalytic properties of small AuNPs<sup>12</sup> might be in relation with the present oxidation.

As for the electrocatalytic response of ethanol on Pd, it has been established that the rate determining step is the interaction between the absorbed species, OH<sub>ads</sub> and CH<sub>3</sub>CO<sub>ads</sub>.<sup>5,10</sup> The eliminative desorption of CH<sub>3</sub>COOH to bring about free Pd sites to allow the electrocatalytic oxidation of ethanol. With referring this mechanism and considering the present unique phenomena only observed on the surface of nano-Au/Pd for water, the elimination of the surface adsorbed species, OH<sub>ads</sub>, at the nano-Au/Pd boundary would be inferred to be a key to enhance the oxidation current of water. As shown in the scheme, the formation of OH<sub>ads</sub> would be possible both on Pd and Au in the present electrode. If the elimination of H<sub>2</sub>O<sub>2</sub> occurs on the nano-Au/Pd, the catalytic enhancement of the oxidation current should be expected by a simple mechanism.



**Scheme.** Plausible electrocatalytic oxidation of water on nano-Au/Pd electrode.

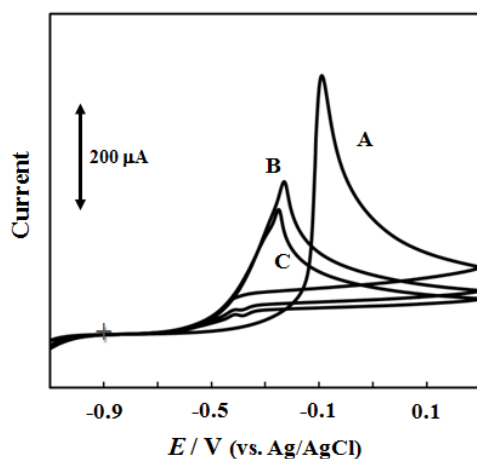
During this catalytic oxidation of water, we confirmed that no gas formation was occurred by eye inspection on a nano-Au/Pd plate electrode. Thus, H<sub>2</sub>O<sub>2</sub> and the related species might be the products of this electrocatalytic oxidation. However, as for the product analysis, further studies would be necessary, e.g., using a rotating ring disc electrode.

Although the exact products were not clear at this moment, here, we would like to emphasise that water could be oxidized using a specific combination of nano-Au and bulk Pd. In addition, judging from the potential range and the result of the eye inspection, the reaction is apparently different from a normal oxidation of water to form O<sub>2</sub>, that would be normally a positive end of the potential window. The peak-shaped oxidation in Fig. 1A would be inferred as a specific surface phenomenon involving water.

As a practical appealing point, the potential range of the new electrocatalytic oxidation of water was negative enough and comparable to those of the well-known electrocatalytic oxidation

of methanol and ethanol in aqueous solutions (see Fig. 3). This indicates a possibility that water can be used as a fuel in the anodic (fuel) reaction of direct fuel cells if we choose specific electrode materials. Of course, the cathodic (air) reaction is a reversible reaction of the normal oxidation of water to form O<sub>2</sub>, so that the normal oxidation of water cannot give energy differences. However, the present CV results have shown that the specific electrocatalytic oxidation occur at negative potentials and can lead to a new design of direct fuel cells with the electrocatalytic oxidation of water as the anodic reaction instead of alcohol fuels. In this “direct water fuel cells”, the huge merit is that water fuel can be used as is, though normally it need to be split into H<sub>2</sub> or the alternative alcohols or others need to be used as fuels.

The present results are preliminary ones. As a difficult point in the CV measurements at present, the values of the maximum oxidation current around -0.09 V were not constant, but varied in some experiments even when we prepared several Pd electrodes using the identical AuNPs' solution. This might be due to some variation of the attached amount of AuNPs. For this point, some further works would be necessary. Also, for more practical views, we confirmed the stability of AuNPs on Pd by the repeated CV and chronoamperometric measurements. As the result, the peak potential shifted to the negative potential as in Fig. 4, and the magnitude of the current was decreased in the second and the third scans. However, after the measurements of repeated CVs or chronoamperometry for several minutes at positive potentials, e.g., 0.3V, the electrochemical response was recovered to show the CV similar to that of the second scan. So, we believe neither significant removal nor passivation occur for AuNPs during the measurements. However, the results of the first scan were observed only in the initial uses after the modification, so that the further mechanistic studies would be necessary on this point.



**Fig. 3** Cyclic voltammograms recorded 1.0 M NaOH aqueous solution with a nano-Au/Pd electrode. The result of (A) first scan, (B) second scan, (C) third scan. Scan rate; 50 mVs<sup>-1</sup>.

The present result was obtained using the nano-Au/Pd electrode, so that further designs of the nano-Au/Pd electrodes should be necessary for constructing actual “direct water fuel cells”. If the bulk characteristics of Pd are essential for the

present electrocatalytic oxidation of water in combining with AuNPs, the cost and availability of Pd might be a problem over the merits of water as the fuel. However, the same electrocatalytic oxidation of water might be possible on other metal-nanocomposites, and, if so, it would be possible to obtain electricity from water and air without emitting CO<sub>2</sub>. So, we believe that the revealed presence of the new electrocatalytic reaction of water may lead to a new paradigm of direct fuel cells.

## Notes and references

Department of Material Chemistry, Graduate School of Engineering,  
Kyoto University, Nishikyo-ku, Kyoto 615-8520, Japan. Fax: +81 75 383 3074; Tel: +81 75 383 3074; E-mail: oyama.munetaka.4m@kyoto-u.ac.jp

- 1 C. Koenigsmann and, S. S. Wong., *Energy Environ. Sci.*, 2011, **4**, 1161.
- 2 X. Zhao, M. Yin, L. Ma, L. Liang, C. Liu, J. Liao, T. Lu and W. Xing, *Energy Environ. Sci.*, 2011, **4**, 2736.
- 3 E. H. Yu, U. Krewer and K. Scott, *Energies*, 2010, **3**, 1499.
- 4 E. Antolini and E. R. Gonzalez, *J. Power Sources*, 2010, **195**, 3431.
- 5 C. Bianchini and P. K. Shen, *Chem. Rev.*, 2009, **109**, 4183.
- 6 B. Braunschweig, D. Hibbitts, M. Neurock, A. Wieckowski, *Catal. Today*, 2013, **202**, 197.
- 7 N. R. Jana, L. Gearheart and C. J. Murphy, *J. Phys. Chem. B*, 2001, **105**, 4065.
- 8 M. Kambayashi, J. Zhang and M. Oyama, *Cryst. Growth Des.*, 2005, **5**, 81.
- 9 M. Oyama, S. Yamaguchi and J. Zhang, *Anal. Sci.*, 2009, **25**, 249.
- 10 Z. X. Liang, T. S. Zhao, J. B. Xu and L. D. Zhu, *Electrochim. Acta*, 2009, **54**, 2203.
- 11 X. W. Zhou, Y. L. Gan, Z. X. Dai and R. H. Zhang, *J. Electroanal. Chem.*, 2012, **685**, 97.
- 12 (a) M. Haruta, *Catal. Today*, 1997, **36**, 153; M. Haruta and M. Date, *Appl. Catal. A*, 2001, **222**, 427.

## Table of Contents Graphics

