Determination of the Acid Strength Distribution of Manganese Dioxide by the Modified Indicator Method

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Synopsis. A new procedure for determining the distribution of acid and base centers of dark colored solids by the indicator method has been proposed. By this method weak acidic sites were found to be present on a manganese dioxide surface.

As a method for measuring the acidity of white colored solid samples such as silica-alumina, the fundamental titration procedure based on Johnson's method[1] is generally used. The acidity of colored solid samples, however, can not be measured by this method. In this case a modified procedure[2] such as the titration of the mixture of the sample and a white standard sample with known acidity is usually applied. By this modified method it is impossible to measure the acidity of black colored solids such as electrolyte manganese dioxide (EMD), because the color change of the Hammett indicator is difficult to observe.

On the EMD surface the presence of acidic sites should be predictable from the cation-exchange ability of its surface OH groups.[3,4] The understanding of the acidic properties on the EMD surface can help to improve the life of dry batteries.[5]

Recently we succeeded in determining the amounts of acid and basic areas on black colored solid samples by our modification of the indicator method. This paper describes this procedure and the distribution of the acidic sites on the EMD surface.

Experimental

Samples. EMD (type FM-H) was supplied by Toyo Soda Manufacturing Co. Ltd., and its particle size was 100—200 mesh (149—79 μ). Before the measurements it was preheated at 110—500 °C for 1 h in air. MnO was obtained by thermal decomposition of manganese carbonate at 500 °C in a stream of nitrogen. Silica-alumina (Catalysts & Chemicals Ind. Co. Ltd.; SiO_2 87%) dried at 110 °C and magnesium oxide (Wako Pure Chem. Co. Ltd.) calcined at 700 °C in air were used as a white standard probe with known acidity and basicity, respectively.

As shown in Fig. 1, a vessel developed by us is composed of a commercially available separate ground-glass Gooch crucible equipped with a cover on the head and a receiver (content volume 15 ml) on the bottom. The pore size of the glass filter is 20—30 μ (3G type).

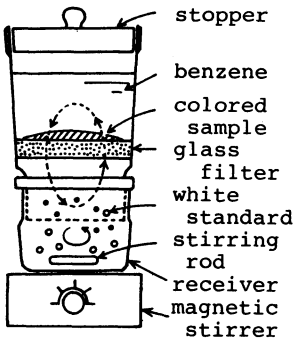

Fig. 1. The vessel to measure the acidic and basic properties of the dark colored solid samples.

Procedure. The standard probe of silica-alumina and a magnetic stirring rod are put into the receiver, to which the paired ground-glass Gooch crucible is attached. Dry benzene is poured into the crucible. When the inner pressure of the crucible is reduced by use of an aspirator, the vessel can be then degassed. The inner part of the vessel can then be easily filled with dry benzene. The known amount of preheated EMD is rapidly placed into the crucible in a stream of dry nitrogen. The weight of the EMD is about three times that of the silica-alumina. A few drops of Hammett indicator with the known pK_a is introduced into the EMD-benzene solution and stirred for 3 h, followed by standing for 12 h. At first 0.1 M† butylamine benzene solution equivalent to the amount of the acid in the silica-alumina is added to the crucible. Butylamine benzene solution is then added at 3-h intervals until the acidic color of the Hammett indicator on the silica-alumina is no longer observed. Stirring is continued all through the titration. A drop of 0.05 M trichloroacetic acid in benzene is added to ensure whether there is appreciable excess of butylamine at the end point or not.

Using benzoic acid instead of butylamine the basicity of dark colored samples can be determined in the same manner as described above.

Results and Discussion

In order to verify our method, the acidity of the white standard solid, silica-alumina, instead of black colored sample was first measured. The same results for the acidity were obtained by our method as for fundamental Johnson's method (Table 1). The silica-alumina, which has an acid strength distribution for the weak acidic sites, is suitable for the white standard probe to measure the acid amount of the EMD.

Our method showed a considerable amount of weak acidic sites were present on the EMD surface. The acid strength distribution of the EMD preheated at the various temperature were given in Table 1. A large amount of acid sites at $+6.8 \leqq H_o < +1.5$ was observed on the EMD surface preheated at 110 °C. When phenolphthalein ($pK_a = +9.3$) was used as a Hammett indicator, the basic sites could not be detected on the EMD surface. While the amount of basic sites at $H_o = +9.3$ on the MnO surface was 0.297 mmol/g.

Many OH groups are known to be present on the EMD surface.[5,6] The relation between the amount of surface OH groups determined by the KI method in *N,N*-dimethylformamide solvent[7] and the total acid amount on the EMD heat-treated at various temperature were shown in Fig. 2. Both the amounts of the surface OH groups and of the total acidic sites

† 1 M = 1 mol dm^{-3}.

Table 1. Acidic properties of electrolytic MnO_2

Sample	Calcinating temperature (°C)	Surface area (m^2/g)	Acid amount(mmol/g)			Total acid amount (mmol/g)
			$+1.5>H_o\geqq+3.3$	$+3.3>H_o\geqq+4.8$	$+4.8>H_o\geqq+6.8$	
MnO_2	110	33.2	0.006	0.072	0.023	0.101
MnO_2	200	28.5	0.005	0.046	0.037	0.088
MnO_2	300	16.3	0	0.019	0.064	0.083
MnO_2	500	12.9	0	0.015	0.025	0.040
SiO_2-Al_2O_3[a)]	110	302	0.142	0.339	0.384	0.865
SiO_2-Al_2O_3[b)]	110	302	0.144	0.333	0.381	0.858

a) By our modified method. b) By Johnson's method.

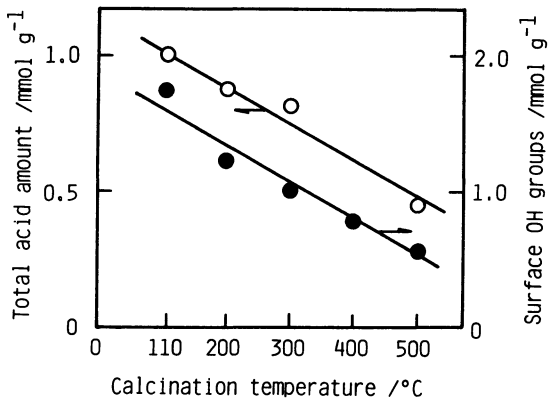

Fig. 2. Relation between both the amount of total acid and of surface OH groups on the electrolytic MnO_2 heat-treated at various temperatures.

decreased in nearly the same ratio as the pretreatment temperature was raised. These results suggest that the surface OH groups are the important factor associated with the acidic property of the EMD. The difference between the surface OH groups and the total acid amount should be expected to be either weak acid OH groups below the acid strength at H_o=+6.3 or the oxidation sites on the EMD. We propose to investigate the surface characterization for the acidic properties on the EMD in further detail.

Thus both the acidity and basicity of the dark colored solid samples can be measured satisfactorily by our method provided one selects suitable standard probes and indicators.

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