Decomposable Slurry to Form Dense Manganese Oxide Layer For Tantalum Solid Electrolytic Capacitors

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Abstract

The decomposable slurry composed of $\text{Mn(OH)}_2 \cdot \text{NH}_4\text{NO}_3 \cdot \text{Mn(NO}_3)_2 \cdot \text{H}_2\text{O}$ has been developed. The slurry was prepared by the addition of aqueous NH_4OH to the aqueous $\text{Mn(NO}_3)_2$ solution. It was a viscous slurry with a pale pink color. The slurry decomposed at lower temperatures with increased amount of aqueous NH_4OH added to the aqueous $\text{Mn(NO}_3)_2$ solution. The lower temperature decomposition reaction of the slurry was attributed to the exothermic reaction which was not observed in the case of the decomposition of the aqueous $\text{Mn(NO}_3)_2$ solution. The manganese oxide prepared from the slurry showed several interesting properties; dense and uniform structure, small surface area, high apparent density, and low electrical resistivity. The application of the slurry to the tantalum solid electrolytic capacitors provided highly performed electrical characteristics of the capacitors with the shortened period for the preparation of the manganese oxide layer in sufficient thickness.

1 INTRODUCTION

Manganese oxide has widely been used as the cathode material of the tantalum solid electrolytic capacitors for its semiconductivity and electrochemical activity ¹⁾. Many studies have been carried out to improve the capacitor characteristics in correlation with the preparation of the manganese oxide layer. Included are the studies of the chemical reduction of a permanganate to manganese oxide ²⁾, the electrolytic deposition of manganese oxide ³⁻⁵⁾, the electrodeless deposition of manganese oxide ⁶⁾, the sputter deposition of manganese oxide ⁷⁾, and the pyrolysis of $\text{Mn(NO}_3)_2$ ⁸⁾. We have found a novel material which is pyrolytically decomposable to form a uniform and a dense manganese oxide layer ⁹⁾. The material was a viscous slurry composed of Mn(OH)_2 , NH_4NO_3 , $\text{Mn(NO}_3)_2$, and H_2O ¹⁰⁾. The slurry decomposed pyrolytically to form a highly performed manganese oxide layer for the cathode of the tantalum solid electrolytic capacitors.

In this paper are discussed, (1) a preparation method and some properties of the slurry, (2)

properties of the manganese oxide layer formed from the slurry, (3) a decomposition process of the slurry, and (4) application of the manganese oxide formed from the slurry to the tantalum solid electrolytic capacitors.

2 EXPERIMENTAL

The slurry was prepared with the addition of aqueous NH_4OH to a $\text{Mn(NO}_3)_2$ solution. When the aqueous NH_4OH was added to the aqueous $\text{Mn(NO}_3)_2$ solution, the small particles of Mn(OH)_2 began to precipitate and disperse in the solution, resulting in the formation of a pale pink colored viscous slurry. The viscosity of the slurry increased with the amount of Mn(OH)_2 which could be controlled by the amount of NH_4OH added. The aqueous NH_4OH reacted sufficiently with the $\text{Mn(NO}_3)_2$ solution by a mixing with the dispersion mill to attain an uniform dispersion of the ingredients; Mn(OH)_2 , NH_4OH , $\text{Mn(NO}_3)_2$, and H_2O . The concentration of the aqueous NH_4OH was 28 % of NH_3 . The concentration of the aqueous $\text{Mn(NO}_3)_2$ solution examined was in the range 57~60 % of $\text{Mn(NO}_3)_2$ by weight in H_2O . The viscosity of the slurry was measured with a B-type viscosity meter of Tokyo Keiki Inc. at room temperature. The slurry was decomposed pyrolytically to form the manganese oxide layer with a convec-

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tion furnace in which heat was transferred to the slurry through the circulating hot air ¹¹⁾.

For measurements of properties of the manganese oxide except for the electrical resistivity, the slurry was decomposed in a porcelain crucible to form the manganese oxide block followed by being pulverized. The pyrolysis of 50 ml of the slurry was carried out at 200, 250, and 300 °C for 5 h in air. The manganese oxide powder pulverized was washed with flowing hot deionized water for 5 h to remove completely the unreacted residues.

The surface area of the samples was measured by the BET method with Digisorb 2500 of Micromeritics Inc. The apparent densities of the pulverized samples were measured with a density meter IH-1000 of Seishin Enterprise Co., Ltd. The oxygen content in the manganese oxide, *i.e.* x-values in MnO_x , was determined from chemical analysis.

For measurement of the electrical resistivity of the manganese oxide layer formed, the four point probe method was used at temperatures from 10 to 75°C. The manganese oxide layer was formed by pyrolyzing the slurry (2ml) on an alumina substrate ($50 \times 50 \times 0.5\text{mm}$). The pyrolysis was carried out at 200, 250, and 300°C for 15 min. The unreacted residue in the manganese oxide layer formed was removed completely with flowing hot deionized water for 5 h. Four isolated Au electrodes were formed on the manganese oxide layer by vacuum evaporation. The ohmic contact between the manganese oxide and Au electrodes was confirmed. The thickness of the manganese oxide layer ranged from 10 to 50 μm , depending on the preparation conditions.

Both the thermogravimetric analysis (TG) and the differential thermal analysis (DTA) of the slurry were carried out with a thermal analyzer Model M-8076 of Rigakudenki Co., Ltd. The weight of samples examined and the scanning speed of the temperature in the analysis were 20 mg and 10°C/min, respectively.

For characterization of the manganese oxide layer formed from the slurry as the cathode material of the tantalum solid electrolytic capacitors, the manganese oxide layer was applied on a tantalum sintered body in the

following procedure. The tantalum sintered body of 6.7 mm in diameter and 12.5 mm in length with an anodic tantalum oxide dielectric film was impregnated at first in the aqueous solution of 35 weight % $\text{Mn}(\text{NO}_3)_2$, followed by being heated in the convectional furnace at 250°C for 10 min. After the three times-repetition of the impregnation-heating process was carried out, the sintered body with the manganese oxide layer was again impregnated in the viscous slurry. The slurry used in the experiment was a mixture of the aqueous $\text{Mn}(\text{NO}_3)_2$ solution with NH_4OH added by 8 volume %. Then the body with the slurry was heated in the convection furnace at 250°C for 10 min. The cycle was repeated three times. The conductive counter electrode formed with a colloidal carbon layer, a silver paste layer, and a solder layer, was provided onto the manganese oxide layer to complete a capacitor construction. Several capacitor characteristics of capacitance, $\tan\delta$, and their frequency dependences were measured with an LCR (Inductance-Capacitance-Resistance) meter Model 4261A of YHP.

3 RESULTS AND DISCUSSION

A. Properties of the slurry

Figure 1 shows a relationship between the viscosity of the slurry formed and the amount of

Figure 1. Relationship between the viscosity of the slurry and the amount of the addition of aqueous NH_4OH to the aqueous $\text{Mn}(\text{NO}_3)_2$ solution

Figure 2. SEM of the manganese oxide layer
a); manganese oxide from the slurry, b); manganese oxide from the aqueous $\text{Mn}(\text{NO}_3)_2$ solution

NH_4OH added to the $\text{Mn}(\text{NO}_3)_2$ solution. Precipitation of pale pink color was formed in the $\text{Mn}(\text{NO}_3)_2$ solution with addition of NH_4OH . As the amount of NH_4OH added to $\text{Mn}(\text{NO}_3)_2$ increases, the viscosity of the solution steeply increases: 7×10^1 cp for the solution with 2.5 volume % NH_4OH added and 5×10^4 cp for 15 volume % added. The slurry thus formed was a pale pink colored viscous material, and was composed of $\text{Mn}(\text{OH})_2$, NH_4NO_3 , $\text{Mn}(\text{NO}_3)_2$, and H_2O . The sufficient mixing and uniform dispersion of the ingredients were required to obtain a stable slurry forming the uniform manganese oxide layer.

B. Properties of the manganese oxide from the slurry

Figures 2-a) and b) show SEM of the manganese oxide layers on the tantalum sintered body formed from the slurry and the conventional

Figure 3. Surface area of the manganese oxide layer

aqueous $\text{Mn}(\text{NO}_3)_2$ solution, respectively. The manganese oxide layer formed from the slurry has smooth surface and is constructed by the uniformly distributed particle. Judging from Fig. 2, the average particle size of the manganese oxide from the slurry was $2.8 \mu\text{m}$ in diameter. The conventional manganese oxide layer from the aqueous $\text{Mn}(\text{NO}_3)_2$ solution was porous, thick, and ragged with very large particles, *e.g.* $100 \mu\text{m}$ in diameter.

Figure 3 shows the surface area of the manganese oxide formed from the slurry. The surface area of the manganese oxide formed from the aqueous $\text{Mn}(\text{NO}_3)_2$ solution are also shown in Fig. 3 for comparison. The surface area is much less in the manganese oxide formed pyrolytically than in the manganese oxide formed electrolytically. In the figure, γ - MnO_2 describes for the manganese oxide electrolytically deposited and the γ - β - MnO_2 describes for the heat treated γ - MnO_2 ; heat treatment temperature was 250°C . The manganese oxide from the slurry shows much lower specific surface area than the manganese oxide from the aqueous $\text{Mn}(\text{NO}_3)_2$ solution, which agrees with the result of the SEM observation; the very dense layer was formed from the slurry.

Figure 4 shows the X-ray diffraction patterns of the manganese oxide formed. Pyrolysis of

Figure 4. X-ray diffraction pattern of the manganese oxide layer

both the aqueous $\text{Mn}(\text{NO}_3)_2$ solution and the slurry resulted in $\beta\text{-MnO}_2$, regardless of the pyrolysis temperatures. From a chemical analysis, x-values in MnO_x of 1.97-2.00 were obtained for the manganese oxide both from the slurry and the aqueous $\text{Mn}(\text{NO}_3)_2$ solution.

The apparent density of the manganese oxide from the slurry and from the aqueous $\text{Mn}(\text{NO}_3)_2$ solution were 1.76 g/cm^3 and 1.49 g/cm^3 , respectively. The high apparent density of the manganese oxide from the slurry agreed again with the observation by SEM and surface area measurements.

Figure 5 shows the electrical resistivities as a function of the inverse temperature for manganese oxide prepared from the slurry and from the aqueous $\text{Mn}(\text{NO}_3)_2$ solution. The numerals in the figure indicate the temperatures at which the slurry or the aqueous $\text{Mn}(\text{NO}_3)_2$ solution was pyrolyzed. The resistivities of the manganese oxide from the slurry was lower than those from the aqueous $\text{Mn}(\text{NO}_3)_2$ solution. The pyrolysis at higher temperatures results in the higher resistivities, although the resistivities of the manganese oxide from the slurry show the smaller dependence on the pyrolysis temperatures.

Figure 5. Electrical resistivities of the manganese oxide layer

C. Thermal analysis of decomposition of the slurry and the aqueous $\text{Mn}(\text{NO}_3)_2$ solution

Figures 6 and 7 are the results of the differential thermal analysis (DTA) and the thermogravimetric analysis (TG) of $\text{Mn}(\text{NO}_3)_2$ and the slurries, respectively. Both figures show the results for the aqueous $\text{Mn}(\text{NO}_3)_2$ solution of 58 weight %, the slurry from the addition of 1, 3, 6, and 10 volume % NH_4OH to the aqueous $\text{Mn}(\text{NO}_3)_2$ solution, denoted for a), b), c), d), and e), respectively. In the case of the aqueous solution of 58 weight % of $\text{Mn}(\text{NO}_3)_2$, Fig.6-a) shows a broad endothermic band below 150°C (dehydration), a steep endothermic band at 198°C (band A), and a small endothermic band at 227°C (band B). Judging from the TG results in Fig. 7-a), in the temperature range above 298°C , the decomposition was completed; *i.e.* monophase of the manganese oxide was present. Both bands A and B correspond to the decomposition reaction of $\text{Mn}(\text{NO}_3)_2$ into the manganese oxide.

With the addition of aqueous NH_4OH to the aqueous $\text{Mn}(\text{NO}_3)_2$ solution, both bands A and B shift toward lower temperatures. Also with the addition of aqueous NH_4OH , the intensity of the band B decreases and an exothermic band (band C) newly appears. The temperature at which the decomposition reaction completes also shifts toward lower temperatures with the addition of aqueous NH_4OH . Consequently, the DTA curve of the slurry obtained by mixing the aqueous

Figure 6. Differential thermal analysis of the aqueous $\text{Mn}(\text{NO}_3)_2$ solution and the slurries

a); aqueous $\text{Mn}(\text{NO}_3)_2$ solution of 58 weight %, b); slurry from the addition of 1 volume % of aqueous NH_4OH , c); slurry from the addition of 3 volume %, d) slurry from the addition of 6 volume %, e); slurry from the addition of 10 volume %

$\text{Mn}(\text{NO}_3)_2$ solution and aqueous NH_4OH by 10 volume % shows a distinguishable difference from the curve of the aqueous $\text{Mn}(\text{NO}_3)_2$ solution: a broad endothermic band below 150°C with a small dip at 140°C , corresponding to the dehydration, and the strong exothermic and endothermic bands in the very narrow temperature range between 168°C and $170\text{--}174^\circ\text{C}$, are obtained as shown in Fig.6-e). The both bands at 168°C and $170\text{--}174^\circ\text{C}$ suggest that the synthesis and decomposition of the Mn-compound occurred. The band B completely disappeared in Fig. 6-e). Judging from Fig.7-e), the decomposition was completely finished in the temperature range above 192°C .

As seen from Figures 6-a) and 7-a), the aqueous $\text{Mn}(\text{NO}_3)_2$ solution began to decompose at

Figure 7. Thermogravimetric analysis of the aqueous $\text{Mn}(\text{NO}_3)_2$ solution and the slurries

a); aqueous $\text{Mn}(\text{NO}_3)_2$ solution of 58 weight %, b); slurry from the addition of 1 volume % of aqueous NH_4OH , c); slurry from the addition of 3 volume %, d) slurry from the addition of 6 volume %, e); slurry from the addition of 10 volume %

about 150°C and finished at 298°C . The decomposition reaction proceeded in a wide temperature region (for about 148 degree). It is expected that the manganese oxide layer formed in the early stage of the reaction is affected significantly by the decomposition reaction followed: the NO_2 gas generated in the continuing reaction gives a bad effect to the manganese oxide layer formed earlier, *i.e.* a porous structure of the layer is accumulated in the reaction process.

On the other hand, the slurry decomposed in the temperature region of $168\text{--}192^\circ\text{C}$ as shown in Figures 6-e) and 7-e). The decomposition reaction proceeded in a very narrow temperature region (for about 24 degree). As mentioned in the previous section, the slurry decomposed with strong exothermic and endothermic process in the narrow temperature range, *i.e.* the much higher rate of the reaction proceeding in the lower temperature range was found in the

slurry decomposition reaction. It is expected that the higher rate of the decomposition reaction prevents the layer formed from being attacked with a generating NO_2 gas, resulting in dense and uniform layer with small particles of the manganese oxide.

The small particle structure (Fig.2), the low specific surface area (Fig.3), and the high apparent density of the manganese oxide layer from the slurry attribute to the decomposition reaction process of the slurry mentioned above. The high electric conductivity (Fig.5) also attributes to the high apparent density of the layer. As crystalline structure of the manganese oxide formed predominantly depends on the decomposition reaction temperature in the pyrolysis, $\beta\text{-MnO}_2$ is obtained both from the slurry and the aqueous $\text{Mn}(\text{NO}_3)_2$ solution in the present temperature range. The x -value in MnO_x from chemical analysis predominantly attributes to the crystalline structure of the manganese oxide, resulting in almost the same x -value with the manganese oxide from the slurry and from the aqueous $\text{Mn}(\text{NO}_3)_2$ solution.

Figure 8 shows the relationships between the temperatures of the band A, B, and the reaction finishing temperature and the amount of the

Figure 8. Relationship between characteristic temperatures in DTA and TG and the amount of NH_4OH added

○; band A, ●; band B, ●; decomposition finishing temperatures

addition of aqueous NH_4OH . The reaction finishing temperature was defined as the temperature at which the weight of the reaction product of the decomposition became constant in TG. In the early stage of the pyrolytic decomposition process, condensation of the slurry by a heating resulted in a formation of concentrated HNO_3 and $\text{Mn}(\text{NO}_3)_2$. In the slurry of the present composition, two kinds of continuing reaction schemes are expected.

In the first reaction scheme, the concentrated HNO_3 obtained in the early stage reacted with the $\text{Mn}(\text{OH})_2$ to form $\text{Mn}(\text{NO}_3)_2$; this is an exothermic reaction. The $\text{Mn}(\text{NO}_3)_2$ obtained decomposed to form the manganese oxide. It is expected that if the exothermic reaction occurs at just before the decomposition of $\text{Mn}(\text{NO}_3)_2$, the $\text{Mn}(\text{NO}_3)_2$ absorbs the heat released and the decomposition of the $\text{Mn}(\text{NO}_3)_2$ is accelerated.

In the second reaction scheme, the concentrated $\text{Mn}(\text{NO}_3)_2$ obtained in the early stage reacted with the $\text{Mn}(\text{OH})_2$ to form directly the manganese oxide particles: this reaction is also exothermic. The particles of the manganese oxide thus formed acted as multiple nuclei for the formation of the manganese oxide in the pyrolytic decomposition reaction of $\text{Mn}(\text{NO}_3)_2$. It is expected that the formation of the nuclei by the process also accelerates the decomposition reaction.

As the amount of aqueous NH_4OH increased, the effect of reaction acceleration mentioned above was much more reinforced, resulting in the earlier completion of the decomposition reaction. The acceleration of the decomposition helped the formation of the uniform and dense manganese oxide layer.

The decomposition at lower temperatures of the slurry provided an additional advantage to the capacitor manufacturing process that the thin dielectric film of Ta_2O_5 was slightly damaged by a heating during the manganese oxide formation.

D.Application of the slurry to capacitors

The slurry obtained in this study was applied to the tantalum solid electrolytic capacitor of 20V-180 μF . Table 1 shows a typical example of capacitor characteristics obtained. The dissipation factor ($\tan\delta$) and the leakage current are

Table 1 Electrical characteristics of the tantalum capacitors

	Capacitor with manganese oxide layer from the slurry	Capacitor with manganese oxide layer from $\text{Mn}(\text{NO}_3)_2$ soln.*
Capacitance	180 μF	180 μF
$\tan \delta$ (at 120 Hz)	4.0 %	6.0 %
Leakage current (20 V, 5 min)	0.2 μA	0.5 μA
Capacitance decrease (10 kHz/120 Hz)	-2.0 %	-2.0 %
Repetition times of pyrolysis	6	8

*) The conventional manganese oxide layer was formed by the three times-repetition of the impregnation-heating process of the aqueous solution of 35 weight % $\text{Mn}(\text{NO}_3)_2$ followed by three-times repetition of the process for 58 weight % $\text{Mn}(\text{NO}_3)_2$.

significantly improved in comparison with the capacitor of the conventional manganese oxide layer.

The roles of the manganese oxide layer in the tantalum solid electrolytic capacitors are, (1) as cathode for the dielectric tantalum oxide film which governs the carrier concentration at the manganese oxide-tantalum oxide interface and (2) as oxygen donor to supply the oxygen ions to the electrically defective portions of the tantalum oxide film which is well known as the self-healing action¹²⁾. The lower electric resistivity of the manganese oxide layer, the better electrical contact between the dielectric tantalum oxide film and the manganese oxide layer, and the sufficient thickness of the manganese oxide layer, result in the lower dissipation factor and the lower leakage current of capacitors.

The low electric resistivity, high apparent density, and uniform distribution of particle size (2-8 μm) of the manganese oxide layer formed from the slurries in the present work resulted in the highly performed tantalum solid electrolytic capacitors.

The higher rate of decomposition reaction proceedings of the slurry gave several advantages to the formation of the manganese oxide in micro pores of the tantalum sintered body: bad effects caused by the generated NO_2 gas were suppressed in the shorter reaction period and lower temperature range. Consequently,

dense and uniform manganese oxide layer with a sufficient thickness was obtained both inside of the sintered body and a surface of the sintered body, which also resulted in the highly performed characteristics of the capacitors.

Besides, since the amount of the manganese oxide deposited on the tantalum sintered body per one dip in the slurry was greater than that of the dip in the aqueous $\text{Mn}(\text{NO}_3)_2$ solution, the impregnation-heating process of the slurry could be shortened to obtain a satisfied amount and quality of the manganese oxide layer for the capacitors; 8 times-repetition decreased to 6 times-repetition.

4 SUMMARY

The novel decomposable slurry composed of $\text{Mn}(\text{OH})_2\text{-NH}_4\text{NO}_3\text{-Mn}(\text{NO}_3)_2\text{-H}_2\text{O}$ has been studied. The results are summarized as follows:

(1) The addition of aqueous NH_4OH to the aqueous $\text{Mn}(\text{NO}_3)_2$ solution resulted in the viscous pink colored slurry of $\text{Mn}(\text{OH})_2\text{-NH}_4\text{NO}_3\text{-Mn}(\text{NO}_3)_2\text{-H}_2\text{O}$.

(2) The manganese oxide prepared from the slurry showed several interesting properties in comparison with the manganese oxide from the aqueous $\text{Mn}(\text{NO}_3)_2$ solution;

- a) dense manganese oxide layer composed of the uniform and small size of particles,
- b) small surface area,
- c) high apparent density,
- d) low electrical resistivity.

(3) The highly performed properties of the manganese oxide attributed to the decomposition behavior of the slurry. The high rate of the reaction proceeding in the lower temperature range with a strong exothermic process resulted in the dense and uniform manganese oxide layer.

(4) The addition of aqueous NH_4OH to the aqueous $\text{Mn}(\text{NO}_3)_2$ solution lowered the decomposition temperature of the slurry and the reaction finishing temperature. The endothermic reaction band shifted from 198°C to $170\sim 174^\circ\text{C}$ and the reaction finishing temperature shifted from 298°C to 192°C .

(5) Condensation of the slurry by a heating resulted in a formation of concentrated HNO_3 and $\text{Mn}(\text{NO}_3)_2$. Two kinds of continuing reaction schemes were expected.

a) the concentrated HNO_3 obtained reacted exothermically with the $\text{Mn}(\text{OH})_2$ in the slurry to form $\text{Mn}(\text{NO}_3)_2$, which decomposed to form the manganese oxide.

b) the concentrated $\text{Mn}(\text{NO}_3)_2$ obtained reacted exothermically with the $\text{Mn}(\text{OH})_2$ to form directly the manganese oxide particles.

It was expected that the exothermic reaction lowered the temperature at which the decomposition of the slurry completed. The formation of the manganese oxide nuclei in the process also accelerated the decomposition reaction.

(6) The application of the slurry to the tantalum solid electrolytic capacitors provided

a highly performed electrical characteristics of the capacitors and the shortened period for the formation of the manganese oxide layer in adequate thickness.

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