Malaysian Journal of Chemistry, 2004, Vol. 6, No. 1, 067 - 071

Determination of AgO in AgO/Ag_2O Mixture by Thermogravimetric Analysis

Riaz Qadeer[*], Rizwan Hussain[**], Sumeera Ikram[**], Fiaz Ahmed[**] and Arshad Munir[**]
[*]Pakistan Atomic Energy Commission, P.O. Box 1611, Islamabad, Pakistan
[**]National Development Complex. P.O. Box 2216, Islamabad, Pakistan

Abstract : AgO is considered to be a prime source for producing high-energy zinc-silver batteries, and Ag_2O is always accompanied with AgO during the production of AgO. The presence of Ag_2O in AgO decreases the potential of the battery. Determination of AgO purity is a tedious job for the analytical chemist. It usually involves laborious and lengthy wet chemistry processing and very expensive analytical technique such as XRD, SEM, XPS spectroscopy etc. We have developed and standardized a simple, fast and economical method based on thermo-gravimetry for the determination of AgO in AgO/Ag_2O. This method is being applied successfully for the purity determination of AgO during its production.

Received : 28.08.03; accepted : 08.04.04

Introduction

Zinc-silver oxide couple has long been recognized as the leading system for high energy density zinc-silver batteries either on a weight or on a volume basis. Two types of silver oxide i.e., mono-valent silver oxide (Ag_2O) and divalent silver oxide (AgO) are being used as cathode materials [1]. The latter has a higher theoretical potential (1.8V) and because of an additional chemical reduction from AgO to Ag_2O, it has higher capacity too [2]. Owing to the higher potential and capacity, AgO is widely used as a cathode material. During the production of AgO, Ag_2O is produced at the same time. For a better performance of the battery, the concentration of Ag_2O in AgO should be as low as possible. This can be controlled by controlling the experimental conditions during the synthesis of AgO.

Wet chemical method [3] and various physical analytical techniques such as x-ray diffraction spectrometer (XRD)/ gas chromatography (GC) [4], x-ray photon spectroscopy (XPS) [5-6], and electron microscope are used to measure the concentration of AgO in a mixture of AgO/Ag_2O. These methods are time consuming and expensive for routine analysis and also these equipment are not readily available in every laboratory. In view of this, a simple, economical, fast and reliable method based on thermo-gravimetry for the estimation of AgO in AgO/Ag_2O mixture has been developed and standardized. Parkhurst et al. [7] used this technique for the analysis of silver oxide mixture precisely, and need further work to establish the accuracy of the method based on thermal analysis. The present paper describes the details of the method for the precise and accurate determination of the purity of AgO in AgO/Ag_2O mixture by thermo-gravimetric analysis.

Experimental

Chemicals used in this study were: Silver (I) oxide, Ag_2O [Merck, item No. 1015037) and silver (II) oxide, AgO [Aldrich, item No. 22,368-8].

Different standard mixtures of AgO and Ag_2O were prepared in different ratios and the mixtures were homogenized using an agate mortar.

TG curves were recorded in dynamic argon atmosphere (40 ml/min) on a TGA –7 thermo-gravimetric analyzer (Perkin Elmer). Samples were heated from ambient temperature to 1000 ^oC at a heating rate of 20 ^oC/min.

Result and Discussion

TG curves of standard mixtures containing known amounts of AgO and Ag_2O are shown in Figures 1-6. It is evident from Figure 1 that AgO decomposes in two steps. The initial decomposition starts after 100 ^oC, whereas second decomposition step starts around 330 ^oC. In both decomposition steps, half oxygen molecule is liberated to produce silver residue according to the following mechanism:

$$AgO \text{ ------------> } Ag_2O + \tfrac{1}{2} O_2 \qquad \text{Step 1}$$
$$Ag_2O \text{ ----------- > } 2Ag + \tfrac{1}{2} O_2 \qquad \text{Step 2}$$

Weight losses of 6.325% and 7.125% were calculated by using a computer program for the first and second decomposition, respectively. Ag_2O decomposes in a single step starting at 330 ^oC. Residue analyzed by ICP-AES at the end of thermo-gravimetric analyses confirmed the formation of silver.

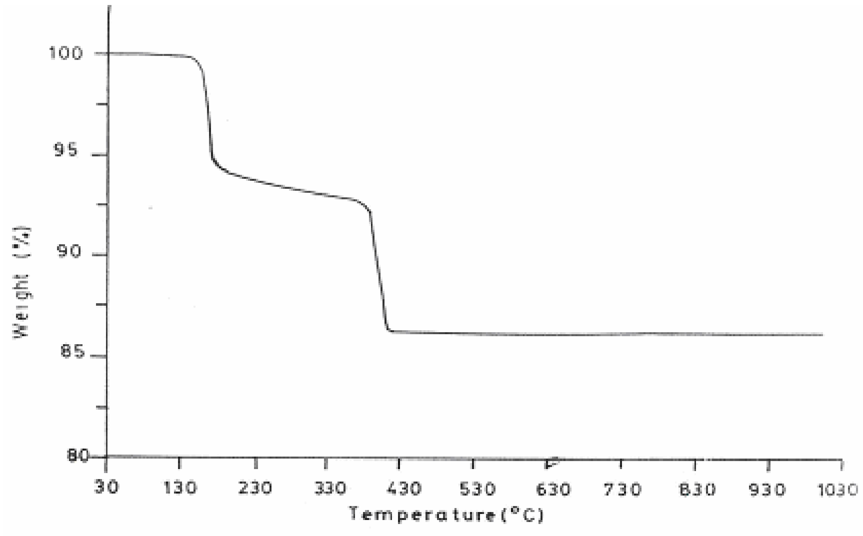

Figure 1 : TG curve of AgO

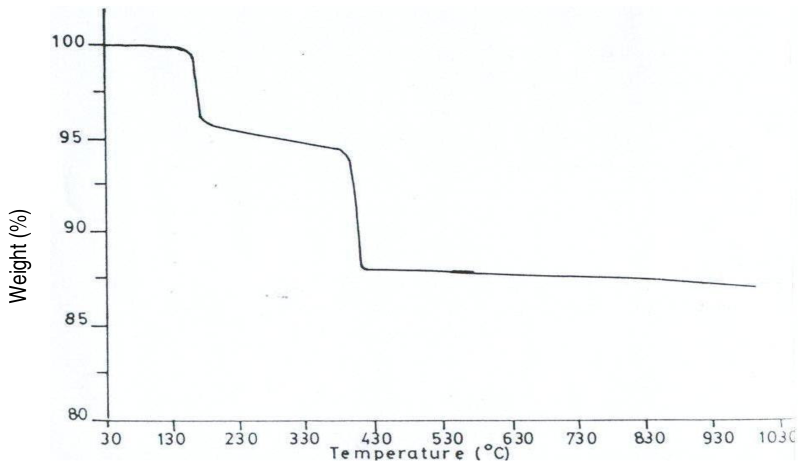

Figure 2 : TG curve of a mixture containing 0.2 g AgO and 0.05 g Ag_2O.

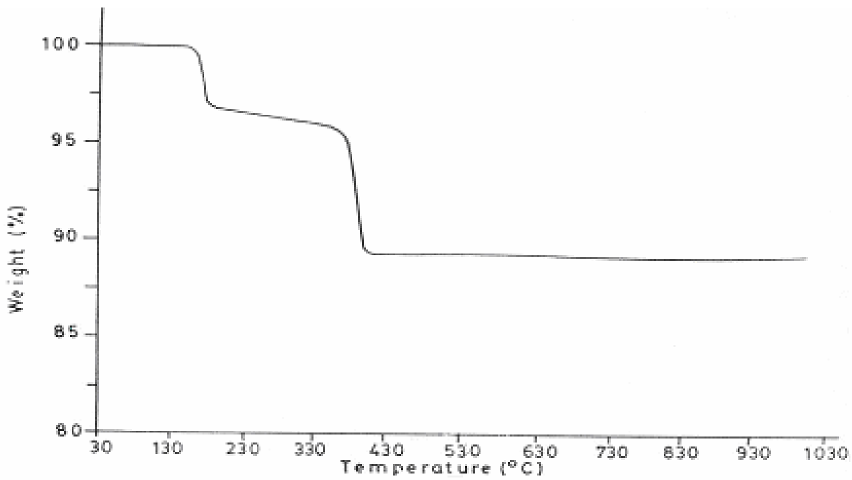

Figure 3 : TG curve of a mixture containing 0.15 g AgO and 0.10 g Ag_2O.

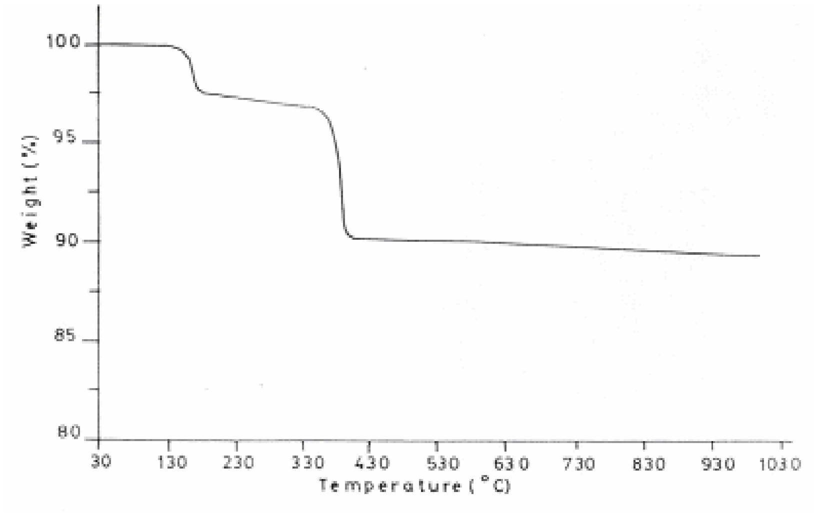

Figure 4 : TG curve of a mixture containing 0.10 g AgO and 0.15 g Ag_2O.

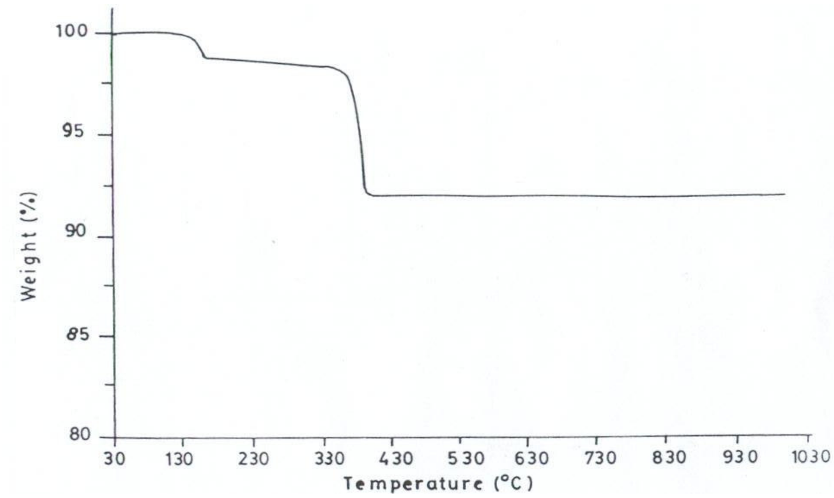

Figure 5 : TG curve of a mixture containing 0.05 g AgO and 0.20 g Ag_2O.

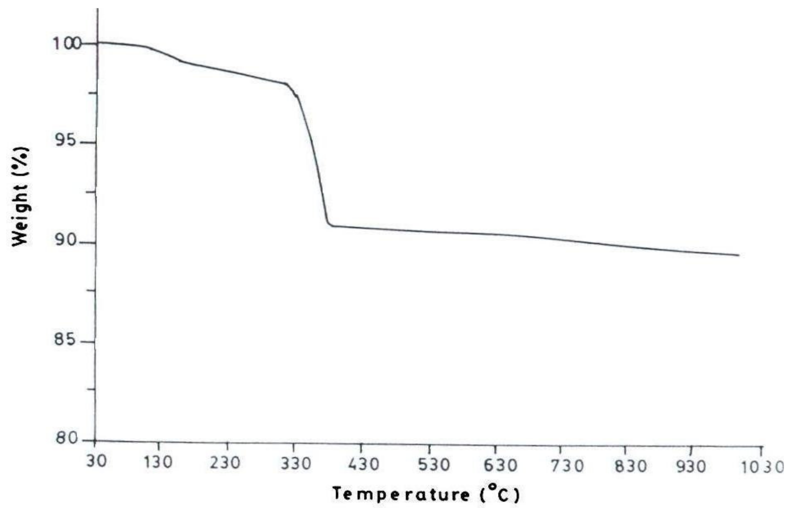

Figure 6 : TG curve of Ag_2O.

Weight loss of the first step of decomposition was utilized to determine the concentration of AgO in the AgO/Ag_2O mixtures. Weight losses observed for different standard samples are presented in Table 1. It is evident from Table 1 that the value of % weight loss decreases as the concentration of AgO in AgO/Ag_2O mixture decreases. A calibration curve plotted between concentration of AgO (%) and weight loss (%) is shown in Figure 7. The following mathematical relation was obtained after subjecting the calibration curve data to linear regression:

$$\text{Weight loss (\%)} = 0.1158 + 0.608 \times \text{Conc.}_{AgO} (\%)$$

The correlation coefficient (r) of 0.9938 indicated a good fit of the data to a straight line. The above equation was applied to deternine the concentration of AgO and the measured values are given in Table 2. These samples were also sent to another laboratory for the determination of AgO concentration by XRD spectrometer for comparison. The results measured by XRD (Table 2) match fairly well with the results obtained by our TG method.

Table 1 : Determined values of weight losses of the first step of decomposition for different standard mixtures of AgO/Ag_2O.

Std. No.	AgO:Ag_2O ratio, %	Weight loss,%
1.	98:02	6.325
2.	80:20	4.756
3.	60:40	3.556
4.	40:60	2.674
5.	20:80	1.393
6.	0.5:9.5	1.227

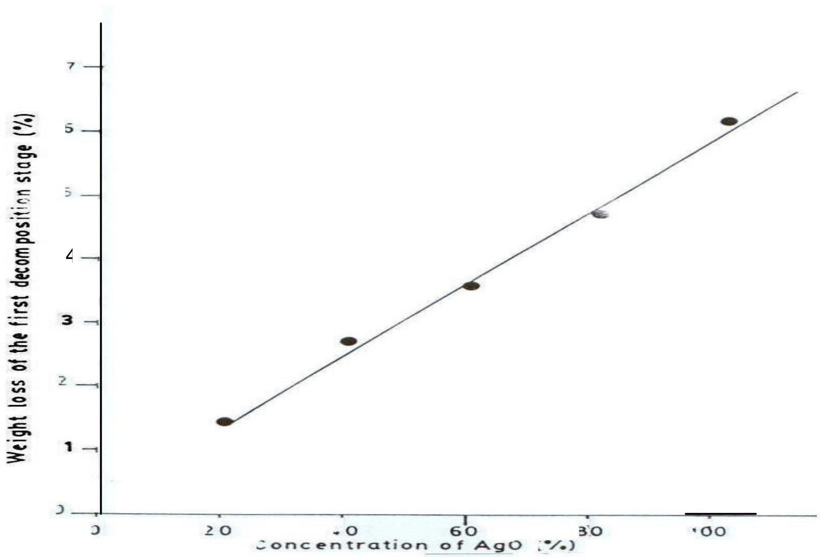

Figure 7 : Calibration curve for AgO concentration measurement

Table 2 : Measured Concentration of AgO

Batch No.	AgO (%)	
	TG Method	XRD Method
1.	93.25 ± 0.17	93.56 ± 0.13
2.	96.70 ± 0.10	96.63 ± 0.20
3.	92.55 ± 0.34	93.00 ± 0.35
4.	97.36 ± 0.22	97.02 ± 0.23

Conclusion

The developed TG method for the determination of AgO concentration in AgO /Ag_2O mixture is precise, fast, and easy to operate and require no chemical for analysis. This method is used successfully for the routine determination of AgO concentration in our laboratory. The method is also cost effective since it does not require any extra efforts and equipment for sample preparation.

References

1. Fleischer A. and Lander J.J. (1971) Zinc Silver Oxide Batteries, *Willey, New York*.
2. James M.D. and Elliot M.M. (1994) In Hand Book of Batteries, 2nd Edition, editor-in-chief, D. Linden, *McGraw Hill Inc., New York*, **18.1 - 18.14**.
3. Dehua Yi. and Baogui H. (1991) Kuangye Gongcheng, **11**, 66; Chemical Abstract No. 116:75173f (1992).
4. Dehua Yi. and Baogui H. (1992) Kuangye Gongcheng, **11**, 66; Chemical Abstract No. 116:75173f.
5. Mansour A.N and Dallek S. (1990) *J. Electrochemical Society*, **137**, 1467.
6. Hoflund G.B., Weaver J.F. and Epling W.S. (1995) *Surface Science Spectra*, **3,** 157 & 163
7. Hoflund G.B., Hazos Z.F. and Salaita G.N. (2000) Phy. Rev. B: Condens. *Mater. Phys*., **62**, 11126.
8. Parkhurst W.A., Dallek S. and Larrik B.F. (1982) Naval Staff Weapon Center Report No. NSWS/TR-82-420 SBI–AD-F500115, **30**, Chemical Abstract, 99:63436m.
9. Parkhurst W.A., Dallek S. and Larrik B.F. (1983) Naval Staff Weapon Center Report No. NSWS/TR-82-420 SBI–AD-F500115, **30**, Chemical Abstract No. 99:63436m.