

## Electrochemical Oscillations during Reduction of Nitrate Ions on Cu and Ag

S. Yamamoto<sup>1</sup>, Y. Mukouyama<sup>1</sup>, S. Nakanishi<sup>2</sup>  
and H. Okamoto<sup>1</sup><sup>1</sup>Tokyo Denki University

Hatoyama, Saitama 350-0394, Japan

<sup>2</sup>The University of Tokyo

Meguro-ku, Tokyo 153-8904, Japan

## INTRODUCTION

The electrochemical reduction of nitrate ions,  $\text{NO}_3^-$ , has been extensively studied, for many years, concerning the mechanism of the nitrate reduction, the influence of electrolysis conditions and the applications of the nitrate reduction, etc., as summarized in recent reviews [1, 2].

It has been reported that the electrocatalytic activities toward the nitrate reduction increase in the order  $\text{Au} < \text{Ag} < \text{Cu}$  [2]. Then, we studied the nitrate reduction on Cu in strong acid solutions and found that two new types of oscillations appeared under potential controlled and current controlled conditions [3]. The oscillation which appeared at a higher potential or a lower current (in absolute value) region was called oscillation I and that which appeared at a lower potential or a higher current region was called oscillation II (see Figures 1a or 1d).

As shown in our previous paper [3], oscillations I and II appeared when both the nitrate reduction reaction and a hydrogen evolution reaction (HER) occurred. Impedance measurements indicated that the appearance of oscillation I was attributed to the negative differential resistance which was probably caused by the suppression of the nitrate reduction due to the formation of adsorbed H on Cu. Oscillation II was accompanied with an intense bubble evolution due to the HER.

We recently have studied the nitrate reduction on Ag and Au which have lower electrocatalytic activity for the reduction than Cu. The oscillations were found to appear during the reduction on Ag as well as on Cu. However, they did not appear during the reduction on Au. In this presentation, we will discuss the relationship between the electrocatalytic activities of metals and the appearance of the oscillations as well as the mechanism of them.

## RESULTS

Figure 1 shows current ( $I$ )–potential ( $E$ ) curves for Cu-wire, Ag-wire and Au-wire electrodes in 0.2 M  $\text{H}_2\text{SO}_4$  and 0.2 M  $\text{HNO}_3$ , observed under potential controlled and current controlled conditions. The onset potentials for the HER attributed to the reduction of  $\text{H}^+$  ions in 0.2 M  $\text{H}_2\text{SO}_4$  were ca. -0.5 V vs. SHE for Cu, at -0.65 V for Ag, and at -0.4 V for Au. The nitrate reduction started to occur in 0.2 M  $\text{HNO}_3$  at 0 V for Cu (not shown in Fig. 1) and at -0.2 V for Ag, which were more positive than the onset potentials for the HER. The nitrate reduction hardly occurred on Au. These corresponded well to the order in the catalytic activities toward the reduction.

As shown in Figures 1a and 1d, oscillation I appeared as a current oscillation in the potential region between ca. -0.5 and -1.0 V, where the reductions of both nitrate ions and hydrogen ions occurred as discussed in the previous paper [3]. It also appeared as a potential oscillation under current controlled conditions. Oscillation II also appeared as a current oscillation and a potential oscillation in the potential region of the HER.

In reference to the Ag electrode, a current oscillation appeared under potential controlled conditions in the potential region between -0.65 and -1.3 V, which

corresponded to the region where the HER had occurred due to the  $\text{H}^+$  reduction on Ag. Hence, the oscillation can be assigned as oscillation I. On the other hand, two types of potential oscillations appeared under current controlled conditions. The potential oscillation that appeared at a low reduction current can be assigned as oscillation I, because the potential range of the oscillation corresponded to the region where the oscillation I appeared as the current oscillation. The other potential oscillation that appeared at a high reduction current can be assigned as oscillation II because the amplitude of the potential oscillation was larger than that of potential oscillation I, similarly to the potential oscillations I and II for the Cu electrode.

As for the Au electrode, oscillations I and II did not appear probably because the electrocatalytic activity toward the nitrate reduction was low. These results indicate that the oscillations appear during the nitrate reduction only on the metals which have high electrocatalytic activities toward the reduction.

## CONCLUSION

We have found two types of oscillations during the nitrate reduction, not only on Cu electrode, but also on the Ag electrode. The oscillations appeared when the metals that have high electrocatalytic activities toward the reduction were used.

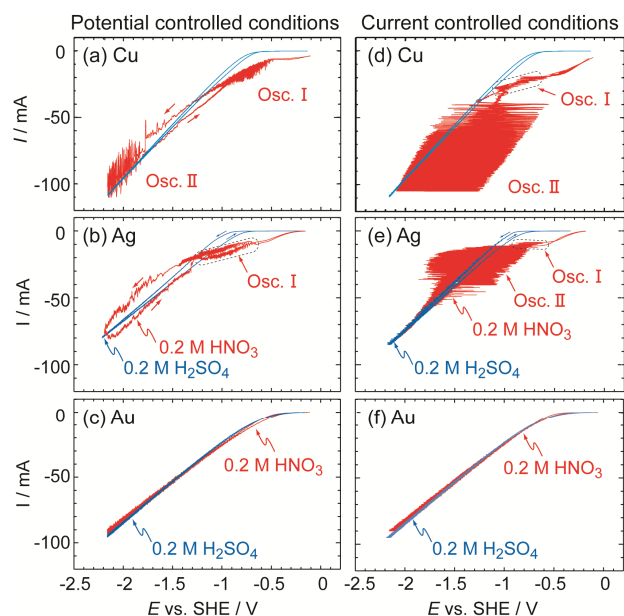


Figure 1. The  $I$ – $E$  curves for various metal electrodes, (a, d) Cu, (b, e) Ag and (c, f) Au, in 0.2 M  $\text{H}_2\text{SO}_4$  and 0.2 M  $\text{HNO}_3$ , measured (left) under potential controlled conditions at a sweep rate of  $10 \text{ mVs}^{-1}$  and (right) under current controlled conditions at a rate of  $0.2 \text{ mAs}^{-1}$ .

## REFERENCES

- [1] C. Milhano and D. Pletcher, in *Modern Aspects of Electrochemistry* 45, R. E. White, Editor, p. 1, Springer, New York (2009).
- [2] V. Rosca, M. Duca, M. T. de Groot and M. T. M. Koper, *Chem. Rev.* 109, 2209 (2009).
- [3] Y. Mukouyama, S. Yamamoto, R. Nakazato, S. Nakanishi and H. Okamoto, *ECS Trans.*, 50 (2013) in press.

This work is partially supported by the Research Institute for Science and Technology of Tokyo Denki University under Grants Q12E-02.