

Temperature-Dependence of Oxygen Reduction Reaction Activity at Platinum Alloy Electrocatalysts

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Development of the highly active cathode catalysts for oxygen reduction reaction (ORR) is one of the most important subjects to achieve a high efficiency at polymer electrolyte fuel cells (PEFCs). For the screening process of the catalyst, it is essential to evaluate precisely kinetically controlled ORR activities at the electrodes and to quantify a reaction by-product, H_2O_2 , which may deteriorate the polymer electrolyte membrane or gaskets, over wide temperature range. Recently, we found that Pt alloys such as Pt-Fe, Pt-Co, and Pt-Ni exhibited very high ORR activity.¹⁾ In the present research, we evaluated their ORR activities and H_2O_2 production rate by using channel flow double electrodes (CFDE)²⁾ at 20-90°C.

$\text{Pt}_{54}\text{Fe}_{46}$, $\text{Pt}_{68}\text{Co}_{32}$, $\text{Pt}_{63}\text{Ni}_{37}$, and Pt films sputtered on gold substrate were used as working electrodes. Pt collecting electrode was located at the downstream of the working electrode in order to detect H_2O_2 . A Pt wire was used as the counter electrode. A reversible hydrogen electrode [RHE(*t*)], kept the temperature at the same as that of the cell (*t*°C), was used as the reference electrode.

Figure 1 shows hydrodynamic voltammograms for ORR at 20°C in O_2 saturated 0.1 M HClO_4 solution at $\text{Pt}_{54}\text{Fe}_{46}$, $\text{Pt}_{68}\text{Co}_{32}$, $\text{Pt}_{63}\text{Ni}_{37}$, and Pt electrodes and simultaneously acquired currents at the collecting electrode. The ORR at the alloy electrodes commences around 0.95 V vs. RHE which is higher than that at Pt electrode by ca. 0.1 V. Formation of H_2O_2 indicated by the current at the collecting electrode was always below the detection limit at pure Pt electrode in the whole temperature and potential ranges, but small H_2O_2 yield of 0.17-1.2% were observed at the alloy electrodes.

Voltammograms for the ORR at each electrode were recorded at 20-90°C by changing the mean flow rate of electrolyte to obtain kinetically controlled currents i_K . Apparent rate constants k_{app} were calculated from the i_K values by correcting the change in oxygen concentration with temperature²⁾; $i_K/4FA = -k_{\text{app}}[\text{O}_2][\text{H}^+]$.

Arrhenius plots of the k_{app} values at a constant overpotential of -0.525 V vs. E° (0.760 V vs. RHE at 30°C) are shown in Fig. 2. Linear relationships between $\log k_{\text{app}}$ and $1/T$ are seen at all electrodes below 60°C. In this temperature region, the ORR activities at the alloy electrodes are larger than that at the Pt electrode by a factor of 4.0 ($\text{Pt}_{54}\text{Fe}_{46}$), 3.1 ($\text{Pt}_{68}\text{Co}_{32}$), and 2.4 ($\text{Pt}_{63}\text{Ni}_{37}$). However, the k_{app} values at the alloy electrodes decrease with elevating temperature above 60°C, and settle to almost the same value at the Pt electrode. The H_2O_2 production was not detected at the alloy electrodes once heated at the high temperature in the solution. This is probably due to dissolution of non-precious metal components (Fe, Co, Ni) from the alloys to form thick Pt layers on the surface.

The apparent activation energy of 41 kJ mol⁻¹ obtained at these alloy electrodes at $t < 60^\circ\text{C}$ is comparable to that at the Pt electrode. These results suggest that the high ORR activities at the alloy electrodes are ascribed to a

large pre-exponential factor such as high coverage of adsorbed oxygen.

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References

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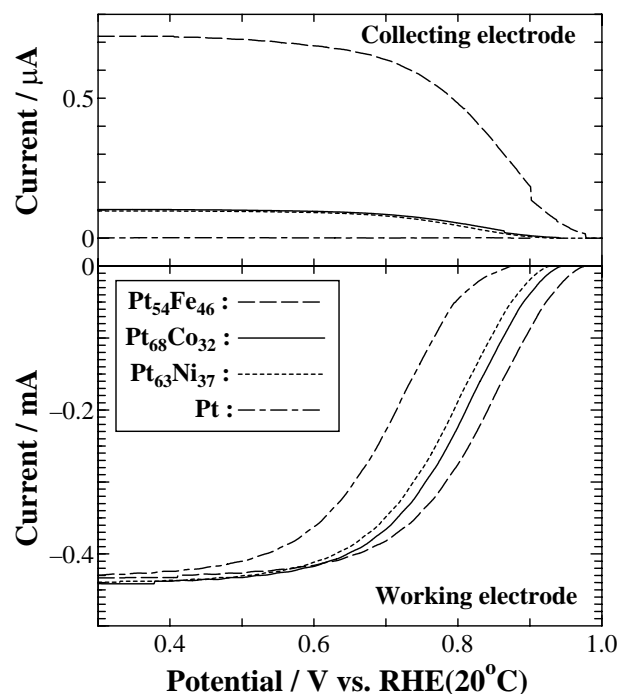


Fig. 1. Hydrodynamic voltammograms for ORR in O_2 saturated 0.1 M HClO_4 solution at $\text{Pt}_{54}\text{Fe}_{46}$, $\text{Pt}_{68}\text{Co}_{32}$, $\text{Pt}_{63}\text{Ni}_{37}$, and Pt electrodes at 20°C and simultaneously acquired currents at Pt collecting electrode. Potential scan rate = 0.5 mV/s. Potential of the collecting electrode = 1.2 V. Mean flow rate of electrolyte = 50 cm/s.

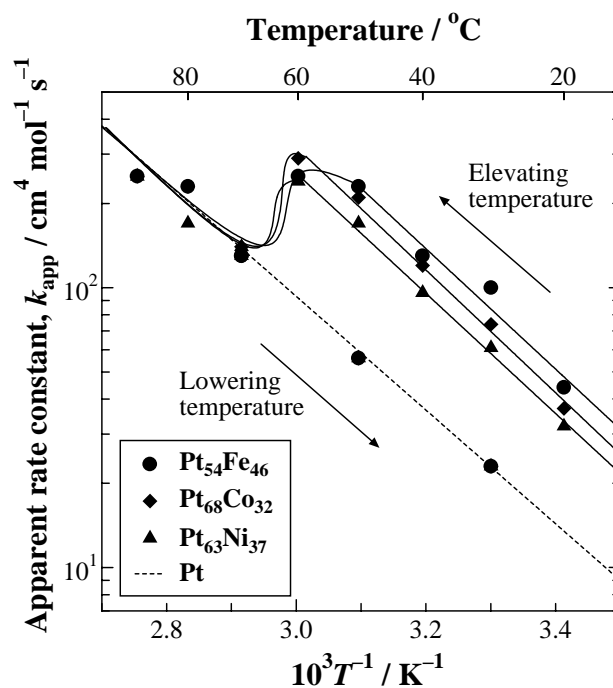


Fig. 2. Arrhenius plots of apparent rate constants for ORR in O_2 saturated 0.1 M HClO_4 solution at $\text{Pt}_{54}\text{Fe}_{46}$, $\text{Pt}_{68}\text{Co}_{32}$, $\text{Pt}_{63}\text{Ni}_{37}$, and Pt electrodes. $E - E^\circ = -0.525$ V.