Electrocatalytic properties for oxygen reduction reaction (ORR) of Pt(111) epitaxial layers on a Pd(111) substrate are investigated. Scanning tunneling microscopy images of the as-prepared 0.6-nm- and 1.2-nm-thick Pt(111) epitaxial layers on Pd(111) (Pt0.6nm/Pd(111) and Pt1.2nm/Pd(111)) revealed that the topmost surface has atomically flat, 50–100-nm-wide terraces. Remarkable current features due to hydrogen storage and emission by the Pd(111) substrate dominated the cyclic voltammograms of Pt0.6nm/Pd(111) in the potential range of 0.15–0.4 V vs. a reversible hydrogen electrode. In contrast, the curve of Pt1.2nm/Pd(111) exhibited a shrinkage in the hydrogen charges (QH) in the potential range of 0.25–0.4 V, accompanied by the emergence of symmetrical redox features at 15 mV on the positive potential side, relative to Pt(111) “butterfly” feature. Both Pt0.6nm/Pd(111) and Pt1.2nm/Pd(111) showed ca. four times higher ORR activity than clean Pt(111), although their hydrogen-related behaviors and activity changes during applying potential cycles were much different. The results suggest that shrinkage in QH and positive shift in the onset potential of hydroxyl species are common features of the CV of highly ORR-active well-defined Pt–M(111) bimetallic surfaces and that the activity enhancements and the structural stabilities fairly depend on the surface structure of the epitaxial Pt(111) lattice.

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High-performance low-cost polymer electrolyte membrane fuel cells (PEMFC) are required for wide-spread use in fuel cell vehicles. Developments in highly active oxygen reduction reaction (ORR) catalysts are one of the top priorities for developing PEMFC stacks. Since the pioneering work on Pt–M (M is a more affordable, low-cost material) alloys by Watanabe and co-workers,1 numerous studies on the ORR properties of Pt–M bimetallic alloy with nanosized structures have been intensively performed. To date, several types of nanosized structures of Pt–M have been proposed for use as high-performance ORR catalysts, e.g., Pt-shell and M-core core–shell nanoparticles (NPs),2–5 especially electrochemically de-alloyed M from Pt–M NPs,6–9 nanostructured thin films of Pt–M10,11 shape-controlled Pt–M NPs,12–15 and nanoframe structures of Pt–Ni alloys.16

Irrespective of the proposed nature of the nanosized structures, the generation of electrochemically stable Pt-shell layers at the topmost surfaces is the consensus for synthesizing Pt–M ORR catalysts with high activity and durability.17–20

The topmost atomic-level structures of the Pt-shell layers for the Pt–M bimetallic alloys determine ORR performance. However, because ORR is governed by many factors, the discussions of ORR enhancement mechanisms are intricate. For example, atomic arrangements of the topmost Pt-shell, thickness of the Pt-shell layers, and interface structures between the surface Pt-shell and underlying M (Pt–M core)21–24 are expected to have a serious influence on the ORR activities. When studying the topmost surface structures and the evaluation of the electrochemical (EC) properties, experimental approaches using single crystals of Pt–M alloys are powerful techniques that allow the atomic and molecular understanding of ORR proceeding on the Pt–M alloy surfaces. Notably, Adzic and co-workers discussed a trend in the ORR activity enhancement of electrochemically prepared Pt monolayers onfcc metal single-crystal surfaces.25 Furthermore, Stamenkovic et al. reported a remarkable dependence of ORR performance on the surface crystallographic arrangements of Pt3Ni.26 Such well-defined approaches enable us to discuss the initial as-prepared EC properties of the atomically flat topmost surfaces of the Pt–M bimetallic surfaces. From these viewpoints, we have presented the effectiveness of molecular beam epitaxy and ultra-high vacuum (UHV) techniques for the preparation of model electrode catalyst surfaces for ORR, the initial as-prepared ORR activities and ORR responses under specific EC conditions were discussed for the Ni/Pt(111),27–31 Co/Pt(hkl),32,33 and Pt/Au(hkl) bimetallic surfaces.34,35

In this study, we focused on the ORR activities of the Pt/Pd(111) bimetallic surfaces prepared through vacuum depositions of Pt on a Pd(111) substrate in UHV. We performed cyclic voltammetry (CV), linear sweep voltammetry (LSV) and applying potential cycling to the as-prepared Pt/Pd(111) in 0.1 M HClO4. The CV characteristics, ORR activity and structural stability for the Pt/Pd(111) surfaces are discussed based on the topmost structures of the Pt(111) epitaxial layers.

**Experimental**

Pt epitaxial layers with various thicknesses were prepared on a clean Pd(111) substrate using two UHV systems. The base pressure of one UHV system was ca. 3 × 10−10 Torr. The Pd(111) single-crystal substrate, with less than 0.1° miscut (φ = 12 mm), was cleaned by repeated Ar+ sputtering and annealing at 1273 K under UHV. The surface atomic arrangement of the cleaned Pd(111) substrate was verified using reflection high-energy electron diffraction (RHEED). The diffraction patterns were analyzed quantitatively using a computer-controlled charge-coupled device camera and a data acquisition system (KSA 400). Pt (99.99% pure) was deposited on the clean Pd(111) substrate at 1273 K using electron-beam evaporation method. The deposition thickness was monitored using a quartz crystal microbalance, and the deposition rate was fixed at ca. 0.1 nm/min. In this study, bimetallic surfaces of Pt with various nm thickness (nmnm) grown on Pd(111) are designated as Pt_xnm/Pd(111). After the confirmation of the surface atomic arrangement of Pt_xnm/Pd(111) based on the separation of RHEED streaks, infrared reflection-absorption spectroscopy (IRRAS) was performed for adsorbed carbon monoxide (CO) on the resulting surfaces. The exposure of the surfaces to CO was carried out through a variable leak valve at ca. 3 × 10−9 Torr at a substrate temperature of 300 K. IRRAS spectra were recorded with 2 cm−1 resolution, with an average of 128 scans, using a Fourier transform infrared spectrometer (Bruker Vertex 70) equipped with a liquid-nitrogen-cooled HgCdTe detector. Here, each spectrum has been presented as a ratio with the spectrum before CO exposure. Scanning tunneling microscopy (STM) observations were performed for the resulting Pt_xnm/Pd(111) surfaces in another UHV system (JEOL 400). Pt (99.99% pure) was deposited on the clean Pd(111) substrate with less than 0.1° miscut (φ = 8 mm) was cleaned by repeated Ar+ sputtering (PSP ISIS3000) and annealing at 1273 K under UHV. After the surface cleaning procedure, Pt was deposited on the cleaned Pd(111) using...
electron beam evaporators (Beamtron); the pressure during the deposition was less than $1 \times 10^{-7}$ Pa. The deposition rate for Pt was fixed at 0.1 nm/min, which was estimated using a flux monitor installed in the evaporator. Then, UHV-STM observations were performed on the Pt$_{0.6nm}$/Pd(111) surfaces.

The EC setup and UHV-EC sample transfer system have been described in a previous study. CV curves of the UHV-prepared surfaces were recorded in N$_2$-purged 0.1 M HClO$_4$ (Merck, Suprapur), without sample disk rotation, using a glass cell that included a platinum counter electrode and a reversible hydrogen electrode (RHE). All potentials in this study have been presented with respect to the RHE. Subsequently, LSV curves were collected in O$_2$-saturated 0.1 M HClO$_4$ with various disk rotation rates. ORR activities of Pt$_{0.6nm}$/Pd(111) were evaluated from the kinetic-controlled current density $(j_{oc})$ at 0.9 V, estimated using a Koutecky–Levich plot. The electrochemical stabilities of the samples were investigated by applying a square-wave signal with 3s each at 0.6 V and 1.0 V in an O$_2$-saturated 0.1 M HClO$_4$ solution. The samples after the potential cycles were retransferred to the UHV-STM system to evaluate the potential-cycle-induced topmost surface structural changes.

Results and Discussion

Figure 1 shows the UHV-STM images and corresponding RHEED patterns for the substrate Pd(111), Pt$_{0.6nm}$/Pd(111), and Pt$_{1.2nm}$/Pd(111). The RHEED pattern before the Pt deposition shows sharp streaks, with the expected lattice spacing for the ⟨110⟩ direction of Pd(111). As can be observed from Fig. 1, the separations of the RHEED streaks remained nearly unchanged by the Pt depositions. The difference in the lattice constants of Pt (0.392 nm) and Pd (0.389 nm) is only ca. 1%. Therefore, the RHEED results suggest that Pt grows on Pd(111) epitaxially under these conditions. The UHV-STM images for the corresponding surfaces clearly show 50–100-nm-wide atomically flat terraces. The results indicate that the Pt depositions on the Pd(111) substrate at 673 K generate the topmost surface of an epitaxial Pt(111) lattice, having atomically flat 50–100 nm wide terraces.

Because C–O stretching frequencies for adsorbed CO depend on the surface morphologies and atomic ratios in the bimetallic surfaces, we have performed IRRAS for adsorbed CO on the Pd$_{0.6nm}$/Pd(111) and Pt$_{2nm}$/Pd(111) surfaces; the results are summarized in Fig. 2. IRRAS spectra for CO adsorption on the clean Pt(111) and Pt(111) surfaces are also presented for reference. With regard to the clean Pt(111), a broad absorption feature at 1933 cm$^{-1}$ dominates the spectrum. Frequencies of the bands due to adsorbed CO on Pd(111) are strongly correlated with adsorbed CO coverage, $\theta$. For example, a band is located at 1936 cm$^{-1}$ for $\theta = 0.5$, at which the c(4 × 2) ordered structure was formed. Based on the C–O stretching frequency, the 1930 cm$^{-1}$ band can be ascribed to bridge-bonded CO on Pd(111). The IRRAS spectrum of the clean Pt(111) is characterized by two distinct bands at 2095 and 1853 cm$^{-1}$, which can reliably be assigned to adsorbed CO on the top- and bridge sites of surface Pt atoms, respectively.

The IRRAS spectrum of Pd$_{0.6nm}$/Pd(111) shows linear- and bridge-bonded CO bands at 2097 cm$^{-1}$ and 1857 cm$^{-1}$, respectively. These frequencies are slightly higher than those for the clean Pt(111); slight blue shifts might arise from the influence of the Pd(111) substrate in the topmost Pt(111) epitaxial layers. The Pt$_{1.2nm}$/Pd(111) shows the linear- and bridge-bonded CO bands at the frequencies same as those shown by Pd$_{0.6nm}$/Pd(111). The results (Fig. 2) clearly indicate that the topmost surfaces of Pd$_{0.6nm}$/Pd(111) and Pt$_{2nm}$/Pd(111) comprise almost pure Pt(111) epitaxial layers, i.e., the substrate Pt(111) is completely covered by the Pt epitaxial growth above 0.6 nm in deposition thickness. Considering the atomic radius of Pt (0.139 nm), a deposition thickness of 0.3 nm might be equivalent to a one-monolayer-thick Pt layer. However, under these preparation conditions, with a substrate temperature of 673 K, the intermixing of the deposited Pt atoms with the substrate Pd atoms is unavoidable during the Pt depositions on Pd(111). Therefore, the actual Pt(111) epitaxial layer thicknesses might be thinner in comparison to the described mass thickness of the deposited Pt. The corresponding surface models for Pd$_{0.6nm}$/Pd(111) and Pt$_{2nm}$/Pd(111) derived from RHEED, STM, and IRRAS results are depicted at the right hand side of Fig. 2.

CV curves with a potential range of 0.15 to 1.0 V for the UHV-prepared Pd$_{0.6nm}$/Pd(111) and Pt$_{2nm}$/Pd(111) surfaces, in addition to those for the clean Pt(111) surface, are summarized in Fig. 3. The hydrogen adsorption and desorption characteristics for low-index single-crystal planes of Pt are well known to be very sensitive to the surface atomic arrangements. The curve of the clean Pt(111) (black dashed line) is characterized by symmetrical features located at 0.05–0.35 V (hydrogen-related peaks) and around 0.8 V (hydroxyl-related peaks), forming a so-called “butterfly”. In contrast, the CV curve of Pd$_{0.6nm}$/Pd(111) (top) at 0.05–0.35 V is characterized by strong EC charges that might originate from hydrogen storage and emission by the Pd(111) substrate. Although STM and IRRAS results sug-
Figure 2. IRRAS spectra for CO adsorption at saturation coverage on Pt0.6nm/Pd(111) and Pt1.2nm/Pd(111). Surface models are depicted on the right hand side.

Figure 3. CV curves for Pt0.6nm/Pd(111) and Pt1.2nm/Pd(111) recorded in N2-purged (sweep rate: 50 mV/s) 0.1 M HClO4. Top Pt0.6nm/Pd(111) (black line), inset is enlarged CV from 0.6 to 1.0 V. Bottom Pt1.2nm/Pd(111) (gray line). CVs of clean Pt(111) (black dashed line) are also presented for reference.

suggested that the topmost Pt0.6nm/Pd(111) surface is covered by atomically flat epitaxial Pt(111) layers in UHV (Fig. 1), the remarkable hydrogen storage and emission features, which emerged on the CV curve shown in Fig. 3, suggest that hydrogen atoms present at the topmost surface of Pt0.6nm/Pd(111) can access the Pd(111) substrate through ultra-thin Pt(111) epitaxial layers in the hydrogen-related potential region. Notably, similar hydrogen features are present on the CV curve of the EC-prepared Pt monolayers formed on a Pd(111) substrate. In other words, the thickness of the 0.6-nm-thick Pt(111) epitaxial layers (Pt0.6nm/Pd(111)) is insufficient to prevent the access of hydrogen to the Pd(111) substrate, i.e., the Pt(111) epitaxial layers might be influenced by the hydrogen storage and emission behavior of the Pd substrate. Moreover, the topmost surface structure, e.g., the surface atomic ratio of Pt and Pd in Pt0.6nm/Pd(111), has not yet been resolved because hydrogen-related features of the topmost Pt(111) epitaxial layer are hidden by the significant features resulting from hydrogen storage and emission by the substrate Pd(111). Furthermore, the Pt0.6nm/Pd(111) shows a rather weak redox feature due to the adsorption and desorption of the OH-related species (around 0.8 V, inset).

In contrast, the CV curve of Pt1.2nm/Pd(111) indicates that almost pure Pt(111) layers actually cover the Pd(111) substrate under EC conditions. Although the hydrogen storage peak of the substrate Pd(111) is still present in potentials between 0.15 and 0.25 V, hydrogen charges (QH) in the region of 0.25–0.4 V markedly shrink relative to the clean Pt(111). Furthermore, a symmetric redox feature is located at ca. 15 mV on the positive potential side, compared with the “butterfly” peak of the clean Pt(111). This feature is ascribable to the adsorption and desorption of OH-related species on the topmost epitaxial Pt(111) lattice. Zhou et. al. investigated the interaction between Pt monolayers and single-crystal supports, and their Density functional theory calculation results show that the binding energy of OH on Pt/Pd(111) is 20 meV weaker than that on Pt(111). Furthermore, recent theoretical calculations for the multilayered Pt shells on the cubic shape-controlled Pd show that OH binding energies on Pt/ Pd(100) depend on the Pt layer thickness and are 12–29 meV lower than those on Pt(100).44 Zhang et al. demonstrated that compressive surface strains of the Pt(111) monolayer on Pd(111) and Pt shells on the Pd core correlate with the ORR activity enhancements of Pt–Pd bimetallic alloys.3,25,42,45 Therefore, the slight positive shift (ca. 15 mV) of the OH-related symmetric redox can be explained by compressive surface strains on the topmost Pt(111) lattice that are induced by a lattice mismatch between the topmost Pt(111) and substrate Pd(111) lattices.

LSV curves for the Pt0.6nm/Pd(111) and Pt1.2nm/Pd(111) surfaces before and after the 1000 potential cycles (PCs) are presented in Fig. 4a. The curves for the clean Pt(111) and Pd(111) surfaces are shown for reference. The initial LSV curves of the Pt0.6nm/Pd(111) and Pt1.2nm/Pd(111) surfaces are almost identical; half-wave potentials for both surfaces are positively shifted about 45 mV relative to the clean Pt(111). Kinetic-controlled current densities (i) at 0.9 V of the UHV-prepared Pt0.6nm/Pd(111) and Pt1.2nm/Pd(111) surfaces are evaluated from Koutecky–Levich plots resulting in values of about 2.5 mA/cm²: the value of which (0.63 mA/cm²) is four fold higher than clean Pt(111). Nevertheless, the ORR activities after the 1000-PCs application were completely different. The half wave potential for the Pt0.6nm/Pd(111) shifted to lower potential by 30 mV, indicating that the activity is ca. 60% of the initial value after applying the 1000-PCs. As for the Pt1.2nm/Pd(111), the LSV curve is almost unchanged. The UHV-STM images for the samples collected after the 1000-PCs (Figs. 4b and 4c) clearly show the outermost surface structures are much different from each other. For the Pt0.6nm/Pd(111), single-nm-sized islands and some pits having an atomic height emerged on the atomically flat terraces, though the topmost surface of Pt1.2nm/Pd(111) is slightly roughened (height modulations of 0.1–0.15 nm) by the PCs. Because of the higher oxygen affinity of the less-noble Pd, the substrate Pd atoms might diffuse to the topmost surface through surface defects in the epitaxial Pt(111) layers during potential sweeps in LSV measurements. The standard electrode potential of Pd is ca. 0.95 V,
and thus, Pd atoms located at the topmost surface and subsurface regions tend to dissolve during the LSV measurements. Therefore, the change in the atomic-level structures of the topmost Pt\textsubscript{1.2nm}/Pd(111) should be considered in the discussion of the EC properties. The small lattice parameter of Pd (a = 0.389 nm) should induce surface compressive strains of the topmost Pt(111) lattice (a = 0.392 nm). Because the actual Pt thickness of the Pt\textsubscript{0.6nm}/Pd(111) is thinner than that of the Pt\textsubscript{1.2nm}/Pd(111), the influence of the Pd(111) substrate on the topmost Pt(111) epitaxial lattice, i.e., the influence induced by lattice mismatch between the topmost Pt(111) epitaxial layer and the underlying Pd(111) substrate, appears to be noticeable for Pt\textsubscript{0.6nm}/Pd(111). Actually, the CV curve for the Pt\textsubscript{0.6nm}/Pd(111) surface shows significant hydrogen storage and emission currents of the substrate Pd(111) (Fig. 3). Furthermore, the topmost surface after applying the 1000-PCs (Fig. 4b) shows pits having atomic level depth on the terrace, suggesting that the 0.6-nm-thick Pt(111) epitaxial layer is too thin to stabilize the topmost Pt(111), and thereby, narrow domains of the substrate Pd(111) can be exposed to the solution during the LSV measurements. Because the Pd(111) surface shows less ORR activity than Pt(111) and is easily dissolved into the solution, Pd atoms at the topmost and/or subsurface regions could lead to a reduction in the ORR activity. Actually, Climent et. al. has reported that Pd overlayers on Pt(111) shows much lower ORR activity than Pt(111) substrate.46

With regard to Pt\textsubscript{1.2nm}/Pd(111), the induced compressive strains should be low in comparison with Pt\textsubscript{0.6nm}/Pd(111). On the other hand, the topmost epitaxial layers of Pt(111) appear to be sufficient to cover the Pd(111) substrate in the EC environment, i.e., a thickness of 1.2 nm should stabilize the topmost Pt(111) epitaxial lattice. Notably, the results of the CO-IRRAS (Fig. 1) and CV (Fig. 3) experiments show that the Pt(111) epitaxial layers above 0.6 nm thickness completely cover the substrate Pd(111). Consequently, the same ORR activity enhancement factors might be obtained for the Pt\textsubscript{0.6nm}/Pd(111) and Pt\textsubscript{1.2nm}/Pd(111) surfaces in this study. On the other hand, unlike the Pt\textsubscript{0.6nm}/Pd(111), the Pt\textsubscript{1.2nm}/Pd(111) maintains the initial activity even after the 1000-PCs. We have previously reported the thickness dependence of the Pt-enriched multilayer shell surfaces that formed through the additional Pt epitaxial growth on the Pt-enriched surface obtained by Ni deposition on an 823 K-Pt(111) substrate28 (η-ML Pt/Ni/Pt(111)). The results clearly show that the ORR activities and the structural stabilities seriously depend on the Pt-enriched multilayer shell thicknesses and the Pt-enriched multilayer shells over 3 MLs stabilize the topmost shell surfaces through suppression of the underlying Ni atom dissolution. The results obtained in this study (Pt/Pd(111) well agree with the results of n ML-Pt/Ni/Pt(111). In addition, recent work on Pt-Pd aerogel catalysts has shown that the Pt surface enrichment induced by deoxygenation leads to enhancement of both the activity and the stability.47 The result for the nanosized catalysts correspond to that for the present extended surfaces.

On the CV curve of Pt\textsubscript{1.2nm}/Pd(111), a shrinkage in QH in the potential region of 0.25–0.4 V and positive shift in the onset potential for the adsorption of OH-related species are obvious. These CV characteristics are also reported for highly ORR-active well-defined Pt–M bimetallic surfaces, e.g., Pt–Ni,26 Pt–Cu surface alloys,48 and our UHV-prepared Ni–Pt and Co–Pt.49 On the other hand, the CV of the Pt(111) epitaxial layers with tensile surface strains for the UHV-prepared Pt/Au(111) (lattice constant of Au is a = 0.407 nm)34,35 is almost the same as that for the clean Pt(111), except for the “butterfly” peaks at 0.8 V, i.e., the aforementioned CV characteristics are absent for the Pt/Au(111) bimetallic surface. Considering the CV and LSV results obtained in this study (Pt/Pd(111)), the shrinkage in QH and a positive shift in the onset potential of hydroxyl species are common CV characteristics for highly active Pt–M(111) bimetallic surfaces. Because lattice mismatch between Pt and Pd is less than 1%, the much smaller changes in QH and the positive shift in the hydroxyl species of Pt\textsubscript{1.2nm}/Pd(111) relative to those of Ni or Co\textsubscript{Pt(111)} might result from the relatively low compressive strains of the topmost Pt(111) lattice.

Conclusions

In the present study, the EC properties of the UHV-prepared Pt/Pd(111) bimetallic surfaces were evaluated in a 0.1 M HClO\textsubscript{4} solution. UHV-STM and IRRAS for adsorbed CO at saturation coverage on Pt\textsubscript{0.6nm}/Pd(111) and Pt\textsubscript{1.2nm}/Pd(111) prepared at 673 K showed that the Pt(111) epitaxial layers with atomically flat 50–100-nm-wide terraces covered the Pd(111) substrate surface. In contrast, in the EC environments, current features due to hydrogen storage and emission by the Pd(111) substrate were noteworthy on the CV curve of Pt\textsubscript{0.6nm}/Pd(111); moreover, when compared with the clean Pt(111), the Pt\textsubscript{1.2nm}/Pd(111) surface exhibited a shrinkage in QH at a potential of 0.25–0.4 V, accompanied by a 15 mV positive shift of the symmetrical “butterfly-like” redox feature. The ORR activities of Pt\textsubscript{0.6nm}/Pd(111) and Pt\textsubscript{1.2nm}/Pd(111) were estimated to be ca. four times higher than those of the clean Pt(111). However, the activity for the Pt\textsubscript{0.6nm}/Pd(111) after 1000-PCs of 0.6–1.0 V decreased by about 60% relative to that of the corresponding as-prepared surfaces. In contrast, the Pt\textsubscript{1.2nm}/Pd(111) retained almost same activity even after the 1000-PCs. The results clearly reveal that that shrinkage in QH and positive shift in the onset potential of hydroxyl species are common features of the CV of highly ORR-active well-defined Pt–M(111) bimetallic surfaces and that the Pt multilayer shell thicknesses above 3 MLs stabilize the topmost surface, thereby, enhancing ORR durability of the Pt-M(111) surfaces.

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References

1. T. Toda, H. Igarashi, H. Uchida, and M. Watanabe, J. Electrochem. Soc., 146, 3750 (1999).
2. Y. C. Hsieh, Y. Zhang, D. Su, V. Volkov, R. Si, L. Wu, Y. Zhu, W. An, P. Liu, P. He, S. Ye, R. R. Adzic, and J. X. Wang, Nat. Commun., 3, 1115 (2012).
3. R. Adzic, J. Zhang, K. Saatsi, M. Vukmirovic, M. Shao, J. Wang, A. Nilekar, M. Mavrikakis, J. Valerio, and F. Uribe, Top. Curr. Chem., 146, 249 (2007).
4. T. Cochell, W. Li, and A. Manthiram, J. Phys. Chem. C, 117, 3865 (2013).
5. C. Koenigsmann, A. C. Santulli, K. Gong, M. B. Vukmirovic, W.-P. Zhou, E. Sutter, S. S. Wong, and R. R. Adzic, J. Am. Chem. Soc., 133, 9783 (2011).
6. Y. Liu, C. M. Hangarter, U. Bertocci, and T. P. Mofﬁat, J. Phys. Chem. C, 116, 7848 (2012).
7. L. Gan, M. Heggen, S. Rudi, and P. Strasser, Nano Lett., 12, 5423 (2012).
8. P. Mani, R. Srivastava, and P. Strasser, J. Power Sources, 196, 666 (2011).
9. S. Koh and P. Strasser, J Am Chem Soc, 129, 12624 (2007).
10. D. F. van der Vliet, C. Wang, D. Tripkovic, D. Strmcnik, X. F. Zhang, M. K. Debe, R. T. Atanaseski, N. M. Markovic, and V. R. Stamenkovic, Nat. Mater., 11, 1051 (2012).
11. D. van der Vliet, C. Wang, M. Debe, R. Atanaseski, N. M. Markovic, and V. R. Stamenkovic, Electrochim. Acta, 56, 8695 (2011).
12. M. Shao, J. Odeli, M. Humbert, T. Yu, and Y. Xia, J. Phys. Chem. C, 117, 4172 (2013).
13. C. Cui, L. Gan, M. Heggen, S. Radi, and P. Strasser, Nat. Mater., 12, 765 (2013).
14. J. Wu, A. Gross, and H. Yang, Nano Lett., 11, 798 (2011).
15. J. Zhang, H. Yang, J. Fang, and S. Zou, Nano Lett., 10, 638 (2010).
16. C. Chen, Y. Kang, Z. Huo, Z. Zhu, W. Huang, H. L. Xin, J. D. Snyder, D. Li, J. A. Herron, M. Mavrikakis, M. Chi, K. L. More, Y. Li, N. M. Markovic, G. A. Somorjai, P. Yang, and V. R. Stamenkovic, Science, 343(6177), 1339 (2014).
17. N. Hodnik, M. Bele, and S. Hocevar, Electrochem. Commun., 23, 125 (2012).
18. C. Wang, M. Chi, D. Li, D. Strmcnik, D. van der Vliet, G. Wang, V. Komnicky, K. C. Chang, A. P. Paulikas, D. Tripkovic, J. Pearson, K. L. More, N. M. Markovic, and V. R. Stamenkovic, J. Am. Chem. Soc., 133, 14396 (2011).
19. F. Maillard, L. Dubau, J. Durst, M. Chatenet, J. André, and E. Rossinot, Electrochem. Commun., 12, 1161 (2010).
20. V. R. Stamenkovic, B. S. Mun, K. J. J. Mayrhofer, P. N. Ross, and N. M. Markovic, J. Am. Chem. Soc., 128, 8813 (2006).
21. M. D. Maciá, J. M. Campiña, E. Herrero, and J. M. Felu, J. Electroanal. Chem., 564, 141 (2004).
22. N. M. Markovic, R. R. Adžić, B. D. Cahan, and E. B. Yeager, J. Electroanal. Chem., 377, 249 (1994).
23. A. Kuzume, E. Herrero, and J. M. Felu, J. Electroanal. Chem., 599, 333 (2007).
24. A. Hitotsuyanagi, M. Nakamura, and N. Hoshi, Electrochim. Acta, 62, 512 (2012).
25. J. Zhang, M. B. Vukmirovic, Y. Xu, M. Mavrikakis, and R. R. Adzic, Angew. Chem. Int. Ed., 44, 2132 (2005).
26. V. R. Stamenkovic, B. Fowler, B. S. Mun, G. Wang, P. N. Ross, C. A. Lucas, and N. M. Markovic, Science, 315, 493 (2007).
27. T. Wadayama, N. Todoroki, Y. Yamada, T. Sugawara, K. Miyamoto, and Y. Iijima, Electrochem. Commun., 12, 1112 (2010).
28. N. Todoroki, Y. Asakimori, and T. Wadayama, Phys. Chem. Chem. Phys., 15, 17771 (2013).
29. N. Todoroki, T. Takahashi, Y. Iijima, Y. Yamada, T. Hayashi, and T. Wadayama, Materials Transactions, 54, 1735 (2013).
30. N. Todoroki, T. Dasai, Y. Asakimori, and T. Wadayama, J. Electroanal. Chem., 724, 15 (2014).
31. N. Todoroki, Y. Iijima, T. Takahashi, Y. Asakimori, and T. Wadayama, J. Electrochem. Soc., 160, F1591 (2013).
32. T. Wadayama, H. Yoshida, K. Ogawa, N. Todoroki, Y. Yamada, K. Miyamoto, Y. Iijima, T. Sugawara, K. Aihara, S. Sugawara, and K. Shinozara, J. Phys. Chem. C, 115, 18589 (2011).
33. Y. Yamada, K. Miyamoto, T. Hayashi, Y. Iijima, N. Todoroki, and T. Wadayama, Surf. Sci., 607, 54 (2013).
34. Y. Iijima, T. Kondo, T. Takahashi, Y. Bandou, N. Todoroki, and T. Wadayama, J. Electrochem. Soc., 160, F998 (2013).
35. Y. Iijima, Y. Takahashi, K. Matsumoto, T. Hayashi, N. Todoroki, and T. Wadayama, J. Electroanal. Chem., 685, 79 (2012).
36. A. M. Bradshaw and F. M. Hoffmann, Surf. Sci., 72, 513 (1978).
37. E. Ozerysny, D. C. Meier, and D. W. Goodman, J. Phys. Chem. B, 106, 9367 (2002).
38. G. Ruppertche, in Adv. Catal., C. G. Bruce and K. Helmut Editors, p. 133, Academic Press (2007).
39. A. Crossley and D. A. King, Surf. Sci., 95, 131 (1980).
40. N. M. Marković and P. N. Ross Jr, Surf. Sci. Rep., 45, 117 (2002).
41. A. Hitotsuyanagi, S. Kondo, M. Nakamura, and N. Hoshi, J. Electroanal. Chem., 657, 123 (2011).
42. J. Zhang, Y. Mo, M. B. Vukmirovic, R. Klö, K. Sasaki, and R. R. Adzic, J. Phys. Chem. B, 108, 10955 (2004).
43. W. P. Zhou, X. F. Yang, M. B. Vukmirovic, B. E. Koel, J. Sao, G. W. Peng, M. Mavrikakis, and R. R. Adzic, J. Am. Chem. Soc., 131, 12755 (2009).
44. S. Xie, S. I. Choi, N. Lu, L. T. Roling, J. A. Herron, L. Zhang, J. Park, J. Wang, M. J. Kim, Z. Xie, M. Mavrikakis, and Y. Xia, Nano Lett., 14, 3570 (2014).
45. M. B. Vukmirovic, J. Zhang, K. Sasaki, A. U. Nilekar, F. Urbe, M. Mavrikakis, and R. R. Adzic, Electrochim. Acta, 52, 2257 (2007).
46. V. Climent, N. M. Markovic, and P. N. Ross, J. Phys. Chem. B, 104, 3116 (2000).
47. W. Liu, P. Rodriguez, L. Borchardt, A. Foelske, J. Yuan, A. K. Herrmann, D. Geiger, Z. Zheng, S. Kaska, N. Gaponik, R. Kotz, T. J. Schmidt, and A. Eychmuller, Angew. Chem. Int. Ed., 52, 9849 (2013).
48. I. E. L. Stephens, A. S. Bondarenko, F. J. Perez-Alonso, F. Calle-Vallejo, L. Bech, T. P. Johansson, A. K. Jepsen, R. Frydendal, B. P. Knudsen, J. Rossmeisl, and J. Chorkendorff, J. Am. Chem. Soc., 133, 5485 (2011).
49. D. F. van der Vliet, C. Wang, D. Li, A. P. Paulikas, J. Greesly, R. B. Rankin, D. Strmcnik, D. Tripkovic, N. M. Markovic, and V. R. Stamenkovic, Angew. Chem., 124, 3193 (2012).
50. M. Wakisaka, S. Morishima, Y. Hyuga, H. Uchida, and M. Watanabe, Electrochem. Commun., 18, 55 (2012).