

## CHAPTER TWO

### CYCLIC VOLTAMMETRY: SOME THEORETICAL ASPECTS

#### 2.1. Voltammetric Techniques and Their Applications to Adsorption Studies

##### 2.1.1. Introduction

Linear sweep voltammetry and cyclic voltammetry are examples of several potential-sweep techniques in which the electrode potential is ramped between two limits at a particular rate while the electrode current is monitored. The resulting curve is known as a voltammogram and provides information on the rate of electrochemical reactions as a function of potential. From the sweep-rate dependence of the voltammetric data several quantitative properties of the charge-transfer reaction can be determined. It is, however, in qualitative mechanistic investigations that sweep techniques, in particular, cyclic voltammetry, are most useful.

##### 2.1.2. Linear sweep voltammetry (LSV)

Linear sweep voltammetry involves applying a linear potential sweep to the working electrode (the electrode under study) whilst monitoring simultaneously the current flowing in the circuit. A signal generator produces a voltage sweep from  $E_i$  to  $E_f$  and a potentiostat applies this potential wave to the electrode under study. The scan direction can be positive or negative and in principle, the sweep rate can possess any constant value:

$$\text{Sweep rate} = dE/dt$$

This method of analysis is commonly employed in polarography whereby under well-defined conditions, the limiting current derived from a redox process in solution during LSV may be used to quantitatively determine the concentration of electroactive species in solution.

##### 2.1.3. Cyclic voltammetry (CV)

Cyclic voltammetry is a method for investigating the electrochemical behaviour of a system. It was first reported in 1938 and described theoretically by Randles [1]. In this technique current flowing between the electrode of interest (whose potential is monitored with respect

to a reference electrode) and a counter electrode is measured under the control of a potentiostat. The voltammogram determines the potentials at which different electrochemical processes occur. The working electrode is subjected to a triangular potential sweep, whereby the potential rises from a start value  $E_i$  to a final value  $E_f$  then returns back to the start potential at a constant potential sweep rate. The sweep rate applied can vary from a few millivolts per second to a hundred volts per second. The current measured during this process is often normalised to the electrode surface area and referred to as the current density. The current density is then plotted against the applied potential, and the result is referred to as a cyclic voltammogram. A peak in the measured current is seen at a potential that is characteristic of any electrode reaction taking place. The peak width and height for a particular process may depend on the sweep rate, electrolyte concentration and the electrode material [2,3].

Cyclic voltammetry makes possible the elucidation of the kinetics of electrochemical reactions taking place at electrode surfaces [4,5]. In a typical voltammogram, there can be several peaks. From the sweep-rate dependence of the peak amplitudes, widths and potentials of the peaks observed in the voltammogram, it is possible to investigate the role of adsorption, diffusion, and coupled homogeneous chemical reaction mechanisms [3,6].

#### **2.1.4. Electrochemical processes that occur at an electrode surface**

The reaction taking place between the electrode surface and species within the solution can proceed through two different processes, which are either Faradaic or non-Faradaic [7].

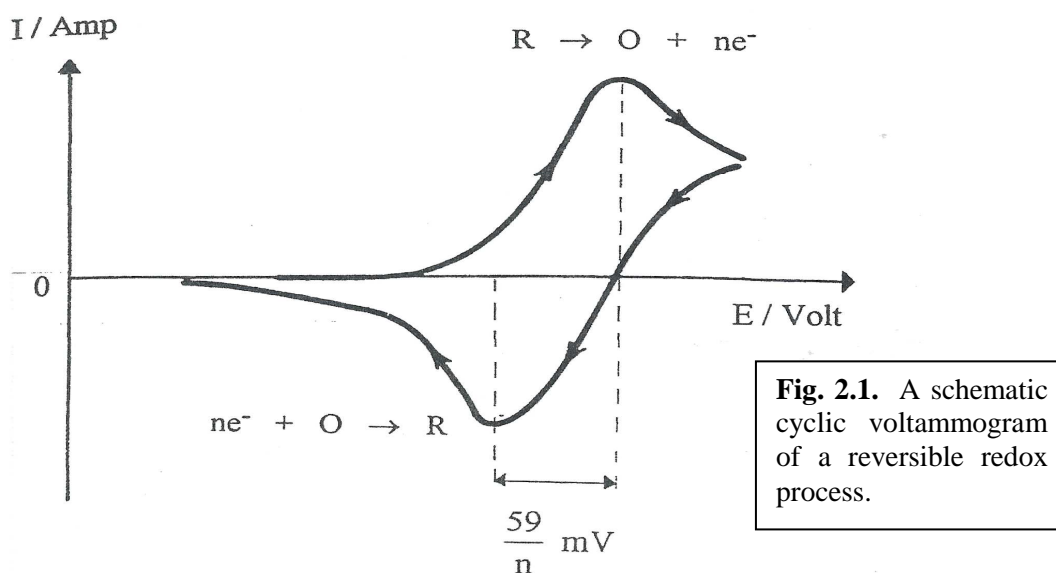
##### **2.1.4.1. Cyclic voltammetry of Faradaic processes**

Faradaic processes are non-adsorptive processes arising from electron transfer across the metal/electrolyte interface. The resulting redox reaction of solution species that takes place is controlled by Faraday's laws [3,8], that is, the amount of electricity which is passed (charge) is proportional to the number of moles of reactant converted. Electrode surfaces where Faradaic processes take place are classified as charge transfer electrodes, since the extent of reaction depends on the measured charge passing through the electrode surface. The redox reaction taking place in the solution can be expressed as:  $O + ne^- \rightleftharpoons R$  where O and R are the oxidised and reduced forms of the redox couple, respectively. When the electron

transfer rate in both the forward and reverse directions at the electrode is high, the reduction is described as reversible, and the cathodic and anodic peaks are separated by a potential of approximately  $59/n$  mV at  $25^\circ\text{C}$  (Fig. 2.1), where  $n$  is the number of electrons transferred. If  $n$  electrons are transferred in a reaction that is reversible, the peak separation is:

$$\left| E_p^{ox} - E_p^{red} \right| = 2.218 \frac{RT}{nF} \quad (2.1)$$

where  $E_p^{ox}$  and  $E_p^{red}$  are the potentials at which the oxidation and reduction processes occur,  $R$  is the universal gas constant,  $T$  is absolute temperature in Kelvin and  $F$  is Faraday's constant.



For a charge transfer process under the same reversible conditions, as in Equation 2.1, the peak current density  $I_p$  is given by the following equation:

$$I_p = 2.75 \times 10^5 n^{3/2} D^{1/2} C^o \nu^{1/2} \quad (2.2)$$

where  $I_p$  is the current at the peak maxima ( $\text{Amp cm}^{-2}$ ),  $D$  is the diffusion coefficient ( $\text{cm}^2 \text{s}^{-1}$ ),  $C^o$  is the concentration of the bulk solution ( $\text{mol cm}^{-3}$ ) and  $\nu$  is the sweep rate ( $\text{Volt s}^{-1}$ ).

The peak height should therefore increase with sweep rate since the peak current is proportional to the square root of the sweep rate.

Another useful parameter in the analysis of CVs is the halfwave potential  $E_{1/2}$  which may be used to identify qualitatively components that may be overlapping and interfering and is related to  $E_p$  by the following equation:  $E_p = E_{1/2} - 1.1 \frac{RT}{nF}$

Under irreversible conditions, i.e. where the rate of the backward reaction is negligible and is described by the reaction scheme:  $O + ne^- \longrightarrow R$ ,  $E_p$  is not independent of sweep rate since the system is no longer at equilibrium. The following equations now hold for  $E_p$  and  $I_p$ :

$$|I_p| = 3.01 \times 10^5 n \left( \frac{2.3RT}{bF} \right)^{1/2} D^{1/2} C^o v^{1/2} \quad (2.3)$$

$$E_p = E_{1/2} - b \left[ 0.52 - \frac{1}{2} \log(b/D) - \log k_s + \frac{1}{2} \log v \right] \quad (2.4)$$

where  $b$  is the Tafel slope (Volts), i.e. the gradient of  $\log_e I$  against  $E$ ,  $k_s$  the specific rate constant at the standard potential can be calculated from a plot of  $E_p$  versus  $\log v$  provided that the diffusion coefficient is known.

In contrast to Faradaic processes, non-Faradaic reactions give rise to a linear relationship between current density  $j$  and sweep rate [7], because they are not diffusion controlled (see below):

$$j = \sigma_m \frac{nF}{RT} \theta(1-\theta)v \quad (2.5)$$

where  $\sigma_m$  is the charge associated with adsorption of a complete monolayer and  $\theta$  is the surface coverage.

For irreversible processes, values for the rate constant can be obtained by measuring the difference in potential between the anodic and cathodic peak currents, as a function of the sweep rate. The voltammetry of a Faradaic process may provide mechanistic and kinetic information [7], including the detection of intermediates in organic redox reactions [2,3]. A typical cyclic voltammogram of a reversible process is shown in Fig. (2.1), where the total current density measured derives from the sum of the Faradaic and non-Faradaic pseudo-capacitive charging of the double layer. This “extra” charge contribution associated with the double layer has to be accounted for in any charge determination (in order to measure the charge associated with a charge transfer reaction, the non-Faradaic pseudo-capacitive charging of the double layer needs to be subtracted from the total current).

#### 2.1.4.2. Cyclic voltammetry of non-Faradaic processes

Non-Faradaic processes take place when the adsorption and desorption of ions from the electrode surface result in an electric current due to charging of the double layer. Non-

Faradaic processes may cause a physical change in the structure of the electrode surface depending on the applied potential and/or the concentration of the electrolyte solution. The adsorption of species, such as metals or ions, is classified as non-Faradaic.

In reversible adsorption processes, the potential of the anodic and cathodic peaks are the same. This behaviour is observed when the sweep rate is sufficiently low to avoid depletion of the reactant at the electrode surface (concentration polarisation). The symmetry with respect to the potential axis of anodic and cathodic current is assigned to the reduction/oxidation of the same amount of surface species.

The rate of adsorption of a metal ion  $M^{Z+}$  (of an oxidised species) at an electrode surface is dependent on the rate of the reaction:  $M_{(aq)}^{Z+} + Ze^{-} \longrightarrow M_{(ads)}$ .

For a first order reaction, the rate of the forward reaction ( $V_F$ ) may be expressed as:

$$V_F = k_F [M^{Z+}] (1 - \theta) \quad (2.6)$$

where  $\theta$  is the fraction of surface sites which are covered with adsorbate  $M$ ,  $k_F$  is the rate constant for the forward reaction, and  $[M^{Z+}]$  is the concentration of the oxidised state of species  $M$ . For the reverse process, the rate of the reverse reaction ( $V_R$ ) is expressed as:

$$V_R = k_R \theta \quad (2.7)$$

where  $k_R$  is the rate constant of the reverse reaction and also potential dependent. At equilibrium, the rate of reaction is:

$$V_F = V_R \quad (2.8)$$

and, therefore, from equations (2.6) and (2.7) a Langmuir adsorption isotherm can be derived:

$$\frac{\theta}{(1 - \theta)} = \frac{k_F}{k_R} [M^{Z+}] \quad (2.9)$$

This is a Langmuir-type adsorption equation, differing from its gas phase counterpart in that the adsorption constant ( $k_F/k_R$ ) is potential dependent since the adsorption reaction involves a transfer of charge across the metal-electrolyte interface. For a reaction taking place with a complete charge transfer, i.e. the formation of a neutral metal adatom at the electrode surface, the Gibbs energy of adsorption ( $\Delta G_{ads}$ ) is given by:

$$\Delta G_{(ads)} = \underbrace{\Delta G_{(ads)}^o}_{\text{chemical potential of } M} + \underbrace{nFE}_{\text{electrochemical potential of } M^{Z+}} \quad (2.10)$$

where  $E$  is the electrode potential and  $\Delta G^o_{(ads)}$  is the Gibbs energy of adsorption in the absence of an electric field. Thus, the adsorption constant may be expressed as:

$$K = \frac{k_F}{k_R} = \exp\left(\frac{-\Delta G^o_{(ads)}}{RT}\right) \quad (2.11)$$

From equation (2.10):

$$k = \frac{k_F}{k_R} = \exp\left(\frac{-\Delta G^o_{(ads)} - nFE}{RT}\right) \quad (2.12)$$

$$k = \exp\left(\frac{-\Delta G^o_{(ads)}}{RT}\right) \exp\left(\frac{-nFE}{RT}\right) \quad (2.13)$$

But at constant temperature:

$$\exp\left(\frac{-\Delta G^o_{(ads)}}{RT}\right) = \text{constant} = k' \quad (2.14)$$

By combining equations 2.13 and 2.14 into equation (2.9):

$$\frac{\theta}{(1-\theta)} = k' \exp\left(\frac{-nFE}{RT}\right) [M^{z+}] \quad (2.15)$$

where  $K'$  is the adsorption equilibrium constant in the absence of an electric field.

If an interaction exists between adsorbed species on the electrode surface then the peak height and width will be modified. Attractive lateral interactions narrow the peak with an increase in magnitude while repulsive lateral interactions broaden and lower the intensity of the peak. Frumkin modified the adsorption isotherm of (2.15) to account for the fact that surface active species could interact repulsively or attractively [9]:

$$\frac{\theta}{(1-\theta)} \exp\left(A\left(\theta - \frac{1}{2}\right)\right) = K' \exp\left(\frac{-nFE}{RT}\right) [M^{z+}] \quad (2.16)$$

where  $\exp\left(A\left(\theta - \frac{1}{2}\right)\right)$  is the van der Waals term for adlayer interactions, with  $A$  representing the magnitude of the attractive ( $-A$ ) and repulsive interactions ( $+A$ ).

With the development of highly sensitive equipment to detect very low currents flowing at the working electrode ( $< 1 \mu\text{A cm}^{-2}$ ), adsorbate coverages of  $< 5\%$  of a monolayer can be determined.

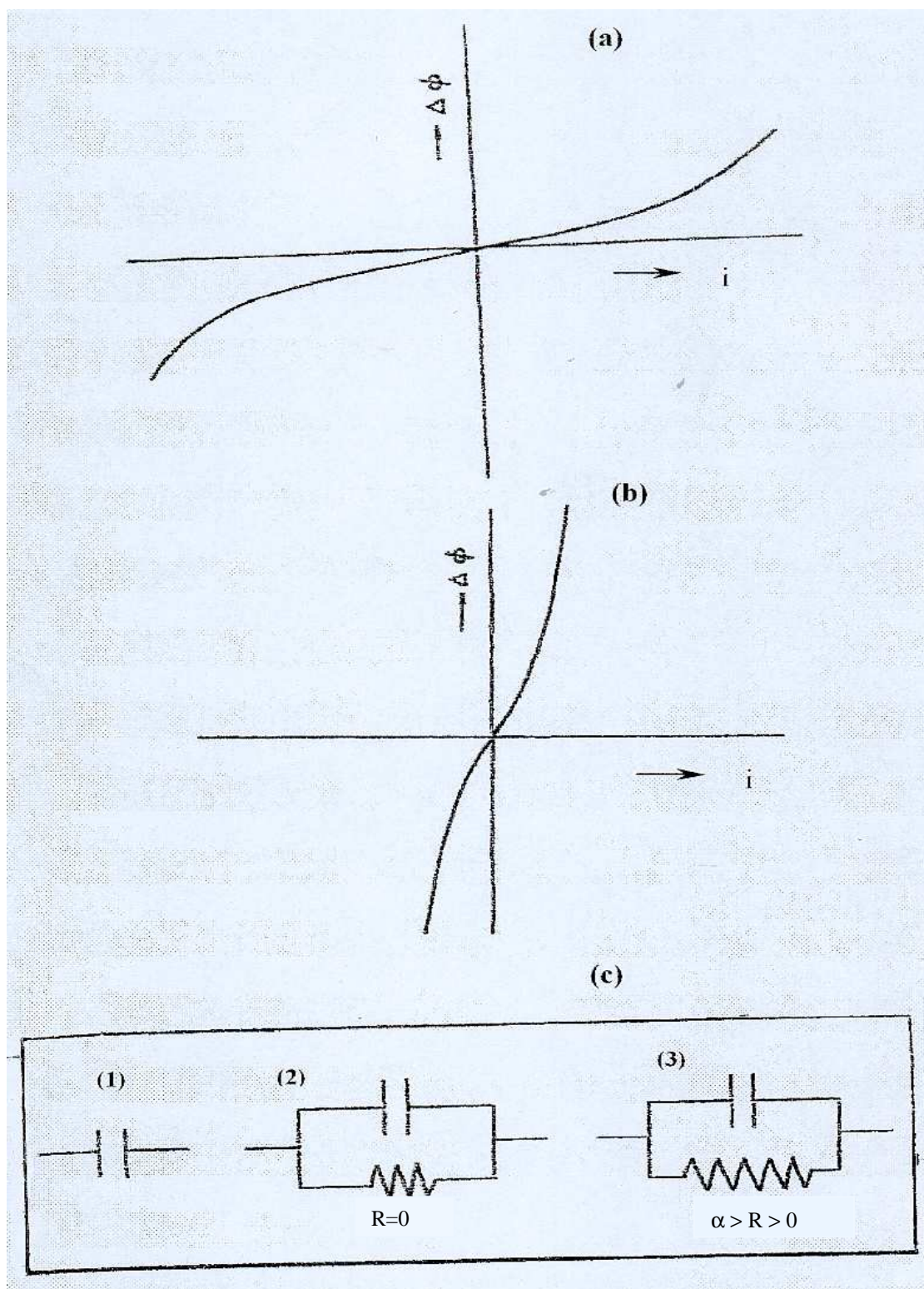
The success of the method in determining adsorbate coverages is critically dependent on knowing precisely the number of electrons transferred per adsorbate molecule. Hence, if this quantity is determined, by measuring the total charge, the surface coverage can be estimated,

providing no impurities are present. Impurity levels can be estimated by, for example, calculating the decrease in charge associated with the hydrogen adsorption region and comparing the value with the theoretical value associated with that particular crystal surface. Under equilibrium conditions, voltammograms provide information about the Gibbs energy of the adsorbed species in terms of the peak potential with respect to the potential of bulk deposition. It could therefore be regarded as analogous to thermal desorption spectroscopy (TDS), giving a “spectrum” of adsorbed surface states, although TDS is kinetic in nature and does not in general give simple thermodynamic information.

## 2.2. Polarisable and non-Polarisable Interfaces

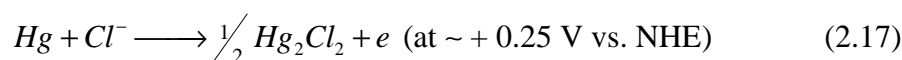
All electrode-solution interfaces can be classified as polarisable or non-polarisable. An electrode for which an electron can pass easily across the interface is called non-polarisable. In this case, external application of a change of potential may result in more electrons passing rapidly across the interface. Thus, there is a negligible build-up of excess charge on the electrode surface, i.e. the interface does not polarise. Fig. 2.2 (a) displays the response of a nonpolarisable interface. It can be inferred from this that a small change in the electrode potential produces a large change in current flow. Platinum in contact with hydrochloric acid is a non-polarisable interface. In contrast, when the transfer of electrons is difficult, a potential change from outside will induce a substantial build-up of excess charges at the interface, hence, the electrode is termed polarisable. Fig. 2.2 (b) shows the behaviour of a polarisable interface: mercury in contact with a solution of potassium chloride ions is an example. When a potential is applied externally to the electrode, the transfer of electrons through the interface is negligible. That is, a small change in current flow causes a large change in electrode potential. An ideally polarisable interface is one which can allow the passage of current without causing a change in the potential difference across it. Figs. 2.2 (c1) and Fig. 2.2(c2) illustrate the electrical analogous of the ideally polarisable and nonpolarisable situations and Fig. 2.2 (c3) shows an intermediate real case [10].

In addition, when the current associated with charging the electrode-electrolyte interface arises purely from capacitive effects, such an interface is termed an ideally polarisable electrode (IPE) [10]. While no real electrode behaves ideally over the entire potential range, some electrode-solution systems, over limited potential ranges, can show behaviour which is approximately, ideal, for instance, a mercury electrode in contact with a de-aerated potassium chloride solution which behaves as an IPE at potentials in excess of 1.5 V. At very



**Fig. 2.2.** (a) Current-potential response of highly non-polarisable electrode. (b) Current-potential response of highly polarisable electrode (c) Electrical equivalent of: (1) ideal polarisable electrode; (2) ideal non-polarisable electrode; (3) partially polarisable electrode. Reprinted from [2].

positive potentials the mercury is able to oxidise in a charge transfer reaction leading to depolarisation [3]:



similarly, at very negative potentials  $K^+$  can be reduced:



### 2.3. Electrode Charge

The electrode charge is defined as the amount of electricity to be supplied to an electrode when its surface area increases by unity with the concentration of solution components remaining constant [10].

Charge transfer reactions occurring at clean or surface-modified platinum single crystal surfaces in aqueous media may be understood in terms of various models (Helmholtz, Gouy-Chapman, Stern, Grahame, Bockris Devanathan and Muller) of the electrode-solution interface. These models, which have been developed in order to establish the distribution of various particles (ions, electrons, and solvent molecules) and the effect on these particles of an applied potential, are set out in standard texts [11-19].

Total charge may be determined by measurement of the amount of electricity flowing in an external circuit when the electrode surface area increases by unity at constant potential. In this method, no charge must arise on the electrode surface from interaction with oxidants or reductants present in solution and the concentrations of all adsorbed species must be kept constant.

The charge on an electrode surface is crucial in determining the rate of electron transfer and the arrangement of monolayer, dipoles and neutral molecules within the double layer. It has been shown by Frumkin [20,21] and others [22,23] that there exists a unique electrode potential at which the free substrate charge on the metal side of the double layer is zero.

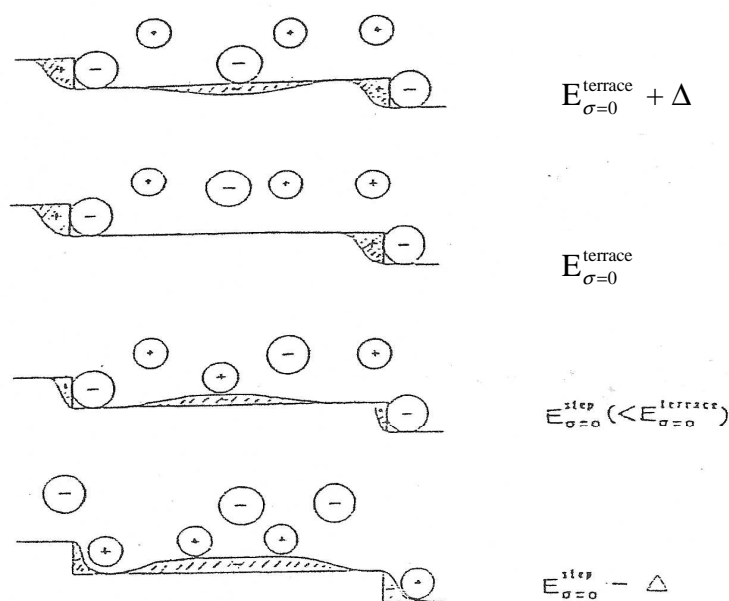
This potential is called the potential of zero charge (PZC) and may be related to the work function of the electrode surface via a Born-Haber cycle [24]:

$$E_{\sigma=0}^{(hkl)} = \frac{\Phi}{e}(hkl) + [\delta x^M - g^S(\text{dip})](hkl) + K \quad (2.19)$$

where  $E_{\sigma=0}^{(hkl)}$  is the potential of the metal M (hkl) at its PZC with respect to a reference electrode,  $\delta_x^M$  is the change of the surface potential of M(hkl) when it comes into contact with the solvent,  $g^s$  is the contribution to the potential at the metal/solution interface due to the orientation of solvent dipoles, and K is a constant due to the potential drop at the reference electrode-solution interface (it remains constant if the same type of reference electrode is used).

For metals, such as platinum, which give rise to strong chemisorption, this equation does not apply and an alternative definition in this case has been given by Frumkin [25].

In relation to the present study, it should be noted that the singular voltammetric responses of single crystal platinum electrodes are derived from local values of work function (step, terrace, kink) and hence local values of PZC [26]. Hence the various voltammetric peaks can be associated with the adsorption/desorption of cations/anions at local values of PZC (Fig. 2.3). For sp-metals such as gold and silver,  $E_{\sigma=0}^{(hkl)}$  may be readily measured using capacitance and provides good experimental support for various proposed models of the double layer.



**Fig. 2.3.** Conceptual model representing the electrostatic interactions between the inhomogeneous electron density distribution on the step-terrace surface and ions in solution.  $-\Delta$  indicates the shift of potential of electrode lower than PZC and  $+\Delta$  indicates the shift of potential of electrode more positive than PZC. Reprinted from [27].

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