

AN INSIGHT INTO THE ORIGIN OF CORROSION POTENTIAL — A CRITICAL REVIEW

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Measurement of corrosion potential of metals is a non destructive tool to understand the changes occurring on the corroding surface. Galvani (1791) observed the flow of current between dissimilar metals. Faraday (1820) gave quantitative relationship between metal dissolved or deposited with the quantity of electricity. Evans and Hoar (1932) proposed the heterogeneous theory of corrosion and Wagner and Traud (1938) presented the homogeneous theory of corrosion and the concept of mixed potential. In 1960 the corrosion potential was understood in terms of the area ratios of anodic and cathodic sites. Pourbaix (1966) correlated the energetics of the corrosion process with solution pH. In 1978, it was seen that the corrosion potential to be dependent on solution parameters. Recently, the physical meaning of corrosion potential was understood in terms of ionic and electronic energy levels in metals. Various ideas presented are reviewed and discussed in detail.

Keywords: Corrosion potential

INTRODUCTION

The electrochemical understanding of the phenomenon of corrosion starts with the observation of Galvani in 1791 [1] where dissimilar metals were connected to the legs of a frog and brought into contact with each other the nerve twitched showing some reaction. Subsequently volta who constructed a pile of dissimilar metals to show that the electric current flows through an electrolyte. Faraday [2] in 1820 put forward the two basic laws which govern the relationship between the metal dissolved and the quantity of electricity flowed.

The spontaneity of corrosion processes came to be more emphasized after the application of thermodynamic data showing the free energy decrease that took place when metals were converted to oxides, sulphides and carbonates. Except gold and platinum, all other metals showed a decrease in free energy by undergoing reaction with environment.

Thermodynamics of corrosion processes

The magnitude of the change in Gibbs free energy, ΔG is a measure of the tendency of any chemical reaction to go and is represented by the work

capacity or maximum electric energy available in the system. A large negative value of ΔG indicates a pronounced tendency for the reaction to proceed whereas a positive value indicates that the reaction has no tendency to proceed and a metal cannot corrode. For oxidation of a transition metal M the reaction is represented by $2 M + H_2O + 3/2 O_2 \rightarrow M_2O_3 \cdot H_2O$. The ΔG for the reaction is expressed in terms of potential $\Delta G = -nFE$. The application of thermodynamics to corrosion phenomenon has been generalized by means of potential - pH diagrams or Pourbaix diagrams [3]. The diagrams were constructed using the energetics of chemical reactions to calculate the equilibrium potentials and Nernst equations. At potentials above the equilibrium potentials of the metal/metal ion reaction, oxidation reaction takes place whereas at potentials below the equilibrium potential the reduction occurs.

Electrochemical corrosion kinetics

Nernst and Caspari [4] referred the difference between the equilibrium potential E_e and the potential E , when the current flows as η . It was Tafel [5] who found the first rational empirical relation between over potential and current

density. $\eta = a + b \log i$. Butler [6] 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. Erdy Gnuz and Volmer [7] in 1930 recognised that these processes should be studied by applying the laws of reaction kinetics. In 1933 Frumkin [8] showed that the structure of the electrical double layer at the electrode/solution interface affected the kinetics of the electrode processes.

In 1932 Evans and Hoar [9] demonstrated that a cell was set up between the upper and lower portions of a steel specimen vertically immersed in KCl solution. They measured current flowing between the upper and lower portions when these were cut and joined together with wax coating of the cut edges. They also plotted potential against current for the two regions and got a polarization (change of potential with current) diagrams known as Evan's diagrams. The current corresponding to the intersection point in this diagram correlated with the weight of the metal dissolution in accordance with Faraday's laws. The above ideas were based on the assumption that the anodic and cathodic reactions should take place at spatially separated areas.

Mears and Brown [10] showed that the corrosion of aluminium in salt solution could be explained in terms of the current flowing between scratched and unscratched portions. Thus the electrochemical mechanism of corrosion came to be widely accepted as the best explanation of corrosion process in aqueous media.

In practice, more often occasions arise when two or more electrode processes may take place independent of each other on the same surface. Iron dissolves in acid solutions giving rise to ferrous ions. Simultaneously hydrogen evolves at a certain potential. These two reactions occur at the same potential known as mixed potential. The mixed potential is decided by the extent of the polarization of iron dissolution reaction and hydrogen evolution reaction from their respective equilibrium potentials. These concepts of mixed potential and homogeneous theory of corrosion were proposed by Wagner and Traud [11] in 1938.

The inter relation between current and potential of corroding system caused a delay in the understanding of corrosion potential and further understanding awaited the developments in heterogeneous electron transfer processes.

Heterogeneous electron transfer

The transfer of electron from a metal to solution across the interface was thought by Gurney who considered the tunneling of electrons [12-14]. He showed the exponential dependence of current on potential. He understood the electron transfer as neutralization of gaseous ions at an electrode. He assumed that the energy of the electron on the left and the right sides of the energy barrier at the electrode/solution interface is the same (e.g. an electron in an electrode) is equal to that of the electron in the acceptor (electron in solution).

Fig. 1 presents the schematic diagram of the potential energy barrier at the interface of a metal electrode and protons in solution. These protons are affected by the solvation energy L and after neutralization the repulsion energy between H atom and H_2O molecules, R together with the adsorption energy, A has to be taken into account. The Fermi level of the metal is below the ground state of H^+ ions in solution under zero applied potential V . The energy of the electron in the E_f was made less negative than the energy of the vacant electron level in the H^+ ions in solution. It was Gurney who pointed out that not all ion-solvent bonds are in their ground states and corresponding to each vibrational level there should be a solvation energy. H_3O^+ will have a large number of vibrational and rotational levels in which the levels would be distributed as dictated by Boltzmann's law. These levels of ions are sufficiently blurred by the interaction with the adjacent solvent molecules that they may be treated as forming a continuous spectrum of levels. As a result the single value of the energy level of the ion in solution must be replaced by a band of levels. According to the Boltzmann's distribution function the electron energy levels in H_3O^+ corresponding to its different vibrational-rotational energy levels can be expressed as $N(U_n) = N(U_0) \exp(-U_n - U_0 / RT)$ where U_0 is the vibrational rotational energy of the $H^+ - H_2O$ bond

when it is in the ground state and U_n is that when it is in the n th vibrational-rotational state. Since $(E_n - E_0) > (U_n - U_0)$ then $(U_n - U_0) = \beta (E_n - E_0)$ where E_0 is the electron energy when the $H^+ - H_2O$ bond is in the ground vibrational-rotational state. E_0 is the electron energy in the n th state; β is the symmetry factor. The acceptor ions in solution at any electron E and at any distance from the electrode can be got by

$$N(E) = N(E_0) \exp = \frac{\beta (E - E_0)}{RT} \quad (1)$$

The heterogeneous charge transfer processes were found to be affected by interfacial potentials. These interfacial potentials were modified by adsorption of ions or molecules from solution. It was Frumkin (Loc, cit) who demonstrated the influence of adsorption of species from solution affecting hydrogen evolution reaction. An attempt was made by Antropov [15] who made a systematic study of adsorption of organic molecules and correlated with inhibition of hydrogen evolution reactions. The effectiveness of inhibitors of acid corrosion was directly related to

the lowering of interfacial tension at the mercury/solution interface. The corrosion potential relative to the point of zero charge (P_{zc}) was considered to be important to understand adsorption. Adsorption of organic molecules affecting corrosion potential was explicit in his work.

In 1970's heterogeneous electron transfer reactions were understood in terms of surface area. The reaction rates were found to be influenced by area of the active surface and interfacial potential. The corrosion potential was understood in terms of local area ratios of anodic and cathodic sites. The dissolution of metal under activation controlled conditions was directly proportional to area of the anodic sites and the cathodic reaction to that of area of cathodic sites. The effectiveness of inhibitors and passivators were understood in terms of corrosion potential.

At corrosion potential, the rate of metal dissolution reaction and the rates of cathodic reactions were equated to corrosion current. It was found that [16]

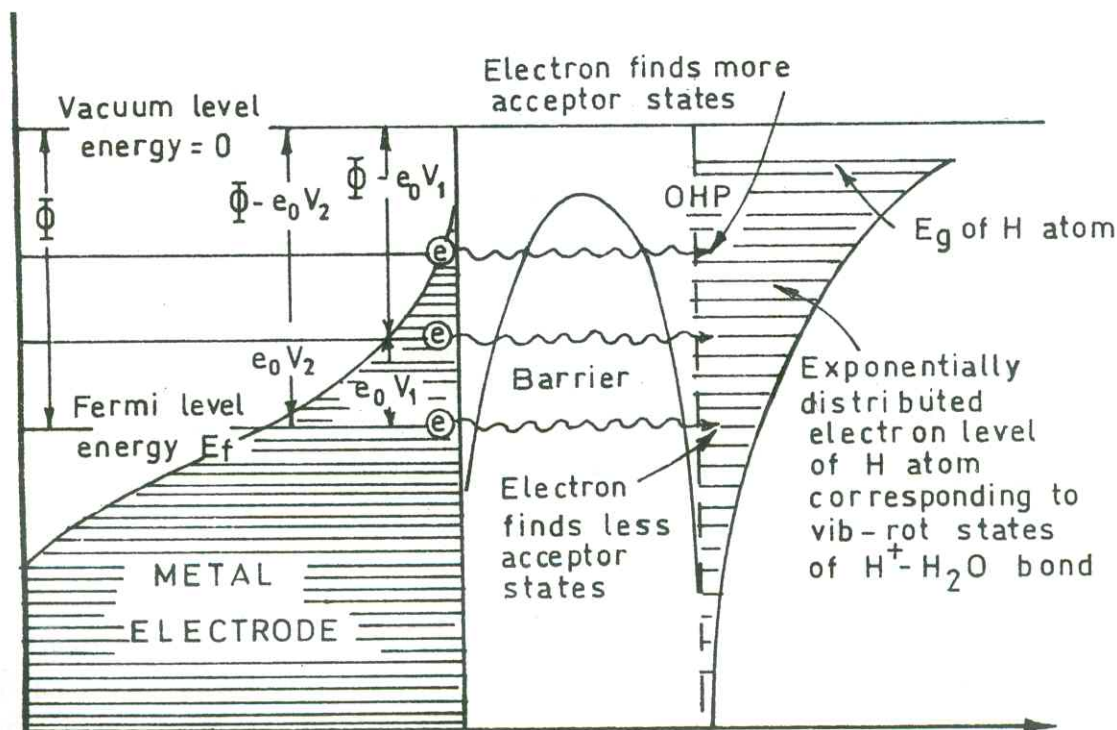


Fig. 1: The schematic diagram of the potential energy barrier at the interface. The ground state energy electron energy level of H atom and the exponentially distributed electron level of H atom corresponding to vibrational-rotational states of $H^+ - H_2O$ bond

$$E_{\text{corr}} = E_{\text{corr}}^x + \frac{RT}{(\alpha_a + \alpha_c)F} \ln \left(\frac{A_c}{A_a} \right) \quad (2)$$

where α_a and α_c are the transfer coefficients of anodic and cathodic reactions; A_c and A_a are the area of anodic and cathodic sites on the corroding surface respectively. The variation of E_{corr} with time over a period of minutes, hours or days was understood as due to the changes in area ratios. When the ratio of (A_c/A_a) is greater than one corrosion potentials would become noble. the corrosion potentials would become active when the ratio of $A_c/A_a < 1$. The surface conditions due to the changes in areas in which oxidation and electronation occur also decide the absolute value of E_{corr} .

When the metal dissolution reaction was under activation controlled and molecular O_2 reduction as cathodic reaction was under diffusion controlled then

$$E_{\text{corr}} = E_{\text{corr}}^x + \frac{RT}{\alpha_a F} \ln \left(\frac{A_c}{A_a} \right) \quad (3)$$

This situation occurs normally in flowing electrolytes and it was observed that corrosion potential of materials under static conditions was different from those obtained under flow conditions [17].

As the solution properties decided the absolute value of corrosion potential, in 1970's attempts were made [18-19] to correlate E_{corr} with solution parameters. To achieve this end, analytical expressions were obtained. The identification of anodic and cathodic reactions was done. This was done using potential - pH diagrams. The number of electrons involved in the corrosion process was calculated by coulombic analysis. Once the identification of individual reactions was completed the anodic and cathodic reactions were studied. The rate equations for individual rate determining steps were equated to i_{corr} .

$$i_{\text{corr}} = \frac{\text{current due to rds of dissolution}}{\text{current due to rds of cathodic reaction}} \quad (4)$$

Then expressions for E_{corr} were obtained. the anodic and cathodic reactions proceed simultaneously at distinguished anodic and

cathodic sites. These sites arise due to electrochemical heterogeneity of surfaces.

Electrochemical heterogeneity of surfaces

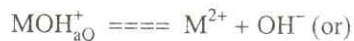
Multielectrode galvanic corrosion cells on a surface are due to this effect. Macroheterogeneous corrosion arises due to the differences in concentrations of neutral salts or of pH or of oxygen or other oxidizing agents. Microheterogeneity arises due to different crystal orientations, presence of grain boundaries, segregations, pores in protective films. If the grain boundaries happen to be the anodic portions very dangerous intergranular corrosion results. The galvanic current flow in these areas decide the value of E_{corr} .

Adsorption of oxygen from the solution causes passivity. The corrosion and passivation is decided by the species present in the medium.

Passivation and depassivation

The adsorbed oxygen interacts electronically with the metal forming a chemisorbed bond. A second layer of O_2 molecules may chemisorb on the top of first monoatomic layer but is less energetically bound than the first. This adsorption is considered to interpose a stable barrier of O_2 atoms and O_2 molecules between the metal and the solution displacing water molecules and increasing the activation energy for metal dissolution.

Metal dissolution can occur as [20-21]



The dissolution or passivation phenomena depend on θ_{MOH} and OH^- concentration [22-23]. When $\theta_{\text{MOH}} = 1$, a continuous film is formed on the surface. They could become more than a monolayer thick. The continuous film formation theories could be applied to the transpassive region by taking into account the increase of the

film dissolution current density ($i_{d,p}$) with potentials.

The passive film covered surface exhibits a potential which is a sum of the interfacial potential differences of metal/film and film/solution interfaces. The film growth can occur either by hopping-motion of metallic ions or place exchange mechanism [24- 25].

$$E = \eta_{m/f} + \eta_f + E_f \quad (10)$$

The E_f is the Flade potential of the film formation. $\eta_{m/f}$ is the potential drop at the metal/film interface. η_f is film forming overpotentials.

The adsorption of aggressive anions from solution on the film surface may lead to depassivation [26,27,28] sometimes preferential depassivation can cause pitting. The pitting potential was a subject of continuing interest. The film surface/solution interface acts as a double layer. Depending on the potential of zero charge (pzc) the extent of adsorption of aggressive anions, charges present on the solution side of the double layer can decide pitting. The adsorbed anions may favour the formation of soluble complexes with metal ions. The concept of non uniform dissolution with special reference to inhomogenities and local stress points and adsorption of anions is also known [29,30]. Pitting is considered as a specific case of crevice corrosion [31,32]. The surface of the initiating pits will be covered by an adsorbed layer or by a salt film resulting from metal dissolution.

The origin of pitting potential [33] was thought to occur due to film fracture through the application of stress. The pitting potential is due to a critical potential above which an internal film pressure exceeds the compressive stress for the film fracture. The film pressure was determined as the sum of two terms, the electrostriction effect and the interfacial tension. The occurrence of pitting potential [34] is also due to the formation of pores through the passive film. This corrosion potential is the lowest potential value for pore formation below which the passive film is resistant to electrocapillary breakdown. The corrosion potential of the pit is decided by the acidity of the local areas [35]. In neutral solutions the pitting potential is given by the following:

$$E_{pit} = E_0 + \eta + \Phi \quad (11)$$

where E_{pit} is the corrosion potential at the pit, E_0 is the corrosion potential in acidified solutions; η is the polarization necessary to obtain a current density high enough to maintain acidity inside the pit, Φ is the potential drop inside the pit.

Physical meaning of corrosion potential

In 1986, the physical meaning of electrode potential based on the energy level of electron and ion in the electrode was discussed by Trasatti [36,37]. It was sato who tried to understand the origin of electrode potential in terms of ion energy in solution. A discussion on the electron and ionic energy levels in metal is essential to understand the meaning of mixed potential.

Fig. 2 presents the energy level of electron in an electrode partially immersed in an electrolyte. The electron may be transferred from vacuum to solution and then from solution to metal. Otherwise there would be a direct transfer of electrons from vacuum to metal. The energy

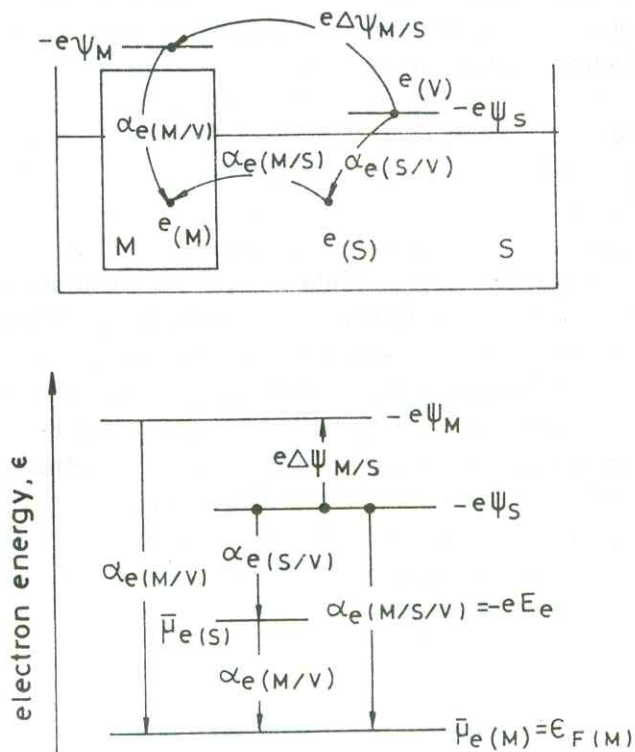


Fig. 2: Energy level of electron in electrode partially immersed in electrolyte solution. $\Delta\psi_{M/S}$ = The outer potential difference between the electrode and solution

needed for transferring electrons from the outer potential $[\mu_e(\text{std}) - e\psi_s]$ through the solution to the $E_{F(M)}$ is the real potential of an electron in the electrode $\alpha_e(M/S/V) = \mu_e(\text{std})$ is the chemical potential of gaseous electron in the standard state. $\alpha_e(M/S/V) = \mu_e(M) - e\Delta\Phi_{M/S} - eX_{s/v} = eE_e$, where $X_{s/v}$ is the surface potential. The reference level for E_e is the electronic level at the point of the outer potential ψ_s of the solution and hence at $\mu_e(r) = -e\psi_s$. To measure the electronic electrode potential, a reference electrode is needed. The relative electrode potential can be given by the potential difference ΔE between the test potential E_e and the reference electrode potential E_e^0 . When the outer potentials ψ_s of the two electrodes is identical, ΔE_e represents the difference in the electrochemical potential $\mu_e^*(M)$ and of the $E_{F(M)}$ of electron in the two electrodes.

Electron energy concept of corrosion process

Let us consider the corrosion of pure iron indeoxygenated acid solutions. At the E_{corr} , iron dissolution rate becomes equal to hydrogen evolution rate. Iron dissolution would occur at potentials anodic to $E_{A(eQ)}$. At anodic potentials the electron energy levels of the electrons in the metal decreased and the ionization energy of metallic atom also decreased. This facilitated the transfer of metallic ions from the metal lattice to solution. The energy level of electrons in the metal are increased by cathodic polarization. Hydrogen evolution reaction would occur at potentials cathodic to E_e of hydrogen electrode, $E_{e(eQ)}$. When a metal, iron, corrodes the electron energy level lies in between $E_{e(eQ)}$ and $E_{c(eQ)}$. The anodic overvoltage, $\eta_a = E_{\text{corr}} - E_{A(eQ)}$; if η_a is related to anodic reaction affinity as $A^+ = 2e\eta_a$. The cathodic reaction affinity is $A^- = 2e\eta_c$ where $\eta_c = E_{\text{corr}} - E_{c(eQ)}$ (Fig. 3). It may be seen that $E_F(M^{2+}/M) > E_{F(M)}$ while $E_F(H^+/H_2)$ and $E_{F(M)}$ the energy of electron in the metal is related to E_{corr} .

$$E_{\text{corr}} = \frac{-\mu_e(M)}{2e} + \Delta\Phi_{M/S} + X_s \quad (13)$$

The corroding metal surface may also be considered as having distinct anodic and cathodic areas. The different sites may assume a different

interfacial potential difference at the interface (Fig. 4). The overall corrosion potential expressed as

$$\delta(\Delta\Phi)_{M/s} = (\Delta\Phi)_{(M/s)(a)} - (\Delta\Phi)_{(M/s)(c)} \quad (14)$$

DISCUSSION

The metal dissolution/deposition reaction has a distinct equilibrium potential which is governed by Nernst equation. The corrosion potential arises due to the departure from the equilibrium potentials of anodic and cathodic reactions. The departure, overvoltage is decided by the flow of current (either externally or internally). The corrosion potential has no thermodynamic significance unlike equilibrium potentials.

The corroding metal consists of a sea of electrons and metallic ions. The ionization energy of the metal atom in the metal decides the leaching of the metallic ions away from the surface. This

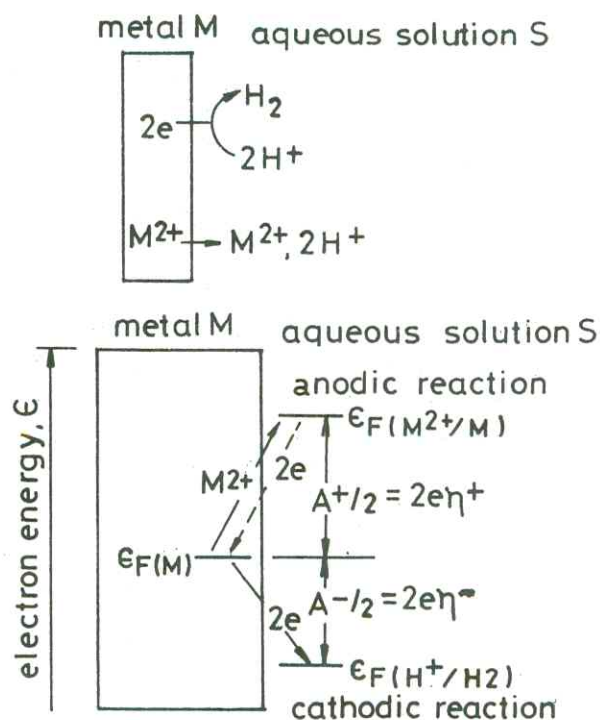


Fig. 3: Energy level of electron in homogeneously corroding metal

$E_{F(M)}$ = Fermi level of electrode electron

$E_{F(M^{2+}/M)}$ = Hypothetical Fermi level equivalent to metal ion transfer equilibrium

$E_{F(H^+/H_2)}$ = Fermi level of redox reaction in equilibrium of hydrogen electrode reaction

A^+/A^- = are the affinities of anodic and cathodic reactions
 η^+/η^- are the overvoltages

ionization energy is lowered by surface heterogeneities and impurities. Dissolution of metal atoms involves the solvation of metal ions which is governed by the solvation energy. The hydration of metallic ions and diffusion in the solution are decided by the properties of solution. The presence of anions, aquo and other ligands decide the extent of hydration. The corrosion potential is decided not only by the solution properties but also by the reactions occurring at the surface. The dissolution, formation of soluble or insoluble species, precipitation on the corroding surface may alter the active surface areas and thereby E_{corr} . The complete coverage of the surface by insoluble film causes passivation and ennoblement in E_{corr} . When two different metals in the electrochemical series are connected, the metal with most electronegative potential is more prone to dissolve in electrolytes. However, it can be shown that the standard electrode potential values as given in the emf series of metals are irrelevant in predicting galvanic phenomenon. For example aluminium ($E^0 = -1.66 \text{ V}$) and lead ($E^0 = -0.13 \text{ V}$) resist dilute H_2SO_4 while iron ($E^0 = -0.44 \text{ V}$) dissolves. Both zinc ($E^0 = -0.76 \text{ V}$) and steel corrode by themselves in aqueous solutions but when coupled the former corrodes and the latter is protected. Hence the galvanic voltage of the couple does not depend on $E_{\text{F(M)}}$ of individual metals. Nature of the corrosion products and kinetics of reactions decide the voltage. So also micro and macro heterogeneities on corroding surface decide the absolute value of E_{corr} .

The ideas based on ionic and electronic levels in the metal may not be able to explain the variation of E_{corr} with time. The observed variation in corrosion potential of metals in static and under flow conditions is due to the diffusion of the reducible species to the metal surface. It is the kinetics that controls E_{corr} . The local cell theory of corrosion (loc, cit) was explained assuming different $\Delta\Phi_{\text{M/s}}$ at anodic and cathodic sites. As E_{F} for the corroding metal being constant for a given metal, anodic and cathodic areas cannot exhibit different $\Delta\Phi_{\text{M/s}}$. The surface potentials variation at different sites causing E_{corr} variation

at anodic and cathodic sites in an over simplification.

The electronic and ionic concepts of corroding metal may help in the understanding of protection potential, a value of potential which lies in the immune region of the potential -pH diagram. If the ionization energy of the metallic atoms are raised so high that virtually no metal atom leaves the lattice. The electron energy of the electrode electron should be raised to prevent metal atom ionisation but not to cause hydrogen evolution.

Heterogeneous theory of corrosion advocates the flow of current between anodic and cathodic sites on the surface. The magnitude of the micro and macrogalvanic current depends on the distance of separation and the resistance offered by the medium. The corrosion potential thus involve contributions by galvanic current multiplied by the resistance of the medium (IR drop). As the resistance of the medium contributes significantly to corrosion potential errors occur during the

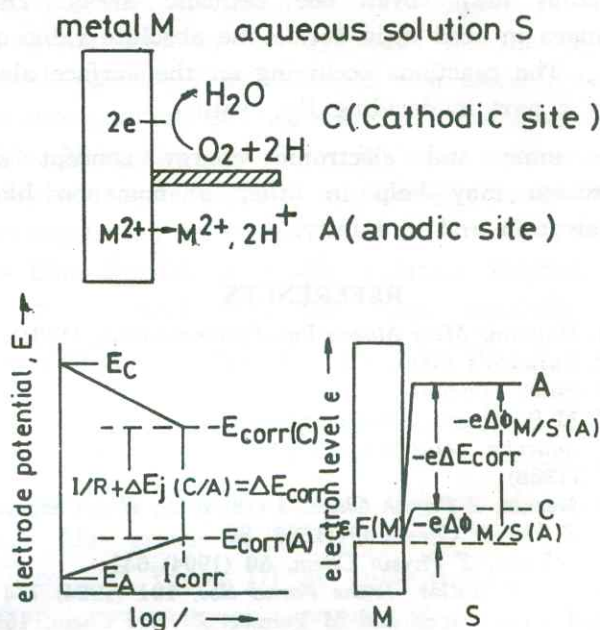


Fig. 4: Polarisation curves of anodic and cathodic reactions of localised metal corrosion
 E_C, E_A are the equilibrium potentials of cathodic and anodic reactions
 $E_{\text{corr}}^C, E_{\text{corr}}^A$ are the corrosion potentials at cathodic and anodic sites
 $\Delta E_j(C/A)$ liquid junction potentials

measurement of corrosion potential. The contribution by system resistance would be enormous when the metal is buried in sand, soil and in concrete structures.

The elimination of errors in measurements involves in the development of reference electrodes [41]. The position of the Luggin capillary or the tip of the reference electrode helped to minimise this error. Embeddable electrodes have been developed [42,43] to eliminate or to minimise IR contribution in the measurement of corrosion potential in buried structures.

CONCLUSION

The corrosion potential arises due to the departure from the respective equilibrium potentials of anodic and cathodic reactions. A flow of micro galvanic current decides the extent of polarization. Solvent molecules and other ligands in solution decide the extent of dissolution. Formation of soluble and insoluble products reduces the active anodic areas whereas adsorption of species from solution may cover the cathodic areas. The changes in area ratio decide the absolute value of E_{corr} . The reactions occurring on the surface also play a part in deciding E_{corr} values.

The ionic and electronic energy concept of corrosion may help in other phenomenon like passivation and immunity.

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