Effects of the Cathode Current Density in the Karl Fischer Coulometric Titration Method

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The Karl Fischer(KF) coulometric titration method is currently used extensively since it can easily detect even the presence of trace water. Since the anode reaction determines the accuracy of this analytical method, the composition of anolyte has been investigated in detail in order to increase the current efficiency up to 100%. On the other hand, the cathode reactions have not in detail been studied quantitatively, since they do not participate in the KF reaction. The authors¹ have investigated these reactions using the electrolytes applicable to the KF titration and the electrolytic cell, both of which are now available on the market.

It has generally been considered that if a reducible compound, such as carbon tetrachloride, is present in the catholyte, that compound will undergo reduction; meanwhile, if such a compound is not present, hydrogen gas will be produced and sulfur dioxide will be reduced. These two reactions seem to occur simultaneously.

Nichugovskii^{2,3} detected hydrogen gas generation when the cathode current density was high; however, his observation was not quantitative. At present, an electrolytic cell without a diaphragm, which hitherto existed between the anode and the cathode, and an electrolyte exclusively usable for the cell are obtainable on the market.⁴ However, the cathode reaction should be carefully studied before the cell and the electrolyte are actually put to use.

In the present work the authors investigated the effect of the cathode current density on the cathode reactions as well as the relation between the kinds of electrolytes and the cathode reactions.

Experimental

To study the cathode reactions an electrolytic cell with a diaphragm was used; the same method as that described in a previous paper¹ was applied to analyze the reaction products. The cathode comprised platinum wire. Its surface area was changed, using platinum wires of different diameters and lengths, in order to alter

the cathode current density.

Two analyzers were especially manufactured for the present study. One was a moisture analyzer that was used to carry out pulse electrolysis with a constant electrolytic current of 400 mA; the other was a moisture analyzer that was used to carry out continuous electrolysis, in which the electrolytic current was controlled in proportion to the polarization voltage (maximum electrolytic current: 400 mA).

The electrolytes of various basic compounds were prepared as follows:

Basic compound	1.5 M
Sulfur dioxide	1.0 M
Iodine(as iodide ion)	0.1 M
Propylene carbonate	15% by volume
Solvent	methanol

The basic compounds used were as follows: pyridine, imidazole, diethanolamine, 4-dimethylaminopyridine and 1,3-di(4-pyridyl) propane. To simplify the analysis of the reaction products, the same electrolyte was used in the cathode compartment, as well as that of the anode.

Moreover, an electrolytic cell without a diaphragm was prepared, and its performance confirmed using the electrolytes mentioned above.

Results

Relation between the cathode current density and reactions at the cathode

Using different electrolytes, a series of experiments were carried out in order to obtain a relation between the cathode current density and the proportion of hydrogen gas generation reactions to the total number of cathode reactions. The results are given in Fig. 1.

A moisture analyzer, which applied pulse electrolysis with a constant electrolytic current of 400 mA, was used. Differences were observed which depended on the basic compounds used. Except for the electrolyte containing

pyridine, the proportion of hydrogen gas generation reaction to the total number of cathode reactions was around 100% for all of the electrolytes used, as long as the cathode current density was kept above a certain level. When the electrolyte contained diethanolamine, however, the amount of generated hydrogen could not be measured accurately, because of a decrease in the volume of the catholyte. It could not be understood why the volume of the catholyte decreased only when diethanolamine was used.

When imidazole was used as the basic compound, the hydrogen gas generation remained smaller than 100% when the current density was less than about 1 A/cm². Moreover, when the current density was 0.05 A/cm² the hydrogen generation was negligible and the reduction of sulfur dioxide, which could not be identified at higher current densities, increased.

On the other hand, in electrolytes comprising 4-dimethylaminopyridine and a mixture of 1,3-di(4-pyridyl)propane and diethanolamine, quantitative hydrogen gas

generation was observed over a wide range of cathode current densities. When pyridine was used as a basic compound, quantitative hydrogen gas generation was not obtained, even when the cathode current density was increased. If the proportion of the hydrogen gas generation reaction to the total cathode reactions is 100%, the reduction product of sulfur dioxide which reacts with iodine is not produced. As a result it is theoretically unnecessary to separate the anolyte from the catholyte with a diaphragm.

Effects of the diaphragm between the cathode and anode

If the reduction at the cathode produces only hydrogen gas, it may be possible to measure the water contents accurately without a diaphragm between the cathode and the anode. The effect of the diaphragm was studied by comparing the measured values of water at the cathode current density that generates 100% hydrogen with those obtained at the cathode current density that generates lower percentages of hydrogen. The results are tabulated in Table 1.

It was found that when the proportion of hydrogen gas generation reaction was 100%, the water contents could be measured accurately, even if the diaphragm was removed. However, when the proportion was lower, higher values were observed, since reduction products of sulfur dioxide capable of reacting with iodine was produced. When the proportion was still lower, the measured values were several times higher than the accurate ones, or the end point of titration was not gained. Nichugovskii reported that the reduction product of sulfur dioxide was S₂O₄²⁻; he did not, however, confirm this hypothesis.^{2,3} The authors tried to confirm it, but could not identify the reduction product of sulfur dioxide.¹ Nevertheless, the authors also supposed that a compound which is likely to react with iodine was produced.

Effects of different electrolysis methods

Because the current density at the cathode greatly influences the proportion of hydrogen gas generated at the cathode, pulse electrolysis under a constant electrolytic current was supposed to be suitable for a

Fig. 1 Relation between the proportion of hydrogen gas generation in cathode reaction and cathode current density: $\diamond$, pyridine; $\triangle$, 4-dimethylaminopyridine; $\circ$, imidazole; $\square$, a mixture of 1,3-di(4-pyridyl)propane and diethanolamine.

Table 1 Effect of diaphragm

Cathode current density/A cm ⁻²	Diaphragm	Electrolyte A ^a		Electrolyte B ^b	
		Observed value ^c /μg	RSD, % ^d	Observed value ^c /μg	RSD, % ^d
1.43	present	10007.3	0.27	9935.8	0.39
	no	10051.2	0.34	10053.7	0.32
0.85	present	10021.3	0.23	—	—
	no	11722.4	0.90	—	—
0.05	present	—	—	10466.8	1.30
	no	—	—	End point was not gained.	

a. Imidazole was used as a basic compound. b. A mixture of 1,3-di(4-pyridyl)propane and diethanolamine was used as a basic compound. c. 10 μl of water was injected. d. Number of measurements was 3.

Table 2 Comparison of different electrolysis methods

Water amount added/ μg	Electrolyte A ^c			Electrolyte B ^d		
	Method A ^e / μg	Method B ^f / μg	Method A/ Method B	Method A ^e / μg	Method B ^f / μg	Method A/ Method B
50 ^a	69.6	57.2	1.22	60.4	53.3	1.13
200 ^a	219.2	208.1	1.05	206.0	211.3	0.97
1000 ^a	1031.1	1034.2	1.00	1033.1	1021.1	1.01
5000 ^b	5047.6	5127.0	0.98	5072.3	5054.5	1.00
10000 ^b	10176.2	10317.7	0.99	10110.9	10029.9	1.01

a. Water-methanol solution (4 mgH₂O/ml) was added by a microsyringe. b. Water was added by a microsyringe. c. Imidazole was used as a basic compound. d. A mixture of 1,3-di(4-pyridyl)propane and diethanolamine was used as a basic compound. e. Continuous electrolysis method in proportion to polarization voltage. f. Pulse electrolysis method with constant electrolytic current. Each value is the average of three determinations. A titration cell without a diaphragm was used and cathode surface area was 0.28 cm².

coulometric titration cell without a diaphragm.

To evidence whether this is correct, the moisture analyzer which applied pulse electrolysis was compared with a moisture analyzer in which the electrolytic current is proportionally controlled according to the polarizing voltage. The results are tabulated in Table 2.

When the amount of water was very small, in case of the latter analyzer, the electrolytic current decreased and the current density at the cathode also decreased. As a result, a sulfur dioxide reduction product that could react with iodine was produced. It was supposed that this is the reason why the measured values were so high. However, when the amount of water was large, the effect of different electrolysis methods became relatively small, and it became difficult to distinguish the effect. Table 2

illustrates this supposition.

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