The Decomposition of AgO in Alkaline Solutions

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ABSTRACT

The gassing rate, r, of powder AgO samples, made by the chemical oxidation of $AgNO_3$, was measured in gassing pipettes. The mean r of 52 AgO samples at 200 hr (AgO content $\geqq$95%, $r_{200} \leqq 35$ µl/day/g) was 23.0 µl/day/g. Gassing rates at different times and in different solutions, respectively, are correlated. r increased with increasing NaOH concentration, temperature, and pelletizing pressure, and with ball milling. r of AgO samples made in the presence of transition elements (added as compounds) were, in general, larger than r of samples with nontransition elements. The effect of Co and Ni is especially catastrophic. Pb suppressed r of highly gassing AgO samples regardless of the method of addition.

Silver(I)-silver(III) oxide, commonly designated as AgO, is thermodynamically unstable in alkaline electrolytes (KOH, NaOH) but has a reasonable degree of metastability (1). Oxygen evolution is the end result of the decomposition reaction

$$2AgO \rightarrow Ag_2O + \tfrac{1}{2} O_2 \qquad [1]$$

Denison (2), however, claimed that AgO is stable in 20-40% KOH solutions.

Oxygen overvoltage of the local cell action and formation of a protective Ag_2O film on the AgO is thought to be the reason for its metastability (1, 3). The decomposition of AgO (*a*) is light sensitive (4, 1), (*b*) increases with increasing temperature (1, 3, 5-8), and (*c*) increases with increasing KOH concentration (1, 7, 8). The decomposition of "Ag_2O_3" (a reaction product of $AgNO_3$ and $K_2S_2O_8$) in KOH ($< 1N$) was found by Stehlik (6) to be a first order reaction with an activation energy of 22 kcal/mole.

The stability of AgO seems to depend on its mode of preparation (9) and the various AgO samples were found to decompose at different rates (1, 5, 7). Unoxidized silver metal increased the rate of decomposition of AgO (3, 7) whereas Ag_2O did not affect the stability of AgO (3). Boer and Ormondt (10) found that the incorporation of Mn, Cu, and Co into AgO during its preparation decreased its stability, whereas Cd increased the stability of $(Ag_3O_4)_a \cdot AgSO_4$ (where a varies from 2 to 2.5). The presence of carbon in AgO battery plates is claimed to have no adverse effects (11), whereas CO_2 decomposes AgO (10).

The addition of Al_2O_3 to alkaline electrolytes is said (12) to inhibit the oxygen evolution. The addition of ZnO to KOH electrolytes decreases the decomposition rate of AgO to Ag_2O (1, 5) and prevents the reduction of Ag_2O to Ag (5). According to Amlie and Rüetschi (1), the addition of zincate ions has little influence because the addition of ZnO to KOH electrolyte reduces its OH^- activity and this causes the decrease of the decomposition rate. Cahan (13) showed that the addition of PbO to 40% KOH (and other electrolytes) markedly reduced the gassing rate of AgO; 1% PbO was found to be the optimum.

Yoshizawa and Takehara (14) have shown that the formation of AgO was retarded by Te and Sb which lowered the oxygen overvoltage or made the decomposition of AgO easier.

The effect of intentionally added inorganic additives on the electric resistivity of AgO was described in a previous paper (15). It was found that the AgO content of samples was very low in the presence of small amounts of Co and Ni indicating either an inhibited formation or an accelerated decomposition of AgO during its preparation in alkaline medium. Since AgO is mainly used in sealed cells, it is very important to know its gassing rate in the absence or presence of beneficial or detrimental additives.

The gassing, *i.e.*, decomposition rate of AgO samples (prepared by chemical oxidation of $AgNO_3$) was determined in alkaline electrolytes as a function of time, NaOH concentration, temperature, porosity, surface area, pelletizing pressure, and intentionally added inorganic additives.

Experimental

The AgO samples were prepared by the chemical oxidation of $AgNO_3$ with alkaline $K_2S_2O_8$ (16). The inorganic additives were incorporated into AgO during its preparation (15), initially at one concentration level: 1000 parts (element) per million parts of Ag, *i.e.*, 1000 ppm (Ag). Subsequently, some of the beneficial and detrimental impurities were studied as a function of concentration.

The amount of oxygen evolved in contact with alkaline solutions was determined in a modified Amlie-Rüetschi microvolumetric apparatus (1), "gassing pipette." The ground glass joint of their apparatus was replaced by an 18/7 O-ring joint (Pyrex, Buna N rubber ring) to eliminate "freezing" of the joint. Furthermore, filling of the gassing pipette (0.2, 0.5, or 1.0 ml capacity) with the electrolyte and joining of the two parts is easier with an O-ring than with a ground glass joint. Loose AgO powder (0.5000 ± 0.0002g) was used for the determinations unless otherwise mentioned.

The assembled gassing pipettes were placed in a constant temperature oil bath and allowed to equilibrate for 1 hr. The position of the meniscus of the electrolyte column after this time is considered as the zero hour reading; at least two parallel measurements were made on each sample at 37.78 ± 0.02°C (100°F) unless otherwise mentioned. The measurements were made in the presence of light.

The gassing rate is calculated at various time intervals from the volume of the evolved gas. This gassing rate is a cumulative average gassing rate and is not corrected for water vapor pressure.

The decomposition of AgO was measured in two alkaline electrolytes, unless otherwise mentioned. One of them contained $8.6N$ NaOH and $2.2N$ Na_2ZnO_2, whereas the other had $9.7N$ KOH and $2.8N$ K_2ZnO_2.

The data were subjected to statistical analysis. The "mean" parameter refers to the average of the samples the distribution of which tends to normality. The least square method was used for regression and curve fittings. If the coefficient of correlation, R of linear regression was low, the data were subjected to polynomial regression analysis.

Results and Discussion

Gas evolution as a function of time.—Figure 1 shows the gas evolution and the gassing rate of an AgO sample (98.1% AgO content) as a function of time in

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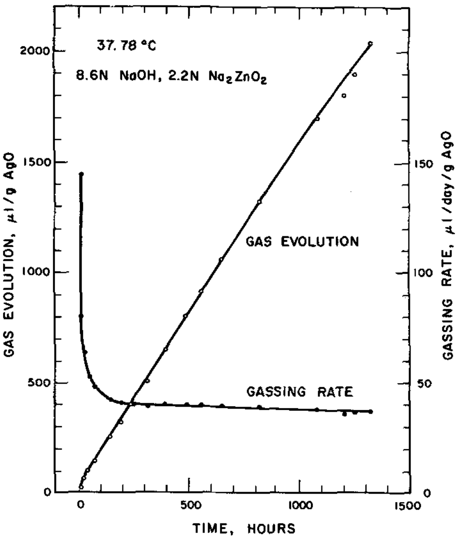

Fig. 1. Gas evolution and gassing rate of AgO as a function of time

8.6*N* NaOH and 2.2*N* Na_2ZnO_2 electrolyte. It can be seen that gas evolved almost linearly with time. The initial nonlinearity shows up clearly in the rapid decrease of the gassing rate. After approximately 200 hr the decrease of the gassing rate is small. On the basis of these results and other considerations, the minimum duration of the gassing test was chosen to be about 200 hr and this is the gassing rate, r_{200}, given, unless otherwise mentioned.

This test is time consuming (200 hr) and the long delay in obtaining the gassing rate is not well suited for routine testing. It was observed that the gassing rate-time curves were more or less parallel to each other. Figure 2 shows an approximately linear relation ($R = 0.896$) between the gassing rates of 114 AgO samples at 20 and 200 hr (samples with $r_{20} > 150$ µl/day/g are not shown in Fig. 2 but were taken into the consideration in the regression analysis). The analysis of variance for a quadratic regression reveals that the linear term is dominating (degree of freedom, $df = 1$, mean square, $MS = 13{,}791$), the increase due to the quadratic term is negligible ($df = 1$, $MS = 24.58$), and the deviation about regression is small ($df = 111$, $MS = 30.18$). Because of low R, the gassing rate at 20 hr (approximately overnight) and the linear regression equation in Fig. 2 can be used only for semiquantitative prediction of the gassing rates of AgO samples. This test, however, may be useful in the production of AgO and in testing a new batch of chemicals for sealed-cell electrolytes.

The mean gassing rates, $\bar{r}_{200}$, of AgO samples (AgO content $\geqq$ 95.0%) were calculated for arbitrarily chosen levels and are shown in Table I. The majority of the considered AgO samples had $r_{200} \leqq 25.0$ µl/day/g which clearly shows up in mean gassing rates. The standard deviation of $\bar{r}_{200}$ becomes smaller mainly due to the narrower gassing rate levels. These results support the observation of several workers (1, 5, 7, 9) that various AgO samples decompose at different rates.

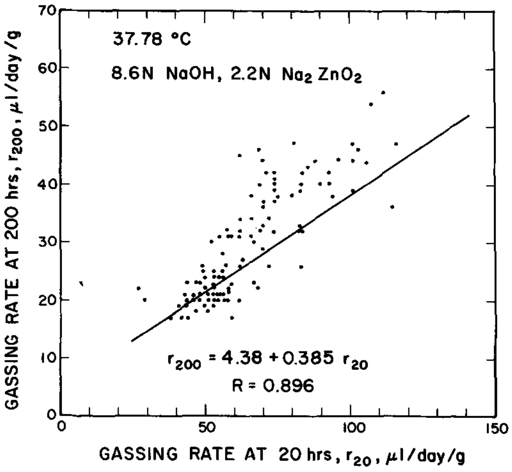

Fig. 2. Gassing rates of AgO samples at 20 and 200 hr.

Table I. The mean gassing rate of AgO samples in 8.6*N* NaOH, 2.2*N* Na_2ZnO_2 solution

r_{200}, µl/day/g	Number of samples	Mean		Standard deviation	
		r_{200}, µl/day/g	AgO content, %	r_{200}, µl/day/g	AgO content, %
$\leqq$35.0	52	23.0	98.1	4.62	0.82
$\leqq$25.0	37	20.6	98.2	2.32	0.75
$\leqq$20.0	15	18.3	98.1	1.23	0.64
$\leqq$18.0	5	16.8	97.8	0.82	1.00

It can be seen in Table I that the mean AgO content of the AgO samples did not change appreciably with the gassing rate. No correlation was found between the gassing rate and AgO content down to 60%.

According to Eq. [1], ½ mole oxygen gas is obtained from 2 moles of AgO at its complete conversion to Ag_2O. Thus, 50,483 µl O_2, a, would evolve per gram AgO (98.1% AgO content) at 37.78°C and 760 mm Hg. If the decomposition is a first order reaction

$$\log \frac{a}{a-x} = \frac{k}{2.303} t \qquad [2]$$

should be linear. In this equation x is the volume of the evolved gas/g AgO at time t and k is the rate constant. Figure 3 shows this to be the case with $R = 0.9988$. The rate constant is calculated from the slope to be 3.09×10^{-5}/hr, *i.e.*, 0.271/year in 8.6*N* NaOH and 2.2*N* Na_2ZnO_2 solution at 37.78°C. It should be mentioned that others consider the decomposition to be zero (7, 8), pseudo zero (7), or first order (6) reaction.

Influence of concentration and temperature.—Figure 4 shows the gassing rate of AgO at 42 hr (98.4% AgO content) to increase with increasing NaOH concentration at all temperatures (these solutions do not contain ZnO). This is in agreement with the results in KOH (1, 7, 8). In view of the large gassing rates at 60°C, r_{42} was chosen instead of r_{200} even though some uncertainty may exist (see Fig. 1), mainly at lower temperatures. Linear regression analysis of the data in Fig. 4 ($R \geqq 0.983$) yielded physically incorrect nega-

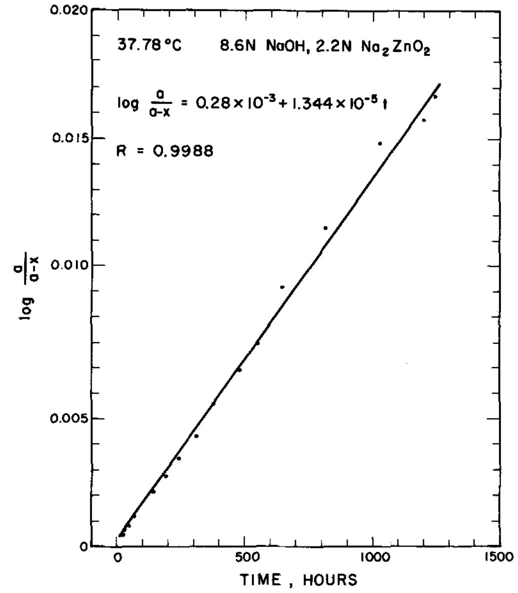

Fig. 3. First-order reaction plot of the decomposition of AgO in alkaline solution.

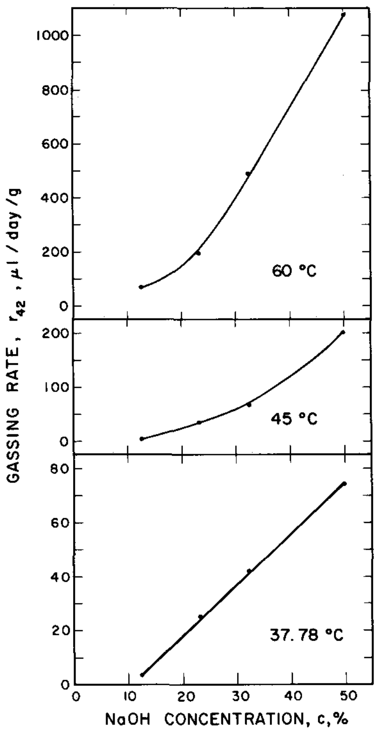

Fig. 4. Gassing rates of AgO as a function of NaOH concentration at various temperatures.

tive intercepts, *i.e.*, no gassing would take place below a certain NaOH concentration. This would be contrary to the results obtained by others in KOH (6-8). Polynomial regression analysis revealed that the curves in the investigated concentration range are predominantly linear and the increase due to the quadratic and cubic terms is slight. The slope of the log r_{42} – log c curve was found to be 2.2, 2.7, and 2.0 at 37.78°, 45°, and 60°C, respectively ($R \geqq 0.973$).

Figure 4 reveals also the known temperature dependence of the gassing rate in alkaline solutions (1, 3, 5-8); the gassing rate increased with increasing temperature. The rate constants, k in various NaOH solutions were calculated by the half-life method from r_{42} and r_x, the gassing rate at the longest available time ($x \geqq 42$ hr). The activation energies, E were calculated from the slopes of log k *vs.* $1/T$ curves. The activation energy of the complex decomposition reaction of AgO (1, 3, 5, 7, 8, 17) was calculated from all data to be 26 kcal/mole. E calculated from r_{42} was found to be 24 kcal/mole whereas E from r_x is 28 kcal/mole. These results are close to the following values obtained by other workers: (*a*) 28.4 kcal/mole in 10-50% KOH solutions (8), it was calculated from gassing rates at approximately 35 hr; (*b*) 22 kcal/mole for "Ag_2O_3" in solutions up to 1*N* KOH (6); and (*c*) 30 kcal/mole for the decomposition of AgO in air (18).

Calculating E from Otto's gassing rates in 11.6*M* (44%) KOH solution [(7), Table I] through the half-life method, one obtains 18.9 kcal/mole. This is considerably lower than the aforementioned E values for AgO. If the gassing rate at 100°C, *i.e.*, r at approximately 20 hr is neglected, 17.2 kcal/mole is obtained from gassing rates at approximately 200 hr and more. The difference in activation energies of the two groups is probably due to the decrease of gassing rate with time, mainly in the beginning of the test.

Figure 5 shows log k *vs.* $1/T$ in two zincate-containing electrolytes. The E values calculated from their slopes are: 21.0 and 23.6 kcal/mole in 9.7*N* KOH, 2.8*N* K_2ZnO_2 and 8.6*N* NaOH, 2.2*N* Na_2ZnO_2 solutions, respectively. The k values were obtained from gassing rates at 100 hr and more. These lower E values seem to support the aforementioned explanation for the difference of E.

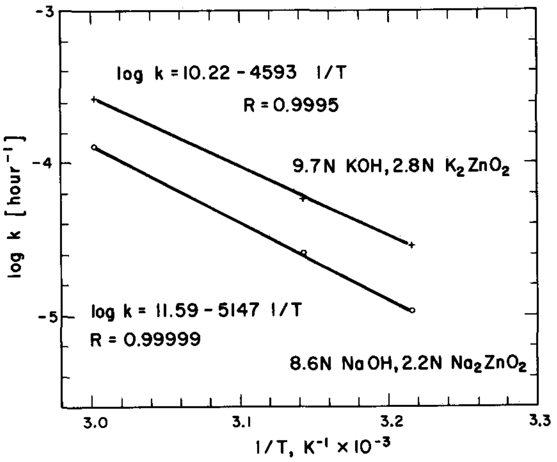

Fig. 5. Rate constants as a function of temperature

Correlation of r in various solutions.—The composition of the electrolyte in AgO cells is varied and the gassing rates are usually determined in each of them. This is, however, time consuming. Figure 6 shows the correlation of the gassing rates (r_{200}) in two frequently used battery electrolytes. It can be seen that the gassing rate in 9.7*N* KOH, 2.8*N* K_2ZnO_2 solution is approximately three times larger than in 8.6*N* NaOH, 2.2*N* Na_2ZnO_2 solution. Even though the data are scattered ($R = 0.887$), the linear relation allows a semiquantitative prediction of the gassing rate in one of the solutions if r is known in the other one.

Amlie and Rüetschi (1) found that the decomposition rate is larger in 10*N* KOH (40%) solution than even in 13.8*N* (40%) NaOH. This could be explained by the different activities of KOH and NaOH. The activity, a is given by $a = \gamma m$ where γ is the mean molal activity coefficient and m is the molality of the solutions. Since $m_{KOH} = 8.96$, $m_{NaOH} = 12.71$, $\gamma_{KOH} = 4.82$, and $\gamma_{NaOH} = 6.12$ [obtained by linear interpolation of the published values (19)], activities are: $a_{KOH} = 43.2$, $a_{NaOH} = 77.8$. It can be seen that the activities are opposite to the gassing rate values and thus, the activities of KOH and NaOH cannot account for the difference in gassing rates. Unfortunately, the individual ionic activities are not available for correlation.

Effect of pressure.—The gassing rate of loose AgO powder samples is measured in this work. AgO, however, is usually compressed in actual cells and therefore it was of interest to investigate the gassing rate of AgO as a function of pelletizing pressure. Figure 7 shows the increase of the gassing rate with increasing pelletizing pressure in both cases. It is evident that

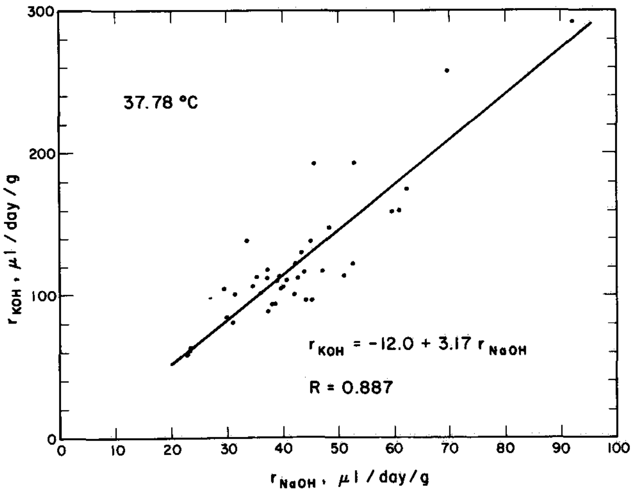

Fig. 6. Gassing rates of AgO samples in 9.7*N* KOH, 2.8*N* K_2ZnO_2 (r_{KOH}) and 8.6*N* NaOH, 2.2*N* Na_2ZnO_2 (r_{NaOH}) solutions.

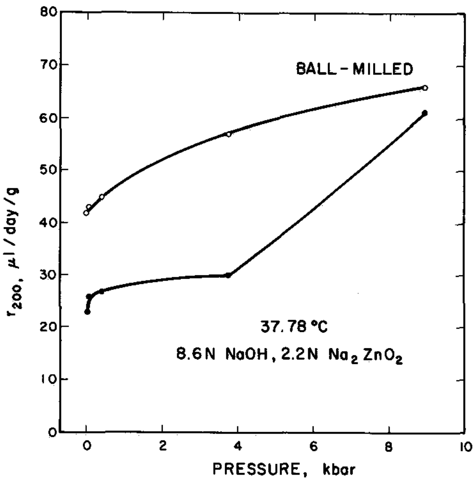

Fig. 7. Gassing rate of AgO as a function of pelletizing pressure

ball-milling of the AgO sample is detrimental. The gassing rate of pellets made from ball-milled AgO was markedly higher than that of unmilled AgO sample at pressures up to approximately 4 kbar; at the highest pressure the difference became small. In view of these results and the pressure dependence of resistivity (15), the pressure of the pelletizing of AgO should be kept to an optimized minimum.

Influence of surface area.—The BET surface area of AgO samples did not correlate with gassing rate of AgO samples contrary to the observation of Amlie and Rüetschi (1) who found a slight correlation. The mean surface area of 13 AgO samples is 1.12 m^2/g (standard deviation, $s = 0.39$) and the $\bar{r}_{200}$ is 22.8 μl/day/g ($s = 3.2$). The surface area increased with decreasing AgO content of the samples (0.86 to 1.79 m^2/g between 98.8 and 71.8%, respectively) and with increasing rate of $AgNO_3$ addition during the preparation of AgO (0.63 to 0.99 m^2/g between 4.25 and 34g $AgNO_3$/min). The surface area increased by *ca.* 50% in the presence of 1000 ppm (Ag) Pb (1.62 m^2/g) but Sn and Hg did not influence it.

The pore volume of AgO samples (determined by mercury intrusion in an Aminco-Winslow porosimeter) showed no correlation with the gassing rate. The mean pore volume of 43 AgO samples ($r_{200} \leq 35.0$ μl/day/g) was found to be 0.57 ml/g ($s = 0.05$) at a mean gassing rate of 23.7 μl/day/g ($s = 4.5$). The pore volume (0.525 ml/g) of Otto's AgO sample (7) is close to the mean pore volume. The gassing rates of this section were measured in the 8.6*N* NaOH, 2.2*N* Na_2ZnO_2 solution.

Effect of inorganic additives.—The influence of various inorganic additives on the resistivity of AgO samples was described separately (15). Here, their effect on the gassing rate of AgO samples is described. Tables II and III show the results for the investigated elements (added as compounds) at a concentration of 1000 parts by weight per million parts of silver used for the preparation of AgO, *i.e.*, 1000 ppm (Ag). The AgO content should not decrease due to this small amount of additive unless it is detrimental. The AgO contents of samples made in the presence of nontransition elements varied slightly but all were > 96.0%. Samples with transition elements had, in general, lower AgO contents and Co and Ni caused the largest drop.

AgO samples made in the presence of nontransition elements had, in general, low gassing rates (Table II). Sb leads the list with a gassing rate of 46 μl/day/g and only samples with Mg, Ba, and Sn show gassing rates above 30 μl/day/g. On the other hand, AgO samples with Pb, Al, Cd, and Zn have gassing rates ≤ 20 μl/day/g.

The incorporation of Cd was found (10) to increase the stability of $(Ag_3O_4)_a \cdot AgSO_4$ (where a varies from 2 to 2.5) and the addition of Al_2O_3 (12) and PbO (13) to alkaline electrolyte, to inhibit and markedly reduce, respectively, the oxygen evolution from AgO. The corresponding low gassing rates of Table II support these findings. The decrease of gassing rate of AgO in the presence of large amounts of ZnO (1, 5) is said (1) to be due to the decrease of OH^- activity of the alkaline solution and the zincate ions have little influence (1). The 20 μl/day/g gassing rate in the presence of 1000 ppm (Ag) Zn is only slightly below the mean gassing rate and the addition of Zn seems to have little influence. Yoshizawa and Takehara (14) found that the AgO formation is retarded on a silver alloy anode containing 2% Te or Sb because the oxygen overvoltage is decreased or the decomposition of AgO is easier in their presence. Table II shows that the sample with Sb has the highest gassing rate. According to Amlie and Rüetschi (1), the decomposition rate of AgO must depend on the oxygen overvoltage. Yoshizawa and Takehara (14) measured the anode potential of silver and its alloys (2% alloying element) during oxygen evolution and found the oxygen overvoltage to decrease by *ca.* 100 mV according to following series (20): pure Ag > Cd > Au > Pb > In > Cu > Te > Sb. The corresponding gassing rates are: 16.8,[2]

Table II. Effect of nontransition element impurities (added as compounds) on the AgO content and gassing rate of AgO samples in 8.6*N* NaOH, 2.2*N* Na_2ZnO_2

Periodic Table group	Element, 1000 ppm (Ag)	AgO content, %	Gassing rate, μl/g AgO/day
—	—	98.1	$\bar{r}_{200} = 23$*
II A	Mg	97.2	32
	Ca	98.5	23
	Sr	97.8	21
	Ba	97.4	33
II B	Zn	98.5	20
	Cd	97.7	16
	Hg	97.5	22
III	Al	98.5	17
	In	97.1	27
	Tl	96.0	22
IV	Ge	98.3	22
	Sn	97.2	32
	Pb	98.5	17
V	As	98.3	25
	Sb	96.8	46
	Bi	98.4	23

* See Table I.

Table III. Effect of transition element impurities (added as compounds) on the AgO content and gassing rate of AgO samples in 8.6*N* NaOH, 2.2*N* Na_2ZnO_2 solution

Transition element	Elements, 1000 ppm (Ag)	AgO content, %	Gassing rate, μl/g AgO/day
—	—	98.1	$\bar{r}_{200} = 23$*
First series	V	96.0	18
	Cr	97.7	18
	Mn	95.3	60
	Fe	96.4	55
	Co	37.7	8800[1]
	Ni	38.0	9000[2]
	Cu†	97.3	65
Second series	Y	96.5	44
	Zr	88.0	5800[3]
	Mo	98.5	28
	Pd	97.3	174
Third series	Ta	92.2	43
	W	98.5	171
Lanthanides	Ce	95.7	648[4]
	Pr	96.9	24
	Eu	97.5	39
Actinides	Th	96.7	72

* See Table I.
† Considered as transition element, see ref. (15).
[1] At 5.5 hr.
[2] At 5.0 hr.
[3] At 4.0 hr.
[4] At 69.0 hr.

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[2] The lowest $\bar{r}_{200}$ used (Table I).

16, —, 17, 27, 65, —, 46 μl/day/g in 8.6*N* NaOH, 2.2N Na_2ZnO_2 at 37.78°C. It can be seen that the gassing rate increases with decreasing oxygen overvoltage of silver alloys mainly in the second half of the aforementioned series.

Table III shows the gassing rates of AgO samples made in the presence of transition elements (15) to be, in general, larger than the gassing rates of samples with nontransition elements. The presence of 1000 ppm (Ag) Co, Ni, and Zr is catastrophic from the viewpoint of gassing rates. Samples with Ce, Pd, and W have intolerably large gassing rates. On the other hand, AgO samples made in the presence of the common V, Cr, and Mo have low gassing rates because they were oxidized and washed out from the precipitate as meta-vanadate, chromate, and molybdate, respectively. When Mn was incorporated, part of it was oxidized to permanganate (red-wine colored mother liquor) and part of it precipitated with AgO. This supports the similar observation of Boer and Ormondt (10). The large gassing rates support their observation (10) that the incorporation of Mn, Cu, and especially Co into AgO during its preparation decreased its stability, *i.e.*, increased the amount of oxygen evolved at 20°C and 77% relative humidity.

Gassing rate as a function of additive concentration.—In view of the aforedescribed, mainly detrimental, effects of the additives, it was of interest to determine the effect of additive concentration. Their influence on the resistivity of AgO and other pertinent information were described elsewhere (15). It should be emphasized that reagent-grade chemicals and additives were used for the preparation of AgO samples without recrystallization or other purifying treatments.

Figure 8 shows the gassing rate of AgO samples as a function of additive concentration. This concentration represents the metal content of the additive used in the preparation of AgO and does not necessarily correspond to its content in the sample (15). It can be seen that the gassing rate of AgO samples increased with increasing additive concentration. The gassing rate in the presence of Cd (not shown) increased only slightly to 34 μl/day/g at 10^5 ppm (Ag) Cd.

The resistivity of AgO samples decreased in the presence of Pb, Sn, Hg, and Bi (15). The gassing rate increased slowly with increasing Sn concentration and it went through a small minimum in the presence of Pb. The latter supports Cahan's similar observation (13). In the presence of small amounts of Hg, the gassing rate was small but started to rise rapidly above 10^4 ppm (Ag) Hg. The gassing rate of AgO samples with Bi was high already at moderate Bi concentrations. Sb and As yielded samples of high gassing rates without beneficially affecting their resistivity.

Ni and Co, which are common trace impurities in most chemicals, drastically increased the gassing rate of AgO samples at 1000 ppm (Ag) concentration (Table III). Therefore, it was of interest to determine the gassing rate at lower Ni concentrations. Table IV shows the gassing rates at 5 hr to be still intolerably high even at 1 ppm (Ag) Ni addition. The volume of the evolved gas increased linearly with time up to 5 hr except at 1 ppm (Ag) Ni where a break occurred after 2 hr.

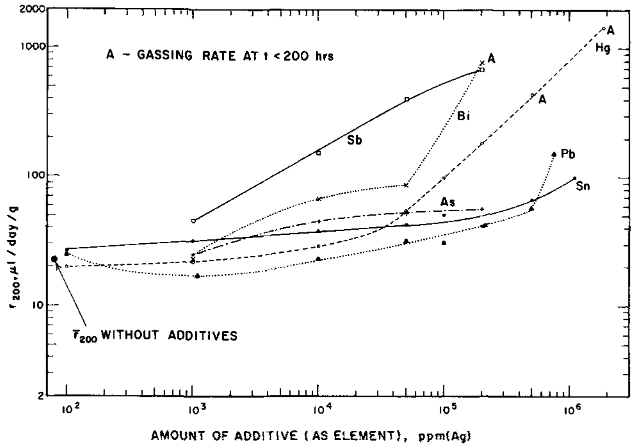

Fig. 8. Gassing rate of AgO samples with additives which were intentionally added in various amounts during their preparation.

Table IV. Gassing rate and AgO content of AgO samples made in the presence of Ni, r_5 in 8.6*N* NaOH, 2.2*N* Na_2ZnO_2 solution

Ni, ppm (Ag)	AgO content, %	r_5, μl/day/g
1000	38.0	8900
100	83.1	8300
10	96.2	1150
1	98.2	176

The explanation of the effect of these inorganic additives cannot be ascertained on the basis of the performed experiments. A correlation of the gassing rates with some meaningful parameters may shed some light on the influence of these additives. This, however, will not be attempted here. The possibilities are numerous. According to Amlie and Rüetschi (1), the gassing rate depends on the oxygen overvoltage and the physical characteristics (structure and porosity) of the surface Ag_2O film. The BET surface area of AgO sample with 1000 ppm (Ag) Pb was *ca.* 50% higher than the mean surface area of AgO samples without additives. In view of the smaller gassing rates in the presence of small amounts of Pb and higher surface areas, the porosity does not seem to be a controlling factor. Cahan (13) ascribed the decrease of gassing rate to the presence of a silver plumbate surface film. The limited number of oxygen overvoltage data on silver alloys (14, 20) seem to correlate with the gassing rates but not without exception.

The effect of transition metal additives, mainly Ni, Co, Zr, and Ce, on the gassing rate seems to point to catalytic action. The thermodynamic, but more likely the kinetic metastability of AgO in alkaline solution can be also affected by their presence. The charge transfer may take place in the bulk or at the surface of AgO by several possible mechanisms (injection, tunneling, transition state).

Suppression of gassing.—In order to determine the effect of beneficial additives (from the viewpoint of resistivity and gassing rate) as gassing suppressors, AgO samples were made in the presence of 5 ppm (Ag) Ni with and without 10^4 ppm (Ag) Hg, Sn, and Pb. The results are shown in Table V. Hg increased the gassing rate by the same amount whether the $Hg(NO_3)_2$ was added to the $AgNO_3$ or to the alkaline persulfate solution. Sn decreased the gassing rate moderately, whereas Pb decreased it markedly neutralizing the affect of Ni to some degree. Replacing part of Pb by Hg, the gassing rate increased indicating the aforementioned detrimental effect of Hg. The resistivity of

Table V. Effect of additives included during the preparation of AgO in the presence of 5 ppm (Ag) Ni

Additive		AgO content, %	ρ, ohm-cm at 2.1 kbar	r_{200}, μl/day/g, 37.78°C, in 8.6*N* NaOH, 2.2*N* Na_2ZnO_2
Element	ppm (Ag)			
—	—	95.7	64.0	280
Hg	10^4	96.7	2.84	405†
Hg	10^4	94.7	3.71	400‡
Sn	10^4	93.4	4.05	222
Pb	10^4	95.5	2.63	84*
Hg Pb	5×10^3 5×10^3	95.8	1.77	122*

† At 117 hr.
‡ $Hg(NO_3)_2$ was added to the alkaline persulfate solution.
* At 165 hr.

Table VI. Effect of additives, incorporated into the 8.6*N* NaOH, 2.2*N* Na_2ZnO_2 solution, on the gassing rate of AgO

Additive, 10^4 ppm (Ag) element	Gassing rate, μl/day/g 37.78°C, 8.6*N* NaOH, 2.2*N* Na_2ZnO_2	Duration of *r* determination, hr
—	249	185
HgO	292	161
Na_2SnO_3	246	209
GeO_2	147	209
PbO	105	209

AgO samples containing Pb, Sn, and Hg are lower as found earlier (15). The AgO content of the samples are generally lower due to the presence of Ni. The addition of Pb to AgO during its preparation is beneficial not only from the viewpoint of electric resistivity but also of gassing rate. Thus, it is advantageous to have Pb as one of the components in any combination of beneficial additives.

In view of the aforementioned beneficial affect of Pb, etc. on the gassing rate and Cahan's results with PbO (13), it was of interest to determine their influence on the gassing rate when they are incorporated in the alkaline solution. An AgO sample with high gassing rate was chosen (98.2% AgO content). The results of Table VI show that Hg increased, Sn did not influence, and Ge and Pb decreased the gassing rate of the AgO sample. Since the trend of the gassing rates in Table V and VI is nearly the same, the effectiveness of the additives is due to their presence and is independent of the method of incorporation.

Summary

The volume of the oxygen evolved from AgO samples in contact with alkaline solutions was measured in a modified microvolumetric appartus of Amlie and Rüetschi (1) and the gassing rates (cumulative average) were calculated. The AgO samples were prepared by the chemical oxidation of $AgNO_3$ with alkaline $K_2S_2O_8$ (16) in the absence or presence of intentionally added metal additives (as compounds). The gas evolved almost linearly with time and the decrease of gassing rate, r after 200 hr was small. In view of the approximately linear relation between the gassing rates at 20 and 200 hr, r_{20} can be used for the rapid semiquantitative prediction of gassing rates. The gassing rates varied somewhat and the mean r_{200} of 52 AgO samples (AgO content $\geqq 95\%$, $r_{200} \leqq 35$ μl/day/g) was 23.0 μl/day/g. Assuming the decomposition of AgO to be a first order reaction, 0.271/year was obtained for the rate constant in 8.6*N* NaOH, 2.2*N* Na_2ZnO_2 solution at 37.78°C.

The gassing rate increased with increasing NaOH concentration and temperature. With NaOH concentration, r_{200} increased approximately linearly. The activation energy for the complex O_2 evolution reaction was calculated from all data to be 26 kcal/mole. The correlation of the gassing rates in two solutions of different composition was found to be approximately linear. The gassing rate of AgO powders increased with ball milling and increasing pelletizing pressure. No correlation was found between the gassing rate and surface area or porosity.

The gassing rates of AgO samples made in the presence of transition elements were, in general, larger than the gassing rates of samples with nontransition elements. The presence of 1000 ppm (Ag) Co, Ni, and Zr is catastrophic from the viewpoint of decomposition and samples with Ce, Pd, and W have intolerably large gassing rates. The gassing rate of AgO samples increased with increasing additive concentration with the exception of Pb at small concentration. The addition of Pb is advantageous also from the viewpoint of electric resistivity (15).

Sn, Ge, and especially Pb suppressed the large gassing rates of AgO samples regardless whether they were incorporated with 5 ppm (Ag) Ni during their preparation or only added to the alkaline solutions.

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