



Experimental Research of Electrochemical Behaviour of Zinc in Ammonium Chloride Solutions

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Abstract: A present study was investigated “Experimental Research of Electrochemical Behaviour of Zinc in Ammonium Chloride Solutions.” The study was investigated by the electrochemical corrosion of zinc is a problem of high significance both in the fundamental and applied fields of electrochemistry. Hence investigations were undertaken to study the corrosion of zinc in storage systems, the electrodeposition and characterisation of zinc and the electrodeposition and characterisation of Sintered nickel alloy. Results show that Potential-pH diagram for zinc in $\text{ZnCl}_2/\text{NH}_4\text{Cl}$ electrolyte, as used in Laclanche's cell. When the surface composition of polished zinc. A freshly polished Zn surface was immersed in 0.5M NH_4Cl for 45 seconds and then analysed for energy measurements by ESCA. The composition of the modified zinc surface is summarised in table-1, When the binding energy was scanned in a narrow range of 1021 to 1010 eV, the participation of Zn 2P electrons in the bond formation was confirmed. The investigations on the zinc- NH_4Cl system were hence carried out with the following specific objectives: IC⁴ find out the structure and nature of the species formed on the surface of zinc when introduced in NH_4Cl solutions.

Keywords: Electrochemical Behaviour, zinc- NH_4Cl , Laclanche's cell, $\text{ZnCl}_2.2\text{NH}_3$ and, Experimental Research

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INTRODUCTION

A distinction is made between chemical, biochemical and electrochemical corrosion of metals. In chemical corrosion of metals, spontaneous destruction governed by the laws of ordinary heterogeneous chemical reactions take place. The destruction of metals attacked at high temperature by aggressive gases which prevent condensation of moisture on the metal surface and also evidently the dissolution of metals in contact with non-conducting organic media belong to this type. The biochemical corrosion or biocorrosion is caused by the vital activity of various microorganisms using a metal as a culture medium or evolving products which attack the metal.

This type of corrosion usually accompanies other types of corrosion. Soils of definite composition, stagnant waters and certain organic products greatly favour the progress of biochemical corrosion. Electrochemical corrosion is encountered more frequently than other types of corrosive destruction and is the most dangerous to metals. It may also occur in a gaseous atmosphere when moisture condenses on the metal surface, in solids and in solution.

Electrochemical Theory of Corrosion- A historical review of how the electrochemical theory of corrosion starts with the observation of Galvani where dissimilar metals were connected to the nerve of the Frog and brought into contact with each other, the nerve twitched showing some reaction. This observation

was subsequently made use of when Volta constructed this pile of dissimilar metals to show that electric current flows when dissimilar metals are connected to each other through an electrolyte. The baser metal dissolved when current was generated.

Nicholson and Charlislie and Davy and subsequently Faraday in 1834, established the close relationship between current and chemical reaction. Faraday, put forward the two basic laws which govern the relationship quantitatively and nomenclature for electrolytic cells. In 1827 Bacquerel, has proposed that corrosion took place when there was difference in oxygen concentration in a flowing stream which could give rise to a flow of current between two pieces of iron or zinc. De La Rive pointed out that if zinc was impure, it dissolved faster in acid solutions.

Spontaneity of Corrosion Processes- The posteriority of corrosion processes came to be more emphasised after the application of thermodynamic data showing the free energy decrease that took place when metals are converted to oxides, sulphates and carbonates. Except gold and platinum, all other metals showed a decrease of free energy by undergoing reaction with environments. This thermodynamic interpretation of the corrosion processes is mostly the work of Pourbaix who used the energetics of chemical reactions to calculate the equilibrium potentials and the Nernst equation of many metals in many environments and provided what was known as the potential-pH diagrams. At potentials above the equilibrium potentials of the metal/metal ion reaction, oxidation reaction takes place and below the equilibrium potentials, the reduction reaction takes place.

Heterogeneous theory of Corrosion

An experimentalist Evans and Hoar demonstrated that a cell was set up between the upper and lower portions of a steel specimen vertically immersed in potassium chloride solution. They measured the current flowing between the upper and lower portions when these are cut and joined together with wax coating at the cut edges.

The investigations were aimed at studying the corrosion of zinc. Zinc is used as anode in LeClanche's cell and many alkaline batteries. Zinc is used as a coating on iron and steel to prevent corrosion. Zinc-nickel alloy coatings are cost-effective if they offer twice as great corrosion resistance as zinc. Hence investigations were aimed at the development of non-cyanide and non-polluting baths for obtaining higher corrosion resistant electrodeposits.

This is now widely known as the Evans diagram. The current corresponding to the intersection point in this diagram correlated with the weight of the metal dissolved in accordance with the Faraday's laws. This is also known as the heterogeneous theory of corrosion and is best illustrated by the Peroxyl indicator test.

Homogeneous theory of Corrosion- It is not necessary that the anodic and cathodic reactions should take place at spatially separated areas. Often two or more electrode processes may take place independent of each other on the same metal surface. For example, iron dissolves in acid solutions giving rise to ferrous ions. Simultaneously hydrogen ions are reduced and liberated as hydrogen gas. These reactions can take place on the metal surface at the observed electrode potential.

These different approaches to the phenomenon of corrosion showed that corrosion is an electrochemical

process consisting of simultaneous oxidation of metal, its transfer into solution as metal ion and reduction of reducible species in solution both taking place at the same rate. The rate of corrosion process is therefore determined by the kinetics of the two types of electrode reactions. Hence further understanding of the rate of corrosion awaited the developments in electrochemical kinetics.

Progress in Electrochemical Kinetics:- The difference between the equilibrium potential E^0 when current flow through an electrode and the potential E when the current flows i. e. , $\eta = E - E^0$, was referred to as over voltage by Nernst and Caspar, Tafel found that the first rational empirical relation between overpotential and current density $\eta = a + b \log i$ Butler published in 1924 a kinetic treatment of the reversible electrode in which the concept of partial cathodic and anodic- currents are expressed as exponentially dependent on potential but the first explicit deduction of the relation between current density and potential under charge transfer control was made by Erdy Cruz and Volmer in 1930. They colonised that these processes should be studied by applying the laws of reaction kinetics and that the electrolytic hydrogen overvoltage is due to the slow neutralisation of hydrogen ions which in turn is caused by the high activation energy of this process.

The first attempt to describe a model of charge transfer was that of Horiuti and Polanyi in 1935. The treatment of electrode reaction as example of consecutive kinetic processes in which one reaction is rate determining was implicit in much of the work of Frumkin's school during 1930 and was clearly discussed by Bowden and Agar in 1938. The further important step in the development of electrode kinetics was made by Frumkin in 1933 who showed that the structure of electrochemical double layer at the electrode solution interface affected the kinetics of the electrode process.

AIMS OF THE STUDY

The electrochemical corrosion of zinc is a problem of high significance both in the fundamental and applied fields of electrochemistry. Hence investigations were undertaken to study the corrosion of zinc in storage systems, the electrodeposition and characterisation of zinc and the electrodeposition and characterisation of Sintered nickel alloy. The work carried out is discussed.

Electrochemical Behaviour of Zn- NH_4Cl

Zinc dissolution on discharge affects the shelf life of systems based on Zn- NH_4Cl The dissolution behaviour was studied using BAS 100 electrochemical Analyser and mechanisms proposed for the reactions occurring. The influence of anions on the Zn- NH_4Cl system was studied.

Electrochemical Behaviour of Zinc in KOH Zinc passivation in KOH, the effect of carbonation on the Zn/KOH system, and the inhibition of corrosion of Zn in the system by sulphur compounds, were investigated in detail and the results presented. Electrodeposited zinc is used extensively to protect iron and steel components from environmental corrosion. In view of the desire in the context of pollution abatement, to replace cyanide plating processes with new ones. attention has been directed towards using non-toxic and non-hazardous complexing agents. Rochelle's salt, viz., potassium sodium tartrate is one such agent, known to produce fine-grained deposits. Hence a bath based on Rochelle's salt was developed for zinc electrodeposition and characteristics of the deposits studied.

Renewed interest in the zinc-nickel alloy has come to replace cadmium in the automobile industry. The development of a Zn-Ni deposit with 82% and above zinc was achieved from a sulphate bath. Characteristics of the deposits were studied.

For both Zn and Zn-Ni electrodeposition, the data relating to the baths and deposits included: Hull cell patterns, current efficiency studies, polarisation of cathodes, throwing power experiments, anode corrosion and bath conductivity. The deposits were characterised for adhesion, micro-hardness, porosity and structure and were compared with conventional baths.

For the evaluation of corrosion resistance of the deposits, salt-spray, weight-loss and immersion studies were used as non-electrochemical methods and potentiation and linear polarisation and galvanic current measurements were employed as electrochemical methods.

State of Art- In the 1860's George Leclanche developed the highly important Zn(Hg)/NH₄Cl/MnO₂ cell. In this cell was used an amalgamated zinc rod anode and MnO₂, mixed with carbon surrounding a carbon current collector, all in a porous container as a cathode. The electrolyte was a saturated solution of NH₄Cl. These cells had a relatively low self-discharge rate. The use of metal halides and halogens as cathode reactants in zinc-anode primary cells with alkaline electrolyte was studied in the 1880s and 1890s. Carbon was the most common electrode for the reduction of halogens, although in some cases a platinum catalyst was added to the carbon.

The Leclanche cell electrolyte represents a special case in that other solid reaction products such as diamines (e.g. ZnCl₂·2NH₃) can be formed. Brouillet and Jalas have constructed a potential-pH diagram for zinc in a Leclanche's cell electrolyte. In actual cell operation, the electrolyte pH can vary between 4 and 9. Below a pH of 5.8, the discharge product is zinc ion. In the pH interval 5.8 to 7.85 crystalline diamine (Zn(NH₂)₂) is formed. Above pH 7.85, the diamine dissolves to form Zn(NH₂)₄ ions.

Table-1 Parameters derived from small spot ESCA studies on Zinc electrodes

Polished zinc				Zinc surface dipped in 0.5M NH ₄ Cl			
Energy	Width	Area	%	Energy	Width	Area	%
Zn2P ₃							
1014.81	1.55	73648	23.0	1015.32	1.29	33517	22.2
1015.85	1.78	246701	77.0	1016.44	1.63	117350	77.8
C1s							
279.18	1.42	1039.43	82.6	279.69	1.29	136361	82.6
260.79	1.25	11055	8.8	281.05	1.34	15670	9.5
282.89	1.67	10828	8.6	282.63	1.30	6538	4.0
				263.97	1.14	6561	4.0

Table-1 Are Potential-pH diagram for zinc in ZnCl₂/ NH₄Cl electrolyte, as used in Leclanche's cell.

Research Programme-

In the Leclanche's cell, corrosion and its effect on cell water balance constitutes important limitations on the storage or shelf life. Detailed investigations on the zinc- NH₄Cl system were hence carried out with the

following specific objectives: IC⁴ find out the structure and nature of the species formed on the surface of zinc when introduced in NH₄Cl solutions.

RESULTS

Electrochemical Behaviour of Zn in NH₄Cl - Surface composition of the zinc electrode dipped in NH₄Cl

Solutions: - In order to identify the structure of the species formed on zinc when introduced in 0.5 M NH₄Cl solutions, X-ray photoelectron spectroscopic studies (XPS) or also known as Electron Spectroscopy for chemical Analysis (ESCA) studies were carried out. It is known that low energy photoelectrons emerge from the outer surface layers of solid materials. Zinc electrode (99.99% purity) of 1 cm area was polished to a mirror finish using 0/1 to 0/4 emery papers, degreased with trichloroethylene and then introduced in the ESCA equipment for energy measurements. Small spot ESCA plots of counts in Binding Energy table-1 showed the presence of Zn 2P_{1/2}, Zn 2P_{3/2} peaks and the formation of surface oxide films formed before the introduction of the specimens into the ESCA chamber. The appearance of IS carbon peak may be due to the inclusion of emery particles, or the non-evaporated, adsorbed trichloroethylene molecules.

It is summarising the surface composition of polished zinc. A freshly polished Zn surface was immersed in 0.5M NH₄Cl for 45 seconds and then analysed for energy measurements by ESCA. The composition of the modified zinc surface is summarised in table-1, When the binding energy was scanned in a narrow range of 1021 to 1010 eV, the participation of Zn 2P_{1/2} electrons in the bond formation was confirmed. The number of electrons involved in the formation of zinc complexes with the binding energy of 1015 eV was confirmed from the reduction in the area of the electrons Zn in NH₄Cl.

DISCUSSION

From the above discussions it is understood that zinc dissolves in NH₄Cl solutions involving DSP electrons and the Binding Energy (eV). The XPS studies revealed that zinc dissolves in NH₄Cl with the 4 2 involvement of dSP² electron and forms a tetrahedral species having probably the structure Zn(NH₃)₂pCl₂. An increase in ammonium ion and chloride ion concentrations increased the corrosion rate of zinc. Potentiostatic polarisation curves revealed that corrosion currents decreased in presence of ZnCl₂, with the shift of E_{corr} to more positive values. The presence of ZnCl₂ hindered the dissolution reaction. The corrosion of zinc in NH₄Cl solutions involves the dissolution of zinc as the anodic and the reduction of oxygen as the cathodic process. The dissolution reaction involves ZnCl₂ + NH₄⁺ → Zn(NH₃)(Cl) as the slow steps. The presence of anions increased the corrosion of zinc in NH₄Cl solutions. Corrosion was more in presence of chromate > borate > silicates > phosphates > oxalates. Soluble zinc complexes are formed which cause the depassivation.

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