# Effect of composition change in the ternary PdIrY alloy on the activity towards oxygen reduction reaction

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**Abstract:** Pd-based catalysts have been studied to replace the Pt catalyst. To increase the activity for oxygen reduction reaction (ORR), transition metals that give strain and electronic effects were incorporated to form an alloy. It is revealed previously that Ir enhances durability and catalyst activity when decorated into the Pd alloy. Amount of Y in the ternary PdIrY alloy catalyst is investigated for improved ORR activity. The $Pd_4IrY/C$ showed the best specific activity and mass activity, 0.812mA/cm$^2$ and 0.324A/mg$_{Pd}$ at 0.6V, which is attributed to the result of simultaneous strain and electronic effects of Ir and Y.

**Keywords:** Pd-based ternary alloy, Oxygen reduction reaction, Polyol method

## 1. Introduction

Many researchers research about Pd-based catalysts because Pd is more similar to Pt, which has the best electrocatalyst but too expensive. However, Pd has five times lower activity towards oxygen reduction reaction (ORR) catalyst activity than Pt. To improve the ORR activity, most of research is focused on the development of Pd-based alloy catalysts. According to the d-band theory, transition metals in the alloy catalysts modify the electronic structure of surface atom so they can increase the catalyst activity when the d-band center decreased lower than fermi energy of catalyst.[1] Cui *et al.* reported that nanoporous PtY alloy enhanced electrocatalytic activity due to the strain effect and electronic effect.[2] You *et al.* reported that Ir-decorated PdCu/C catalyst has higher single cell performance than PdCu/C catalyst.[3] This research suggests that the Ir can increase not only durability but also catalyst activity because of the core-shell structure like PdCu@PdIr alloy catalyst.

In this study, the dependency of ORR activity of the PdIrY ternary alloy catalyst is investigated by controlling of the amount of Y in the ternary alloy in acidic condition. PdIrY alloy catalysts were prepared by polyol method to change the atomic ratio of Y.

## 2. Experimental

$Pd_4IrY_M/C$ (M=0.5, 1, 1.5, 2) catalysts of 40 wt.% loading level were prepared by a polyol method. A carbon black (Ketjen black, KB 600JD) as a carbon support was dispersed in ethylene glycol and deionized (DI) water using ultra-sonication. $(NH_4)_2PdCl_4$ and $YCl_3\cdot 6H_2O$ previously dissolved in ethylene glycol and $(NH_4)_2IrCl_6$ dissolved in DI water, and then these metal solutions added to the dispersion solution of carbon support. With 1M NaOH aqueous solution, the pH value of reaction mixture was adjusted to about 11. This solution refluxed for 2 hours at 110 ℃ and then freeze-dried for 10 h after filtering and washing with DI water and acetone. Pd/C and $Pd_4Ir/C$ alloy catalysts were prepared by the same process to be used as comparative samples.

X-ray diffraction (XRD) patterns was measured to identify the crystalline structure and size of catalysts. Those catalysts were scanned between 10° and 80° at a scan rate of 2°/min. Electrocatalytic performance was evaluated by cyclic voltammetry (CV) and linear sweep voltammetry (LSV) tests. CV curves were drawn in $N_2$-purged 0.1M $HClO_4$ solution at a scan rate of 50mV/s. LSV tests were done in $O_2$-purged 0.1M $HClO_4$ solution at a scan rate of 5mV/s. Through these tests, the specific activity (SA) and mass activity (MA) for the ORR as properties of electrocatalytic performance is estimated.

## 3. Results and discussion

Fig. 1a shows XRD patterns of each catalyst. A ratio of 1st and 2nd intense peaks demonstrates all of catalysts corresponds to a face centered cubic structure of Pd, which is the dominant element in the alloy. And their crystalline sizes of are distributed between 2 and 3nm for the all alloy catalyst except Pd/C. In

TEM image (not shown here), Pd/C particles had large sizes between 5 ~ 20nm however, other alloy catalyst particles were smaller than Pd/C.

According to electrochemical evaluation by CV and LSV, the $Pd_4IrY/C$ showed not only the large electrochemical active surface area (ECSA) value but also the highest specific activity and mass activity as observed from the Fig. 1b, which displays an I-V curve of each catalyst towards ORR. This enhancement of ORR activity could be accounted for the decreasing of the d-band center of Pd and Ir by incorporation of Y atom in the alloy and the occurring of strain effect in the structure. Further study for reasons of this results will be elucidated through various physicochemical analysis.

**Table 1.** The properties of Pd/C, $Pd_4Ir/C$, and $Pd_4IrY_M/C$ (M=0.5, 1, 1.5, 2)

| Catalyst | Crystalline size (nm) | ECSA ($m^2/g_{Pd}$) | $i_k$ at 0.6V (mA) | SA at 0.6V ($mA/cm^2$) | MA at 0.6V ($A/mg_{Pd}$) |
|---|---|---|---|---|---|
| Pd/C | 4.40 | 18.5 | 0.0603 | 0.083 | 0.015 |
| $Pd_4Ir/C$ | 2.10 | 24.8 | 0.0820 | 0.122 | 0.030 |
| $Pd_4IrY_{0.5}/C$ | 2.44 | 35.3 | 0.1732 | 0.195 | 0.069 |
| $Pd_4IrY/C$ | 2.00 | 39.9 | 0.7645 | 0.812 | 0.324 |
| $Pd_4IrY_{1.5}/C$ | 2.61 | 36.0 | 0.3972 | 0.497 | 0.179 |
| $Pd_4IrY_2/C$ | 2.89 | 38.1 | 0.1586 | 0.199 | 0.076 |

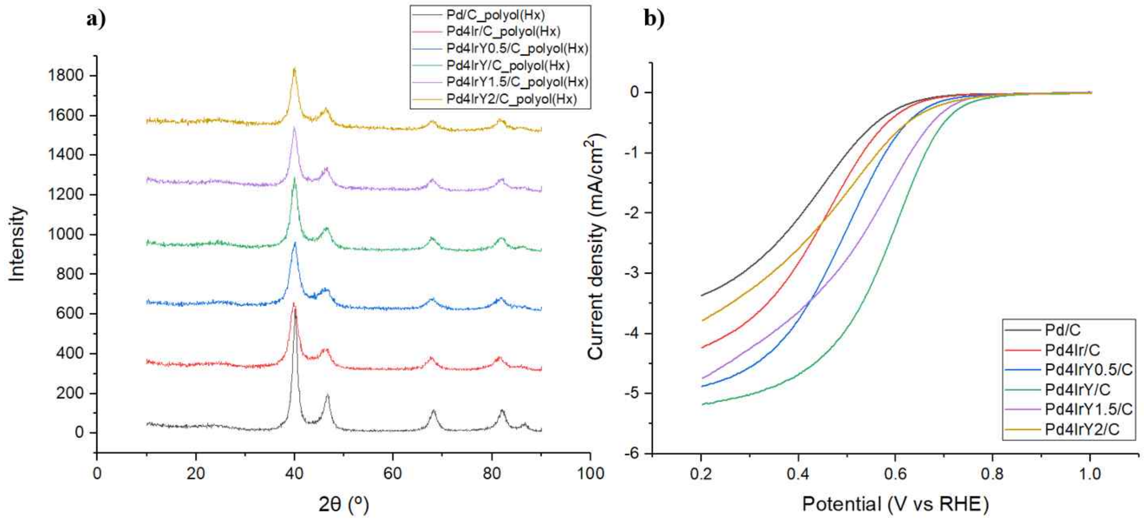

**Figure 1.** a) XRD patterns and b) ORR polarization curves of Pd/C, Pd4Ir/C, and Pd4IrYM/C (M=0.5, 1, 1.5, 2)

## 4. Conclusions

Pd-based alloy catalyst is expected to increase catalyst activity by d-band theory and strain effect, however, many transition metal in the Pd alloy have a bad influence of the catalyst role. The $Pd_4IrY/C$ showed the best catalysts activity among the prepared catalysts, which could be attributed to the alloying effect of Y, which provide the decreasing the d-band center and the strain effect in the alloy nanoparticle.

## References

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