Mass Change of Ruthenium Oxide During Methanol Oxidation†

Sang-Eun Bae[1,2], Jung-Hyun Yoon[1,*] and Chi-Woo Lee[1,*]

[1]Department of Advanced Materials Chemistry, Korea University, 2511 Sejongro, Sejong, 339-700, Republic of Korea
[2]Nuclear Chemistry Research Division, Korea Atomic Energy Research Institute, 989-111 Daedeok-daero, Yuseong-gu, Daejeon 305-353, Republic of Korea

*Corresponding authors: Fax: +82 44 8601331; E-mail: yoonjh@korea.ac.kr, cwlee@korea.ac.kr

An electrochemical quartz crystal microbalance was employed to investigate the electrochemical dynamics of a ruthenium oxide (RuOx) film in aqueous solutions. The ruthenium oxide film was prepared by electrochemical deposition, where 5 H_2O molecules per Ru were incorporated into the film. During the potential cycles of the ruthenium oxide film in an electrolyte, a proton ion is deserted and inserted repeatedly, where two water molecules are always accompanied. The prepared ruthenium oxide film exhibits electrocatalytic activity toward the oxidation reaction of methanol. During the electrocatalytic reaction, the mass of the ruthenium oxide increases slightly, indicating that there are adsorptions of some intermediates on the ruthenium oxide film produced in the oxidation reaction of methanol.

Key Words: Ruthenium oxide, Electrochemical quartz crystal microbalance, Methanol oxidation, Catalyst.

INTRODUCTION

Ruthenium oxide (RuOx) has attracted a lot of attention because it has been applied to the catalysts for an oxidation of methanol[1] and gas evolutions, such as oxygen[2], chlorine[3] and hydrogen[4] as well as the supercapacitor materials[5]. Particularly in the development of a direct methanol fuel cell, ruthenium oxide has been known to enhance the electrode kinetics of the methanol oxidation and thus it has been used as a pivotal element within catalyst systems for a direct methanol fuel cell[6,7].

Ruthenium oxide can be prepared though various techniques, such as electrodeposition[1,8], sol-gel synthesis[9] and an electrostatic spray technique[5]. The redox reactions of the prepared ruthenium oxide film are accompanied by a proton desertion and insertion in the film as shown in following equation[6]:

$$RuO_{x-z}(OH)_{y+z} \rightleftharpoons RuO_x(OH)_y + z\,e^- + z\,H^+ \qquad (1)$$
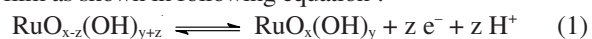
The number of water molecules involved in the reactions depends on the applied potential as well as the preparation procedures of ruthenium oxide. The dynamics of the proton and water during the redox reactions of ruthenium oxide plays an important role in the electrocatalysis for methanol oxidation reactions and charge storage as a pseudocapacitance.

Electrochemical quartz crystal microbalance is known to be a powerful tool for the studies of a mass change on a electrode surface[10]. A few groups have employed an electrochemical quartz crystal microbalance to investigate the mass changes of ruthenium oxide films. Vukovic and Cukman[11] reported the mass changes during an electrodeposition and potential cycle of ruthenium oxide film. Kim and Kim[5] investigated the charge storage mechanism of ruthenium oxide using an electrochemical quartz crystal microbalance[5]. The Santos group has reported the mass change of a ruthenium oxide film during methanol oxidation, where they proposed that there was no CO adsorption on the ruthenium oxide film[12]. However, it was difficult to evaluate the CO adsorption on the ruthenium oxide surface in their work since the results were not exactly compared. More recently, Sopcic et al.[6] also investigated the mass changes of ruthenium oxide under different experimental condition.

In this work, ruthenium oxide film was prepared using a potential cycle between -200 mV and +900 mV vs. SCE. The electrocatalytic effect of ruthenium oxide on the oxidation reaction of methanol was investigated using an electrochemical quartz crystal microbalance. To study the mass changes of the ruthenium oxide film during the potential cycle, we also carried out the electrochemical quartz crystal microbalance measurements of a ruthenium oxide film in aqueous and D_2O solutions and compared the mass changes of the ruthenium oxide film under both conditions.

EXPERIMENTAL

All chemicals used in this work were of the best quality available from Aldrich and were used without further purification. Solutions were made up with Milli-Q grade water.

†Presented to the 4th International Symposium on Applications of Chemical and Analytical Technologies in Nuclear Industries, Daejeon, Korea

A ruthenium oxide thin film was electrodeposited on a gold coated quartz crystal surface. After the electrodeposition of ruthenium oxide, the cell was rinsed with Milli-Q grade water and the solution was poured in the cell. For the D_2O solution, the cell was rinsed with D_2O. Before the experiments, all solutions were purged by ultra pure argon and the measurements were conducted under an argon atmosphere. The electrochemical quartz crystal microbalance system consists of a well-type Teflon cell, PC-controlled M283 potentiostat (EG & G) and QCA 917 (EG & G).

RESULTS AND DISCUSSION

Fig. 1 shows a set of cyclic voltammograms and changes in the resonant frequency of the gold quartz crystal simultaneously obtained when the potential was cycled continuously between -0.2 V and +0.9 V in a 20 mM $HClO_4$ aqueous solution containing 2 mM $RuCl_3$. Here, cyclic voltammetric technique was employed to produce a porous ruthenium oxide (RuOx) film. The proton insertion and desertion processes repeatedly take place during the cyclic voltammograms measurements, which may result in micro-pores on the ruthenium oxide film. As a result, we expect that the whole ruthenium oxide film can be electroactive during the electrochemical measurements. In first cycle, there is a small bump around 0 V, which can be attributed to the $Ru(OH_2)_6^{3+/2+}$ redox reactions[1]. The current increase observed above +750 mV is associated with a further oxidation of the ruthenium oxide species and induces the formation of the RuO_2 film[11].
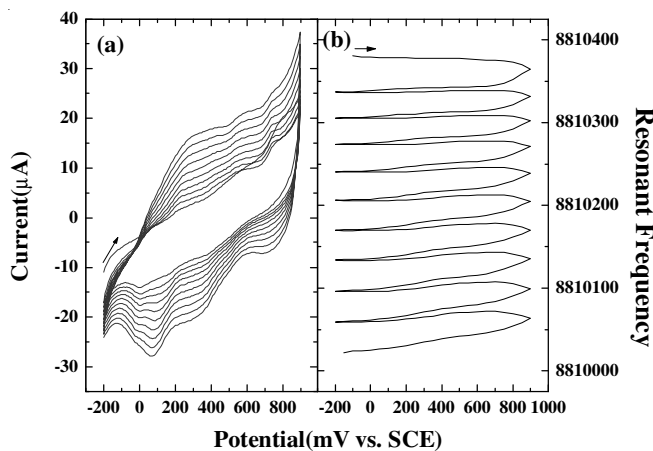

Fig. 1. Cyclic voltammograms (a) and resonant frequency change (b) obtained from a quartz crystal in 2 mM $RuCl_3\cdot xH_2O$ + 20 mM $HClO_4$. The scan rate was 50 mV/s

On the returning sweep, there is no corresponding reduction current detectable. As the number of cycles increase, the current continuously increases, indicating that an electroactive thin film accumulated on the electrode surface. The change in resonant frequency displayed in Fig. 1(b) supports the electrodeposition of a ruthenium oxide film on the electrode surface. The resonant frequency in Fig. 1(b) remains constant until +700 mV and starts to decrease at a potential more positive than +750 mV. On the returning sweep, the frequency is still decreasing up to +700 mV and then stays at a constant value until the end of the sweep. In the next sweep, the same processes are repeated. According to the Sauerbrey equation, the

1 Hz resonant frequency change allow the quartz crystal (0.2 cm electrode area) in this work to probe 5.47 ng/cm² mass changes on the surface[10]. During the 10 cycles, the resonant frequency decreased by 356 Hz and thus the mass of the ruthenium oxide thin film was estimated to be 1.95 µg/cm². Assuming that the oxidation state of the Ru is + 4 at + 900 mV[11,13], the molar mass obtained from the cyclic voltammograms and resonant frequency changes is estimated to be 229 g/mol. This value indicates that the 5 H_2O molecules per Ru are incorporated into RuO_2 film, which is comparable to the value in the literature[11].
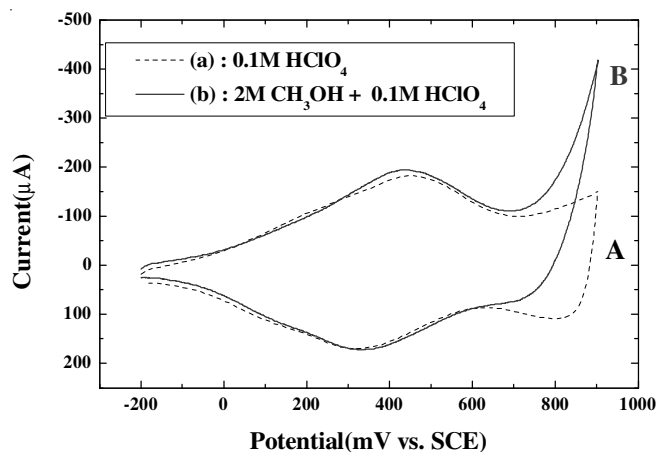

Fig. 2. Cyclic voltammograms obtained from a quartz crystal in 0.1 M $HClO_4$ (a) and 2 M methanol + 0.1 M $HClO_4$ (b). The scan rate was 50 mV/s

To investigate the mass changes of a ruthenium oxide thin film on a quartz crystal during the methanol oxidation, cyclic voltammetric measurements were performed in 0.1 M $HClO_4$ without (a) and with (b) 2 M CH_3OH. In Fig. 2(a), there are broad peaks centered at + 400 mV, which results from the oxidation state shift of the deposited ruthenium oxide thin film. Curve (b) shows the cyclic voltammogram obtained in a methanol solution. It is well-known that ruthenium oxide exhibits an electrocatalytic activity toward the electro-oxidation of methanol[1,8]. Here, the anodic and cathodic currents of the ruthenium oxide film below +0.7 V are exactly the same as that in curve (a) of Fig. 2. On the other hand, the anodic current in curve (b) abruptly increases over +0.7 V, which agrees with the voltammogram of ruthenium oxide on a BPG electrode obtained in a methanol solution previously[8]. Therefore, it is obvious that the ruthenium oxide film electrodeposited in this work shows the electrocatalytic activity for the oxidation reaction of the methanol. The cyclic voltammetric measurement performed in the D_2O (not shown here) leads to the same result as the curve (a).

Fig. 3 reveals the resonant frequency changes of a quartz crystal simultaneously obtained during the cyclic voltammograms measurements. Herein, several potential cycles were repeated until constant change of the resonant frequency was obtained. As the applied potential is moved to positive values, the resonant frequency continuously increases in all cases (Fig. 3). It is well-known that this feature is associated with a proton desertion from the electrodeposited ruthenium oxide film[5,11]. In a negative potential sweep, the resonant frequency

decreases, which is attributable to the insertion of protons, and returns the origin point at -200 mV, indicating that these proton desertion and insertion processes are reversible. A molar mass of 34 g/e⁻ mol was obtained for the cyclic voltammograms, which implies that two water molecules per proton are lost during the oxidation of the ruthenium oxide film. If the resonant frequency changes obtained in the solutions with (Fig. 3a) and without (Fig. 3b) methanol are compared, both resonant frequencies are almost the same at the potential below + 400 mV. Above + 400 mV, there is some discrepancy between the two. The increasing rate of the resonant frequency measured in the methanol solution is slightly reduced with respect to the one without methanol between + 400 and 600 mV and the difference between the two systems becomes noticeable at a potential of more than 600 mV. Coincidently, the potential at which the oxidation reaction of methanol takes place is approximately consistent with the one in which the discrepancy of the resonant frequency is observed. Therefore, it is presumed that the discrepancy is associated with the oxidation reaction of methanol.

The change in resonant frequency displayed in Fig. 3c was obtained in the D_2O solution. If only proton ions are moving during the potential scan, the change in the resonant frequency obtained from the D_2O solution should be twice that in an aqueous solution under the same condition. However, there are about 10 % differences in the resonant frequencies between aqueous and D_2O solutions, implying that the protons are moving as a form of hydronium ions or with water molecules during the redox reactions of the ruthenium oxide film, which agrees well with the results in Fig. 3a and those reported in the literature[12].
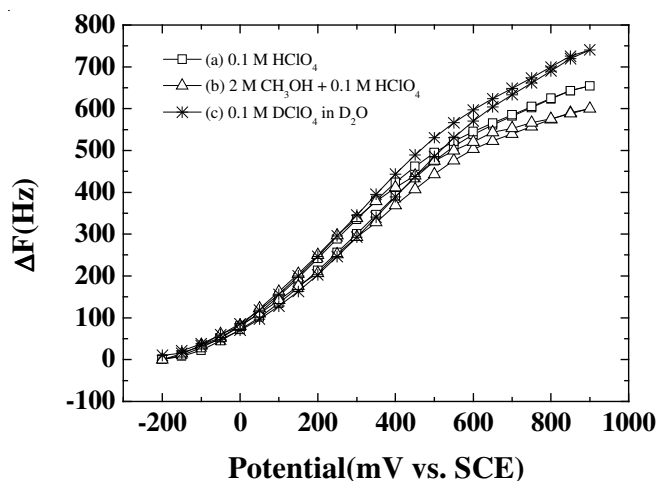

Fig. 3. Resonant frequency changes obtained from a quartz crystal in aqueous solutions containing 0.1 M $HClO_4$ (a) and 2 M methanol + 0.1 M $HClO_4$ (b) and in D_2O solution containing 0.1 M $DClO_4$ (c). The scan rate was 50 mV/s

A relative reduction of the increasing rate of resonant frequency change during the oxidation reaction of methanol can be explained by an interaction between ruthenium oxide film and the intermediates of the oxidation reaction of methanol. Deprotonation and oxygenation reactions of methanol take place during methanol oxidation reaction where the intermediates such as CO, COH and COOH are produced. It is known

that CO and COOH are adsorbed on the ruthenium oxide surface[14,15]. Therefore, it can be concluded that a lesser increment in the resonant frequency during the oxidation reaction of methanol can be attributed to the adsorption of the intermediates such as CO and COOH on a ruthenium oxide. According to Kulesza[16], a discharge reaction of water on the ruthenium oxide film below 1 V, $H_2O \rightarrow OH_{ads} + H^+ + e^-$, occurs. It might be a plausible explanation that smaller mass change may be associated with an instantaneous interaction between OH_{ads} on ruthenium oxide and the intermediates such as CO and COOH, which might enhance the electrode kinetics of the oxidation reactions[17].

Conclusion

An electrochemical quartz crystal microbalance was employed to investigate the electrochemical dynamics of a ruthenium oxide film during an oxidation reaction of methanol. The electrochemical quartz crystal microbalance results show that 5 H_2O molecules per Ru are inserted into the ruthenium oxide film during the electrodeposition. During the potential cycle between -200 mV and +900 mV, the proton ions are deserted and inserted repeatedly, where two water molecules per Ru are accompanied, which was also supported by the change in resonant frequency measured in a D_2O solution. During the oxidation reaction of methanol, intermediates such as CO and COOH are adsorbed on the ruthenium oxide film, in which the weak interaction between OH_{ads} and CO might take place and enhance the electrode kinetics of the oxidation reaction of methanol.

REFERENCES

1. C.N. Shi and F.C. Anson, *J. Electroanal. Chem.*, **362**, 273 (1993).
2. L.D. Burke, O.J. Murphy, J.F. Oneill and S. Venkatesan, *J. Chem. Soc. Faraday Trans. I*, **73**, 1659 (1977).
3. L.D. Burke and J.F. Oneill, *J. Electroanal. Chem.*, **101**, 341 (1979).
4. A. Cornell and D. Simonsson, *J. Electrochem. Soc.*, **140**, 3123 (1993).
5. I.H. Kim and K.B. Kim, *J. Electrochem. Soc.*, **151**, E7 (2004).
6. S. Sopcic, M.K. Rokovic, Z. Mandic, A. Róka and G. Inzelt, *Electrochim. Acta*, **56**, 3543 (2011).
7. T. Iwasita, *Electrochim. Acta*, **47**, 3663 (2002).
8. C.H. Lee, S.-E. Bae, C.-W. Lee, D.-H. Jung, C.-S. Kim and D.-R. Shin, *Int. J. Hydrogen Energy*, **26**, 175 (2001).
9. P.J. Kulesza and M. Bandoch, *J. Electroanal. Chem.*, **323**, 131 (1992).
10. J.H. Jin, C.W. Lee, S.E. Bae and D.S. Shin, *Bull. Korean Chem. Soc.*, **17**, 975 (1996).
11. M. Vukovic and D. Cukman, *J. Electroanal. Chem.*, **474**, 167 (1999).
12. M.C. Santos, L. Cogo, S.T. Tanimoto, M.L. Calegaro and L.O.S. Bulhoes, *Appl. Surf. Sci.*, **253**, 1817 (2006).
13. M.C. Santos, A.J. Terezo, V.C. Fernandes, E.C. Pereira and L.O.S. Bulhões, *J. Solid State Electrochem.*, **9**, 91 (2005).
14. W.F. Lin, M.S. Zei, M. Eiswirth, G. Ertl, T. Iwasita and W. Vielstich, *J. Phys. Chem. B*, **103**, 6968 (1999).
15. Y. Ishikawa, M.-S. Liao and C.R. Cabrera, *Surf. Sci.*, **463**, 66 (2000).
16. P.J. Kulesza, *J. Electroanal. Chem. Interf. ElectroChem.*, **220**, 295 (1987).
17. M.-S. Löffler, B. Groß, H. Natter, R. Hempelmann, Th. Krajewski and J. Divisek, *Phys. Chem. Chem. Phys.*, **3**, 333 (2001).