COPPER ELECTRODEPOSITION ON IRIDIUM, RUTHENIUM AND ITS
CONDUCTIVE OXIDE SUBSTRATE

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The aim of this thesis was to investigate the physical and electrochemical properties of sub monolayer and monolayer of copper deposition on the polycrystalline iridium, ruthenium and its conductive oxide. The electrochemical methods cyclic voltammetry (CV) and chronocoulometry were used to study the under potential deposition. The electrochemical methods to oxidize the ruthenium metal are presented, and the electrochemical properties of the oxide ruthenium are studied.

The full range of CV is presented in this thesis, and the distances between the stripping bulk peak and stripping UPD peak in various concentration of CuSO_4 on iridium, ruthenium and its conductive oxide are shown, which yields thermodynamic data on relative difference of bonding strength between Cu-Ru/Ir atoms and Cu-Cu atoms. The monolayer of UPD on ruthenium is about 0.5mL, and on oxidized ruthenium is around 0.9mL to 1.0mL. The conductive oxide ruthenium presents the similar properties of ruthenium metal. The pH effect of stripping bulk peak and stripping UPD peak of copper deposition on ruthenium and oxide ruthenium was investigated. The stripping UPD peak and stripping bulk peak disappeared after the pH ≥ 3 on oxidized ruthenium electrode, and a new peak appeared, which means the condition of pH is very important. The results show that the Cl\(^-\), SO\(_4\)\(^{2-}\), Br\(^-\) will affect the position of stripping bulk peak and stripping UPD peak: the stripping bulk peak will shift and decrease if the concentration of halide ions is increasing, and the monolayer of UPD will increase at the same time.
ACKNOWLEDGMENTS

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1.1 History of metal UPD deposition and its application

1.1.1 What is the metal under potential deposition?

In 1912, Hevesy [1] was the first person to report the effect of under potential deposition, that is, the deposition of a sub monolayer amount (≤ ca. one monolayer) of a metal on a foreign metal electrode at potentials positive from the reversible Nernst potential. His curves show unsymmetrical tail for positive potentials, which mean metal adsorption to take place up to several tenths of a volt positive from the Nernst potential. Since then this effect, definition as under potential deposition has been studied intensively by means of electrochemical methods. The Cyclic Voltammetry is the fast and convenient way to study this layer. From then, many metal deposition of sub monolayer were studied, such as Cu\(^{2+}\), Pb\(^{2+}\), Ag\(^{+}\), Cd\(^{2+}\), Bi\(^{3+}\), Ti\(^{+}\) and Li\(^{+}\) [2]. It was clearly seen that the monolayer deposition on a foreign substrate at under potential because a strong interaction between monolayer atoms and the substrate. The structure of first monolayer is related to the shape of next 5-6 layer of deposited copper atoms (bulk peak), which is about 20-100 nm height and is most interesting area on semiconductor industry.
1.1.2 The copper application and its barrier in IC industry

For the semiconductor industry, the copper deposition behavior is very important. It has been the soul of semiconductor industry since the historic announcement by International Business Machines (IBM) in 1997 about copper (Cu) that the integrated circuit (IC) industry replaced aluminum (Al) by Cu as a favorable interconnects material. The reason chose Cu over Al is higher electrical conductivity and superior resistance to electromigration, and then, the research of copper deposition on the foreign metal surface which is the barrier are quite interesting, which will help the circuit industry to improve the skill to make the smaller and faster chips. The electrodeposition method is really cheaper than the physical vapor deposition.

Due to the scaling down, the contribution of interconnects should become preponderant for the performance of IC. IC fabrication requires processing temperatures as high as 450 °C, which can make the Copper to diffuse and mix into silicon (Si). To prevent such a problem, diffusion barriers like tantalum (Ta), tantalum nitride (TaN) have been or are still in use to contain the Cu interconnects in the vias, contacts and trenches. (Fig. 1.1)

From further investigation (Fig. 1.1), Ruthenium (Ru) and Iridium (Ir) are the proposed metal to be used as the barrier of Copper. The behavior of Copper deposited on Ru or Ir surface is studied by electrochemistry by the next chapters. The Ru and Ir metal have high melting point, and less resistivity by comparing the Ta and TaN. It is easy to electrodeposit copper on Ru and Ir,
and the Ta will react with water at the same conditions.

(a) Proposed  
(b) Current

Figure 1.1 A via feature bifurcated (a) with Ru or Ir as a proposed Cu barrier for the future sub 0.13 µm ICs and (b) current technology using Ta/TaN barriers.

1.2 Physical and Chemical property of Ruthenium and Iridium

1.2.1 Property of ruthenium

Some physical property of ruthenium: melting point 2334°C; boiling point 4150°C; density of solid 12370 kgm⁻³; electrical resistivity: 7.1 Ωcm¹⁰. RuO₄ is a toxic gas.

\[
\text{Ru(s) + O}_2 \ (g) \rightarrow \text{RuO}_2 \ (s);
\]
Ru(s) + 2O₂ (g) → RuO₄ (g)

Information of crystal structure of ruthenium

Space group: P6₃/mmc; Structure: hcp (hexagonal close-packed);

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1.2.2 Property of iridium

Some physical property of iridium: melting point 2466°C; boiling point 4428°C; density of solid 22650 kgm⁻³; electrical resistivity: 4.7 Ωcm.¹¹

Iridium is largely immune to atmospheric attack. On heating with oxygen, iridium metal gives iridium (IV) oxide, IrO₂ [black].¹¹

Ir(s) + O₂ (g) → IrO₂(s)

Information of crystal structure of iridium

Space group: Fm-3m; Structure: ccp (cubic close-packed);

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1.3 Electrochemical Methods

1.3.1 Linear Sweep Voltammetry (LSV)

A simple potential waveform that is often used in electrochemical experiments is the linear wave; the potential is continuously changed as a linear function of time. The rate of change of potential with time is referred to as the scan rate \( v \). The simplest technique that uses this wave form is Linear Sweep Voltammetry (LSV).

The potential-time dependence that is used for LSV measurements is presented in Figure 1.2. The potential is from \( E_1 \) to \( E_2 \) to obtain a current response that characterizes the electro active species present qualitatively and quantitatively.

![Potential-time profiles used for Linear Sweep Voltammetry (LSV)](image)

Figure 1.2 Potential-time profiles used for Linear Sweep Voltammetry (LSV)
1.3.2 Cyclic Voltammetry (CV)

Cyclic voltammetry is an extension of LSV with the voltage scan back after the current maximum of the reduction process has been passed. (Figure 1.3) The Cyclic voltammetry is a very popular technique for the initial electrochemical studies of new cells. It has been proven very useful in getting information about complicated electrode reactions.

The Figure 1.4 shows the reaction of $K_3Fe(\text{CN})_6$ on ruthenium electrode surface.

$$Fe(\text{CN})_6^{3-} + e = Fe(\text{CN})_6^{4-}$$

The three-electrode cell has a platinum foil as counter electrode, ruthenium electrode as working electrode and Ag/AgCl as reference electrode. The solution contains 4mM $K_3Fe(\text{CN})_6$ and 0.1M $K_2SO_4$ as electrolyte. The separation of reductive peak and oxidized peak is 60 mV, which is related to the 60mV/n. (n is the transfer electron number). From reversible peak current height $i_p$ (figure 1.4), the area of working electrode can be calculated from the below equation:

$$i_p = (2.69 \times 10^5) n^{3/2}AD^{1/2}C^*v^{1/2}$$  \hspace{1cm} (1.1)

$n$ is the transfer electron number, $A$ is the working electrode area in cm$^2$, $C^*$is the bulk concentration of electroactive species in mol cm$^{-3}$, $v$ is the scanrate of cyclic voltammetry in Vs$^{-1}$ and $D$ is the diffusion coefficient in cm$^2$s$^{-1}$. 

Figure 1.3 Potential-time profiles used for Cyclic Voltammetry (CV)

Figure 1.4 Cyclic Voltammetry of 4mM $K_3Fe(CN)_6$ on polycrystalline Ruthenium electrode, 0.1M $K_2SO_4$ as electrolyte, Platinum foil as the CE, Scanrate=10mV/s
1.3.3 Chronocoulometry (CC)

Figure 1.4 describes the time sequence of four steps used in the data acquisition and processing. The work electrode was held at the initial potential $E_i$, from which the ion’s absorption happened, for 120 seconds. This time is long enough for the adsorption equilibrium, which is built between the ions at the work electrode surface and in the bulk of the solution. Then: the scope begins the acquisition of data; after 1 ms a wave pulse is sent to trigger the potentiostat, which is happened as $t=0$ for all further events; (Figure 1.4) this signal forced the potential to jump from $E_i$ to $E_f$; the potential was held at $E_f$ for 100ms while the current transients were recorded; after 100ms, $E$ came back to $E_i$. The potential $E_f$ is always equal to the potential where the total desorption is occurred from the surface of working electrode. It means that desorption rather than adsorption of ion is measured. The current transients recorded over a 10ms time window are captured and are showed later.

![Diagram](image)

Figure 1.5 Chronocoulometry from trigger of $E_i$ to $E_f$, process in 0.1 M HClO$_4$ on polycrystalline Au electrode.
The linear part of the charge versus the time graph, which is related to the steady-state current, and is extrapolated by linear regression to \( t=0 \). The charge difference \( \Delta \sigma_M \) between the electrode charge densities \( \sigma_M \) at \( E_f \) and a given value of \( E_i \) is promised by this method. \(^{12-14}\)

\[
\Delta \sigma_M (E_i) = \sigma_M (E_i) - \sigma_M (E_f) \quad (1.2)
\]

From this experiment data, the Gibbs surface excess, \( \Gamma \) is obtained for adsorbates on solid electrodes\(^{12-14}\). The interfacial tension \( \gamma \) may be determined by back integration of the electrode charge densities, \( \sigma_M \), which can be determined from chronocoulometric experiments.

The following of processing data steps is used and will be shown on the following part of work:

(a) Measurement of the relative charge density \( \Delta \sigma_M \) from \( E_i \) to \( E_f \) where no adsorption of ions happen.

(b) The absolute charge density \( \sigma_M \) is calculated from \( \Delta \sigma_M \). By using the potential of zero charge, which has been independently measured, and from equation (1), \( \sigma_M (E_f) \) was obtained:

\[
\Delta \sigma_M (pzc) = \sigma_M (pzc) - \sigma_M (E_f) = -\sigma_M (E_f) \quad (1.3)
\]

(c) The relative interfacial tension is determined by integrating \( \sigma_M \) with respect to \( E \):

\[
\gamma (E_i) = - \int \sigma_M \, dE + \gamma (E_f) \quad (1.4)
\]

\( \gamma (E_f) \) is not known but if its value is independent of the ions concentration for the ion is no adsorption at \( E_f \). \( \pi \) can be determined:
\[ \pi (E) = \gamma_{\theta=0} - \gamma_{\theta} = - (\int \sigma_{M, \theta=0} dE - \int \sigma_{M, \theta} dE) \quad (1.5) \]

(d) The relative surface excess is calculated by differentiating \( \pi \) with respect to \( \ln c \) (\( c \) is the bulk ion concentration):

\[ \Gamma = \frac{\partial \pi}{RT \partial \ln c} \quad \text{T.P.E.} \quad (1.6) \]

The max concentration of ions in the bulk of solution studied is quite low. This is sufficiently small and the Henry’s law \(^{[12-16]}\) can be followed. Then, concentrations instead of activities are used to obtain \( \Gamma \).

1.4 How to prepare the Ruthenium and Ruthenium Oxide electrode.

After getting the metal shot of Ruthenium from the company, I need to make the electrode by using the epoxy and hardener. First I just solder the shot with the wire which is about 15 cm, and shot should be held solidly and heated up totally, then I use the plastic mold (show in figure) to hold the shot and let the parafilm hold the bottom of the mold tightly. I prepare the epoxy and hardener by the ration 100:15 and mix them up totally. After filling in the plastic mold and cover all the shot and wire in the plastic mold, I let the mixture stay 48 hours and made it dry.
After making sure the epoxy has dried, I remove the mold from the dried epoxy by making little cuts on the plastic mold with the wire cutters. The plastic mold should fracture into pieces, which makes the removal of the plastic mold extremely easy. So I already have an unpolished electrode. I placed the stainless steel puck (shown in figure) on the heat plate, and heated it for 5 minutes. After applying a thin layer of clear hot mounting wax on the surface of the steel puck, I placed the unpolished electrode with the backside on the wax.
Last steps will help me to polish the electrode with different silicon carbide (SiC) pads and diamond suspensions. From the coarse step to the fine grind, each step need 2 minutes. After using the different polishing pad and diamond suspensions, I finished the steps and get a perfect electrode. Every working electrode is cleaned in 0.5M H$_2$SO$_4$ by 20 cycles of CV from -0.5V to 0.6V before the experiments.

1.5 Experiment equipments and chemicals

1.5.1 Chemical

All electrochemical experiments were performed by using a polycrystalline ruthenium or iridium electrode. The counter electrode (CE) was a platinum coil cleaned by 15% HNO$_3$ from fisher scientific. The reference electrode (RE) was silver-silver chloride electrode (Ag/AgCl) from CH instrument.

Water was purified in a Millipore Milli-Q® Elix5® ultrapure water system (> 18.2 MΩ/cm). The supporting electrolyte was either 0.5 M H$_2$SO$_4$ or 0.5M K$_2$SO$_4$ (from fisher scientific). Both of them are the ACS grade chemicals. The
supporting electrolytes were purged with argon or nitrogen to remove oxygen.

The Cyclic Voltammetry (CV) experiments were performed using polycrystalline metal electrodes polished and cleaned according to the procedure described in the preparation of electrode part. The electrode was washed by nitride acid before each experiment. The measurements were conducted in a glass-Teflon cell equipped with a Pt CE and an Ag/AgCl reference electrode ([Cl⁻] =3M). Millipore water was used for solution preparation. All electrochemical measurements were conducted at room temperature (25°C).

1.5.2 Equipment

The electrochemical experiments were performed using a CH instrument model 400 potentiostat and controlled by a PIII computer. Custom software was used to record cyclic voltammograms (CVs) and to perform the chronocoulometric experiments.

1.6 How to oxidize the ruthenium electrode

From the introduction part of ruthenium properties, the ruthenium can be oxidized in a certain conditions, which is critical for the further experiments of this thesis. The main reason is that the ruthenium oxide is conductive, which has interesting properties to compare with the ruthenium electrode, and it’s behavior is progressive as the polycrystalline ruthenium electrode. Now, it is no literature to report the copper electrodeposition on oxidized ruthenium.
The experiment is prepared in the three-electrode cell. The reference electrode is Ag/AgCl, and counter electrode is platinum. The solution is in the 0.5M H$_2$SO$_4$, 0.1M HClO$_4$, and 0.1M K$_2$SO$_4$. Then, by using the regular potential step, jumping from the OCP (0.6V) to 1.3 V, and holding there for 180 seconds, the ruthenium electrode is oxidized. From the picture 1.9, the colorful surface of oxidized ruthenium electrode is obviously different with the former ruthenium electrode that has the metal shining surface. The different color area means that the different thickness of oxide on the surface.

![Colorful surface of oxidized ruthenium electrode](image)

Figure 1.9 Surface of ruthenium electrode after oxidizing 180 seconds at 1.3 V. captured by the light microscope (10 time zoom)
Reference


3. Back to the Future: Copper Comes of Age,  


CHAPTER 2

ELECTROCHEMISTRY OF POLYCRYSTALLINE RUTHENIUM ELECTRODE

2.1 CV of polycrystalline ruthenium electrode in 2mm CuSO₄

Prior to UPD experiments, the ruthenium electrodes were prepared by CV cleaning with a few sweeps in the range -0.5V to 0.5V. Figure (2.1c) shows voltammograms obtained with a polycrystalline ruthenium electrode in 0.5 M H₂SO₄, which is the CV as the background. The current height of this background is 1.2X10⁻⁴ Acm⁻², which is almost ten times smaller than the striping bulk peak of copper from figure2.1a. Then the progressive scan series CVs were obtained in 2mM CuSO₄ and 0.5M H₂SO₄ as electrolyte by macro command of CH instrument software. From the background CV, the anodic range obviously has no peak exist. So comparing the CVs of ruthenium electrode in 2mM CuSO₄ solution, the two peaks appear which were defined as the strip bulk peak and strip UPD peak. In this thesis, I just discuss the strip bulk peak and strip UPD peak, both of them are easy to recognize and have a good shape, and I just use the “Bulk peak” and “UPD peak” with ignoring the word “strip”. From the CV of polycrystalline ruthenium electrode (figure 2.1a), the strip UPD peak has almost constant height after potential went to more negative from 0.03V (vs. Ag/AgCl). The height of strip bulk peak is related with the concentration of CuSO₄, according to figure 2.2 to figure2.5.

The copper monolayer of this UPD is around 0.5 ML, which can be
explained by the structure of polycrystalline ruthenium surface, and are similar to those reported in the literature.\textsuperscript{1-2} From the table (2.1), the UPD ML is almost constant which is related to the surface structure of the polycrystalline ruthenium.

The crystal cell of ruthenium is HCP (Hexagonal Close-Packed) from the part of introduction.\textsuperscript{3} From the introduction part of properties of Ruthenium metal, one monolayer on ruthenium single crystal of surface Ru (0001) is about $1.65 \times 10^{15}$ atom cm$^{-2}$, which means that calculated monolayer coverage is higher than what we experimentally obtained (0.5ML). One of the Reasons is that the atoms of copper do not crowd compactly on first monolayer with the coabsorption of SO$_4^{2-}$. From the literature\textsuperscript{6}, the structure of this coabsorption should be like sandwich.
Fig 2.1 (a) The progressive scan CVs of polycrystalline ruthenium electrode in 2mM CuSO₄ and 0.5 M H₂SO₄ as electrolyte. Scanrate = 20mV/s. (b) The monolayer of the UPD peak (peak1) versus the lowest potential of each CV. (c) The background of ruthenium electrode in 0.5 M H₂SO₄

From the table 2.1, the UPD peak of copper deposition is increasing gradually from 0.11V to -0.05V, and then it is constant from -0.05V to -0.20V. The calculation of monolayer was presented:

\[ ML = \frac{Q}{nFNA} \]

When the switching potential move more positive than -0.01V, the bulk stripping peak does not show up. From -0.01V to 0.11V, the monolayer of UPD peak is still dependent on the cathodic potential in a non-equilibrium situation. The potential distance between the bulk peak and UPD peak is an important data, which can explain the difference of stability between the monolayer and next several layers. From the reported literatures \(^{[4-8]}\), the distance is around 150mV. The experiments show that the distance is about 130 ± 20 mV. From the equation below:

\[ \Delta G = nF\Delta E \]

The Gibbs energy difference between stripping UPD peak and stripping bulk peak is about 25 ± 4 kJmol\(^{-1}\).

<table>
<thead>
<tr>
<th>Lowest E /V</th>
<th>Monolayer of Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.11</td>
<td>0.04</td>
</tr>
<tr>
<td>0.07</td>
<td>0.17</td>
</tr>
<tr>
<td>0.03</td>
<td>0.34</td>
</tr>
<tr>
<td>-0.01</td>
<td>0.42</td>
</tr>
<tr>
<td>-0.05</td>
<td>0.47</td>
</tr>
</tbody>
</table>
Table 2.1 Monolayer of copper on polycrystalline ruthenium electrode

<table>
<thead>
<tr>
<th>Potential (V)</th>
<th>Current Density (mA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.09</td>
<td>0.49</td>
</tr>
<tr>
<td>-0.13</td>
<td>0.48</td>
</tr>
<tr>
<td>-0.17</td>
<td>0.47</td>
</tr>
<tr>
<td>-0.20</td>
<td>0.46</td>
</tr>
</tbody>
</table>

2.2 Polycrystalline ruthenium electrode in different concentration of CuSO$_4$

The ruthenium electrode in different concentration of CuSO$_4$ will help us to find the unique property of copper UPD peak. As the concentration of copper is increasing, the bulk peak will shift from 0.05V to 0.12V, which is around 60 mV. According to Nernst’s law, a shift will happen in the reversible equilibrium potential with the respective copper concentration in the solutions.[1] Around 30 mV shift to positive values was observed for the bulk peak according to the reference[1], but the value of these experiments is about 60 mV and has the same trend.

The same effect on UPD peak should exist. The data from the experiments is around 10 mV shifts, which the bulk peak could cause is too high and the UPD peak is tiny and not easy to observe. The shifting trend of UPD peak is also same as the Bulk peak. The Gibbs energy decreases from 35 ± 4 kJmol$^{-1}$ to 30 ± 4 kJmol$^{-1}$ by increasing the concentration of CuSO$_4$ (Figure 2.2 to 2.5).
Figure 2.2  Polycrystalline ruthenium electrodes in 1mM CuSO₄ with 0.5M H₂SO₄ as the electrolyte. Scan rate = 20 mV/s.

Figure 2.3  Polycrystalline ruthenium electrodes in 2mM CuSO₄ with 0.5M H₂SO₄ as the electrolyte. Scan rate = 20 mV/s.
Figure 2.4 Polycrystalline ruthenium electrodes in 5mM CuSO$_4$ with 0.5M H$_2$SO$_4$ as the electrolyte. Scan rate = 20 mV/s.

Figure 2.5 Polycrystalline ruthenium electrodes in 10mM CuSO$_4$ with 0.5M H$_2$SO$_4$ as the electrolyte. Scan rate = 20 mV/s.

The ruthenium electrode in different concentration of CuSO$_4$ is to test the monolayer of Copper UPD existence and see the bulk peak shift.

The figure 2.6 shows the monolayer and bulk peak position versus the different concentration of CuSO$_4$. It is reasonable to assume that the UPD influences the further growth of the bulk peak, for the first monolayer structure.
will decide what the next couple of monolayer grow up. From the figure 2.6, the UPD peak shifts less than the bulk peak, it means that deposition of bulk on ruthenium electrode is becoming easier in higher concentration of CuSO$_4$. The monolayer of UPD is slightly decreasing when the concentration of CuSO$_4$ is increasing. For the error bar of measurement is bigger in the high concentration solution, it should be constant of UPD monolayer. From these data, the first monolayer completed under the potential of -0.01V, and the second layer and next few layers are from the bulk peak. From this assumption, the first layer mainly interacts with atoms on the surface of ruthenium electrode. After the first layer, the copper atoms and anions cover the surface, which will block the interaction, and then, the bulk peak will appear.

![Figure 2.6 Concentration of CuSO$_4$ Vs bulk peak position and monolayer](image)

2.3 pH effect on the UPD and bulk peak of ruthenium electrode

23
The pH of CuSO$_4$ solution is one of critical aspects to investigate the copper deposition on ruthenium electrode. The solution contains 0.5M K$_2$SO$_4$, and pH was adjusted by H$_2$SO$_4$ and NaOH solution in order to avoid the effect of other cathodic anions. From the figure 2.7, pH above 4 the bulk and UPD peaks become smaller, even disappear, which means the pH value of solution is important to these experiment. From all the data from figure 2.1 to 2.6, the 0.5M H$_2$SO$_4$ is the electrolyte, and the pH = 0.

Figure 2.7 CV of ruthenium electrode in different pH 2mM CuSO$_4$ solution and 0.5M K$_2$SO$_4$ as electrolyte; pH is adjusted by H$_2$SO$_4$ and NaOH; Scanrate = 20mV/s.

2.4 Anion effects on ruthenium electrode in 2mM Cu (ClO$_4$)$_2$ solution

It was well known for some time that anion adsorption may have a strong influence on the deposition behavior on the polycrystalline ruthenium
In this part, the technique of cyclic voltammetry was used to obtain data of the system with anions and without anions. By comparing the regular CV, the influences of anions are identified. First, the under potential peak shift $\Delta E$ is decreased, which is related to a reduction in bond strength between copper adatom and ruthenium surface. This change of bond energy caused by the interaction of the anions with the ruthenium, and it is obviously stronger than that with the adsorbates. Second, the area of UPD peak was enlarged. The reason is that the copper atom adsorption is now accompanied by anions desorption; both sides contribute to the current in the same direction and thus make a larger apparent surface charge.\(^\text{[6]}\)

From the reference\(^\text{[1,5,7-9]}\), the anions effect sequence is $\text{ClO}_4^- < \text{SO}_4^{2-} < \text{Cl}^- < \text{Br}^-$. In this case, the effect of anions is more complex than what the reference said. From the figure 2.8, the ruthenium electrode in 2mM Cu ($\text{ClO}_4$)$_2$ solution, and the influence of ClO$_4^-$ is so small that do not need to count it in the experiments. The result is similar as the ruthenium electrode in 2mM CuSO$_4$ solution, the UPD and bulk peak still there, which means that the SO$_4^{2-}$ may help to build the UPD peak, but it is not critical reason for the UPD peak formation. It also excludes the suspicion that the UPD peak actually is the absorption of SO$_4^{2-}$ and no copper at all. The monolayer of UPD peak in figure 2.8 is about 0.13 ML, which is smaller than the monolayer in 2mM CuSO$_4$
solution. One of reasons is that the ClO₄⁻ does not coadsorb easily on the ruthenium electrode surface with copper atoms. There is an assumption that the anions form a compound or bond strongly on the ruthenium electrode surface, and then, the copper deposits on this surface. With a complex process-taking place on ruthenium surface, the anions go up to the copper monolayer that has built on the surface of ruthenium. Finally, the anions may help to build the copper monolayer more densely by the strong interaction with the ruthenium surface.

Figure 2.8 CV of ruthenium electrode in 2mM Cu (ClO₄)₂ and 0.1 M HClO₄ as electrolyte; Scanrate = 20mV/s

2.4.1 The influence of Cl⁻ on the ruthenium surface

From the figure 2.9 to figure 2.11, the influence of Cl⁻ is bigger as the concentration of Cl⁻ increases by comparing the shape of CVs. The bulk peak position is shifting from 0.11 V to 0.01 V (from table 2.2) and its height decreases while the concentration of Cl⁻ increases. This phenomenon is
corresponding to the reference \cite{1,5-9}. The monolayer of UPD peak is increasing while the concentration of Cl$^-$ is higher. This is because the copper atom adsorption is accompanied by Cl$^-$ desorption, both of them contributes to the current in the same way. Then, this process, which can explain the shrink of its height, affects the bulk peak.

The distance between the bulk peak and UPD peak can help us to understand whether the monolayer takes place easily or difficultly. From the table 2.2, the distance from 120 mV increases to 205 mV, which means the monolayer of copper deposition happens easier. The Gibbs excess is increasing from 23.16kJmol$^{-1}$ to 39.57kJmol$^{-1}$.

<table>
<thead>
<tr>
<th>conc. of KCl</th>
<th>bulk position / V</th>
<th>UPD position / V</th>
<th>UPD / uC</th>
<th>Monolayer</th>
<th>$\Delta E$ / mV</th>
<th>$\Delta G$ / kJmol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.11</td>
<td>0.23</td>
<td>13</td>
<td>0.12</td>
<td>120</td>
<td>23.16</td>
</tr>
<tr>
<td>1mM</td>
<td>0.08</td>
<td>0.22</td>
<td>30</td>
<td>0.29</td>
<td>140</td>
<td>27.02</td>
</tr>
<tr>
<td>10mM</td>
<td>0.05</td>
<td>0.2</td>
<td>77</td>
<td>0.76</td>
<td>150</td>
<td>28.95</td>
</tr>
<tr>
<td>20mM</td>
<td>0.01</td>
<td>0.215</td>
<td>229</td>
<td>2.28</td>
<td>205</td>
<td>39.57</td>
</tr>
</tbody>
</table>

Table 2.2 Influence of x mM Cl$^-$ on ruthenium in 2 mM Cu (ClO$_4$)$_2$ solution
Figure 2.9 CV of ruthenium electrode in 2mM Cu (ClO$_4$)$_2$ + 1mM KCl and 0.1 M HClO$_4$ as electrolyte; Scanrate = 20mV/s

Figure 2.10 CV of ruthenium electrode in 2mM Cu (ClO$_4$)$_2$ + 10mM KCl and 0.1 M HClO$_4$ as electrolyte; Scanrate = 20mV/s
Figure 2.11 CV of ruthenium electrode in 2mM Cu (ClO$_4$)$_2$ + 20mM KCl and 0.1 M HClO$_4$ as electrolyte; Scanrate = 20mV/s

2.4.2 The influence of SO$_4^{2-}$ on the ruthenium surface

From the figure 2.12 to figure 2.14, the influence of SO$_4^{2-}$ is bigger as the concentration of SO$_4^{2-}$ increases by comparing the shape of CVs. The bulk peak position is shifting from 0.11 V to 0.075 V (from table 2.3) and its height decreases while the concentration of SO$_4^{2-}$ increases. This phenomenon is corresponding to the reference $^{[1, 5-9]}$. The monolayer of UPD peak is increasing while the concentration of SO$_4^{2-}$ is higher. This is because the copper atom adsorption is accompanied by SO$_4^{2-}$ desorption, both of them contributes to the current in the same way. Then, this process, which can explain the shrink of its height, affects the bulk peak.

The distance between the bulk peak and UPD peak can help us to understand whether the monolayer takes place easily or difficultly. From the table 2.3, the distance from 120 mV increases to 194 mV, which means the
monolayer of copper deposition happens easier. The Gibbs excess is increasing from 23.16kJmol$^{-1}$ to 37.44kJmol$^{-1}$. In the solution of 20mM $K_2SO_4$, the behavior of copper deposition on ruthenium electrode is quite like in the 2mM CuSO$_4$ solution, $\Delta E$ and $\Delta G$ are almost same from table 2.3.

<table>
<thead>
<tr>
<th>conc. / $K_2SO_4$</th>
<th>bulk position / V</th>
<th>upd position / V</th>
<th>upd charge uC</th>
<th>Monolayer</th>
<th>$\Delta E$ / mV</th>
<th>$\Delta G$ kJmol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 mM</td>
<td>0.11</td>
<td>0.23</td>
<td>13</td>
<td>0.12</td>
<td>120</td>
<td>23.16</td>
</tr>
<tr>
<td>1 mM</td>
<td>0.105</td>
<td>0.233</td>
<td>22</td>
<td>0.21</td>
<td>128</td>
<td>24.70</td>
</tr>
<tr>
<td>10 mM</td>
<td>0.075</td>
<td>0.256</td>
<td>43</td>
<td>0.42</td>
<td>181</td>
<td>34.93</td>
</tr>
<tr>
<td>20 mM</td>
<td>0.075</td>
<td>0.269</td>
<td>57</td>
<td>0.56</td>
<td>194</td>
<td>37.44</td>
</tr>
</tbody>
</table>

Table 2.3 Influence of $x$ mM SO$_4^{2-}$ on ruthenium in 2mM Cu (ClO$_4$)$_2$ solution

![Figure 2.12 CV of ruthenium electrode in 2mM Cu (ClO$_4$)$_2$ + 1mM $K_2SO_4$ and 0.1 M HClO$_4$ as electrolyte; Scanrate = 20mV/s](image)
Figure 2.13 CV of ruthenium electrode in 2mM Cu (ClO$_4$)$_2$ + 10mM K$_2$SO$_4$ and 0.1 M HClO$_4$ as electrolyte; Scanrate = 20mV/s

Figure 2.14 CV of ruthenium electrode in 2mM Cu (ClO$_4$)$_2$ + 20mM K$_2$SO$_4$ and 0.1 M HClO$_4$ as electrolyte; Scanrate = 20mV/s
2.4.3 The influence of Br\(^{-}\) on the ruthenium surface

From the figure 2.15 to figure 2.17, the influence of Br\(^{-}\) is bigger as the concentration of Br\(^{-}\) increases by comparing the shape of CVs. The bulk peak position is shifting from 0.11 V to 0.03 V (from table 2.4) and its height decreases while the concentration of Br\(^{-}\) increases. This phenomenon is corresponding to the reference \[1, 5-9\]. The monolayer of UPD peak is decreasing while the concentration of Br\(^{-}\) is higher. This is because the copper atom adsorption is accompanied by Br\(^{-}\) desorption, both of them contributes to the current in the same way. Then, this process, which can explain the shrink of its height, affects the bulk peak.

The distance between the bulk peak and UPD peak can help us to understand whether the monolayer takes place easily or difficultly. From the table 2.4, the distance from 120 mV increases to 255 mV, which means the monolayer of copper deposition happens easier. The Gibbs excess is increasing from 23.16kJmol\(^{-1}\) to 49.21kJmol\(^{-1}\). The influence of Br\(^{-}\) is so strong that the bulk peak almost disappeared from figure 2.15 to figure 2.17, plus the decreasing of monolayer of UPD. It means that the structure of monolayer on the surface of ruthenium may be changed by the strong bond energy of Br\(^{-}\) with ruthenium atoms.
Table 2.4 Influence of x mM Br⁻ on ruthenium in 2 mM Cu (ClO₄)₂ solution

<table>
<thead>
<tr>
<th>conc. of KBr</th>
<th>bulk position / V</th>
<th>upd position / V</th>
<th>upd uC</th>
<th>Monolayer</th>
<th>ΔE/ mV</th>
<th>ΔG kJmol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 mM</td>
<td>0.11</td>
<td>0.23</td>
<td>13</td>
<td>0.12</td>
<td>120</td>
<td>23.16</td>
</tr>
<tr>
<td>1 mM</td>
<td>0.061</td>
<td>0.255</td>
<td>97</td>
<td>0.96</td>
<td>194</td>
<td>37.44</td>
</tr>
<tr>
<td>10 mM</td>
<td>0.015</td>
<td>0.268</td>
<td>73</td>
<td>0.72</td>
<td>253</td>
<td>48.82</td>
</tr>
<tr>
<td>20 mM</td>
<td>0.03</td>
<td>0.285</td>
<td>59</td>
<td>0.58</td>
<td>255</td>
<td>49.21</td>
</tr>
</tbody>
</table>

Figure 2.15 CV of ruthenium electrode in 2 mM Cu (ClO₄)₂ + 1 mM KBr and 0.1 M HClO₄ as electrolyte; Scanrate = 20 mV/s
Figure 2.16 CV of ruthenium electrode in 2mM Cu (ClO$_4$)$_2$ + 1mM KBr and 0.1 M HClO$_4$ as electrolyte; Scanrate = 20mV/s

Figure 2.17 CV of ruthenium electrode in 2mM Cu (ClO$_4$)$_2$ + 1mM KBr and 0.1 M HClO$_4$ as electrolyte; Scanrate = 20mV/s
2.4.4 Summary the influence of anions on the ruthenium surface

From the part 2.4.1 to 2.4.3, the influences of three anions on copper deposition process are described, which shows the strong influence on the ruthenium electrode surface.

First, compare the Cl\textsuperscript{-} SO\textsubscript{4}\textsuperscript{2-} and Br\textsuperscript{-} influences, the Br\textsuperscript{-} affect the surface quite a lot and even the bulk peak almost disappeared which may suggest that the structure of first monolayer on the ruthenium surface is changed, it will block the further bulk peak building at the same lowest potential.

Second, the change plot of CV in SO\textsubscript{4}\textsuperscript{2-} is smaller than the other two anions, and the distance of peak separation is the smallest one in the three anions. It means the influence of SO\textsubscript{4}\textsuperscript{2-} is smallest. So the anions effect sequence is SO\textsubscript{4}\textsuperscript{2-} < Cl\textsuperscript{-} < Br\textsuperscript{-} from the experiments.

Third, the monolayer of UPD is increasing when the concentration SO\textsubscript{4}\textsuperscript{2-} and Cl\textsuperscript{-} are increasing, but the monolayer of UPD is decreasing in Br\textsuperscript{-} solutions.
Reference

1. Dieter M. Kolb, Advances in electrochemistry and electrochemical engineering Vol 11


CHAPTER 3

ELECTROCHEMISTRY OF OXIDIZED POLYCRYSTALLINE RUTHENIUM ELECTRODE

3.1 Oxidized ruthenium electrodes in 2mM CuSO$_4$ solution

The RuO$_x$H$_y$ electrode is made from ruthenium electrode, which is oxidized by 180 second with 1.3 voltages in 0.5 M H$_2$SO$_4$. The surface is looked like more dark than the Ruthenium electrode that is shining. Some unique properties of this type of electrode will be presented below. Since the second part of ruthenium electrode discussion, the behavior of oxidized ruthenium electrode is also similar like the polycrystalline ruthenium electrode.

The capacitance of this electrode is much higher than the ruthenium electrode $^{[1-2]}$. From the back ground which is the voltammograms that run in 0.5M H$_2$SO$_4$. The current height is 11.2X10$^{-4}$ Acm$^{-2}$, which is about the ten times bigger than the background of ruthenium electrode ($1.2e^{-4}$ Acm$^{-2}$). The strip bulk peak of copper (from fig3.1a) on RuOxHx electrode is 25X10$^{-4}$ Acm$^{-2}$, which is two times bigger than the back ground, which is related to the copper bulk deposition peak. The height of strip UPD peak (from fig3.1a) on RuO$_x$H$_y$ electrode is almost constant after the potential goes to more negative from 0.05 V, which is related with copper UPD peak. The monolayer of UPD peak is about 0.9 to1 ML, which is almost double of monolayer of Ruthenium electrode. From table 3.1, the monolayer coverage of copper UPD is increasing at the beginning, and then is keeping constantly after it reaches the potential 0.05 V.
The position of stripping UPD peak is shifting a little bit when the potential is going to negative and this may be explained by forming structure of deposited copper and need to be studied further.

The distance between the stripping UPD peak and stripping bulk peak is critical for the thermodynamic study, which will help us to understand the difference of copper deposition between UPD peak and bulk peak. It is about $170\pm20\text{mV} \ (\Delta E)$ between of these two peaks. $\Delta E$ can convert to $\Delta G$, which is the kinetic information of the difference between the copper bulk deposition and the copper UPD deposition. This means that $\Delta G$ is much bigger; the UPD deposition is much easier. From table 3.1, the $\Delta G$ is around $33\pm4\text{kJmol}^{-1}$, which is almost $10\text{kJmol}^{-1}$ more by comparing the data from the ruthenium electrode (Table2.1).

$$\Delta G = n \ F \ \Delta E$$
Figure 3.1 (a) CV of oxidized ruthenium electrode in 2mM CuSO₄ solution and 0.5M H₂SO₄ as electrolyte (b) CV of oxidized ruthenium electrode in 0.5M H₂SO₄ as the background (c) The monolayer of copper UPD versus the lowest potential of every CV.

<table>
<thead>
<tr>
<th>Lowest E / V</th>
<th>UPD Position / V</th>
<th>Bulk position / V</th>
<th>ΔEₚ / V</th>
<th>ΔGₚ / kJmol⁻¹</th>
<th>Mono layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03</td>
<td>0.172</td>
<td>no</td>
<td></td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>-0.01</td>
<td>0.184</td>
<td>no</td>
<td></td>
<td>0.91</td>
<td></td>
</tr>
<tr>
<td>-0.05</td>
<td>0.187</td>
<td>0.017</td>
<td>0.170</td>
<td>32.81</td>
<td>1.00</td>
</tr>
<tr>
<td>-0.09</td>
<td>0.189</td>
<td>0.023</td>
<td>0.166</td>
<td>32.03</td>
<td>1.00</td>
</tr>
<tr>
<td>-0.13</td>
<td>0.192</td>
<td>0.026</td>
<td>0.166</td>
<td>32.03</td>
<td>1.00</td>
</tr>
<tr>
<td>-0.17</td>
<td>0.192</td>
<td>0.026</td>
<td>0.166</td>
<td>32.03</td>
<td>0.98</td>
</tr>
<tr>
<td>-0.2</td>
<td>0.191</td>
<td>0.030</td>
<td>0.161</td>
<td>31.07</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Table 3.1 Copper depositions on oxidized polycrystalline ruthenium electrode

3.2 Oxidized Polycrystalline ruthenium electrode in different concentration of CuSO₄

The oxidized ruthenium electrode in different concentration of CuSO₄ will help us to find the unique property of copper UPD peak. As the concentration of copper is increasing, the bulk peak will shift from 0.02V to 0.07V, which is around 50 mV. According to Nernst's law[^3] a shift will happen in the reversible equilibrium potential with the respective copper concentration in the solutions. Around 30 mV shift to positive values was reported[^1] for the bulk peak according to the reference, but the value of these experiments is about 50 mV and has the same trend. The same effect on UPD peak should exist. The data from the experiments is around 30 mV shift, which can be explained by
the bulk peak is too high and the UPD peak is tiny and not easy to observe. The shifting trend of UPD peak is also same as the Bulk peak. The Gibbs energy decreases from 40 ± 4 kJmol$^{-1}$ to 35 ± 4 kJmol$^{-1}$ by increasing the concentration of CuSO$_4$ (Figure 3.2 to 3.5).

![Graph showing cyclic voltammograms](image)

Figure 3.2 Oxidized polycrystalline ruthenium electrodes in 1mM CuSO$_4$ with 0.5M H$_2$SO$_4$ as the electrolyte. Scan rate = 20 mV/s.
Figure 3.3 Oxidized polycrystalline ruthenium electrodes in 2mM CuSO\(_4\) with 0.5M H\(_2\)SO\(_4\) as the electrolyte. Scan rate = 20 mV/s.

Figure 3.4 Oxidized polycrystalline ruthenium electrodes in 5mM CuSO\(_4\) with 0.5M H\(_2\)SO\(_4\) as the electrolyte. Scan rate = 20 mV/s.
Figure 3.5 Oxidized polycrystalline ruthenium electrodes in 10mM CuSO₄ with 0.5M H₂SO₄ as the electrolyte. Scan rate = 20 mV/s.

The oxidized ruthenium electrode in different concentration of CuSO₄ is to test the monolayer of Copper UPD existence and see the bulk peak shift. It is reasonable to assume that the UPD influences the further growth of the bulk peak. For the UPD peak shifts less than the bulk peak, it means that deposition of bulk copper on oxidized ruthenium electrode is becoming easier in high concentration of CuSO₄. From these data, the first monolayer is not completed under the potential of -0.01V, and the second layer and next few layers are from the bulk peak.
Comparing the ruthenium electrode, the oxidized ruthenium electrode behavior is similar but the data also has significant difference. First, the monolayer of copper on oxidized ruthenium electrode is double as the ruthenium electrode, which has the same electrode area. Second, the distance between the bulk peak and UPD peak on the oxidized ruthenium electrode is bigger than the ruthenium electrode, which is about 10kJmol$^{-1}$ more. Third, the capacity of oxidized ruthenium electrode is bigger than the ruthenium electrode because the background is almost ten times higher than ruthenium electrode in 0.5M H$_2$SO$_4$.

3.3 pH effect on the UPD and bulk peak of oxidized ruthenium electrode

The pH of CuSO$_4$ solution$^{[4-6]}$ is one of critical aspects to investigate the
copper deposition on oxidized ruthenium electrode. The solution contains 0.5M K$_2$SO$_4$, and pH is adjusted by H$_2$SO$_4$ and NaOH solution in order to avoid the effect of other cathodic anions. From the figure 3.7, pH above 4 the bulk and UPD peaks become smaller, even disappear, and a new peak appears, it is the copper deposition peak from the related XPS data of Yibin Zhang. It means the pH value of solution is important to these experiments. From all the data from figure 3.1 to 3.5, the 0.5M H$_2$SO$_4$ is the electrolyte, and the pH = 0.

![Figure 3.7 CV of oxidized ruthenium electrode in different pH 2mM CuSO$_4$ solution and 0.5M K$_2$SO$_4$ as electrolyte; pH is adjusted by H$_2$SO$_4$ and NaOH; Scanrate = 20mV/s.](image)
3.4 Effect of different oxidized potential on ruthenium electrode

Oxidized potential on ruthenium electrode is one of critical aspects to investigate the behavior of oxidized ruthenium electrode, which also help to distinguish the oxidized ruthenium and ruthenium electrodes. [5-8]

From the figure 3.9, the capacity of oxidized ruthenium electrode is increasing, as the oxidized potential is higher. As the oxidized potential increases, the bulk peak will shift to negative; the monolayer of UPD peak becomes clear, the monolayer of UPD peak also becomes more; the distance between the bulk peak and UPD peak is increasing, it means that the copper deposition becomes easier and the under potential deposition happens at the more positive potential by comparing the bare ruthenium electrode from table
3.2.

The oxidized potential above 1.4 V makes the ruthenium electrode excessively oxidized, which turns Ru to RuO$_4$ (gas). Therefore, the best-oxidized potential is 1.3 V.

Figure 3.9 Various oxidized potential on ruthenium electrodes in 2mM CuSO$_4$ with 0.5M H$_2$SO$_4$ as the electrolyte. Scanrate 20mV/s

<table>
<thead>
<tr>
<th>Oxidized potential</th>
<th>Bulk peak / V</th>
<th>UPD peak / V</th>
<th>$\Delta E_p$ distance</th>
<th>$\Delta G_p$ KJmol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3v 180s</td>
<td>0.018</td>
<td>0.204</td>
<td>0.186</td>
<td>35.9</td>
</tr>
<tr>
<td>1.1v 180s</td>
<td>0.023</td>
<td>0.193</td>
<td>0.170</td>
<td>32.8</td>
</tr>
<tr>
<td>0.8v 180s</td>
<td>0.048</td>
<td>0.215</td>
<td>0.167</td>
<td>32.2</td>
</tr>
<tr>
<td>Bare Ru</td>
<td>0.064</td>
<td>0.176</td>
<td>0.112</td>
<td>21.6</td>
</tr>
</tbody>
</table>

Table 3.2 Various oxidized potential on ruthenium electrodes in 2mM CuSO$_4$ with 0.5M H$_2$SO$_4$ as the electrolyte.

3.5 Effect of different oxidized time on ruthenium electrodes
Oxidized time on ruthenium electrode is one of critical aspects to investigate the behavior of oxidized ruthenium electrode, which also help to distinguish the oxidized ruthenium and ruthenium electrodes.\[8\]

From the figure 3.10, the capacity of oxidized ruthenium electrode is increasing, as the oxidized time is larger. As the oxidized time increases, the bulk peak position is constant; the distance between the bulk peak and UPD peak is also constant, it means that the copper deposition is same inspite of the oxidized time, and the oxidized potential is more important than the oxidized time to determine the interactions between Cu/RuO$_x$H$_y$.

![Graph showing various oxidized time on ruthenium electrodes in 2mM CuSO$_4$ with 0.5M H$_2$SO$_4$ as the electrolyte. Scanrate 20mV/s](image)

<table>
<thead>
<tr>
<th>Oxidized time</th>
<th>Bulk peak position / V</th>
<th>UPD peak position / V</th>
<th>$\Delta E_p$ / V</th>
<th>$\Delta G_p$ kJmol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3v 180s</td>
<td>0.018</td>
<td>0.204</td>
<td>0.186</td>
<td>35.9</td>
</tr>
<tr>
<td>1.3v 120s</td>
<td>0.01</td>
<td>0.183</td>
<td>0.173</td>
<td>33.4</td>
</tr>
</tbody>
</table>
Table 3.3 Various oxidized time on ruthenium electrode in 2mM CuSO₄ with 0.5M H₂SO₄ as the electrolyte.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>1.3v 60s</th>
<th>1.3v 30s</th>
<th>1.3v 5s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.02</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>0.21</td>
<td>0.215</td>
<td>0.218</td>
</tr>
<tr>
<td></td>
<td>0.19</td>
<td>0.195</td>
<td>0.188</td>
</tr>
<tr>
<td></td>
<td>36.7</td>
<td>37.6</td>
<td>36.3</td>
</tr>
</tbody>
</table>

3.6 Anion effects on oxidized ruthenium electrode in 2mM Cu (ClO₄)₂ solution

It is well known for some time that anion adsorption may have a strong influence on the deposition behavior on the polycrystalline ruthenium electrodes. But no literature shows the halide anions influence on oxidized ruthenium electrode systematically.

In this part, the technique of cyclic voltammetry is used to obtain data of the system with anions and without anions. By comparing the regular CV, the influences of anions are identified. First, the under potential peak shift $\Delta E$ is decreased, which is related to a reduction in bond strength between copper adatom and oxidized ruthenium surface. This change of bond energy is caused by the interaction of the anions with the oxidized ruthenium, and it is obviously stronger than that with the adsorbates. Second, the area of UPD peak is enlarged. The reason is that the copper atom adsorption is now accompanied by anions desorption; both sides contribute to the current in the same direction and thus make a larger apparent surface charge.

From the reference [3-4], the anions effect sequence is ClO₄⁻ < SO₄²⁻ < Cl⁻ < Br⁻. In this case, the effect of anions is more complex than what the reference said. From the figure 3.10, the oxidized ruthenium electrode in 2mM Cu (ClO₄)₂
solution, and the influence of ClO$_4^-$ is so small that do not need to count it in the experiments. The result is similar as the oxidized ruthenium electrode in 2mM CuSO$_4$ solution, the UPD and bulk peak still there, which means that the SO$_4^{2-}$ may help to build the UPD peak, but it is not critical reason for the UPD peak formation. It also excludes the suspicion that the UPD peak actually is the absorption of SO$_4^{2-}$ and no copper at all. The monolayer of UPD peak in figure 3.11 is about 0.57 ML, which is smaller than the monolayer in 2mM CuSO$_4$ solution. One of reasons is that the ClO$_4^-$ does not coadsorb easily on the oxidized ruthenium electrode surface with copper atoms.

The oxidized surface of ruthenium electrode may help to build the first monolayer of copper deposition much easier by comparing the bare ruthenium electrode in the same solution. From ignoring the anions influence, the bulk peak will be higher on the oxidized ruthenium electrode in the same conditions. It means that the efficiency of copper deposition is better on the oxidized ruthenium electrode. One of the explanations is that the electroactive area increase after the oxidization. By using the equation 1.1, the calculation of the area of oxidized ruthenium electrode is two times as big as the ruthenium electrode (the original one).
Figure 3.11 CV of oxidized (1.3V 180s) ruthenium electrode in 2mM Cu (ClO$_4$)$_2$ and 0.1 M HClO$_4$ as electrolyte; Scanrate = 20mV/s

3.6.1 The influence of Cl$^-$ on oxidized (1.3V 180s) ruthenium surface

From the figure 3.12 to figure 3.14, the influence of Cl$^-$ is bigger as the concentration of Cl$^-$ increases. The bulk peak position is shifting from 0.078 V to 0.016 V (from table 2.2) and its height decreases while the concentration of Cl$^-$ increases. This phenomenon is similar as the ruthenium reference$^{[4-6]}$. The monolayer of UPD peak is increasing while the concentration of Cl$^-$ is higher. This may be caused by the copper atom adsorption is accompanied by Cl$^-$ desorption, both of them contributes to the current in the same way. Then, this process, which can explain the shrink of its height, affects the bulk peak.

The distance between the bulk peak and UPD peak can help us to understand whether the monolayer takes place easily or hardly. From the table 3.4, the distance from 152 mV increases to 206 mV, which means the monolayer of
copper deposition happens easier. The Gibbs excess is increasing from 29.3kJmol\(^{-1}\) to 39.7kJmol\(^{-1}\).

<table>
<thead>
<tr>
<th>Conc.</th>
<th>Bulk Position / V</th>
<th>UPD Position / V</th>
<th>(\Delta E_p / \text{V})</th>
<th>(\Delta G_p / \text{kJmol}^{-1})</th>
<th>Monolayer</th>
<th>Charge / (\mu\text{C})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0mM</td>
<td>0.078</td>
<td>0.23</td>
<td>0.152</td>
<td>29.3</td>
<td>0.58</td>
<td>58.6</td>
</tr>
<tr>
<td>1mM Cl</td>
<td>0.084</td>
<td>0.278</td>
<td>0.194</td>
<td>37.4</td>
<td>1.10</td>
<td>111</td>
</tr>
<tr>
<td>10mM Cl</td>
<td>0.047</td>
<td>0.232</td>
<td>0.185</td>
<td>35.7</td>
<td>0.72</td>
<td>73</td>
</tr>
<tr>
<td>20mM Cl</td>
<td>0.016</td>
<td>0.222</td>
<td>0.206</td>
<td>39.7</td>
<td>0.87</td>
<td>88</td>
</tr>
</tbody>
</table>

Table 3.4 Influence of \(\text{xmM Cl}^-\) on oxidized (1.3V 180s) ruthenium in 2mM \(\text{Cu (ClO}_4)_2\) solution

Figure 3.12 CV of oxidized (1.3V 80s) ruthenium electrode in 2mM \(\text{Cu (ClO}_4)_2\) + 1mM KCl and 0.1 M HClO\(_4\) as electrolyte; Scanrate = 20mV/s
Figure 3.13 CV of oxidized (1.3V 80s) ruthenium electrode in 2mM Cu (ClO_4)_2 + 10mM KCl and 0.1 M HClO_4 as electrolyte; Scanrate = 20mV/s

Figure 3.14 CV of oxidized (1.3V 80s) ruthenium electrode in 2mM Cu (ClO_4)_2 + 20mM KCl and 0.1 M HClO_4 as electrolyte; Scanrate = 20mV/s
3.6.2 The influence of SO$_4^{2-}$ on the oxidized (1.3V 80s) ruthenium surface

From the figure 3.15 to figure 3.17, the influence of SO$_4^{2-}$ is bigger as the concentration of SO$_4^{2-}$ increases. The bulk peak position is shifting from 0.078 V to 0.084 V (from table 3.5) which has the similar position and its height keeps the same while the concentration of SO$_4^{2-}$ increases. The monolayer of UPD peak is increasing while the concentration of SO$_4^{2-}$ is higher. This may be caused by the copper atom adsorption is accompanied by SO$_4^{2-}$ desorption, both of them contributes to the current in the same way. Then, this process affects the bulk peak. \cite{4-6}

The distance between the bulk peak and UPD peak can help us to understand whether the monolayer takes place easily or hardly. From the table 3.5, the distance from 152 mV increases to 238 mV, which means the monolayer of copper deposition happens easier. The Gibbs excess is increasing from 29.3kJmol$^{-1}$ to 45.9kJmol$^{-1}$. In the solution of 20mM K$_2$SO$_4$, the behavior of copper deposition on ruthenium electrode is quite like in the 2mM CuSO$_4$ solution, $\Delta E$ and $\Delta G$ are almost same from table 3.5.

<table>
<thead>
<tr>
<th>Conc.</th>
<th>Bulk position /V</th>
<th>UPD position / V</th>
<th>$\Delta E_p$ / V</th>
<th>$\Delta G_p$ / kJmol$^{-1}$</th>
<th>Monolayer</th>
</tr>
</thead>
<tbody>
<tr>
<td>0mM</td>
<td>0.078</td>
<td>0.23</td>
<td>0.152</td>
<td>29.3</td>
<td>0.58</td>
</tr>
<tr>
<td>1mM SO$_4^{2-}$</td>
<td>0.088</td>
<td>0.295</td>
<td>0.207</td>
<td>39.9</td>
<td>0.78</td>
</tr>
<tr>
<td>10mM SO$_4^{2-}$</td>
<td>0.086</td>
<td>0.309</td>
<td>0.223</td>
<td>43.0</td>
<td>0.98</td>
</tr>
<tr>
<td>20mM SO$_4^{2-}$</td>
<td>0.084</td>
<td>0.322</td>
<td>0.238</td>
<td>45.9</td>
<td>1.07</td>
</tr>
</tbody>
</table>

Table 3.5 Influence of $x$mM SO$_4^{2-}$ on oxidized (1.3V 180s) ruthenium in 2mM Cu (ClO$_4$)$_2$ solution
Figure 3.15 CV of oxidized (1.3V 180s) ruthenium electrode in 2mM \( \text{Cu}^{(\text{ClO}_4)_2} \) + 1mM \( \text{K}_2\text{SO}_4 \) and 0.1 M \( \text{HClO}_4 \) as electrolyte; Scanrate = 20mV/s

Figure 3.16 CV of oxidized (1.3V 180s) ruthenium electrode in 2mM \( \text{Cu}^{(\text{ClO}_4)_2} \) + 10mM \( \text{K}_2\text{SO}_4 \) and 0.1 M \( \text{HClO}_4 \) as electrolyte; Scanrate = 20mV/s
3.17 CV of oxidized (1.3V 180s) ruthenium electrode in 2mM Cu

\[(\text{ClO}_4)_2 \quad + \quad 20\text{mM K}_2\text{SO}_4 \quad \text{and} \quad 0.1 \quad \text{M HClO}_4 \quad \text{as electrolyte;}
\]

Scanrate = 20mV/s

3.6.3 The influence of Br\(^{-}\) on oxidized (1.3V 180s) ruthenium surface

From the figure 3.18 to figure 3.20, the influence of Br\(^{-}\) is bigger as the concentration of Br\(^{-}\) increases. The bulk peak position is shifting from 0.078 V to -0.002 V (from table 3.6) and its height decreases while the concentration of Br\(^{-}\) increases. The monolayer of UPD peak is increasing while the concentration of Br\(^{-}\) is higher. This may be caused by the copper atom adsorption is accompanied by Br\(^{-}\) desorption, both of them contributes to the current in the same way. Then, this process, which can explain the shrink of its height, affects the bulk peak.

The distance between the bulk peak and UPD peak can help us to understand whether the monolayer takes place easily or hardly. From the table 3.6, the distance from 152 mV increases to 252 mV, which means the
monolayer of copper deposition happens easier. The Gibbs excess is increasing from 29.3kJmol\(^{-1}\) to 48.6kJmol\(^{-1}\).

<table>
<thead>
<tr>
<th>Conc.</th>
<th>Bulk position / V</th>
<th>UPD position / V</th>
<th>(\Delta E_p / \text{V})</th>
<th>(\Delta G_p / \text{kJmol}^{-1})</th>
<th>Monolayer</th>
<th>Charge/ \text{uC}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0mM</td>
<td>0.078</td>
<td>0.23</td>
<td>0.152</td>
<td>29.3</td>
<td>0.58</td>
<td>58.6</td>
</tr>
<tr>
<td>1mM Br(^-)</td>
<td>0.081</td>
<td>0.313</td>
<td>0.232</td>
<td>44.7</td>
<td>0.60</td>
<td>61</td>
</tr>
<tr>
<td>10mM Br(^-)</td>
<td>0.01</td>
<td>0.26</td>
<td>0.25</td>
<td>48.2</td>
<td>3.59</td>
<td>360</td>
</tr>
<tr>
<td>20mM Br(^-)</td>
<td>-0.002</td>
<td>0.25</td>
<td>0.252</td>
<td>48.6</td>
<td>4.67</td>
<td>469</td>
</tr>
</tbody>
</table>

Table 3.6 Influence of \(x\)mM Br\(^-\) on oxidized (1.3V 180s) ruthenium in 2mM Cu \((\text{ClO}_4)_2\) solution

Figure 3.18 CV of oxidized (1.3V 180s) ruthenium electrode in 2mM Cu \((\text{ClO}_4)_2\) + 1mM KBr and 0.1 M HClO\(_4\) as electrolyte; Scanrate = 20mV/s
Figure 3.19 CV of oxidized (1.3V 180s) ruthenium electrode in 2mM $\text{Cu (ClO}_4\text{)}_2 + 10\text{mM KBr and 0.1 M HClO}_4$ as electrolyte; Scanrate = 20mV/s

Figure 3.20 CV of oxidized (1.3V 180s) ruthenium electrode in 2mM $\text{Cu (ClO}_4\text{)}_2 + 20\text{mM KBr and 0.1 M HClO}_4$ as electrolyte; Scanrate = 20mV/s
3.6.4 Summary the influence of anions on the oxidized ruthenium surface

From the part 3.6.1 to 3.6.3, the influences of three anions on copper deposition process are described, which shows the strong influence on the oxidized ruthenium electrode surface. First, compare the Cl\(^{-}\), SO\(_4^{2-}\) and Br\(^{-}\) influences, the Br\(^{-}\) affect the surface quite a lot and even the bulk peak almost disappeared which may suggest that the structure of first monolayer on the ruthenium surface is changed, it will block the further bulk peak building at the same lowest potential. Second, the change plot of CV in SO\(_4^{2-}\) is smaller than the other two anions. It means the influence of SO\(_4^{2-}\) is smallest. So the anions effect sequence is SO\(_4^{2-}\) < Cl\(^{-}\) < Br\(^{-}\) from the experiments.

3.7 Scanrate dependent investigation on oxidized ruthenium electrode

The kinetics of the oxidized ruthenium electrode process was obtained by the voltammograms recorded at the different scanrate\(^{[10]}\). The peak potentials and current maxima are related with the scan rate. The figure 3.21 shows the CVs of different scan rate of copper deposition on the oxidized ruthenium in 2mM CuSO\(_4\) solution. The CV shows that the bulk disappears after the scanrate is above 200 mVs\(^{-1}\). The figure 3.22 shows the monolayer of copper deposition at different scan rate. From which, the monolayer is almost constant while the scanrate from 1 mVs\(^{-1}\) to 1000 mVs\(^{-1}\), and it which means that the scan rate can not affect the UPD deposition, and it also suggests that the building process of UPD on oxidized ruthenium is so fast that the bulk peak can not be
built at the high scan rate.

The figure 3.23 shows that the linear dependence of the UPD position on the square root of the sweep rate is obvious. Bosco and Rangarajan \cite{11} have shown that this is the characteristic of an instantaneous nucleation and growth process. From the figure 3.22, it means that the same nucleation of copper happened and the structure of copper deposition is same on the oxidized ruthenium electrode.

Figure 3.21 Different scanrate of CVs on oxidized (1.3V 180s) ruthenium electrode in 2mM CuSO$_4$ with 0.5M H$_2$SO$_4$ as the electrolyte.

Scanrate: 1, 3, 5, 10, 20, 50, 100, 200, 500, 1000 mV/s
Figure 3.22 Monolayer of copper deposition on oxidized ruthenium electrode vs. scanrate.

Figure 3.23 Copper UPD in the CV as a function of the square root of the scan rate.
Reference


4. Dieter M. Kolb, Advances in electrochemistry and electrochemical engineering Vol 11


CHAPTER 4

ELECTROCHEMISTRY OF POLycRYSTALLINE IRIDIUM ELECTRODE

4.1 CV of polycrystalline iridium electrode in 1mm CuSO₄

The polycrystalline Iridium has the similar physical properties as the polycrystalline ruthenium, which was also considered as the one of options the copper barriers. The electrochemical method is the best way to investigate the deposition of copper on the Iridium.[1-3]

Prior to UPD experiments, the iridium electrodes were prepared by CV cleaning with a few sweeps in the range -0.5V to 0.5V. Figure (4.1) shows voltammograms obtained with a polycrystalline iridium electrode in 0.5 M H₂SO₄, which is the CV as the background. The current height of this background is 300 uAcm⁻², which is almost five times smaller than the striping bulk peak of copper from figure4.2. Then the series CVs were obtained in 1mM CuSO₄ and 0.5M H₂SO₄ as electrolyte by macro command of CH instrument software. From the background CV, the anodic range obviously has no peak exist. So comparing the CV of iridium electrode in 1mM CuSO₄ solution, the two peaks appear which were defined as the bulk peak and UPD peak. From the CV of polycrystalline iridium electrode (figure 4.2), the peak1 has almost constant height after potential went to more negative from 0.03V (vs. Ag/AgCl) which is defined as the under potential deposition (UPD) peak. The peak2 is the bulk peak that its height is related with the concentration of CuSO₄, according to figure 4.3 to figure4.6. The copper monolayer of this UPD is
around 0.5 ML, which can be explained by the structure of polycrystalline iridium surface, which are similar to those reported in the literature.\textsuperscript{[1-2]}

From the table (4.1), the UPD ML is almost constant which is related to the surface structure of the polycrystalline iridium. The crystal cell of iridium is CCP (Cubic Close-Packed) from the part of introduction.

Figure 4.1 The back ground of polycrystalline iridium electrode in 0.5 M H$_2$SO$_4$; Scanrate = 20mVs$^{-1}$

Fig 4.2 The progressive scan CV of polycrystalline Iridium electrode in 1mM
CuSO₄ and 0.5 M H₂SO₄ as electrolyte. Scanrate = 20 mV/s.

<table>
<thead>
<tr>
<th>Cu Conc. /mM</th>
<th>UPD Position (V)</th>
<th>Charge / uC</th>
<th>ML</th>
<th>Bulk position/V</th>
<th>ΔEₚ / V</th>
<th>ΔGₚ kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>0.263</td>
<td>23.2</td>
<td>0.25</td>
<td>0.032</td>
<td>0.231</td>
<td>44.58</td>
</tr>
<tr>
<td>0.5</td>
<td>0.265</td>
<td>14.7</td>
<td>0.16</td>
<td>0.013</td>
<td>0.252</td>
<td>48.63</td>
</tr>
<tr>
<td>1</td>
<td>0.309</td>
<td>28.3</td>
<td>0.31</td>
<td>0.044</td>
<td>0.265</td>
<td>51.14</td>
</tr>
<tr>
<td>2</td>
<td>0.465</td>
<td>19.9</td>
<td>0.22</td>
<td>0.063</td>
<td>0.402</td>
<td>77.58</td>
</tr>
<tr>
<td>5</td>
<td>0.467</td>
<td>24.3</td>
<td>0.26</td>
<td>0.085</td>
<td>0.382</td>
<td>73.72</td>
</tr>
</tbody>
</table>

Table 4.1 Monolayer of copper on polycrystalline iridium electrode in different CuSO₄ solution; Scanrate = 20 mVs⁻¹

![Cyclic voltammogram](image)

Fig 4.3 The progressive scan CV of polycrystalline Iridium electrode in 0.25mM CuSO₄ and 0.5 M H₂SO₄ as electrolyte. Scanrate = 20 mV/s.
Fig 4.4 The progressive scan CV of polycrystalline Iridium electrode in 0.5mM CuSO₄ and 0.5 M H₂SO₄ as electrolyte. Scanrate = 20mV/s.

Fig 4.5 The progressive scan CV of polycrystalline Iridium electrode in 1mM CuSO₄ and 0.5 M H₂SO₄ as electrolyte. Scanrate = 20mV/s.
4.2 Anion effects on iridium electrode in 1mM Cu (ClO$_4$)$_2$ solution

It was well known for some time that anion adsorption may have a strong influence on the deposition behavior on the polycrystalline iridium electrodes [2-6]. However, no one study the detail of halide anions influence systematically.

In this part, the technique of cyclic voltammetry was used to obtain data of the system with anions and without anions. By comparing the regular CV, the influences of anions are identified. First, the under potential peak shift $\Delta E$ is decreased, which is related to a reduction in bond strength between copper adatom and iridium surface. This change of bond energy caused by the interaction of the anions with the iridium, and it is obviously stronger than that with the adsorbates. Second, the area of UPD peak was enlarged. The reason is that the copper atom adsorption is now accompanied by anions desorption;
both sides contribute to the current in the same direction and thus make a larger apparent surface charge.\textsuperscript{[6-7]}

From the reference\textsuperscript{[8-9]}, the anions effect sequence is \(\text{ClO}_4^- < \text{SO}_4^{2-} < \text{Cl}^- < \text{Br}^-\). In this case, the effect of anions is more complex than what the reference said. From the figure 4.7, the iridium electrode in 1mM Cu (\(\text{ClO}_4\))\textsubscript{2} solution, and the influence of \(\text{ClO}_4^-\) is so small that do not need to count it in the experiments. The result is similar as the iridium electrode in 1mM CuSO\textsubscript{4} solution, the UPD and bulk peak still there, which means that the \(\text{SO}_4^{2-}\) may help to build the UPD peak, but it is not critical reason for the UPD peak formation. It also excludes the suspicion that the UPD peak actually is the absorption of \(\text{SO}_4^{2-}\) and no copper at all. The monolayer of UPD peak in figure 4.7 is about 0.53 ML, which is bigger than the monolayer in 1mM CuSO\textsubscript{4} solution. The anions may block the copper monolayer more densely by the strong interaction with the iridium surface.
Figure 4.7 CV of iridium electrode in 1mM Cu (ClO$_4$)$_2$ and 0.1 M HClO$_4$ as electrolyte; Scanrate = 20mV/s

4.2.1 The influence of Cl$^-$ on the iridium surface

From the figure 4.8 to figure 4.10, the influence of Cl$^-$ is bigger as the concentration of Cl$^-$ increases. The bulk peak position is shifting from 0.072 V to -0.028 V (from table 4.2) and its height decreases while the concentration of Cl$^-$ increases. The UPD peak position shifts to negative potential while the concentration of Cl$^-$ is higher. This may be caused by the copper atom adsorption is accompanied by Cl$^-$ desorption, both of them contributes to the current in the same way. Then, this process, which can explain the shrink of its height, affects the bulk peak.

The distance between the bulk peak and UPD peak can help us to understand whether the monolayer takes place easily or difficult. From the
Table 4.2, the distance from 400 mV decreases to 156 mV, which means the monolayer of copper deposition happens difficult. The Gibbs excess is decreasing from 76.2 kJ mol\(^{-1}\) to 30.1 kJ mol\(^{-1}\).

<table>
<thead>
<tr>
<th>KCl /mM</th>
<th>Bulk position/ V</th>
<th>UPD position / V</th>
<th>Charge / uC</th>
<th>ML</th>
<th>(\Delta E_p / V)</th>
<th>(\Delta G_p / kJ mol^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.072</td>
<td>0.467</td>
<td>52</td>
<td>0.53</td>
<td>0.395</td>
<td>76.2</td>
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<td>32</td>
<td>0.33</td>
<td>0.415</td>
<td>80.0</td>
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<tr>
<td>10</td>
<td>0.015</td>
<td>0.093</td>
<td>29</td>
<td>0.30</td>
<td>0.078</td>
<td>15.0</td>
</tr>
<tr>
<td>20</td>
<td>-0.028</td>
<td>0.128</td>
<td>78</td>
<td>0.80</td>
<td>0.156</td>
<td>30.1</td>
</tr>
</tbody>
</table>

Table 4.2 Influence of x mM Cl\(^{-}\) on iridium in 1 mM Cu (ClO\(_4\))\(_2\) solution

Figure 4.8 CV of iridium electrode in 1 mM Cu (ClO\(_4\))\(_2\) + 1 mM KCl and 0.1 M HClO\(_4\) as electrolyte; Scanrate = 20 mV/s
Figure 4.9 CV of iridium electrode in 1mM Cu (ClO$_4$)$_2$ + 10mM KCl and 0.1 M HClO$_4$ as electrolyte; Scanrate = 20mV/s

Figure 4.10 CV of iridium electrode in 1mM Cu (ClO$_4$)$_2$ + 20mM KCl and 0.1 M HClO$_4$ as electrolyte; Scanrate = 20mV/s
4.2.2 The influence of $\text{SO}_4^{2-}$ on the iridium surface

From the figure 4.11 to figure 4.13, the influence of $\text{SO}_4^{2-}$ is bigger as the concentration of $\text{SO}_4^{2-}$ increases. The bulk peak position is constant (from table 4.3) and its height decreases while the concentration of $\text{SO}_4^{2-}$ increases. The monolayer of UPD peak is decreasing while the concentration of $\text{SO}_4^{2-}$ is higher. This may be caused by the copper atom adsorption is accompanied by $\text{SO}_4^{2-}$ desorption, both of them contributes to the current in the same way. Then, this process, which can explain the shrink of its height, affects the bulk peak.

The distance between the bulk peak and UPD peak can help us to understand whether the monolayer takes place easily or difficult. From the table 4.3, the distance from 395 mV increases to 434 mV, which means the monolayer of copper deposition happens easier. The Gibbs excess is increasing from 76.2kJmol$^{-1}$ to 83.7kJmol$^{-1}$. In the solution of 20mM $\text{K}_2\text{SO}_4$, the behavior of copper deposition on iridium electrode is quite like in the 1mM CuSO$_4$ solution; $\Delta E$ and $\Delta G$ are almost same from table 4.3.

<table>
<thead>
<tr>
<th>$\text{K}_2\text{SO}_4$ /mM</th>
<th>Bulk position / V</th>
<th>UPD position / V</th>
<th>Charge / uC</th>
<th>ML</th>
<th>$\Delta E_p$ / V</th>
<th>$\Delta G_p$ / kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.072</td>
<td>0.467</td>
<td>52</td>
<td>0.53</td>
<td>0.395</td>
<td>76.2</td>
</tr>
<tr>
<td>1</td>
<td>0.075</td>
<td>0.5</td>
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<td>0.22</td>
<td>0.425</td>
<td>82.0</td>
</tr>
<tr>
<td>10</td>
<td>0.074</td>
<td>0.503</td>
<td>15</td>
<td>0.15</td>
<td>0.429</td>
<td>82.7</td>
</tr>
<tr>
<td>20</td>
<td>0.072</td>
<td>0.506</td>
<td>11</td>
<td>0.11</td>
<td>0.434</td>
<td>83.7</td>
</tr>
</tbody>
</table>

Table 4.3 Influence of xmM $\text{SO}_4^{2-}$ on iridium in 1mM Cu ($\text{ClO}_4$)$_2$ solution
Figure 4.11 CV of iridium electrode in 1mM Cu (ClO$_4$)$_2$ + 1mM K$_2$SO$_4$ and 0.1 M HClO$_4$ as electrolyte; Scanrate = 20mV/s

Figure 4.12 CV of iridium electrode in 1mM Cu (ClO$_4$)$_2$ + 10mM K$_2$SO$_4$ and 0.1 M HClO$_4$ as electrolyte; Scanrate = 20mV/s
4.4.3 The influence of Br\(^{-}\) on the iridium surface

From the figure 4.14 to figure 4.16, the influence of Br\(^{-}\) is bigger as the concentration of Br\(^{-}\) increases. The bulk peak position is shifting from 0.072 V to -0.072 V (from table 4.4) and its height decreases while the concentration of Br\(^{-}\) increases. The monolayer of UPD peak is decreasing while the concentration of Br\(^{-}\) is higher. This may be caused by the copper atom adsorption is accompanied by Br\(^{-}\) desorption, both of them contributes to the current in the same way. Then, this process, which can explain the shrink of its height, affects the bulk peak.

The distance between the bulk peak and UPD peak can help us to understand whether the monolayer takes place easily or hardly. From the table 4.4, the

Figure 4.13 CV of iridium electrode in 1mM Cu (ClO\(_4\))\(_2\) + 20mM K\(_2\)SO\(_4\) and 0.1 M HClO\(_4\) as electrolyte ; Scanrate = 20mV/s
distance from 395 mV decreases to 325 mV, which means the monolayer of copper deposition happens harder. The Gibbs excess is decreasing from 76.2kJmol\(^{-1}\) to 62.7kJmol\(^{-1}\). The influence of Br\(^-\) is so strong that the bulk peak almost disappeared and the shape of UPD peak was changed. It means that the structure of monolayer on the surface of iridium was changed by the strong bond energy of Br\(^-\) with iridium atoms.

<table>
<thead>
<tr>
<th>KBr /mM</th>
<th>Bulk position / V</th>
<th>UPD position / V</th>
<th>Charge / uC</th>
<th>ML</th>
<th>(\Delta E_p / V)</th>
<th>(\Delta G_p / kJmol^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.072</td>
<td>0.467</td>
<td>52</td>
<td>0.53</td>
<td>0.395</td>
<td>76.2</td>
</tr>
<tr>
<td>1</td>
<td>0.055</td>
<td>0.413</td>
<td>9</td>
<td>0.09</td>
<td>0.358</td>
<td>69.0</td>
</tr>
<tr>
<td>10</td>
<td>0.024</td>
<td>0.222</td>
<td>17</td>
<td>0.17</td>
<td>0.198</td>
<td>38.2</td>
</tr>
<tr>
<td>20</td>
<td>-0.072</td>
<td>0.253</td>
<td>22</td>
<td>0.22</td>
<td>0.325</td>
<td>62.7</td>
</tr>
</tbody>
</table>

Table 4.4 Influence of x mM Br\(^-\) on iridium in 1mM Cu (ClO\(_4\))\(_2\) solution

Figure 4.14 CV of iridium electrode in 1mM Cu (ClO\(_4\))\(_2\) + 1mM KBr and 0.1 M HClO\(_4\) as electrolyte ; Scanrate = 20mV/s
Figure 4.15 CV of iridium electrode in 1mM Cu (ClO$_4$)$_2$ + 1mM KBr and 0.1 M HClO$_4$ as electrolyte; Scanrate = 20mV/s

Figure 4.16 CV of iridium electrode in 1mM Cu (ClO$_4$)$_2$ + 1mM KBr and 0.1 M HClO$_4$ as electrolyte; Scanrate = 20mV/s
Reference

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CHAPTER 5

CONCLUSIONS

The progressive scan CVs of copper electrodeposition on ruthenium electrode is presented, which shows the bulk peak and UPD peak exist. From the CVs, the copper deposition on ruthenium is easily controlled. The influence of different CuSO$_4$ concentration on copper deposition is investigated, which the strip bulk peak shifts to positive potential when the concentration is increasing. The monolayer of UPD is almost constant in the different CuSO$_4$ concentration, which is about 0.5ML. Some errors measurement happened from the Figure 2.6, so the line slightly decreases. The reason is that the bulk peak is so huge in the high concentration and it is not easy to measure the charge UPD peak in the software. The pH effect the copper deposition is studied, the bulk peak has a decreasing trend when the pH is increasing. The influences of Cl$^-$, SO$_4^{2-}$ and Br$^-$ on copper deposition process are described, which shows the strong influence on the ruthenium electrode surface. First, compare the influences, the Br$^-$ affect the surface quite a lot and even the bulk peak almost disappeared which may suggest that the structure of first monolayer on the ruthenium surface is changed, it will block the further bulk peak building at the same lowest potential. Second, the change plot of CV in SO$_4^{2-}$ is smaller than the other two anions, and the distance of peak separation is the smallest one in the three anions. It means the influence of SO$_4^{2-}$ is smallest. So the anions effect sequence is SO$_4^{2-}$ < Cl$^-$ < Br$^-$ from the
experiments. Third, the monolayer of UPD is increasing when the concentration $\text{SO}_4^{2-}$ and $\text{Cl}^-$ are increasing, but the monolayer of UPD is decreasing in $\text{Br}^-$ solutions.

The progressive scan CVs of copper electrodeposition on oxide ruthenium electrode is presented, which shows the bulk peak and UPD peak exist, and is similar with the ruthenium electrode. From the CVs, the copper deposition on ruthenium is easily controlled. The influence of different CuSO$_4$ concentration on copper deposition is investigated, which the strip bulk peak shifts to positive potential when the concentration is increasing. The monolayer of UPD is almost constant in the different CuSO$_4$ concentration, which is about 1ML. Some errors measurement happened from the Figure 3.6, so the line is not linear. The reason is that the bulk peak is so huge in the high concentration and it is not easy to measure the charge UPD peak in the software. The pH effect the copper deposition is studied, the bulk peak has a decreasing trend when the pH is increasing. When pH is above 3, the bulk peak and UPD peak disappear, and a new peak will appear. It is the copper deposition peak from Yibin Zhang’s XPS data. The oxidized potential of ruthenium electrode is investigated. The height of bulk peak increased when oxidized potential was increasing. The monolayer of UPD will increasing from 0.5ML to 1ML when the oxidized potential is increasing. The oxidized time of ruthenium electrode is also studied. The capacitance of ruthenium is increasing a lot when the oxidize time increases from 5s to 180s. At the same time the monolayer is also
increasing. The influences of Cl$^{-}$ SO$_4^{2-}$ and Br$^{-}$ on copper deposition process are described, which shows the strong influence on the oxidized ruthenium electrode surface. First, compare the Cl$^{-}$ SO$_4^{2-}$ and Br$^{-}$ influences, the Br$^{-}$ affect the surface quite a lot and even the bulk peak almost disappeared which may suggest that the structure of first monolayer on the ruthenium surface is changed, it will block the further bulk peak building at the same lowest potential. Second, the change plot of CV in SO$_4^{2-}$ is smaller than the other two anions. It means the influence of SO$_4^{2-}$ is smallest. So the anions effect sequence is SO$_4^{2-}$ < Cl$^{-}$ < Br$^{-}$ from the experiments. The scanrate dependent experiment is studied and interesting information are obtained. The UPD peak is observed at the high scanrate that is over 200mVs$^{-1}$, but the bulk peak disappears. After processing the data of square root of scanrate versus the strip UPD peak position, I got a linear line (figure3.23) which means that the same nucleation of copper happened and the structure of copper deposition is same on the different scanrate.

The progressive scan CVs of copper electrodeposition on iridium electrode is presented, which shows the bulk peak and UPD peak exist. From the CVs, the copper deposition on iridium is easily controlled. The influence of different CuSO$_4$ concentration on copper deposition is investigated, which the strip bulk peak shifts to positive potential when the concentration is increasing. The monolayer of UPD is almost constant in the different CuSO$_4$ concentration, which is about 0.25ML. The influences of Cl$^{-}$ SO$_4^{2-}$ and Br$^{-}$ on copper
deposition process are described, which shows the strong influence on the iridium electrode surface. First, compare the influences, the Br⁻ affect the surface quite a lot and even the bulk peak almost disappeared when [KBr]=20mM which may suggest that the structure of first monolayer on the ruthenium surface is changed, it will block the further bulk peak building at the same lowest potential. Second, the change plot of CV in SO₄²⁻ is smaller than the other two anions, and the distance of peak separation is the smallest one in the three anions. It means the influence of SO₄²⁻ is smallest. So the anions effect sequence is SO₄²⁻ < Cl⁻ < Br⁻ from the experiments.
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