Chlorine Evolution Reaction on Amorphous Palladium-Phosphorus Alloys Containing Iridium, Rhodium or Platinum

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The mechanism of a chlorine evolution reaction on amorphous palladium-phosphorus alloys containing iridium, rhodium or platinum in a hot concentrated sodium chloride solution was studied. The chlorine evolution reaction on all the amorphous palladium-phosphorus alloys examined seemed to proceed by the discharge-electrochemical desorption mechanism in which the electrochemical desorption was the rate determining step. An X-ray photoelectron spectroscopic study revealed that the chlorine evolution occurred on the passive film in which iridium, rhodium or platinum cations were significantly concentrated. The corrosion resistance during the chlorine evolution was due to the formation of these passive films. The electrocatalytic activity of amorphous iridium-containing alloys was higher than other amorphous alloys containing rhodium or platinum, and hence the rate of the chlorine evolution reaction was dependent on these cations of the platinum group metals contained in the passive film. Furthermore, high total concentrations of cations of the platinum-group metals in the passive film were effective for chlorine evolution. This fact indicates that active sites for the chlorine evolution was platinum group cations in the passive film. In addition, the passive film containing a small amount of palladium ions and major cations of another platinum group metal formed on amorphous alloys was more effective for the chlorine evolution than the passive film formed on single metals of the platinum group. This was attributed to high concentrations of effective platinum group cations in the passive film formed on the amorphous alloys and possibly to a synergistic effect of mixing of palladium ion with other platinum group cations.

1 Introduction

The anode for electrolysis of sodium chloride solution is required to have a high electrocatalytic activity for chlorine evolution and a low activity for parasitic oxygen evolution along with resistance to corrosion in the extremely aggressive chloride-containing environment of a high oxidizing power. Although the anodic characteristics of platinum group metals in sodium chloride solutions have been extensively studied^{1~9)}, these metals have not been used in the chlor-alkali industry because none of them possesses both the electrocatalytic activity and corrosion resistance for the chlorine evolution in hot concentrated sodium chloride solutions.

The present authors^{10~12)} recently attempted

to prepare amorphous palladium-base alloys possessing both the high corrosion resistance and high electrocatalytic activity for the chlorine evolution in hot concentrated sodium chloride solutions. It has become apparent from these attempts that amorphous ternary palladium-phosphorus alloys containing sufficient amounts of rhodium, iridium or platinum possess a high corrosion resistance under the conditions for evolution of a good deal of chlorine^{11~13)}. Among them amorphous palladium-iridium-phosphorus alloys showed particularly high electrocatalytic activity for chlorine evolution and a low activity for oxygen evolution, which could not be observed in the crystalline platinum group metals^{11,12)}.

Their activity for chlorine evolution and corrosion resistance are dependent upon the nature of the passive film since the chlorine evolution takes place on the film. Actually it was confirmed our X-ray photoelectron spec-

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troscopic studies^{14,15)} that the electrocatalytic properties of crystalline platinum group metals and amorphous palladium-titanium-phosphorus alloys for chlorine evolution correlated with the composition of the surface film.

The present work was undertaken to determine the mechanism of a chlorine reaction on amorphous palladium-phosphorus alloys containing iridium, rhodium or platinum in connection with the composition and thickness of the surface film formed on the amorphous alloys which were examined by means of X-ray photoelectron spectroscopy.

2 Experimental

2.1 Preparation of specimens

Palladium-base alloy ingots were prepared as follows: After prescribed amounts of palladium chips and red phosphorus were vacuum-sealed in a quartz ampoule so as to put palladium chips on red phosphorus, the reaction of phosphorus with palladium was carried out overnight at 400°C and then the temperature was gradually raised to melt the palladium phosphide for homogenization. After the palladium phosphide was melted with various amounts of iridium, rhodium, platinum and/or titanium under an argon atmosphere, the alloy ingots were prepared by sucking up the melt into a quartz tube and subsequent water-quenching. After the ingot was remelted in a quartz tube under an argon atmosphere, a jet of the molten alloy was impinged by pressurized argon gas onto the outer surface of a rapidly rotating wheel. By this method, amorphous alloy ribbons of 0.6~1.5 mm width and 10~30 μ m thickness were prepared. The nominal compositions of amorphous alloys prepared are shown in Table 1. Crystalline iridium, rhodium and platinum metal sheets of about 1.0 mm width and 0.1~0.5 mm thickness were also prepared for comparison. Prior to electrochemical measurements, the amorphous alloy ribbons and metal sheets were polished with energy paper to No. 1000,

Table 1 Potential ranges of Tafel relation and values of Tafel slopes for various amorphous palladium alloys and platinum group metals. They were estimated from galvanostatic anodic polarization curves measured in 4 M NaCl solution of pH 4 and 80°C

Electrode	Range (V vs. SCE)	Tafel slope (V/decade)
Amorphous Alloy		
Pd ₄₁ Ir ₄₀ P ₁₉	<1.10	0.045
Pd ₃₉ Ir ₄₀ Ti ₁₂ P ₁₉	<1.10	0.048
Pd ₄₆ Ir ₃₀ Ti ₁₃ P ₁₉	<1.10	0.045
Pd ₄₁ Ir ₃₀ Ti ₁₀ P ₁₉	<1.10	0.045
Pd ₆₁ Rh ₂₀ P ₁₉	<1.10	0.050
Pd ₅₆ Rh ₂₅ P ₁₉	<1.10	0.048
Pd ₅₁ Rh ₃₀ P ₁₉	<1.10	0.050
Pd ₅₄ Rh ₂₅ Ti ₁₂ P ₁₉	<1.10	0.050
Pd ₅₁ Rh ₂₅ Ti ₁₃ P ₁₉	<1.11	0.050
Pd ₄₆ Rh ₂₅ Ti ₁₀ P ₁₉	<1.11	0.050
Pd ₄₁ Rh ₂₅ Ti ₁₃ P ₁₉	<1.11	0.052
Pd ₅₁ Pt ₃₀ P ₁₉	<1.10	0.050
Pd ₄₁ Pt ₄₀ P ₁₉	<1.10	0.050
Pure platinum group metal		
Ir	<1.10	0.050
Rh	<1.10	0.070
Pt	<1.10	0.050

degreased ultrasonically in acetone, and finally dried in air.

2.2 Anodic polarization measurements

Anodic polarization measurements were carried out galvanostatically by polarization for 300 sec at each current density for investigation of the gas evolution mechanism on alloys. The ohmic drop was corrected by the interrupter method. A 4 M NaCl solution of pH 4 was used as an electrolyte, whose pH was adjusted by the addition of 4 M HCl. The solutions were prepared by using reagent grade chemicals and de-ionized water. During measurements, the electrolyte was open to air and kept at 80°C. An H-shaped electrolytic cell was used, in which anode and cathode compartments were separated by an asbestos diaphragm. The solution filled in each compartment was about 1.5×10^{-4} m³. A platinum gauze and a saturated calomel electrode were used as counter and reference electrodes, respectively.

2.3 Measurements of X-ray photoelectron spectra

After the amorphous alloy and platinum group metal specimens were polarized potentiostatically for 3600 sec at a potential in the gas evolution region in the 4 M NaCl solution of pH 4 and 80°C, they were rinsed with de-ionized water and placed in a vacuum system of an AEI ES 200 X-ray photoelectron spectrometer. X-ray photoelectron spectra of the specimens were measured with the $MgK\alpha_{1,2}$ excitation at a constant temperature of 50°C. The composition and thickness of the surface film were determined from the integrated intensities of the spectral peaks. The detailed procedure of the energy calibration and the quantitative determination have been reported previously¹⁶⁻¹⁸. It was assumed for the determination that the thickness of the surface film was uniform and all constituents of the surface film distributed homogeneously through the film, the surface of which was covered by a uniform contaminant hydrocarbon layer. Ratios of photo-ionization cross-

Fig. 1 Galvanostatic anodic polarization curves of amorphous Pd-P alloys containing Ir, Rh or Pt measured in 4 M NaCl solution of pH 4 and 80°C

Fig. 2 Correlation between logarithmic current density after polarization for 3600 sec at 1.10 V (vs. SCE) and logarithmic concentration of chloride ion in the solution

sections of elements relative to that of 01s electrons, which were used for the quantitative determination, have been summarized elsewhere^{14,15}.

3 Results and Discussion

3.1 Mechanism of chlorine evolution reaction

Figure 1 shows galvanostatic anodic polarization curves for amorphous $Pd_{41}Ir_{40}P_{19}$, $Pd_{51}Rh_{30}P_{19}$ and $Pd_{41}Pt_{40}P_{19}$ alloys measured in a 4 M NaCl solution of pH 4 and 80°C. A sharp increase in current density in the potential region higher than about 1.0 V (vs. SCE) corresponds mostly to chlorine evolution on the alloy specimens because they have a low activity for competitive oxygen evolution and a high corrosion resistance¹¹. A linear increase in logarithmic current density with polarization potential (Tafel relation) appears up to about 1.1 V (vs. SCE). At still high potentials the current density deviates from the Tafel relation and is not increased linearly with the potential. This is due to a change in composition and property of the surface film or an increase in amount of chlo-

Table 2 Rate equations and related kinetic parameters for anodic chlorine evolution reactions

Reactions	Rate-determining step	Rate equation	Tafel slope $b = (\partial E / \partial \log i)_{\text{Cl}^-}$	Reaction order with Cl^- $(\partial \log i / \partial \log [\text{Cl}^-])_E$
Volmer-Tafel	Volmer	$i/F = k_1 [\text{Cl}^-] \exp (FE/2 RT)$	$2.303 \cdot 2 RT/F$ (0.140 V/decade)*	1
	Tafel	$i/F = (k_1/k_{-1}) k_2 [\text{Cl}^-]^2 \exp (2 FE/RT)$	$2.303 \cdot RT/2 F$ (0.035 V/decade)*	2
Volmer-Heyrovsky	Volmer	$i/F = k_1 [\text{Cl}^-] \exp (FE/2 RT)$	$2.303 \cdot 2 RT/F$ (0.140 V/decade)*	1
	Heyrovsky	$i/F (k_1/k_{-1}) k_3 [\text{Cl}^-]^2 \exp (3 FE/3 RT)$	$2.303 \cdot 2 RT/3 F$ (0.047 V/decade)*	2

*at 80°C

rine molecules adsorbed on the surface film with increasing potential as will be reported subsequently¹⁹⁾.

The potential ranges where the Tafel relation was observed are summarized in Table 1 along with the Tafel slope of polarization curve, $b = (\partial E / \partial \log i)$, for amorphous palladium phosphorus alloys containing iridium, rhodium, platinum and/or titanium. Table 1 also includes data of crystalline platinum group metals for comparison. The Tafel slope of the amorphous alloys and platinum-group metals for the chlorine evolution reaction is in the range of 0.045~0.050 V/decade except that of rhodium metal. Since the temperature is 80°C, the Tafel slope, b , can be represented by

$$b \approx 2.303(2 RT/3 F) \quad (1)$$

where R is the gas constant and F is the Faraday constant.

The change in chlorine evolution rate on amorphous palladium alloys with the concentration of chloride ion in the solution was examined in order to reveal the mechanism of the chlorine evolution reaction. Figure 2 shows the relation between the logarithmic current density of typical amorphous alloys after polarization for 3600 sec at 1.10 V (*vs.* SCE) and the logarithmic concentration of chloride ion. A linear relationship between them is detected for each amorphous alloy. The slopes for amorphous $\text{Pd}_{41}\text{Ir}_{40}\text{P}_{19}$, $\text{Pd}_{41}\text{Pt}_{40}\text{P}_{19}$ and $\text{Pd}_{51}\text{Rh}_{30}\text{P}_{19}$ alloy were 2.12, 1.96 and 1.75, respectively. Accordingly, the slopes were nearly 2, and hence

$$(\partial \log i / \partial \log [\text{Cl}^-])_E \approx 2 \quad (2)$$

where $[\text{Cl}^-]$ is the concentration of chloride ion.

A linear increase in logarithmic current density with the logarithmic concentration of chloride ion was also observed for other amorphous palladium-base alloys containing iridium, rhodium, platinum and/or titanium, and the slopes were about 2. The reaction rate of the chlorine evolution on the amorphous palladium-base alloys, which is independent of the chemical composition of the amorphous alloys, may be expressed by using Eqs. 1 and 2 as:

$$i/F \approx k [\text{Cl}^-]^2 \exp (3 FE/2 RT) \quad (3)$$

where k is the apparent rate constant for the chlorine evolution reaction.

The chlorine evolution mechanism on noble metals^{5,7)}, their oxides^{20~23)} and graphite^{24,25)} have been studied, and the following two mechanisms have been proposed:

I. Volmer-Tafel mechanism

II. Volmer-Heyrovsky mechanism

The reaction rate equation for the chlorine evolution was estimated similarly to that for a hydrogen evolution²⁶⁾ on the basis of the following assumptions: The surface coverage of adsorbed chlorine involved in the chlorine evolution reaction is much less than unity; the Langmuire adsorption isotherm can be applied for the low coverage of adsorbed chlorine; the

Table 3 Current densities of various amorphous palladium-phosphorus alloys and crystalline platinum group metals after polarization for 3600 sec at 1.10 V (*vs.* SCE) in 4 M NaCl solution of pH 4 and 80°C, and film thicknesses, cationic fractions, average valence of cations and ratio of number of platinum group cations to the sum of number of oxygen atom and chloride ion in passive films formed on the alloys by the polarization

Electrode	Current density A/m ²	Passive film analyzed by XPS					
		Film thickness nm	Cationic fraction			Average valence of cations	[Pt group cations]
							[O]+[Cl ⁻]
Pd-Ir-P alloy			Pd	Ir	Ti		
Pd ₄₁ Ir ₄₀ P ₁₉	290	6.16	0.026	0.974	—	3.23	0.138
Pd ₃₉ Ir ₄₀ Ti ₂ P ₁₉	200	3.34	0.021	0.971	0.008	3.15	0.158
Pd ₄₆ Ir ₃₀ Ti ₅ P ₁₉	300	3.11	0.016	0.959	0.026	3.25	0.139
Pd ₄₁ Ir ₃₀ Ti ₁₀ P ₁₉	290	4.59	0.025	0.860	0.115	3.22	0.132
Iridium metal	67	2.00	—	1	—	3.32	0.099
Pd-Rh-P alloy			Pd	Rh	Ti		
Pd ₈₁ Rh ₂₀ P ₁₉	22	2.37	0.081	0.919	—	3.54	0.116
Pd ₃₈ Rh ₂₅ P ₁₉	30	2.61	0.119	0.881	—	3.57	0.193
Pd ₅₁ Rh ₃₀ P ₁₉	31	2.25	0.084	0.916	—	3.46	0.269
Pd ₅₄ Rh ₂₅ Ti ₂ P ₁₉	30	2.36	0.159	0.807	0.034	3.46	0.156
Pd ₅₁ Rh ₂₅ Ti ₅ P ₁₉	22	2.20	0.070	0.738	0.192	3.43	0.112
Pd ₄₆ Rh ₂₅ Ti ₁₀ P ₁₉	18	2.36	0.053	0.557	0.390	3.58	0.087
Pd ₄₁ Rh ₂₅ Ti ₁₅ P ₁₉	15	2.25	0.077	0.437	0.487	3.55	0.072
Rhodium metal	8	3.08	—	1	—	3.00	0.102
Pd-Pt-P alloy			Pd	Pt			
Pd ₅₁ Pt ₃₀ P ₁₉	36	2.33	0.182	0.818		2.88	0.139
Pd ₄₁ Pt ₄₀ P ₁₉	20	2.13	0.151	0.849		2.39	0.120
Platinum metal	40	1.19	—	—		2.39	0.219

rate is determined by one of the two consecutive reactions of (4) and (5) or (4) and (6) and another elementary reaction is in equilibrium; and a symmetry factors is 0.5. Table 2 shows the rate equations of chlorine evolutions for individual mechanisms and related kinetic parameters. In the reaction rate equations, k_1 and k_{-1} are the specific rate constants for the forward and reverse reactions in the discharge reaction, and k_2 and k_3 are specific rate constants for forward reactions in the recombination and the electrochemical desorption, respectively. The reaction rate of the chlorine evolution on the amorphous palladium-base alloys in the potential region lower than 1.10 V (*vs.* SCE) in the hot concentrated NaCl solution was expressed by Eq. 3, and hence the reaction seemed to occur by the discharge-electrochemical desorption mechanism in which the latter is the rate determining step. From the Tafel slope

shown in Table 1, the same mechanism is presumed for the chlorine evolution on platinum group metals. Tilak⁸⁾ reported that the slopes, b , for the chlorine evolution reaction on iridium and rhodium metals in 5 M NaCl solution of pH 3.5 and 95°C were 0.046 and 0.054 V/decade, respectively, and suggested that the chlorine evolution reaction took place possibly due to the same mechanism as that found in the present work for the amorphous palladium-base alloys.

3.2 Chlorine evolution reaction and surface film

The rate equation for the chlorine evolution reaction on the amorphous palladium-base alloys examined was written by Eq. 3 regardless of alloy composition. Nevertheless the activity for the chlorine evolution was dependent upon the alloy composition. Accordingly, the surface films on which the chlorine evolution took place were analyzed by means of the X-ray photoelectron

spectroscopy.

X-ray photoelectron spectra were measured after potentiostatic polarization for 3600 sec in the gas evolution region. The spectra measured over the wide binding energy region indicated the existence of platinum group metals, phosphorus, oxygen, chlorine and carbon in the specimen surface. Titanium was also detected from the titanium-bearing alloys. The C 1s spectrum found arose from a contaminant hydrocarbon layer covering the specimen surface¹⁷⁾. Spectra of core electron levels of the platinum group metals such as Pd 3d_{5/2}, Rh 3d_{5/2}, Pt 4f_{7/2} and Ir 4f_{7/2} electron levels were all composed of three peaks of different valence states. The binding energies of these levels for each valence state were¹⁵⁾:

335.3, 336.8 and 337.6 eV
for Pd ⁰ , Pd ²⁺ and Pd ⁴⁺
307.9, 308.5 and 309.7 eV
for Rh ⁰ , Rh ³⁺ and Rh ⁴⁺ ,
71.2, 72.2 and 74.8 eV
for Pt ⁰ , Pt ²⁺ and Pt ⁴⁺ , and
61.0, 62.0 and 63.7 eV
for Ir ⁰ , Ir ³⁺ and Ir ⁴⁺ ,

where the superscript 0 denoted the metallic state. The Ti 2p_{3/2} spectrum consisted of two peaks at about 454.7 and 459.0 eV corresponding to Ti⁰ and Ti⁴⁺ states, respectively¹⁵⁾. The P 2p spectrum was also composed of two peaks at about 130.0 and 133.3 eV caused by the P⁰ state and the P⁵⁺ state in PO₄³⁻²⁷⁾. The O 1s spectrum consisted of a main peak at about 532 eV corresponding to oxygen in metal-OH and metal-OH₂ bonds (OH oxygen; OH⁻ and H₂O) and a low binding energy shoulder at about 530 eV from oxygen in metal-O-metal bond (OM oxygen; O²⁻)¹⁷⁾. Oxygen constituting PO₄³⁻ was also contained in OH oxygen²⁸⁾. The Cl 2p_{3/2} and 2p_{1/2} spectra were not completely separated, and the Cl 2p spectrum measured was composed of four peaks indicating presence of two kinds of chlorine species. The main Cl 2p_{3/2} peak at 198.2 eV was assigned

to Cl⁻ and a high binding energy shoulder of Cl 2p_{3/2} at about 200.2 eV arose from Cl⁰ which was covalently bonded or not ionized¹⁵⁾. Consequently, the X-ray photoelectron spectroscopy revealed that the chlorine evolution occurred on the surface film consisting of cations of the platinum group metals, Ti⁴⁺, Cl⁻, Cl⁰, PO₄³⁻, O²⁻, OH⁻ and H₂O, the thickness of the film being several nanometers since the metallic signals from the substrate alloy such as Pd⁰ 3d, Rh⁰ 3d, Ir⁰ 3d and/or Pt⁰ 3d were always observed on the X-ray photoelectron spectra.

As shown above, cations of each platinum group metal were a mixture of two kinds of cations of different valences. Under the assumption of homogeneous distribution of these cations in the surface film, the cationic ratio of these two species of each platinum group metal is equal to the ratio of integrated intensities of their X-ray photoelectron spectra.

Fig. 3 Correlation between current density and ratio of number of platinum group cations to the sum of numbers of oxygen atom and chloride ion in the surface film after polarization at 1.10 V (*vs.* SCE) for 3600 sec in 4 M NaCl solution at pH 4 and 80°C

1: Pd₄₁Ir₄₀P₁₉, 2: Pd₃₉Ir₄₀Ti₂P₁₉, 3: Pd₄₃Ir₃₀Ti₅P₁₉,
4: Pd₄₁Ir₃₀Ti₁₀P₁₉, 5: Pure Ir
a: Pd₅₁Rh₂₀P₁₉, b: Pd₅₀Rh₃₅P₁₉, c: Pd₅₁Rh₃₀P₁₉,
d: Pd₅₄Rh₂₅Ti₂P₁₉, e: Pd₅₁Rh₂₅Ti₅P₁₉, f: Pd₄₆Rh₂₅
Ti₁₀P₁₉, g: Pd₄₁Rh₂₅Ti₁₅P₁₉, h: Pure Rh
A: Pd₅₁Pt₃₀P₁₉, B: Pd₄₁Pt₄₀P₁₉, C: Pure Pt

After integrating the 3d or 4f spectrum corresponding to the individual valence states, we estimated the relative amounts of platinum group metal cations in the surface film and hence their average valence.

After integration of all the spectra obtained from each specimen, the composition and thickness of the surface film were quantitatively determined. Some of the analytical results are shown in Table 3 for the surface films formed on the amorphous palladium-base alloys and platinum-group metals after polarization for 3600 sec at 1.10 V (*vs.* SCE) in the 4 M NaCl solution of pH 4 and 80°C.

The current density after polarization for 3600 sec at 1.10 V (*vs.* SCE) is also included in the table. As described previously, the rate equation of the chlorine evolution reaction is independent of the chemical composition of amorphous alloys and is expressed by Eq. 3. Hence, the change in reaction rate with the alloy composition is attributable to the change in the apparent rate constant, k , in Eq. 3 when the concentration of chloride ion in the solution and the polarization potential are constant. In this connection, the current densities of amorphous iridium-bearing alloys are higher than those of amorphous alloys containing rhodium or platinum. This is consistent with the fact that the current density of iridium metal is higher than that of rhodium or platinum metal. Thus the reaction rate of the chlorine evolution on the amorphous palladium-base alloys is dependent upon the additional platinum group metal.

As can be seen in Table 3, no correlation was observed between the film thickness and reaction rate of chlorine evolution despite the fact that the film thickening sometimes depicts the incomplete protectivity of the passive film and may change the rate of electron exchange reactions on the film. Furthermore, the electrocatalytic activity was not appreciably related to the average valence of cations in the surface

film, although the change in cationic valence in the surface film would generally lead to the change in electronic property of the film.

The concentration of cations of additional platinum group elements in the surface film is significantly higher than that of palladium ion. It was known¹¹⁾ that the corrosion resistance of amorphous palladium-phosphorus alloys during active evolution of chlorine was largely improved by additions of sufficient amounts of iridium, rhodium or platinum. It seems, therefore, reasonable that the addition of sufficient amounts of iridium, rhodium or platinum leads to formation of a iridium-, rhodium- or platinum-enriched passive film which provides high corrosion resistance under the chlorine evolution conditions as well as the change in electrocatalytic activity for the chlorine evolution.

It is interesting to note that the iridium-enriched passive film formed on the amorphous palladium-iridium-phosphorus alloys is more active for the chlorine evolution than the passive film on the crystalline iridium metal since the iridium-containing alloys exhibit higher rates of chlorine evolution than the crystalline iridium metal. The current densities of amorphous palladium-rhodium-phosphorus alloys are also higher than those of the rhodium metal. In this connection, there is a general trend that the current density for the chlorine evolution increases with increasing ratio of the number of cations of the platinum group metals to the sum of oxygen and chlorine ion in the surface film as shown in Fig. 3. This ratio corresponds to the concentration of platinum group cations in the surface film. For instance, this ratio in the surface film on the amorphous palladium-iridium-phosphorus alloys is higher than that on the iridium metal. A nearly linear increase in current density with the concentration of platinum group cations in the surface film is observed for each series of amorphous alloys. This suggests that the active sites for the chlorine evolution on the amorphous palladium-

base alloys are platinum-group cations in the surface film. As described previously, the mechanism of the chlorine evolution reaction is not changed by the change of additional platinum group metal in the amorphous palladium-base alloys. Accordingly the difference in the slope by the change of additional platinum group metals in Fig. 3 suggests the fact that the electrocatalytic activity for the chlorine evolution reaction is dependent upon cations of the additional platinum group metals contained in the surface film. Hence the electrocatalytic activity of cations in the surface film formed on palladium-iridium-phosphorus alloys for the chlorine evolution reaction is higher than that on the amorphous alloys containing rhodium or platinum.

Morita *et al.*²⁹⁾ claimed that a higher electrocatalytic activity for the chlorine evolution on an MnO_2 electrode containing 2 at% palladium than the activity estimated from the PdO electrode is due to the fact that palladium, which dispersed on the MnO_2 surface, serves effectively as active sites for the chlorine evolution reaction and is further activated by mixing of catalysts. Such a synergistic effect of mixing was also observed for the SnO_2 -Pt catalysts^{30, 31)}. In the present work, the iridium-, rhodium- and platinum-enriched passive films formed on the amorphous palladium-base alloys contained a small amount of palladium ion. As reported previously¹¹⁾, the electrocatalytic activity of palladium metal for the chlorine evolution is significantly higher than that of iridium, rhodium or platinum metal. Accordingly, mixing of a small amount of palladium ion with other platinum group cations in the surface film may increase synergistically the electrocatalytic activity of amorphous palladium-base alloys for the chlorine evolution.

4 Conclusions

The mechanism of a chlorine evolution was investigated for amorphous palladium-phospho-

rus alloys containing rhodium, iridium or platinum which are known to possess excellent electrocatalytic activity for chlorine evolution along with great corrosion resistance in hot concentrated sodium chloride solutions. The rate equation was $i/F \approx k[\text{Cl}^-]^2 \exp(3FE/2RT)$, suggesting that the chlorine evolution occurred by the discharge-electrochemical desorption mechanism in which the reaction rate was determined by the electrochemical desorption.

The X-ray photoelectron spectroscopic study revealed that the electrocatalytic activity was different with cations of platinum group metals contained in the passive film, on which the chlorine evolution took place, and increased with increasing total concentrations of cations of platinum group metals in the passive film. In addition, mixing of a small amount of palladium ion with major cations of other platinum group metals in the passive film seemed to be more effective for the chlorine evolution than the passive film containing cations of a single metal of the platinum group.

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会員のページ

第3回夏の学校

電気化学協会関東支部主催の第3回夏の学校は、8月5～7日の3日間温泉の街草津の国立大学共同施設草津セミナーハウスに、50名を越える参加者を迎えて活況のうちに終了した。

今回は“電気化学の新展開”を主テーマとし、冒頭に東工大の井上先生より“新しい電気化学測定法”の特別講演があった。続いて2つの分科会の話題として、職訓大の青柿先生が“電極反応におけるゆらぎの役割”と題して、また山梨大の渡辺先生が“電極の機能設計”と題して講演された。

分科会のテーマは“電極反応解析のフロンティア”で学生による発表に先立ち、東大の渡辺先生より赤外・ラマン分光を用いた in-situ な電極反応解析についての紹介があった。電気分解、光電気化学および電池の3つの分野で計10件の学生発表があったが「主テーマの“電極反応解析”」まで突っ込んだ研究発表は少なく、電極反応の複雑さを痛感するとともに、反応解析手法の学習そして新しい電気化学測定法の開発について、気を新たにする有意義な分科会であった（東大 山形）。

一方、分科会2は“電気化学と機能設計”で農工大の松岡先生から、センサー、電子材料等の設計に果たす電気化学的手法の役割に関する概説／があり、表面処理、新電極材料、固体化学および生物電気化学の4つの分野で計9件の学生発表があった。分科会2は“機能設計”という言葉では言い尽くせない、さまざまな問題が議論された。これらの講演・討論を通じて、各種材料の設計において、電気化学システムの利用が実験室レベルで既に良好な成績を収めている現状や、機能性電極の製作にお

いて、他分野の技術の利用がより一層活発になっている現状が明らかになった（慶応大 村主）。

勉強会の間には、親睦を深めるために懇親会やソフトボールが企画された。懇親会では研究室での苦労話や果ては失敗談まで飛び出し、またソフトボールでは熱い声援（？）が飛び交う中、熱戦が繰り広げられ、気分をリフレッシュさせるよい機会であった。

全体を通して、発表形式に関する問題点等も指摘されたが、私自身としては収穫の多い、また刺激を受けた3日間であったと思う。特に、最終日の総合討論の場において、「若い世代の人達は今までのカラを打ち破り、電気化学を大きく飛躍させねばならない」といった主旨の東工大 大瀧先生の話は印象深かった。

なお、懇親会の席上では来年の学生幹事の選出も行なわれ、今年以上に盛り上がることを期待している。

最後に、企画をして下さった関東支部の先生方、それに運営に尽力された東工大小泉、千葉大菊池、横国大岡田、および分科会の報告を送っていただいた2人の学生幹事の諸氏に感謝します。（横国大 大内）