Effects of Aging on Electrocatalytic Activities of Pt and Pd Nanoparticles

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ABSTRACT

Although the time dependences of the electrocatalytic activities of Pt and Pd nanoparticles during electrochemical operations have been widely studied, the time dependences under nonpolarized conditions have never been investigated in depth. This study reports the changes in the electrocatalytic activities of Pt and Pd nanoparticles with aging in air and in solution. Pt (or Pd) nanoparticle-modified electrodes are obtained by adsorbing citrate-stabilized Pt (or Pd) nanoparticles on amine-modified indium-tin oxide (ITO) electrodes, or by electrodeposition of Pt (or Pd) nanoparticles on ITO electrodes. The electrocatalytic activities of freshly prepared Pt and Pd nanoparticles in the oxygen reduction reaction slowly decrease with aging. The electrocatalytic activities decrease more slowly in solution than in air. An increase in surface contamination may cause electrocatalytic deactivation during aging. The electrocatalytic activities of long-aged Pt (or Pd) nanoparticles are significantly enhanced and recovered by NaBH_4 treatment.

Keywords : Pt nanoparticles, Pd nanoparticles, electrocatalytic activity, oxygen reduction reaction, aging

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1. Introduction

Pt and Pd nanomaterials are excellent catalysts in many electrochemical reactions [1,2], and such nanomaterials enable fast energy conversion (in fuel cells) [3-5] and high electrochemical signals (in sensors) [6-8] to be obtained. Much effort has been devoted to obtaining high electrocatalytic activities with minimal use of Pt and Pd nanomaterials on supporting materials [9,10]. Morphology or composition control and electrochemical or chemical treatment [11-17] have been used to further enhance the electrocatalytic activities. However, if the high electrocatalytic activities obtained just after synthesis and/or pretreatment

of the nanomaterials change with time, the initial activities are not the normal ones. Nanomaterial-based fuel cells and electrochemical sensors are generally stored for long periods in air or solution before use. It is therefore important to understand the changes in electrocatalytic activities with aging.

We have previously shown that the electrocatalytic activities of Au nanoparticles prepared via electrodeposition or chemical reduction of Au ions slowly decrease with aging, both in air and in solution [18]. We have also reported that the enhanced electrocatalytic activities of Au or Pt electrodes after chemical and electrochemical pretreatments slowly decrease with aging [19,20]. Although most recent studies have

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been performed using Pt and Pd nanomaterial-based electrodes rather than Pt and Pd electrodes, and the time dependences of the electrocatalytic activities of Pt and Pd nanoparticles during electrochemical operations have been widely studied, the changes in the electrocatalytic activities of Pt and Pd nanoparticles with aging under nonpolarized conditions have never been investigated in depth.

Here, we report the time dependences of the electrocatalytic activities of two metal nanoparticles (Pt and Pd nanoparticles) in the oxygen reduction reaction in air and in solution after their synthesis. The changes in the electrocatalytic activities of two types of nanoparticles (electrodeposited and chemically reduced ones) on indium-tin oxide (ITO) electrodes were evaluated, because two synthesis methods are commonly employed for the preparation of the nanoparticles and because low electrocatalytic ITO electrodes are suitable for the test of the activities of highly electrocatalytic metal nanoparticles. Probable reasons for the changes are discussed.

2. Experiment

All chemicals were obtained from Sigma-Aldrich Co. ITO electrodes were purchased from Corning (Daegu, Korea). Citrate-stabilized Pt nanoparticles were synthesized using a reported method [21]. Briefly, 5 % H_2PtCl_6 solution (1.3 mL) was added to distilled water (68 mL) and the mixture was stirred at 80°C. A fresh stock solution of 1% aqueous sodium citrate (20 mL) was slowly dropped into the solution, and the mixture was stirred for 10 min. Then, 0.1 M ascorbic acid solution (10.7 mL) was added and the final mixture was stirred for 20 min at 80 °C. ITO electrodes were modified with freshly prepared Pt nanoparticles as follows. The electrodes were immersed in an ethanolic solution containing 2 % (3-aminopropyl)triethoxysilane (APTES) (v/v) for 12 h to form an amine-terminated monolayer. The solution of Pt nanoparticles was dropped on and spread over the APTES-modified ITO electrodes for 1 h, and the electrodes were then washed with distilled water. Citrate-stabilized Pd nanoparticles were synthesized similarly to citrate-stabilized Pt nanoparticles, using a K_2PdCl_4 precursor. Pt nanoparticles were electrodeposited on ITO electrodes by performing two cyclic scans (from 0.1 to -1.15 V, at a scan rate of 50 mV/s) in a deaerated solution containing 1 M H_2SO_4 and 1 mM

H_2PtCl_6 . Pd nanoparticles were electrodeposited on ITO electrodes by performing 10 cyclic scans (from 0.9 to -0.1 V, at a scan rate of 50 mV/s) in a deaerated solution containing 1 mM K_2PdCl_4 . A precursor solution aged for more than 1 h with Ar purging was used to obtain electrodeposited Pd nanoparticle-modified ITO electrodes. A moderately aged precursor solution gives better electrocatalytic activities of Pd nanoparticles than a fresh precursor solution. NaBH_4 treatment was performed by dipping the electrodes for 15 min in a tris buffer solution (100 mM, pH 9.3) containing 10 mM NaBH_4 .

Electrochemical measurements were performed using a CHI 617B electrochemical workstation (CH Instruments, Austin, TX, USA). The electrochemical cell consisted of a working electrode, a Pt-wire counter electrode, and an Ag/AgCl (3 M NaCl) reference electrode. The geometric areas of the Pt and Pd nanoparticle-modified ITO electrodes exposed to the solution were ca. 0.28 cm². Every experiment was performed using newly prepared electrodes, i.e., if an electrode was used for an electrochemical measurement, it was not used for another measurement. All electrochemical data were obtained at room temperature (25 °C).

3. Results and Discussion

We investigated the time dependences of the electrocatalytic activities of two types of freshly prepared Pt or Pd nanoparticle-modified ITO electrode in the oxygen reduction reaction. To obtain Pt nanoparticle-modified electrodes, citrate-stabilized Pt nanoparticles were adsorbed on amine-modified ITO electrodes, or Pt nanoparticles were electrodeposited on ITO electrodes. Fig. 1a shows a transmission electron microscopy (TEM) image of the as-synthesized Pt nanoparticles. Fig. 1b shows cyclic voltammograms of citrate-stabilized Pt nanoparticle-modified ITO electrodes. The cathodic peak potential shifted to a negative potential with aging in ambient air. This indicates that the electrocatalytic activity (in the oxygen reduction reaction) achieved with freshly prepared Pt nanoparticles was higher than those achieved with aged ones and that the higher activities decreased with aging in air. Fig. 1c shows a scanning electron microscopy (SEM) image of a Pt nanoparticle-electrodeposited ITO electrode. Fig. 1d shows that the electrocatalytic activity just after electrodeposition was higher than

Fig. 1. (a) TEM image of citrate-stabilized Pt nanoparticles; (b) cyclic voltammograms obtained (at a scan rate of 100 mV/s) using APTES-modified ITO electrodes on which citrate-stabilized Pt nanoparticles were adsorbed, in O_2 -saturated solution containing 0.1 M $HClO_4$, for different periods of nanoparticle aging in air after synthesis; (c) SEM image of Pt nanoparticle-electrodeposited ITO electrode; and (d) cyclic voltammograms obtained (at a scan rate of 100 mV/s) using Pt nanoparticle-electrodeposited ITO electrodes in O_2 -saturated solution containing 0.1 M $HClO_4$, for different periods of nanoparticle aging in air after synthesis.

Fig. 2. Cyclic voltammograms obtained (at a scan rate of 100 mV/s) in O_2 -saturated solution containing 0.1 M $HClO_4$ (a) using APTES-modified ITO electrodes on which citrate-stabilized Pt nanoparticles were adsorbed just after synthesis and after 7 days aging in solution and (b) using Pt nanoparticle-electrodeposited ITO electrodes just after electrodeposition and after $NaBH_4$ treatment of the electrode aged for 7 days in air.

those after aging, and the higher activities decreased with aging. When Pt nanoparticles were stored in solution after synthesis, the decrease in the electrocatalytic activity (Fig. 2a) was much slower than the decrease

for those stored in air (Fig. 1b).

It has been reported that the contribution of the two-electron reduction pathway for O_2 conversion to H_2O_2 compared with that of the four-electron reduc-

Fig. 3. (a) TEM image of citrate-stabilized Pd nanoparticles; (b) cyclic voltammograms obtained (at a scan rate of 100 mV/s) using APTES-modified ITO electrodes on which citrate-stabilized Pd nanoparticles were adsorbed, in O_2 -saturated solution containing 0.1 M $HClO_4$, for different periods of nanoparticle aging in air after synthesis; (c) SEM image of Pd nanoparticle-electrodeposited ITO electrode; and (d) cyclic voltammograms obtained (at a scan rate of 100 mV/s) using Pd nanoparticle-electrodeposited ITO electrodes in O_2 -saturated solution containing 0.1 M $HClO_4$, for different periods of nanoparticle aging in air after synthesis.

tion pathway increases with increasing surface contamination of Pt electrodes with organic impurities, even if the change in surface contamination is not large, and that the electrochemical active surface area decreases with increasing surface contamination [22]. These two effects of surface contamination decrease the electrocatalytic activities of Pt electrodes. The decrease in the electrocatalytic activity of Pt nanoparticles during aging in air also seems to be caused by increased surface contamination. Deactivation by contamination in solution is much slower than that in air. In our previous study, it was shown that $NaBH_4$ treatment reproducibly enhances the electrocatalytic activities of Pt electrodes [20]. Fig. 2b shows that the voltammogram obtained just after preparation of a Pt nanoparticle-electrodeposited ITO electrode was similar to that obtained just after $NaBH_4$ treatment of an electrode aged for 7 days in air. This clearly indicates that the electrocatalytic activities of long-aged Pt nanoparticles were signifi-

cantly enhanced and recovered by $NaBH_4$ treatment.

We also investigated the effect of aging on Pd nanoparticle-modified ITO electrodes. Citrate-stabilized Pd nanoparticles were adsorbed on amine-modified ITO electrodes, or Pd nanoparticles were electrodeposited on ITO electrodes. Fig. 3a shows a TEM image of as-synthesized Pd nanoparticles. The electrocatalytic activity of a citrate-stabilized Pd nanoparticle-modified ITO electrode just after synthesis was much higher than those after aging the nanoparticles in air (Fig. 3b). The negative shift of the cathodic peak potential increased with increasing aging in air. Fig. 3c shows a SEM image of a Pd nanoparticle-electrodeposited ITO electrode. A negative shift with aging was also observed for the Pd nanoparticle-electrodeposited ITO electrode (Fig. 3d). The electrocatalytic activity just after electrodeposition was much higher than those after aging. We also measured the effect of aging on citrate-stabilized Pd nanoparticles in solution. Similar to the case

Fig. 4. Cyclic voltammograms obtained (at a scan rate of 100 mV/s) in O_2 -saturated solution containing 0.1 M $HClO_4$ (a) using APTES-modified ITO electrodes on which citrate-stabilized Pd nanoparticles were adsorbed just after synthesis and after 7 days aging in solution and (b) using Pd nanoparticle-electrodeposited ITO electrodes just after electrodeposition and after $NaBH_4$ treatment of the electrode aged for 7 days in air.

for Pt nanoparticles, the decrease in the electrocatalytic activity of Pd nanoparticles in solution (Fig. 4a) was much slower than that in air (Fig. 3b). Although the electrocatalytic activities of Pd nanoparticles decrease with aging, $NaBH_4$ treatment can enhance the decreased activities. The voltammogram obtained just after preparation of the Pd nanoparticle-electrodeposited ITO electrode was similar to that obtained just after $NaBH_4$ treatment of the electrode aged for 7 days in air (Fig. 4b).

It seems that freshly synthesized Pt and Pd nanoparticles, formed chemically or electrochemically, are less contaminated and more electrocatalytically active than aged ones. The surfaces of Pt and Pd nanoparticles are slowly contaminated with carbon-based materials and organic materials with aging. When the nanoparticles are stored in solution, the rate of contamination is slower than that in air, which leads to a slower decrease in the electrocatalytic activity in solution. These findings are important in investigating the electrocatalytic activities of nanoparticles. Essentially, the aging effect should be considered when the electrocatalytic activities of nanoparticles are compared with those of other nanomaterials.

4. Conclusions

The electrocatalytic activities of freshly prepared Pt and Pd nanoparticles cannot be maintained for a long period under nonpolarized conditions (in air and in solution). The electrocatalytic activities of freshly prepared Pt and Pd nanoparticles in the oxygen reduction reaction slowly decrease with aging. The

decreases in the electrocatalytic activities in solution are much slower than those in air. Increased surface contamination might cause deactivation of electrocatalytic activities during aging. $NaBH_4$ treatment can significantly enhance the electrocatalytic activities of long-aged Pt and Pd nanoparticles. The results of this study imply that, when the electrocatalytic activities of Pt and Pd nanoparticles are compared with those of other nanomaterials, the aging effect should be considered.

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References

- [1] F. Godínez-Salomón, E. Arce-Estrada and M. Hallen-López, *Int. J. Electrochem. Sci.*, **7**, 2566 (2012).
- [2] A. Datta, S. Kapri and S. Bhattacharyya, *Green Chem.*, **17**, 1572 (2015).
- [3] M. K. Debe, *Nature*, **43**, 486 (2012).
- [4] A. Sáez, J. Solla-Gullón, E. Expósito, A. Aldaz and V. Montiel, *Int. J. Electrochem. Sci.*, **8**, 7030 (2013).
- [5] H. J. Park and S. H. Hur *J. Korean Electrochem. Soc.*, **17**, 201 (2014).
- [6] E. Spain, H. McArdle, T. E. Keyes and R.-J. Forster, *Analyst*, **138**, 4340 (2013).
- [7] S. H. Lim, J. Wei, J. Lin, Q. Li and J. K. You, *Biosens. Bioelectron.*, **20**, 2341 (2005).
- [8] M. Rashid, T.-S. Jun and Y. S. Kim, *J. Korean Electrochem. Soc.*, **17**, 18 (2014).
- [9] V. T. T. Ho, C.-J. Pan, J. Rick, W.-N. Su and B.-J.

- Hwang, *J. Am. Chem. Soc.*, **133**, 11716 (2011).
- [10] S. Y. Ang and D. A. Walsh, *Appl. Catal., B*, **98**, 49 (2010).
- [11] V.-D. Dao and H.-S. Choi, *Electrochim. Acta*, **93**, 287 (2013).
- [12] R. C. Cerritos, M. Guerra-Balcázar, R. F. Ramírez, J. Ledesma-García and L. G. Arriaga, *Materials*, **5**, 1686 (2012).
- [13] B. N. Wanjala, B. Fang, J. Luo, Y. Chen, J. Yin, M. H. Engelhard, R. Loukrakpam and C.-J. Zhong, *J. Am. Chem. Soc.*, **133**, 12714 (2011).
- [14] J. Bao, M. Dou, H. Liu, F. Wang, J. Liu, Z. Li and J. Ji, *ACS Appl. Mater. Interfaces*, **7**, 15223 (2015).
- [15] S. Garbarino, A. Pereira, C. Hamel, E'. Irissou, M. Chaker and D. Guay, *J. Phys. Chem. C*, **114**, 2980 (2010).
- [16] G. He, Y. Song, X. Kang and S. Chen, *Electrochim. Acta*, **94**, 98 (2013).
- [17] J. Das, H. Kim, K. Jo, K. H. Park, S. Jon, K. Lee and H. Yang, *Chem. Commun.*, 6394 (2009).
- [18] H. J. Kang, S. Patra, J. Das, A. Aziz, J. Jo and H. Yang, *Electrochem. Commun.*, **12**, 1245 (2010).
- [19] G. Dutta, K. Jo, H. Lee, B. Kim, H. Y. Woo and H. Yang, *J. Electroanal. Chem.*, **675**, 41 (2012).
- [20] G. Dutta, A.-M. Jiaul and H. Yang, *Electrochim. Acta*, **141**, 319 (2014).
- [21] M. Huang, Y. Shao, X. Sun, H. Chen, B. Liu, and S. Dong, *Langmuir*, **21**, 323 (2005).
- [22] M. S. El-Deab, F. Kitamura and T. Ohsaka, *J. Electrochem. Soc.*, **160**, F651 (2013).