Effect of hydrophobic cations on the oxygen reduction reaction on single-crystal platinum electrodes

Tomoaki Kumeda1, Hiroo Tajiri2, Osami Sakata3, Nagahiro Hoshi1 & Masashi Nakamura1

Highly active catalysts for the oxygen reduction reaction are essential for the widespread and economically viable use of polymer electrolyte fuel cells. Here we report the oxygen reduction reaction activities of single-crystal platinum electrodes in acidic solutions containing tetralkylammonium cations with different alkyl chain lengths. The high hydrophobicity of a tetralkylammonium cation with a longer alkyl chain enhances the oxygen reduction reaction activity. The activity on Pt(111) in the presence of tetra-n-hexylammonium cation is eight times as high as that without this cation, which is comparable to the activities on Pt3Co(111) and Pt3Ni(111) electrodes. Hydrophobic cations and their hydration shells destabilize the adsorbed hydroxide and adsorbed water. The hydrophobic characteristics of non-specifically adsorbed cations can prevent the adsorption of poisoning species on the platinum electrode and form a highly efficient interface for the oxygen reduction reaction.
The development of highly active catalysts for the oxygen reduction reaction (ORR) is a prominent issue in terms of decreasing Pt loading in cathode catalysts for polymer electrolyte fuel cells (PEFCs). Model electrocatalysts with atomically well-defined surfaces have provided detailed information regarding activation sites, optimal atomic arrangement, and the surface composition of catalysts, which have been applied to nanomaterials for practical use. In the case of Pt-based materials, the introduction of heterometals drastically improves ORR activity, depending on the surface structure. PtM (M = Ni, Co, etc.) bimetal alloys perturb the density of state (DOS) of the d-band and compress the lattice strain of the surface layer. Consequently, the ORR activities on PtM(111) are increased by one order of magnitude as high as that of Pt(111) electrode. In many heterogeneous catalysts, the catalytic activity has a volcano-shaped relationship with the atomic arrangement and alloy composition of the substrate. The variation of the d-band DOS of the substrate modifies the adsorption energy of the reaction products and the intermediate species. Therefore, the center position of the d-band DOS strongly correlates with the ORR activity. Pt,Ni and Pt,Co are located near the top in the volcano-shaped dependency between the activity and the d-band center. The introduction of step and kink structures also activates the ORR; the high-index planes of Pt give the maximum activity for the ORR on the surfaces with 3–4 atomic rows of (111) terrace. The catalyst development through substrate modification has reached a maturity stage, and other approaches are required for further enhancement of the ORR activity.

The activity of electrochemical reactions is affected by the solvent and electrolyte ions as well as the substrate. At the electrode/electrolyte interface, such solution species construct the electric double layer (EDL), which governs the ORR activity on Pt surfaces significantly. It is well known that strongly adsorbed anions, such as halide and sulfate ions, on the Pt surface inhibit the ORR severely. The adsorbed hydroxide (OH$_\text{ads}$) species is formed on Pt surfaces in electrolytic solutions containing ions that weakly interact with Pt surfaces. The stability of OH$_\text{ads}$ depends on the surface structure and on the electronic state of the substrate. Since OH$_\text{ads}$ is also an inhibitor for the ORR, the control of OH$_\text{ads}$ is a key factor in activating the ORR.

In the EDL, some hydrated cations located at the outer Helmholtz plane (OHP) are stabilized as non-specifically adsorbed species through non-covalent interactions, such as hydrogen bonds and electrostatic interactions. Non-covalent interactions in the EDL shift the adsorption equilibrium and the phase transition potential of the adsorbed layer. In alkaline media, the ORR activity of Pt(111) is improved exponentially as the hydration energy of the OHP cations decreases; the activity in CsOH is one order of magnitude higher than that in LiOH. Cations with a high affinity toward oxygen species, such as Li$^+$, strongly stabilize OH$_\text{ads}$, which then deactivated the ORR. Therefore, appropriate control of the structure and hydrophobicity of the interfacial cations can improve ORR activity.

In PEFCs, which use proton-exchange membranes, the control of hydrophobicity is necessary in acidic solutions. In this study, we focus on tetraalkylammonium (TAA) cations of which the hydrophobicity and interfacial structure can be controlled by the alkyl chain length. Variation of the alkyl chain length can change the hydration structure of TAA$^+$ dramatically. We have evaluated the ORR activity on single-crystal Pt electrodes in acidic solutions containing TAA$^+$ with different alkyl chains lengths. The interfacial structures have been also determined by in situ X-ray scattering and infrared (IR) spectroscopy measurements.

**Results**

**Electrochemical characterization.** We used four types of TAA$^+$ with different alkyl chains lengths ($n$): tetramethylammonium (TMA$^+$) $n = 1$, tetraethylammonium (TEA$^+$) $n = 2$, tetra-n-butylammonium (TBA$^+$) $n = 4$, and tetra-n-hexylammonium (THA$^+$) $n = 6$. Figure 1a shows cyclic voltammograms (CVs) in 0.1 M HClO$_4$ containing 10$^{-3}$ M TBA$^+$ and 10$^{-3}$ M THA$^+$; the solubility of TAA$^+$ in acidic solution decreases with the increase of alkyl chain length. The concentrations of TBA$^+$ and THA$^+$ used in this study are approximately equal to the saturation. The CV data show the hydrogen adsorption/desorption region between 0.05 and 0.40 V, the double layer charging/discharging region between 0.40 V and 0.60 V, and the Pt oxidation region between 0.60 V and 0.90 V. In the presence of TBA$^+$ and THA$^+$, the onset potentials for the adsorption of hydrogen and Pt oxidation shift negatively and positively, respectively, whereas the CV data in solutions containing 10$^{-3}$ M TMA$^+$ and TEA$^+$ are identical to those without TAA$^+$ (Supplementary Figure 1a). This indicates that TAA$^+$ with longer alkyl chains affects the adsorption of hydrogen and Pt oxidation, even at low concentrations.

No IR absorption band for the alkyl chain of TAA$^+$ appears, as shown in Supplementary Figure 2. Previous IR study has revealed that the specific adsorption of TAA$^+$ on Pt does not occur above 0 V. Therefore, the potential shift of hydrogen adsorption is not due to site blocking by specifically adsorbed TAA$^+$. The hydrogen adsorption step is governed by the proton-transfer process in the EDL, which depends on the conformation and hydrogen-bonding interactions of hydration water. Density functional theory (DFT) calculations suggest that hydrogen adsorption energy is affected by proton transfer in the water bilayer. These results indicate that TBA$^+$ and THA$^+$ located near the electrode induce the reconstruction of interfacial water, and the inhibition of proton transfer in the EDL results in the potential shift for hydrogen adsorption. In the solutions containing 10$^{-3}$ M TMA$^+$ and TEA$^+$, no potential shift appears even though the concentrations of TMA$^+$ and TEA$^+$ are larger by two or three orders of magnitude than those of TBA$^+$ and THA$^+$. Since the enthalpy of hydration water with TAA$^+$ is reduced by an increase of the alkyl chain length, the enhancement of hydrophobicity with longer alkyl chains strongly perturbs the interfacial water, changing the equilibrium potentials for the adsorption of hydrogen and Pt oxidation on Pt(111).

Figure 1b shows linear sweep ORR voltammograms in 0.1 M HClO$_4$ containing TBA$^+$ and THA$^+$ (voltammograms in TMA$^+$ and TEA$^+$ containing solutions are shown in Supplementary Figure 1b). The specific activities ($j_0$) at 0.90 V in TAA$^+$-containing solutions are shown in Fig. 1c. The ORR activity increases in the sequence THA$^+$ $>$ TBA$^+$ $>$ TEA$^+$ $>$ TMA$^+$. Figure 1c shows a correlation with the hydrophobicity of TAA$^+$. The ORR activity in THA$^+$ is eight times greater than that in 0.1 M HClO$_4$. The structural effects of the substrates on the ORR were investigated using the other typical index planes of Pt, as shown in Fig. 1d (CVs and linear sweep ORR voltammograms are shown in Supplementary Figure 3). There is no significant enhancement effect of THA$^+$ on Pt(100) and Pt(110). However, THA$^+$ enhances the activity on Pt(331) $= 3$(111)−(111), which gives the highest activity for the ORR on stepped surfaces, by 1.3 times. The specific activities on Pt(111) and Pt(331) in THA$^+$-containing solution are comparable with those of Pt$_3$Co and Pt$_3$Ni.
CVs were measured in solutions saturated with Ar. The scanning rate is 0.050 V s⁻¹. The potential was scanned from 0.05 V in the positive direction. The scanning rate is 0.010 V s⁻¹ and the rotation rate of the electrode is 1600 rpm.

δ potential dependence of the band intensity for saturated with O₂, and the potential was scanned from 0.05 V in the positive direction. The scanning rate is 0.010 V s⁻¹ and the rotation rate of the electrode is 1600 rpm.

The positive- and negative-absorption bands at 1650 and 1610 cm⁻¹ are assigned to the in-plane OH adlayer (111), Pt(100), Pt(110), and Pt(331) oxidized Pt(111) between 0.30 and 1.0 V, as shown in Supplementary Figure 2. This fact suggests that the structure of the interfacial THA⁺ is not changed by the electrode potential.

New IR bands appear on THA⁺-modified Pt(111) at 1510 cm⁻¹, which are assigned to the HOH binding mode of adsorbed water monomers at 0.30 V. Since this band overlaps the broad positive-going band around 1570 cm⁻¹, an accurate absorption frequency is unclear. The red shift from 1510 cm⁻¹ to 1090 cm⁻¹ in D₂O solvent indicates that these bands are derived from water (Supplementary Figure 4). On Ni(111), Rh(111), and Ru(0001) under ultra-high vacuum condition, the δHOH shifts from 1595 cm⁻¹ (isolated monomer) to 1560 cm⁻¹ (adsorbed monomer) by the adsorption via oxygen lone pair29-31. The action spectroscopic method using scanning tunneling microscopy also reveals that the signal for water monomer adsorbed on Pt(111) appears around 1550 cm⁻¹. The solid liquid interface, since the interfacial water molecules are hydrogen bonded with neighboring oxygen species and electrolyte ions. The generation of OH adlayer above 0.50 V decreases the coverage of adsorbed water relative to that at the background potential of 0.3 V. The increase in the intensity of δHOH above 0.5 V also involves the orientation change of water induced by the electrode potential, because the water dipole responds sensitively to the electric field in the EDL. The band intensities of non-adsorbed and adsorbed water are also reduced by the modification with THA⁺, indicating the decrease of the coverage of OH adlayer. No IR bands in the CH stretching and CH bending regions appear on THA⁺ modified Pt(111) between 0.30 and 1.0 V, as shown in Supplementary Figure 2. This fact suggests that the structure of the interfacial THA⁺ is not changed by the electrode potential.

The positive- and negative-absorption bands at 1650 and 1610 cm⁻¹ are assigned to the HOH binding mode (δHOH) of non-adsorbed and adsorbed hydrogen bonded water, respectively26,27. The δHOH of non-adsorbed water corresponds to those in the liquid phase (1645 cm⁻¹) and the solid phase (1650 cm⁻¹). It is known that δHOH shifts to lower frequency by adsorption on metal surfaces. These frequencies are higher than δHOH for an isolated water monomer (1595 cm⁻¹ from matrix isolation measurements)28. Therefore, these water molecules are hydrogen bonded with neighboring oxygen species and electrolyte ions. The generation of OH adlayer above 0.50 V decreases the coverage of adsorbed water relative to that at the background potential of 0.3 V. The increase in the intensity of δHOH above 0.5 V also involves the orientation change of water induced by the electrode potential, because the water dipole responds sensitively to the electric field in the EDL. The band intensities of non-adsorbed and adsorbed water are also reduced by the modification with THA⁺, indicating the decrease of the coverage of OH adlayer. No IR bands in the CH stretching and CH bending regions appear on THA⁺ modified Pt(111) between 0.30 and 1.0 V, as shown in Supplementary Figure 2. This fact suggests that the structure of the interfacial THA⁺ is not changed by the electrode potential.

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cation and its hydration shell. The hydronium cation facilitates the construction of a tetrahedral configuration, stabilizing the ice-like structure. Conversely, the hydration shell around hydrophobic cations such as THA\textsuperscript{+} disrupts the tetrahedral hydrogen-bonding network. As a consequence, the monomeric species may be stabilized on the surface.

**X-ray crystal truncation rod measurement of interfacial structures.**

Electron density profiles along the surface normal direction were estimated from X-ray specular crystal truncation rod (CTR) scattering. Figure 3a shows the specular CTR profiles of Pt(111) in 0.1 M HClO\textsubscript{4} with and without 10\textsuperscript{-6} M THA\textsuperscript{+}. The CTR profiles were obtained at 0.5 and 0.9 V, which are the double layer and the OH adsorption regions, respectively. Normalized CTR profiles are shown in Supplementary Figure 5a. While the CTR profiles with and without THA\textsuperscript{+} at 0.50 V are nearly identical, the CTR at 0.90 V is clearly altered by the addition of THA\textsuperscript{+}. Since THA\textsuperscript{+} is composed of nitrogen, carbon, and hydrogen, the electron density in the EDL is significantly lower than that of Pt. Therefore, the primary factor for this variation in the CTR is the structural change in the substrate Pt. The initial model used for structural optimization comprises three Pt layers and one oxygen layer of water molecule or OH ad layer. The vertical atomic position, occupancy factor, and Debye-Waller factors for the Pt and oxygen layers were optimized by the least-squares method. The electron density profiles and the structural parameters of the optimized model are shown in Supplementary Figure 5b and Supplementary Table 1, respectively.

Schematic models of the interfacial structure are shown in Fig. 3b. At 0.50 V, the layer distance between oxygen and the 1st Pt layer is 2.14 Å, while the layer distance between oxygen and the 1st Pt layer is 2.37 Å. At 0.90 V, the layer distance between oxygen and the 1st Pt layer is 2.29 Å, while the layer distance between oxygen and the 1st Pt layer is 2.28 Å.

**Fig. 2** Infrared spectroscopic measurement of species adsorbed on platinum(111). a Specular potential dependence of infrared spectra on Pt(111) and Pt(111) modified with tetra-n-hexylammonium cation (THA\textsuperscript{+}) in 0.1 M acidic solutions saturated with Ar. The potential of the background spectra is 0.30 V versus reversible hydrogen electrode (RHE). The potentials of the sample spectra are stepped in the positive direction. b Potential dependence of the charge density of Pt oxidation and the band intensity of δ\textsubscript{POH}.

**Fig. 3** X-ray crystal truncation rod measurement of interfacial structure on platinum(111). a Specular crystal truncation rod (CTR) profiles of Pt(111) in 0.1 M HClO\textsubscript{4} with and without 10\textsuperscript{-6} M tetra-n-hexylammonium cation (THA\textsuperscript{+}) saturated with Ar at 0.50 V and 0.90 V versus reversible hydrogen electrode (RHE). The dots are the data points and the solid lines are the structure factors calculated using the optimized model. b Schematic models of the interfacial structure.
The hydration energies of tetraalkylammonium cations were calculated using the following equation:

$$\Delta_h^{\text{hydr}} = -2.14 \text{ Å}.$$  

The hydration structures of interfacial cations were assumed by Monte Carlo simulations and X-ray measurements. The increase of the hydration energy of alkali metal cations is inversely correlated to the ORR activity in TMA$^+$. The order of the hydration energy of alkali metal cations (Li$^+ > Na^+ > K^+ > Cs^+$) is inversely correlated to the ORR activity (Cs$^+ > K^+ > Na^+ > Li^+$). Previous IR and X-ray studies have revealed that Li$^+$ located at the OHP inhibits the surface oxidation of Pt(111) due to the stabilization effect between Li$^+$ and OH$_{ad}$, whereas high-order oxidation accompanied by surface roughness proceeds in solution containing Cs$^+$. Thus, OH$_{ad}$ is stabilized by the interaction with species that have high-hydration affinity. The hydration structures of interfacial cations were assumed from the OH stretching band frequency$^{21,22}$. The hydration water around hydrophilic cations, such as H$^+$ and Li$^+$, is coordinated with the dipole moment pointed outward and the hydrogen atoms of the hydration water, which can link with the oxygen species located in the secondary hydration sphere. Conversely, hydrophobic cations such as TAA$^+$ weaken the bonding with hydration water and strengthen intermolecular hydrogen bonding in the primary hydration shell. Consequently, the hydration shell around the hydrophobic cation is restricted to coordination with the outer oxygen species because of the complete hydrogen-bonding network within the shell. The ORR activity in TMA$^+$ is comparable with that in HClO$_4$ without TAA$^+$, indicating that TMA$^+$ does not contribute the enhancement of the ORR. Since the hydration shell size of TMA$^+$ is smaller than those of the other TAA$^+$, the complete hydrogen-bonding network may not be constructed in the shell.

The OHP cations interact with the charged species in the EDL as well as the substrate. Therefore, cations electrostatically interacting with adsorbed anions can approach the surface at the potentials more positive than the potential of zero charge (pzc)$^{17,20,46,47}$. The coverage of the OHP cations is balanced with that of the adsorbed anions and the surface charge depending on the electrode potential. On the surface at a constant coverage of adsorbed counter anions, the coverage of the OHP cation decreases with increasing potential$^{17}$. As described above, the IR spectra indicate that the coverage of TAA$^+$ is approximately constant in the potential region examined in this study. The increase in the coverage of the negatively charged species, i.e., OH$_{ad}$ and O$_{ad}$, is balanced by positive surface charge so that the coverage of the TAA$^+$ remains constant.

While the ORR activity on Pt(111) is dramatically enhanced by the presence of TAA$^+$, there is no significant enhancement of the ORR on Pt(100), Pt(110) and Pt(331) by TAA$^+$. In acidic solution above 0.6 V, the hydration water around H$^+$ is linked with OH$_{ad}$ through hydrogen bond (Fig. 5a). H$^+$–H$_2$O–OH$_{ad}$ formation stabilizes the OH$_{ad}$ layer and inhibits the ORR. According to studies on the Pt(111) surface under the ultra-high vacuum condition, the coadsorption of OH$_{ad}$ and H$_2$O forms a well-defined 3 x 3 honeycomb structure because the symmetry and OH–O distance in the coadsorbed layer fit well with the Pt(111) lattice$^{14,48}$. The approach of the hydration shell around TAA$^+$ to the Pt surface disrupts the stabilization effect between the hydration water and the OH$_{ad}$ layer (Fig. 5b). The coverage of OH$_{ad}$ is decreased by this destabilization effect, which induces the disruption of stable hydrogen-bonding network in the coadsorbed layer. These multiple effects are enhanced by the hydrophobicity of cation and promote the access of oxygen molecules to the Pt(111) surface.

The IR spectra on Pt(100) indicate that the addition of TAA$^+$ results in a slight reduction of the band intensity and band broadening of $\delta$$_{\text{OH}}$ as shown in Supplementary Figure 6. The charge densities for surface oxidation also decrease on Pt(110) and Pt(331) above 0.7 V after the addition of TAA$^+$. For Pt(100), the coverage of OH$_{ad}$ is not adsorbed at 0.50 V. Conversely, in the presence of THA$^+$, the coverage of the OHP cations decreases with increasing potential$^{17}$. As described above, the IR spectra indicate that the coverage of TAA$^+$ is approximately constant in the potential region examined in this study. The increase in the coverage of the negatively charged species, i.e., OH$_{ad}$ and O$_{ad}$, is balanced by positive surface charge so that the coverage of the TAA$^+$ remains constant.

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Fig. 5 Schematic of interfacial hydrated cations and adsorbed hydroxide species. a hydrophilic cation and (b) hydrophobic cation. Arrows indicate the direction of water dipole within the hydration shell. (Platinum is represented by gray spheres, oxygen by blue spheres, and hydrogen by pink spheres.)

Pt(111), and Pt(331), although OH adsorption is inhibited by the approach of the THA⁺ hydration shell, the ORR enhancement effect by the disruption of OH_ads + H₂O hydrogen-bonding network is weak due to the narrow (111) terrace and the lattice mismatch of the OH_ads + H₂O honeycomb layer with the substrate. The Pt(331) surface having a (111) terrace shows high-ORR activity in HClO₄ without TAA⁺ 8. DFT calculations suggest that the OH_ads on stepped Pt surfaces is destabilized by deforming the hydrogen bonds of interfacial water surrounding the adsorption sites, and the destabilization of oxygen species cause the enhancement of the ORR on the (111) terrace.⁵⁹

The ORR activity on Pt(111) in THA⁺ is comparable with those on Pt₃Co(111) and Pt₃Ni(111) in HClO₄. The activation factor for the ORR with these Pt alloys is also due to decrease in the coverage of OH_ads. Therefore, a similar inhibiting effect of OH_ads can be achieved by the structural improvement in EDL species. Furthermore, the supply of oxygen molecules to the electrode may be improved by weakening the hydrogen-bonding strength around the hydrophobic cations.

In summary, we evaluated the ORR activities of single-crystal Pt electrodes in HClO₄ solutions containing TAA⁺ with various alkyl chain lengths. The ORR activity increased in the following sequence THA⁺ n = 6 » TAA⁺ n = 4 > TMA⁺ n = 2 > TMA⁺ n = 1 = HClO₄ and the ORR activity on Pt(111) in THA⁺ was comparable with those on Pt₃Co(111) and Pt₃Ni(111) in HClO₄. In situ IR and X-ray CTR measurements indicated that the coverage of OH_ads on Pt(111) at 0.90 V in the presence of THA⁺ is decreased. The weaker interaction between the hydration shell around THA⁺ and OH_ads destabilizes the OH_ads + H₂O coadsorbed layer and forms a highly efficient interface for the ORR.

Methods

Electrochemical measurement: Single-crystal Pt beads for CV measurement were prepared by the Clavilier’s method.⁵⁹ The crystal beads were oriented to (111), (100), (110), and (331) using Laue back reflection of X-ray, and then mechanically polished with diamond slurries. A Pt(111) disk (8 mm in diameter, MatTech) was used for the X-ray CTR measurement. The samples were annealed in H₂ or Ar atmosphere. The annealed surfaces were protected with ultrapure water (Milli-Q Advantage A10, Millipore). The solutions were prepared with HClO₄ (Kanto Chemical), HF (Kanto Chemical), tetraethylammonium salts, and ultrapure water. The tetraalkylammonium salts used were tetramethylammonium perchlorate (Tokyo Chemical Industry), tetraethylammonium perchlorate (Tokyo Chemical Industry), tetra-n-butylammonium perchlorate (Sigma-Aldrich), and tetra-n-hexylammonium perchlorate (Alfa Aesar). The reference electrode used in all measurements was a reversible hydrogen electrode (RHE). The ORR voltammograms were measured in the hanging meniscus rotating disk electrode (RDE) configuration using an electrochemical analyzer (ALS 702DH, BAS) and a rotating ring-disk electrode apparatus (RDE-E3.3 A, BAS).⁵⁵ The ORR activity was estimated from the kinetic current density (specific activity, j) at 0.90 V versus RHE according to the Koutecky-Levich equation: 1/j = 1/jₘ + 1/jₙ, where jₘ and jₙ are the total current density and the limiting current density, respectively. The current densities were normalized to the geometrical surface area of the Pt surface.

Infrared spectroscopy: In situ infrared reflection absorption spectroscopy (IRAS) measurement was performed using a Fourier transform (FTIR) spectrometer (Bruker Vertex 70v). An electrochemical IR cell with a tapered BaF₂ or CaF₂ window beveled at 60° was attached to the spectrometer with a narrow band mercury-cadmium-telluride (MCT) detector. A polypropylene film (Chempex Industries) with a thickness of 6 µm was intercalated between the BaF₂ prism and the Pt(111) and Pt(100) surfaces to prevent the dissolution of the BaF₂ material.⁵⁰ A layer of water was placed between the BaF₂ prism and the polymer film to compensate for the gap of the refractive index. The interferograms were averaged over 640 scans by subtractively normalized interfacial FTIR (SNIFTIRS) with p-polarized light at a resolution of 4 cm⁻¹. In THA⁺ containing solution, the adsorption of OH_ads is inhibited by the repetitive potential steps of SNIFTIRS measurement because THA⁺ assembles on the surface at the negative potentials. Therefore, after the Pt(111) and Pt(100) electrodes were immersed in 0.1 M HClO₄ and 0.1 M HF containing THA⁺ for 5 min, IR measurement was performed in the solution without THA⁺. We confirmed that Pt(111) modified with THA⁺ shows the same voltammograms and ORR activity.

X-ray crystal truncation rod scattering: In situ X-ray CTR measurement was performed with a multi-axis diffractometer at BL13XU (Spring-8). The X-ray energy used was 20 keV. Integrated intensities were measured by rocking scans, and then corrected for Lorentz and area factors. Spectral CTR was measured along the surface normal direction L in units of c⁻¹ |k| = 0.6797 nm. Structure refinements were conducted using the least-squares method with the ANA-ROD program.⁵⁴

Data availability

The data that support the findings of this study are available within the paper and Supplementary Information, as well as from the corresponding author upon request.

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References

1. Zhang, C., Shen, X., Pan, Y. & Peng, Z. A review of Pt-based electrocatalysts for oxygen reduction reaction. Front. Energy 11, 268–285 (2017).

2. Lv, H. et al. Recent advances in the design of tailored nanomaterials for efficient oxygen reduction reaction. Nano Energy 29, 149–165 (2016).

3. Gomez-Marín, A. M., Rizo, R. & Felu, J. M. Oxygen reduction reaction at Pt single crystals: a critical overview. Catal. Sci. Technol. 4, 1685–1698 (2014).

4. Stamenkovic, V. et al. Changing the activity of electrocatalysts for oxygen reduction by tuning the surface electronic structure. Angew. Chem. Int. Ed. 45, 2897–2901 (2006).

5. Strasser, P. et al. Lattice-strain control of the activity in dealloyed core–shell fuel cell catalysts. Nat. Chem. 2, 454–460 (2010).

6. Stamenkovic, V. R. et al. Improved oxygen reduction activity on Pt₃Ni(111) via increased surface site availability. Science 315, 493–497 (2007).

7. Kobayashi, S., Nakamura, M. & Hoshi, N. The oxygen reduction reaction on Pt(111) in acid solutions: intrinsic kinetic parameters and anion adsorption effects. J. Electroanal. Chem. 599, 333–343 (2007).

8. Sugimura, F., Nakamura, M. & Hoshi, N. The oxygen reduction reaction on Pt(111) and Pt(100) in solutions containing chloride ions. J. Phys. Chem. C. 112, 11234–11240 (2017).

9. Kuzume, A., Herrero, E. & Felu, J. M. Oxygen reduction on stepped platinum surfaces in acidic media. J. Electroanal. Chem. 599, 333–343 (2007).

10. Sugimura, F., Nakamura, M. & Hoshi, N. The oxygen reduction reaction on stepped Pt surfaces. J. Electroanal. Chem. 1698, 46–50 (2017).

11. Kobayashi, S., Nakamura, M. & Hoshi, N. Effect of alloy composition and crystal face of Pt on the oxygen reduction reaction. Ind. Eng. Chem. Res. 51, 285–289 (2012).

12. Markovic, N. M., Gasteiger, H. A., Grgur, B. N. & Ross, P. N. Oxygen reduction reaction on Pt(111): effects of bromide. J. Electroanal. Chem. 467, 157–163 (1999).

13. Stamenkovic, V. R., Markovic, N. M. & Ross, P. N. Structure-relationships in electrocatalysis: oxygen reduction and hydrogen oxidation reactions on Pt and Pt(100) in solutions containing chloride ions. J. Electroanal. Chem. 500, 44–51 (2001).

14. Wang, J. X., Markovic, N. M. & Adzie, R. R. Kinetic analysis of oxygen reduction on Pt(111) in acid solution: intrinsic kinetic parameters and anion adsorption effects. J. Phys. Chem. B 108, 4127–4133 (2004).

15. Wakisaka, M., Udagawa, Y., Suzuki, H., Uchida, H. & Watanabe, M. Structural effects on the surface oxidation processes at Pt single-crystal electrodes.
Nakamura, M., Sato, N., Hoshi, N. & Sakata, O. Outer Helmholtz plane of the
aqueous electrolyte formed at the solid liquid interface. *ChemPhysChem* 12, 1430–1434 (2011).

Nakamura, M., Nakajima, Y., Sato, N., Hoshi, N. & Sakata, O. Structure of the
electrical double layer on Ag(100): promotive effect of cationic species on Br
adlayer formation. *Phys. Rev. B* 84, 165433 (2011).

Srirmuk, D. et al. The role of non-covalent interactions in electrocatalytic
fuel cell reactions on platinum. *Nat. Chem.* 1, 466–472 (2009).

Nakamura, M., Nakajima, Y., Hoshi, N., Tajiiri, H. & Sakata, O. Effect of non-
specifically adsorbed ions on the surface oxidation of Pt(111). *ChemPhysChem*
14, 2426–2431 (2013).

Yamakata, A. & Osawa, M. Destruction of the water layer on a hydrophobic
surface induced by the forced approach of hydrophilic and hydrophobic
cations. *J. Phys. Chem. C.* 114, 1487–1491 (2010).

Yamakata, A. & Osawa, M. Cation-dependent restructuration of the electric
double layer on CO-covered Pt electrodes: difference between hydrophilic and
hydrophobic cations. *J. Electroanal. Chem.* 800, 19–24 (2016).

Duwell, M., Wang, J. & Xu, B. Surface enhanced spectroscopic investigations of
adsorption of cations on electrochemical interfaces. *Phys. Chem. Chem. Phys.*
19, 971–975 (2017).

Skulasen, E. et al. Density functional theory calculations for the hydrogen
evolution reaction in an electrochemical double layer on the Pt(111) electrode.
*Phys. Chem. Chem. Phys.* 9, 3241–3250 (2007).

Marcus, Y. Tetraalkylammonium ions in aqueous and non-aqueous solutions.
*J. Chem. Phys.* 111, 1998–2008 (2000).

Osawa, M., Tsuchiya, M., Mogami, H., Samjeske, G. & Yamakata, A.
Structure of water at the electrified platinum-water interface: a study by
surface-enhanced infrared absorption spectroscopy. *J. Phys. Chem. C.* 112,
4248–4256 (2008).

Nakamura, M., Ito, H. & Hoshi, N. Infrared spectroscopy of water adsorbed on
M(111) (M = Pt, Pd, Rh, Au, Cu) electrodes in sulfuric acid solution.
*J. Phys. Chem. C.* 112, 9458–9463 (2008).

Bentwood, R. M., Barnes, A. J. & Orville-Thomas, W. J. Studied of
intermolecular interactions by matrix isolation vibrational spectroscopy:
Self-association of water. *J. Mol. Spectrosc.* 84, 391–404 (1980).

Nakamura, M. & Ito, M. Ring hexamer like cluster molecules of water formed
on a Ni(1 1 1) surface. *Chem. Phys. Lett.* 384, 256–261 (2004).

Yamamoto, S., Beniya, A., Mukai, K., Yamashita, Y. & Yoshinobu, J.
Water adsorption on Rh(111) at 20 K: from monomer to bulk amorphous ice.
*J. Phys. Chem. B* 109, 5816–5823 (2005).

Nakamura, M. & Ito, M. Infrared spectroscopic study of water adsorbed on
Na on the Ru(001) surface. *Surf. Sci.* 502–503, 144–148 (2002).

Motoyabashi, K. et al. Adsorption of water dimer on platinum(111): identification
of the -OH+Pt hydrogen bond. *ACS Nano* 8, 11583–11590 (2014).

Shingaya, Y. & Ito, M. Coordination number and molecular orientation of
hydronium cation/bisulphate anion adlayers on Pt(111). *Surf. Sci.* 368, 318–323
(1996).

Kondo, T., Masuda, T., Aoki, N. & Usoski, K. Potential-dependent structures and
potential-induced structure changes at Pt(111) single-crystal electrode/
sulfuric and perchloric acid interface in the potential region between hydrogen
underpotential deposition and surface oxide formation by in situ surface X-
ray scattering. *J. Phys. Chem. C.* 120, 16118–16131 (2016).

Michaelides, A., Ranae, V. A., de Andres, P. L. & King, D. A. General model
for water monomer adsorption on close-packed transition and noble metal
surfaces. *Phys. Rev. Lett.* 90, 216102 (2003).

Meng, S., Wang, E. G. & Gao, S. Water adsorption on metal surfaces: a general
picture from density functional theory studies. *Phys. Rev. B* 69, 195404 (2004).

Gruder, Y. & Lucas, A. C. Surface X-ray diffraction studies of single crystal
electrocatalysts. *Nano Energy* 29, 378–393 (2016).

Hirota, K., Song, M., -B. & Ito, M. In-situ infrared spectroscopy of water and
electrolytes adsorbed on a Pt(111) electrode surface in acid solution. Structural
changes of adsorbed water molecules upon an electrode potential. *Chem.
Phys. Lett.* 255, 335–341 (1996).

Arthara, K., Kitamura, F., Ohsaka, T. & Tokuda, K. Characterization of the
adsorption state of carbonate ions on the Au(111) electrode surface using in situ
IRAS. *J. Electroanal. Chem.* 510, 128–135 (2001).

Seitsonen, A. P., Zhu, Y., Bedurflich, K. & Over, H. Bonding mechanism and
atomic geometry of an ordered hydroxyl overlayer on Pt(111). *J. Chem.
Phys.* 123, 7347–7351 (2001).

Rai, V., Aryanpour, M. & Pitsch, H. First-principle analysis of oxygen-
containing adsorbates formed from the electrochemical discharge of water on
Pt(111). *J. Phys. Chem. C.* 112, 9760–9768 (2008).