High-throughput screening of binary catalysts for oxygen reduction
산소 환원 반응을 위한 2성분계 촉매의 고속 분석연구

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1. Introduction

Combinatorial screening method was first introduced into the field of electrochemical catalysis by Mallouk and co-workers in 1998 [1]. Since then, this method has also been adopted by Woo [2, 3] and Chu [4] in discovering anode catalysts with higher and more stable electrocatalytic activity, as well as investigating the influence of Nafion on the activity of electrocatalysts, respectively. However, there exists difficulty in applying high-throughput screening method to the study of oxygen reduction cathode catalyst. Because the solubility of oxygen in the electrolyte is relatively low, it is rather difficult to consume the protons contained in the electrolyte rapidly. As a result, the pH variation in the vicinity of the catalyst spot is too small to be observed by use of proton indicator. At 25 ℃ the solubility of oxygen in pure water is only 2.6×10^{-4} mol/l, and lower in the electrolyte solution. In this work, we have first adopted fluoresceinas pH fluorescence indicator for high-throughput optical screening of oxygen reduction catalysts. A series of Pt based and non-Pt catalysts have been prepared and evaluated as oxygen reduction catalysts in order to find out compositions with higher catalytic activity.

2. Experimental

Serving as working electrode, the array was mounted in a three-electrode cell for fluorescence screening, with Ag/AgCl as reference electrode and platinum foil as counter electrode. All potentials were presented with respect to the reversible hydrogen electrode (RHE). The electrolyte solution was composed of 100 μM fluorescein sodium salt as pH indicator. pH of the electrolyte was adjusted to 4 by H_2SO_4 [5]. Fig. 1 shows the micro-dispensing system used for preparation of arrays.

3. Results and Discussion

Fig. 2 shows the fluorescence image taken at 0.55 V versus RHE. The results of image analysis revealed that Pt(67)Bi(33) had the highest activity, and several other spots located near Pt(67)Bi(33) had higher activities than Pt and other spots in the array, which included several compositions of PtCu, PtSe and PtTe. Besides these compositions, Pt(44)Ir(56) also showed higher activity than Pt.

Combinatorial array of Non-Pt binary catalysts were prepared with six transition metals including Ru, Fe, Co, Ni, Cu and Cr. The fluorescence image taken at potential of 0.55 V is presented in Fig. 3. The analysis results revealed that Ru(56)Fe(44) showed the highest activity. Besides, both Ru(44)Fe(56) and Ru(67)Co(33) had higher activities than Pt.

4. Conclusion

A series of Pt based and non-Pt binary catalysts have been prepared and evaluated towards the oxygen reduction, by high-throughput optical screening. Fluorescein was first used as pH indicator for detecting pH change in the vicinity of cathode caused by oxygen reduction. Arrays of catalyst spot comprised of binary catalysts and pure Pt were all prepared by using robotic micro-dispenser. Some of Pt based binary catalysts including PtBi, PtCu, PtSe, PtTe and PtIr, as well as non-Pt catalysts, such as RuFe, showed higher activities than pure Pt. All the active binary catalysts exhibited better methanol tolerance than Pt, especially RuFe catalyst.

Acknowledgement

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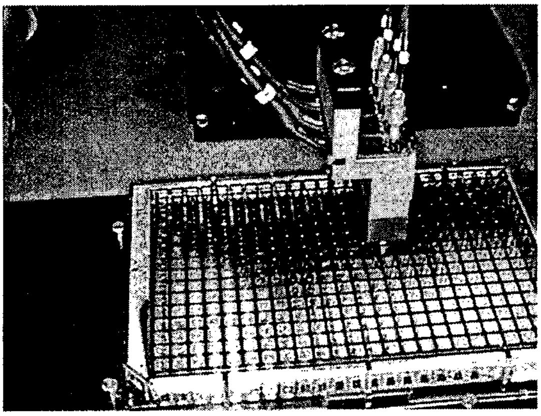

Figure 1. The stock solutions, delivered from four metal precursor solutions, in a 384-well plate.

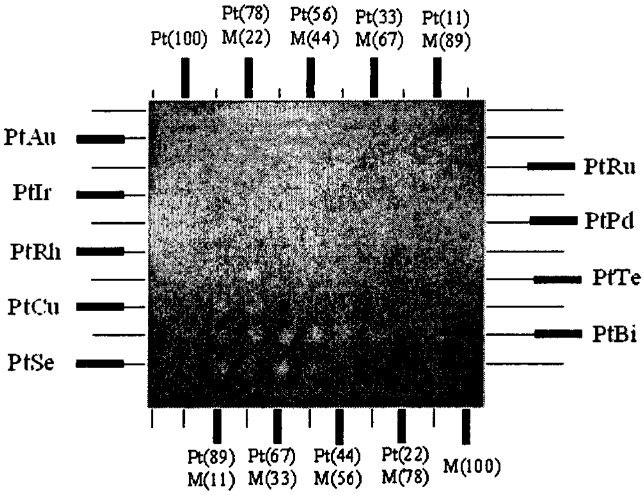

Figure 2. Fluorescence image of Pt based binary array at 0.5 V versus RHE in oxygen saturated electrolyte (pH 4).

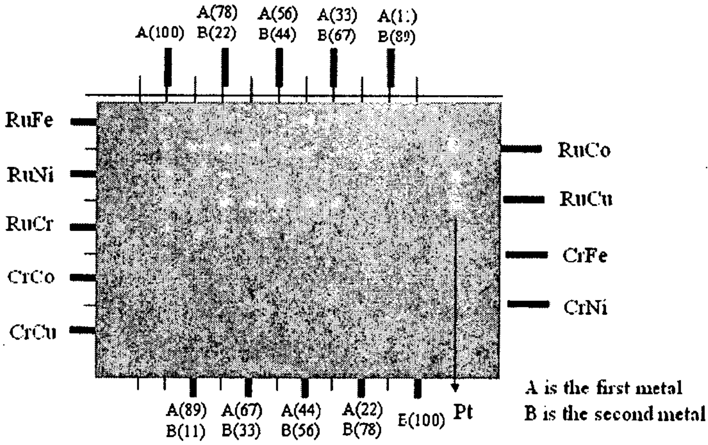

Figure 3. Fluorescence image of non-Pt binary array at 0.5 V versus RHE in oxygen saturated electrolyte (pH 4).

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