Effect of Frequency of Differential Capacities at Various Anodes in Aqueous Acetate or Propionate Solutions

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The interfacial differential capacities at platinum, gold, palladium, lead dioxide, and graphite anodes were measured with an a.c. bridge at different frequencies in aqueous solutions of acetate or propionate. The measured capacity varied almost linearly with the reciprocal of the square root of frequency ($f^{-1/2}$), and at the same time, decreased with the increase of frequency for all the tested anodes in both carboxylate solutions. The resistance also decreased linearly with the increased frequency. The rate constants (k_s 's) of the charge-transfer process of the anodic reaction were calculated from the capacitance data. The value of k_s was smallest, 2.8×10^{-7} cm/sec, at the platinum anode, the greatest value was 4.2×10^{-2} cm/sec at the palladium anode undergoing only the oxygen evolution reaction. It was found that k_s at the anodes tends to increase with increasing frequency and with decreasing carboxylate concentration.

1 Introduction

For the electrolytic oxidation reaction of carboxylate solutions, only a few papers appear to have been reported so far on the basis of the determination of kinetic parameters. Conway *et al.* measured the exchange current density (i_0) in formate solution¹⁾. Their values of i_0 are fairly close to those obtained by the authors in glacial acetic acid²⁾. The exchange current density found in glacial acetic acid is less than 1×10^{-10} A/cm², which is small as compared with the value of i_0 of general reversible electrode processes. This implies that the electrode processes are irreversible in glacial acetic acid and formate solution.

In the present work, the frequency dependence of the differential capacity at the anode interface has been studied with various anode materials in aqueous acetate or propionate solution. From the results of the capacity, resistance and their frequency dependence, the rate constant of charge-transfer process of the elec-

trolytic oxidation was calculated using a theoretical equation of the faradaic impedance. Then, the electrode processes in both carboxylate solutions were discussed on the basis of k_s .

2 Experimental

Measurements of the capacity were carried out by an a.c. bridge similar to that reported in the previous paper³⁾. The test anodes used were platinum, gold, palladium, lead dioxide, and graphite. The pretreatment of the surface of these anodes was the same as that described previously³⁾. The frequency was arbitrarily adjusted to 0.1, 0.5, 1, 5, or 10 KHz by a Tōa-Dempa oscillator model CR-200 J. The capacity, for example, on the platinum anode was measured to a precision of about $\pm 2\%$ at 2.0V with 10 KHz in 5 M acetate concentration. The test solutions were prepared by mixing aqueous solution of acetate*¹ (0.5, 1, 2, 5 M) or propionate*² (0.5, 1, 2 M) and 0.5 M pota-

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*¹ Aqueous solution of the equimolar mixture of acetic acid and potassium acetate.

*² Aqueous solution of the equimolar mixture of propionic acid and potassium propionate.

ssium sulfate supporting electrolyte. All the measurements were carried out at 25°C.

3 Results and Discussion

3.1 Relationship between capacity and frequency

According to the theory of faradaic impedance, the double layer capacity at the anode-electrolyte interface can be obtained from the measured impedance at high frequencies. However, it is usually necessary to plot the capacity against the reciprocal of the square root of frequency, and to extrapolate it to an infinite frequency.

The relationship between the capacity and $f^{-1/2}$ value at 1.3 V and 2.0 V for various anodes in 5 M aqueous potassium acetate solution is shown in Fig. 1. In the case of the platinum anode in aqueous acetate solution, the oxygen evolution was found to begin to

occur at around 1.3 V, and the Kolbe reaction took place simultaneously at 2.0 V, giving the Kolbe products. However, with other anodes, or in the aqueous propionate solution, the same did not occur at the same potential as that observed at the platinum anode in the acetate solution. Potentials of 1.3 V and 2.0 V in Fig. 1 were chosen as the reference potentials for the comparison of the anode materials. Except the case of lead dioxide the measured capacities at both potentials increased almost linearly with $f^{-1/2}$. The capacity value and its dependence on $f^{-1/2}$ at the platinum anode shown in Fig. 1 were the smallest of all the anodes within the frequency range employed. Although the linearity of the capacity vs. $f^{-1/2}$ relation was not good enough for anodes other than platinum to obtain the exact value from the extrapolation to an infinite frequency, we tried to obtain the value at infinite frequency. The obtained values were: 32 $\mu F/cm^2$ at 1.3 V and 21 $\mu F/cm^2$ at 2.0 V at the platinum, 25 $\mu F/cm^2$ at 2.0 V at the palladium, and 31 $\mu F/cm^2$ at 2.0 V at the gold electrodes, respectively.

In the case of a lead dioxide electrode, the capacities at both 1.3 V and 2.0 V show maxima at 5 KHz. At present it is not clear why the maxima appear. Also, the capacity at 1.3 V at the high frequency of 10 KHz on a graphite was found to be 46 $\mu F/cm^2$, which is close to 32 $\mu F/cm^2$ at the platinum. As a comparison, the data obtained by Girina^{(4), (5)} at the platinum anode in acetate solution are also plotted in Fig. 1 as filled circles. These values are extrapolated to an infinite frequency at 1.3 V to obtain 32 $\mu F/cm^2$ which agrees well with those obtained by the authors. The fact that the capacity lowers linearly with increasing frequency has also suggested by Sarmousakis and Prager⁽⁶⁾ at platinum in 1 N aqueous solutions of KCl, KBr, and KI, respectively.

Fig. 2 shows the relationship between the capacity and $f^{-1/2}$ value at various anodes at 1.3 V in 2 M aqueous potassium propionate solution. In this figure, it is clearly seen that the capacity value at any given anode decreases almost linearly with increasing frequency, which is similar to that obtained in acetate solutions. Especially, the capacity on the gold

Fig. 1 Relationship between capacity and frequency at various anodes in 5 M aqueous acetate solution

—○— : Pt, —×— : Au, —△— : Pd, —□— : PbO₂, —◇— : Graphite, —●— : Pt (Girina)

Fig. 2 Relationship between capacity and frequency at various anodes in 2M aqueous propionate solution

—○— : Pt, —×— : Au, —△— : Pd, —□— : PbO₂, —◇— : Graphite

is shown to be the lowest value in the whole frequency range employed. The capacity values extrapolated to an infinite frequency are 8 $\mu\text{F}/\text{cm}^2$ on the gold, 23 $\mu\text{F}/\text{cm}^2$ on the platinum, and 32 $\mu\text{F}/\text{cm}^2$ on the palladium electrodes, respectively. However, extrapolation can not be made for lead dioxide and graphite, because of the fairly steep slope of the line in Fig. 2.

Because of the above mentioned difficulties for obtaining the capacity value at infinite frequency, a conventional value was obtained by extrapolating the plots to 10 KHz, the values for various anodes being summarized in Table 1.

The capacity values 126 $\mu\text{F}/\text{cm}^2$ for gold and 172 $\mu\text{F}/\text{cm}^2$ for lead dioxide in acetate solutions were fairly large, but the other anodes showed the values of about 50 $\mu\text{F}/\text{cm}^2$. These values are in good agreement with those obtained from the capacity current density curves by the authors⁷⁾ who, employing a galvanostatic single pulse method at 10 mA/cm² in 5 M acetate solution, obtained the capacity values as high as 144 $\mu\text{F}/\text{cm}^2$ at gold and lead dioxide, 67 $\mu\text{F}/\text{cm}^2$ at platinum, 58 $\mu\text{F}/\text{cm}^2$ at palladium, and 50 $\mu\text{F}/\text{cm}^2$ at graphite.

The value obtained here appears to be reliable, since two different methods gave nearly the same value. Besides, in propionate solution the capacity at 2.0 V is lower than the one at 1.3 V, and the capacity in propionate solution is also lower than the one in acetate solution. This result is in agreement with the results given in the previous paper⁸⁾, in which a single pulse method was employed. Such differences in the capacity between the two solutions may be related to the fact that the reaction of formation of olefin (ethylene) occurs in propionate solution and it does not occur in acetate solution. The results in the present investigation by an impedance method consequently seems to support the explanation given in the previous paper⁸⁾.

3.2 Relationship between resistance and frequency

Fig. 3 shows an example of plots of resistance (R) against frequency at platinum in acetate solution. The log resistance decreases almost linearly with increasing log frequency. Such a tendency in resistance was also found at the other anodes, or in aqueous propionate solution.

Table 1 Differential capacities in 10 KHz of various anodes ($\mu\text{F}/\text{cm}^2$)

Anode	Acetate				Propionate			
	1.3 V vs. S.C.E.		2.0 V vs. S.C.E.		1.3 V vs. S.C.E.		2.0 V vs. S.C.E.	
	0.5 M	5 M	0.5 M	5 M	0.5 M	2 M	0.5 M	2 M
Pt	35	32	48	23	32	25	12	7
Au	45	126	45	48	17	10	12	6
Pd	45	64	70	38	45	35	—	—
PbO ₂	128	172	104	160	10	20	10	25
Graphite	41	46	—	—	20	10	—	15

Fig. 3 Relationship between resistance and frequency at a platinum anode in aqueous acetate solution

The results of the resistance values at various anodes in both acetate and propionate aqueous solutions are listed for comparison in Table 2. As is evident from this table, the resistance is generally greater in propionate than in acetate solution. In addition, as for the variation of the resistance with carboxylate concentration, the resistance in acetate solution is lowered with increasing concentration, but in propionate solution the reverse is found. Such a tendency in resistance was recognized at each anode used. For example, the resistance at 2.0 V at 10 KHz on the platinum anode in 0.5 M acetate solution is 105 Ω , but it is small as 65 Ω in 5 M. On the other hand, in 0.5 M propionate solution the resistance is 240 Ω , but it becomes greater as 265 Ω in 2 M.

These results might be related to the dissociation constant of fatty acids, which is smaller for propionic acid (1.4×10^{-5}) than acetic acid (1.86×10^{-5}).

3.3 Rate constant

From the above data of the dependences of capacity and resistance on frequency, the rate constant as a kinetic parameter of charge-transfer process was calculated by the theoretical equation of the faradaic impedance^{9),10)}. These values are summarized in Table 3. The k_s values are seen to increase with decreasing carboxylate concentration and also with increasing frequency.

In general, it is probable to analyze the mechanism of the electrode reaction using the character of the faradaic impedance, especially for the case of the highly reversible process. In the electrolytic oxidation reaction of carboxylate solutions, the authors have already reported the irreversibility in the adsorption and desorption processes of hydroxyl ions or carboxyl ions on the anode-solution interface^{12),13)}, the irreversibility being located in the discharge reaction of these ions and the values of i_0 being determined in glacial acetic acid²⁾. Taking these facts into consideration, it is presumed that the k_s values are too small.

The k_s value in the present investigation was 2.8×10^{-7} cm/sec at 2.0 V, 0.1 KHz on a platinum anode in 5 M acetate, which is the smallest, and the value was 4.2×10^{-2} cm/sec at 1.3 V, 5 KHz on a palladium anode in 2 M propionate solution, which is the largest.

These k_s values are close to the i_0 values obtained in glacial acetic acid containing 2% water, as reported in the previous paper²⁾. The i_0 value was 1.5×10^{-13} A/cm² at platinum,

Table 2 Resistances at various anodes (Ω)

Anode	5 M acetate				2 M propionate			
	1.3 V vs. S.C.E.		2.0 V vs. S.C.E.		1.3 V vs. S.C.E.		2.0 V vs. S.C.E.	
	0.1 KHz	10 KHz	0.1 KHz	10 KHz	0.1 KHz	10 KHz	0.1 KHz	10 KHz
Pt	1210	59	1620	65	1583	95	1027	265
Au	203	58	432	155	4860	120	975	90
Pd	994	50	—	—	975	90	—	—
PbO ₂	1625	317	—	—	588	441	—	—
Graphite	139	64	—	—	234	144	—	—

Table 3 Rate constants at various anodes (cm/sec)

Anode	f (KHz)	Acetate				Propionate			
		1.3 V vs. S.C.E.		2.0 V vs. S.C.E.		1.3 V vs. S.C.E.		2.0 V vs. S.C.E.	
		0.5 M	5 M	0.5 M	5 M	0.5 M	2 M	0.5 M	2 M
Pt	0.1	5.2×10^{-6}	4.9×10^{-7}	3.4×10^{-5}	2.8×10^{-7}	2.5×10^{-6}	2.3×10^{-4}	1.3×10^{-4}	2.7×10^{-5}
	5	3.3×10^{-4}	2.8×10^{-5}	3.0×10^{-4}	9.2×10^{-6}	6.2×10^{-5}	7.5×10^{-5}	2.4×10^{-4}	1.8×10^{-5}
Au	0.1	1.3×10^{-5}	2.3×10^{-6}	2.0×10^{-5}	2.8×10^{-6}	2.1×10^{-6}	7.2×10^{-6}	3.4×10^{-4}	—
	5	2.2×10^{-4}	1.9×10^{-5}	3.9×10^{-4}	7.0×10^{-5}	1.4×10^{-5}	1.7×10^{-5}	9.2×10^{-4}	—
Pd	0.1	1.3×10^{-4}	3.8×10^{-6}	—	—	1.7×10^{-3}	8.2×10^{-4}	—	—
	5	4.7×10^{-3}	2.9×10^{-5}	—	—	2.1×10^{-3}	4.2×10^{-2}	—	—
PbO ₂	0.1	4.1×10^{-5}	3.4×10^{-6}	—	—	3.1×10^{-4}	1.6×10^{-4}	1.2×10^{-3}	—
	5	8.1×10^{-5}	1.9×10^{-4}	—	—	3.5×10^{-4}	1.0×10^{-3}	5.3×10^{-4}	2.0×10^{-4}
Graphite	0.1	2.4×10^{-5}	4.4×10^{-6}	—	—	2.5×10^{-4}	2.4×10^{-4}	—	7.1×10^{-4}
	5	2.0×10^{-4}	6.1×10^{-5}	—	—	2.5×10^{-4}	4.5×10^{-5}	1.5×10^{-4}	3.8×10^{-5}

which is relatively small, and 5.3×10^{-8} A/cm² at palladium, which is relatively large, 4.7×10^{-10} at gold, 1.0×10^{-14} at lead dioxide, and 1.4×10^{-11} A/cm² at graphite.

Consequently, these differences in k_s can be explained as follows: When the oxygen evolution due to the discharge of hydroxyl ion is the predominant reaction as is the case of palladium, the effect of carboxylate ion is scarcely discernible. Because of the oxygen evolution reaction proceeded, the k_s value will probably be increased.

However, the k_s value in the case of platinum evolving the Kolbe products will most likely be decreased for the reason that the adsorption and discharge reaction of carboxylate ion is fairly inhibited by hydroxide ion.

4 Summary

- (1) The differential capacities of platinum, gold, palladium, lead dioxide, and graphite anodes in aqueous acetate and propionate solutions were varied almost linearly with $f^{-1/2}$, and decreased with increasing frequency.
- (2) The resistance also decreased linearly with increasing frequency.
- (3) The rate constant ranged from the smallest value 2.8×10^{-7} cm/sec at platinum when the Kolbe reaction occurs to the greatest value 4.2×10^{-2} cm/sec at palla-

dium when only the oxygen evolution reaction takes place.

- (4) It was found that the rate constants tend to increase with increasing frequency and with decreasing carboxylate concentration.

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