JOURNAL OF APPLIED ELECTROCHEMISTRY **16** (1986) 565–574

Anodic characteristics of amorphorous palladium-base alloys in sodium chloride solutions

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Received 26 July 1985

The anodic characteristics of a variety of amorphous palladium–base alloys were examined with a view to their use for the production of sodium hypochlorite by electrolysis of dilute sodium chloride solutions at ambient temperature. The corrosion resistance of palladium–metalloid alloys was obtained by alloying with platinum group metals and/or valve metals. Among these alloys, rhodium-containing alloys showed high electrocatalytic activities for chlorine evolution. Surface activation treatment was, however, necessary to obtain sufficiently high activities for chlorine evolution at low overpotentials. Surface-activated amorphous alloys possessed considerably higher current efficiency for chlorine evolution in comparison with currently used anodes.

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1. Introduction

Since the extremely high corrosion resistance of melt-spun amorphous alloys was discovered [1], a variety of further unusual, unique and attractive chemical properties have been found [2]. Amorphous alloys are suitable in preparing materials having specific properties by alloying with complicated compositions because they are chemically homogeneous even though the alloys with the same compositions are solidified without rapid quenching into crystalline multiple phases with poor mechanical properties (low strength and sometimes brittleness).

It is required that the anode for electrolysis of sodium chloride solutions has 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 high oxidizing power. Some of the present authors [3–5] recently attempted to prepare amorphous palladium-base alloys possessing both the high corrosion resistance and the high electrocatalytic activity required for chlorine evolution in hot concentrated sodium chloride solutions similar to the solutions used in the chlor-alkali industry.

On the other hand, in industrial plants using seawater as a coolant, sodium hypochlorite is injected into the coolant at the intake of the cooling system for protection against marine life such as barnacles which decrease cooling efficiency and sometimes clog the system. Sodium hypochlorite is produced by the reaction of chlorine with sodium hydroxide. Both reactants can be produced by electrolysis of seawater on the anode and cathode, respectively, and hence the electrolysis of seawater results in the formation of sodium hypochlorite. It is required that the anode materials have much higher activity for chlorine evolution in seawater in comparison with the activity for chlorine evolution in hot concentrated sodium chloride solutions since the concentration of chloride ion in seawater is only one eighth as high as the solutions used in the chlor-alkali industry. In addition the electrolysis of sea water takes place at ambient temperature. The different conditions encountered in sea water and chlor-alkali cells are summarized in Table 1.

The anodic characteristics of platinum group

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Table 1. Conditions encountered in sea-water and chlor-alkali cells

	Chlor-alkali cells	*Sea-water cells*
Sodium chloride concentration	$\sim 300\,\mathrm{g\,l^{-1}}$	$\sim 30\,\mathrm{g\,l^{-1}}$
Anolyte pH	~2–4	~7–8
Temperature	80–90° C	10–30° C

metals in sodium chloride solutions have been extensively studied [6–9]. Among platinum group single metals, palladium has the highest activity for chlorine evolution and low activity for the oxygen evolution in sodium chloride solutions at ambient temperature, but has a very low corrosion resistance [4]. Other platinum group single metals have either a low activity for chlorine evolution or high activities for both chlorine and oxygen evolutions [4]. Currently used electrodes are generally composed of platinum group metals, alloys or metal oxides and a titanium substrate. Their oxygen overpotentials are not sufficiently high and hence their efficiency for chlorine evolution in dilute sodium chloride solutions at ambient temperature is not always high.

The present work aims to investigate the anodic characteristics of amorphous palladium–metalloid alloys containing ruthenium, rhodium, iridium, platinum and/or valve metals for production of sodium hypochlorite in sodium chloride solutions.

2. Experimental procedure

Alloy ingots were prepared as follows. Prescribed amounts of palladium chips and red phosphorus were vacuum-sealed in a quartz ampoule so that the palladium chips were on the red phosphorus. The reaction of palladium with phosphorus was carried out at 400° C for about a day, and then the temperature was gradually raised to melt the palladium phosphide for homogenization. The palladium phosphide thus prepared was melted with various amounts of palladium, ruthenium, rhodium, iridium, platinum, titanium, zirconium, tantalum and/or silicon under an argon atmosphere, and the alloy ingots were prepared by sucking 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 1 to 5 mm width and 10 to 30 μm thickness were prepared. The nominal compositions of alloys are given in Tables 2 and 3. Prior to electrochemical measurements, the amorphous alloy ribbons were polished in cyclohexane with silicon carbode paper up to No. 1000, degreased ultrasonically in acetone and finally dried in air. Currently used commercial electrodes were also used for comparison.

The enhancement of the electrocatalytic activity of amorphous alloys was carried out by the surface activation treatment [10, 11], which consisted of electrodeposition of zinc on the amorphous alloys, heat treatment at lower temperatures than crystallization temperatures of the amorphous alloys for diffusion of zinc into the alloys and leaching of zinc from the alloys into 6 N KOH at 80° C.

The electrolytes used were 0.5 to 4 N NaCl, solutions open to air at 30 ± 1° C. Anodic polarization curves of specimens were measured potentiodynamically with a potential sweep rate of $2.6\,\mathrm{ks\,V^{-1}}$ without separating the anode and cathode compartments. Corrections for ohmic drop were carried out by the current interruption method. Galvanostatic polarization was performed at 500 to $2000\,\mathrm{A\,m^{-2}}$ in the 0.5 N NaCl solution at 30 ± 1° C and at a ratio of the solution volume to the specimen surface area of 30 to 400 cm in order to determine the current efficiency for chlorine evolution on the alloys at $1000\,\mathrm{coulomb\,l^{-1}}$. Because the anode and cathode compartments were not separated from each other, chlorine formed on the anode partly reacted with sodium hydroxide formed on the cathode with a consequent formation of sodium hypochlorite. Both chlorine and sodium hypochlorite liberates iodine from potassium iodide. Accordingly, after electrolysis an excess of potassium iodide was added to the electrolyte and the amount of chlorine produced was estimated by iodometry using 0.025 N $Na_2S_2O_3$ solution. The end point was confirmed by the decoloration of iodostarch reaction product by

Table 2. Nominal compositions of amorphous Pd–P alloys (at %)

Alloy	*Pd*	*Ru*	*Rh*	*Ir*	*Pt*	*Ti*	*Zr*	*Ta*	*P*	*Si*
Pd–P	81	–	–	–	–	–	–	–	19	–
Pd–Si	81	–	–	–	–	–	–	–	–	19
Pd–Ti–P	79	–	–	–	–	2	–	–	19	–
	65	–	–	–	–	16	–	–	19	–
Pd–Ta–P	71	–	–	–	–	–	–	10	19	–
Pd–Ru–P	71	10	–	–	–	–	–	–	19	–
	61	20	–	–	–	–	–	–	19	–
	51	30	–	–	–	–	–	–	19	–
Pd–Rh–P	71	–	10	–	–	–	–	–	19	–
	66	–	15	–	–	–	–	–	19	–
	61	–	20	–	–	–	–	–	19	–
	56	–	25	–	–	–	–	–	19	–
Pd–Ir–P	61	–	–	20	–	–	–	–	19	–
	51	–	–	30	–	–	–	–	19	–
	41	–	–	40	–	–	–	–	19	–
Pd–Pt–P	61	–	–	–	20	–	–	–	19	–
	41	–	–	–	40	–	–	–	19	–
Pd–30Ir–Ru–P	46	5	–	30	–	–	–	–	19	–
	41	10	–	30	–	–	–	–	19	–
Pd–30Ir–Rh–P	46	–	5	30	–	–	–	–	19	–
	41	–	10	30	–	–	–	–	19	–
Pd–30Ir–Pt–P	46	–	–	30	5	–	–	–	19	–
	41	–	–	30	10	–	–	–	19	–
Pd–30Ir–Ti–P	46	–	–	30	–	5	–	–	19	–
	41	–	–	30	–	10	–	–	19	–
Pd–30Ir–5Ti–Ru–P	45	1	–	30	–	5	–	–	19	–
	44	2	–	30	–	5	–	–	19	–
Pd–30Ir–5Ti–Rh–P	45	–	1	30	–	5	–	–	19	–
	44	–	2	30	–	5	–	–	19	–
Pd-30Ir–5Ti–Pt–P	45	–	–	30	1	5	–	–	19	–
	44	–	–	30	2	5	–	–	19	–

the addition of a small amount of starch near the end point.

3. Results and discussion

3.1. *Effects of various elements*

The corrosion potential of amorphous Pd–19P and Pd–19Si alloys was about −0.12 V (SCE) in 0.5 N NaCl solution and the alloys dissolved rapidly by anodic polarization up to about 1.0 and 0.7 V (SCE), respectively. Since the anodic dissolution current of the Pd–19P alloy was lower than that of the Pd–19Si alloy, an improvement of corrosion resistance of the Pd–19P alloy by alloying additions was carried out.

Alloying with titanium or tantalum ennobled the corrosion potential up to about 0.3 V (SCE), and ternary Pd–P alloys containing these elements exhibited a peak current density of active dissolution at about 0.8 V (SCE). Although these alloys could be passivated by polarization at potentials which were still rather high, they had very low activities for chlorine evolution, which began to occur at about 1.0 V (SCE).

In order to enhance both the corrosion resistance and electrocatalytic activity for chlorine evolution, the second platinum group metals were added to the amorphous Pd–19P alloys. When various amounts of ruthenium were added, the anodic current density for active dissolution was not changed. Although the amorphous Pd–30Ru–19P alloy showed an active–

Table 3. Nominal compositions of amorphous Pd–Rh–metalloid alloys (at %)

Alloy	*Pd*	*Ru*	*Rh*	*Ir*	*Pt*	*Ti*	*Zr*	*Ta*	*P*	*Si*
Pd–Rh–Ta–P	61	–	10	–	–	–	–	10	19	–
	56	–	10	–	–	–	–	15	19	–
	56	–	15	–	–	–	–	10	19	–
Pd–Rh–Ti–P	54	–	25	–	–	2	–	–	19	–
	51	–	25	–	–	5	–	–	19	–
	46	–	25	–	–	10	–	–	19	–
Pd–25Rh–5Ti–Ru–P	46	5	25	–	–	5	–	–	19	–
Pd–25Rh–5Ti–Ir–P	46	–	25	5	–	5	–	–	19	–
Pd–25Rh–5Ti–Pt–P	46	–	25	–	5	5	–	–	19	–
Pd–25Rh–5Ti–Zr–P	46	–	25	–	–	5	5	–	19	–
Pd–25Rh–5Ti–Ta–P	46	–	25	–	–	5	–	5	19	–
Pd–25Rh–P–Si	56	–	25	–	–	–	–	–	10	9
	56	–	25	–	–	–	–	–	5	14
Pd–25Rh–Si	56	–	25	–	–	–	–	–	–	19
Pd–25Rh–10Ti–P–Si	46	–	25	–	–	10	–	–	10	9
Pd–25Rh–5Ti–Ru–P–Si	46	5	25	–	–	5	–	–	10	9
Pd–25Rh–5Ti–Ir–P–Si	46	–	25	5	–	5	–	–	10	9
Pd–25Rh–5Ti–Pt–P–Si	46	–	25	–	5	5	–	–	10	9
Pd–Rh–Pt–Ti–P–Si	64	–	10	–	5	2	–	–	10	9
	59	–	10	–	10	2	–	–	10	9
	59	–	15	–	5	2	–	–	10	9
Pd–Rh–Ru–Pt–Ti–P–Si	59	5	10	–	5	2	–	–	10	9
	49	5	20	–	5	2	–	–	10	9
	59	5	5	–	10	2	–	–	10	9

passive transition, it could not be used as the anode in the sodium chloride solution because of its high corrosion rate.

Fig. 1 shows anodic polarization curves of amorphous Pd–Ir–P alloys measured in the 0.5 N NaCl solution. The alloy containing 20 at % Ir was actively corroded and could not be passivated by anodic polarization. The Pd–30Ir–19P alloy showed active–passive transition and evolved chlorine at potentials higher than about 1.0 V (SCE), but the active dissolution current was considerably high. The alloy containing 40 at % Ir showed a sufficiently low active dissolution current, but its activity for chlorine evolution was not sufficiently high.

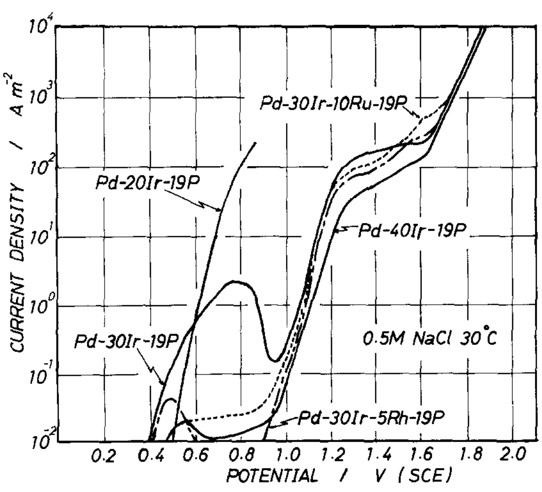

Fig. 1. Anodic polarization curves of various Pd–Ir–P alloys measured in a 0.5 M NaCl solution at 30° C.

Since the Pd–30Ir–19P alloy was more active for chlorine evolution than the Pd–40Ir–19P alloy, enhancement of the corrosion resistance of the Pd–30Ir–19P alloy by alloying was attempted. Additions of ruthenium, rhodium, platinum and/or titanium improved the corrosion resistance. As seen in Fig. 1, the active dissolution current was significantly lowered by the addition of 5 at % Rh or 10 at % Ru to the Pd–30Ir–19P alloy, and their activity for chlorine evolution exceeded the activity of the Pd–40Ir–19P alloy by factors of about 3 or 4.5, respectively, at about 1.2 V (SCE). Although

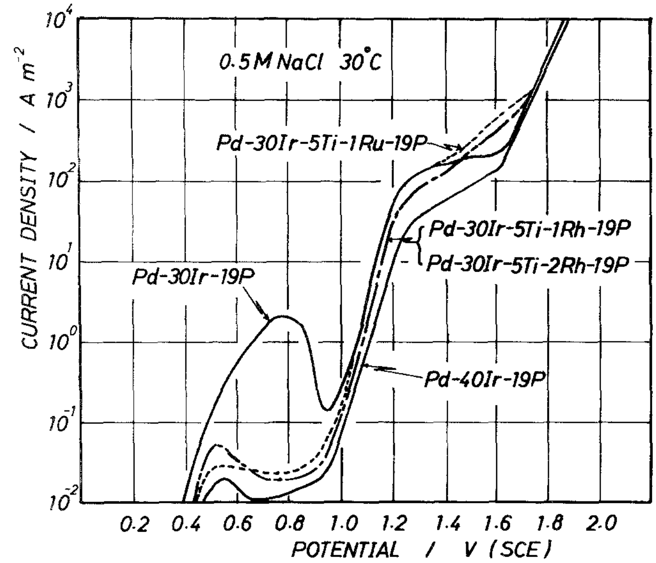

Fig. 2. Anodic polarization curves of various Pd–Ir–P alloys measured in a 0.5 M NaCl solution at 30° C.

their corrosion resistance was still slightly lower in comparison with the Pd–40Ir–19P alloy, it was remarkable that the addition of ruthenium or rhodium was effective in improving the corrosion resistance.

The addition of platinum to amorphous Pd–P and Pd–Ir–P alloys were also quite effective in improving the corrosion resistance. The electrocatalytic activities of these platinum-containing alloys were initially very high but decreased with time of electrolysis. This fact was often observed for platinum metal [12] and platinum-containing alloys [13] and was interpreted in terms of formation of a surface film having a low electronic conductivity due to an increase in the higher valent platinum ion, Pt^{4+} in the film.

On the other hand, the addition of titanium to the amorphous Pd–30Ir–19P alloy effectively decreased the corrosion rate but also decreased considerably the activity for chlorine evolution. Accordingly, an attempt was made to improve the corrosion resistance by the addition of a small amount of ruthenium or rhodium without addition of a large amount of titanium. As shown in Fig 2, a combined addition of titanium and rhodium or titanium and ruthenium was quite effective in decreasing the active dissolution current without appreciably impairing the electrocatalytic activity for chlorine evolution.

In the Pd–Rh–19P alloy family, the alloys containing 20 at % Rh showed active–passive transition. The suppression of active dissolution by a combined addition of rhodium and tantalum was not effective since it became quite difficult to recover a severe decrease in the electrocatalytic activity for chlorine evolution. As shown in Fig 3, the active dissolution current of the amorphous Pd–25Rh–19P alloy was almost identical to that of Pd–40Ir–19P alloy, and hence an improvement of the corrosion resistance of the amorphous Pd–25Rh–19P alloy by alloying was tried. A combined addition of 5 at % titanium and another element of platinum

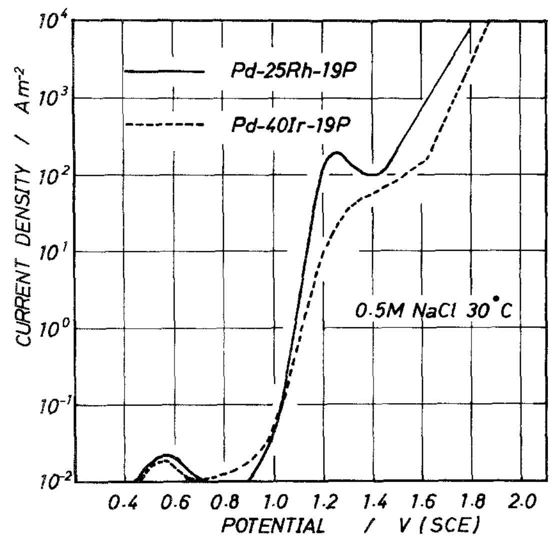

Fig. 3. A comparison of anodic polarization curves between amorphous Pd–25Rh–19P and Pd–40Ir–19P alloys measured in a 0.5 M NaCl solution at 30° C.

group metals or valve metals to the amorphous Pd–25Rh–19P alloy lowered the dissolution current density in the active region to a value lower than $10^{-2}\,\mathrm{A\,m^{-2}}$, although the activity for chlorine evolution was decreased, depending upon the alloying addition.

3.2. *Difference between rhodium and iridium as an alloying element*

It was noteworthy that the activity of the amorphous Pd–25Rh–19P alloy for chlorine evolution at about 1.2 V (SCE) was almost an order of magnitude higher than that of the amorphous Pd–40Ir–19P alloy as shown in Fig. 3. This was in contrast to the fact that the activity of the amorphous Pd–40Ir–19P alloy for chlorine evolution in a 4 N NaCl solution of pH 4 and 80° C exceeded that of the amorphous Pd–Rh–19P alloys containing 20 at % or more rhodium at least by a factor of 6 [4]. The differences in conditions between previous and present experiments were the concentration, temperature and pH of the solution and the absence of separation between anode and cathode compartments in the present experiment.

Fig. 4 shows the effect of the concentration of sodium chloride on the chlorine evolution current on the amorphous Pd–25Rh–19P alloy. The equilibrium potential for the chlorine evolution reaction ennobles by about 30 mV with an order of magnitude decrease in the concentration of chloride ion. Accordingly, the polarization curve shifted in the noble direction with decreasing concentration of sodium chloride but an appreciable change in the Tafel relation was not observed. In contrast, as shown in Fig. 5, an apparent Tafel slope of the polarization curve of the amorphous Pd–40Ir–19P alloy for chlorine evolution increased with decreasing concentration of sodium chloride, and hence the electrocatalytic activity of the Pd–40Ir–19P alloy significantly decreased with decreasing concentration of sodium chloride. It is difficult to interpret the gradual change in the mechanism of chlorine evolution with change in the concentration of sodium chloride and this may be due to the change in the nature of the surface film on which the chlorine evolution takes place.

In previous experiments [4] the electrolysis of 4 N NaCl solution of pH 4 at 80° C was carried out by using an electrolytic cell in which anode

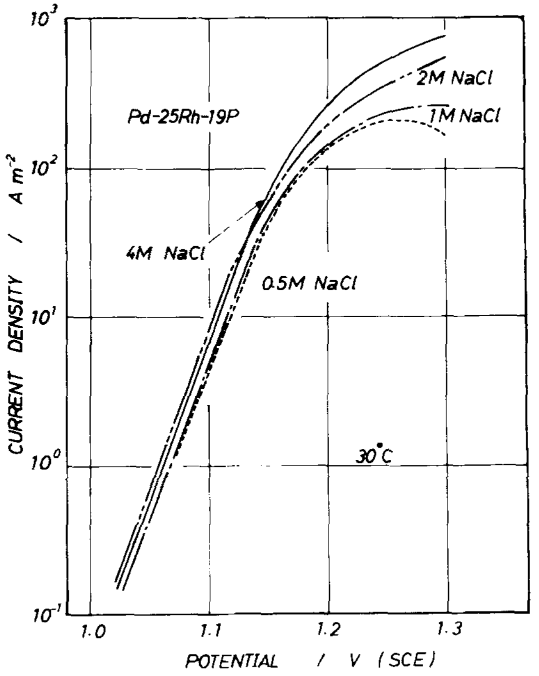

Fig. 4. Change in anodic polarization curve of an amorphous Pd–25Rh–19P alloy as a function of concentration of sodium chloride in electrolytes at 30° C.

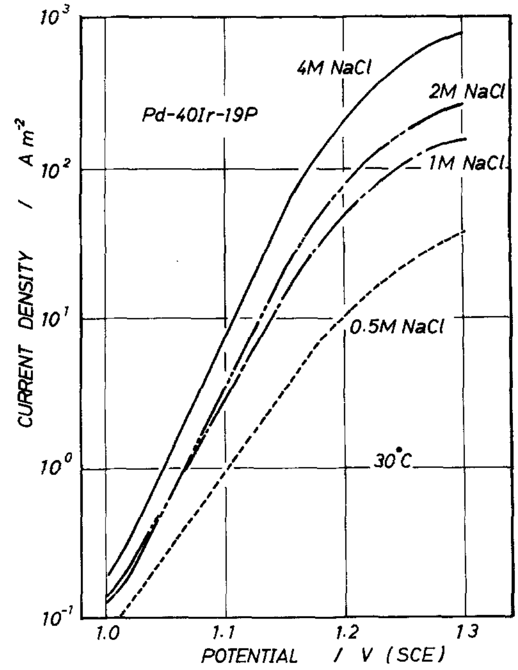

Fig. 5. Change in anodic polarization curve of an amorphous Pd–40Ir–19P alloy as a function of concentration of sodium chloride in electrolytes at 30° C.

and cathode compartments were separated by a diaphragm. Under these conditions the lower activity of the amorphous rhodium-containing alloys for chlorine evolution than that of the iridium-containing alloys was mainly due to the difficulty of the release of the final product, that is, adsorbed molecular chlorine from the rhodium-containing alloy electrode [13] and rhodium metal electrode [12]. In the present experiment anode and cathode compartments were not separated from each other and the solution was neutral. It seems, therefore, easy to release the final product, molecular chlorine, from the anode, because chlorine molecules are able to react with sodium hydroxide formed on the cathode with a consequent formation of sodium hypochlorite. Consequently rhodium-containing alloys have good activity as chlorine evolution electrodes in sodium chloride solutions in which both the anode and cathode are immersed without separation.

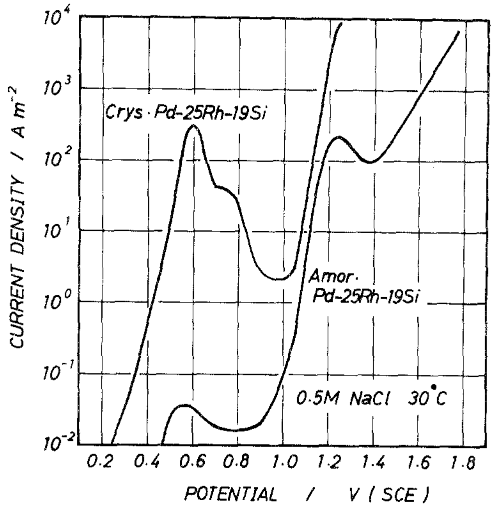

Fig. 6. A comparison of anodic polarization curves of amorphous and crystalline Pd–25Rh–19Si alloys measured in a 0.5 M NaCl solution at 30° C.

Since the activity of the rhodium-containing alloy was more than an order of magnitude higher than that of the iridium-containing alloy at about 1.2 V (SCE), further investigations were performed by using alloys whose corrosion resistance was provided mainly not by iridium addition but by the rhodium addition.

3.3. *Effect of vitrification*

The change in anodic behaviour by vitrification was examined by using an amorphous alloy and the crystalline counterpart before vitrification. Fig. 6 shows the effect of vitrification on the anodic polarization behaviour of Pd–25Rh–19Si alloy. The amorphous Pd–25Rh–19Si alloy showed a low active dissolution current and evolved chlorine gas at potentials higher than about 1.0 V (SCE). In contrast the crystalline counterpart, namely the cast alloy, exhibited a very high active dissolution current, and evolved chlorine gas with dissolution of the alloy at high potentials.

It is well known [14–16] that crystallization of corrosion resistant amorphous alloys results in a significant increase in their corrosion rates due to an introduction of chemical heterogeneity in the alloys which produces active surface sites for corrosion. According to a comparison of the corrosion behaviour of amorphous palladium-base electrode materials with crystalline counterparts in a hot concentrated sodium chloride solution [17], a palladium-rich metallic phase in the crystalline alloy was preferentially corroded during the chlorine evolution.

Consequently, virtrification is required in providing the sufficiently high corrosion resistance necessary for the anode in the electrolysis of sodium chloride solutions.

3.4. *Effects of metalloids*

It is known [18, 19] that the corrosion resistance of amorphous metal–metalloid alloys is greatly affected by metalloids contained in the alloys. Both phosphorus- and silicon-containing palladium-base alloys are vitrified by rapid quenching from the liquid state. Hence the effect of these metalloids on the corrosion resistance and electrocatalytic activity was examined by the change in relative amounts of phosphorous and silicon as shown in Fig. 7. There was no significant difference in both the active dissolution current and electrocatalytic activity for chlorine evolution with change of metalloid. The alloys containing both phosphorus and silicon, however, showed slightly lower active dissolution current and chlorine evolution current in

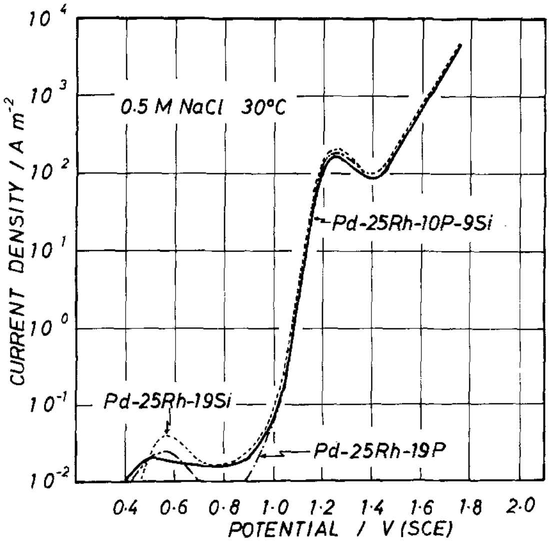

Fig. 7. Effect of metalloids on anodic polarization curves of amorphous Pd–25Rh–metalloid alloys measured in a 0.5 M NaCl solution at 30° C.

comparison with the alloys containing only a single metalloid element.

It is known that the active sites for the chlorine evolution on the amorphous palladium-base alloys containing a second platinum group metal are mainly platinum group cations in the passive film [20] and that the passive film formed on the palladium-base alloys containing rhodium during the chlorine evolution in a hot concentrated sodium chloride solution is composed exclusively of rhodium ion as a cation [13]. Hence, the passive film on which the chlorine evolution took place would be composed mainly of rhodium ion on the amorphous palladium–rhodium–metalloid alloys in sodium chloride solutions at ambient temperature. Since the major cations in the passive film which were responsible for the corrosion resistance were not different with metalloid, a slightly lower anodic current density for the alloy containing both phosphorus and silicon suggested a slightly better corrosion resistance of the alloys.

Accordingly, the palladium–rhodium–metalloid alloys containing both phosphorus and silicon might be superior for a long service life to the alloys containing only a single metalloid element.

3.5. *Surface activation treatment*

The production of sodium hypochlorite by electrolysis of seawater is generally carried out at a current density of about 1000 A m^{-2}. In order to prepare an energy saving corrosion resistant anode which is able to electrolyse seawater at high current densities at low overpotentials, the chlorine evolution current of the palladium–rhodium–metalloid alloys must be increased more than an order of magnitude. A surface activation treatment was, therefore, applied to the alloys. It is known [11] that the electrochemically effective surface area of palladium-base alloys can be increased by about two orders of magnitude by surface activation treatment. If the activity for chlorine evolution is increased sufficiently by surface activation treatment, alloys having a higher corrosion resistance are more suitable for the anode than alloys which do not possess a sufficiently high corrosion resistance but have a high electrocatalytic activity before the surface activation treatment. Accordingly, a surface activation treatment was applied to the highly corrosion resistant alloys containing various metallic elements beneficial in increasing the corrosion resistance.

Fig. 8 shows an example of the change in activity for chlorine evolution as a function of

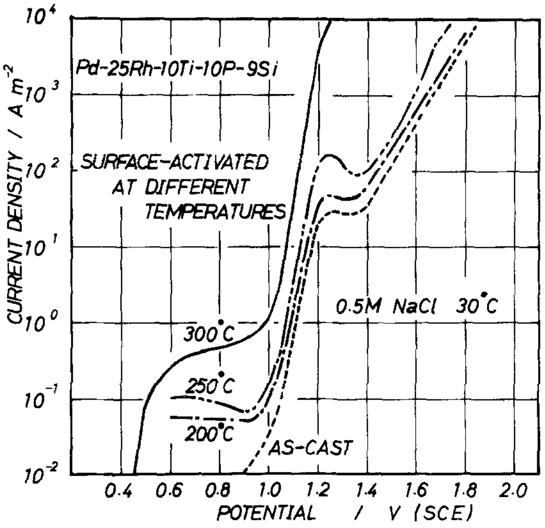

Fig. 8. Change in anodic polarization curve of an amorphous Pd–25Rh–10Ti–10P–9Si alloy measured in a 0.5 M NaCl solution at 30° C as a function of temperature of heat treatment included in the surface activation treatment.

Table 4. Activities for chlorine and oxygen evolutions in solutions at 30° C

Electrode	*Current density at 1.15 V(SCE) ($A\,m^{-2}$)*				
	As-cast	*0.5 M NaCl Surface-activated at*			*0.25 M Na_2SO_4 Surface-activated at 300° C*
		200° C	250° C	300° C	
Amorphous alloy					
Pd–25Rh–10P–9Si	18.0	28.0	200	800	35.0
Pd–25Rh–10Ti–10P–9Si	4.6	9·5	27.0	600	23.0
Pd–25Rh–5Ti–5Ru–10P–9Si	17.0	40.0	50.0	1300	22.0
Pd–25Rh–5Ti–5Pt–10P–9Si	9.0	27.0	45.0	260	22.0
Currently used electrode					
Pt/Ti	–	12.0	–	–	1.4
PdO/Ti	–	250	–	–	36.0
Pt–Ir/Ti	–	750	–	–	64.0

temperature of heat treatment for diffusion of zinc in the surface activation treatment. The activity for chlorine evolution was increased by increasing the temperature for heat treatment, and the alloy treated at 300° C exhibited a sufficiently high chlorine evolution current as the anode for the production of sodium hypochlorite by the electrolysis of seawater.

Table 4 shows the change in the activity of various alloys for the chlorine evolution by the surface activation treatment. Since both chlorine and oxygen were evolved in sodium chloride solutions, the activity of these alloys for oxygen evolution was estimated by using the current density measured in 0.25 M Na_2SO_4 solution at 30° C in which only oxygen was evolved. The activities of amorphous alloys for both chlorine and oxygen evolution were compared with those of currently used anodes in which a titanium substrate was covered by platinum, platinum–iridium or palladium oxide. The activity of as-cast amorphous alloys for chlorine evolution was not high, but the surface-activated amorphous alloys possessed very high activities. On the other hand, the activities of the surface-activated amorphous alloys for oxygen evolution were lower than the activity of the Pt–Ir/Ti anode which is known to have the highest activity among the currently used anodes for the production of sodium hypochlorite.

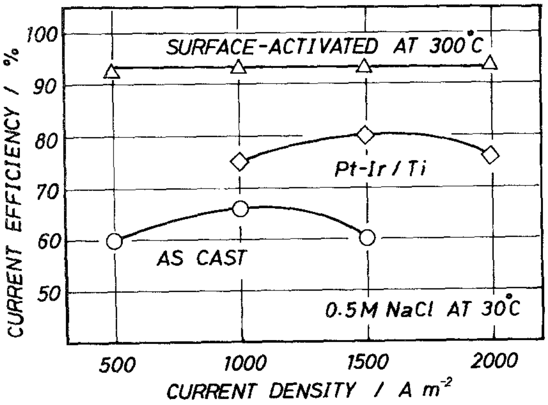

Fig. 9. Current efficiency for chlorine evolution in a 0.5 M NaCl solution at 30° C on surface-activated and unactivated amorphous Pd–25Rh–10P–9Si alloys and a currently used Pt–Ir/Ti anode.

The high current efficiency of the surface-activated amorphous alloy anode for chlorine evolution was confirmed by the analysis of chlorine produced by electrolysis under galvanostatic conditions. Fig. 9 shows an example of a comparison of current efficiency for chlorine production. When galvanostatic polarization was carried out, the overpotential of the anode having a low activity for chlorine evolution became very high and hence a large amount of oxygen was evolved with a consequent low current efficiency for the chlorine evolution. The current efficiency for chlorine evolution on the surface-activated amorphous Pd–25Rh–10P–9Si alloy was 10 to 20% higher than that on the Pt–Ir/Ti anode.

4. Conclusions

Anodic characteristics of amorphous palladium-base alloys for the production of sodium hypochlorite in dilute sodium chloride solutions at 30° C were examined. The following conclusions were drawn:

1. The corrosion resistance necessary for the anode was provided by alloying with a sufficient amount of platinum group metals and/or valve metals.
2. The high electrocatalytic activity for chlorine evolution was maintained when the amorphous palladium–metalloid alloys were further alloyed with rhodium.
3. Surface-activation treatment was necessary to provide a sufficiently high activity for chlorine evolution in dilute sodium chloride solutions at ambient temperature.
4. The surface-activated corrosion resistant amorphous alloys showed significantly higher current efficiency for chlorine evolution in comparison with currently used anodes.

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