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Self-Decomposition Processes in Silver Electrodes

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ABSTRACT

The self-decomposition of silver oxide (AgO) electrode material in KOH electrolyte has been studied to determine the effects of metallic additions, preparation techniques, and carbonate content. The study employed a multi-technique approach that involved direct gas evolution measurements, thermal analysis, and electrical resistivity measurements. The results indicate that small amounts (10 ppm) of cobalt and nickel substantially increase the rate of decomposition in electrolyte. High levels of copper also increase the decomposition rate, but to a lesser extent. Other metals, such as indium and gold, tend to suppress AgO decomposition. A third group, including lead and mercury, have little or no effect on the decomposition rate. Binary mixtures of several elements were also tested as a means of counteracting the destabilizing properties of cobalt in particular. Of these, coadditions of cadmium with cobalt decrease the latter's adverse effects on AgO decomposition.

The performance of silver oxide/zinc batteries can be degraded by excessive decomposition of the silver oxide (AgO) cathode material during storage. The spontaneous decomposition of AgO to the monoxide (Ag_2O) reduces battery capacity. In addition, the decomposition process produces oxygen which can react with the zinc electrode forming a zinc oxide film on the anode which retards the initial voltage rise upon battery activation. These concerns have lead the current investigation into the self-decomposition processes of AgO active cathode material. Reported here are the effects of the inclusion of metals as oxides in chemically prepared AgO on its sample composition, decomposition rate, and electrical resistivity.

A number of investigators have studied silver oxide stability. Earlier work was reviewed by Ruetschi (1), who indicated that the potential of the AgO/Ag_2O electrode depends on OH^- ion activity and H_2O activity in the same way as the oxygen electrode, and that at any KOH concentration the AgO/Ag_2O electrode is 0.200V above the oxygen electrode. Therefore AgO is thermodynamically unstable in a Ag-Zn cell. The kinetics of decomposition of AgO (wet) have been reported earlier by Tvarusko (2) and Moses *et al.* (3). They concluded that certain impurities such as nickel catalyze oxygen evolution and that others such as lead oxide and cadmium oxide suppress the gassing rate. Ohya and Shimizu reported (4) that the ternary addition of Cd, Te, and other elements stabilized AgO.

The present work encompasses a study of those materials which catalyze the decomposition of AgO and the effects of other materials stabilizing AgO in combination. Early reports of this work were by Parkhurst *et al.* (5), Freeman *et al.* (6), and West *et al.* (7).

Experimental

A multi-technique approach has been used to investigate the effects of trace elements, processing procedures, and surface treatments on the stability of AgO cathode material. The techniques used include: direct gas evolution measurements in potassium hydroxide using a modified Amlie-Ruetschi gassing cell (1), thermogravimetry (TG) (8), and electrical resistivity using the van der Pauw techniques (9). The samples of AgO investigated were either obtained from commercial sources or prepared using the inorganic synthesis technique described by Hammer and Kleinberg (10). Trace elements were added in known quantities by coprecipitating metal oxides with the silver oxide using a modification of the inorganic synthesis technique, as described below.

Sample preparation.—Samples were prepared from reagent grade $AgNO_3$ in an alkaline (1.8*M* KOH or NaOH) oxidizing solution. The oxidizing agents were 0.28*M* $K_2S_2O_8$ or $KMnO_4$. Metals for addition were dissolved in a minimal amount of concentrated nitric acid and added to the silver nitrate solution prior to the addition of the oxidizing agent. The metallic additions are listed in Table I. Elements were added in concentrations of 10, 100, 1000, and 10,000 ppm relative to the metallic silver except in the binary experi-

Table I. Trace element additions used to investigate silver oxide stability

Addition method	
Coprecipitated	Binary addition
Cadmium	Cadmium-tellurium
Cobalt	Cadmium-cobalt
Copper	Selenium-mercury
Gold	Thallium-indium
Indium	Lead-cadmium
Iron	Lead-cobalt
Lead	Lead-copper
Mercury	Lead-iron
Nickel	Lead-nickel
Selenium	
Tellurium	
Thallium	

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ments where only selected concentrations were used. The oxidation reaction was conducted for 15 min at 363 K (90°C). The precipitated AgO was washed with slightly alkaline water and vacuum dried at 333 K (60°C) for 16h. Distilled water was used in all preparations. The concentration of additives in the AgO samples was confirmed by atomic absorption (AA) spectrophotometric analyses using a Perkin-Elmer 5000 instrument. The purity (trace metals) of the distilled water was checked by a commercial testing service (Century Laboratories, Thorofare, NJ). Selected AgO samples were treated with a mild reducing agent to determine the effects of surface reduction. The reducing agent selected was dilute aqueous hydrazine in concentrations of 0.01, 0.05, and 0.10 volume percent (v/o). The AgO was washed for several (5-10) minutes with the reducing agent and then rinsed and redried as above.

Oxygen evolution measurements.—The amount of oxygen evolved upon decomposition of AgO in potassium hydroxide was measured by a displacement technique using a modified Amile-Ruetschi microvolumetric gassing vessel (1). A 0.5g sample (± 1 mg) was placed in the bottom half of the vessel and then 30 weight percent (w/o) KOH was added. The pipette section was partially immersed in KOH to fill the lower portion of the pipette with electrolyte and the two pieces clamped together between a neoprene O-ring. The apparatus was immersed in a thermostatically controlled (298 K) temperature bath and allowed to equilibrate for 1h prior to beginning the measurements. The change in the electrolyte level in the pipette was observed for periods ranging from 10 to 500h. The observations were corrected for barometric pressure fluctuations by using a blank consisting of a tube filled only with electrolyte. The effects of sample preparation procedures (grinding and precipitation rate) on gas evolution rates were found to be negligible. Stirring the samples during gassing likewise produced no change in results. The gas evolution studies were conducted in darkened containers due to the photosensitivity of the samples. Reported gassing rates are corrected to standard temperature and pressure.

Thermogravimetry.—The thermogravimetry-gas chromatography technique has been described elsewhere for the analysis of silver oxide electrodes containing only AgO, Ag_2O, Ag_2CO_3, and Ag (8). This technique was used to determine the relative amounts of AgO in pure, additive-free samples and in samples containing coprecipitated metal additions (10-10,000 ppm). Studies were performed with a du Pont 1090 thermal analysis system interfaced with a 951 thermogravimetric analyzer module. Samples (50-100 mg) were run in platinum boats at a heating rate of 20 K/min from 303 to 823 K in a flowing atmosphere (*ca.* 50 cm^3/min) of dry helium.

Resistivity measurements.—The electrical resistivity of powders is a function of intergranular contact and thus a function of pressure. At increased pressure, the powder is forced into more intimate contact resulting in lower overall resistance. The resistivity of samples in this study has been measured using the van der Pauw technique (9, 11). In brief, this technique employs four contacts to a sample of irregular shape (in this case a sample under compression) and determines the sample resistivity through an analysis of current and voltage through specified contacts. If the contacts are labeled A, B, C, and D, the specific resistance of the sample is given by the implicit relation

$$\exp(-\pi R_1 d/p) + \exp(-\pi R_2 d/p) = 1$$

where p = specific resistance of sample, d = thickness of sample, R_1 = voltage difference between D and C divided by the current through A and B, R_2 = voltage difference between A and D divided by the current through B and C. An explicit approximation is found in (9).

The apparatus used to measure the electrical resistance is a modified version of the one recommended by Hottman and Pohl (11). The sample is placed on a Delrin disk, 1.90 cm in diameter and 0.635 cm thick in the center. The disk has a flat portion in the center, *ca.* 0.89 cm in diameter. The annulus between this portion and the edge of the disk is tapered slightly to a reduced thickness. Four gold-plated wires (28 gauge) placed at the circumference of the flat portion of the disk serve as the electrical contacts. The sample holder is embedded in a stainless steel base. The base is 6.35 cm in diameter. Compression of the sample is provided through a Delrin faced plunger 3.175 cm in diameter and 8.64 cm in height. Pressure is applied by placing the entire assembly in a laboratory press. Vernier calipers are mounted on the press plates to record sample thickness with changes in pressure. Measurements were taken by applying pressure to the assembly, recording the currents and voltages necessary to calculate R_1 and R_2, and noting the sample thickness on the calipers.

Results and Discussion

The multi-technique approach employed in this study, in particular the complimentary gas evolution and thermogravimetry methods, has provided new insight into the effect of metal additives on the formation and stability of chemically prepared AgO cathode material. The electrical resistance data provides additional information on the effect of trace elements on the performance of silver (II) oxide. The results of gas evolution studies for various metallic additions (both single and binary additions), carbonate content, method of production, and surface treatment are discussed below.

Effect of metallic additions on AgO stability.—The effect of adding metals to chemically prepared AgO varies as a function of the type and amount of the metal added. Three general categories are used to classify the added elements; elements which promote gassing (oxygen evolution), those which do not significantly change the gassing rate, and those which somewhat reduce gassing. The first category contains cobalt, nickel, and copper, with cobalt and nickel being much more active than copper. The other elements studied in this investigation (listed in Table I) fall in the second and third categories. The gas evolution results are summarized in Fig. 1. Figure 2, showing the gas evolved as a function of time for various cobalt concentrations, is an example of the data used in preparing Fig. 1; the gas evolution rate for a particular concentration is simply equivalent to the slope for the corresponding curve in Fig. 2. The TG method (8) was used to determine the amount of AgO in the samples. A TG curve of pure, chemically prrepared AgO (98.0%) is shown in Fig. 3. The first weight loss, A, is caused by the decomposition of AgO to Ag_2O. The second weight loss, B, is caused by the decomposition of Ag_2O to Ag. The composition of the sample can then be determined from the weight loss measurements and the appropriate gravimetric factors.

The presence of cobalt or nickel was previously reported (2) as being catastrophic to the stability of AgO cathode material. A series of TG curves of cobalt-containing cathode material is shown in Fig. 4. It is seen that, by comparison with the TG curve of pure AgO in Fig. 3, as little as 10 ppm Co results in a large decrease in the amount of AgO formed. Furthermore, the TG curves in Fig. 4 show that no AgO at all is formed in the presence of higher (100, 1,000, and 10,000 ppm) Co concentrations, the samples being essentially pure Ag_2O. In addition, the effect of Co on the Ag_2O stability is clearly seen as a shift in the Ag_2O decomposition reaction to lower temperatures with increasing Co concentration. Thus, the high rate of gassing noted for the coprecipitated samples containing the higher concentrations of Co is caused by the decomposition of Ag_2O instead of AgO. It is clear that, under these conditions, Co is such a strong catalyst that no AgO forms; it should be noted that cobalt-containing samples were analyzed with 24h of preparation.

Nickel also caused highly increased gassing rates even at low concentrations, although the effect is not as pronounced as with cobalt. The gassing rate of samples containing 10 ppm Ni was an order of magnitude higher than the gassing rate of the reference material. For samples containing 100 ppm or less of Co or Ni, the first-order rate constant was about 3 times greater for the Co-containing samples. Since Co is a common impurity in Ni, the possibility that the decomposition of Ni-containing samples was catalyzed in part by trace amounts of Co should not be ignored.

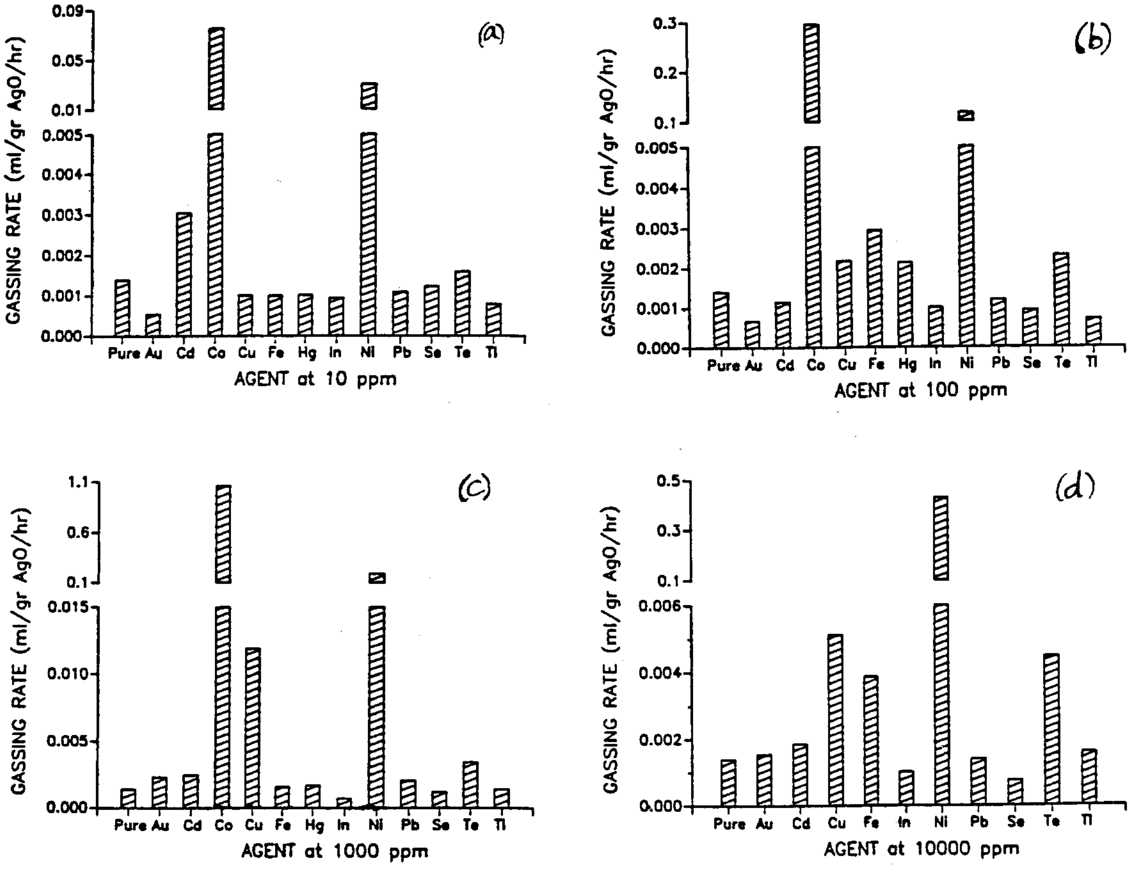

Fig. 1. Gassing rates of silver oxides with coprecipitated additives at concentrations of (a) 10 ppm; (b) 100 ppm; (c) 1,000 ppm; and (d) 10,000 ppm

The other additives shown in Fig. 1 all have a much less dramatic impact on the stability of the silver oxide. Copper, iron, and tellurium appear to be somewhat detrimental to the oxide's stability. Indium, thallium, selenium, and gold all consistently reduce the gassing rate. The results for lead, mercury, and cadmium are not as consistent in their effect, but all, on the average, appear beneficial.

Binary additions.—Binary additions were performed for two distinct purposes: to determine if a synergistic increase in stability was possible for certain binaries, and to determine the ability of certain additives to counteract the deleterious effect of elements such as nickel or cobalt. The results of the binary element additions are presented in Table II. Listed in the table are the binary pairs chosen to investigate synergistic activities. As single components, mercury and selenium tend to stabilize the silver oxide. The binary mercury-selenium addition (100 ppm each) resulted in a minor increase in the AgO stability. Indium and thallium also act to reduce the decomposition rate when added singly. No synergistic effect was noted when the two are present simultaneously. The final couple, lead and cadmium, caused an increase in gassing when combined and effectively negated the positive effects of each single element.

The ability of additives to counteract the catalytic effect of certain elements has also been investigated and is summarized in Fig. 5 and 6. These results show that cadmium (Fig. 5) and lead (Fig. 6) are both successful in reducing the gassing rate with cobalt, but are not capable of negating the cobalt effect. Cadmium at 10,000 ppm is somewhat more effective than lead at the same level. A beneficial effect of lead on nickel-catalyzed gassing is also observed, but the amount of reduction is substantially less. Copper, which has been shown to be mildly catalytic, does not respond to lead additions in the same way, as increased gassing activity was observed.

Effect of carbonate.—The effect of carbonate content on gas evolution and resistivity was analyzed by studying two samples of commercial origin, which differed only in their carbonate content. One sample contained 0.75 w/o silver carbonate and the second contained 2.75 w/o. The amount

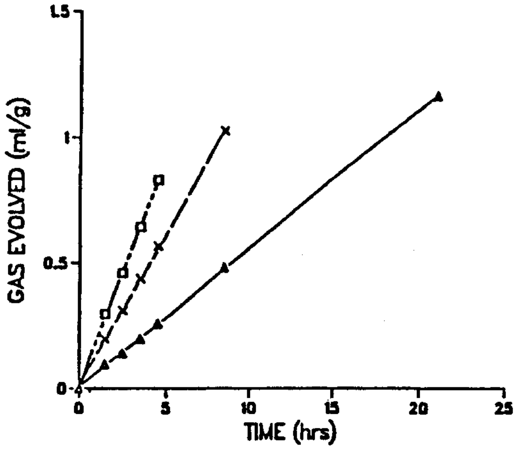

Fig. 2. Oxygen evolution of silver oxide with cobalt additions (△ – 10 ppm; x – 100 ppm; and □ – 1000 ppm).

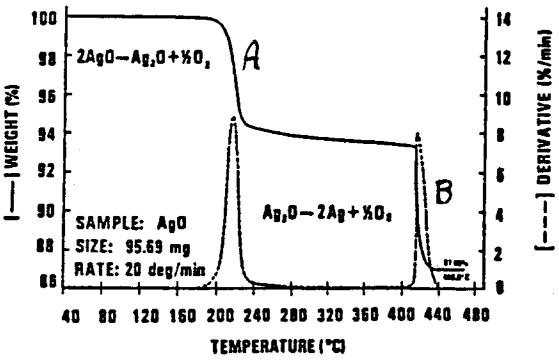

Fig. 3. Thermogravimetry curve of pure (98.0%) AgO

Table II. Decomposition of AgO formed with selected binary metallic additions

Elements (ppm)		Gassing rate ($\times 10^{-4}$ ml/g/h) of AgO with		
A	B	A only	B only	Binary
Hg(100)	Se(100)	21.3	9.3	8.7
Hg(100)	Se(10,000)	21.3	7.5	9.3
Hg(1,000)	Se(10)	16.6	12.3	15.1
Hg(1,000)	Se(100)	16.6	9.3	22.0
Te(10)	Cd(10,000)	15.9	18.5	15.7
Te(100)	Cd(10,000)	23.2	18.5	12.4
Te(1,000)	Cd(100)	33.9	11.3	28.5
Te(1,000)	Cd(10)	33.9	30.3	56.2
In(100)	Tl(10,000)	9.9	15.9	14.4
In(1,000)	Tl(1,000)	6.8	13.8	17.7
In(10,000)	Tl(100)	10.1	7.1	7.2

of carbonate was determined by thermogravimetry and gas chromatography as described in (8).

Gas evolution was found to increase significantly in the presence of carbonate, increasing from 7.7×10^{-5} to 3.4×10^{-4} ml/g/h. Although decomposition of the carbonate will produce carbon dioxide, the gas evolution measurement is thought to represent oxygen production because carbon dioxide is highly soluble in potassium hydroxide. These results indicate that the presence of carbonate may increase the rate of silver (II) oxide or silver (I) oxide decomposition. The decomposition of silver carbonate has been discussed by Anderson *et al.* (12). It should be noted that the gas evolution process for the high carbonate sample exhibited a lag of about 50h before significant gassing was observed; however, the total amount of carbon dioxide produced by decomposition is estimated as being less than 2 ml.

The presence of silver carbonate also had a detrimental effect on the conductivity of the electrode material. The low carbonate silver oxide had a measured resistivity of 87 Ωcm, whereas the high carbonate material measured 352 Ωcm. This is attributed to the high concentration of carbonate on the surface of the particles (12).

Methods of preparation.—The preparation of silver (II) oxide involves oxidation of silver nitrate and precipitation in an alkaline solution. The effect of both the oxidizer chosen and the nature of the base on silver (II) oxide formation and stability have been investigated. The alkalis were potassium hydroxide and sodium hydroxide. Thermogravimetric analysis results are summarized in Fig. 7, which indicates that only potassium persulfate is successful in generating silver (II) oxide under these conditions. Figure 7 also indicates that potassium hydroxide produces a higher purity silver (II) oxide. The results of gas evolution measurements, illustrated in Fig. 8, indicate that the silver (II) oxide produced by using potassium hydroxide is more stable, evolving gas at a rate of 1.38×10^{-3} ml/g/h compared to 4.704×10^{-3} ml/g/h for the material prepared in sodium hydroxide. The samples prepared with potassium permanganate as the oxidizer exhibited substantially less gassing than expected because low levels of silver (II) oxide were obtained.

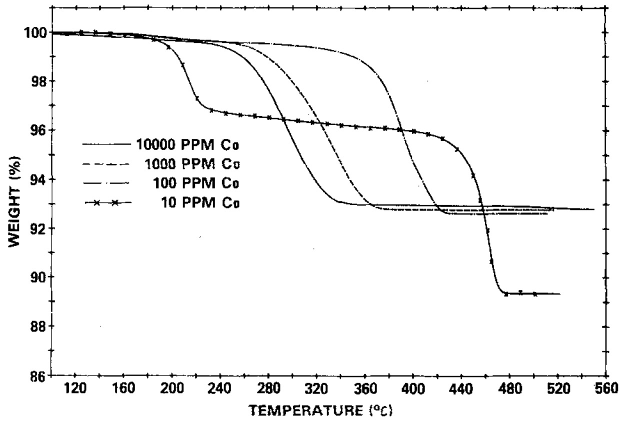

Fig. 4. Thermogravimetric curves of AgO with cobalt additions. Heating rate: 20 K/min. Atm: He (50 cm^3/min).

The sample resistances were also consistent with the silver (II) oxide content. The sample prepared with potassium hydroxide had a resistance of 11.4 Ωcm, while that prepared with sodium hydroxide had a resistance of 584 Ωcm, reflecting the lower content of the more conductive silver (II) oxide. These values are at a pressure of 9.65×10^7 Pa and compare favorably with the value of 59.3 Ωcm at 2.10×10^8 Pa reported by Tvarusko for silver (II) oxide (2). The sample prepared with potassium permanganate exhibited a resistance of 1×10^{-6} Ωcm, a value typical of the monovalent silver oxide (13, 14).

Hydrazine reduction.—Mild reduction of chemically prepared silver (II) oxide by dilute solutions of hydrazine was investigated as a possible means of increasing the stability of the silver (II) oxide. The treatment had a negligible effect on the rate of gassing and substantially increased the resistance of the sample for the lower concentrations of reducing agent used. The resistivity of samples treated with 0.01% and 0.05% hydrazine solutions were 711 and 505 Ωcm, respectively. Reduction with a 0.1% solution produced a sample with a resistivity of only 48 Ωcm. These results can be explained if it is assumed that the hydrazine reduces the silver (II) oxide first to silver (I) oxide and in a second step reduces the silver (I) oxide to metallic silver. The reduction will take place on the surface of the particles and the initial reduction will result in an increase in re-

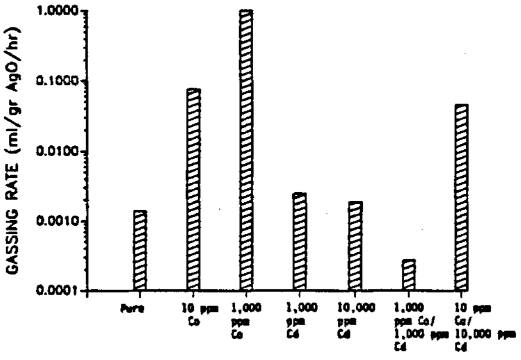

Fig. 5. The effect of cadmium additions as an anticatalyst in cobalt-containing silver oxides.

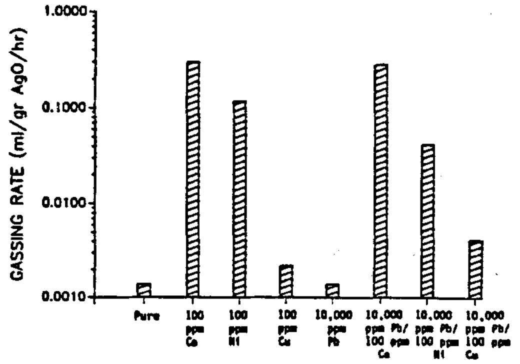

Fig. 6. The effect of lead as an anticatalyst in high gassing silver oxides.

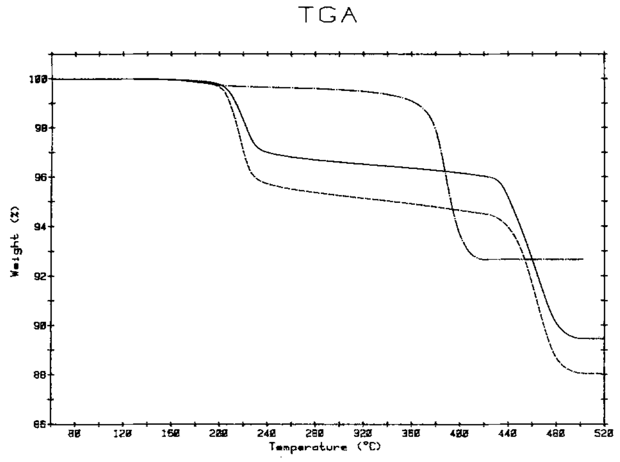

Fig. 7. Thermogravimetric curves for AgO prepared with various reagents. — · — · — KOH/MnO_4. ——— $NaOH/K_2S_2O_8$. ---- $KOH/K_2S_2O_8$. Heating rate: 20 K/min. Atm: He (50 cm^3/min).

sistance due to the presence of the low conductivity material (Ag_2O) surrounding the particles. As the amount of reduction increases, some highly conductive silver metal is formed on the surface of the particles, reducing the sample resistivity. This assumption is validated by TG results for samples treated with higher concentrations of hydrazine; in this case, the entire sample can be reduced to Ag_2O or even silver, depending on the treatment time.

Resistivity measurements.—The resistivity of silver oxide samples was measured using the van der Pauw technique described previously. This gives resistivity as a function of applied pressure. For purposes of comparison, the values obtained at 9.65 × 10^7 Pa, an intermediate pressure in the range investigated, are reported. The resistivity results are presented in Table III.

The measured resistivity for the silver oxide reference material, 11.30 Ωcm at 9.65 × 10^7 Pa, is comparable to the 59.3 Ωcm value reported by Tvarusko (13). The effects of the metal additive are dependent on the metal type and its concentration as indicated by the data in Table III. Small amounts (10 ppm) of either cobalt or nickel increase the resistivity of silver oxide substantially; however, a further increase in concentration to 100 ppm reduces the resistivity by an order of magnitude or more. Further additions of these materials then raise the resistivity. It is speculated that changes in the composition of the particle surface account for this phenomenon. Small amounts of catalyst produce Ag_2O on the surface, increasing the resistivity above that for AgO. (Dirske (14) reported a 10^8 Ωcm increase in ohmic resistance for Ag_2O over that for AgO.) Added catalyst further reduces the surface to metallic silver which reduces the resistivity. At high additive concentrations, the conductivity of the additive itself overides that of the silver oxide particles in the measurements. Other additives, lead in particular, greatly decrease the resistivity of the sample. Additives of this type should act to improve battery performance by reducing the ohmic resistance of the electrode material under discharge conditions.

Table III. Effect of additives on the electrical resistivity of silver oxide

Additive concentration		Measured resistivity (Ωcm/g)
Reference (98% AgO)		11.39
Cobalt	10	14,343
	100	1,701
	1,000	157
	10,000	1,801
Nickel	10	7,182
	100	1.971
	1,000	7.815
	10,000	38.01
Lead	10	0.006
	100	0.090
	1,000	0.200
	10,000	2.5
Copper	100	1.0
Iron	100	18.0
Cadium	100	8.3
Tellurium	100	3.0

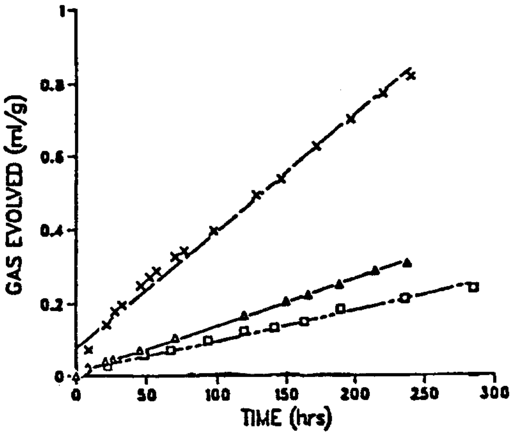

Fig. 8. Oxygen evolution of silver oxides prepared with various reagents (x – via $NaOH/K_2S_2O_8$; △ – via $KOH/KMnO_4$; and ☐ – via $KOH/K_2S_2O_8$).

Summary

A multi-technique approach, utilizing direct gas evolution measurements, thermal analysis, and electrical resistivity measurements, was used to study the self-decomposition of the silver oxide electrode. The results of this investigation indicate that trace quantities of cobalt or nickel substantially increase the rate of decomposition of silver (II) oxide. Large quantities of these metals incorporated in the coprecipitation process inhibited the production of AgO. High levels of copper also increased the decomposition rate, but to a lesser extent. Indium and gold additions, however, were found to decrease oxygen evolution in the silver oxides.

Binary mixtures of several elements were studied to determine the ability of selected elements as anticatalysts and also to note any synergistic effects. While no synergism was noted, both cadmium and lead additions countered the destabilizing properties of other additives to a limited extent.

We have recently reported on a TG decomposition kinetics study of AgO cathode material (15). The results relate to the self-discharge of AgO in reserve AgO/Zn batteries that are stored without electrolyte in the cells. Correlations are being made between the thermal stability of these electroformed cathodes and the presence of electrochemically incorporated metal additives (16).

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Analysis of Electrokinetic Data by Parameter Estimation and Model Discrimination Technqiues

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ABSTRACT

An alternative approach to classical methods of electrochemical data analysis is presented. This alternative method is based on nonlinear parameter estimation and model discrimination techniques. The method is used to obtain the relevant kinetic and transport parameters and to elucidate the kinetic mechanism of O_2 reduction at carbon and silver electrodes in alkaline electrolytes.

Conventional methods for electrochemical data analysis generally tend to focus on a narrow range of the kinetic expressions describing the electrochemical process, such as the Tafel or the linear segments of typical polarization curves. Focus on these sections of the polarization curves produces a set of parameter values which electrochemists have traditionally used to elucidate the mechanisms of electrochemical reactions. However, in most instances, the linear and Tafel segments of these curves are distorted by diffusion processes, the reverse reaction in the neighborhood of the equilibrium potential, and coupling effects of other reactions. Therefore, parameters estimated from the Tafel or linear regions of the polarization curves, especially for complex electrode reaction systems, may not reflect the true values of the parameters of the electrode reactions under consideration. For instance, where the electrode reaction is relatively fast, the Tafel segment may be so short as to create difficulty in accurately estimating the parameters. On the other hand, for slow electrode reactions, the polarization curves can have several Tafel segments with transition regions, where the reaction from one segment could be coupled with that in another segment. McIntyre (1) noted the coupling effect of a regenerative process of a heterogeneous catalytic electrode reaction over the complete potential range in which the electroactive species was reduced and recommended that the coupling effect be taken into account if kinetic parameters characteristic of the charge-transfer reaction are to be obtained. On the other hand, the linear region extends only a few millivolts beyond the equilibrium or open-circuit potential. As pointed out by Nagy *et al.* (2), measurements at such low overpotentials are often hampered by signal-to-noise ratio problems, and extrapolation from the linear to higher overpotential range as commonly done in electrochemical studies is generally questionable.

Most kinetic models, in addition to relating the overall process and the component steps to the potential driving force and to the concentrations of reactants, products, and intermediates, must also take into account the transport of reacting species, intermediates, and products to and from the electrode surface. Furthermore, consideration of homogeneous reactions in the solution and heterogeneous non-charge transfer reactions at the electrode surface increases the complexity of the system of model equations needed to evaluate the kinetic parameters. This system of model equations is normally described by a set of differential equations containing the unknown parameters, some of which may enter into the boundary conditions. In classical electrokinetic data analysis, a number of simplifying assumptions are made in order to adapt the problem to analytical solutions (3). This approach tends to limit the kinetic models to a narrow range of the variables over which only a limited number of the parameters can be estimated at once. On the contrary, the development of numerical algorithms for the solution of electrochemical problems (4-7) makes it possible for the investigator to predict the behavior of such complex electrochemical systems over a wide range of the variables. This facilitates the simultaneous estimation of the parameters from experimental data. Consequently, more rigorous kinetic expressions can be developed to cover the range of variables of practical interest.

Only a few attempts have been made to estimate electrokinetic parameters by parameter estimation techniques. A multiparameter least square curve fitting program was developed by Meites and Meites (8). This program was based on a trial-and-error search pattern in which each parameter is successively varied while the others are held constant until the optimum point is reached. This program was applied to problems in titrimetry, polarography, and chronoamperometry, and could estimate up to five parameters. Gorodestskii *et al.* (9) used a nonlinear technique—the method of steepest descent—to estimate the transfer coefficients and exchange current densities of bismuth discharge reactions on a stationary amalgam electrode. Vert and Pavlova (10) used the method of least squares to calculate the exchange current density of the slow step of an electrochemical reaction and the potential correspond-

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