

Formation of Mercury Adatom Layer by Simple Dipping Method for the Oxygen Reduction and Its Application to an Al-air Fuel Cell[†]

Guang Shan Xuan, Yan-Ling Gong, Hyung Joo Kim,[‡] and Sunghyun Kim^{§,*}

Department of Pharmacy, Qingdao University of Science & Technology, Qingdao, 266042, China

[‡]Department of Microbial Engineering, Konkuk University, Seoul 143-701, Korea

[§]Department of Bioscience and Biotechnology, Konkuk University, Seoul 143-701, Korea. *E-mail: skim100@konkuk.ac.kr

Received July 3, 2010, Accepted August 7, 2010

Key Words: Hg adatom layer, O₂/H₂O₂ reduction, Al-air fuel cell

The electrocatalytic reduction of oxygen is of prime importance in view of its practical applications for developing cathodes in fuel cells and metal-air batteries.¹⁻⁴ Since the cathode performance is directly affected by the oxygen reduction overpotential, a lot of effort has been poured on the development of better electrocatalysts having less potential loss. Reaction mechanisms and rates vary with electrode materials,^{5,6} crystallographic orientations,^{7,8} and reaction environments.⁹ In aqueous solution, oxygen reduction usually proceeds *via* consecutive two-electron processes, being reduced to hydrogen peroxide and then to water. There is no doubt that the best way is to reduce oxygen directly to water. This four-electron process, however, is not easy to achieve. Despite the fact that many ingenious methods and new materials have been devised, the search for the four-electron reduction electrocatalysts is still under way. They include various materials such as carbon-supported platinum,¹⁰ metal macrocycles,^{11,12} and 1,4,5,8-naphthalenetetrone-modified gold.¹³ Biological systems such as laccase¹⁴ and cytochrome c oxidase¹⁵ have also been investigated.

Recently Matsumoto and coworkers^{16,17} reported that mercury adatom-modified gold electrodes prepared by underpotential deposition (upd) showed catalytic activities toward both oxygen and hydrogen peroxide reduction. Oxygen reduction, notably enough, proceed by four-electron reduction to water on the Au/Hg electrodes, while two-electron process has been observed both on Au and Hg electrodes.¹⁸

In this work, we report a simple and reproducible way to prepare mercury-deposited gold electrodes by simply dipping Au in a mercury ion-containing solution. Thus prepared electrodes were used as a cathode in an alkaline-air fuel cell.

Fig. 1 shows XPS spectra for Hg-adlayers formed on the Au surface by dipping and UPD. Two peaks at 84.6 eV (or 84.5 eV) and 88.3 eV (or 88.2 eV) correspond to Au4f_{7/2} and Au4f_{5/2}, respectively, and two peaks at 100.5 eV (or 100.4 eV) and 104.5 eV (or 104.4 eV) to Hg4f_{7/2} and Hg4f_{5/2}, respectively.¹⁹ The essentially same Hg peak positions within experimental error indicate that the oxidation state of Hg in both electrodes is identical. Metallic mercury gives a binding energy of 4f_{7/2} at 99.9 eV.¹⁹ Upon oxidation to Hg²⁺ it increases to 100.5 eV with 104.6 eV for 4f_{5/2}.^{19,20} Our XPS results indicate that mercury in both electrodes exists in a divalent state. Hg²⁺ ions are adsorbed on the Au surface by dipping. The possible reason why

Hg is still in +2 state for Au-Hg(upd) is that Hg is oxidized by oxygen in air during sample transfer.

Panel A of Fig. 2 is the linear sweep voltammetry (LSV) of oxygen reduction at a Au-Hg(dip) (solid) and a Au-Hg(upd) (dotted) electrode. Molecular oxygen is irreversibly reduced at both electrodes. Almost identical voltammograms indicate that Hg adatom layers prepared by dipping and UPD have the same effect on the oxygen reduction. Charges under the peak were plotted against the dipping time (Panel B). Charges quickly increased with time and reached a limiting value within 100 s. This implies that further Hg atoms are not adsorbed on the Au surface once a full Hg adlayer is formed. In this experiment, we fixed the dipping time at 120 s.

The electrocatalytic nature of the Au-Hg(dip) toward oxygen reduction is demonstrated in Fig. 3, in which LSVs at a bare Au (curves a and c) and a Au-Hg(dip) (b, d) for N₂- (a, b) and O₂-saturated (c, d) solutions. Two consecutive reduction waves were observed at a polycrystalline bare Au.¹⁶ Oxygen is reduced to HO₂⁻ and then to OH⁻ although the direct reduction to OH⁻ has been reported.²² The different results are due to the different crystallographic faces exposed on the Au surface.²³ At a Au-Hg(dip) electrode, however, only a single reduction wave was observed and the peak potential was shifted to -0.18 V from -0.43 V for a bare Au, indicating the catalytic nature of this electrode toward the oxygen reduction.

The irreversible reduction of molecular oxygen is thought to

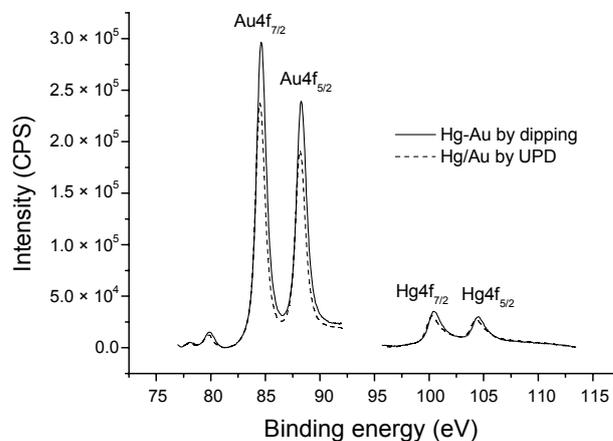


Figure 1. Au4f and Hg4f peaks by X-ray photoelectron spectroscopy for Hg adatom layers prepared by dipping (solid) and underpotential deposition (dashed) methods.

[†]This paper is dedicated to Professor Hasuck Kim for his outstanding contribution to electrochemistry and analytical chemistry.

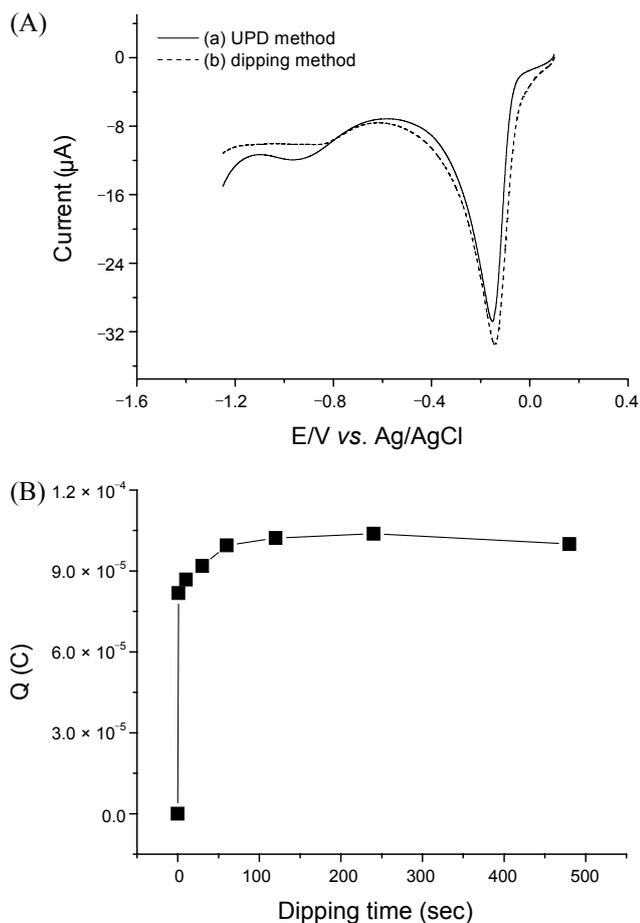


Figure 2. (A) Linear sweep voltammety at Au-Hg(upd) (solid) and Au-Hg(dip) (dashed) electrodes in air-saturated 0.1 M KOH solution. Scan rate = $50 \text{ mV}\cdot\text{sec}^{-1}$. (B) Plot of charge vs. dipping time for the oxygen reduction peak shown in (A).

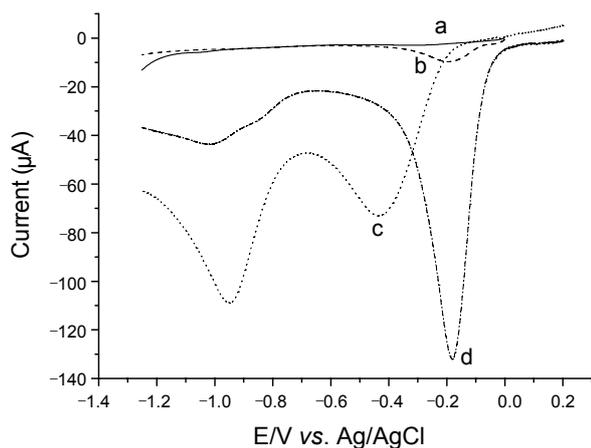


Figure 3. Linear sweep voltammety at a bare Au (a and c) and a Au-Hg(dip) (b and d) electrodes for N_2 -saturated (a and b) and O_2 -saturated (c and d) 0.1 M KOH solutions. Scan rate = $50 \text{ mV}\cdot\text{sec}^{-1}$. Inset: cyclic voltammograms for oxygen reduction at a Au-Hg(dip) electrode for various oxygen percentages.

proceed to produce hydroxide ion *via* the formation of hydrogen peroxide. Fig. 4 is cyclic voltammograms of H_2O_2 of various concentrations in 0.1 M KOH solution. Although the reduction

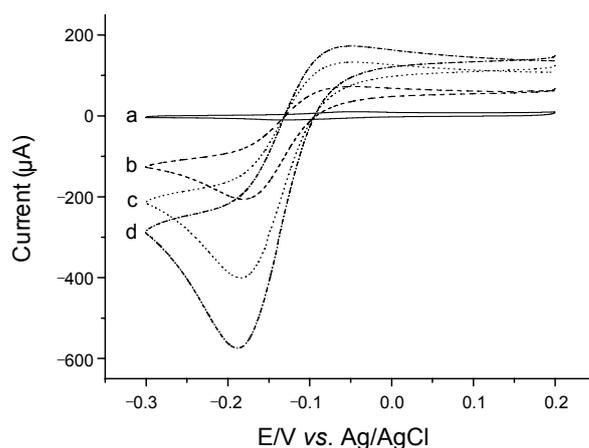
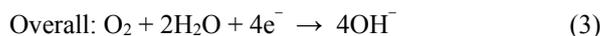
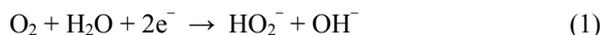


Figure 4. Cyclic voltammety at a Au-Hg(dip) electrode for different H_2O_2 concentrations of (a) zero, (b) $4.3 \times 10^{-5} \text{ M}$, (c) $8.7 \times 10^{-3} \text{ M}$, and (d) $1.3 \times 10^{-2} \text{ M}$. Scan rate = $50 \text{ mV}\cdot\text{sec}^{-1}$.

current does not seem to linearly increase with the increase in H_2O_2 concentration, the reduction potential is very close to that of oxygen reduction. Molecular oxygen is reduced to hydrogen peroxide (HO_2^-) by the two-electron process (Eq. 1 below) and produced HO_2^- is further reduced to peroxide ion (Eq. 2) by the two-electron process. The overall reaction is the four-electron reduction of oxygen to OH^- . This was confirmed by Matsumoto *et al.*¹⁶ who showed in their rotating ring disk electrode experiments that no oxidation current at the ring electrode was observed for the oxygen reduction occurred at the disk electrode, indicating that OH^- was formed by the four-electron reduction process. The following reduction mechanism at a Au-Hg(dip) could be written.



Another possibility is the decomposition of H_2O_2 in highly alkaline solutions into oxygen and water. Even in this case, produced oxygen undergoes a series of reduction reactions to OH^- as shown above.

Adsorbed hydroxides (OH_{ads}^-) may play an important role in the reduction of oxygen. Adzic and coworkers²⁴ reported in their Au single crystal works that the origin of the catalytic activity was attributed to the formation of partly discharged OH^- species ($\text{OH}_{\text{ads}}^{(1-\delta)-}$) on the surface. The same explanation was given to the Hg adatom-modified Au surface by UPD. In our case of Au-Hg(dip) electrodes, we also observed the formation of adsorbed OH^- species (data not shown). The higher amount of adsorbed OH^- species on the Au-Hg(dip) surface than on the bare Au surface explains a better catalytic activity of the former compared to the unmodified Au surface.

Au-Hg(dip) electrodes have been applied to the aluminum-air semi-fuel cell as a cathode. While there has been much effort to develop aluminum-hydrogen peroxide fuel cells as green power sources,^{25,26} a relatively small number of researches have

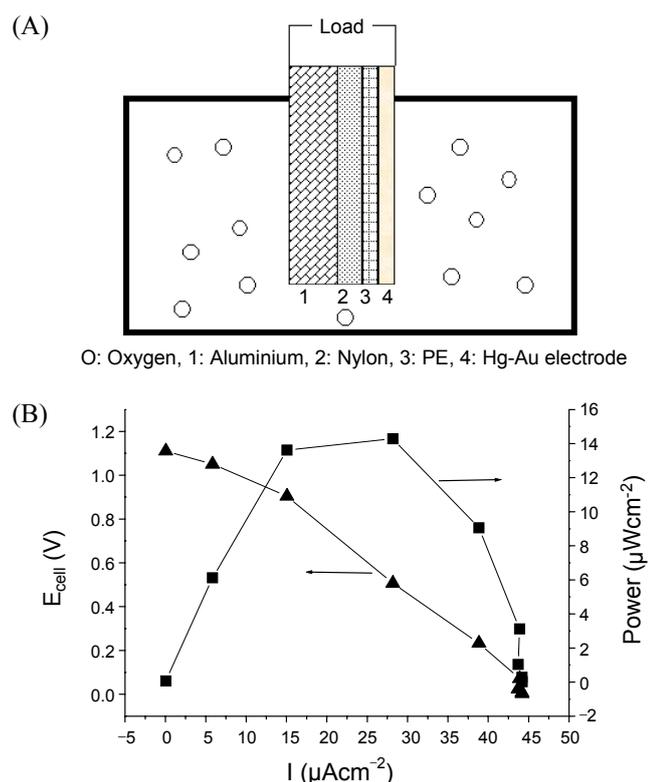
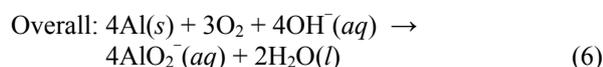
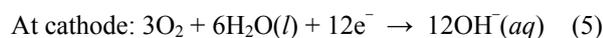
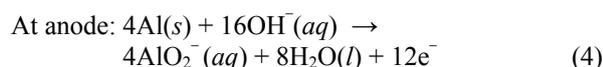


Figure 5. (A) Schematic diagram of an aluminum-air semi-fuel cell constructed using a Au-Hg(dip) cathode. (B) Polarization (▲) and power density (■) curves in an air-saturated 0.1 M KOH solution.

been conducted on the aluminum-oxygen fuel cells. We constructed an Al-O₂ cell that consisted of an Al foil anode (0.8 cm²), a Au-Hg(dip) cathode (0.6 cm²) prepared from a Au-sputtered PVC, and an air-saturated 0.1 M KOH solution (Fig. 5A). A nylon membrane was set between the anode and the cathode. The following reactions take place:



A polarization curve was constructed by changing external loads (Fig. 5B). The initial open circuit voltage of about 1.5 V gradually decreased to 1.1 to 1.2 V due to the aluminum hydroxide layer formation on the aluminum surface.²⁵ The maximum power density of 14.3 μW·cm⁻² is quite lower than those of chemical fuel cells. This result, however, shows the possibility of using oxygen as a cathodic fuel and Au-Hg(dip) as an electro-catalyst for oxygen reduction.

In this paper we have shown that Hg adatom-modified Au surface could be easily prepared by simply dipping a Au surface into a Hg²⁺-containing solution and thus prepared surface exhibited four-electron reduction activity for molecular oxygen in strongly alkaline solutions. An Al-O₂ semi-fuel cell using

this electrode as a cathode was constructed and its performance was tested.

Experimental

All the chemicals were of reagent grade otherwise stated. For voltammetric experiments, gold disk electrodes (0.071 cm²) were employed as a working electrode. They were sequentially polished with 1.0, 0.3, and 0.05 μm alumina until mirror finish. After removing trace alumina from the surface by rinsing with deionized water and brief cleansing in an ultrasonic bath, they were immersed in a freshly prepared 10⁻² M mercury acetate solution for 2 min. Thus prepared Hg-adsorbed gold electrodes (denoted as Au-Hg(dip)) were again rinsed with deionized water. The same adsorption procedure was followed on Au-sputtered PVC (Nuricell, Korea) for a fuel cell work. For comparison purpose, Hg adlayer was formed by underpotential deposition (UPD).¹⁶ Hg UPD was done by dissolving HgO in 0.1 M H₂SO₄ to prepare 1 mM Hg²⁺ solution. After purging dissolved oxygen with N₂, potential was scanned between 1.05 and 0.75 V at 10 mV·s⁻¹. Thus prepared electrodes are denoted as Au-Hg(upd).

The electrochemical set-up consisted of a classical three electrodes system (Autolab PGSTAT 30, Ecochemie, Netherlands). The reference and counter electrodes were Ag|AgCl|KCl (3.5 M) and a platinum wire, respectively.

X-ray photoelectron spectra were collected by an XPS spectrometer (VG Microtech ESCA2000, England). Binding energy was calibrated with respect to carbon 1 s peak at 285 eV.

Acknowledgments. This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST) (No. 2010-0015726).

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