

Electrodeposition of Pt onto RuO₂(110) Single-Crystal Surface

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The electrodeposition of Pt on RuO₂(110) from acid solutions of several Pt complexes was studied using programmed potential step or potential sweep methods. The RuO₂(110) single-crystal surface was obtained by gas-phase oxidation of Ru(0001). The electrodeposition process is characterized by a large crystallization overpotential and three-dimensional growth from a Pt adlayer. The mismatch between the RuO₂(110) and Pt lattices is the likely origin of that overpotential. The nucleation is instantaneous, as verified by potential step experiments. The process starts with depositing a 0.25 ML of Pt, with Pt atoms arranged in a $c(2 \times 2)$ array, which is followed by the growth of Pt islands and three-dimensional clusters as in the Stranski–Krastanov growth mode. Density functional theory calculations were used to help in elucidating atomically resolved electrochemical scanning tunneling microscopy (ECSTM) images of the initial stages of Pt deposition. A Pt adlayer on RuO₂(110) has lower catalytic activity for the oxygen reduction reaction compared to Pt, which is in agreement with a large calculated upshift of the d-band center of a low-coverage Pt deposit on RuO₂(110) as well as a lack of the oxygen adsorption in a bridge configuration on that surface.

1. Introduction

There are only a handful of studies of metal electrodeposition on conductive metal oxide surfaces. Likewise, the catalytic properties of electrodeposited metal/metal oxide systems are largely unexplored. These systems have a considerable potential as electrocatalysts, despite some restrictions that the electrochemical media can impose. Platinum monolayer/multilayer deposits on metal oxides are candidate electrocatalysts for improving the oxygen reduction reaction (ORR) due to the plausible effects of the oxide's OH or O and vacancy sites on the OH coverage on Pt and possible enhanced splitting of the O–O bond.¹ Furthermore, increased stability of the Pt deposits on oxide surfaces may result from adsorption of Pt cations on oxide surfaces.² Beside the above features, an appropriate metal oxide support must be stable under the oxidizing conditions of oxygen reduction and preferably conductive.

We selected the RuO₂(110) surface as a model system because of its rare suitability for atomic-scale surface chemistry and its conductivity and stability under the oxidizing conditions of an oxygen cathode. The electrodeposition of metals on compound substrates (metal oxides, chalcogenides, carbides, etc.) differs considerably from that on foreign metal substrates since usually at least two chemically different kinds of atomic sites are available on the surface of compound substrates. The RuO₂ possesses metallic conductivity³ due to ruthenium d-electrons.⁴ The only work on electrodeposition of metals on RuO₂ is apparently the study of Ag electrodeposition by Hepel et al.^{5,6}

The objective of this work is to obtain basic information on the initial phases of Pt monolayer-level deposition on Ru oxide surfaces. Such information would be valuable for elucidating the initial phases of metal growth on metal oxide surfaces under electrochemical conditions. In addition, the catalytic properties of such surfaces could be determined and the potential for electrocatalysis estimated. Electrochemical experiments showed that Pt deposition involves large crystallization overpotential.

A deposition of a 0.25 ML of Pt (Pt coverage was calculated in relation to Ru atoms), with Pt atoms arranged in a $c(2 \times 2)$ array, is followed by Pt island growth. Density functional theory (DFT) is used to calculate deposits of various Pt coverages and to compare them with atomically resolved electrochemical scanning tunneling microscopy (ECSTM) images of the initial stages of Pt deposition on RuO₂(110).

2. Experimental Section

The RuO₂(110) single-crystal surface was obtained by gas-phase oxidation of Ru(0001).⁷ A disk-shaped Ru(0001) single crystal, 8 mm in diameter and 2 mm thick, was obtained from Metal Crystal and Oxides, Cambridge, England. It was mechanically polished with 1 μm diamond paste. After the cleaning procedure, the crystal was placed inside a quartz tube. Inductive heating in a stream of a mixture of Ar and ~ 100 ppm O₂ gas produced chemical oxidation. The oxide was formed in samples held for about 2 min at temperatures between 600 and 800 K. From the flow rate of the gas mixture we estimated that the O₂ pressure in the quartz tube was around 0.1 mbar. The sample was transferred to the electrochemical cell protected with a droplet of sulfuric acid. This procedure yields a well-ordered RuO₂(110) single-crystal surface, which was verified by atomically resolved images obtained by ECSTM. The ECSTM images were obtained in 50 mM H₂SO₄ at open circuit potential (OCP). Voltammetry curves obtained from such surfaces confirmed that they were well ordered, being similar to those obtained for ordered bulk RuO₂(110). The in situ scanning tunneling microscopy (STM) studies were performed using a Molecular Imaging Pico STM with a 300S scanner and a 300S Pico Bipotentiostat. The tunneling tips were made of a polycrystalline Pt–20% Ir wire and coated with Apiezon wax. The platinum wires served as the reference and counter electrodes in ECSTM experiments. The voltammetry experiments were carried out in a standard three-electrode electrochemical cell with a Ag/AgCl/KCl (3 M) reference electrode and a Pt foil counter electrode. All the potentials in the text are reported versus a reversible

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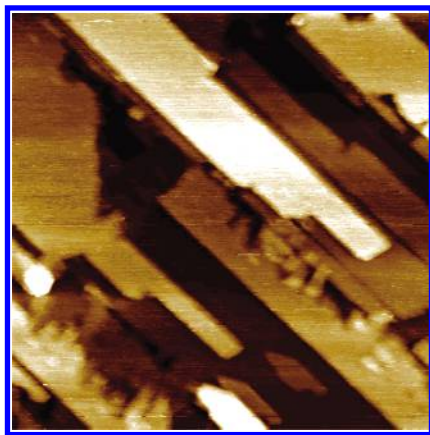


Figure 1. ECSTM image of the RuO₂(110) oxide obtained by chemical oxidation of Ru(0001). Image obtained in 50 mM H₂SO₄ at open circuit condition (0.95 V); size 200 nm × 200 nm, Z range 1 nm.

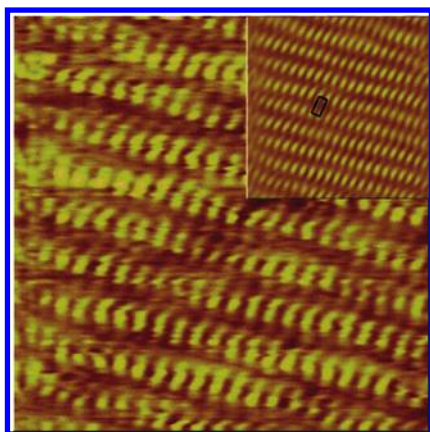


Figure 2. Atomically resolved ECSTM image of RuO₂ stripes (and its Fourier transform shown in the inset) obtained in 50 mM H₂SO₄ at open circuit condition (0.95 V); size 5.8 nm × 5.8 nm.

hydrogen electrode (RHE). Pt was deposited by programmed potential pulses or potential sweeps from K₂PtCl₄ or K₂Pt(NO₂)₄ dissolved in 50 mM H₂SO₄ or 10 mM HCl. Concentrations of Pt salts range from 10⁻⁶ to 10⁻³ M. All the solutions were made with high-purity grade chemicals and Millipore Q UV plus water.

3. Results and Discussion

3.1. Synthesis and Characterization of RuO₂(110) Single-Crystal Surface. The oxidation of the Ru(0001) surface was performed in a stream of Ar containing about 100 ppm O₂ at temperatures between 600 and 800 K. The ECSTM image of such a surface is given in Figure 1. To prevent surface contamination, the oxidized Ru surface was examined in 50 mM H₂SO₄ under open circuit conditions (~0.95 V). Figure 1 shows that oxide grows as long parallel stripes. The step height of these stripes is about 3 Å, corresponding to one monolayer of Ru oxide. The covering of the surface by oxide was examined by probing the surface in several places by ECSTM. In each of them the surface was completely covered with oxide suggesting that the whole surface was covered by oxide. Additional evidence comes from voltammetry, which is discussed in the following section. Atomically resolved ECSTM pictures unveil the nature of the oxide stripes, Figure 2. The structure of the oxide stripes displays a rectangular 6.3 Å × 3.1 Å unit cell. Within the limits of accuracy of the ECSTM technique, this unit cell corresponds to the rutile structure of RuO₂ with the (110) orientation (6.38 Å × 3.11 Å).⁸ Similar rectangular stripes

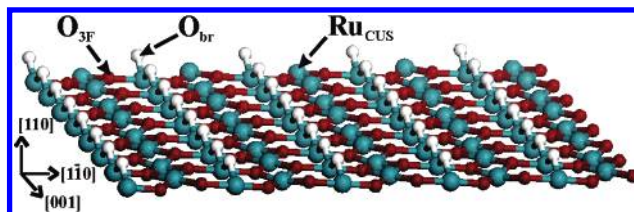


Figure 3. Model of RuO₂(110) surface in perspective view.

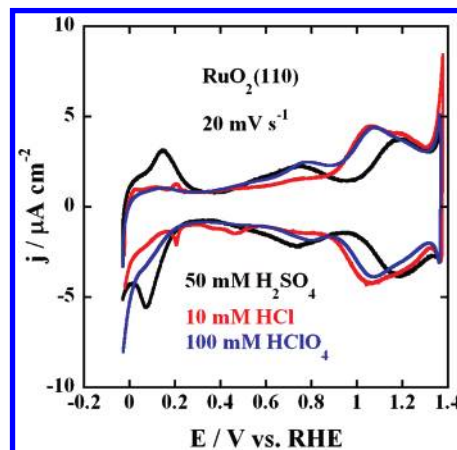


Figure 4. Voltammetry curves of a RuO₂(110) surface in deoxygenated 50 mM H₂SO₄, 10 mM HCl, and 100 mM HClO₄.

and internal structures with the same unit cell were observed in images from the ultrahigh vacuum (UHV) gas-phase oxidation of Ru(0001) with high doses of O₂ at 600–800 K.⁹ Low-energy electron diffraction (LEED) and STM data showed that this is a RuO₂(110) oxide film, growing epitaxially on the Ru(0001) surface as an incommensurate layer.^{9,10} The misfit between RuO₂(110) with cell dimensions of 6.38 Å × 3.11 Å and the nonprimitive rectangular cell for Ru(0001) with cell dimensions of 4.70 Å × 2.70 Å is too large to expect a pseudomorphic growth of oxide. This incommensuration between Ru and RuO₂ suggests that the oxide film is not strained.

A ball-and-stick model of the RuO₂(110) surface is shown in Figure 3. The RuO₂(110) surface contains two kinds of coordinatively unsaturated (CUS) atoms: twofold bridging O (O_{br}) and fivefold Ru (Ru_{CUS}). The O_{3F} sites are O atoms that lie in the plane of the Ru atoms and possess its bulklike threefold coordination. The interpretation of atomically resolved ECSTM images of oxides is difficult because of strong variations in the local electronic structure, as well as geometric effects. UHV experiments of O and CO adsorption on a RuO₂(110) surface as well as its partial reduction by CO, together with DFT calculations,^{9,10} showed that bright rows should be interpreted in terms of rows of bridging oxygen.

3.2. Voltammetry of RuO₂(110) Surface in Sulfuric, Perchloric, and Hydrochloric Acids. Polarization curves of a RuO₂(110) surface in deoxygenated sulfuric, perchloric, and hydrochloric acids are shown in Figure 4. The curve in sulfuric acid is very similar to that obtained for bulk (naturally grown) RuO₂.^{11–13} In the case of hydrochloric acid, a comparison with the curve in ref 14 is precluded by vastly different potential limits in the two experiments. The voltammetric curve for RuO₂(110) in perchloric acid exhibits much better resolved features, yet qualitatively it does not differ substantially from those for polycrystalline samples.¹⁵ The symmetrical shape of the polarization curves suggests reversible surface redox processes of RuO₂ in the potential range between H₂ and O₂ evolution. These surface redox processes apparently involve a change of the oxidation state of Ru and proton transfer through

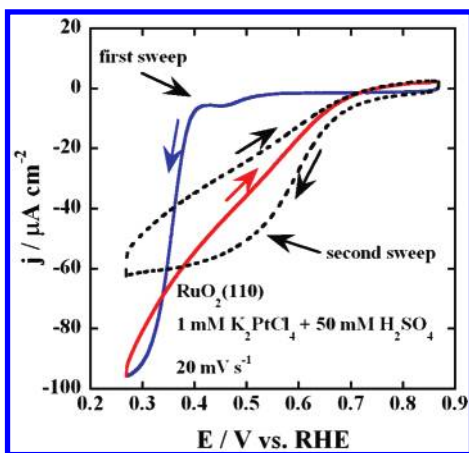


Figure 5. Voltammetry curves for the first and second sweep of Pt deposition on RuO₂(110) obtained from 1 mM K₂PtCl₄ + 50 mM H₂SO₄.

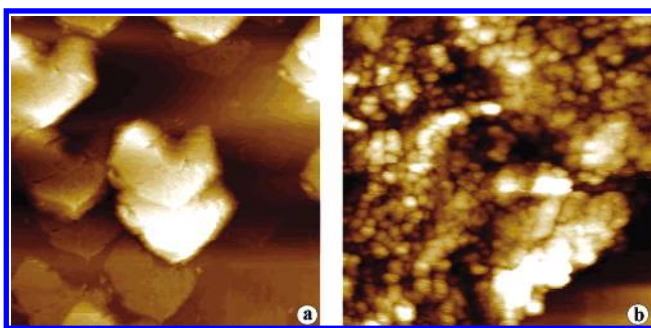


Figure 6. ECSTM images of the rectangularly shaped multilayer deposit of Pt on RuO₂(110) obtained in 50 mM H₂SO₄ at open circuit condition (0.95 V). (a) 1250 nm × 1250 nm, Z range 100 nm. (b) Zoom of (a) 80 nm × 80 nm, Z range 5 nm.

conversion of O²⁻ ions to OH⁻ in order to maintain a charge balance. The differences among the polarization curves obtained in sulfuric, perchloric, and hydrochloric acids reflect the specific influence of the corresponding anions on the surface redox processes. The absence of characteristic Ru peaks is an indication that the Ru surface is fully covered with RuO₂.

3.3. Electrochemical Deposition of Pt onto RuO₂(110).

Figure 5 shows a cyclic voltammogram for the electrodeposition of Pt on RuO₂(110) in 1 mM K₂PtCl₄ + 50 mM H₂SO₄ at a scan rate of 20 mV s⁻¹. The process is characterized by a large overpotential causing the appearance of the so-called “nucleation loop” that makes the current in the anodic sweep larger than the current in the cathodic sweep. This type of the current loop in the cyclic voltammogram appears associated with the nucleation and growth processes and is due to an easier nucleation on a partially Pt-covered RuO₂ surface (anodic in comparison with cathodic sweep). In addition, the real surface area of the Pt deposit is larger in the anodic sweep and it can support a larger current. The deposition starts at an overpotential of about 0.3 V (equilibrium potential is 0.642 V). There is one likely reason for the large overpotential, viz., the mismatch between the RuO₂(110) and Pt lattices. An IR drop due to resistivity of RuO₂ cannot be the reason for the large overpotential because RuO₂ possesses metallic conductivity.³ Further support for the above analysis comes from the second sweep, Figure 5, which shows that there is no overpotential for Pt deposition on Pt islands.

Figures 6–8 show a multilayer deposition of Pt on RuO₂(110) obtained under various conditions. Figure 6 shows a rectangularly shaped layered deposit. It was obtained from 1 mM K₂PtCl₄ + 10 mM HCl by stepping the potential from OCP

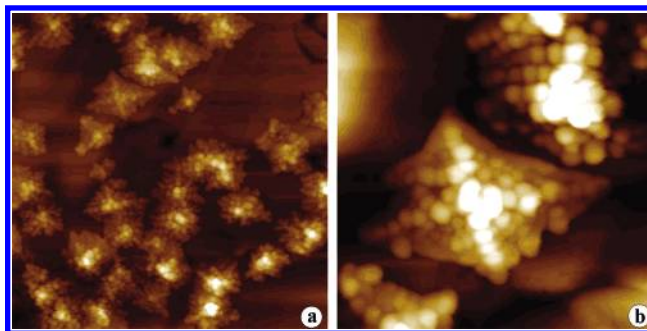


Figure 7. ECSTM images of the pyramidal multilayer deposit of Pt on RuO₂(110) obtained in 50 mM H₂SO₄ at open circuit condition (0.95 V). (a) 250 nm × 250 nm, Z range 18 nm. (b) Zoom of (a) 70 nm × 70 nm, Z range 11 nm.

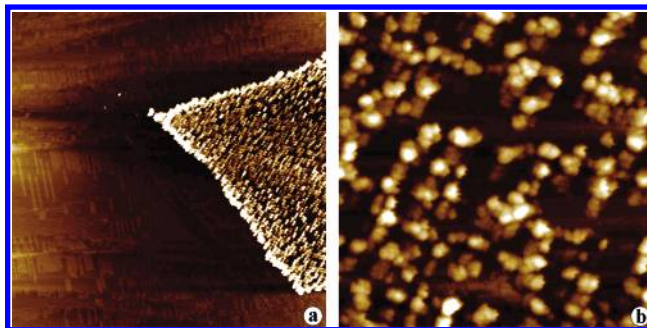


Figure 8. ECSTM images of the columnar multilayer deposit of Pt on RuO₂(110) obtained in 50 mM H₂SO₄ at open circuit condition (0.95 V). (a) 800 nm × 800 nm, Z range 6 nm. (b) Zoom of (a) 100 nm × 100 nm, Z range 6 nm.

to 0.268 V until 1750 μC of total charge was passed. The size of these structures is as large as 410 nm × 360 nm × 56 nm. One can see that rectangularly shaped layered deposits grow along two orthogonal directions of RuO₂ and thus sometimes make L-shaped structures. The pyramidal deposit shown in Figure 7 was obtained from 0.1 mM K₂PtCl₄ + 10 mM HCl in eight sweeps between 0.87 and 0.02 V. The surface is covered with rectangular-based pyramids with their sides oriented along two orthogonal directions of RuO₂. Some of them stand alone, but others merged into a larger deposit. The side of the pyramid could be as large as 35 nm and the height about 8 nm. Figure 8 shows a columnar deposit. It was obtained from 10⁻³ mM K₂PtCl₄ + 50 mM H₂SO₄ by stepping the potential from OCP to 0.22 V and keeping it at that potential for 2 h. The columns are about 5 nm in height, and their base is about 9 nm in diameter, which usually consists of several Pt islands. The common features of Pt deposition in Figures 6–8 are (i) three-dimensional growth, (ii) nonuniform coverage, and (iii) three-dimensional deposit consisting of Pt islands of 2–3 nm in diameter. A three-dimensional growth could be expected for Pt deposition on RuO₂(110) because of the high surface energy of Pt (2.691 J m⁻²)¹⁶ compared to RuO₂(110) (1.136 J m⁻²).¹⁷ Hepel et al.^{5,6} report similar properties of Ag deposition on RuO₂ under similar growth conditions to ours.

The potential step deposition was used to obtain information on the mechanism of electrochemical deposition of Pt onto RuO₂(110). The current transient following a potential step, in 10 mM K₂PtCl₄ + 50 mM H₂SO₄, is presented in Figure 9a. The potential was stepped from open circuit to 0.068 V, just before hydrogen evolution. To determine the type of the nucleation process involved in Pt deposition, we compared the experimental plot of the dimensionless ratio I^2/I_m^2 versus t/t_m , with the theoretical curves for instantaneous and progressive nucleation processes under diffusion control (Figure 9b).¹⁸ I and

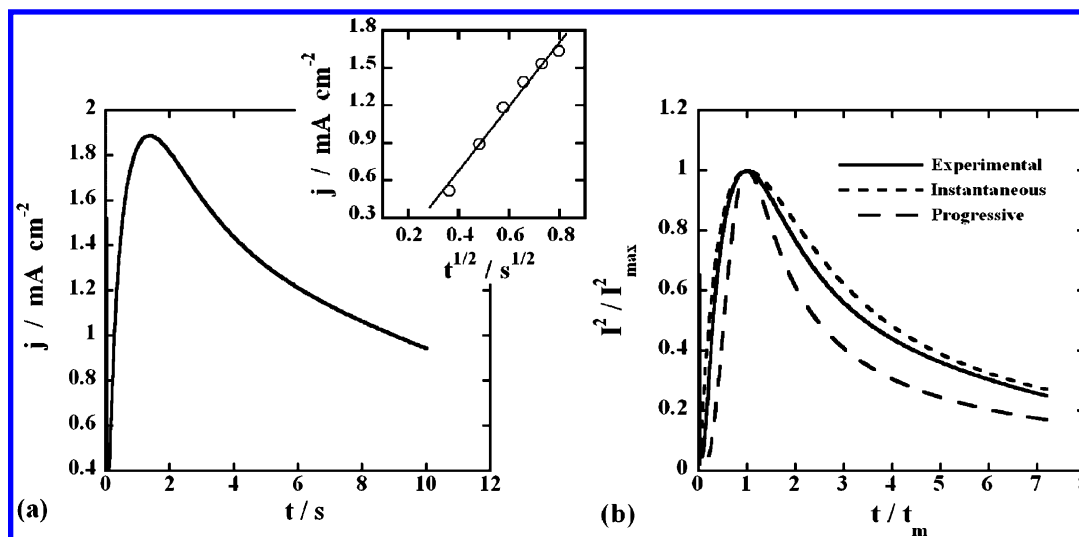


Figure 9. (a) Potentiostatic current transient for Pt deposition on RuO₂(110) obtained from 10 mM K₂PtCl₄ + 50 mM H₂SO₄ by the potential step from OCP to 0.068 V. Inset shows the plot of j vs $t^{1/2}$ obtained from the rising part of the j vs t plot. (b) Dimensionless $I^2 = I_{\max}^2$ vs t/t_m experimental plot of the data in (a) compared with theoretical curves for instantaneous and progressive nucleation processes given by eqs 1 and 2, respectively.

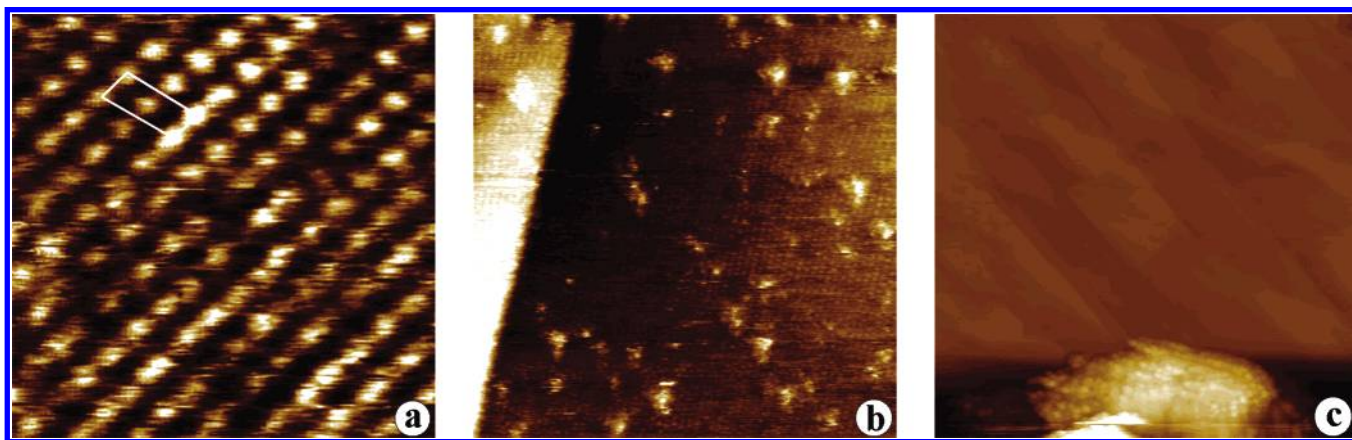


Figure 10. ECSTM images of the evolution of Pt deposit on RuO₂(110) with increasing amount of Pt (see text for details). They are obtained in 50 mM H₂SO₄ at open circuit condition (0.95 V). (a) 3.9 nm × 3.9 nm. (b) 24 nm × 24 nm. (c) 200 nm × 200 nm, Z range 25 nm.

I_m are the current and the current at maximum, respectively, while t and t_m are the corresponding times. Expressions for theoretical curves for the instantaneous and progressive nucleation processes are, respectively,

$$\frac{I^2}{I_m^2} = \frac{1.9542}{t/t_m} \{1 - \exp[-1.2564(t/t_m)]\}^2 \quad (1)$$

and

$$\frac{I^2}{I_m^2} = \frac{1.2254}{t/t_m} \{1 - \exp[-2.3367(t/t_m)^2]\}^2 \quad (2)$$

They show that the dimensionless plot is in good agreement with an instantaneous nucleation process, especially the rising part of the curve which demonstrates a clear linear dependence of j versus $t^{1/2}$ (see the inset of Figure 9a).

3.4. Initial Stage of Electrochemical Deposition of Pt onto RuO₂(110). Figure 10 shows a series of ECSTM pictures describing evolution of Pt deposit with increasing amount of deposited Pt. Figure 10, parts a and b, shows atomically resolved ECSTM images of the oxide stripes after Pt deposition from 1 mM K₂PtCl₄ + 50 mM H₂SO₄ by stepping the potential from OCP to 0.268 V and holding it at that potential until 50 and 80 μ C of total charge was passed, respectively. Figure 10a

consists of bright spots in a rectangular-centered arrangement (5.8 Å × 12.7 Å), while on Figure 10b, besides bright spots arranged in rectangular-centered array one can see small mounds and RuO₂(110) step. Figure 10c depicts the Pt deposit obtained under same conditions as for the Pt deposit shown in Figure 10, parts a and b, except that total charge that was passed was 1000 μ C. That picture reveals a three-dimensional deposit consisting of small Pt islands similar to Pt deposits described in the previous section. In order to better understand atomically resolved ECSTM pictures, DFT calculations¹⁹ were conducted to obtain the geometries and electronic structures of Pt adsorption on the stoichiometric RuO₂(110) surface at different coverages.

DFT calculations of Pt adsorption on the RuO₂(110) surface were performed using the CASTEP code.²⁰ Ultrasoft pseudopotentials expanded in a plane-wave basis in reciprocal space were employed (340 eV cutoff),²¹ and the RPBE gradient-corrected exchange-correlation functional was used.²² RuO₂(110) surfaces were modeled by a two-layer slab geometry (two O–Ru₂O₂–O units, hence six atomic layers) with a vacuum of 11 Å between the slabs. Upon increasing the number of layers to four, the changes in the relative energies for Pt adsorption at the different sites, which are our interest here, were negligible (less than 0.05 eV). The outermost surface layer was allowed to fully relax with the adsorbates. Brillouin zone sampling was

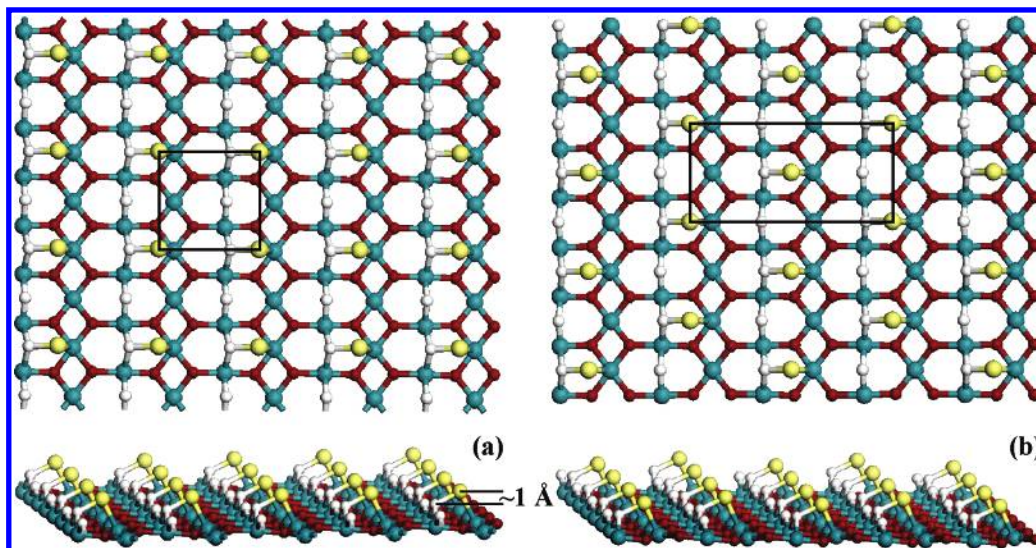


Figure 11. Two possible optimized geometries for 0.25 ML Pt coverage on RuO₂(110) in perspective and side view: (a) 2×1 ($6.234 \text{ \AA} \times 6.442 \text{ \AA}$) and (b) $c(2 \times 2)$ ($6.234 \text{ \AA} \times 12.884 \text{ \AA}$).

on a $4 \times 4 \times 1$ Monkhorst–Pack k -point grid.²³ Increasing the cutoff and the number of k -points had no significant effect on the results. For details of the calculations, see ref 19.

The results revealed that the Pt atoms strongly adsorb on RuO₂ and that two-dimensional growth up to 1.25 ML deposition was energetically favorable. At low coverage, the binding between Pt and RuO₂ is very strong, accompanied by a significant transfer of electron density from Pt to the support and a large downshift of the d-band compared to that of the unsupported Pt. At high coverage, a weak interaction of RuO₂ with the Pt cluster is observed, and the electronic structure of Pt is only slightly modified with respect to that of the unsupported material. The prediction of the DFT calculation that Pt atoms strongly adsorb on RuO₂ is not in accord with experimental observation that there is a large overpotential for Pt deposition on RuO₂. The likely reason for this difference is that in the DFT calculation Pt was deposited under UHV conditions, whereas in experiment Pt was deposited under electrochemical conditions.

Comparison of the atomically resolved ECSTM image of the oxide stripe after Pt deposition, Figure 10a, with possible arrangements of Pt atoms at different Pt coverages predicted by DFT calculations¹⁹ suggests that the image is equivalent to the calculated adlayer of 0.25 ML Pt coverage (Pt coverage was calculated in relation to Ru atoms). But why is only a 0.25 ML Pt coverage observed? Figure 12 displays changes of energies with coverage for Pt adsorption on RuO₂(110), viz., the adsorption energy of a free Pt atom on the RuO₂(110) surface (E_{ads}), formation energy of n free Pt atoms to an unsupported Pt_{*n*} cluster (E_{form}), and desorption energy (E_{des}) which corresponds to the energy cost to desorb a Pt_{*n*} cluster from the RuO₂(110) surface. All three energies have a strong dependence on the coverage. Since DFT calculations were done for 0 K, but the data presented were obtained at room temperature, one could expect some difference caused by the deposition conditions. DFT calculations show that at 0.25 ML Pt coverages of RuO₂ there are two possible Pt atom arrangements, 2×1 ($6.234 \text{ \AA} \times 6.442 \text{ \AA}$) and $c(2 \times 2)$ ($6.234 \text{ \AA} \times 12.884 \text{ \AA}$), and they are related and almost equally probable (only 0.1 eV difference), Figure 11, parts a and b. One is transformed into the other by translating every other row of Pt atoms along the [001] direction for one lattice unit (3.11 Å). ECSTM shows that only the $c(2 \times 2)$ array is observed and that, within the limits of accuracy,

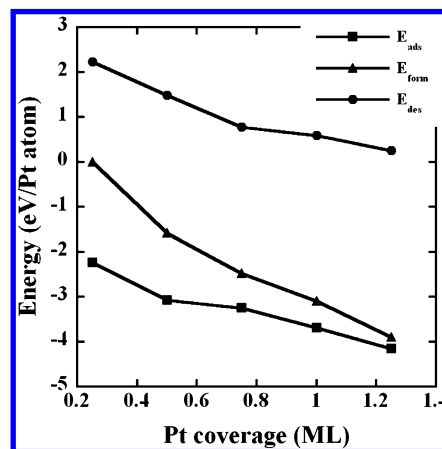


Figure 12. Calculated E_{ads} , E_{form} , and E_{des} energies for the Pt/RuO₂ interface at different Pt coverages.

it agrees with the calculated one. Also, DFT calculations show that Pt atoms lie $\sim 1 \text{ \AA}$ above the plane of bridging O. This prediction is easy to understand. Pt atoms cannot lie in the plane of Ru atoms because the Pt–Ru distance would be too short, making such configurations energetically unfavorable. Thus, assuming that ECSTM image contrast is governed by geometric effects, as in the case of imaging of RuO₂(110), one could expect to see an ECSTM image like the one depicted in Figure 10a. The small mounds observed in Figure 10b appear to be nuclei of Pt islands. Thus, Figure 10 shows the growth of Pt islands, and from them a three-dimensional Pt deposit, which implies the Stranski–Krastanov growth mode.

3.5. Oxygen Reduction Reaction on Pt onto RuO₂(110). Figure 13 shows the ORR on RuO₂(110), a Pt adlayer on RuO₂(110), and Pt(111) stationary electrodes. The cathodic potential limit for the RuO₂(110) and Pt adlayer on RuO₂(110) is set positive to the limiting potential below which formation of metallic Ru sites and surface roughening appears as discussed in ref 24. The polarization curve for RuO₂(110) shows that it is quite inactive for the ORR. In order to compare the activity for ORR of Pt adlayers on RuO₂(110) and Pt(111), one should take into account that there are 6 times more Pt atoms on a Pt(111) surface than in the Pt adlayer on RuO₂(110) (see Figure 10a and Figure 11b). Thus, the current for the Pt/RuO₂(110) surface is obtained by normalizing the measured current by the Pt(111) coverage. Figure 13 shows that the potential for ORR on a Pt

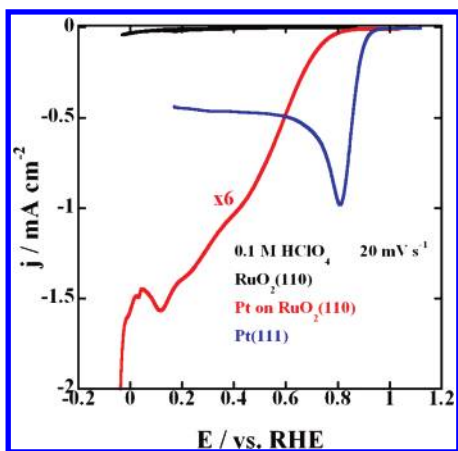


Figure 13. Polarization curves for ORR on RuO₂(110), Pt on RuO₂(110) normalized by Pt coverage, and Pt(111) stationary electrodes in oxygenated 100 mM HClO₄.

adlayer on RuO₂(110) is shifted negatively compared to Pt(111). This shift and smaller kinetic current suggest that the ORR on a Pt adlayer on RuO₂(110) is affected by electronic effects. The lower activity of Pt on RuO₂ compared to Pt(111) could be expected on the basis of a very large upshift of the d-band center of the Pt adlayer on RuO₂(110).¹⁹ Therefore, the supported Pt is too active to catalyze the ORR since it reacts with H₂O and is probably oxidized to Pt–OH, which blocks the ORR. An additional cause of such activity could come from the fact that Pt atoms in the Pt adlayer are fairly distant from each other compared to the Pt–Pt interatomic distance in Pt(111). This might influence the O₂ bonding and orientation toward the Pt adlayer. For this surface there is no possibility for bonding of O₂ with two Pt atoms (bridge model—Yeager¹), but O₂ can only bond to a single Pt atom with two bonds (Griffith model¹) or in an end-on adsorption through a single bond (Pauling model¹). Such an orientation of O₂ molecules is not conducive to the splitting of the O–O bond, thus resulting in a modest activity of such a surface for the ORR. One could argue that the O₂ molecule can bridge between a Pt atom and a Ru atom from the Ru plane and in that way achieve a bridging configuration. Although possible it does not appear to improve the activity if operative. A possible reason for this is that the presence of an oxygen-containing species at a RuO₂ surface in a broad potential range will interfere with the ORR.

4. Conclusions

The electrodeposition of Pt on RuO₂(110) was studied by programmed potential pulses or potential sweeps from several Pt complexes in acid solutions. Electrochemical experiments showed that Pt deposition involves large crystallization overpotential which is likely due to the mismatch between the RuO₂(110) and Pt lattices. The process starts with the deposition of a 0.25 ML of Pt, with Pt atoms arranged in a c(2 × 2) array, which is followed by Pt islands growth and three-dimensional cluster formation. This suggests the Stranski–Krastanov growth mode. The three-dimensional growth is expected since Pt has larger surface energy than RuO₂. Three different kinds of

multilayer deposits were observed as a function of the deposition conditions: rectangular, pyramidal, and columnar. Large deposits grow along two orthogonal directions of RuO₂. The three-dimensional deposit consists of Pt islands 2–3 nm in diameter. The deposition process, however, is not uniform over the whole electrode surface. The nucleation is instantaneous, as inferred from the potential step experiments.

DFT calculations were performed to gain additional insights into the atomically resolved ECSTM images of initial stages of Pt deposition onto RuO₂, as well as activity for ORR. It is shown that Pt adlayer on RuO₂(110) has lower catalytic activity for ORR compared to Pt, which is in agreement with a large calculated upshift of the d-band center, as well as a lack of the oxygen adsorption in a bridge configuration on that surface.

The system offers an interesting possibility to study the catalytic reactions on supported single Pt atoms, which will be reported in the near future.

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