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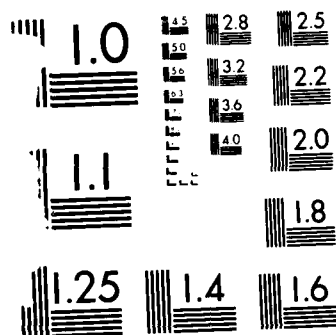
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ELECTRODE PROCESSES IN POROUS ELECTRODES

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1.0 INTRODUCTION

This is the final technical report for ^{at}ONR contract N00014-80-C-0403 covering the period from Sept. 1984 to Nov. 1985. The scope of the effort for this period was to address novel methods of investigation of silver electrodes in order to better understand the chemical and physical processes which occur during charge and discharge.

Three areas of study were covered by this effort. The first was the development of a mass spectrometric procedure to determine the distribution of silver (I) oxide and silver (II) oxide in a silver electrode at any stage of the charge-discharge process. The second was the development of a rapid analytical technique for the determination of silver (II) oxide in a silver electrode. The third was a preliminary study of the application of acoustic analysis to give a more complete understanding of the processes occurring during charge and discharge of silver electrodes.

The results of these investigations are detailed in ^{this report,} ~~the~~ following sections.

2.0 MASS SPECTROMETRY

One part of activity for this year is an investigation of the behavior of silver electrodes through the distribution of oxygen isotopes in the silver oxides. The concept is to oxidize and reduce Ag electrodes in potassium hydroxide electrolyte doped with O^{18} and to analyze the resultant oxide distribution by thermal decomposition mass spectrometry. Since the two oxides have distinctly different decomposition temperatures, the oxygen observed by mass spectrometry will indicate the electrode oxide composition. The first phase of this study was to develop the methods and techniques for sample preparation and analysis.

The test electrodes were prepared in a three electrode single compartment cell. The working electrode was silver wire, polished and degreased. A platinum counter electrode and a Hg/HgO reference electrode were used. The experiments were carried out galvanostatically and the voltage monitored to indicate the state of charge of the silver electrode. The electrolyte was 10 M KOH and prepared with either distilled water or water containing 97% O^{18} . After removal from the cell the electrodes were washed with distilled water and dried.

The initial data indicated that the major product from the thermal decomposition of electrochemically oxidized silver (Ag) wires was carbon dioxide (CO_2). There was very little evidence of oxygen (O_2) as would be expected if silver(I) oxide (Ag_2O) and silver(II) oxide (AgO) were present. The Ag wire electrodes were prepared in electrolyte which was labelled with O^{18} . The evolved CO_2 was labelled with O^{18} . The proportions of O^{18} to O^{16} in the CO_2 suggest that the CO_2 reacts with the electrode after the oxidation and does not arise simply from the solution. This analysis is outlined below.

The mass spectrometry data for the proportions of labelled CO_2 averaged for three samples are:

$\text{CO}^{16}_0^{16}$	0.583 ± 0.024
$\text{CO}^{16}_0^{18}$	0.342 ± 0.021
$\text{CO}^{18}_0^{18}$	0.074 ± 0.003

Water and CO_2 exchange oxygen fairly rapidly, in neutral solutions the exchange is complete in one day (1). On the assumption of complete exchange the isotopic composition of the original solution would be $76.4 \pm 1.6\%$ O^{16} and $27.2 \pm 0.6\%$ O^{18} . This is consistent with the proportion of the mixed isotope CO_2 found, which theoretically would be 0.361 ± 0.026 .

The isotope distribution in the original electrolyte was 78.3% O^{18} and 21.7% O^{16} . The levels of CO_2 in the electrolyte were not measured, but assuming they were relatively small, the isotope distribution would reflect the solution distribution which it clearly does not. If it did the ratios of the three CO_2 's would be:

$\text{CO}^{16}_0^{16}$	0.047
$\text{CO}^{16}_0^{18}$	0.340
$\text{CO}^{18}_0^{18}$	0.613

An alternative explanation is that atmospheric CO_2 reacts with the electrode after it is removed from the electrolyte. This is reasonable since to have the inversion in isotope distribution some additional O^{16} is added to the system which would come from the CO_2 . If the oxygen incorporated in the electrode during oxidation reflects the isotopic composition of the electrolyte, then the molar ratio of atmospheric CO_2 to electrode oxygen would be 1.16.

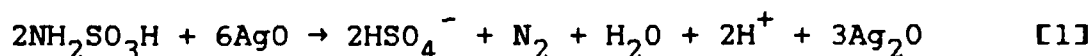
Further elucidation of the CO_2 /electrode interaction was not possible within the scope of this effort. The reaction may occur directly between the silver oxides and CO_2 or it may be mediated by an electrolyte layer. In this case, the isotope ratios may change with time because of continued exchange with essentially pure O^{16}CO_2 in the atmosphere. This interaction is worthy of further study because of the practical importance it may have in the production of commercial silver electrodes and potential silver carbonate contamination.

In order to avoid the formation of carbonate on the silver electrodes, the electrodes were subsequently prepared in an argon atmosphere. This eliminated the problem. The thermal decomposition mass spectrometry of carbonate-free, oxidized silver electrodes clearly showed the oxygen release from Ag_2O at 110°C . The heating rate of thermal probe was insufficient to give a clean peak for the decomposition of Ag_2O , the decomposition yielded a broad peak lasting several minutes. The equipment can be modified to overcome this problem for future studies.

3.0 GASOMETRIC ANALYSIS

Several analytical methods are available for the determination of the chemical composition of Ag/Ag₂O/AgO porous electrodes (e.g. the Wagner wet chemical analysis and the TGA method reported by Parkhurst et. al. (2)). These, in some cases, involve tedious and time consuming procedures and discrepancies of as much as 15% have been observed in the results. As part of the work conducted under the present contract, an investigation of a possible improved alternative method was carried out for the determination of AgO. The method is based on the reaction of AgO and sulfamic acid to produce nitrogen gas and is based on the work of Brasted who studied the reaction of sodium nitrite with sulfamic acid (3).

The reaction of AgO with sulfamic acid has the following stoichiometry



which yields 6 moles of N₂ per 6 moles of AgO, thus, for example, 0.743g of AgO yield 22.4 cm³ of nitrogen at STP. There is no reaction of sulfamic acid with either Ag or Ag₂O.

The apparatus consists of a 100 cm³ graduated, water-jacketed buret inverted with its mouth immersed in a water reservoir. The buret is connected by a gas line to a 50 cm³ reaction flask. The reaction flask is a standard Erlenmyer flask modified by placing a ridge along the bottom to form two compartments.

The determination is carried out by placing a weighed quantity of material containing approximately 0.1g of AgO in one side of the bottom of the reaction flask, and 3 cm³ of 20% sulfamic acid solution in the other. At these ratios, the sulfamic acid is in about 6-fold excess. The buret is filled with water and the system

allowed to come to thermal equilibrium. The reactants are mixed by tipping the flask and gas evolution begins immediately. When the reaction ceases, the buret reading is taken after 5 minutes in order to allow thermal equilibrium. The measured gas volume is corrected for temperature, barometric pressure and water vapor pressure. The corrected volume is compared to the theoretical, based on the sample weight to calculate the percentage of AgO in the sample. The equation for the theoretical gas volume is:

$$\text{volume (cm}^3\text{)} = 22.4 \left(\frac{\text{bp} - \text{vp}}{760} \right) \left(\frac{273}{(273 + t)} \right) \left(\frac{\text{AgO wt (g)}}{0.743} \right)$$

where bp is the barometric pressure in mmHg, and vp is the vapor pressure of water in mmHg at the temperature t °C of the experiment.

A series of determinations were made on standardized AgO and the results showed a standard deviation of $\pm 2.3\%$.

The investigation of the sulfamic acid gasometric determination of AgO has shown it to be a fast, simple and accurate method. In addition, it does not have associated with it the hazards of some methods which involve the generation of ammonia(4).

4.0 ACOUSTIC EMISSION

Acoustic emission analysis has been applied to many areas of materials analysis, including phase transition studies and surface oxide formation (5-8). Since there are crystal structure differences between silver and its oxides, it was decided to determine whether acoustic emission does occur during the charge-discharge cycling of a silver electrode. Then, correlation of acoustic emission with voltage-time data would provide insight into the phase transition processes and perhaps establish if and when other intermediate oxide phases are formed.

The experimental apparatus consisted of a three electrode, one compartment cell. The working electrode was a silver foil with an active area of 1 cm^2 which was polished and degreased. The counter electrode was a porous $\text{Ag}/\text{Ag}_2\text{O}$ electrode and a Hg/HgO reference electrode was used. The electrolyte was 10 M KOH saturated with Ag_2O . The working electrodes were charged and discharged galvanostatically and the time-voltage recorded. The acoustic sensor was a Dunegan model S9222 micro-miniature transducer, 3.59 mm diameter, mounted on the silver foil above the electrolyte level. The transducer signal was recorded with a Dunegan model 8000 Acoustic Emission Analyzer.

Acoustic emissions were observed during the oxidation-reduction of the silver electrode. The data is limited by the limited sensitivity of the transducer. Nonetheless, strong acoustic signals were recorded at the $\text{Ag}_2\text{O}/\text{AgO}$ transition during the charge phase and the strongest signals were recorded during oxygen evolution when the electrode was completely charged. Weaker responses were recorded at other times in both the charge and discharge regimes. The technique appears promising. More sensitive acoustic transducers are available and further work is indicated.

5.0 SUMMARY

This year's effort has centered on the development of novel methods of investigating the processes occurring during the oxidation and reduction of silver electrodes. A method of thermal decomposition mass spectrometry was developed to study the formation and distribution of AgO and Ag₂O in the silver electrode and further to study this distribution by incorporating oxygen-18 into the electrode. A rapid and safe gasometric analysis technique for the determination of AgO was developed. The method is based on the reaction of AgO with sulfamic acid in aqueous solution. Nitrogen gas is the only gaseous product of this reaction and can be quantified easily. Preliminary investigations of acoustic emission techniques applied to charging and discharging electrodes suggest further development of the method is warranted. Acoustic signals are detectable from the electrode which originate in the structural and physio-chemical changes occurring at the electrode.

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