Communications

An Electrochemical Quartz Crystal Microbalance Study of Oxygen Reduction during the Underpotential Deposition of Lead on a Gold Electrode

Youngran Lim and Euijin Hwang*

Electrochemistry Group,
Korea Research Institute of Standards and Science,
Taejon 305-340, Korea

The electrocatalytic reduction of oxygen on solid electrodes has been extensively studied for a long time, and it should still be one of the most addressed topics in the recent literature because of its worldwide interest in energy conversion devices, particularly the fuel cell. Some reviews can be found elsewhere.[1-3] It has been shown that some metal adatoms on foreign substrates cause considerable catalytic effects on oxygen reduction. Lead,[4-7] thallium,[5,7,8] and bismuth[9] are known to promote oxygen reduction at gold substrates in perchloric acid[6,9] and sodium hydroxide solutions,[4,5,8] and in acetonitrile[7] as solvent.

An electrochemical quartz crystal microbalance (EQCM)[10] has been widely used for the studies on the electrode processes that accompany the mass change of electrode, such as electrosorption. Though an EQCM is a powerful *in situ* tool measuring the electrode mass change concurrently with common electrochemical data such as potential and current, it has not been used for the research of oxygen reduction because no mass change is expected according to the oxygen reduction itself. If the oxygen reduction could be influenced by electrosorption, an EQCM should be a useful tool that serves some possible interpretations in the relationship between oxygen reduction and interfacial phenomena.

Recently, we have reported an abnormal reduction current in the presence of dissolved oxygen during the EQCM study on the underpotential deposition (UPD) of lead in 1 mM lead nitrate and 0.1 M nitric acid.[11] In this previous paper,

the catalytic reduction of nitrate or dissolved oxygen by the adsorbed lead species has been proposed as a possible reason for that abnormal current. To clear up the cause some experiments for the lead UPD were carried out in nitric acid and perchloric acid in the presence or in the absence of dissolved oxygen.

Lead nitrate (Aldrich, 99.999%), nitric acid (Merck, pro analysi), PbO (Aldrich, 99.999%), and perchloric acid (Aldrich, double distilled PPB/Teflon grade) were used as received. Argon (99.99+%) was used to purge out dissolved oxygen in the solution. AT cut quartz crystals of 6 MHz resonance frequency were used for the EQCM and their theoretical sensitivity is 12.3 ng/çm$^2 \cdot$Hz. The sensitivity measured by coulometric dissolution of silver was 11.8 ng/cm$^2 \cdot$Hz and the relative standard deviation was about 5%. The measured sensitivity was in good agreement with the theoretical value in 1σ range. The electrodes on quartz crystals were prepared by RF plasma sputtering from chromium (Cerac, 99.95%) and gold (Cerac, 99.999%) targets. Chromium undercoating (50 nm thick) was followed by gold coating (200 nm thick). The detailed experimental conditions were described in the previous paper.[11]

Our low noise EQCM introduced in the previous paper was enough to extract the reduction current associated with the UPD of lead from the total current as shown in Figure 1. The UPD current was calculated from the first order derivative of EQCM frequency change with the assumption that the electrode mass change occurs only due to the deposition and dissolution of lead. This assumption was verified to be valid in the deaerated solution as shown in Figure 2, where the estimated UPD current is almost identical with the total current. The excess reduction current in the cathodic potential region more negative than -0.3 V *vs.* Saturated Calomel Electrode (SCE) seems to be the reduction current of nitrate.

Figure 1(c) shows that the oxygen reduction starts from 0.25 V *vs.* SCE in the presence of lead ions while it occurs at more negative potential in the absence of lead ion as shown in Figure 1(a). It may be described as the potential shift to the positive direction in the presence of lead ions is due to the catalytic reduction of oxygen. There is no doubt that the catalytic sites on the gold surface had to be served by underpotentially deposited lead.

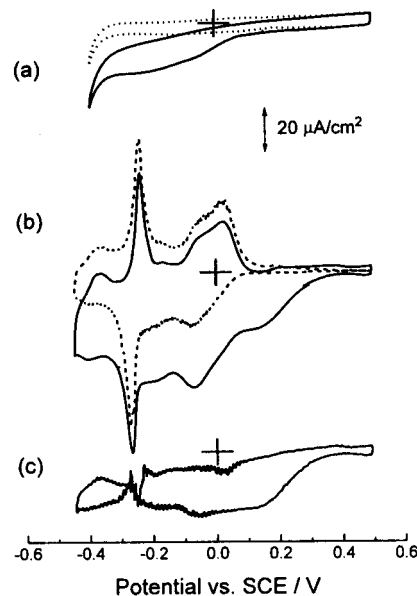*To whom correspondence should be addressed.
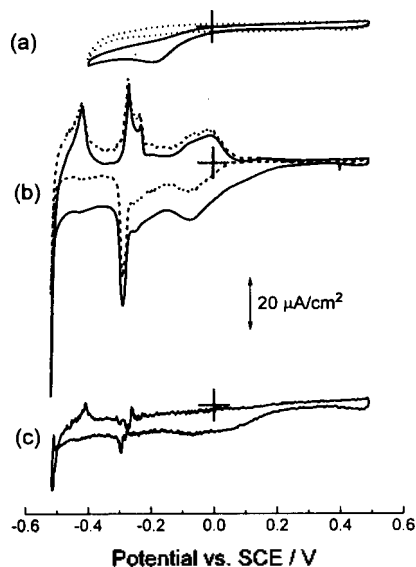
Figure 1. Current-potential curves of gold electrode in 0.1 M nitric acid. Sweep rate, 10 mV/s; sampling interval, 0.2 s. (a) background current in the presence (−) and in the absence (···) of dissolved oxygen, (b) total current (−) in 1 mM $Pb(NO_3)_2$ in the presence of dissolved oxygen and estimated Pb UPD current (---) from EQCM data, and (c) the excess current by eliminating the Pb UPD current from total current.
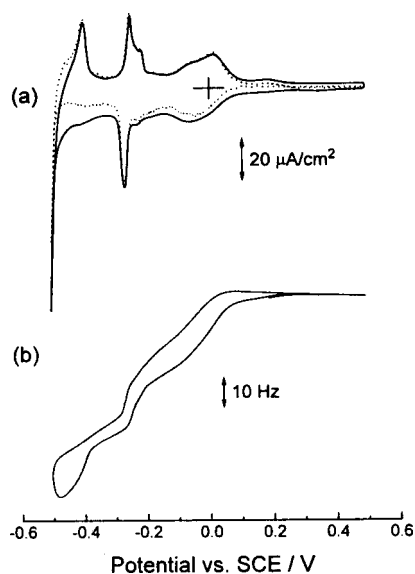
Figure 2. EQCM results in deaerated 1 mM $Pb(NO_3)_2$ and 0.1 M nitric acid. Sweep rate, 10 mV/s; sampling interval, 0.2 s. (a) Current-potential curve (−) and estimated Pb UPD current (---) and (b) frequency change of EQCM *vs.* potential.

The same situation occurred in perchloric acid. Figure 3 clearly shows a positive shift of oxygen reduction wave in the presence of lead ions. This result obtained from perchlorate media supports that the catalytic current in nitric acid was not due to the nitrate reduction, but due to the oxygen reduction itself. The larger UPD current compared with nitrate media is attributed to the larger surface roughness of the electrode used in perchlorate media.

Figure 3. Current-potential curves of gold electrode in 0.1 M perchloric acid. Sweep rate, 10 mV/s; sampling interval, 0.2 s. (a) background current in the presence (−) and in the absence (···) of dissolved oxygen, (b) total current (−) in 1 mM PbO in the presence of dissolved oxygen and estimated Pb UPD current (---) from EQCM data, and (c) the excess current by eliminating the Pb UPD current from total current.

It is well known that the oxygen recombination at lead negative electrode of sealed lead-acid battery occurs through the chemical/electrochemical reactions as follows:[3]

$$Pb + \frac{1}{2}O_2 \rightarrow PbO \tag{1}$$

$$PbO + H_2SO_4 \rightarrow PbSO_4 + H_2O \tag{2}$$

$$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-} \tag{3}$$

where metallic lead is served as a catalyst. The chemical reaction of metallic lead and molecular oxygen (reaction 1) in acidic media is rapid. The rate determining step of oxygen recombination is known to be the diffusion process of molecular oxygen from the positive electrode. The same phenomena can be imagined for our results. The catalytic reduction of oxygen with underpotentially deposited lead occurs probably through the chemical reaction as shown in reaction 1. PbO is very soluble in nitric or perchloric acids and the solved lead ion should be reduced again at the given potential as follows:

$$PbO + 2H^+ \rightarrow Pb^{2+} + H_2O \tag{4}$$

$$Pb^{2+} + 2e^- \rightarrow Pb \tag{5}$$

At the potential region where the oxygen reduction occurs but its current does not reach the diffusion limit, the current flow can be explained as the number of catalytic sites served by adsorbed metallic lead is still not enough to reduce all the oxygen molecules adjacent to the electrode. Actually the UPD current was not so measurable in that potential region even the oxidation current was fairly large during the reverse scan. The catalytic oxygen current reaches its limiting value at the potential where the lead UPD current starts

to flow rapidly.

As conclusion we showed that the underpotentially deposited lead acts as a catalyst for the oxygen reduction at a gold substrate in nitric acid and perchloric acid. The catalytic reduction current of oxygen during the lead UPD could be estimated by elimination of lead UPD current using our low noise EQCM.

References

1. Hoare, J. P. In *Encyclopedia of Electrochemistry of the Elements*; Bard, A. J., Ed.; Marcel Dekker: New York, U. S. A., 1974; Vol. 2, p 305.
2. Scherson, D.; Tryk, D.; Daroux, M.; Xing, X., Eds. *Structural Effects in Electrocatalysis and Oxygen Electrochemistry*; The Electrochemical Society: Pennington, U. S. A., 1992; Proceedings Vol. 92-11.
3. Kinoshita, K. *Electrochemical Oxygen Technology*; John Wiley & Sons: New York, U. S. A., 1992.
4. Adzic, R. R.; Tripkovic, A. V.; Markovic, N. M. *J. Electroanal. Chem.* **1980**, *114*, 37.
5. Amadelli, R.; Molla, J.; Bindra, P.; Yeager, E. *J. Electrochem. Soc.* **1981**, *128*, 2706.
6. Alvarez-Rizatti, M.; Juttner, K. *J. Electroanal. Chem.* **1983**, *144*, 351.
7. Kokkinidis, G.; Sazou, D. *J. Electroanal. Chem.* **1986**, *199*, 165.
8. Amadelli, R.; Markovic, N.; Adzic, R.; Yeager, E. *J. Electroanal. Chem.* **1983**, *159*, 391.
9. Sayed, S. M.; Juttner, K. *Electrochim. Acta*, **1983**, *28*, 1635.
10. Buttry, D. A. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, U. S. A., 1991; Vol. 17, p 1.
11. Hwang, E.; Lim, Y. *Bull. Kor. Chem. Soc.* **1996**, *17*, 39.

Synthesis of Alkyl-Substituted Bispidinones and 3-Aza-1,3,5-trimethylbicyclo[3,3,1]nonan-9-one

Ki-Whan Chi* and Richard J. Lagow†

*Department of Chemistry, University of Ulsan,
Ulsan 680-749 Republic of Korea
†Department of Chemistry,
University of Texas at Austin,
Austin, Texas 78712 U.S.A.*

During the last 20 years, some of perfluorochemicals (perfluorodecalin, perfluorotripropylamine etc.) have drawn much attention on their potential biomedical applications.[1] These chemicals, so-called blood substitutes, appear to be useful for perfusing isolated organs and other clinical applications due to their biological inertness and high capacities for dissolving gases.[2] However, the absence of versatile synthetic method for perfluorination has put restriction upon the development of new perfluorochemicals. One of the authors (RJL) has been interested for decades in the synthesis of new class of perfluoro-organic compounds by the LaMar direct fluorination[3] with F₂. And a cyclic perfluoro(polyketone)[4] was recently synthesized for the first time by the liquid-phase direct fluorination methodology.[5] Thus, we decided to use bispidinone derivatives[6] as the precursor on which liquid-phase direct fluorination would be applied for the development of improved blood substitute.

In this paper, we would like to report the synthesis of various alkyl-substituted bispidinones 1 and 3-aza-1,3,5-trimethylbicyclo[3,3,1]nonan-9-one(2) by the Mannich reaction.[7]
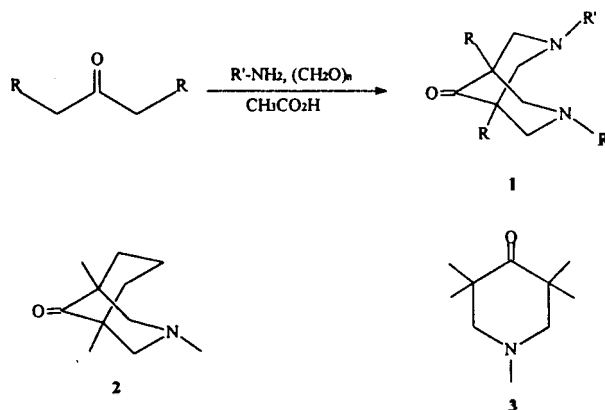
To the solution of a primaryamine (480 mmol), acetic acid (30 mL, 520 mmol) in ethanol (200 mL) at 0 ℃ was added paraformaldehyde (30 g, 1.00 mol) and a ketone (220 mmol). the resulting suspention was heated at reflux for 5 hrs and *ca.* 100 mL of ethanol was distilled off. The reaction mixture was cooled and diluted with ether (500 mL). The solution was acidified with perchloric acid (70%) and the mixture was kept in a refrigerator overnight. The perchlorate salt was collected and partitioned between dichloromethane and an aqueous sodium hydroxide solution (20%). The organic extracts were dried (Na₂SO₄) and concentrated. Re-extraction with hexane and evaporation of solvents gave the crude product. Further purification with vacuum distillation or flash chromatography provided the bispidinone 1 or 2.

As shown in Table 1, the yields of bispidinones 1 are acceptable considering the fact that good yields could be obtained only from the irreversible product formation by crystallization or precipitation.[6a] Also, 3-aza-1,3,5-trimethylbicyclo [3,3,1]nonan-9-one (2) is successfully synthesized from 2,6-dimethylcyclohexanone in 15% yield. The existence of Bohlmann bands[6b] (2843, 2774, 2727 cm⁻¹) in the IR spectrum of 2, the unusual chemical shift (δ 3.017) of one hydrogen

Table 1. The Yields of Bispidinones 1

1	R	R'	Yield[8]
a	CH₃	n-C₃H₇	18
b	C₂H₅	CH₃	44
c	C₂H₅	n-C₃H₇	28
d	n-C₃H₇	CH₃	35