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Anodic Dissolution of Zinc in Potassium Nitrate

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ABSTRACT

The apparent valence of pure zinc dissolving anodically in 3% KNO_3 was determined as a function of current density, temperature, and ultrasonic agitation. The apparent valence of zinc dissolving anodically at $24^{\circ}C$ at current densities < 30 ma.cm^{-2} is 2.01 ± 0.01. From 30-40 ma the valence diminished and from 42 ma up to about 80 ma cm^{-2} it remains constant at about 1.87. The valence is to some extent a function of the previous history of sample preparation in that the value is affected by polishing of the electrode. Under the influence of ultrasonic vibrations, the apparent valence at high current densities is approximately the same as with no ultrasonic vibrations. In both cases a black film (corrosion product) spalls off the anode but to a larger extent with ultrasonics. At elevated temperatures the apparent valence again decreases with increasing current density and appears to vary as a function of metal history. Metallic particles are found in the corrosion product. The average size of the particles increases with increasing temperature. On the basis of the above, it is consluded that the normal valencey of zinc ions, +2 does not change during anodic dissolution in nitrate solutions, but the apparent valence of less than 2 arises as

a consequence of partial disintegration of the anode. The dissolution of zinc aggregates outside the electrical circuit thus accounts for the lower coulombic equivalent.

INTRODUCTION

When either zinc or cadmium (having a normal valence of +2) is dissolved anodically in aqueous neutral salt solutions, containing nitrate or chlorate ions, the number of coulombs required to dissolve one gram equivalent of metal is less than the faradaic weight equivalent, especially at high current densities. Other metals, beryllium, magnesium, aluminum, indium, gallium, thallium, iron and tin also exhibit this phenomenon. The implication here is that these metals dissolve with a mean valence lower than the normal oxidation state.

One mechanism which has received wide acceptance is the concept of the "uncommon valence ion" as proposed by Epelboin[1] for zinc undergoing anodic dissolution in perchlorate solution. Later work on zinc, cadmium and other metals by Davidson and co-workers[2-6] has supported this mechanism and attributed the results to the expulsion of univalent ions.

Another mechanism suggested by Hoey and Cohen[7] proposes the corrosion rate as film controlled. The film of hydroxide or hydrated oxide containing small metallic particles spalls off the surface. The small particles are then slowly oxidized by water or an oxidizing agent. This film controlled mechanism has received much support from Robinson and King[8],

Higgins[9], Roald and Beck[10], and Straumanis and co-workers[11-13].

The purpose of this study was to obtain experimental data for the anodic dissolution of zinc in 3% aqueous KNO_3 as a function of: 1. current density, 2. temperature, and 3. ultrasonic vibrations, and to establish a mechanism consistent with the results.

EXPERIMENTAL

The Effect of Current Density

Apparatus. The apparatus consisted of a 400 ml. cell, a zinc electrode made of either a polycrystalline bar (99.99% purity) or of a single crystal (exposed surface nearly parallel to the basal plane, 99.95% purity), a sensitive milliammeter, a decade type resistance box, dry cells, a knife switch, and a platinum cathode, all connected in series. A micro burette of 10 ml. capacity with 0.02 ml. graduations was used to titrate the zinc content of the electrolyte following electrolysis.

Procedure. The zinc electrodes were polished immediately before each run. Two hundred ml. of a 3% KNO_3 solution was transferred to the thermostated cell. A mounted metal anode and the platinum cathode were then inserted and connected in series with the external circuit and the circuit closed. A timer and milliammeter were used to measure the number of coulombs passed (checked by a copper coulometer). After a sufficient time interval the circuit was broken and the electrodes removed from the beaker. Any adhering film on the anode

was removed by scrubbing with a rubber policeman and the electrolyte treated as follows. Two drops of 6 M HCl were added and the solution was quantitatively transferred to a volumetric flask where it was diluted to 500 ml. with distilled water. Aliquots of 100 ml. volume were withdrawn, heated to about 90°C, buffered to pH of 10, and titrated with standard disodium EDTA using Erichrome Black T as indicator.

Data and results. The apparent valence was determined at $24.0 \pm 0.5°C$ over a current density range of 0.5 to 85 ma.cm^{-2} with a possible error range of ± 1 percent. Since the behavior of polycrystalline and single crystal anodes were apparently the same at this temperature, the resulting data were combined and results are presented graphically in Fig. 1.

At low current densities (< than 30 ma.cm^{-2}) a very thin, usually spotty, black film was observed on the face of the anode. Upon removal from the electrolyte the film turned grayish white after about five minutes exposure. Tests at higher current densities (> 30 ma.cm^{-2}) resulted in a thicker and continuous black film. Also a white precipitate was observed directly below the vertical electrode. An X-ray analysis of the deposit revealed it to be ZnO.

On one occasion, four valence measurements were performed in consecutive order on each zinc electrode. The zinc anodes were not polished between runs; the electrodes were merely transferred (after cleaning with distilled water) to a fresh solution and another run started. The results are tabulated in Table 1.
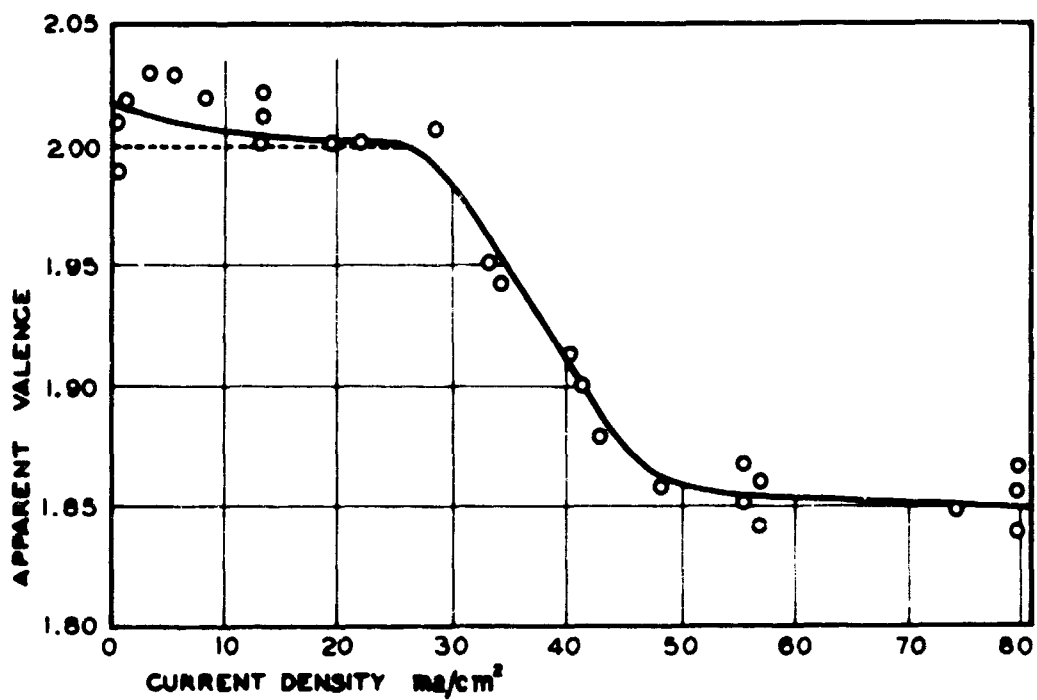
Fig. 1. Apparent valence as a function
of current density for Zn
dissolving anodically in 3 percent
KNO_3.

Table 1

Effect of Successive Valence Measurements of Zinc Ions Going into Solution from Zn Anodes (no polishing between runs).

Sample	Time sec.	C.d. $ma.cm^{-2}$	Wt. of Zn Exptl.	(g) Calcd.	Apparent valence
Monocrystal	2500	28.40	0.04234	0.04239	2.00
	2500	14.20	0.02082	0.02117	2.03
	2500	14.20	0.02424	0.02117	1.75
	1800	28.40	0.03209	0.03049	1.90
Polycrystal	2500	39.70	0.04333	0.04239	1.95
	2500	19.85	0.02123	0.02117	2.00
	2500	19.85	0.02562	0.02117	1.65
	1800	39.70	0.03457	0.03049	1.76

Provided polishing was performed between successive runs, the reproducibility of apparent valence was better than ±0.03.

The Effect of Ultrasonic Vibrations on Apparent Valence of Zinc Dissolved Anodically in a 3% KNO_3 Solution.

Apparatus. The apparatus was essentially the same as previously described except that the 400 ml. cell was replaced with an ultrasonic cell of equivalent diameter. The cell was connected to a G.V. 400 Ultrasonic Generator.

Procedure. The procedure followed the same general pattern as before. Ultrasonic vibrations were passed through the reaction cell during the complete test. The readings on the central dial of the generator corresponded to the maximum visible agitation in the nitrate solution and the maximum audible sound. This energy input occurred at 32,500 kilocycles per second, amplitude of 10 (maximum possible) and "G" impedance setting.

Data and Results. The data showed little difference from those found for zinc in the absence of ultrasonic vibrations. The average values for the apparent valence of zinc in 3% KNO_3 are 1.84 ± 0.03 and 1.86 ± 0.03 with and without ultrasonics respectively.

During electrolysis accompanied by ultrasonic agitation the black film still formed on the surface and the solution became turbid. The gelationous $Zn(OH)_2$ film generally present during electrolysis was not present to any large degree. If the zinc anode was etched slightly with dilute H_2SO_4 before a run, the black film spalled from the anode surface. After about five minutes the solution turned a gray-black murky color and the electrodes were barely visible. Upon terminating the ultrasonic agitation the dark particles settled to the bottom. Upon adding two drops of concentrated HCl to the electrolyte from which the electrodes had been removed, the solid dissolved and hydrogen gas was evolved. Titration of solutions from both etched and non-etched samples gave the same apparent valence.

A sample of the gray black material was collected by decanting the liquid and filtering the dark matter using dry acetone as a wash. Part of the sample turned white during and after filtering

Portions of the sample were viewed under a microscope using oil immersion at 1430 X. In reflected light, the grayer parts of the sample revealed a multitude of bright metallic

particles in a matrix of corrosion product. The diameter of the particles averaged about 10^{-5}cm. A sample taken from the darkest part of the material revealed a similar structure but more metallic particles. A few large chunks of metal (about 10^{-4}cm) could be seen floating in the oil. In transmitted light certain portions of the sample were black or opaque to light whereas in reflected light the corresponding portions appeared as bright reflecting particles.

As another means of identification, the darkest parts of the sediment were subjected to X-ray analysis. The diffraction pattern revealed the presence of zinc, ZnO, and $Zn(OH)_2$. These results are identical to those found by James and Stoner.[14]

Effect of Temperature on Apparent Valence.

Apparatus and procedure. The apparatus and procedure were similar to previous studies. The cell was opened to the atmosphere and any evaporation which occurred during electrolysis was corrected by addition of water at the same temperature to the electrolyte.

Data and Results. The apparent valence as a function of temperature is shown in Fig. 2.

It was speculated that this temperature dependency could be related to an activation energy by assuming that the overall rate constant k was proportional to the normal valence less the apparent valence. Accordingly, an Arrhenius plot of
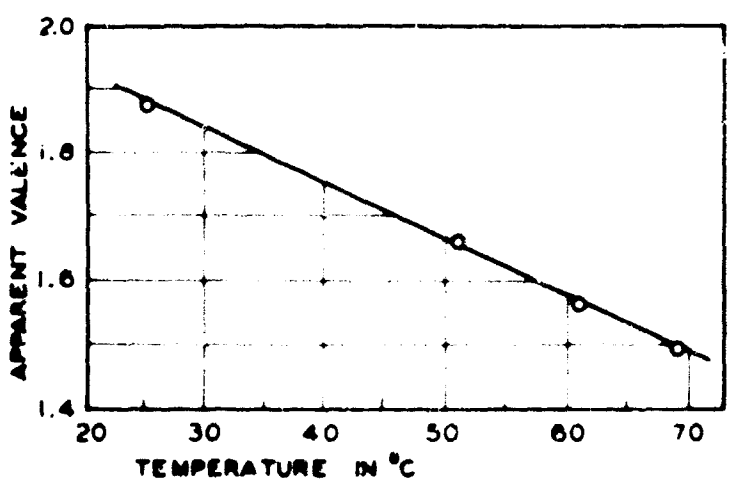
Fig. 2.   Apparent valence as a function of
temperature for Zn dissolving
anodically in 3 percent KNO₃.
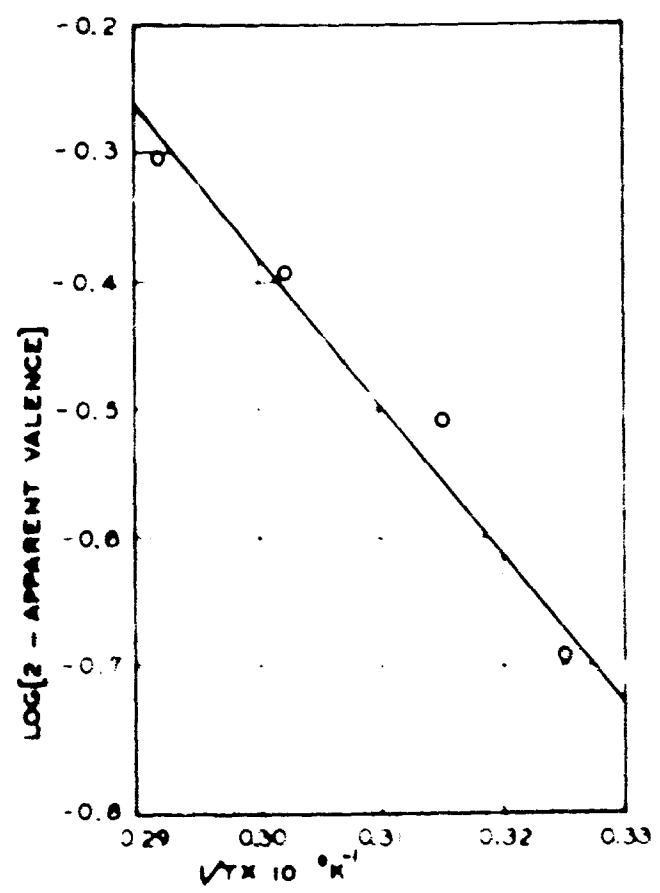

Fig. 3.   The variation of log apparent
apparent valence with reciprocal
absolute temperature

log(2 minus apparent valence) versus reciprocal temperature was made as illustrated in Fig. 3.

An activation energy of 4.2 kcal was found from the slope of the straight line. At the elevated temperatures an appreciable amount of gray corrosion product containing larger particles than were observed at lower temperatures settled to the bottom of the reaction cell. The electrolyte was decanted and a few drops of concentrated HCl were added. The material evolved hydrogen.

A sample of this material viewed under the microscope at 1430 X appeared similar to that previously described except that the number of metallic particles was considerably lower.

The electrolyte contained after the experiments nitrite ions, the amount of which was proportional to the decrease in apparent valence.

DISCUSSION AND CONCLUSIONS

At current densities, 50 to 80 ma.cm^{-2}, the apparent valence of zinc was found to be 1.86 ± 0.01. This value is in agreement with the results of previous works cited.[2,14] However when the current density dropped below 40 ma.cm^{-2} the valence started increasing and below 30 ma.cm^{-2} values close to the normal oxidation state of two were obtained.

These results are more in accord with the concept of anodic disintegration since the rate of mass loss due to anodic breakdown must be a function of instantaneous current density.[15] On this basis one would expect a decrease in the apparent
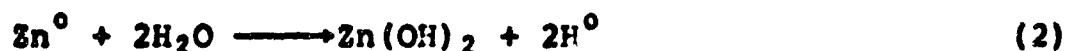
valence with increasing current density possibly to some limiting value. Furthermore it is noteworthy that at extremely low current densities, < 10 ma, the metal surface was in most cases completely free of the black surface film.

At room temperature where the current density studies were made, there was no difference between monocrystalline and polycrystalline zinc within experimental error. This proves that the mechanism does not involve the preferential attack of the electrolyte at grain boundaries to produce chunks of metal, which is in accord with the small size of the particles observed by Stoner.[14]

An interesting occurrence was the change in apparent valence during four consecutive tests performed without polishing the electrodes. It would be difficult to apply the concept of "uncommon valence ion" to explain these results. In any event the danger of attaching quantitative significance of deviations from normal valence without strict adherence to technique is apparent.

The results of the ultrasonic studies proved most interesting. The black film was formed on the anode surface as usual but the white gelatinous film of $Zn(OH)_2$, observed without ultrasonics, did not appear. Apparently the gelatinous film did not adhere well to the surface under ultrasonic agitation and was largely spalled off. If the anode surface is etched prior to electrolysis the spalling is more pronounced. The flakes which are continuously formed contain many metallic

particles originating from disintegration of the zinc anode. These particles appear very active and are oxidized by nitrate or water as follows:

$$Zn^{o} + NO_{3}^{-} + H_{2}O \longrightarrow Zn(OH)_{2} + NO_{2}^{-} \tag{1}$$

$$Zn^{o} + 2H_{2}O \longrightarrow Zn(OH)_{2} + 2H^{o} \tag{2}$$

$$NO_{3}^{-} + 2H^{o} \longrightarrow H_{2}O + NO_{2}^{-}$$

The last equation accounts for the presence of NO^{-} in the anolyte.

The similarity of behavior of the anodes in the presence or absence of ultrasonic agitation suggests the controlling step of anodic disintegration to be independent of this influence. In some way the current density is responsible for the breakdown of the anode. The active particles detached from the surface of the anode then react with the oxidizing electrolyte as proposed in equations 1 and 2 forming an oxide or hydroxide film around the particles. The resulting non-conducting film effectively insulates the unreacted metallic particles from electrical contact with the electrode thus accounting for the lower valence. As the film thickens a combination of compressional stress between the film and an undefined interface coupled with hydrogen pressure (reaction 2) cause the film to spall. The exposed metallic particles are thus free to undergo further hydrolysis to evolve hydrogen; those still protected by inclusion in the hydroxide matrix are preserved sufficiently long to allow their removal and subsequent observation in a water-free environment.

The fact that larger metallic particles could be obtained at higher temperatures together with lower apparent valences suggest that the extent of disintegration is increased. Alternatively the rate at which the particles are attacked at the surface of the metal might be expected to increase with temperature. The activation energy of 4.2 kcal suggests a possible rate determining step of adsorption or some physical process but this is only speculative.

The exact mechanism of anodic disintegration is not elucidated in this work, but it is suggested on the basis of limited information that certain areas or protrusions i.e., active sites, on the surface of the zinc anode adsorb the NO_3^- ion leading to the formation of ZnO as given by:

$$Zn + NO_3^- \quad ZnO + NO_2^-$$

The ZnO could then passivate these points allowing normal anodic dissolution to remove zinc from around the point which eventually would break off. This mechanism of undermining is also in accord with the current density effect in that the adsorption of the NO_3^- ion would be expected to increase with the increase of the positive potential and hence of current density until the surface was effectively saturated with the adsorbed ion.

This investigation shows again that the deviation from Faraday's law can be explained by disintegration of the anode because the particles are visible, their composition proved

by X-ray diffraction, and their reactions, e.g. with reducers, observed. The assumption of formation of lower valence ions, the presence of which cannot be proved, is not necessary and does not account for the experimental data in all respects.

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