单层 FeO 薄膜表面周期性氧缺陷结构的形成

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摘要: 采用扫描隧道显微镜和 X 射线光电子能谱对含有次表层 Fe 的 Pt 表皮结构 (Pt skin), 即 0.4 ML Fe 的 Pt/Fe/Pt(111) 表面, 在 1.1×10^{-7} kPa 氧气气氛退火过程中的变化进行了研究。结果表明, 当退火温度为 600 K 时, 氧气在 Pt/Fe/Pt(111) 表面上解离吸附并诱导表面局域结构的重构; 750 K 时次表层 Fe 可以扩散到表面并被氧化; 当升至 850 K 时, 在样品表面形成单层 FeO 结构, 并且 FeO 表面具有周期性的缺陷。这种缺陷是由于单层 FeO 薄膜的摩尔条纹单胞中 fcc 位上一个或多个氧原子缺失形成的, 其中多原子空位被确定为缺失 6 个氧原子所致。FeO 表面缺陷结构的研究为理解 Fe-Pt 催化剂在氧化气氛中的结构稳定性以及构造表面活性位提供一定的基础。

关键词: 铁; 铂; 双金属催化剂; 氧化亚铁薄膜; 氧空位缺陷; 扫描隧道显微镜

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Formation of Periodic Arrays of O Vacancy Clusters on Monolayer FeO Islands Grown on Pt(111)

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Abstract: The structural evolution of a Pt surface with 0.4 monolayer (ML) subsurface Fe on annealing in 1.1×10^{-7} kPa O₂ was studied by scanning tunneling microscopy and X-ray photoelectron spectroscopy. When the annealing temperature was 600 K, only dissociative adsorption of O₂ occurred, which induced the local restructuring of surface regions. At 750 K, subsurface Fe atoms segregated onto the surface and were oxidized. When the annealing temperature was increased to 850 K, well defined monolayer FeO islands with periodic arrays of defects were formed. The defects were located at the hexagonal closest packed sites (fcc) of FeO Moiré unit cells and were either single oxygen vacancies or multiple oxygen vacancies consisting of six missing O atoms. The formation of periodic defects on monolayer FeO islands may be a way to construct active sites on Pt-Fe model catalysts.

Key words: iron; platinum; bimetallic catalyst; iron oxide film; oxygen vacancy; scanning tunneling microscopy

The slow rate of the oxygen reduction reaction (ORR) at Pt cathodes of polymer electrolyte membrane fuel cells (PEMFC) is one of the main factors that limit the large scale application of PEMFCs in automobiles [1]. This has to be solved by the use of highly efficient catalysts. Modifications of pure Pt catalysts with one or more transition metals often improve ORR activity [1–3]. The performance of Pt-based multi-component catalysts can be enhanced by several orders of magnitude when their surface structures had a sandwich structure [1,4]. This special surface structure consists

of three parts: a pure Pt skin layer, a transition metal enriched subsurface region, and a Pt or Pt-based alloy bulk phase. A Pt₃Ni(111) sample with the surface sandwich structure was found to be 10-fold more active for the ORR in a PEMFC than the corresponding Pt(111) surface and 90-fold more active than current state-of-the-art Pt/C catalysts [1]. The presence of subsurface Ni changed the surface electronic properties of Pt, which consequently weakened the adsorption of non-reactive oxygenated species to increase the number of active sites for O₂ adsorption. The Pt-

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based surface sandwich structures are not only useful in ORR application but also have obvious potential applications in hydrogenation reactions and other systems [5,6]. It has been shown that the surface of the Pt/Ni/Pt(111) structure was active for the selective hydrogenation of acrolein [5].

Although the catalytic activity of the Pt-based surface sandwich structures has been highlighted in many studies [7,8], the stability of the catalysts in potential applications, particularly in oxidizing environments, is also of importance and deserves more attention. In an O₂ atmosphere, the Pt-based surface sandwich structure is thermodynamically unstable and can undergo structural changes [9], which can lower its ORR activity. There have been a few studies that discuss the stability of the catalysts [9–11], but the structural evolution of the catalysts when heated in O₂ is still not well established.

The Pt-based surface sandwich structures are usually prepared by the annealing of Pt(111) single crystals covered with a transition metal film of Cu, Ni, or Co, etc [5,9,12,13]. In this work, we chose Pt/Fe/Pt(111) (with a coverage of subsurface Fe of 0.4 monolayer (ML)) as the model structure and studied its morphological and structural changes during stepwise annealing in 1.1×10^{-7} kPa O₂ by scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). The mechanism of the structural changes of the Pt/Fe/Pt(111) surface is discussed on the basis of in situ investigations.

1 Experimental

All experiments were carried out in an Omicron multi-probe surface analysis system with three UHV chambers, the preparation, spectroscopic, and microscopic chambers [9,14]. The three chambers were connected by a transfer chamber through which samples can be transferred by magnetically coupled probes without breaking the vacuum. The base pressure varied from 1.0×10^{-11} to 3.0×10^{-11} kPa. The preparation chamber had a Fe source for Fe deposition and an ion sputtering gun for surface cleaning. The spectro-

scopic chamber was equipped with XPS, ultraviolet photoelectron spectroscopy, ion scattering spectroscopy, and high resolution electron energy loss spectroscopy. The microscopic chamber was equipped with an Omicron variable temperature STM and a Focus photoemission electron microscope. XPS spectra were acquired with Mg K_α ($h\nu = 1\,253.6$ eV) radiation at a pass energy of 30 eV. The XPS spectra were calibrated with the Pt 4f_{7/2} peak at 71.0 eV. The STM measurements were carried out at room temperature (RT) in the constant current mode using a W tip.

The Pt skin surface with a subsurface region enriched with Fe, Pt/Fe/Pt(111), was prepared by a well established two-step procedure. This comprised the deposition of Fe on the Pt(111) surface at 487 K and ultrahigh vacuum (UHV) annealing at 850 K [9,14]. The Pt(111) surface was cleaned by repeated cycles of oxidation (5.0×10^{-8} kPa O₂) at 800 K, 2.0 kV Ar⁺ sputtering, and UHV annealing at 1 000 K until the STM and XPS did not detect any impurities. The sample temperature was measured by a NiCr–NiAl thermocouple welded onto the back of the Pt(111) crystal. The Fe source consisted of two pairs of 0.5 mm diameter tungsten wires wrapped with a coil of Fe wire (0.1 mm diameter, purity 99.998%, Alfa Aesar). First, an Fe overlayer with the coverage of 0.4 ML was deposited on Pt(111) at 487 K. Before each Fe deposition, the Fe source was degassed for more than 10 min. The vacuum was better than 1.2×10^{-10} kPa during deposition. Subsequently, the Pt skin surface with the 0.4 ML subsurface Fe was prepared in UHV and then annealed stepwise in 1.1×10^{-7} kPa O₂. O₂ (purity of 99.999%) was dosed into the system by backfilling the chambers through a leak valve. The Pt/Fe/Pt(111) surface was annealed in O₂ at each specified temperature for 6 min.

2 Results and discussion

Figure 1 shows the STM images of 0.4 ML Fe deposited on Pt(111) at 487 K and the Fe/Pt(111) surface annealed at 850 K in UHV. It can be seen that Fe islands were distributed randomly on the terraces of Pt(111). The height profile

Fig. 1. STM images of (a) 0.4 ML Fe deposited on Pt(111) at 487 K (400 nm $\times$ 400 nm) and (b) the Fe/Pt(111) surface annealed at 850 K in UHV (400 nm $\times$ 400 nm); (c) Depth profile along the line drawn in (a).

(Fig. 1(c)) showed that these islands had the height of the monatomic γ -Fe(111) layer. On annealing at 850 K in UHV, the 0.4 ML Fe/Pt(111) surface was transformed into a surface sandwich structure called Pt/Fe/Pt(111) (Fig. 1(b)). This structural transformation has been studied in detail in previous works [9,14].

After annealing the Pt/Fe/Pt(111) surface in 1.1×10^{-7} kPa O_2 at 600 K for 6 min, the surface steps became straight (shown in Fig. 2). In addition, a high density of black pits was found to be distributed evenly on the terraces. The depth of these pits was about 0.06 nm, which was much less than the step height of Pt(111). High resolution STM images showed that most of these pits were faceted and their edges were oriented along specific directions. The surface domains outside these pits had the same atomic structure as Pt(111) (Fig. 2).

It is known that O_2 dissociates on Pt(111) above 300 K to

form oxygen islands that would also appear as black pits in STM images [15,16]. Indeed, similar black pits were also observed but with a much lower density and a smaller size (Fig. 3) on the clean Pt(111) surface when this was treated under the same oxidation condition. These pits can be removed by exposing the surface to CO at RT. On the oxygen-exposed Pt/Fe/Pt(111) surface, dissociated atomic oxygen species were not detected by XPS after exposure of the surface to 3 Langmuir (L) CO at 400 K. Also, the surface pits did not show any significant change in density and size after the reaction with CO. Therefore, the appearance of the pits on the Pt skin surface was attributed to surface restructuring induced by oxygen adsorption. By comparison with the Pt(111) surface, the higher density and larger size of the pits on the Pt/Fe/Pt(111) surface can be attributed to the presence of subsurface Fe atoms that enhanced the surface roughening induced by oxygen adsorption.

Fig. 2. STM images of the Pt/Fe/Pt(111) surface annealed in 1.1×10^{-7} kPa O_2 at 600 K. (a) $200 \text{ nm} \times 200 \text{ nm}$; (b) $100 \text{ nm} \times 100 \text{ nm}$; (c) $40 \text{ nm} \times 40 \text{ nm}$; (d) $10 \text{ nm} \times 10 \text{ nm}$; (e) Depth profile along the line drawn in (c).

Fig. 3. STM images of (a) clean Pt(111) surface ($200 \text{ nm} \times 200 \text{ nm}$), (b) Pt(111) annealed in 1.1×10^{-7} kPa O_2 at 600 K ($200 \text{ nm} \times 200 \text{ nm}$), and (c) the same surface as (b) ($100 \text{ nm} \times 100 \text{ nm}$); (d) Depth profile along the line drawn in (c).

When the annealing temperature was increased to 750 K, the size of the pits became large. More important, a new surface phase, which showed the characteristic Moiré patterns of the monolayer FeO structure on Pt(111) [9] (Fig. 4(a)), started to appear. This indicated that the outward diffusion of subsurface Fe atoms onto the surface had occurred

and a surface FeO phase was formed at 750 K. When the annealing temperature was raised to 800 K, more ordered FeO islands grew preferentially along steps, and their periodic superstructure can be clearly distinguished (Fig. 4(b)). Also, many small FeO domains were observed on the terraces as well.

Fig. 4. STM images of the Pt/Fe/Pt(111) surface after annealing in 1.1×10^{-7} kPa O_2 at various temperatures. (a) 750 K (100 nm $\times$ 100 nm); (b) 800 K (100 nm $\times$ 100 nm).

When the Pt/Fe/Pt(111) surface was annealed at 850 K, the FeO islands appeared exclusively near steps. Furthermore, these islands were located at a height lower than the Pt(111) terraces by one platinum layer (Fig. 5(a)) and seemed embedded into the Pt(111) terraces. FeO islands embedded in Pt(111) terraces were also found by directly oxidizing Fe/Pt(111) at 1 000 K [17]. More interestingly,

periodic arrays of uniform protrusions with a height of 0.2 nm and diameter of 1.5 nm were observed in the FeO islands (Fig. 5(b)). These had the same periodicity as the Moiré patterns of the FeO film (the second brightest spots shown in Fig. 5(c)). In addition to the bright protrusions, some small depressions were also seen at the same locations of the FeO islands.

Fig. 5. STM images of the Pt/Fe/Pt(111) surface annealed in 1.1×10^{-7} kPa O_2 at 850 K. (a) 400 nm $\times$ 400 nm ($V_b = 1816$ mV, $I = 0.279$ nA); (b) 100 nm $\times$ 100 nm ($V_b = 1816$ mV, $I = 0.279$ nA); (c) 20 nm $\times$ 20 nm ($V_b = 2565$ mV, $I = 0.349$ nA).

To resolve the surface structure more clearly, atomically resolved STM images of the defective FeO islands and a defect-free monolayer FeO film were acquired using low bias voltages (Fig. 6). The images revealed that the FeO islands were atomically flat but defective at specific sites. Thus, the protrusions observed in the high bias voltage STM images were attributed to the electronic effect induced by surface defects and not to the presence of particles on the surface.

The growth and structure of a monolayer FeO film on Pt(111) has been studied extensively. A monolayer FeO

overlayer consists of a top layer of O atoms and a bottom layer of Fe atoms [18–26]. The O atoms on the top surface can be imaged by STM [20,23]. Our STM images of the defect sites on the FeO islands (Fig. 6) indicated that surface oxygen atoms were missing at the defect sites. The stoichiometry of the defective FeO islands was also determined by XPS. As shown in Fig. 7, the FeO islands have similar Fe 2p and O 1s binding energies to those of the defect-free monolayer FeO film, but with relatively lower intensities due to the lower coverage of FeO on the surface. By taking the O/Fe ratio from the defect-free monolayer

Fig. 6. (a) Atomically resolved STM image of a defective FeO island (15 nm $\times$ 15 nm) ($V_b = -100$ mV, $I = 0.02$ nA); (b) Zoomed O vacancy clusters in (a); (c) Schematic drawing of missing O atoms (the blue balls with dotted lines) at fcc sites; (d) STM image from a perfect 1.0 ML FeO film (10 nm $\times$ 10 nm) ($V_b = 800$ mV, $I = 0.6$ nA).

Fig. 7. Fe 2p and O 1s XPS profiles of the clean Pt(111) surface, the FeO islands with the periodic defects, and the perfect 1.0 ML FeO film grown on Pt(111).

FeO film as normalized at 1.0, the O/Fe ratio from the defective FeO islands was determined to be in a ratio of 0.90. The XPS results in combination with the STM images showed that the observed defects in the FeO islands were oxygen vacancies. The large defects were multiple oxygen vacancies (or oxygen vacancy clusters) and the small ones were single oxygen vacancies. Through the careful analysis of the structure of the large defects (Fig. 6(b)), we suggest that the multiple oxygen vacancy be attributed to six missing oxygen atoms at the hexagonal closest packed (fcc) sites [26] of the monolayer FeO structure. This is illustrated in Fig. 6(c).

On the basis of the above results, we suggest that the oxidation of the Pt skin surface with 0.4 ML subsurface Fe occurs by the following steps: (1) adsorption of atomic oxygen and surface restructuring induced by the oxygen adsorption; (2) exposure of subsurface Fe to atomic oxygen and formation of defective iron oxide clusters, denoted as FeO_{1-x} ($x < 1$); (3) diffusion and aggregation of FeO_{1-x} clus-

ters to form ordered but defective FeO islands at steps. The surface restructuring of the Pt skin structure or the displacing of the surface Pt atoms induced by oxygen promotes the diffusion of subsurface Fe atoms out onto the surface where they react with oxygen to form the oxide clusters. At the same time, the FeO_{1-x} clusters also diffuse toward steps and aggregate into big islands. Both the vertical and lateral diffusion of Fe (FeO_{1-x}) clusters are limited by the surrounding Pt atoms. Because the Fe coverage was only 0.4 ML, the FeO_{1-x} clusters formed were highly dispersed on the terraces in the initial stage of the oxidation. The aggregation of the FeO_{1-x} clusters result in the formation of ordered FeO_{1-x} layers with periodic defects. In the case of a 1.0 ML subsurface Fe underneath the Pt skin, we did not observe these defects during the same oxidation process. Thus, it is the aggregation of submonolayer FeO_{1-x} clusters that cause the periodic defects.

It should be noted that surface defects in FeO films have been well studied [24,25]. For example, a defective FeO

film, named $\text{FeO}_{0.75}$, was formed by reducing $\text{FeO}/\text{Pt}(111)$ with atomic H at 300 K [24]. The $\text{FeO}_{0.75}$ structure determined by LEED and STM was proposed to have triangularly shaped oxygen vacancy dislocation loops at specific sites in the Moiré structure of the film. This structure is quite different from the structure of the periodic arrays of oxygen vacancy clusters in FeO films that are the first reported in the present work.

3 Conclusions

The structural changes of a Pt skin surface with 0.4 ML subsurface Fe on heating in 1.1×10^{-7} kPa O_2 to different annealing temperatures were studied. At 600 K, oxygen adsorption induced surface restructuring of the Pt skin surface. At 750 K, subsurface Fe began to segregate onto the surface and formed FeO_{1-x} structures. At 850 K, FeO islands with periodic arrays of surface defects appeared at steps and were embedded in the Pt terraces. These surface defects were located at fcc sites of monolayer FeO islands and were multiple oxygen vacancies consisting of six missing oxygen atoms and single oxygen vacancies. The monolayer FeO islands with the periodic arrays of O vacancy clusters appear to be a metastable structure that exist during the oxidation of subsurface Fe.

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