

Temperature Dependence of Oxygen Electroreduction Properties on Pt and Pt alloy particles

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Temperature dependence of electrocatalytic properties have been investigated for Pt and Pt alloys particles by high pressure type rotational disc electrode (RDE) measurements. Oxygen electro-reduction reaction (ORR), which is a major potential loss factor of PEFC, at temperature range from 25°C to 120°C have been studied. Electrochemical properties of Pt alloy particle have been measured above 100°C, which is the boiling point of water. Alloy particles of PtFe and PtNi show superior electrocatalytic properties than pure Pt; for example, the kinetically controlled current density of ORR of PtFe is about 10 times larger than that of pure Pt at 120°C, while the overpotential of ORR does not remarkably shifted by the temperature. The present results indicate an importance of the electrochemical characterization of Pt alloys at elevated temperatures when the electrocatalytic materials are designed to be used at higher temperature operation above 100°C, which has recently been recognized as a technological option for advanced PEFC.

Key words: PEFC, Electrocatalyst, Oxygen Reduction, Pt alloy, Temperature Dependence

1. INTRODUCTION

Fuel Cells have been recognized as a promising technological option for future energy system which intrinsically possess higher energy efficiency than the present conversion devices such as internal combustion engines. Among several types of fuel cells, Polymer Electrolyte Fuel Cells (PEFC) have been extensively developed as an alternative batteries for zero-emission vehicles, on-site power generation and mobile phones. However, the PEFC uses electrode reaction at both side of the membrane, hence, the electrocatalytic properties of the electrodes are crucial against the cell's efficiency. The Pt and Pt alloy electrocatalysts suffer from surface poisoning by contaminated carbon monoxide (CO) as well as sulfur species when reformed hydrocarbon gases are used. So, the tolerance against these condensable species is an important issue for the practical application.

Higher temperature operation of PEFC has been pointed out to be a promising option to overcome most of the technological problem of the present PEFC system and new class of polymer electrolyte membranes have been investigated elsewhere⁽¹⁻¹¹⁾. As the operation temperature increases, the poisoning

of the electrocatalysts becomes weaker and cell efficiency becomes larger. However, the electrocatalytic properties of Pt alloys at temperature regions above 100°C have been still poorly studied and reliable catalytic data is necessary for designing electrode materials. Moreover, the electrocatalytic properties of electrodes with particle form have not been sufficiently investigated; most of the works are on Pt bulk crystals or films⁽¹²⁻²¹⁾. The electrode materials morphology used in the experiments of research papers are usually different from those of practical fuel cells conditions and electrode performances are affected by operational parameters such as gas flow, humidity and so on⁽²²⁻²³⁾.

In this paper, the temperature dependence of electrocatalytic oxygen reduction properties of Pt and Pt alloys particles at wide temperature range have been investigated for better understanding of catalyst materials. As ORR is a predominant energy loss factor of the cell, the materials with improved electrode kinetics have been surveyed for higher efficient PEFC design.

2. EXPERIMENTAL

2-1. High pressure rotational disc electrode (RDE) measurements

Usually, the electrocatalytic properties of the electrode materials have been studied either by the polarization properties of the real fuel cell or rotational disc electrode (RDE) measurements at ambient temperature electrochemical cells. However, the former case, electrocatalytic properties are influenced by miscellaneous operational conditions and ,in the latter case, the properties can be measured only in the temperature region below 100°C. The electrochemical properties of the electrode materials at elevated temperature above 100°C have been scarcely investigated.

In the present work, high pressure type RDE apparatus has been designed as shown in fig.1. The electrochemical measurement chamber was autoclave type made from stainless steel (SUS) and interior glass cell was hold inside. The RDE measurements in the aqueous solution can be executed up to 160°C, where

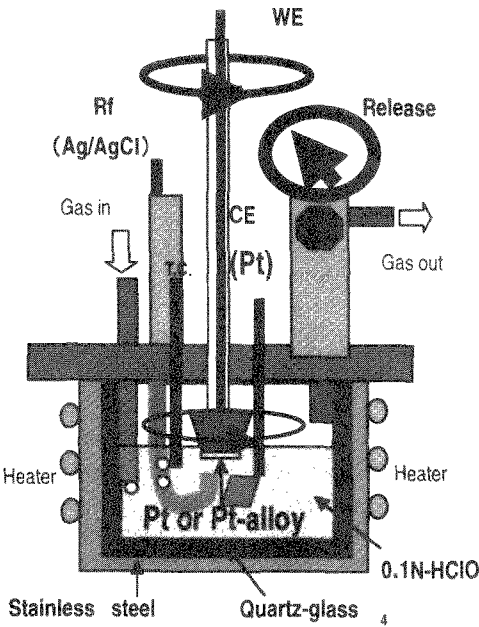


Figure 1
High pressure type RDE apparatus.

the saturated water vapor pressure is about 6 atm. The autoclave type RDE apparatus suppress a boiling of water by the pressure and the temperature dependence of the electrode materials can be measured in the wide temperature range.

2-2. Preparation of the Pt alloy particles

In order to see the electrochemical

properties of the electrode materials much closer to the real cell conditions, the particle samples of Pt alloys have been synthesized by mechanical alloying methods. Source Pt powders and the secondary metal elements (Ni, Fe) are mixed by 1:1 mol% ratios in agate mortar and alloyed by fast-speed mechanical milling for several hours. The Pt binary alloy formation of the particles have been confirmed by X-ray diffraction measurements.

2-3. Electrochemical properties

Mechanically alloyed Pt and Pt alloy particles are first dispersed in the water solution and deposited on to Ti substrates and after dried, Nafion solution are dropped on top of the powders to form a stable coating film. The specimen are set on the RDE apparatus and electrochemical properties have been measured in the temperature region from 20°C to 120°C. Cyclic voltammograms (CV) are measured in 0.1N-HClO₄ solution and the real electrochemical surface area of the particle samples are obtained by an electrical capacity of the hydrogen desorption wave of CV. Hydrodynamic voltammograms of oxygen reduction reaction (ORR) of the samples are measured in O₂ saturated 0.1N-HClO₄ solutions at a rotational speed from 1000 rpm to 2000 rpm. Even at 120°C, CV as well as polarization curve of the particle samples are successfully obtained.

3.RESULTS AND DISCUSSION

3-1. Structure of the Pt alloy powders

The size of the Pt alloy powders are measured by SEM observations. The size of the Pt powders are in the range of 0.1 mm to 1 mm, however, that of PtNi as well as PtFe are 1 mm to 10 mm. The compositions of the Pt alloy powders are determined by EPMA (Electron probe micro analysis) method and they are PtNi = 54 :46 and PtFe = 43 : 57, respectively. Figure 2 shows that the XRD peaks of second elements are disappeared completely after 8.5 hour mechanical milling and form patterns for binary alloy formation (PtFe) with a face centered cubic lattice (FCC).

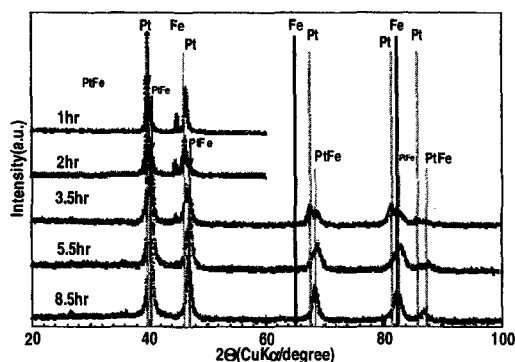


Figure 2
XRD patterns of PtFe alloy particles.

3-2 Oxygen reduction

Cyclic voltammograms of Particle samples were measured at 25°C, 80°C, 100°C and 120°C, respectively. Figure 3 shows a typical CV spectra of Pt, PtNi and PtFe specimen at 25°C, obtained with a scanning rate of 100 mV/sec in a 0.1N-HClO₄ solution. The electrochemical surface area of the particle specimen was obtained by the electrical capacity of the hydrogen desorption wave. The voltammogram are almost identical shape at elevated temperature.

The cyclic voltammograms of PtNi and PtFe alloy particle samples show similar voltammogram patterns in the temperatures range from 25°C and 120°C.

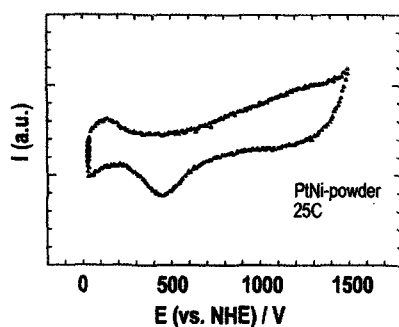


Figure 3
The cyclic voltammograms of PtNi-alloy particle samples.

Electroactive surface areas (S_a) of the particle specimen are determined by the following formula, $S_a = Q_H / 210 \mu\text{Ccm}^{-2}$, where Q_H denotes Faradic capacity of the hydrogen desorption wave of CV and an electrical capacity of $210 \mu\text{Ccm}^{-2}$ for polycrystalline Pt surfaces. The electroactive surface area are measured at each temperatures

and roughness factors of the catalytic surfaces are obtained by the electroactive surface area S_a divided by the apparent surface area, as listed in table1. Although the value is small in PtFe alloys, the roughness factors are increasing with temperature for all of the Pt alloy samples.

Table1.

Polycrystalline Pt surfaces. The electroactive surface area are measured at each temperatures and roughness factors of the catalytic surfaces.

	Temperature/°C				
	25	80	100	120	130
Pt	87	187	164	210	---
PtNi	37	103	112	198	187
PtFe	53	65	64	88	95

Hydrodynamic voltammograms of the oxygen reduction reaction (ORR) properties were measured for Pt particles at 25°C when the O₂ gases were saturated in 0.1N-HClO₄ solution. The polarization curves obtained by RDE with 1000, 1500, 2000 rpm are described in figure 4 . ORR

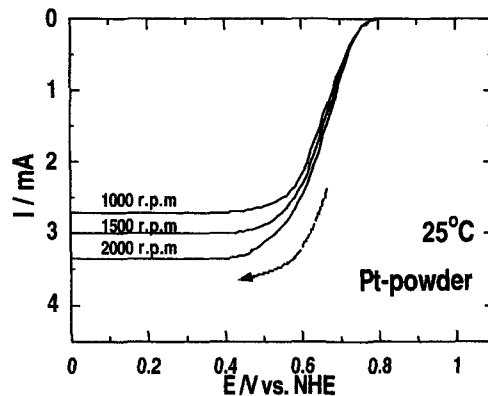


Figure 4
The polarization curves of Pt measured in 0.1N-HClO₄ solution saturated with the oxygen gases by RDE.

starts at around 0.8 V vs. NHE and the limiting current increases with a rotational speed. As the apparatus in the present experiment is a high pressure type, temperature dependence of the polarization curves at 1000 rpm of (a) Pt, (b) PtNi and (c) PtFe particles can be measured from 25 to 120°C which is shown in figure 5.

As a common tendency to three samples, a limiting current is increasing with increasing temperature, while the polarization curves above 100°C has scarcely been studied up to now. The enhancement of the limiting current may not be ascribed to the increased electrocatalytic activity of the particles surfaces but enhanced gas diffusion in the solution.

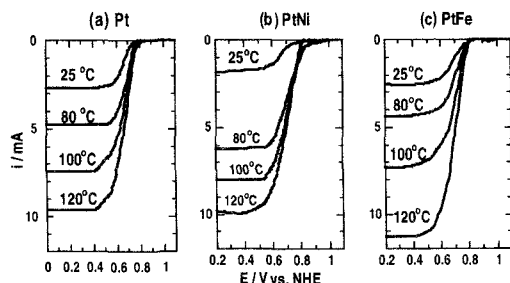


Figure 5
Polarization curves of Pt and Pt-alloys powders on rotating disk electrodes ($\omega=1000$ r.p.m.) at different temperatures.(25-120°C)

Figure 6 shows the polarization curves of Pt, PtNi and PtFe at 120°C with rotational disc speed of 1000 rpm. At this condition, ORR start almost same potential of around 0.8 V vs. NHE and there is minor differences among three particles. The overpotential of ORR at elevated temperature does not change so much from that at room temperature even for PtFe and PtNi alloy particles.

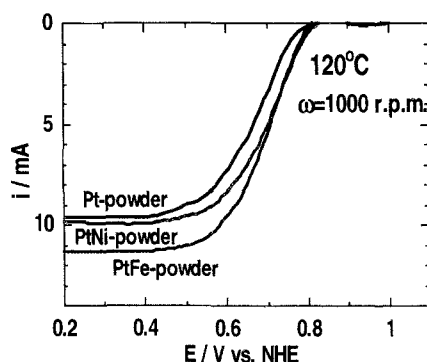


Figure 6
The polarization curves of Pt, PtNi and PtFe at 120°C with rotational disc speed of 1000 rpm.

Figure 7 (a) shows the polarization curves of PtFe alloys at 120°C. The limiting current was increasing with the rotational speed.

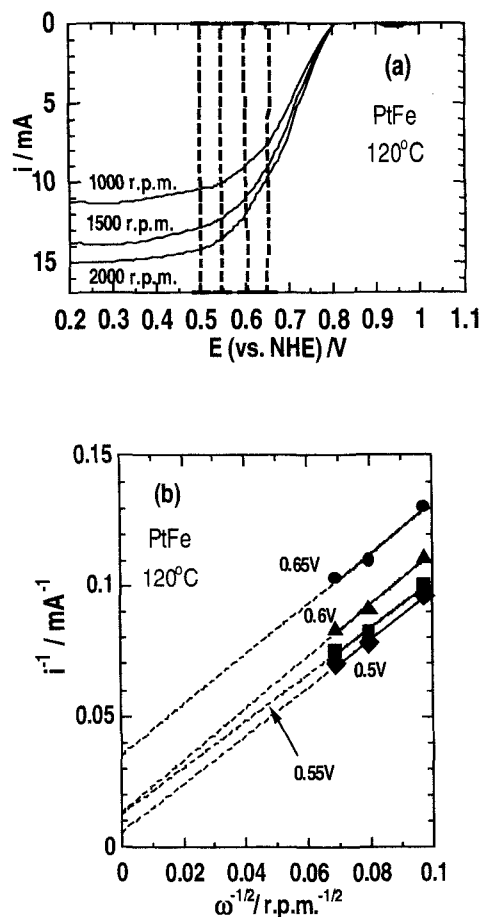


Figure 7
(a) The polarization curves of PtFe alloys
(b) Koutechy-Levich Plot of PtFe-powder at 120°C.

In order to study a real surface electrocatalytic kinetics, Koutechy-Levich plots at the potentials of 0.5, 0.55, 0.60 and 0.65 V were derived as shown in fig. 7 (b). In this characterization, an extrapolation of an inverse current ($1/i$) to the infinite rotational speed ($\omega^{-1/2} = 0$) indicates an real electrocatalytic activity, i.e., charge transfer rate limiting current, at any gas diffusion flux to the electrode surfaces. The current normalized by the electroactive surface area at this limit is considered to be a kinetic current density (j_k), or kinetically controlled current density. The j_k has been measured from 25 to 120°C, and it has been compared among different Pt alloys particles samples. Linear slope in the plot were obtained against different potential and indicates the four electron processes are prevails in the ORR against alloy specimens.

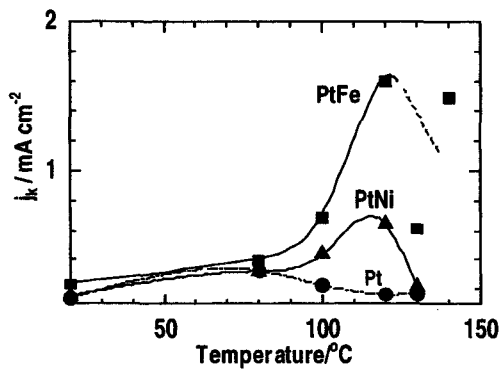


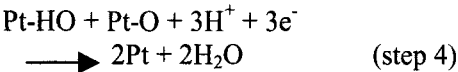
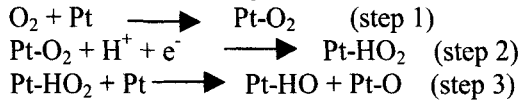
Figure 8
Kinetic current density (j_k) of ORR for Pt, PtNi and PtFe alloy particle samples.

Figure 8 shows j_k of ORR for Pt, PtNi and PtFe alloy particle samples, respectively. Although the electrocatalytic activity of Pt, j_k (Pt), are almost constant from 25°C to 120°C, that of PtNi as well as PtFe increased with the temperature. The difference at the room temperature is almost identical to the previous reports ⁽¹⁴⁾. It is quite interesting that the activity of PtFe alloy increased dramatically when the temperature is above 100°C. At 120°C, the activity of PtFe alloy particle, j_k (PtFe) is about 10 times larger than that of Pt particle although the overpotential is almost the same among three alloy samples. The results are summarized in table 2.

Table 2
The activity of Pt and Pt-alloy particles from j_k .

	Pt	PtNi	PtFe
25C	1	1.4	2.1
120C	1	3.9	9.7

Figure 9 shows Tafel plots for ORR of Pt, PtNi and PtFe alloy samples at 120°C, respectively. Tafel region in the potential from 0.5 V to 0.7 V is in agreement with the previous studies and those potential regions are important from the viewpoint of the practical PEFC. It is widely accepted that predominant electron transfer path at rate determining step (rds) of ORR is a one electron transfer process to form Pt-HO₂ (super hydroperoxides) as described in step 2 in the following reaction schemes.



Tafel slope of ca. -0.12 V/decade indicates the above rate determining step is predominant in the ORR at Pt surfaces. In the fig. 9, the Tafel slopes among Pt, PtNi and PtFe are almost the same, which indicates the rate determining step itself is not changed by alloying. At temperature above 100 °C, PtFe and PtNi were found to have faster electron transfer rate than Pt on the surfaces if the same reaction mechanism are working.

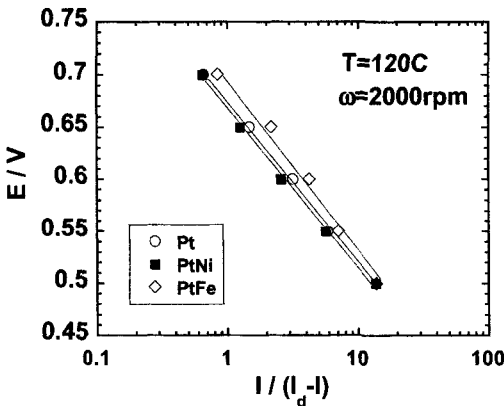


Figure 9
Tafel plots for ORR of Pt, PtNi and PtFe alloy samples at 120°C.

4.SUMMARY

Temperature dependence of electrocatalytic properties have been investigated for Pt and Pt alloys particles by high pressure type RDE measurements. Oxygen reduction reaction (ORR) at temperature range from 25°C to 120°C have been studied by cyclic voltammograms (CV) as well as hydrodynamic polarization curves of those particle samples. The electrochemical properties can be measured above the boiling point of water in the present experiment. Pt alloy powders of PtFe and PtNi show superior electrocatalytic properties than that of pure Pt; for example, the kinetically controlled current density of ORR of PtFe is about 10 times larger than that of pure Pt at 120°C. The present results indicate an importance of the electrochemical characterization of Pt alloys particles at elevated temperatures when the electrocatalytic materials are designed to be used as electrodes at higher operations. A higher temperature operation above 100°C has recently been recognized as a technological option for advanced PEFC.

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