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THERMOGRAVIMETRY OF HIGH-PURITY, CHEMICALLY-PREPARED AgO CATHODE MATERIAL

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ABSTRACT

The purity and stability of chemically-prepared silver(II) oxide material used in AgO/Zn cells for miniaturized electronic devices were determined by thermogravimetry (TG). During storage, high-purity AgO powder slowly reacted with atmospheric CO_2, forming Ag_2CO_3. The increase in Ag_2CO_3 content was determined with high accuracy from measurements of the TG mass plateaus. The accuracy of the TG measurements was corroborated by concurrent gas chromatographic determinations of the evolved CO_2 from the decomposition of the AgO powder. The excellent precision and accuracy attainable with the 951 TGA module of the DuPont 1090 thermal analysis system were demonstrated.

INTRODUCTION

Batteries employing electrochemically-prepared silver oxide cathodes are used in numerous military applications requiring power sources with high power and energy densities. Such cathodes contain various amounts of silver(II) oxide, silver(I) oxide, silver, and silver carbonate impurity. The decomposition of the thermodynamically-unstable AgO component during storage causes performance degradation problems in silver oxide/zinc cells. A new, extremely rapid thermogravimetry–evolved gas analysis (TG–EGA) method for the analysis of the components of silver oxide cathode material has recently been developed [1].

Chemically-prepared silver oxide cathode material is used in cells for applications requiring power sources with low power densities, i.e., for miniaturized electronic devices. This AgO material can be prepared in very pure form. While studying the aging characteristics of the electrochemically-prepared silver oxide cathode material, this pure chemically-prepared AgO material was continually run as a standard for assessing the performance of the TGA module.

Three decomposition reactions occur when silver carbonate or the silver

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oxides are heated [1]

$$Ag_2CO_3 \rightarrow Ag_2O + CO_2 \quad (1)$$

$$2\ AgO \rightarrow Ag_2O + 0.5\ O_2 \quad (2)$$

$$Ag_2O \rightarrow 2\ Ag + 0.5\ O_2 \quad (3)$$

The mass losses that result from the evolution of CO_2 or O_2 are relatively small: 15.960, 6.458 and 6.904% respectively, for the three reactions. The detection by TG of very small mass losses, in the order of 0.006% of the sample mass, is necessary to distinguish between samples that differ in composition by as little as 0.1%.

In this paper, the high accuracy and precision attained with the DuPont 951 TGA module during a study of the purity and stability of chemically-prepared, high-purity AgO cathode material are described.

EXPERIMENTAL

A DuPont 1090 thermal analysis system with a 951 TGA module and a Hewlett-Packard 5710A gas chromatograph were employed in this study. TG samples were run in platinum boats at various heating rates from 0.2 to 40.0 K min^{-1} in a flowing atmosphere (50 cm^3 min^{-1}) of dry argon or helium. Samples identical to those used in the TG run were placed in a specially-constructed glass vessel for GC analysis. After loading the sample, the vessel was evacuated ($p \leqslant 20$ μm Hg), and the sample was decomposed by placing the vessel in the TGA furnace and heating over the same temperature range as in the TG run. The amount of evolved, trapped CO_2 was analyzed by GC for determination of the Ag_2CO_3 content of the sample.

During the course of this work, the removable quartz rod balance beam and its stainless steel clip holder had to be replaced periodically. During replacement, a very tight fit was achieved between the quartz rod and clip and between the clip and the cold beam member. This was followed by careful recalibration of the TGA module with a class M weight. The calibration was then checked by running a standard material such as pure $CaCO_3$ (99.999%, Atomergic Chemetals Corp.) and measuring the mass loss plateaus.

The high-purity AgO cathode material [2] used in this work was obtained from RAYOVAC Corp. in the form of a loose, free-flowing powder. No special sample preparation except thorough mixing was employed. The sample mass was about 100 mg for both the TG and GC analyses.

RESULTS AND DISCUSSION

To demonstrate the accuracy attainable with the 951 TGA module, a TG curve of pure $CaCO_3$ is shown in Fig. 1. The apparent mass increase up to

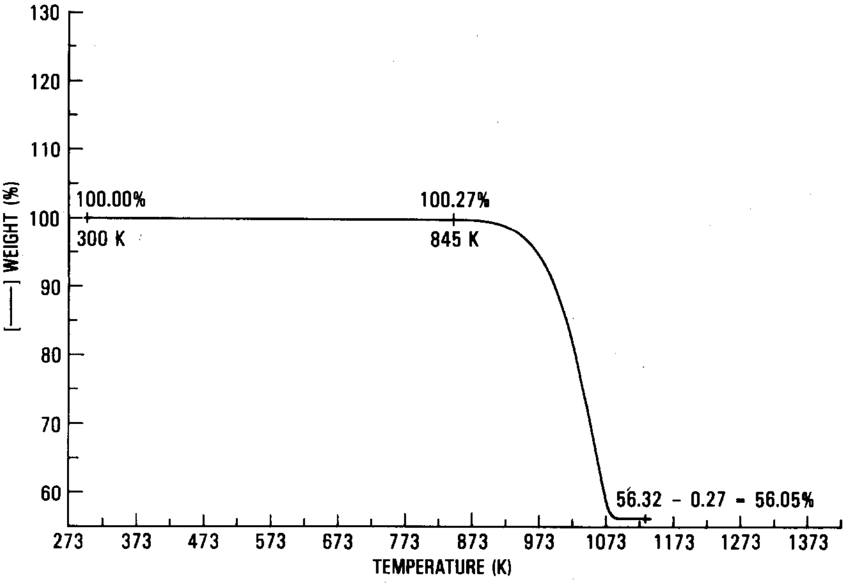

Fig. 1. TG curve for $CaCO_3$, 99.999%. Sample size, 21.407 mg; heating rate, 20 K min^{-1}; atmosphere, argon, 50 cm^3 min^{-1}.

845 K, just prior to decomposition of the sample to CaO, had reached a steady value of 0.055 mg (0.27% of the sample weight). Thus, the corrected value for the final plateau, W_3, is $56.32 - 0.27 = 56.05\%$, compared to a calculated value of $CaO/CaCO_3 \times 100 = 56.03\%$.

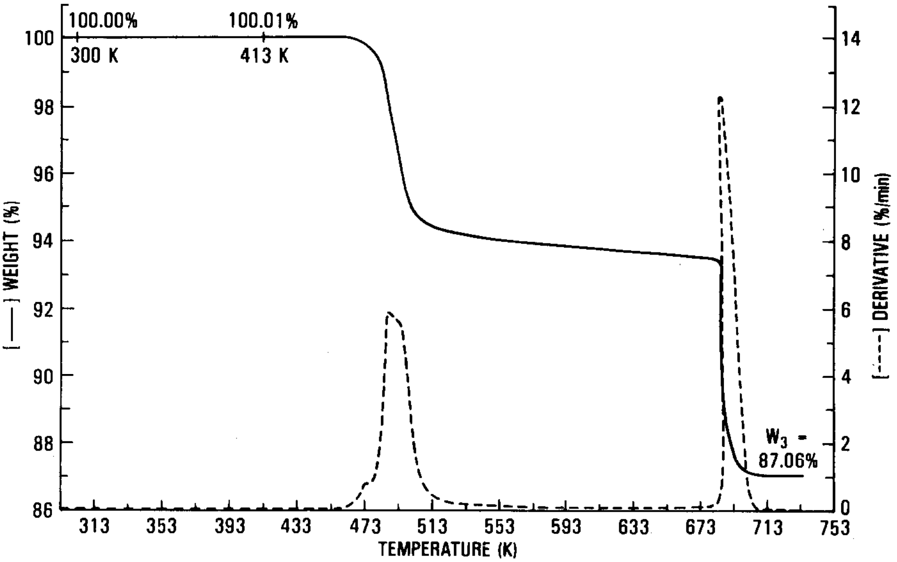

Fig. 2. TG curve and derivative for AgO cathode material. Sample size, 104.87 mg; heating rate, 20 K min^{-1}; atmosphere, helium, 50 cm^3 min^{-1}.

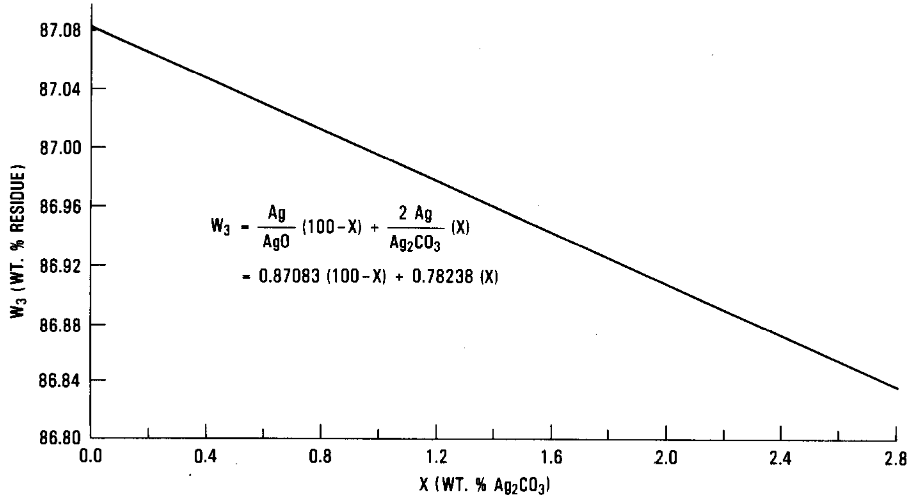

Fig. 3. Theoretical relationship between W_3 and the amount of Ag_2CO_3 contamination in an AgO sample.

A typical TG curve and its derivative for an AgO sample are shown in Fig. 2. In a previous paper [1], the interpretation of such curves for determination of the AgO, Ag_2O, Ag, and Ag_2CO_3 content of silver oxide samples was discussed. The rapid weight loss at about 493 K and the subsequent slow continuing weight loss up to about 683 K are caused by the decomposition of the Ag_2O_3 component of the AgO lattice into Ag_2O *. At about 683 K, the Ag_2O decomposes rapidly to Ag; the endothermicity of this decomposition causes the temperature of the sample thermocouple to decrease by 1–2 K as seen on the primary and derivative curves at about 683 K. The shoulder on the derivative peak at about 473 K is caused by the decomposition of the Ag_2CO_3 impurity according to reaction (1)

$$Ag_2CO_3 \rightarrow Ag_2O + CO_2 \qquad (1)$$

The first decomposition step for AgO is

$$2\ AgO \rightarrow Ag_2O + 0.5\ O_2 \qquad (2)$$

The Ag_2O formed in reaction (1) or (2) then decomposes according to

$$Ag_2O \rightarrow 2\ Ag + 0.5\ O_2 \qquad (3)$$

Thus, for a pure AgO sample, the value of the final plateau, W_3, which is the weight percent remaining, would be Ag/AgO × 100 = 87.083%. The final plateau for a pure Ag_2CO_3 sample would have a value of 2 Ag/Ag_2CO_3 ×

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* It has been well established that the AgO lattice is composed of Ag^{3+} and Ag^{+} species, i.e., $Ag_2O_3 \cdot Ag_2O$ [3].

100 = 78.238%. Figure 3 shows the effect of small amounts of Ag_2CO_3 impurity on the value of W_3 for AgO samples. W_3 is related to the weight percent Ag_2CO_3 impurity, x, according to

$$W_3 = \frac{\mathrm{Ag}}{\mathrm{AgO}}(100 - x) + \frac{2\,\mathrm{Ag}}{\mathrm{Ag_2CO_3}}(x) = 0.87083(100 - x) + 0.78238(x) \quad (4)$$

Thus, for samples containing only AgO and Ag_2CO_3, the amount of Ag_2CO_3 impurity can easily be determined from the measured value of W_3 alone.

The TG results for samples of the pure AgO material analyzed at intervals during a 19-month storage period are summarized in Table 1. The pure AgO material was stored during this period in a glass jar at room temperature in the dark. The excellent precision of the measurements can be seen by comparing multiple runs on the same date, e.g., runs 9–12, 13–15, 25–26 and 27–28 in which the W_3 values are always within ±0.01%.

To establish the validity of this measurement method for samples containing only AgO and Ag_2CO_3, the amount of AgO and Ag_2CO_3 was periodically determined by the TG–GC method that we developed for the analysis of silver oxide cathode material containing AgO, Ag_2O, Ag and Ag_2CO_3 [1]. The excellent agreement between the amount of AgO and Ag_2CO_3 determined by the TG–GC analysis method and that determined from measurement of W_3 alone is seen in Table 1 (runs 9, 21, 26 and 28).

The excellent stability of this AgO material is apparent from the analysis results over a 19-month period. During this time, no attempt was made to exclude atmospheric CO_2 from contact with the AgO. The stability of the AgO would, of course, be even greater after its incorporation as a cathode into a hermetically-sealed cell.

Decomposition reactions involving relatively small mass losses can be studied accurately with the 951 TGA provided that the assembly of the quartz rod and stainless steel spring clip into the cold beam member is performed with great care. The stainless steel spring clip is designed so that its expansion with increasing temperature compensates for the thermal expansion of the quartz rod. A very snug fit must be achieved between the rod and clip and between the clip and the cold beam member to prevent large apparent mass increases caused by movement of the rod or clip outward, thereby increasing the distance from the sample to the balance fulcrum. Another cause of the apparent mass increase during heating is the decrease in density with temperature of the purge gas atmosphere plus evolved gases from decomposition of the sample. The mass increase with an argon purge atmosphere was usually 40–50 μg. Figure 1 shows an example of this phenomenon. The increase was minimized by using helium ($d = 0.179$ g l^{-1}) instead of argon ($d = 1.78$ g l^{-1}) as a purge gas. Thus, with helium purge gas and a tightly-fitted rod and clip, we were able to limit the apparent mass increase to only 10 μg over the temperature range 298–773 K, i.e., 0.01% for a typical 100-mg sample. The same 10-μg mass increase was

TABLE 1

TG results for AgO cathode material

Date (d/m/y)	Run No.	Heating rate (K min^{-1})	Atm.	W_3(%)	Correction (%)	Corrected W_3 (%)	% Ag_2CO_3 [a]	% AgO [b]	% Ag_2CO_3 [c]	% AgO [c]
19/3/82	1	20.0	Ar	87.10	0.04	87.06	0.26	99.74		
25/3/82	2	20.0	Ar	87.12	0.05	87.07	0.15	99.85		
1/4/82	3	40.0	Ar	87.15	0.08	87.07	0.15	99.85		
5/4/82	4	1.0	Ar	87.09	0.04	87.05	0.37	99.63		
10/5/82	5	20.0	O_2	87.13	0.06	87.07	0.15	99.85		
24/5/82	6	20.0	Ar	87.07	0.04	87.03	0.60	99.40		
25/5/82	7	20.0	Ar	87.11	0.06	87.05	0.37	99.63		
30/6/82	8	20.0	Ar	87.07	0.05	87.02	0.71	99.29		
25/10/82	9	20.0	Ar	87.05	0.04	87.01	0.83	99.17	0.75	99.10
25/10/82	10	20.0	Ar	87.05	0.03	87.02	0.71	99.29		
25/10/82	11	20.0	Ar	87.07	0.05	87.02	0.71	99.29		
25/10/82	12	20.0	Ar	87.06	0.04	87.02	0.71	99.29		
9/12/82	13	20.0	Ar	87.06	0.07	86.99	1.05	98.95		

9/12/82	14	20.0	Ar	87.03	0.04	86.99	1.05	98.95		
9/12/82	15	20.0	Ar	87.02	0.03	86.99	1.05	98.95		
25/1/83	16	20.0	Ar	87.02	0.03	86.99	1.05	98.95		
11/3/83	17	20.0	Ar	87.00	0.02	86.98	1.16	98.84		
4/4/83	18	20.0	Ar	86.94	0.02	86.92	1.84	98.16		
6/4/83	19	2.0	Ar	86.99	0.05	86.94	1.62	98.38		
7/4/83	20	0.2	Ar	87.03	0.09	86.94	1.62	98.38		
16/6/83	21	20.0	Ar	86.98	0.06	86.92	1.84	98.16	1.44	98.48
21/6/83	22	20.0	Ar	86.97	0.06	86.91	1.96	98.04		
16/8/83	23	20.0	He	86.89	0.01	86.88	2.30	97.70		
2/9/83	24	20.0	He	86.88	0.02	86.86	2.52	97.48		
28/10/83	25	20.0	He	86.91	0.01	86.90	2.07	97.93		
28/10/83	26	20.0	He	86.92	0.01	86.91	1.96	98.04	1.69	98.17
16/11/83	27[d]	20.0	He	87.06	0.01	87.05	0.37	99.63		
16/11/83	28[d]	20.0	He	87.06	0.01	87.05	0.37	99.63	0.25	99.72

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[a] % Ag_2CO_3 calculated from W_3 alone (eqn. 4).

[b] $AgO = 100 - \% Ag_2CO_3$.

[c] Determined by TG–GC method (ref. 1).

[d] Fresh AgO sample.

obtained in runs with an empty platinum boat or with an inert 100-mg sample, e.g., Ag powder.

CONCLUSIONS

The high purity and excellent stability of chemically-prepared AgO cathode material (RAYOVAC Corporation) were determined by TG using a DuPont 1090 thermal analysis system. The composition of freshly-prepared material was 99.6–99.8% AgO, 0.2–0.4% Ag_2CO_3. The amount of Ag_2CO_3 gradually increased to 2.0–2.5% from reaction of the sample with atmospheric CO_2 during storage for 19 months under ambient conditions.

Excellent precision and accuracy are attainable with the DuPont 951 TGA module provided that the quartz rod balance beam and its retaining stainless steel spring clip are properly installed and further provided that the apparent sample mass increase is known for the temperature range studied and the purge gas employed. With a tightly-fitted rod and clip assembly and a helium-purge atmosphere, the error from the apparent mass increase during heating was limited to about 10 μg from ambient temperature to 773 K.

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