862 Bull. Chem. Soc. Jpn. Vol. 84, No. 8, 862–866 (2011)

Controllable Deposition of Alloy Clusters or Nanoparticles Catalysts on Carbon Surfaces

Yuji Ando,*[1] Kotaro Sasaki,[2] Dong Su,[2] and Radoslav Adzic*[2]

[1]Energy Technology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST),
16-1 Onogawa, Tsukuba 305-8569

[2]Brookhaven National Laboratory, Upton, NY 11973, USA

Received January 11, 2011; E-mail: ando-yuji@aist.go.jp, adzic@bnl.gov

We describe a simple method for controllably depositing Pt–Ru alloy nanoparticles on carbon surfaces that is mediated by Pb or Cu adlayers undergoing underpotential deposition and stripping during Pt and Ru codeposition at diffusion-limiting currents. The amount of surface Pt atoms deposited largely reflects the number of potential cycles causing the deposition and stripping of the metal adlayer at underpotentials, the metal species used as a mediator, and the scan rate of the potential cycles. We employed electrochemical methanol oxidation to gain information on the catalyst's activities. The catalysts with large amounts of surface Pt atoms have relatively high methanol-oxidation activity. Catalysts prepared using this method enhance methanol-oxidation activity per electrode surface area, while maintaining catalytic activity per surface Pt atom; thus, the amount of Pt is reduced in comparison with conventional methanol-oxidation catalysts. The method is suitable for efficient synthesizing various bimetallic catalysts.

Considerable attention has been paid to assuring the controllable deposition of Pt-based alloy clusters on various carbon materials for fuel-cell applications.[1] Thus, certain metal atoms were shown to act as surfactants, promoting layer-by-layer deposition.[2–5] For example, the two-dimensional electrodeposition of silver on gold (111) was demonstrated when lead or copper was present as the mediator.[6] In electrodepositing Au, the large catalytic- and morphological-effects of Sb adsorbates proved invaluable.[7] One important, but difficult to achieve, feature of such deposition processes lies in depositing thin layers on the support materials in a well-controlled manner.

This goal can be met via underpotential deposition (UPD) that involves depositing certain metals on other metal surfaces at a higher potential than the bulk deposition potential. This phenomenon rests upon the greater strength of admetal–substrate bonding than that of admetal–admetal bonding. Several researchers have investigated monolayer- or bilayer-modification of metal surfaces by UPD;[8] for example, Ag on the Pt(111),[9] Ag on Au(111),[10–12] Pt on Co–Pd,[13] Pb on Cu(111),[14] and Ru and Bi on Pt nanoparticles.[15] Brankovic et al.[16] reported the deposition, via UPD, of a submonolayer of Pt, a monolayer of Pd, and a bilayer of Ag on Au(111) surfaces mediated by a Cu adlayer. Further, layer-by-layer overpotential deposition of Ag monolayer and bilayer on Au(111) mediated by Pb UPD/stripping cycles was demonstrated,[17] indicating that the 2-dimensional growth of Ag is enhanced through the coadsorption of Pb that blocks the formation of large Ag islands.

In this paper, we demonstrate a methodology for depositing a controllable thin layer on carbon of one very important catalytic material, viz., the Pt–Ru alloy, mediated by the UPD processes of Pb, Cu, Bi, or Tl on Pt. This approach enhances the utilization of Pt and Ru, and the electrochemical methanol-oxidation activity of this catalyst.

Experimental

Carbon black (Vulcan, XC-72) was oxidized chemically using ammonium persulfate to generate a large coverage of functional groups on the surface of carbon. We detailed the preparation procedure elsewhere.[18] We placed 5 µg of oxidized carbon, suspended in pure water, on the 0.196 cm^2 surface area of a glassy carbon electrode and dried it slowly.

The electrode was immersed in a solution of 0.01 mM K_2PtCl_4, 0.05 mM $RuCl_3$, and 5 mM Metal salt (Metal salt = $PbCl_2$, $CuSO_4 \cdot 5H_2O$, $Bi(NO_3)_3 \cdot 5H_2O$, or Tl_2CO_3), and its potential was cycled by applying a linear potential sweep between −0.5 to 1.0 V vs. Ag/AgCl(3 M Cl^-) reference electrode for 10 to 500 cycles without rotation. Under this potential regime, Pt and Ru deposition on the carbon surface is under diffusion control because of their low concentration; the concentration of the nonnoble metal cation is more than 100 times larger than that of both together. Thus, with first having deposited Pt or Ru atoms on carbon substrate, underpotential deposition on them will take place, followed by the UPD adlayer stripping. This will slow down the nucleation of Pt and Ru that are continuously deposited at overpotentials. This process facilitates growth of a monolayer, rather than three-dimensional (3D) clusters, and thus we achieved the two-dimensional (2D) deposition of Pt and Ru on carbon at every nucleation site afforded by the early Pt clusters. We consider that Ru oxidized at high potential (1.0 V vs. Ag/AgCl) is reduced to metallic Ru at low potential in the potential cycles because Ru is held at high potential for a very short time.[19]

Published on the web July 30, 2011; doi:10.1246/bcsj.20110008

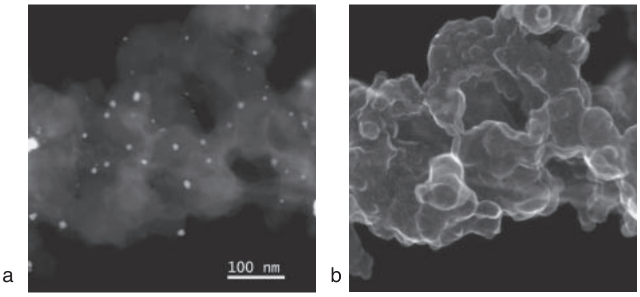

Figure 1. (a) STEM and (b) SEM images of Pt–Ru nanoparticles embedded in carbon prepared by Pt–Ru deposition mediated by Pb UPD (500 potential cycles), taken at magnification 2×10^5.

After depositing Pt and Ru, we placed the electrode in a 0.1 M $HClO_4$ solution to assess the H^+ adsorption/desorption on Pt, and PtOH formation/reduction. The methanol-oxidation activity of this catalyst was measured in a 0.5 M CH_3OH in a 0.1 M $HClO_4$ solution without electrode rotation. We prepared the catalyst and acquired the electrochemical measurements at room temperature in an Ar atmosphere to prevent the oxidation of metallic particles. A Ag/AgCl(3 M Cl^-) electrode was used as the reference; all potentials, E, are quoted with respect to reference electrode. The prepared catalysts were characterized using transmission electron microscopy (TEM) (JEOL-3000F; 300 kV).

Results and Discussion

Figure 1 shows the (a) STEM and (b) SEM images (magnified 2×10^5) of Pt–Ru nanoparticles embedded in carbon prepared by Pt–Ru deposition mediated by Pb UPD (500 potential cycles). Particle sizes vary between 3 and 14 nm, but most are below 10 nm. The size of the Pt–Ru particles we prepared is somewhat larger than that prepared by coimpregnation[20] and vapor deposition,[21] but smaller than those generated by Pt–Ru electrodeposition by applying potential cycles in the absence of mediator.[22] This finding suggests that the catalyst preparation method can control the enlargement of particle size, and inhibit the aggregation of small particles. We determined that the amount of metal in the Pt–Ru/C prepared by Pt–Ru deposition mediated by Pb UPD (100 potential cycles) was 10 nmol of Pt and 2 nmol of Ru, using inductively coupled plasma emission spectroscopy (ICP). The reason for the lower amount of Ru is the preferential deposition of Pt, which has a higher reversible electrode potential. In addition, the rate of Ru deposition on Pt is lowered by the Pb UPD on Pt. The EDS spectrum did not detect the presence of the mediator.

Table 1 shows the amount of surface Pt estimated from proton desorption in perchloric acid. This is an approximate procedure that additionally is affected by the difficulty in separating the charge associated with the formation of RuOH. However, we consider that the proton desorption peak mostly is attributable to Pt atoms because of large bulk composition of Pt (Pt:Ru = 10:2), and the dominant presence of Pt in the surface layers of metal particles. The surface Pt–Ru composition is discussed later. The amount of surface Pt atoms principally is affected by the catalyst preparation procedure. A distinct proton desorption peak was not observed for the catalyst prepared by the mediation of Bi UPD. Others, using rotating ring disk electrode measurements, pointed out that most bismuth remained on a Pt electrode at pH 3.[23] In preparing the catalyst mediated by Bi UPD on Pt, the Bi remaining on Pt may obstruct step-by-step Pt deposition.

Table 1. Amount of Surface Pt Atom on Pt–Ru/Carbon

Catalysts Pt–Ru deposition mediated by	Amount of surface Pt/nmol *(proton desorption in 0.1 M $HClO_4$)*
Pb UPD (10 cycles, 25 $mV\,s^{-1}$)	—[a]
Pb UPD (100 cycles, 25 $mV\,s^{-1}$)	0.64
Pb UPD (500 cycles, 25 $mV\,s^{-1}$)	0.95
Cu UPD (100 cycles, 25 $mV\,s^{-1}$)	0.69
Tl UPD (100 cycles, 25 $mV\,s^{-1}$)	0.20
Bi UPD (100 cycles, 25 $mV\,s^{-1}$)	—[a]
Pb UPD (100 cycles, 10 $mV\,s^{-1}$)	0.56
Pb UPD (100 cycles, 50 $mV\,s^{-1}$)	0.11

a) Distinct proton desorption peak is not observed.

Further information on the distribution of Pt and Ru in the catalysts particles has been obtained using a high-angle annular dark field (HAADF) technique coupled with electron energy loss spectroscopy (EELS). Figures 2a and 2b display the HAADF and EELS intensity profiles obtained in two directions from the edge to the center of the Pt–Ru nanoparticles. Figures 2a and 2b show two different distributions of Ru as a function of the position along the scan from the particle's edge.

Figures 3 and 4 show the HAADF and EELS intensity profiles obtained in scans across the Pt–Ru nanoparticles. EELS shows the distribution of Pt (Figure 3) and Ru (Figure 4). Insert to Figure 3 shows the procedure for the background-subtraction. The normalized Pt EELS intensity around the particle edge is relatively larger than the Ru EELS intensity, indicating the dominant presence of Pt in the surface layers.

Figure 5 shows voltammetry curves of methanol oxidation on Pt–Ru/C prepared by Pt–Ru deposition mediated by Pb, Cu, Tl, and Bi UPD. From Table 1 and the voltammetry curves, it is observed that the catalysts with a large amount of surface Pt atoms have relatively high methanol-oxidation activity. Lead and copper are thought to function as mediators for facilitating the two-dimensional deposition of Pt and Ru on carbon through their UPD on Pt.

Both the numbers of surface Pt atoms and methanol-oxidation activity rise with increasing potential cycles during preparation of the catalyst (Table 1, and Figure 6a). As shown in Figure 6b, the values of methanol-oxidation activity per surface Pt atom of these two catalysts are very close values, regardless of the number of CV cycles. From this result and TEM image of Figure 1, we believe that the number of alloy particle on carbon increases with increasing potential cycles during the catalyst preparation, while the enlargement of the size of the alloy particles is controlled. This preparation method supports possibly increasing methanol-oxidation activity per electrode surface area by repeating the CV cycles, while maintaining catalytic activity per surface Pt atom. The catalyst prepared by 10 CV cycles showed extremely low activity; probably insufficient amounts of Pt and Ru were deposited on carbon during these cycles.

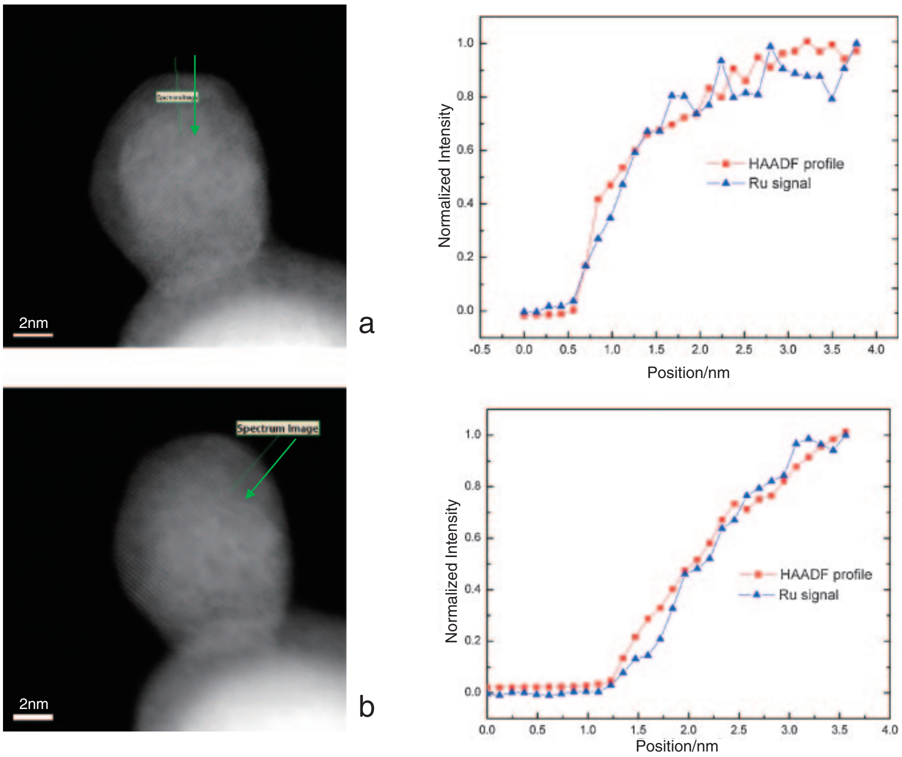

Figure 2. HAADF and Ru EELS intensity profiles obtained in two directions (a and b) from the edge to the center of the Pt–Ru nanoparticles.

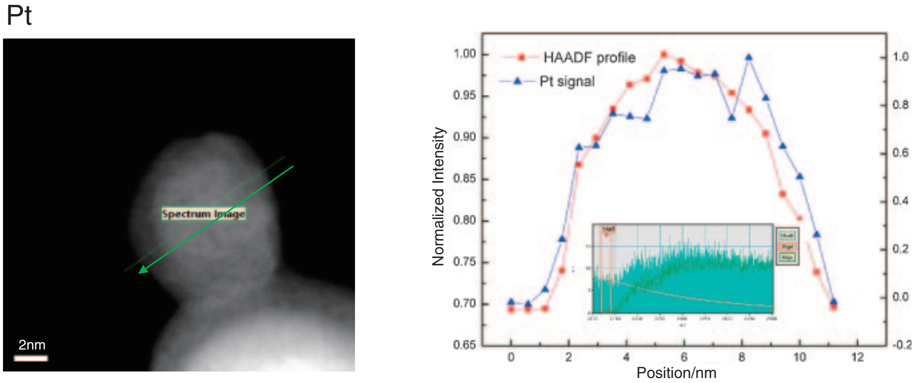

Figure 3. HAADF and Pt EELS intensity profiles obtained in scans across the Pt–Ru nanoparticles.

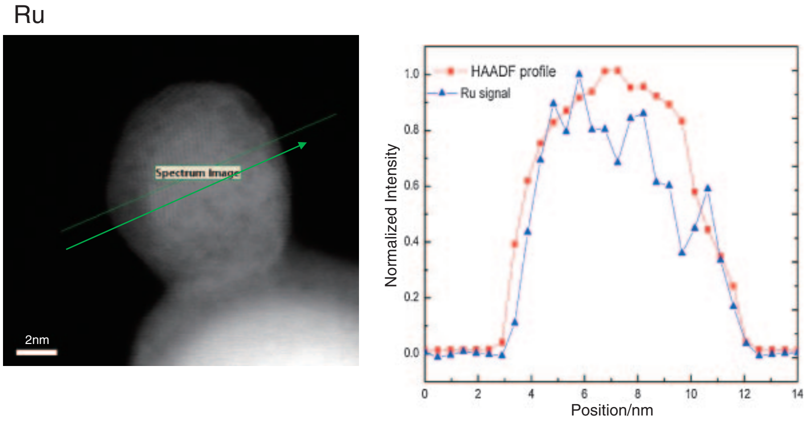

Figure 4. HAADF and Ru EELS intensity profiles obtained in scans across the Pt–Ru nanoparticles.

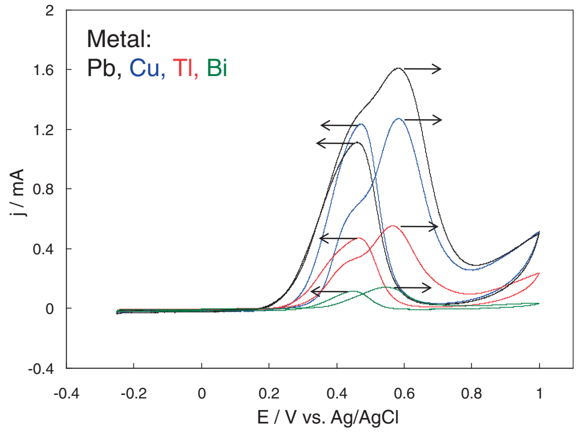

Figure 5. Voltammetry curves of methanol oxidation on Pt–Ru/C prepared by Pt–Ru deposition mediated by Pb, Cu, Tl, or Bi UPD (100 potential cycles), measured in a 0.1 M $HClO_4$ + 0.5 M CH_3OH solution at a scan rate of 25 mV s^{-1}.

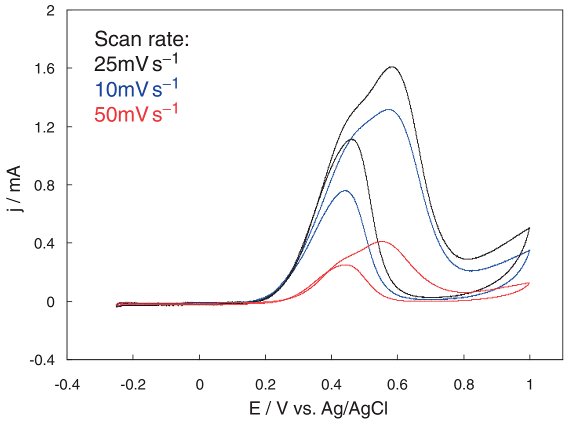

Figure 7. Voltammetry curves of methanol oxidation on Pt–Ru/C prepared by Pt–Ru deposition mediated by Pb UPD (100 potential cycles) at a scan rate of 10, 25, or 50 mV s^{-1}, measured in a 0.1 M $HClO_4$ + 0.5 M CH_3OH solution.

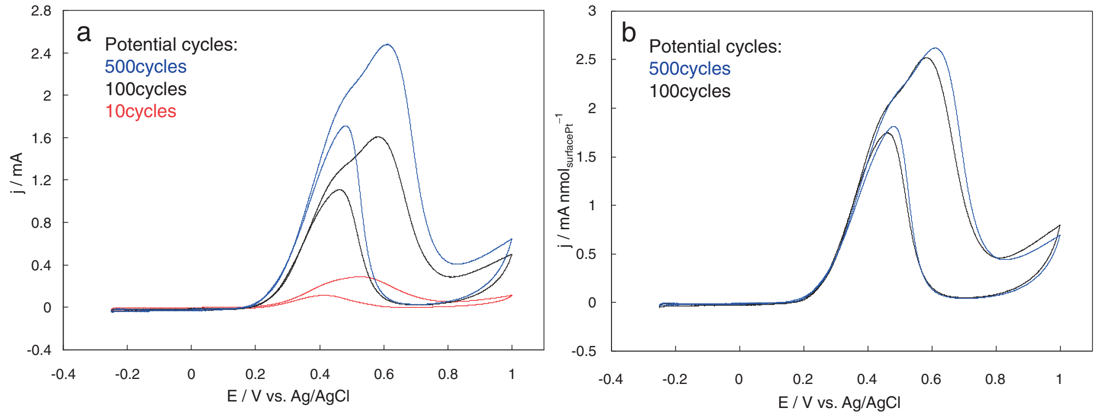

Figure 6. (a) Voltammetry curves of methanol oxidation on Pt–Ru/C prepared by Pt–Ru deposition mediated by Pb UPD (10, 100, or 500 potential cycles), measured in a 0.1 M $HClO_4$ + 0.5 M CH_3OH solution at a scan rate of 25 mV s^{-1}. (b) Voltammetry curves of methanol oxidation on Pt–Ru/C normalized by surface Pt atom prepared by Pt–Ru deposition mediated by Pb UPD (100 or 500 potential cycles), measured in a 0.1 M $HClO_4$ + 0.5 M CH_3OH solution at a scan rate of 25 mV s^{-1}.

Figure 7 shows the effect of scan rate of potential cycles during catalyst preparation for methanol-oxidation activity on Pt–Ru/C. Catalysts with large amounts of surface Pt atoms have relatively high methanol-oxidation activity. These results suggest that the step-by-step deposition of Pt–Ru alloy on carbon can be controllable by altering the scan rate of potential cycles.

Conclusion

We demonstrated a simple method for the controllable deposition of Pt–Ru nanoparticles on carbon surfaces for catalytic applications involving mediation by underpotential deposition and the bulk deposition of Pb or Cu on Pt–Ru. The amount of surface Pt atoms primarily is affected by the procedure for preparing the catalyst. The catalysts with large amounts of surface Pt atoms have relatively high methanol-oxidation activity. We conclude that the number of alloy particle on carbon increases with the increasing number of potential cycles during catalyst preparation, while, at the same time, controlling the enlargement in the size of the alloy particles.

It is noteworthy that the method of preparing the catalyst can control the extent of deposition of the alloy particles on carbon and thereby modulate methanol-oxidation activity per electrode surface area, while maintaining catalytic activity per surface Pt atom.

This work was carried out at Brookhaven National Laboratory under Contract No. DE-AC02-98CH10886 with the U.S. Department of Energy, Office of Science, and supported by its Division of Chemical Sciences, Geosciences and Biosciences and its Division of Materials Sciences and Engineering, within the Office of Basic Energy Sciences. Yuji Ando acknowledges financial support from AIST.

Supporting Information

The cyclic voltammetry curves obtained during Pt–Ru deposition mediated by Pb UPD and OPD on the oxidized carbon particles in an 0.1 M $HClO_4$ solution containing 0.01 mM Pt^{2+}, 0.05 mM Ru^{3+}, and 5 mM Pb^{2+} ions. This material is available free of charge on the Web at http://www.csj.jp/journals/bcsj/.

References

1 E. Antolini, *Appl. Catal., B* **2009**, *88*, 1.
2 M. Copel, M. C. Reuter, M. Horn von Hoegen, R. M. Tromp, *Phys. Rev. B* **1990**, *42*, 11682.
3 M. Horn-von Hoegen, F. K. LeGoues, M. Copel, M. C. Reuter, R. M. Tromp, *Phys. Rev. Lett.* **1991**, *67*, 1130.
4 G. Meyer, B. Voigtländer, N. M. Amer, *Surf. Sci.* **1992**, *274*, L541.
5 H. A. van der Vegt, H. M. van Pinxteren, M. Lohmeier, E. Vlieg, J. M. C. Thornton, *Phys. Rev. Lett.* **1992**, *68*, 3335.
6 K. Sieradzki, S. R. Brankovic, N. Dimitrov, *Science* **1999**, *284*, 138.
7 D. Davidović, R. R. Adzić, *Electrochim. Acta* **1988**, *33*, 103.
8 R. R. Adzic, in *Advances in Electrochemistry and Electrochemical Engineering*, ed. by H. Gerischer, C. W. Tobias, John Wiley & Sons, New York, **1984**, Vol. 13, pp. 159–260.
9 N. S. Marinkovic, J. X. Wang, J. S. Marinkovic, R. R. Adzic, *J. Phys. Chem. B* **1999**, *103*, 139.
10 M. J. Esplandiu, M. A. Schneeweiss, D. M. Kolb, *Phys. Chem. Chem. Phys.* **1999**, *1*, 4847.
11 T. Kondo, J. Morita, M. Okamura, T. Saito, K. Uosaki, *J. Electroanal. Chem.* **2002**, *532*, 201.
12 T. Kondo, S. Takakusagi, K. Uosaki, *Electrochem. Commun.* **2009**, *11*, 804.
13 M. Shao, K. Sasaki, N. S. Marinkovic, L. Zhang, R. R. Adzic, *Electrochem. Commun.* **2007**, *9*, 2848.
14 R. Vasilic, N. Vasiljevic, N. Dimitrov, *J. Electroanal. Chem.* **2005**, *580*, 203.
15 Y. Du, C. Wang, *Mater. Chem. Phys.* **2009**, *113*, 927.
16 S. R. Brankovic, J. X. Wang, R. R. Adžić, *Surf. Sci.* **2001**, *474*, L173.
17 J. X. Wang, B. M. Ocko, R. R. Adzic, *Surf. Sci.* **2003**, *540*, 230.
18 Y. Ando, K. Sasaki, R. R. Adzic, *Electrochem. Commun.* **2009**, *11*, 1135.
19 P. P. Sharma, I. I. Suni, *J. Electrochem. Soc.* **2011**, *158*, H111.
20 Y. Takasu, T. Fujiwara, Y. Murakami, K. Sasaki, M. Oguri, T. Asaki, W. Sugimoto, *J. Electrochem. Soc.* **2000**, *147*, 4421.
21 P. Sivakumar, V. Tricoli, *Electrochim. Acta* **2006**, *51*, 1235.
22 F. J. Rodríguez-Nieto, T. Y. Morante-Catacora, C. R. Cabrera, *J. Electroanal. Chem.* **2004**, *571*, 15.
23 J. Lee, P. Strasser, M. Eiswirth, G. Ertl, *Electrochim. Acta* **2001**, *47*, 501.