

Mobility and Reactivity of Oxygen Adspecies on Platinum Surface

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S Supporting Information

ABSTRACT: The adsorption and mobility of oxygen adspecies on platinum (Pt) surface are crucial for the oxidation of surface-adsorbed carbon monoxide (CO), which causes the deactivation of Pt catalyst in fuel cells. By employing nanoelectrode and ultramicroelectrode techniques, we have observed the surface mobility of oxygen adspecies produced by the dissociative adsorption of H₂O and the surface reaction between the oxygen adspecies and the preadsorbed CO on the Pt surface. The desorption charge of oxygen adspecies on a Pt nanoelectrode has been found to be in proportion to the reciprocal of the square root of scan rate. Using this information, the apparent surface diffusion coefficient of oxygen adspecies has been determined to be $(5.61 \pm 0.84) \times 10^{-10}$ cm²/s at 25 °C. During the surface oxidation of CO, two current peaks are observed, which are attributed to CO oxidation at the Pt/electrolyte interface and the surface mobility of the oxygen adspecies on the adjacent Pt surface, respectively. These results demonstrate that the surface mobility of oxygen adspecies plays an important role in the antipoisoning and reactivation of Pt catalyst.

The adsorption, desorption, mobility, and reactivity of the oxygen adspecies on the surface of catalysts are central to the surface science and heterogeneous catalysis.^{1–7} Faradaic adsorption and desorption are surface processes involving electron transfer. Despite the extensive investigations of the adsorption of oxygen adspecies and carbon monoxide (CO) on Pt surface over the last century, these processes remain as the key issues of fuel cells and water electrolysis.^{8–16} Although surface mobility of oxygen adspecies produced by the dissociative adsorption of water is important in electrocatalysis, the quantitative measurement of such a property of oxygen adspecies have rarely been reported probably due to the complexity of solid/liquid interface as well as the lack of applicable experimental techniques.

The experimental techniques reported for the investigation of surface mobility include field emission microscopy,¹⁷ field ionic microscopy,¹⁸ laser-induced thermal desorption,¹⁹ and scanning tunneling microscopy (STM).²⁰ Except STM,²¹ these methods generally require ultrahigh vacuum or are performed in a solid/gas environment. Methods have also been established for the quantitative analysis of surface mobility in the solid/electrolyte interface.^{22–34} For example, scanning electrochemical microscope induced desorption (SECMID) has been developed for the measurement of lateral diffusion of H⁺ along hydrous metal oxides,²⁷ stearic acid monolayers,²⁸ and phospholipid assem-

blies.²⁹ In addition, electrochemical nuclear magnetic resonance (EC-NMR) has been developed recently to study surface diffusion of CO on Pt surface.^{32,35}

Despite the above-mentioned advances, the influence of the introduced external physical-fields on the surface mobility of adspecies remains unknown. For example, surface mobility of certain adspecies on conductive substrate was measured statistically by rapid STM imaging.^{31,36,37} However, the strong electric field between the tip and substrate introduced by STM can cause the adspecies to migrate on the surface. Surface mobility of oxygen adspecies has also been studied by chronoamperometry and cyclic voltammetry without interference from external physical fields.^{26,38–42} However, the surface diffusion coefficients obtained using these methods in a Pt/Nafion system are as high as 1.49×10^{-4} cm²/s for hydrogen adatoms and 1.65×10^{-3} cm²/s for oxygen adspecies due to the uncertain properties of the reactive interface.^{39–41}

The electrochemical behaviors of ultramicroelectrodes (UMEs) and nanoelectrodes (NEs) are much different from those obtained on macroelectrodes due to their small size of electrode/electrolyte interface, which changes the properties of interfacial structure as well as the mass transfer and charge transfer processes.^{43–53} Using UME and NE techniques, we reinvestigated the Faradaic adsorption and desorption processes of oxygen adspecies on Pt surface. The surface mobility of oxygen adspecies has been observed, and its role on the catalytic oxidation of CO on Pt surface has also been investigated.

The SEM image of a Pt NE after electrochemical experiments showed a coplanar disk-like electrode (Figure 1a). The apparent radius of the electrode was determined to be 262 nm (Figure 1b) by using the steady-state limiting current of Ru(NH₃)₆Cl₃ (diffusion coefficient of 6.3×10^{-6} cm²/s).⁴⁸ The cyclic voltammograms of the Pt NE in a 0.5 M H₂SO₄ solution had no difference from those obtained using a macroscopic electrode. The adsorption/desorption processes for both hydrogen and oxygen adspecies were observed. When the potential for the reverse scan was set at 1.1 V vs RHE, a monolayer of oxygen adspecies (i.e., OH, an important reactant in CO oxidation) was formed on the polycrystalline Pt surface.⁵⁴ Different from that on a macroscopic electrode, Faradaic desorption current of oxygen adspecies on the Pt NE was no longer in proportion to the scan rate (ν), but in proportion to $\nu^{1/2}$ instead. Since the Faradaic desorption current is potential dependent, we integrated the charge in the whole range of the desorption potential and found that the total charge was in a linear relationship with $\nu^{-1/2}$ (Figure 1d). This interesting observation prompted us to reinvestigate

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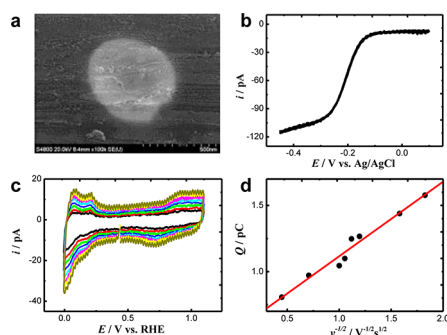


Figure 1. (a) SEM image of the Pt NE after electrochemical experiments. (b) Steady-state voltammogram of the Pt NE in an aqueous solution containing 2 mM $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ and 0.1 M NaCl with a scan rate of 0.05 V/s. (c) Cyclic voltammograms of the Pt NE in an aqueous solution containing 0.5 M H_2SO_4 with the scan rate of 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1 V/s. (d) Linear relationship between the integrated desorption charge of oxygen adspecies and the reciprocal of the square root of scan rate.

the surface electrochemistry of the absorbed oxygen species on Pt NEs, which might involve not only the Faradaic adsorption and desorption but also the surface mobility of the oxygen adspecies.

We have studied previously the surface diffusion and spillover behaviors of hydrogen adatoms on Pt NEs. In these studies, unusually high roughness factors (RF) were obtained using the integrated charge of the desorption of hydrogen adatoms.⁴⁴ The “abnormal” phenomenon could be explained by resorting to [Figure 2](#). When a glass-sealed Pt electrode is immersed in the

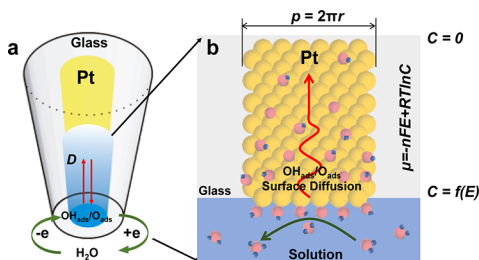


Figure 2. Schematic diagrams of the surface adsorption, mobility, and desorption on Pt surface. (a) The oxygen adspecies are generated by the dissociative adsorption of H_2O at the Pt/electrolyte interface and diffuse along the adjacent Pt surface. (b) Unfolding picture of (a), showing the driving force of surface mobility is actually the surface concentration gradient of oxygen adspecies.

electrolyte solution, there is a Pt surface adjacent to the Pt/electrolyte interface. If adspecies can diffuse from the boundary of the Pt/electrolyte interface to the adjacent Pt surface, the apparent RF can be expressed as $(n_1 + 2l/r)$, where n_1 is the normal RF usually no higher than 3 for a mirror disk electrode, l is the diffusion distance, and r is the electrode radius (see S5 of the [Supporting Information](#) for more details). In the case of a macroscopic electrode with $r \geq 1$ mm, the equation of RF reduces to n_1 because the surface diffusion distance (l) is much smaller than the electrode radius (r). However, if the electrode size is decreased to micrometer or nanometer scale, n_1 can be neglected and the RF simplifies to $2l/r$. It is thus the size effect of NE and UME that makes them suitable for the study of the surface mobility of adspecies.

The surface mobility of oxygen adspecies can be understood using thermodynamics. When H_2O is dissociated at the Pt/

electrolyte interface, the surface concentration of oxygen adspecies in this area is higher than that on the adjacent Pt surface. The concentration difference of oxygen adspecies leads to a chemical potential ($\mu = -nFE + RT \ln C$) gradient between these two areas. As a result, the oxygen adspecies move from the boundary of Pt/electrolyte interface (high chemical potential) onto the adjacent Pt surface (low chemical potential). When the potential scans backward, the oxygen adspecies accumulated on the adjacent Pt surface move back to the boundary of Pt/electrolyte interface and desorb there. The surface mobility of oxygen adspecies should abide by the Fick’s second law. Hence, the Faradaic current associated with the surface mobility can be expressed by the following equation:⁵⁵

$$i = nFp(nF/RT)^{1/2} C^* D^{1/2} \nu^{1/2} \pi^{1/2} \chi(\sigma t) \quad (1)$$

Because the Faradaic current is potential dependent, it is thus better to quantify the integral charge with the scan rate. From [eq 1](#), the integral charge is expressed as follows:

$$Q_d = \int i dt = \left[nFp \left(\frac{nF}{RT} \right)^{1/2} C^* D^{1/2} \pi^{1/2} \int_{E_1}^{E_2} \chi(\sigma t) dE \right] \nu^{-1/2} \quad (2)$$

where Q_d is the integral charge of the Faradaic desorption caused by the surface diffusion of oxygen adspecies, n is the electron transfer number of Faradaic desorption, F is the Faraday constant, p is the perimeter of the disc Pt NE, R is the gas constant, T is the absolute temperature, C^* is the saturate surface concentration of oxygen adspecies, D is the surface diffusion coefficient of oxygen adspecies, E_1 and E_2 are the initial and end potentials for Faradaic desorption, and ν is the scan rate; details of $\chi(\sigma t)$ can be found in the literature.⁵⁶ From the linear relationship between Q and $\nu^{-1/2}$, the apparent surface diffusion coefficient (D) of oxygen adspecies on Pt surface was determined to be $(5.61 \pm 0.84) \times 10^{-10} \text{ cm}^2/\text{s}$ at 25 °C ([Figure 1d](#) and [Figure S4](#) for more details).

The surface diffusion coefficient D can be expressed in an Arrhenius form as⁵⁷

$$D = D_0 \exp(-\Delta E_d/kT) \quad (3)$$

$$D_0 = \nu \lambda^2 \exp(\Delta S_d/k) \quad (4)$$

where ΔE_d is the activation energy of surface diffusion, k is the Plank constant, T is the absolute temperature, ν is the effective vibrational frequency of the adsorbate, λ is the average distance in each jump, ΔS_d is the difference in the entropy of the system, and D_0 is the pre-exponential factor. The activation energy of surface diffusion ΔE_d and the pre-exponential factor D_0 can thus be determined by measuring the temperature dependence of D . Experimentally, the surface diffusion coefficient (D) of oxygen adspecies on Pt NEs was measured under different temperatures from 303 to 333 K ([Figure 3](#)). From these data, the pre-exponential factor D_0 and the activation energy ΔE_d were determined to be $1.62 \times 10^{-7} \text{ cm}^2/\text{s}$ and 13.67 kJ/mol, respectively (see S4 of the [Supporting Information](#) for details).

We next investigated the oxidative desorption of CO on Pt surface using an epoxy-sealed Pt ultramicroelectrode (UME) with a radius of 5 μm . In these experiments, CO was first preadsorbed on the Pt surface and then a potential was applied on the Pt UME (details see S1). When the applied potential enters into the “oxygen” region, a stripping current peak was observed due to the reaction between the surface-absorbed CO

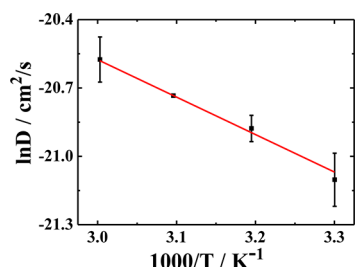


Figure 3. Arrhenius relationship between the apparent surface diffusion coefficient D of oxygen adspecies and the temperature on Pt NEs in an aqueous solution containing 0.5 M H_2SO_4 .

molecules and oxygen adspecies. In the well-known bifunctional mechanism of Pt–Ru catalyst, surface mobility of oxygen adspecies on Ru plays an important role in the oxidative desorption of CO on Pt surface.^{58,59} However, we demonstrated that the surface mobility of oxygen adspecies on the Pt itself can be used for the reactivation of the catalyst. As shown in Figure 4a,

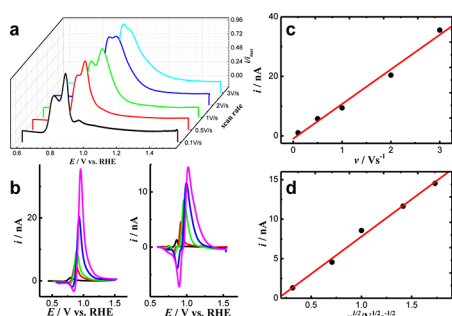


Figure 4. (a) Stripping voltammograms of the preadsorbed CO on an epoxy-sealing Pt UME with a radius of 5 μm in 0.5 M H_2SO_4 solution, the scan rates are 0.1, 0.5, 1, 2, and 3 V/s. (b) Separated current Peak 1 (left) and the separated current Peak 2 (right) after background subtraction. (c) Linear relationship between the first peak currents and the scan rates. (d) Linear relationship between the second peak currents and the square root of scan rates.

two stripping peaks of CO oxidation on Pt UME could be observed even at scan rate as high as 3 V/s. The peak currents of the first and second peaks were found to be in proportion to the scan rate and square root of the scan rate, respectively (Figure 4b–d). These data suggested that first peak was attributed to the oxidative desorption of the CO adsorbed at the Pt/electrolyte interface, and the second one was attributed to the surface mobilities of either oxygen adspecies or CO at the adjacent Pt surface. To distinguish these two possibilities, based on the linear relationship between i and $v^{1/2}$ (Figure 4d), the apparent surface diffusion coefficient is estimated as $6.8 \times 10^{-10} \text{ cm}^2/\text{s}$, which is close to the mobility of oxygen adspecies and much higher than that of CO ($3.6 \times 10^{-13} \text{ cm}^2/\text{s}$) reported previously using EC-NMR.³² It can be concluded that the oxidative desorption of CO on Pt surface is a bimolecular reaction involving the surface mobility of oxygen adspecies.

In conclusion, we have demonstrated that the surface mobility of oxygen adspecies on the Pt surface can be measured using NE or UME. By using this technique, the surface reaction of oxygen adspecies with CO on Pt was also observed. When surface mobility process is involved, the integrated charge is found to be in proportion to $v^{-1/2}$ instead of v . Based on this relationship, the apparent surface diffusion coefficient and the activation energy of surface mobility can be determined, providing valuable

information for the understanding of the catalytic mechanism of surface reaction.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b05259.

Experimental details and more experimental data (PDF)

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Notes

The authors declare no competing financial interest.

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