

Effect of Cu Ad-layers deposited onto Gold Electrodes Surfaces on the Electrocatalytic Reduction of Oxygen in Alkaline Solution: a Rotating Ring-Disk Electrode Hydrodynamic Voltammetry Study

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Underpotential deposition (UPD) of Cu ad-layers onto gold electrodes in an alkaline solution was investigated, for the first time. Modified single crystal Au(111) and polycrystalline Au electrodes were applied to oxygen reduction reaction (ORR) using rotating ring-disk electrode hydrodynamic voltammetry in an O₂-saturated 0.1 M NaOH solution. In comparison to bare substrate, a considerable enhancement of the disproportionation of hydrogen peroxide was observed at all Cu-modified Au electrodes. Additionally, the well-pronounced positive shifts of the reduction waves were attributed to the enhancement of the catalytic activity towards both the two-electron reduction steps of O₂ to HO₂⁻ and OH⁻ at the Cu-modified electrodes. Very interestingly, the direct four-electron ORR took place at potentials more negative than ca. -0.8 V vs. Ag|AgCl, which is ca. 400 mV more positive than what is shown at a bare polycrystalline Au electrode.

Keywords: Electrocatalysis, Oxygen Reduction Reaction (ORR), Underpotential Deposition (UPD), Rotating Ring-Disk Electrode (RRDE), Fuel Cells.

1. INTRODUCTION

Electrocatalysis in oxygen reduction is of major interest and extensive studies have been carried out for, among others, fuel cell applications [1-3]. Gold substrate is known to be a good catalyst for oxygen reduction in alkaline media [4-11]. On Au(100) single crystals, molecular oxygen (O₂) is reduced to water (H₂O) through a four-electron reduction process [4-6]. Polycrystalline Au electrodes as well as single crystal Au(111) electrodes, however, show a two-electron reduction process to form hydrogen peroxide [3,7-11]. To improve the catalytic activity of gold substrate for O₂

reduction, modification of the electrode surface with foreign metal ad-layer(s) could be an effective strategy for it has been proven to greatly enhance the electrocatalysis of various species [12-20] including the ORR itself [3,7,8,10,11,21-23].

Cu ad-layers onto gold surfaces have been reported, so far, to have a negative catalytic effect on ORR [24]. However, in a more recent work, a positive catalytic reduction of O₂ was observed on Au(111) single crystal electrodes in alkaline media when the surfaces were modified with Cu of less than a monolayer [25]. In the present work, under potential deposition (UPD) of Cu in an alkaline solution onto single crystal Au(111) and polycrystalline Au electrodes is presented for the first time. By means of rotating ring-disk electrode (RRDE) hydrodynamic voltammetry, as an easy and powerful tool to understand reaction pathways [3,8,10,26], the positive catalytic activity of the prepared Cu ad-layer on ORR was confirmed.

2. EXPERIMENTAL

NaOH and H₂SO₄ (ultra pure grade, Kanto Chemical Co., Inc.) were used to prepare electrolytes. CuSO₄·5H₂O (99.5%) purchased from Wako Pure Chemical Industries, Ltd., served for UPD experiments. All solutions were prepared using ultra pure water (Milli-Q 18.2 MΩcm, Millipore System Inc.). An RRDE (Nikko Keisoku, Japan) which consisted of a polycrystalline Au disk (ø = 6 mm) and Au ring sealed in a poly-tetrafluoroethylene jacket was used. Prior to each experiment, the electrode was polished with a 0.1 μm alumina polishing suspension (Baikalox[®]) on a polishing cloth (Bioanalytical Systems, Inc.) and then sonicated in Milli-Q water. After being polished to a mirror-like surface, the Au disk was electrochemically pretreated in a 0.1 M H₂SO₄ solution by repeating the potential scan in the range of -0.8 to 0.8 V (vs. Pt-plate: 0 V vs. Pt-plate = ca. 0.79 V vs. Ag|AgCl|KCl(sat)) at 100 mV s⁻¹ for 10 min or until the cyclic voltammogram of a clean Au electrode surface was obtained [11, 27]. In some experiments, an Au(111) single crystal electrode (ca. 0.08 cm² in surface area), which was prepared from an Au wire (99.99% in purity, Tanaka Kikinzoku Kogyo Co., Ltd.) using the flame-annealing-quenching method [25,28], was also used for comparison.

Hydrodynamic voltammetry was carried out using a rotating ring-disk electrode (RRDE-1) system, a dual potentiogalvanostat (DPGS-1) and a motor speed controller (SC-5) (Nikko Keisoku, Japan) along with a function generator 2230 (Toho Technical Research, Japan) and a D-72DG X-Y recorder (Rikken Denshi, Co., Ltd.). Ag|AgCl|KCl(sat) and a spiral Pt wire were employed as reference and counter electrodes, respectively.

The electrolyte was purged with high purity oxygen (>99.999%) for 20 minutes, and during the measurements oxygen was kept flowing over the solution to maintain an O₂-saturated electrolyte. Experiments in an O₂-free solution were carried out under a high purity N₂ gas atmosphere. All experiments were conducted at room temperature (i.e. 23 ± 1 °C).

3. RESULTS AND DISCUSSION

3.1. Underpotential deposition (UPD) of Cu in alkaline solution

Studies on Cu UPD on Au electrodes have been reported in acid media [29-31]. However, to our knowledge, no report has been published on Cu UPD in alkaline solutions. In the present work, both Au(111) single crystal and polycrystalline Au electrodes have been investigated in a Cu(II)-containing 0.1 M NaOH solution. For Cu UPD at a polycrystalline Au electrode, the current started to flow at ca. 0.35 V vs. Ag|AgCl. As the potential is scanned cathodically, two well-defined UPD peaks were observed at ca. -0.1 V and ca. -0.64 V vs. Ag|AgCl (Fig. 1). From the peak areas, a monolayer (ML) of Cu(I) species such as insoluble Cu(OH) or Cu₂O and further reduction of deposited Cu(I) to Cu(0) occurred at these two reduction peaks, respectively. Considering the theoretically estimated total charge of 0.44 C/cm² [29] for a full coverage of Cu ad-atoms (i.e. by reduction of Cu(II) to Cu(0)) onto the Au surface. These peaks were partially coupled with broad re-oxidation peaks appearing at ca. -0.9 V ≤ E ≤ -0.4 V and ca. -0.3 V ≤ E ≤ 0.2 V vs. Ag|AgCl, respectively. The re-oxidation peak at the positive side included the oxidation of multi-layer deposited Cu at potentials more negative than -0.8 V. More clearly, when a rotating disk electrode was used (dotted line in Fig. 1), the peak currents of the sharp anodic peak at ca. -0.2 V depended (not shown) on the switching potential at the negative limit, suggesting that the anodic peak included the oxidation of multi-layer Cu (not Cu ad-layer) deposited at negative potentials. In the present experimental conditions, since the concentration of Cu(II) was rather low (1 × 10⁻⁴ M), Cu deposition took place by only a few layers on the electrode surface and no color change (Au to Cu) was observed.

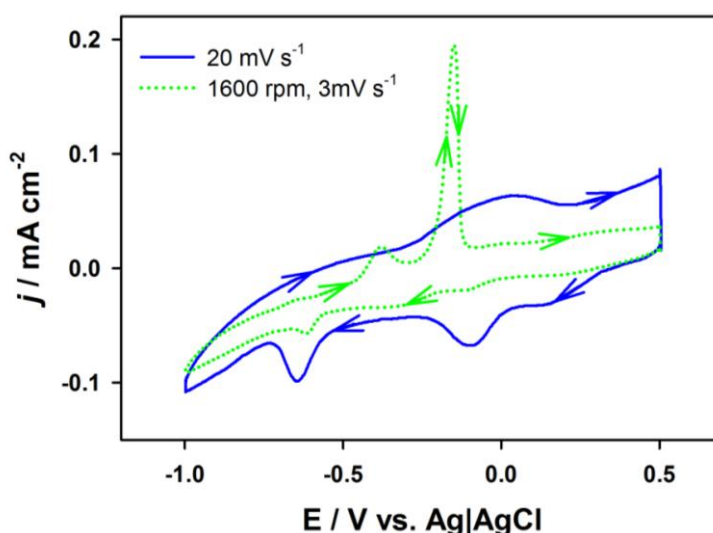


Figure 1. Cyclic voltammograms for Cu-UPD at polycrystalline Au electrode in N₂-saturated (0.1 M NaOH + 5 × 10⁻⁵ M CuSO₄) solution.

Using single crystal Au(111) electrode, sharper peaks compared with the polycrystalline Au electrode, were observed (Fig. 2, where, to enhance the background current in the absence of Cu(II),

the voltammogram of a bare Au(111) electrode at a larger scan rate is also shown by a dotted line for comparison). In the initial stages of Cu UPD, two peaks at ca. -0.05 V and ca. -0.15 V vs. Ag|AgCl (peaks I and II, respectively) were observed. These peaks would correspond to the peak observed at -0.1 V on a polycrystalline Au electrode (Fig. 1), and at these potentials Cu(II) was suggested to be reduced to Cu(I) species such as Cu(OH) or Cu₂O at different sites [25,32 and refs therein]. At more negative potential, two cathodic peaks were observed on an Au(111) electrode at ca. -0.31 V and ca. -0.62 V vs. Ag|AgCl (peaks III and IV), which are probably due to the reduction of the Cu(I) ad-layer. These peaks would correspond to the peak observed at -0.64 V on a polycrystalline Au electrode, owing to the clear similarities in both potential and peak area. Although not fully elucidated, the reason why the peaks are splitted on an Au(111) electrode might be explained as different sites of the Au(111) surface may give separated reduction peaks. At ca. -0.88 V, multi-layer deposition of Cu took place (peak V). On the reverse scan, a first anodic peak is observed at ca. -0.43 V (peak 1 of Fig. 2, which was coupled with the cathodic peak at -0.62 V, peak IV, due to the redox reaction of Cu(I)/Cu(0) species [25,32]) followed by a wave at ca. -0.23 V (peak 2) and a broad re-oxidation peak (peak 3) at ca. -0.07 V vs. Ag|AgCl. The peak 3 would correspond to the re-oxidation peak at a polycrystalline Au electrode appeared at ca. -0.3 V $\leq E \leq 0.2$ V vs. Ag|AgCl.

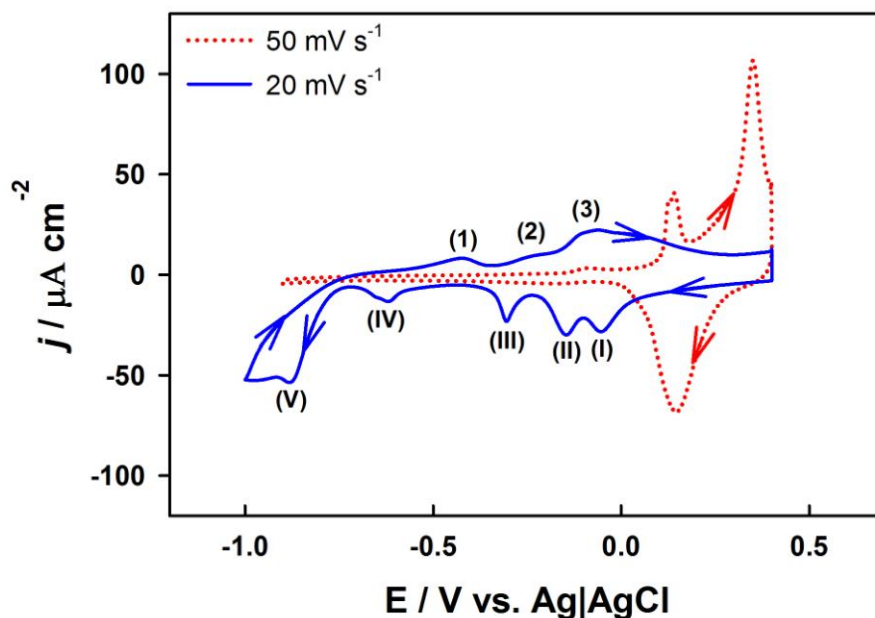


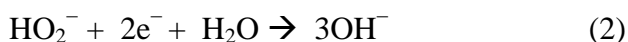
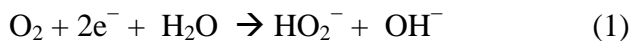
Figure 2. Cyclic voltammograms for Cu-UPD at Au(111) single crystal electrode in N₂-saturated 0.1M NaOH solution in the absence (dotted lines) and the presence (solid line) of 10⁻⁴ M CuSO₄.

The UPD peaks on the Au(111) surface obtained in a (0.1 M NaOH + 0.1 mM CuSO₄) solution (Fig. 2) were similar in terms of potential to those obtained in a 0.1 M NaOH solution for the Cu ad-layer modified Au(111) electrode prepared in a 0.1 M H₂SO₄ solution (cf. Fig. 2C in ref. 25). This suggests that, in the present work conditions, Cu ad-layers behaved exactly the same way, whether they were initially prepared in acid or alkaline solution. To gain more insights on the surface structures

of these Cu ad-layers, a more detailed study using surface techniques (i.e. STM, SEM, TEM, AFM,...etc) would be required and that is beyond the scope of the present work.

3.2. Oxygen reduction at bare and Cu-modified Au electrodes

Oxygen reduction on a polycrystalline gold electrode in an alkaline solution is well known to proceed via a two-electron mechanism to yield hydrogen peroxide (HO_2^-) [7, 8], which is further reduced at more negative potentials to OH^- (Eq. 1 and 2, respectively).



This was clearly confirmed using the steady-state hydrodynamic voltammetry technique (curves a and b in Fig. 3). The disk current started to flow at ca. -0.05 V vs. Ag|AgCl (curve a) and the ring current is also observed at the same potential (curve b) which is due to the oxidation of HO_2^- produced at the disk electrode. The ring current decreased at potentials where HO_2^- was further reduced to OH^- at ca. -0.8 V vs. Ag|AgCl and reached a negligible value at $E \leq$ ca. -1.2 V vs. Ag|AgCl, where a four-electron reduction process of O_2 took place. The observed results are in a good agreement with the literature [3, 7].

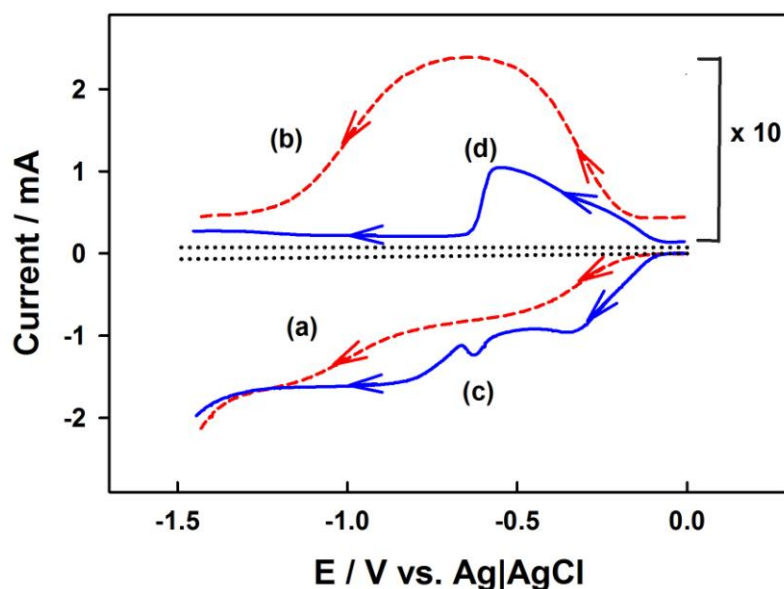
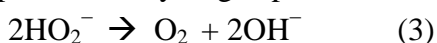


Figure 3. Rotating Ring-Disk voltammograms for a negative going scanning for ORR at (a) bare and (c) Cu-modified polycrystalline Au disk electrodes and for HO_2^- oxidation at (b, d) Au ring electrode at +0.5 V vs. Ag|AgCl in O_2 -saturated 0.1 M NaOH solution with (c, d) and without (a, b) 5×10^{-5} M CuSO_4 . In all cases, 1600 rpm rotation speed and 3mV s^{-1} scan rate were used.

Typical steady-state voltammograms obtained for the O_2 reduction at Au electrode in the presence of 5×10^{-5} M CuSO_4 in an O_2 -saturated 0.1 M NaOH solution are shown in Fig. 3 (curves c

and d). A positive shift in potential and an increase in O_2 reduction current due to a catalytic effect of the Cu ad-layer are well pronounced. At the first reduction wave, the two-electron reduction of O_2 to hydrogen peroxide (HO_2^-) took place, but the detected HO_2^- at the ring electrode (curve d) was much less than that observed for the O_2 reduction at a bare Au electrode (curve b). Thus, since Cu(II) is reduced to Cu(I) in this potential region, the reason behind this catalytic O_2 reduction would be the catalytic disproportionation of HO_2^- by the Cu(I) ad-layer on the Cu-modified Au surface [25]. Very interestingly, a reduction peak in (curve c) at ca. -0.63 V vs. Ag|AgCl was observed with a sudden decrease of the ring current (curve d), indicating the change in reduction mechanism. This peak at ca. -0.63 V vs. Ag|AgCl coincides with the second well-defined reduction peak of the Cu ad-layer on polycrystalline (Fig. 1) and single crystal (Fig. 2) Au electrodes, where the reduction of Cu(I) species to Cu(0) would take place [25,32]. The formed Cu(0) ad-layer at this potential leads to the effective decomposition of hydrogen peroxide:



Being regarded as one of the strongest oxidizing agents, hydrogen peroxide is expected to be most reactive (through the redox process of disproportionation) with the formed Cu(0) species in comparison to Cu(I) which explains the immediate consumption of the produced peroxide in the vicinity of the disk electrode leading to the disappearance of the corresponding ring current as observed here.

The disk current increased further to reach a limiting current at potentials $E \leq$ ca. -0.8 V vs. Ag|AgCl, where the four-electron reduction process took place. The observed shift in O_2 reduction potential was ca. 400 mV (Fig. 3), and the electrode behaved as a Cu electrode.

In order to understand the relationship between the observed catalytic activity and the deposited Cu ad-layers, the RRDE experiment with a positive-going scan from -1.0 V vs. Ag|AgCl was managed (Fig. 4).

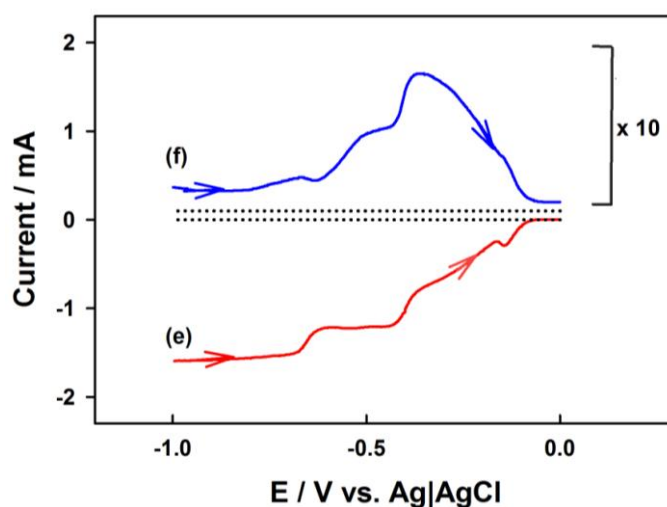


Figure 4. Ring-Disk voltammograms for a positive going scan for O_2 reduction at Cu-modified polycrystalline Au disk electrodes (curve e) and for HO_2^- oxidation at Au ring electrode (curve f) at $+0.5$ V vs. Ag|AgCl in O_2 -saturated (0.1 M NaOH + 5×10^{-5} M $CuSO_4$) solution. In all cases, 1600 rpm rotation speed and $3mV s^{-1}$ scan rate were used.

The O_2 reduction current started to decrease (a little less than the total 4-electron reduction) at ca. -0.9 V vs. Ag|AgCl (see curve e in Fig. 4). In the potential region of -0.9 V $\leq E \leq -0.7$ V, partial dissolution of the deposited Cu layer leading to uncovered bare Au spots occurs leading to the appearance of the small ring current due to the oxidation of HO_2^- . In the potential region of ca. -0.7 V $\leq E \leq -0.4$ V (see Fig.1), the modified Cu ad-layer was gradually oxidized and turns fully into Cu(I) species at ca. -0.4 V [25,32].

At this potential region, further decrease in O_2 reduction current ($n =$ ca. 3 in average and the n value decreased from 4 at -0.7 V to 2 at ca. -0.4 V) was observed with an increase in the ring current, indicating that the HO_2^- formed at the disk electrode was not completely decomposed. At potentials more positive than ca. -0.35 V, where Cu ad-layer would be partially oxidized to Cu(II) species with still remaining Cu(I) species, 2-electron reduction of O_2 to HO_2^- took place with a further increase in the ring current. At potentials more positive than ca. 0 V vs. Ag|AgCl, no reduction of O_2 was observed and the Cu ad-layer would be fully oxidized to Cu(II) species. The RRDE voltammograms shown in Fig. 4 were almost the same as those observed for O_2 reduction using a Cu-disk (Cu-plated Au) Au-ring electrode under the same conditions with no Cu(II) in solution. RRDE experiments at various rotation speeds for both bare and Cu-modified polycrystalline Au electrodes are displayed in Figures 5 and 6, respectively.

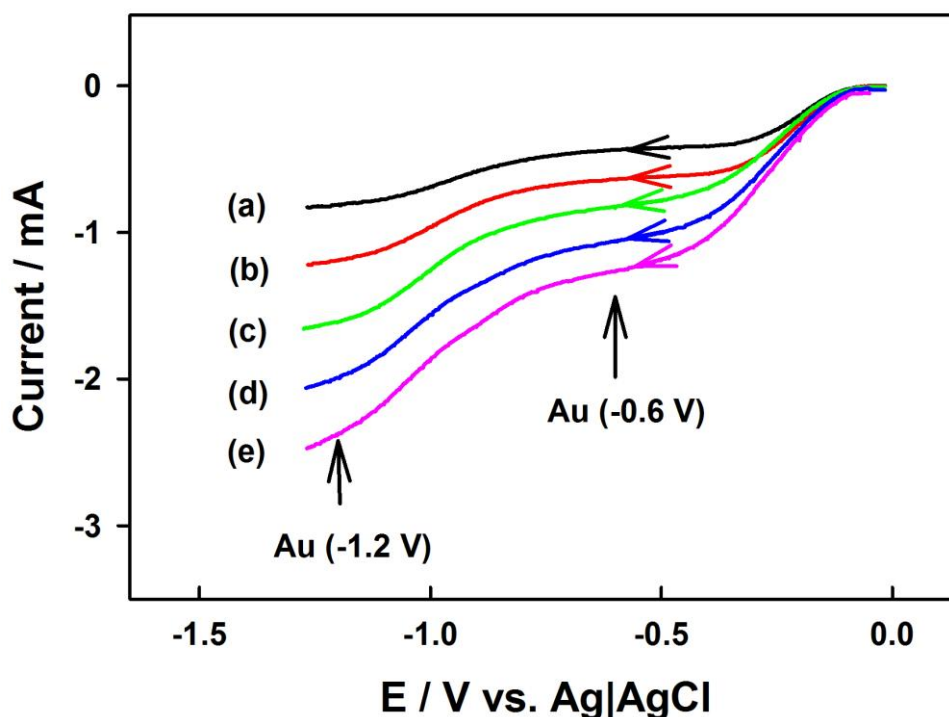


Figure 5. Rotating disk measurements for O_2 reduction on bare polycrystalline Au electrode at (a) 400, (b) 900, (c) 1600, (d) 2500 and (e) 3600 rpm. All experiments were carried out in an O_2 -saturated 0.1 M NaOH solution at a scan rate of 3 mV s^{-1} .

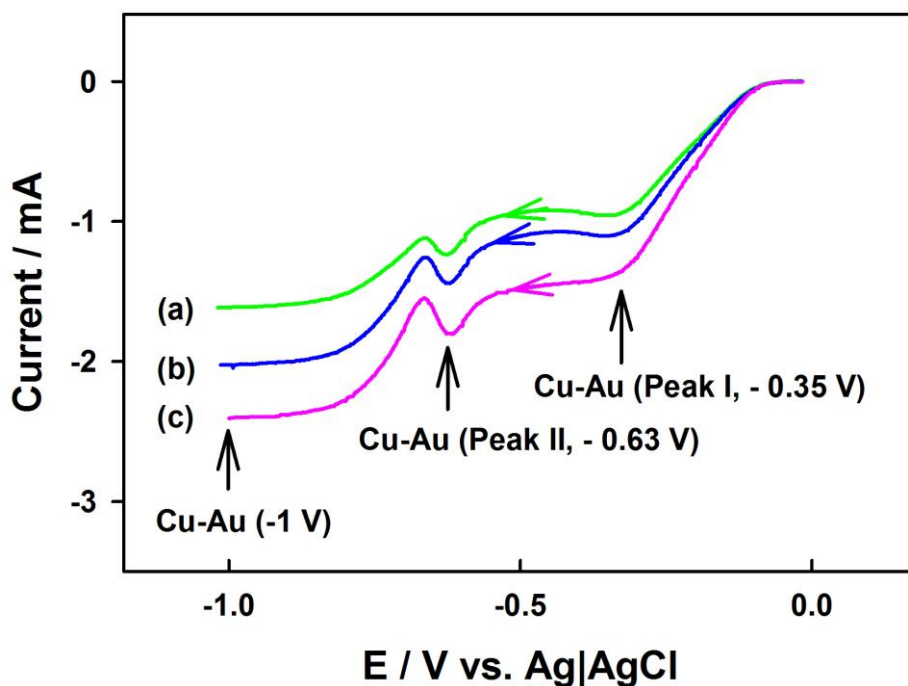


Figure 6. Rotating disk measurements for O_2 reduction on Cu-modified Au electrode at (a) 1600rpm, (b) 2500 rpm and (c) 3600 rpm. All experiments were carried out in an O_2 -saturated ($0.1\text{ M NaOH} + 5 \times 10^{-5}\text{ M CuSO}_4$) solution at a scan rate of 3 mV s^{-1} .

3.3. Koutecky-Levich plots

The Koutecky-Levich (K-L) plots are shown in Fig. 7, where the dependence of the reciprocal of the reduction current (I^{-1}) on the reciprocal of the square root of the rotating angular velocity ($\omega^{-1/2}$) is given, and the number of electrons (n) was calculated from the slope of the (K-L) plots using Eq. 4 [26 and refs. therein],

$$(\text{slope})^{-1} = 0.62 n F A D^{2/3} \nu^{-1/6} c \quad (4)$$

where F is the Faraday constant (96487 C mol^{-1}), A is the disk electrode area (0.283 cm^2), D and c are the diffusion coefficient ($1.65 \times 10^{-5}\text{ cm}^2\text{ s}^{-1}$) and concentration of O_2 ($1.28 \times 10^{-6}\text{ mol cm}^{-3}$) in an O_2 -saturated 0.1 M NaOH solution, respectively, and ν is the kinematic viscosity of 0.1 M NaOH solution ($0.88 \times 10^{-2}\text{ cm}^2\text{ s}^{-1}$) [3, 26,33].

The K-L plots showed that: (i) at bare Au electrode, the oxygen reaction started as a two-electron reduction process ($n = 2.2$ at ca. $-0.6\text{ V vs. Ag|AgCl}$) to produce HO_2^- , and the hydrogen peroxide was reduced to OH^- at a more negative potential ($n = \text{ca. } 4.1$ at ca. $-1.2\text{ V vs. Ag|AgCl}$); (ii) at the Cu-modified Au electrode surface, the first reduction wave obtained at ca. $-0.35\text{ V vs. Ag|AgCl}$ showed $n = \text{ca. } 2.6$, while the second reduction peak at ca. $-0.63\text{ V vs. Ag|AgCl}$ gave $n = \text{ca. } 3.3$, where the catalytic decomposition of hydrogen peroxide at the Cu-modified Au electrode took place because of the absence of any ring current due to HO_2^- oxidation at potentials $E \leq \text{ca. } -0.63\text{ V vs.}$

Ag|AgCl (see curve d in Fig. 3); and (iii) at potentials more negative than ca. -0.8 V vs. Ag|AgCl a four-electron reduction process took place ($n = \text{ca. } 4.0$ at ca. -1.0 V vs. Ag|AgCl).

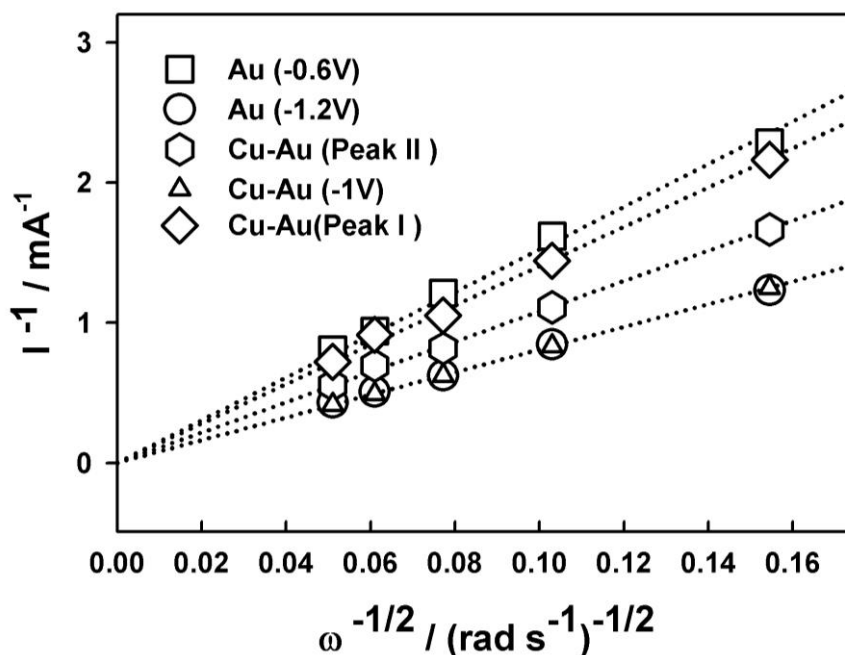


Figure 7. Koutecky-Levich plots for O_2 reduction on bare and Cu-modified polycrystalline Au electrodes in an O_2 -saturated 0.1 M NaOH solution in the presence and absence of 5×10^{-5} M CuSO_4 . The data was extracted from Fig. 5 and Fig. 6. Cu-Au (Peak I) and Cu-Au (Peak II) denote the data extracted from (Fig. 6) at ca. -0.35 V and ca. -0.63 V vs. Ag|AgCl, respectively.

The catalytic ORR observed in the present work at the Cu ad-layer modified Au electrode is in good agreement with our work on Au(111) single crystal electrodes [25]. The positive catalytic effect of Cu ad-layer on gold electrode in an alkaline solution is reasonably expected, since Cu electrode itself is a good catalyst for oxygen reduction in both weak [34,35] and strong (present study) alkaline solutions.

4. CONCLUSION

Catalytic O_2 -reduction at Cu-modified Au electrodes was carried out by hydrodynamic voltammetry. Voltammetric behavior of Cu UPD on polycrystalline and single crystal Au electrodes in an alkaline solution is also presented for the first time. An interesting positive catalytic activity is observed upon the Cu deposition onto the Au electrode surface with a remarkable positive shift in the reduction potential of oxygen. On a Cu-modified Au electrode, catalytic decomposition of hydrogen peroxide was effective at potentials more negative than ca. -0.63 V vs. Ag|AgCl, and the direct four-electron reduction of O_2 to OH^- occurred at potentials of $E \leq -0.8$ V vs. Ag|AgCl, which is ca. 400 mV more positive than those at a bare polycrystalline gold electrode.

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