A NONLINEAR STUDY OF ELECTRODE IMPEDANCE IN SULPHIDE MINERALS

by

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ABSTRACT

A laboratory study of the non-linear characteristics of natural sulphide minerals has been carried out in order to understand and possibly identify the processes controlling the electrode impedance of the minerals. The full non-linear reaction rate equation has been analyzed numerically and used to predict dynamic electrode impedance which is compared with observed results.

It is found that distinct processes are responsible for the non-linear behavior of the sulphide minerals studied. Some of these processes can be identified as being diffusion or charge transfer reaction controlled. Peculiar non-linear characteristics of minerals are found which can ultimately serve as observable signatures of the minerals. Although the diffusion process with its associated Warburg impedance is important, it does not play any universal dominant role under non-linear conditions. A positively charged ion, possibly a cupric ion impurity, has been identified as the diffusing species responsible for the observed non-symmetric feature of the dynamic impedance.

Thesis Supervisor: Theodore R. Madden

Title: Professor of Geophysics

To the memory of 'Kunle Ajaja,

a friend, colleague and scholar.

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CHAPTER ONE

1 Introduction

Although the success of induced polarization (IP) as a geophysical prospecting tool for locating sulphide ore deposits (which include chief sources of copper) is well established (see Madden and Cantwell, 1967; and Phillips and Richards, 1975), the understanding of the microscopic nature of the phenomenon is still obscure. Earlier attempts at the description of the IP effect have been largely phenomenological in nature. Seigel (1949) seeks to explain the chargeability of an IP causing medium by distributing an array of current dipoles while Wait (1959) evokes the Classius-Mossotti theory of dielectrics to account for the IP effect due to particles covered with a concentric film of dielectric material. These studies neglect the electrochemical foundation of the induced polarization effect and have not been of much help in the more practical problem of identifying the IP mechanism or establishing any IP "signature" which can be used to discriminate between different minerals or other sources of induced polarization.

The inception of the field of geo-electrochemistry has probably been initiated by Marshall and Madden (1959) who have investigated the electrochemical cause of IP. Further work on the geo-electrochemical aspects of IP has been reported by Angoran (1975) and Angoran and Madden (1976). These studies indicate that cupric and sulphide ions are active and also provide further evidence as to the significance of diffusional process.

This study is a direct continuation of the recent one reported by Angoran and Madden (1976). It introduces another basic parameter, the shape of the Lissajous patterns in addition to the complex electrode impedance, and is concerned with possible identification of the processes controlling the IP phenomena by investigating the early non-linear character of the electrodic process. The study is reported in two further chapters and the conclusions are summarized in the fourth.

The basic concept of electrode impedance, including both the "linear" electrode impedance and the "non-linear" dynamic impedance, is dealt with in chapter two. Chapter three presents the experimental methods and results which are compared with theoretical predictions from numerical methods. In this chapter, also, possible explanations for the electrodic processes are offered according to whether diffusional or kinetic process is dominant. Since the initial non-linear characteristics appear to be dependent on the electrode-electrolyte system, possible distinction between natural minerals used in laboratory experiments is attempted.

CHAPTER TWO

2. The Kinetic Theory of Electrode Impedance

2.1 Introduction

Metallic minerals such as the sulphide-minerals act as electrodes in their natural environments. When these minerals are in contact with the interstitial fluids, a phase boundary is developed in which the charge carriers are redistributed by the anisotropic interfacial forces. This results in the well-known double-layer. The double layer can be decomposed into three zones: the fixed-layer of adsorbed charges tightly bound to the solid phase, the diffuse layer in the solution phase which consists of a net charge and across which is the zeta potential. The third zone is the diffusion layer which exists only when there is a net current flow through the electrode. Although this layer is almost electrically neutral, there are significant changes in the solution's composition due to the passage of current.

When the mineral-electrode is current driving or driven, there exists some departure from the equilibrium potential, which is called the electrode polarization or better as the overpotential. The passage of current through the mineral-electrode requires two systems of operations. These are the so-called ionics and electrodics. The former involves the transport and interaction of ions in the solvent and the latter a collection of kinetic processes taking place at the electrode boundary and culminating in the conversion of ionic to electronic current. This must involve at least one ionic charge as far as the geophysical application is concerned.

The entire electrodic process is an ensemble of partial reactions or steps which act in parallel or series. These partial reactions can be classified into two major types which always act in series:

(i) the primary reaction which is the charge transfer reaction occurring at the interface and essential to the (geo)electrochemical process, and

(ii) the secondary reaction which is a host of various partial reactions. Among these are:

(a) the addition or removal of materials into or from the crystal lattice, the phase transition or simply crystallization stage.

(b) the transport of the participating species to or from the reaction site. (At least one of these species must be an ion in solution.)

(c) the homogeneous/heterogeneous chemical transformation of the ionic species before or after the charge transfer step. This depends on the concentration of the species but not on the electrode potential.

Any of the above steps could lead to a delay in the overall electrode reactions and hence be the source of an electrode impedance. In other words, the electrode impedance can be resolved into a string of other elementary impedances arising from the partial reactions.

The application of the kinetic theory is in establishing the mechanism of the overall electrode reaction, by providing information on the nature and sequence of the partial reactions and possibly isolate them. This usually can be accomplished by obtaining the current-potential relationship and the polarization impedance with respect to the concentration of the reacting species and the current or voltage excitations. From the geo-electrochemical point of view, this could be used to study the microscopic behavior of the induced polarization of metallic minerals, with the intention of being able to identify the I.P. signatures of the different minerals. The recent studies by the Madden group (see Angoran and Madden, 1976) have been able to isolate certain active species in the sulphide mineral electrolyte system and also provide a firm evidence as to the significance of the diffusion process.

Charge and mass transfer processes are thus very important among the elementary steps in the overall reaction occurring in the mineral-solution system. Angoran (1975), however, reported at least one case in which sulphide mineral electrode impedance was strongly influenced by surface smoothness, probably due to the occurrence of strong crystallization overpotential. It is not believed, though, that minerals in situ could maintain smooth surfaces, as if diamond polished, especially at the two-phase boundaries.

2.2 A Generalized Theory of Linear Electrode Impedance

For a generalized electrodic process all we need to consider is a charge transfer reaction and any combination of other reactions (homogeneous/heterogeneous chemical reactions, mass transfer, etc.). The presence of an indifferent electrolyte will be assumed in order to neglect the zeta potential and the theory of absolute rate of reactions will be used to develop the electrode impedance associated with such a process.

The theory of absolute rate of reactions developed by Eyring is based on the introduction of an intermediate state, called the activated complex between the initial and final states of the reaction. In the activated state, the species are still in equilibrium with the initial state, say, and will proceed to cross the energy barrier at a universal frequency of kT/h which is neither dependent on the reacting species nor the reactions. After crossing the energy barrier they decompose into the final products.

For a reaction

$$\sum \nu_j S_j \rightleftarrows \sum \nu_j' S_j',$$

the rate of reaction is

$$\vec{\tau}_s = \frac{kT}{h} \Pi [A_j]^{\nu_j} \exp\left(-\frac{\vec{\Delta F}^{\dagger}}{RT}\right) \tag{2.1}$$

where $[A_j]$ - the activity of the j^{th} reacting species (S_j)

ν_j - the stoichiometric factor

and $\vec{\Delta F}^{\dagger}$ - Gibb's free energy of activation (the arrow indicates the direction of reaction)

such that,

$$\vec{\Delta F}^{\dagger} = \vec{\Delta H} - T\vec{\Delta S}$$

and $\vec{\Delta H}$ - enthalpy of activation

$\vec{\Delta S}$ - entropy of activation

In the presence of any perturbation effects such as an externally impressed electric field, there is a change in the free energy of activation which also affects the reaction rate. $\overrightarrow{\Delta F}^{\dagger}$ is then replaced by $\overrightarrow{\Delta F}^{\dagger} - \overrightarrow{\Delta F}_f^{\dagger}$, where $\overrightarrow{\Delta F}_f^{\dagger}$ is the change in the free energy due to the applied field.

Equation (2.1) then becomes

$$\overrightarrow{\tau} = \frac{kT}{h}\overrightarrow{\tau}_o \Pi [A_j]^{\nu_j} \exp \frac{\overrightarrow{\Delta F}_f^{\dagger}}{RT} \qquad (2.2)$$

where $\overrightarrow{\tau}_o = \exp - \frac{\overrightarrow{\Delta F}}{RT}$

If the perturbation is simply an applied voltage, then

$\overrightarrow{\Delta F}_f^{\dagger} = n\overrightarrow{\alpha} v_f F$ (molar change, that is)

Also

$\overleftarrow{\Delta F}_f^{\dagger} = -n\overleftarrow{\alpha} v_f F$, and $\overleftarrow{i}_o = \exp - \frac{\overleftarrow{\Delta F}}{RT}$

where n - charge transfer valence

v_f - electrode potential

$\overrightarrow{\alpha}, \overleftarrow{\alpha}$ - transfer coefficients such that $\overrightarrow{\alpha} + \overleftarrow{\alpha} = 1$.

By writing an equivalent form of Equation (2.2) for the opposite direction, we can obtain the net current density

$$i_{net} = (\overrightarrow{\tau} - \overleftarrow{\tau})F = F\frac{kT}{h}\{\overrightarrow{\tau}_o \prod_j [A_j]^{\nu_j} \exp \frac{\overrightarrow{\alpha} n}{RT} v_f F$$

$$- \overleftarrow{\tau}_o \Pi [A_j']^{\nu_j'} \exp (-\overleftarrow{\alpha} n \frac{v_f F}{RT})\} \qquad (2.3)$$

from the relation,

Current density = rate x F

= molar flux x charge per mole.

Under equilibrium conditions the electrode potential is v_o and the net current is zero. The forward and backward currents are equal to the exchange current, i_o.

Hence

$$i_o = \overrightarrow{\tau}_o \frac{kT}{h} F \prod_j [A_{oj}]^{\nu_j}$$

$$= \overleftarrow{\tau}_o \frac{kT}{h} F \prod_j [A'_{oj}]^{\nu'_j} \tag{2.4}$$

where $[A_{oj}]$, $[A'_{oj}]$ are the activities of the reactants and the products respectively at equilibrium.

Equations (2.3) and (2.4) give,

$$i_{net} = i_o \left[\prod_j \{\frac{[A_j]}{[A_{oj}]}\}^{\nu_j} \exp\{\vec{\alpha}\frac{nvF}{RT}\} - \prod_j \{\frac{[A'_j]}{[A'_{oj}]}\}^{\nu'_j} \exp\{(\vec{\alpha}-1)\frac{nv}{RT}F\} \right] \tag{2.5}$$

where $v_f \equiv v$.

Equation (2.5) relates the current to the activities of the reacting species, the products and the voltage. It can be generalized as

$$i_{net} = f([A_j],[A'_j],v) \tag{2.6}$$

or simply as

$$i_{net} = f(c_j,v) \tag{2.7}$$

where $c_j \equiv [c_j]$ is the concentration of the active species, (assuming that the activity coefficients are constant).

When indeed, there exists a rapidly realizable equilibrium condition and any small departures from this are such that

$$v << RT/nF$$

and $\Delta c_j << c_{oj}$ for all participating species, then we can expand Equation (2.7) as a Taylor series to the first order, and the change in the current is

$$i = \sum \frac{\partial f}{\partial c_j} \Delta c_j + \frac{\partial f}{\partial v} v \tag{2.8}$$

If the partial differential coefficients are evaluated from Equation (2.5) then,

$$i = i_o \{\frac{nF}{RT} v + \sum \nu_j \frac{\Delta [A_j]}{[A_{oj}]} - \sum \nu_j' \frac{\Delta [A_j']}{[A_{oj}']}\} \tag{2.9}$$

Angoran and Madden (1976) define the chemical impedance as the change in chemical potential per unit flow rate, in such a way that,

$$Z_j^{(chem)} = \frac{\Delta \xi_j}{-\nu_j i/nF} \quad \text{and} \quad Z_j'^{(chem)} = \frac{\Delta \xi_j'}{\nu_j' i/nF}$$

where the chemical potential, ξ_j, say, is given by

$$\xi_j = \xi_o + RT \,\mathrm{Ln}\, [A_j]. \qquad \text{(thermodynamic relation)}$$

By using the relation

$$\Delta \xi_j = RT \,\Delta \mathrm{Ln}\, [A_j] = RT \frac{\Delta [A_j]}{[A_j]}$$

they obtain an elegant relation between the potential difference across the fixed layer and the faradaic current:

$$v = i\{\theta + Z_j^{(elec)} + Z_j^{'(elec)}\} \qquad (2.10)$$

where

$\theta = RT/nFi_o$, the charge transfer resistance (or simply, the reaction resistance).

The electrical impedance is given by

$$Z_j^{(elec)} = Z^{(chem)} \cdot (\nu/nF)^2.$$

$Z_j^{(elec)}$ and $Z_j^{'(elec)}$ are thus the electrical impedances arising from the overall processes associated with the chemical impedance "seen" by the depletion or accumulation of species.

The implication of Equation (2.10) is that both the accumulation and depletion of species as well as the charge transfer step (the kinetics or activation energy control) combine in series to impede the passage of current through the electrode-electrolyte system.

The above step involves a charge transfer process and hence involves the so-called faradaic current. There exists a non-faradaic current which arises from the charging and discharging of the fixed layer capacitance. This capacitative coupling effect of the fixed layer will act in parallel to the faradaic impedance given by Equation (2.10). Other distinct charge transfer steps with an associated string of "secondary" partial reactions, which are characterized by their chemical impedances, also act in parallel with the capacitative impedance. The overall effect of all these impedances constitute the electrode impedance.

This presents a complete picture of the electrodic process as the variety of the partial reactions only contributes to the electrode impedance through their associated chemical impedances. The nature of the contributions depends on the partial reaction and the boundary conditions imposed on the participating species. The Warburg impedance due to the diffusion of species to and from the reaction and the "surface Warburg" due to the diffusion of species over finite distances on the electrode surface are examples of common chemical impedances (Angoran and Madden, 1976).

Since the diffusing species must contain at least one ion, the diffusion process is modified by the presence of the electrical field in the solution. The effect, however, can be neglected for most practical cases. This has been shown in a classical treatment of the problem by Madden (1961). A similar, but less painful to read treatment is given in Appendix A.

2.3 The Non-Linear Electrode Impedance

The deductions based on the linearization of the electrodic process have been adequate for describing a lot of the observed electrodic phenomena, but they have not completely resolved certain elementary problems. It therefore becomes necessary to resort to the basic non-linear and asymmetric nature of the electrode characteristics. The principal sources of the non-linearity are the diffusion processes and the kinetics. The latter is associated with the change in the activation energy while the former depends on the change in the concentrations of species and the boundary conditions imposed on these species. For instance, only non-negative concentrations are allowed and hence depletion of species beyond zero concentration is forbidden. At low concentration of species, very huge potentials are thus required to maintain relatively small currents.

A feeling for the non-linearity can be had by keeping second order terms in the Taylor series expansion of the reaction rates.

Let the faradaic current be

$$i = f(c_j, v)$$

then

$$i = i_o + \sum_j \frac{\partial f}{\partial c_j}\Delta c_j + \frac{\partial f}{\partial v} v + \frac{1}{2}\,{}_j\,\frac{\partial^2 f}{\partial c_j^2}(\Delta c_j)^2 + \frac{1}{2}\frac{\partial^2 f}{\partial v^2} v^2$$

$$+ {}_j\,\frac{\partial^2 f}{\partial c_j \partial v} v\,\Delta c_j + \sum_{j \neq k} \frac{\partial^2 f}{\partial c_j \partial c_k}\Delta c_j \Delta c_k + \text{HOT} \qquad (2.11)$$

(HOT ≡ higher order terms)

By employing Equation (2.11) to evaluate the forward and backward rates we can obtain the net current as

$$i_{Net} = i_o [\sum_j \nu_j \frac{\Delta[A_j]}{[A_j]} - \sum \nu'_j \frac{\Delta[A'_j]}{[A'_j]} + \frac{nF}{RT} v]$$

$$+ \frac{i_o}{2} [\sum_j \nu_j (\nu_j - 1) \{ \frac{\Delta[A_j]}{[A_j]} \}^2 - \sum_{j'} \nu'_j (\nu'_j - 1) \{ \frac{\Delta[A'_j]}{[A'_j]} \}^2]$$

$$+ i_o [\alpha \sum_j \nu_j \frac{\Delta[A_j]}{[A_j]} + (1-\alpha) \sum_{j'} \nu'_j \frac{\Delta[A'_j]}{[A'_j]}] \frac{nF}{RT} v$$

$$+ i_o [\sum \nu_j \nu_k \frac{\Delta[A_j]}{[A_j]} \frac{\Delta[A_k]}{[A_k]} - \sum \nu'_j \nu'_k \frac{\Delta[A'_j]}{[A'_j]} \frac{\Delta[A'_k]}{[A'_k]}]$$

$$+ i_o (2\alpha - 1) \frac{nF}{RT} v \qquad (2.12)$$

If we use the concept of the chemical impedance, and the associated electrical impedance, then Equation (2.12) becomes

$$i = \frac{i}{\theta} [v/i - \sum z_j^e - \sum z_j'^e] + NL, \qquad (2.13)$$

The non-linear part, NL, is given by

$$NL = \frac{i^2}{i_o \theta^2} [\frac{1}{2} \sum \nu_j^{\#} \{z_j^e\}^2 - \frac{1}{2} \sum \nu_j'^{\#} \{z_j'^e\}^2 + z_j^e * z_k^e - z_j'^e * z_k'^e]$$

$$+ \frac{iv}{i_o \theta^2} [-\alpha \sum z_j^e + (1-\alpha) \sum z_j'^e] + \frac{(2\alpha - 1)}{i_o \theta^2} v^2 \qquad (2.14)$$

where $z^e \equiv z^{(elec)}$

$\nu_j^{\#} = (\nu_j - 1)/\nu_j$

$\theta = RT/nF\, i_o$

[The convolution operator * is such that $Z_j * Z_k = \sum_{r=1} Z_j Z_{j+r}$, for all j; and we have dropped the suffix "Net".]

Although equation (2.13) represents non-linear electrode characteristics, it greatly simplifies the non-linearity. For instance since $\nu_j^{\#}$ and $\nu_j^{'\#}$ are both non-negative and $\alpha \leqslant 1$, the depletion and accumulation processes appear to have cancellation effects in the non-linear terms. It is illustrative to consider an electrode reaction which proceeds simultaneously for each partial step involving a single active species. If we further take $\alpha=0.5$, then Equation (2.13) becomes

$$i(\theta + Z^e + Z'^e) = v\{1 + \frac{0.5}{\theta}\frac{i}{i_o}(Z'^e - Z^e)\} \qquad (2.15)$$

In this case, the non-linearity persists only if $Z^e \neq Z'^e$.

Equation (2.14), nonetheless, predicts even harmonics in the current density given pure sinusoidally varying applied voltage. In general, the current is anharmonic if the voltage pure sinusoidal function of time, and can be analyzed as

$$\delta I = \sum_{s=1} A_s \sin(s\omega t) + \sum_{s=0} B_s \cos(s\omega t),$$

δI can also be written in terms of the changes for each harmonic;

$$\delta I = \sum_{s=1} \delta I(s)$$

and $\delta I(s)$, for each s, can be evaluated as a sum of first order linear terms and higher order non-linear terms as in (2.13).

Also if a sinusoidal current free from harmonics is passed through the electrodes, the resulting alternating potential is anharmonic. Another consequence of the non-linearity is the faradaic rectification. This is as a result of a shift in the time average of the potential, say due to the asymmetric form of the electrode characteristics:

Let the monochromatic current through the electrode be

$$i = I \sin \omega t, \tag{2.16}$$

the electrode current-potential relationship can be written as

$$v = I\,[R_f \sin \omega t - \frac{1}{\omega c_f} \cos \omega t] + \Delta I\,[R_f \sin^2 \omega t - \frac{1}{\omega c_f} \cos^2 \omega t] \tag{2.17}$$

if we limit ourselves to the fundamental and first harmonics. In the above equation, it is assumed that the faradaic impedance can be represented by a series combination of some resistance, R_f and capacitance, c_f (see Grahame, 1952; and Vetter, 1967). For a charge transfer and diffusion controlled electrode impedance

$$R_f = \theta + W$$

where θ = charge transfer resistance

W = the Warburg impedance.

It follows from Equations (2.16) and (2.17) that even though the time average of the current is zero, the average value of the voltage is $\frac{1}{2}\Delta I Z_f^2 \neq 0$, and $Z_f = \{R_f^2 + (1/\omega c_f)^2\}^{1/2}$. This shift in the average potential is the faradaic rectification.

2.3.1 The full non-linear dynamic electrode impedance

The second order non-linear characteristics predict possible cancellation of the electrode non-linearity. Also, there is a tendency for even harmonics to cancel out in a back to back array of "twin" electrodes. These make such non-linear expressions not very useful for studying electrode impedances. As an alternative, the full non-linear rate process will be analyzed. This is, however, accomplished by numerical methods since the expressions are fairly complicated.

We can assume that only one of the participating species is active and the products remain at unity activity, then Equation (2.5) implies

$$i = i_o[\{1 + \frac{\Delta[A]}{[A_o]}\}^{\nu} \exp(\vec{\alpha}\frac{nF}{RT}v) - \exp\{(\vec{\alpha}-1)\frac{nF}{RT}v\}] \qquad (2.18)$$

The active species must diffuse to or from the reaction zones according to the Fickian laws, and are subject to the following initial and boundary conditions.

$c(x,o) = c_o$ {constant concentration before excitation}

$c(\delta,t) = c_o$ {diffusion layer caused by forced or natural convection; it is sufficient to put $\delta = \infty$.}

and

$D\frac{\partial c}{\partial x}\Big|_{x=0} = \frac{I\nu}{nF}\sin\omega t$ {applying Kirchoff's current law to the Fickian and faradaic currents}

By the method of Laplace transform, or other, we can show that the change in concentration at the electrode is

$$\Delta c = c(o,t) - c_o = \frac{I\nu}{nF\sqrt{D\omega}} \sin(\omega t - \pi/4)$$

If we assume there is an excess of indifferent electrolyte in order to justify keeping the activity coefficients unchanged, then

$$\frac{\Delta[A]}{[A_o]} = \frac{I\nu}{[A_o]nF\sqrt{D\omega}} \sin(\omega t - \pi/4) \qquad (2.19)$$

Equation (2.19) enables us to calculate the change in the activity associated with a certain flow of current. We also notice that for each swing of the current, the active species can accumulate or become depleted. While the accumulation process is unlimited, the depletion cannot proceed beyond zero concentration and the diffusional process thus causes asymmetry.

If we let

$D \sim 0.7 \cdot 10^{-5} \mathrm{cm}^2/\mathrm{sec}$,

and $\omega = 0.1$

then,

$$\Delta c_{max} = 1.23 \cdot 10^{-5} \frac{\nu}{n} I \text{ mole/liter} \qquad (2.20)$$

(I is in microamperes)

We can expect $1/2 \leqslant \nu/n \leqslant 4$, and the diffusion coefficients to be higher than the value quoted above, therefore, a general relation for the change in concentration can be written as

$$\frac{\Delta c_{max}}{c_o} = \lambda \frac{1.23 \cdot 10^{-5}}{c_o} \text{ per } \mu A$$

where the factor $\lambda \leqslant 1$, usually.

But from the previous studies (Angoran and Madden, 1976), for the background I.P., $c_o \sim 10^{-5}$ and in the presence of active species $c_o \sim 10^{-3}$. We thus expect non-linearity at currents $\sim 1\mu A$ in the former and $\sim 100\mu A$ in the latter.

We can parametrize Equation (2.18) in the form

$$I_p \sin \omega t = \exp\left(\vec{\alpha}\frac{nF}{RT}v\right) - \exp\left\{(\vec{\alpha}-1)\frac{nF}{RT}v\right\} + \delta \sin(\omega t-\pi/4)\exp\left(\vec{\alpha}\frac{nF}{RT}v\right) \qquad (2.21)$$

where $I_p = \frac{I}{i_o}$ and $\delta = \frac{\Delta c_{max}}{c_o}$,

and we can simulate electrode experiments by choosing I_p, δ and $\vec{\alpha}$ and evaluate (2.21) by numerical methods to obtain the current-potential, I-V, characteristics. "Numerical" experiments with the same electrodes, solution and frequency can be simulated by changing I_p and δ by the same ratio. In general, a wide variety of experiments is possible by specializing the parameters I_p, δ and $\vec{\alpha}$.

Instead of presenting the I-V characteristics directly as Lissajous patterns, a general standardizing technique is adopted by introducing the concept of the dynamic impedance. This is the ratio of the instantaneous voltage and the maximum current. The current is normalized to a range of [-1,1] and the dynamic impedance when traced as a function of the phase describes some Lissajous pattern. Such patterns are completely normalized and are good for direct comparisons.

More complicated processes involving active products and arbitrary ν/n will imply more involved numerical solutions but can be treated similarly.

CHAPTER THREE

3. The Non-Linear Aspects of Electrode Impedance

The faradaic electrode impedance results from an aggregate of partial processes which represent departures from some quiescent conditions, and whose contributions act in series or in parallel. Although different partial processes compete for the dominant role, the resulting I-V characteristic is linear provided the associated departures from equilibrium are sufficiently small. For greater departures, the contributions to the electrode impedance become more complicated and more reactions enter the competition. Asymmetric processes, like the change in the concentration of the participating species and the activation energy are emphasized and the I-V characteristic becomes non-linear.

The case of "sufficiently small" departures from equilibrium and hence the linear electrode concept is a rather special one, since all electrodes are, in fact, principally non-linear. However, the sequence in which certain partial processes begin to contribute to or dominate the electrode impedance and the nature of such processes will depend on the electrode-electrolyte system.

In the non-linear regime, a pure sinusoidal current flowing through an electrode system results in an anharmonic alternating potential, and hence a distorted Lissajous pattern. The shape of the pattern presents an additional parameter for investigating the mechanism of the electrodic process. At low frequencies, the non-faradaic current is very small and little or no non-linearity is expected from the fixed layer and so its contributions to the non-linearity can be neglected.

3.1 Experimental Investigation

The basic set-up consists of an electrochemical cell containing natural minerals and an electronic system for measuring the complex electrode impedance. This has been carefully described by Angoran (1975). We have made slight modification in the electrode spacing which cuts down the solution resistance by a factor of ten, and have used de-ionized double distilled water for preparing electrolytes. Measurements have also been made down to 10^{-2} hertz. The equivalent circuit fitting method using a generalized inverse of the electrode impedance spectra has been employed to investigate the mechanism of the electrodic process where possible.

In addition, a new set-up, especially useful for the non-linear study of electrode impedance is shown in Figure 3.1. The special feature in this case is that of a constant current source (see Figure 3.2(a)) which can deliver a wide range of currents (d.c. or a.c.) and maintain this for all values of the electrode impedance less than 1 megaohm. The stability of this voltage controlled current source is maintained by a differential amplifier of unity gain. The current settings are made in the 1:2:5:10 ratio, just the same as with the amplifier settings of the Tektronix storage oscilloscope used. This enables us to make simultaneous changes in the current and scope settings which we expect would keep the Lissajous pattern the same. This is pretty much so in the linear regime. Non-linearities can easily be detected

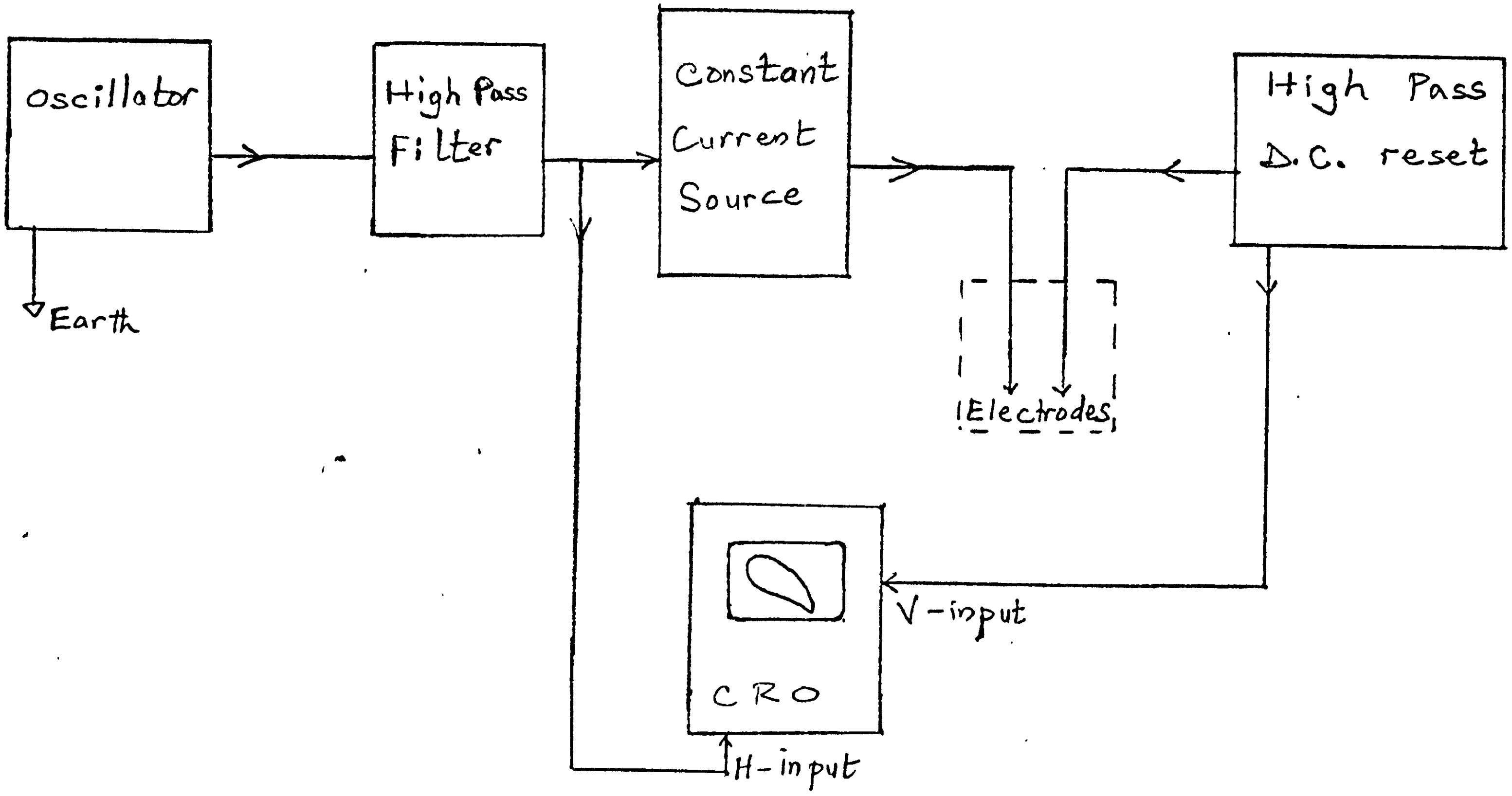


Fig. 3.1 Block Diagram of Experimental Set-up

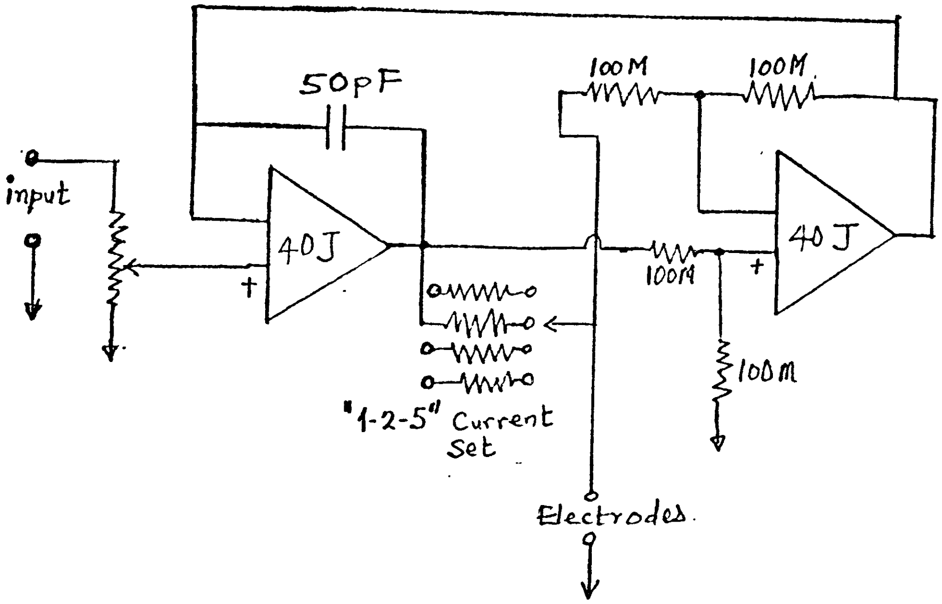


Fig. 3.2(a) Constant Current Source

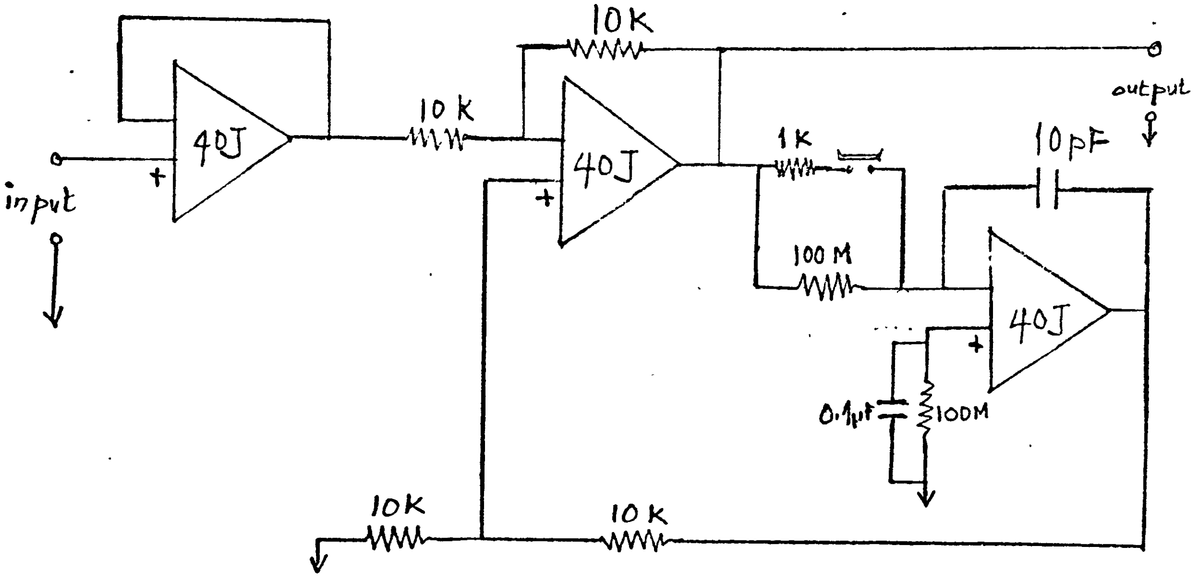


Fig. 3.2(b) High Pass Self-Potential Reset

and an immediate estimate of any impedance changes is possible. The high pass self-potential reset, in Figure 3.2(b) has a large high pass time constant for nulling any d.c. offset which might cause undesirable shift in the displayed patterns.

The mineral-electrodes are ground with silicon carbide abrasives down to grit #600, which could produce a scratch of about 20 microns. Although both 10^{-3} molar $CuSO_4$ and 10^{-3} molar KCl are used, the data on KCl electrolyte are considered more useful for the non-linear study. This is because earlier work by Angoran and Madden (1976) has confirmed that the Cu^{++} ions are active species.

The experimental procedure consists of pre-oxidizing or pre-reducing the electrochemical environment and then quick introduction of the minerals into the electrochemical cell (necessary only for pre-reduced environments). The frequency spectrum of the complex electrode impedance is then determined as a function of the applied current. For low frequency measurements, a constant sinusoidal current free of harmonics is passed through the mineral-electrolyte system and also fed to the horizontal input of a storage scope. The alternating voltage across the electrode is passed through a high input impedance device, sometimes amplified, and fed to the vertical input of the storage scope. Phase determinations can be obtained directly from the Lissajous pattern displayed on the scope, while the magnitude of the impedance is obtained by comparison using standard resistors. Although it is possible to calibrate the device to measure impedance directly, this has not been done.

Observations have not been limited to the mineral-electrolyte-mineral system (the "twin" electrode array). In order to eliminate the effect of possible cancellations of even harmonics and faradaic rectification in the "twin" mineral-electrode array, single mineral electrodes have also been used. Measurements on such arrays are made relative to a less polarizable electrode (Ag-AgCl).

In a few cases, Tafel lines have been obtained from basic direct current experiments in which different currents are forced through the mineral-electrolyte-mineral array and the anodic and cathodic potentials measured relative to some reference electrode (usually calomel).

The suite of minerals studied is the same as used in previous works by the research group, viz.: chalcocite, chalcopyrite, pyrite, and covellite, but the electrolytes have been limited to potassium chloride and copper sulphate. Metallic electrodes like copper and iron have been used for tests only.

3.2 Results and Discussion

3.2.1 Observed Non-Linear Character of Minerals

The typical behavior of the electrode impedance spectra for the minerals studied is presented in Figure 3.3(a)-(d). This corresponds to the earlier experiments in which constant potentials are impressed across the electrodes; such potentials together with the current at 0.1 hertz are marked on the curves. Slight decrease in the electrode impedance with increasing current is observed for chalcopyrite, pyrite and covellite. On the other hand, the electrode impedance of chalcocite tends to increase with applied voltage.

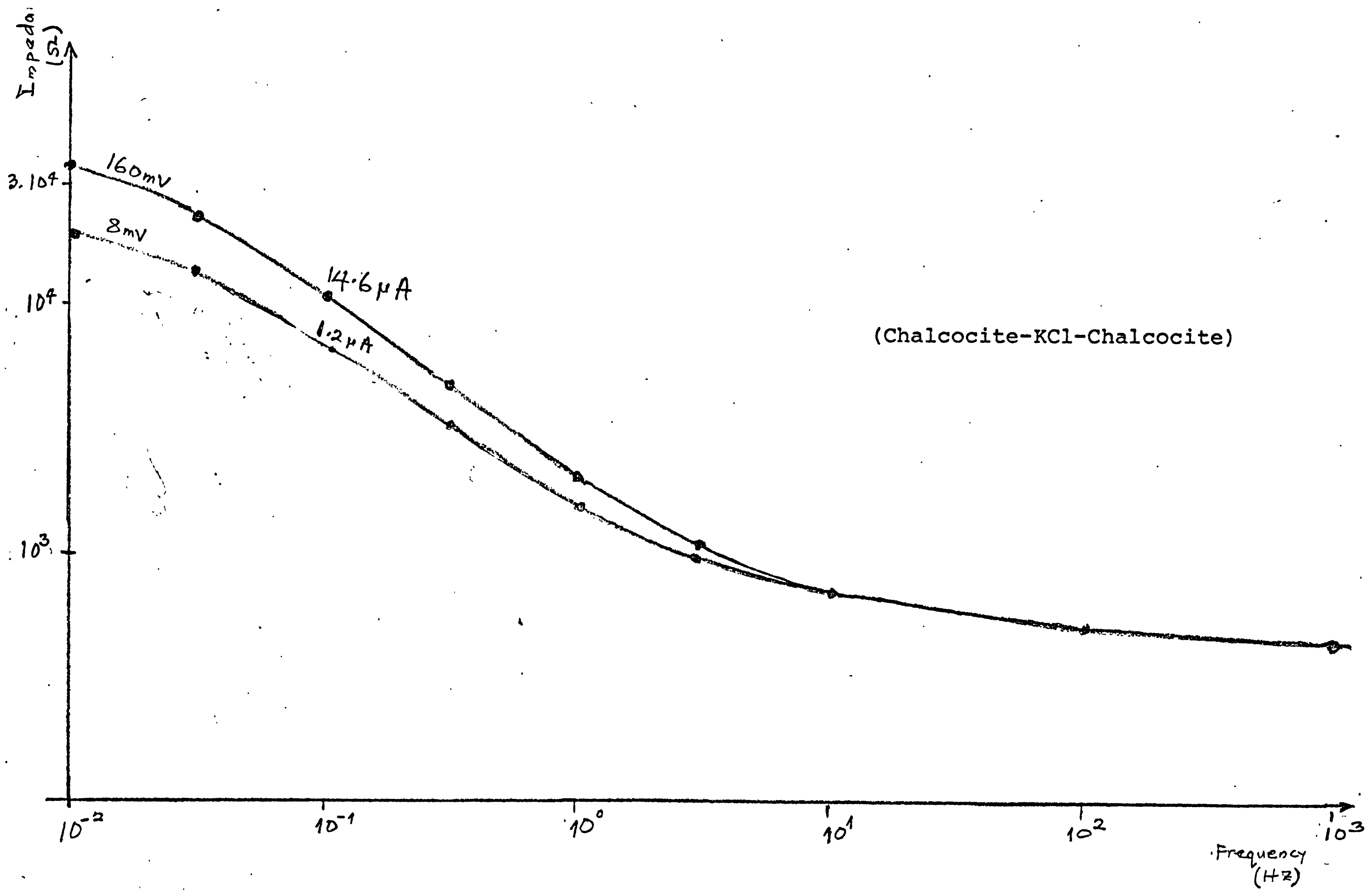


Fig. 3.3(a). Frequency spectra of Chalcocite electrode impedance

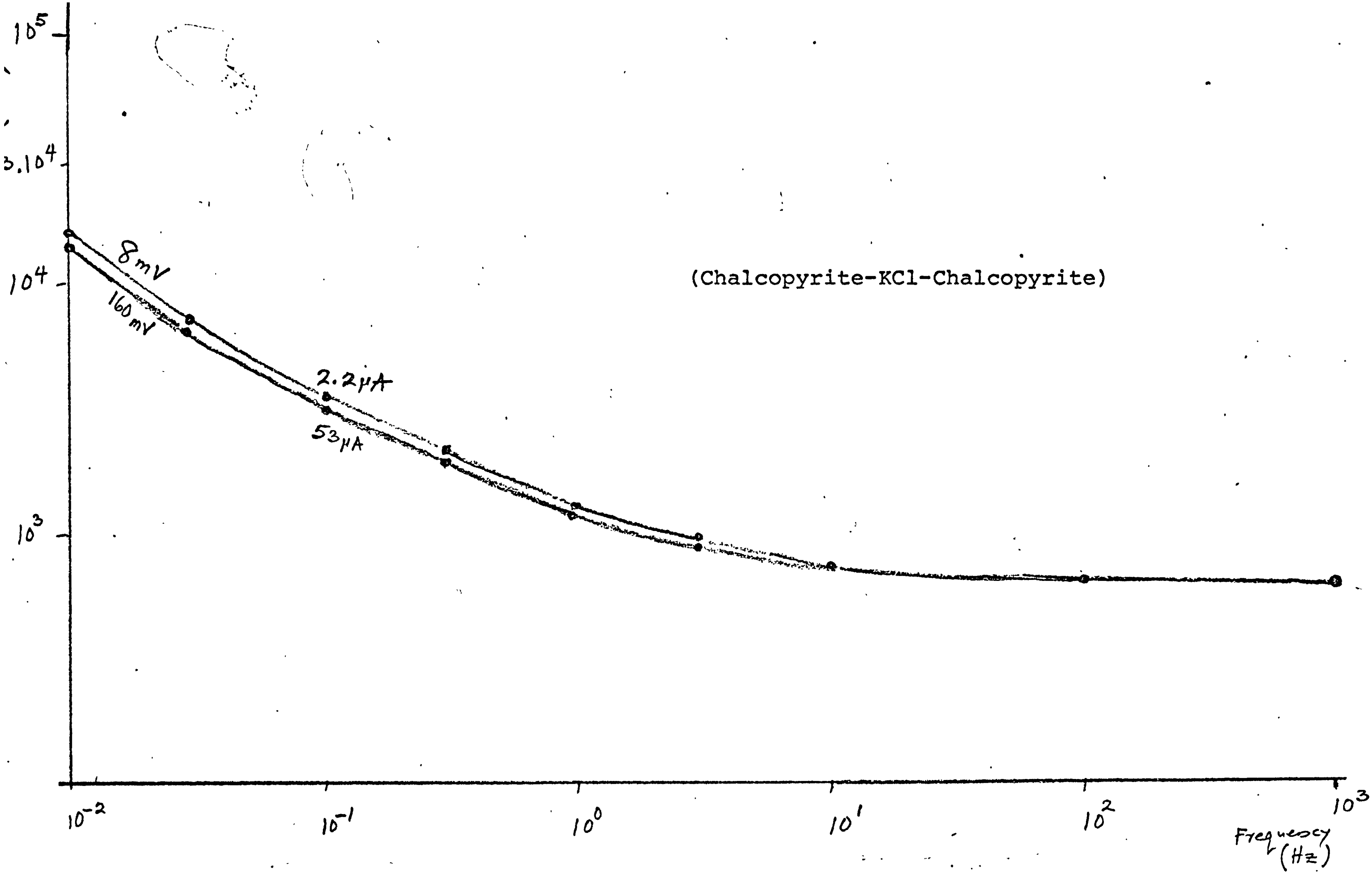


Fig. 3.3(b). Frequency spectra of Chalcopyrite electrode impedance

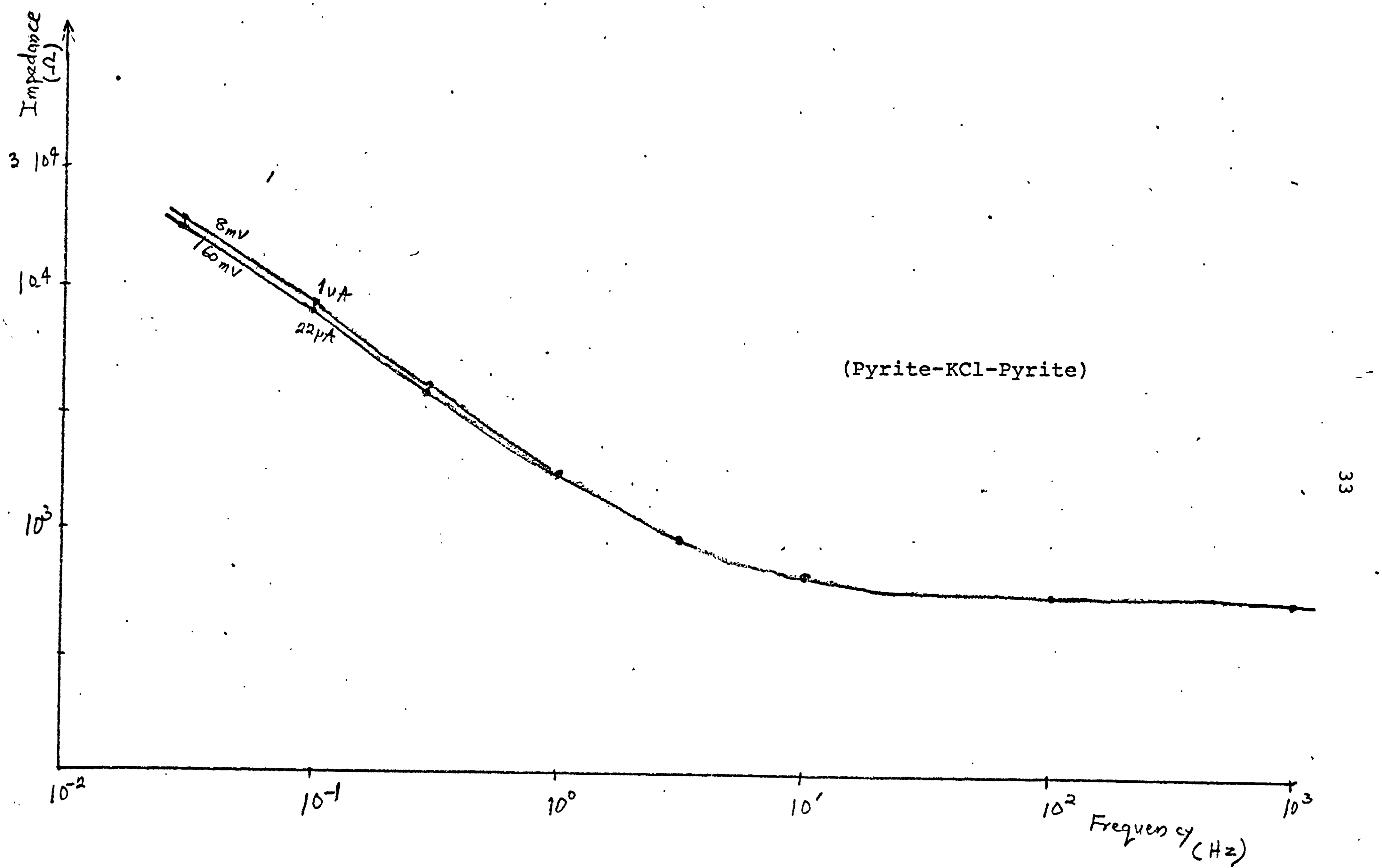


Fig. 3.3(c). Frequency spectra of Pyrite electrode impedance

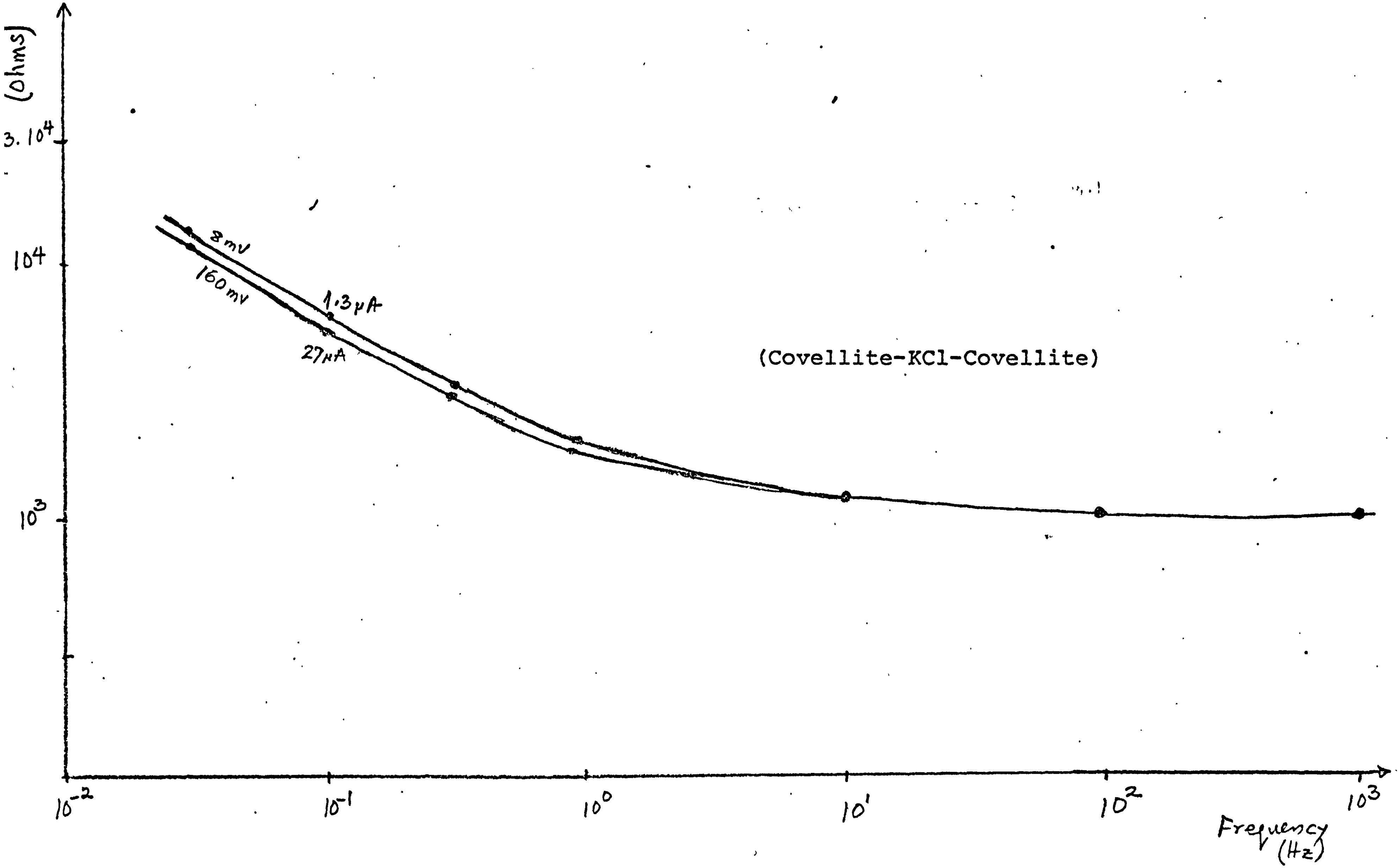


Fig. 3.3(d). Frequency spectra of Covellite electrode impedance

The shapes of the Lissajous patterns characteristic of these minerals are quite distinct. These are shown in Figure 3.4 where they have been re-traced to introduce a phase shift of 180 degrees because such a phase shift has been imposed on the subsequent patterns by a later circuitry. The differences in the shapes of the Lissajous patterns can be interpreted as an indication that different processes dominate the electrode impedance in the mineral-electrolyte systems, and this becomes obvious only in the non-linear regime. Similar experiments have been conducted in copper sulphate solution and on the basis of these, a rough classification of the electrode according as whether they are linear or not can be made. (See Table 3.1; an electrode is said to be linear only when it appears less non-linear.)

Where it is possible the electrode impedance spectra has been inverted by the equivalent circuit fitting procedure. In the case of chalcopyrite, pyrite and covellite the decrease in the electrode impedance can be associated with a decrease in the Warburg impedance. Equivalent models incorporating parallel charge transfer reactions also result in better fit with the almost non-linear data, especially for chalcocite.

Higher currents and hence potential drops are possible with the constant current arrangement, and these are very useful, in particular for cases where the electrode processes are not wholly kinetically controlled and the condition $\nu > RT/nF$ does not guarantee any observable non-linear characteristics. Figure 3.5 shows an example where a twin-pyrite electrode in potassium chloride appears linear while supporting up to 600mV.

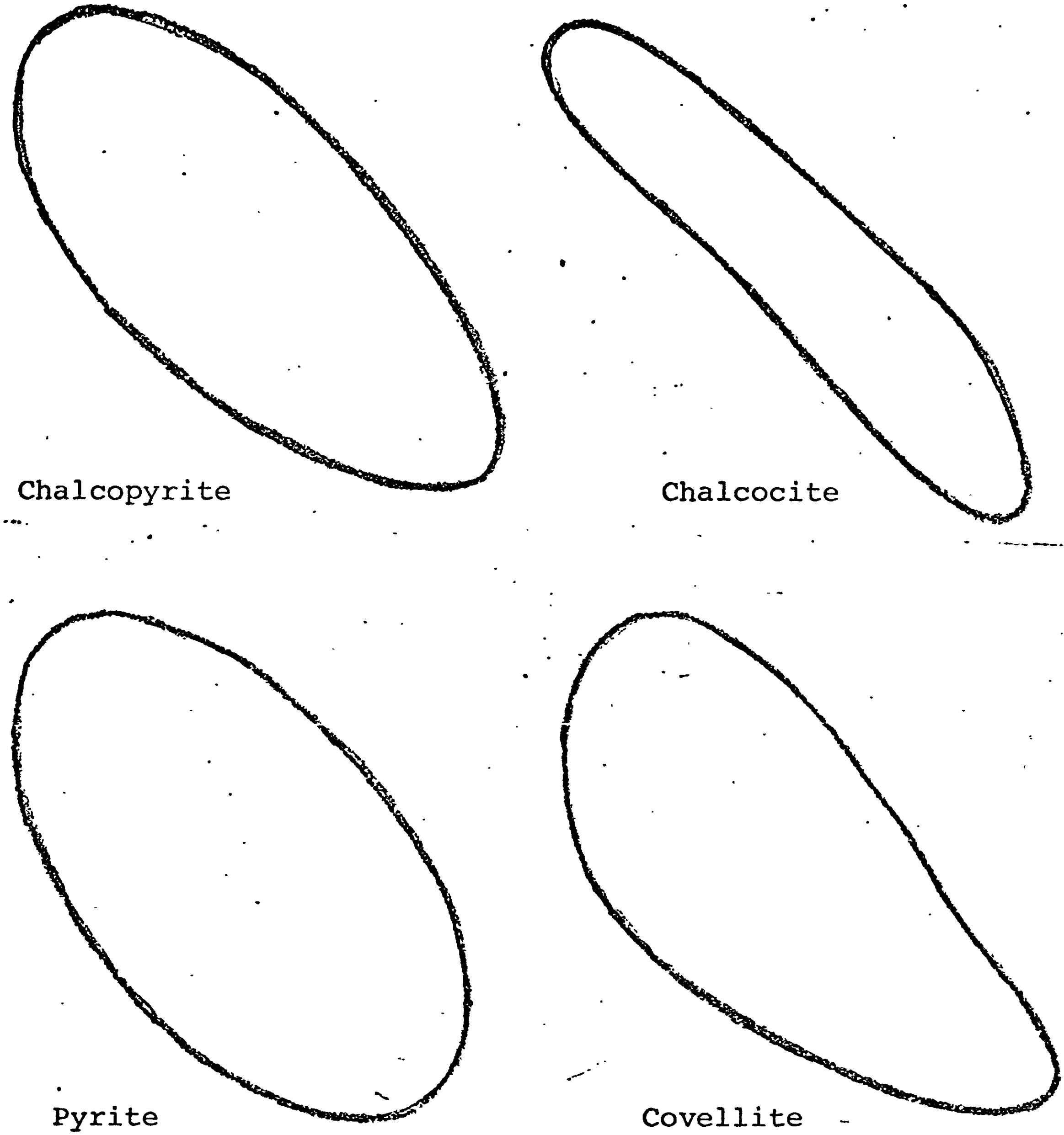


Fig. 3.4 Electrode Lissajous patterns of different minerals in potassium chloride at 0.01 hertz.

Electrode Electrolyte	Chalcopyrite ($CuFeS_2$)	Chalcocite (Cu_2S)	Pyrite (FeS_2)	Covellite (CuS)	Copper (Cu)
Copper Sulphate ($CuSO_4$)	NON-LINEAR	LINEAR	LINEAR	LINEAR	NON-LINEAR
Potassium Chloride (KCl)	NON-LINEAR	NON-LINEAR	LINEAR	NON-LINEAR	NON-LINEAR

Table 3.1. A rough classification of linear and non-linear electrode-electrolyte systems.

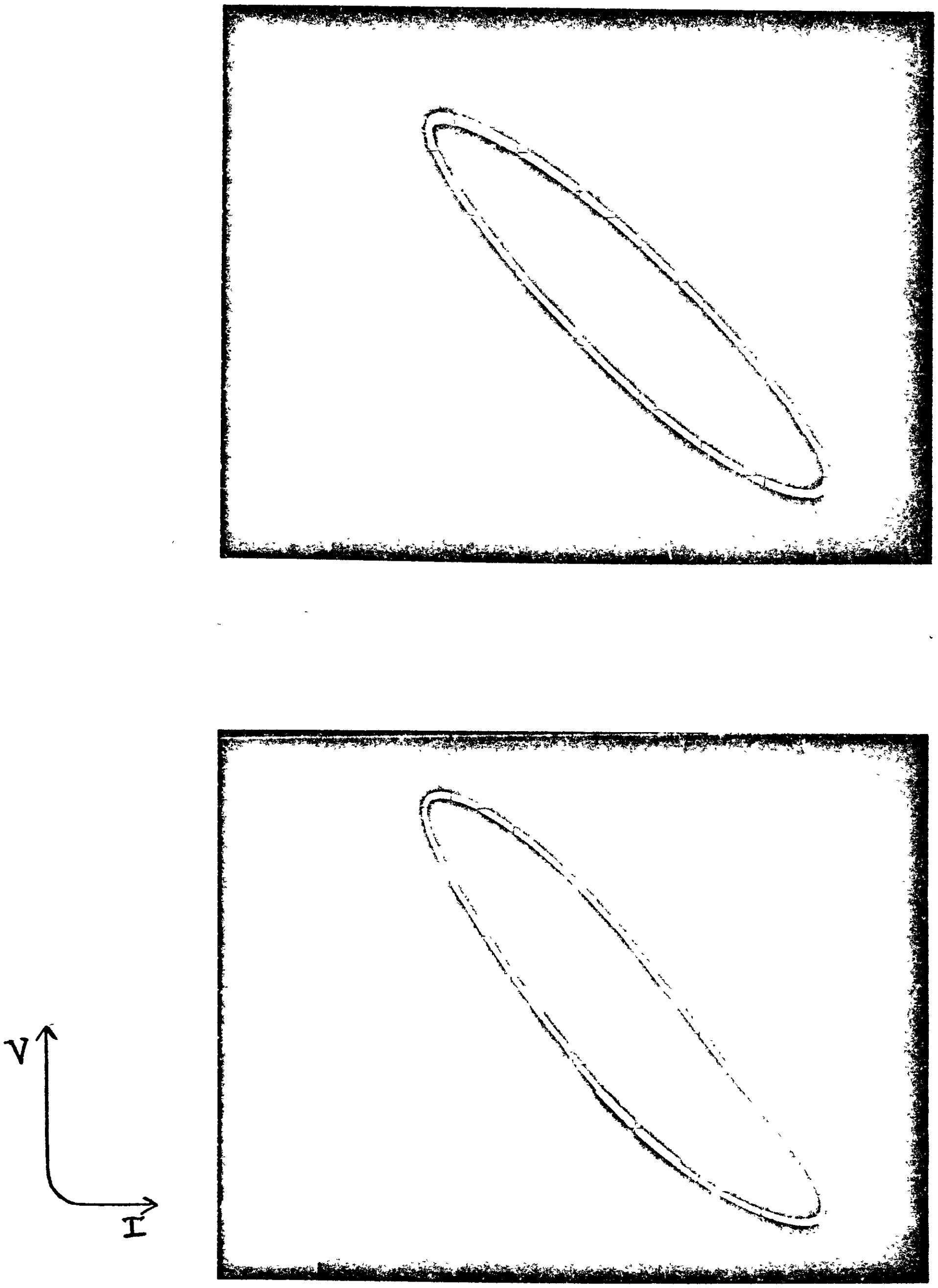


Fig. 3.5 Electrode Lissajous pattern of twin pyrite in KCl at 0.01 hertz.

(a) Top: Applied voltage = 590mV
(b) Bottom: Applied voltage = 695mV

The cancellation of the non-linearity in a back-to-back electrode array can be significant especially at high currents. The anharmonic alternating potential across a "twin" and a single mineral electrode system together with the associated distorted Lissajous patterns are shown in Figure 3.6.

Experiments with single chalcocite electrodes indeed confirm the initial increase in the electrode impedance before any subsequent decrease. Figure 3.7 is a biased but effective representation of this. It is biased because the reference line of each trace has been shifted in such a way that the change in the voltage appears only at one end. Properly oriented and centered traces are shown in Figure 3.8(a and b). We notice that the increase in the voltage during the positive half-cycle of the current is slightly less than that during the negative half-cycle. The electrode impedance appears to be dominated by a diffusional process, and the reacting ion involved must be positively charged. This positive diffusing ion appears to be stable in a potassium chloride environment as a change in the solution concentration from 10^{-3} to 10^{-2}M per liter produces no significant effect other than a cut in the solution resistance (compare Figures 3.8(a) and 3.8(b)). The onset of observable non-linear characteristics occurs at about a current density of $0.13 \mu A\, cm^{-2}$ and the diffusional factors, responsible for the asymmetric increase in the dynamic impedance becomes less effective at $0.52 \mu A\, cm^{-2}$ at 0.01 hertz. This is probably due to the presence of a parallel reaction which is less diffusion dominated.

Chalcopyrite and pyrite show systematic decrease in electrode impedance with the passage of current (see Figure 3.9(a)

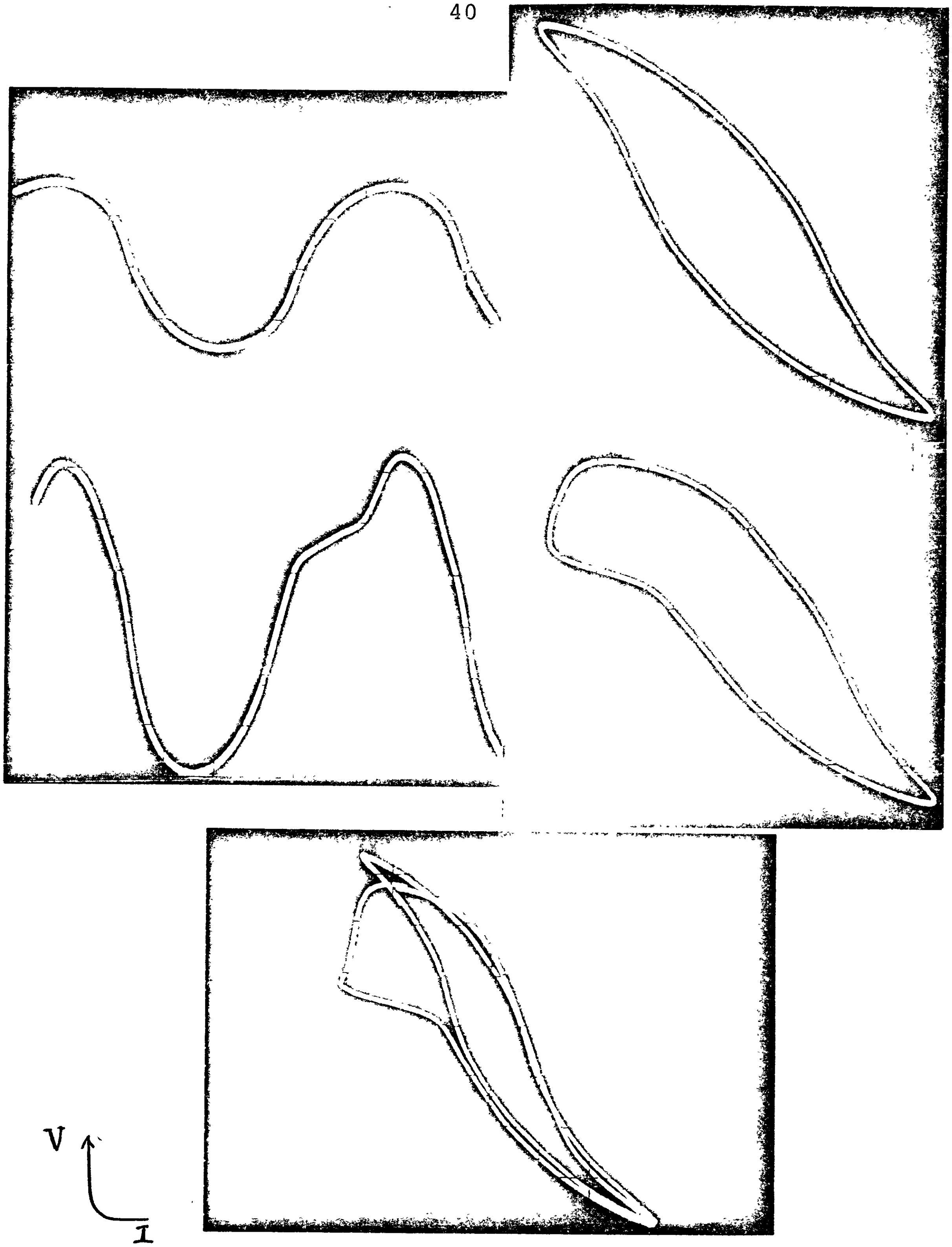
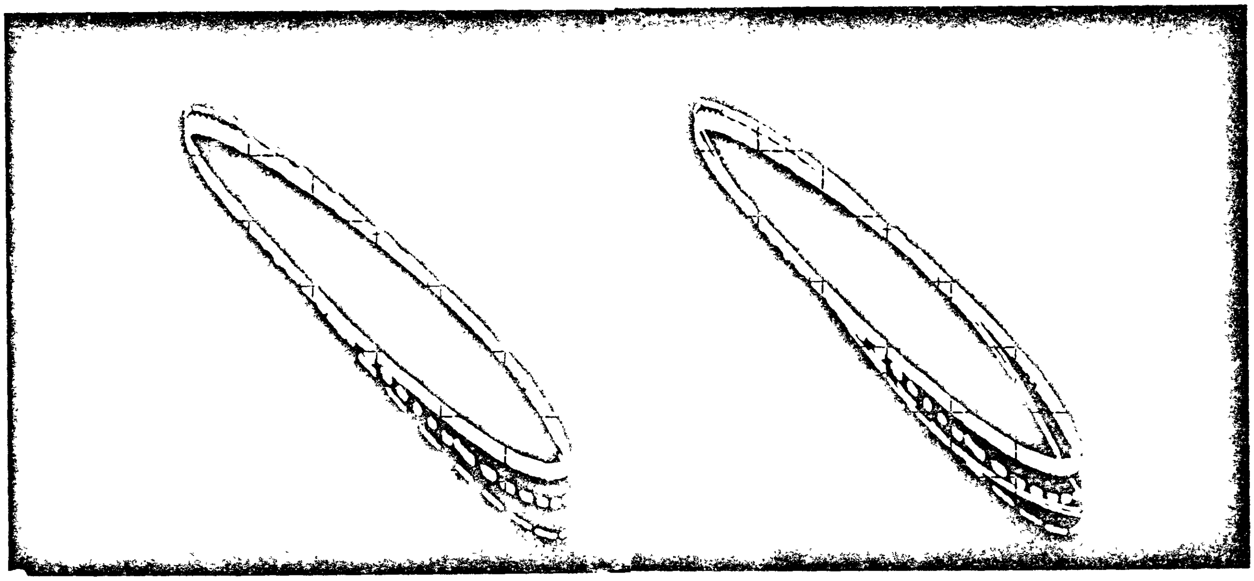


Fig. 3.6 Anharmonic alternating potentials and electrode Lissajous patterns in twin and single chalcocite electrodes.

Top: Twin electrode
Middle: Single electrode (ref. Ag-AgCl)
Bottom: Superimposed patterns



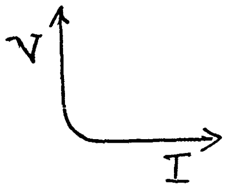


Fig. 3.7 Electrode Lissajous pattern of single chalcocite in KCl at 0.01 hertz.

Legend:

Curves	Current (μA)
Thick continuous line	0.4
Dotted line	0.8
Dashed line	1.6
Thin continuous line (right hand figure only)	4.0

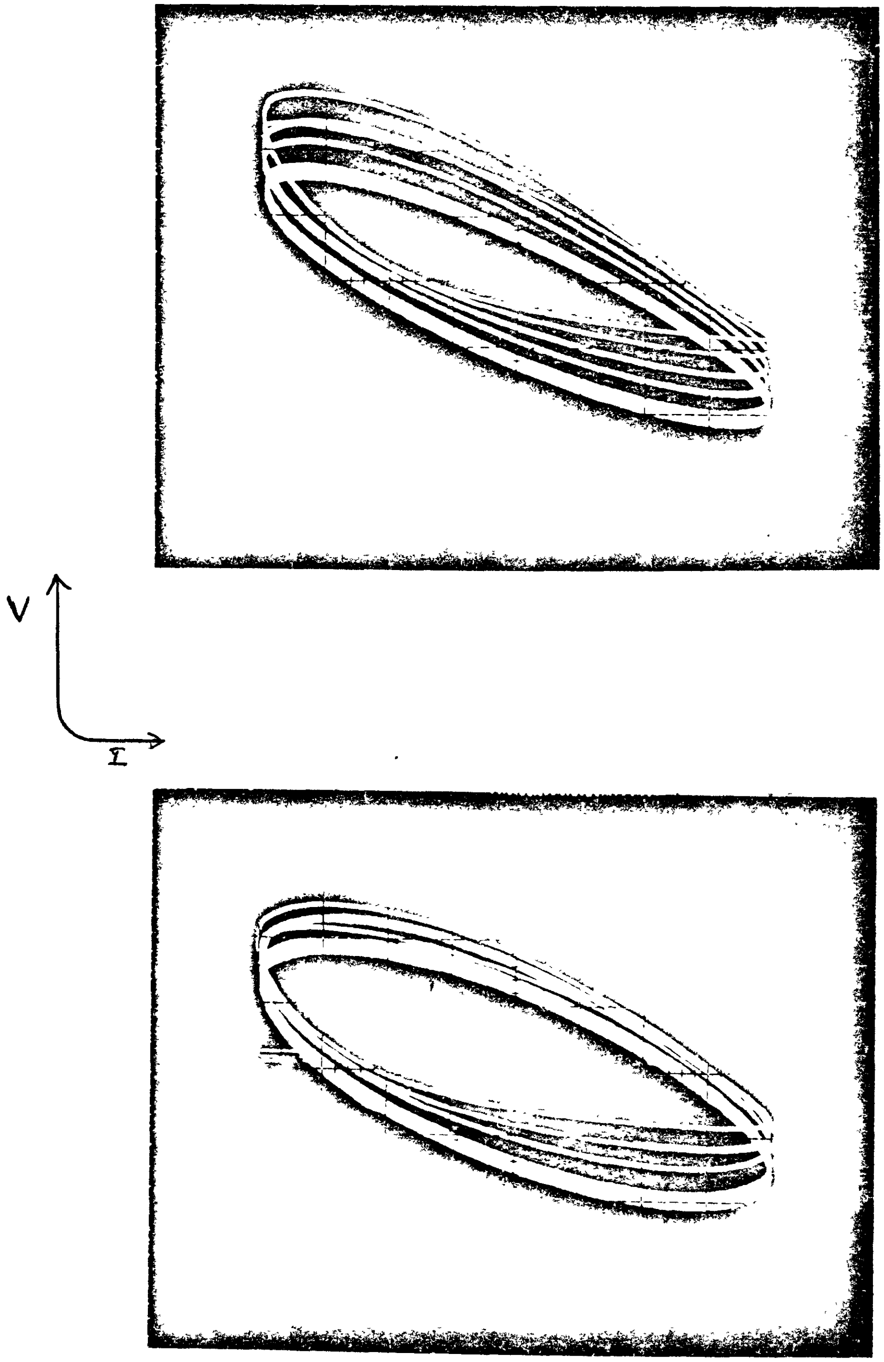


Fig. 3.8 Well centered asymmetric electrode Lissajous patterns of chalcocite at 0.03 hertz at different currents in:

(a) 10^{-3}M per liter KCl (top)
(b) 10^{-2}M per liter KCl (bottom)

[Single mineral-electrodes]

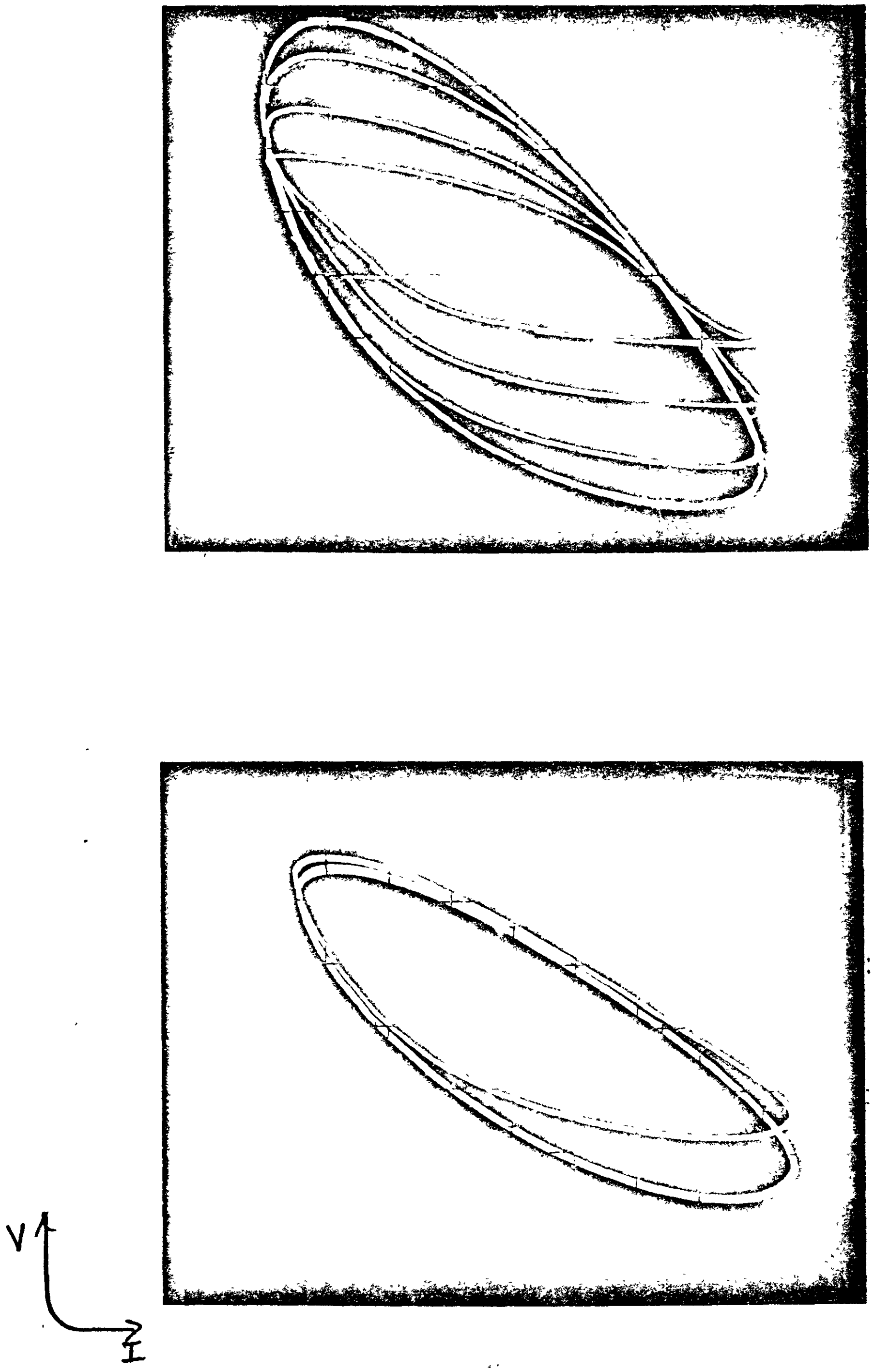


Fig. 3.9 Electrode Lissajous patterns of (a) chalcopyrite (top) and (b) pyrite (bottom). Outer patterns correspond to lower currents. [Single mineral-electrodes]

and (b)). Observable non-linearities commence at 0.7μA cm^{-2}, and 0.6μA cm^{-2} in chalcopyrite and pyrite at 0.01 hertz. The minerals appear distinguishable, however, and the mechanism leading to non-linear features must be different. In pyrite, the decrease in the electrode impedance is also associated with the decrease in the phase angle and the "solution Warburg". Chalcopyrite electrode impedance appears controlled by the kinetics factors. This could explain the decrease of the impedance with current but the simultaneous appearance of wide phase angles even at 7.5μA cm^{-2} which is suggestive of significant diffusion, still remains unresolved.

3.2.2 Comparison with Numerical Solution Prediction

In order to provide better understanding of the non-linear features, the Lissajous figures can be simulated for different experiments and electrode reactions. In this study, the effect of the fixed layer has been neglected which is probably justified at low frequencies. Also only one active reactant is considered and the products are thought to go directly to the solid phase. Furthermore, for convenience, our numerical calculations do not incorporate other parallel charge transfer processes. The parameter $I_p = I/i_o$ is selected in such a way that I is of the same order as in our laboratory experiments and $i_o \sim 10^{-3}$ to 10^{-4} amps which agrees with the estimates from Tafel lines and corresponds to the values of the reaction resistance deduced from our equivalent fitting analysis. The numerical results are plotted as dynamic impedance and an artificial phase shift of 180° has been introduced in the plots so that we can compare them with observed patterns.

Figures 3.10(a) and (b) show the dynamic impedance of an electrode involved in similar experiments at the same frequency. A "linear" Lissajous pattern is shown and the non-linearity caused by doubling the current each time is superimposed on the former. If the diffusion process is unlimited then a change of concentration from 20-80% will occur. The dynamic impedance will continue to increase asymmetrically as shown, and in the limit an infinite voltage will be required to maintain a small current through the electrode at zero concentration. We can compare this behavior with the results on chalcocite, and reinforce our conclusions about the preponderant effort of unlimited diffusional processes at the beginning of the non-linearity. Also, the diffusion ion can be identified as being positively charged. In Figure 3.10(c) we show both the theoretical and observed asymmetries in the dynamic impedance which has led us to identify the charge sign of the diffusing ion.

Figures 3.11 and 3.12 show the numerical experiments involving different choices of I_p and δ which are used to simulate cases which are reaction resistance limited. There is a decrease in the dynamic impedance, loss in phase and a tendency toward symmetry. We also notice that any Warburg-like effect tends to disappear with further reduction in the diffusion effect (see Figures 3.13(a) and (b)). The behavior of pyrite and chalcopyrite can be explained by attributing the decrease in the electrode impedance to some dominant kinetics controlled processes. Such a simple explanation might be adequate for

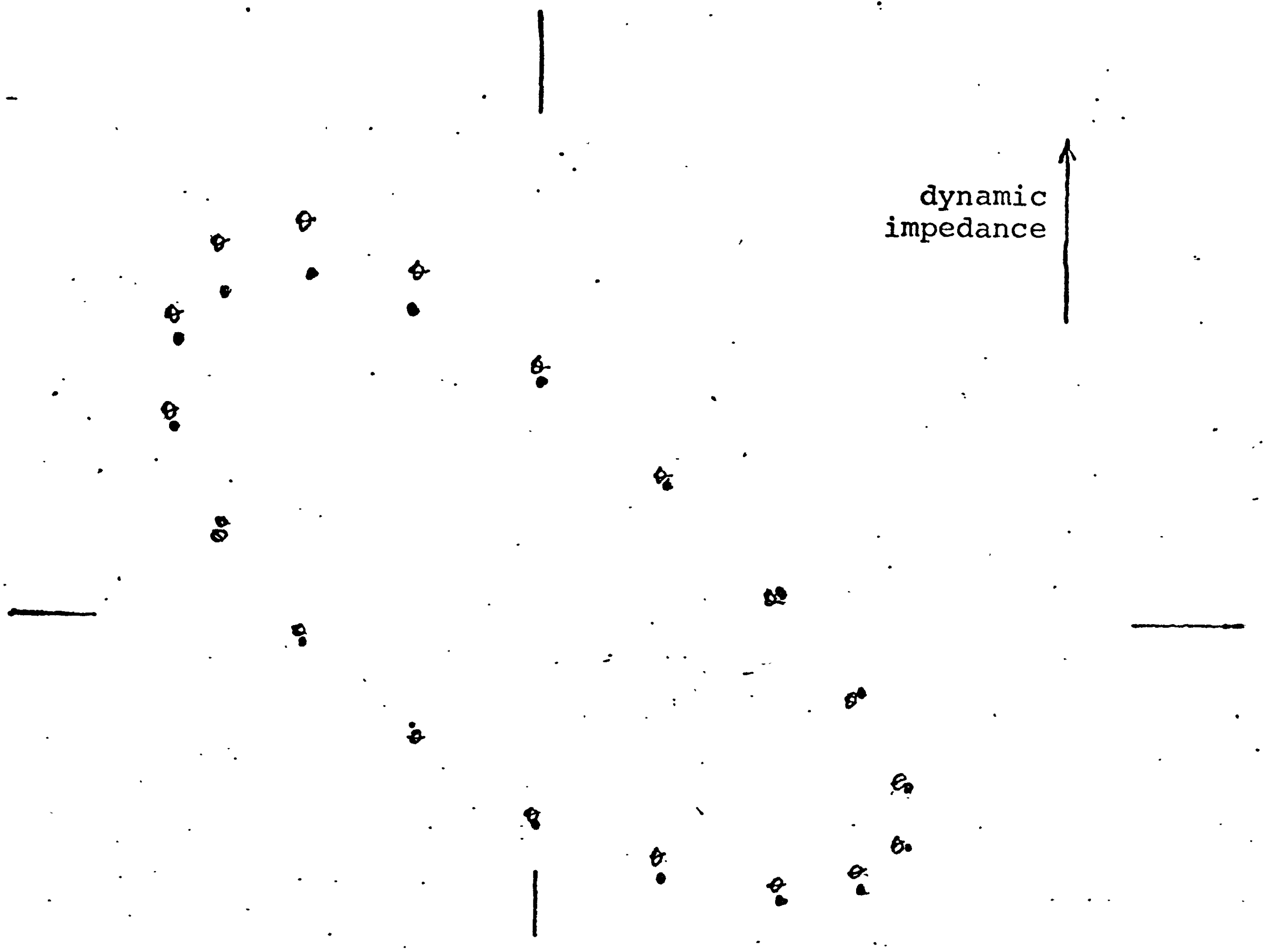


Fig. 3.10(a) Theoretical dynamic impedance

Legend:

• • • $I_p = 0.5\cdot10^{-3}$, $\delta = 0.2$, $\vec{\alpha} = 0.5$

⊖ ⊖ ⊖ $I_p = 10^{-3}$, $\delta = 0.4$, $\vec{\alpha} = 0.5$

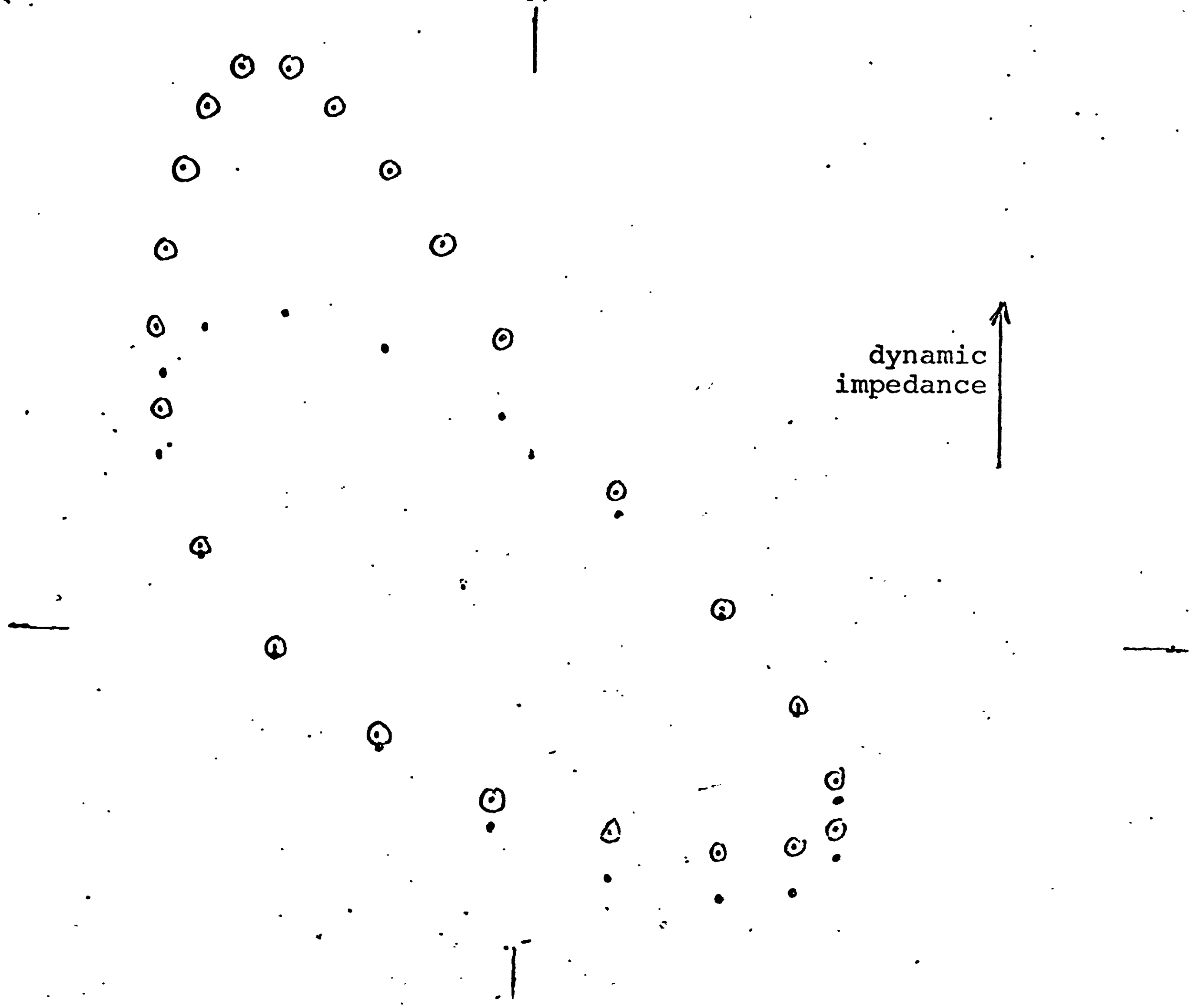


Fig. 3.10(b) Theoretical dynamic impedance

Legend:

• • • ; $I_p = 0.5 \cdot 10^{-3}$, $\delta = 0.2$, $\vec{\alpha} = 0.5$

⊙⊙⊙; $I_p = 2\ 10^{-3}$, $\delta = 0.8$, $\vec{\alpha} = 0.5$

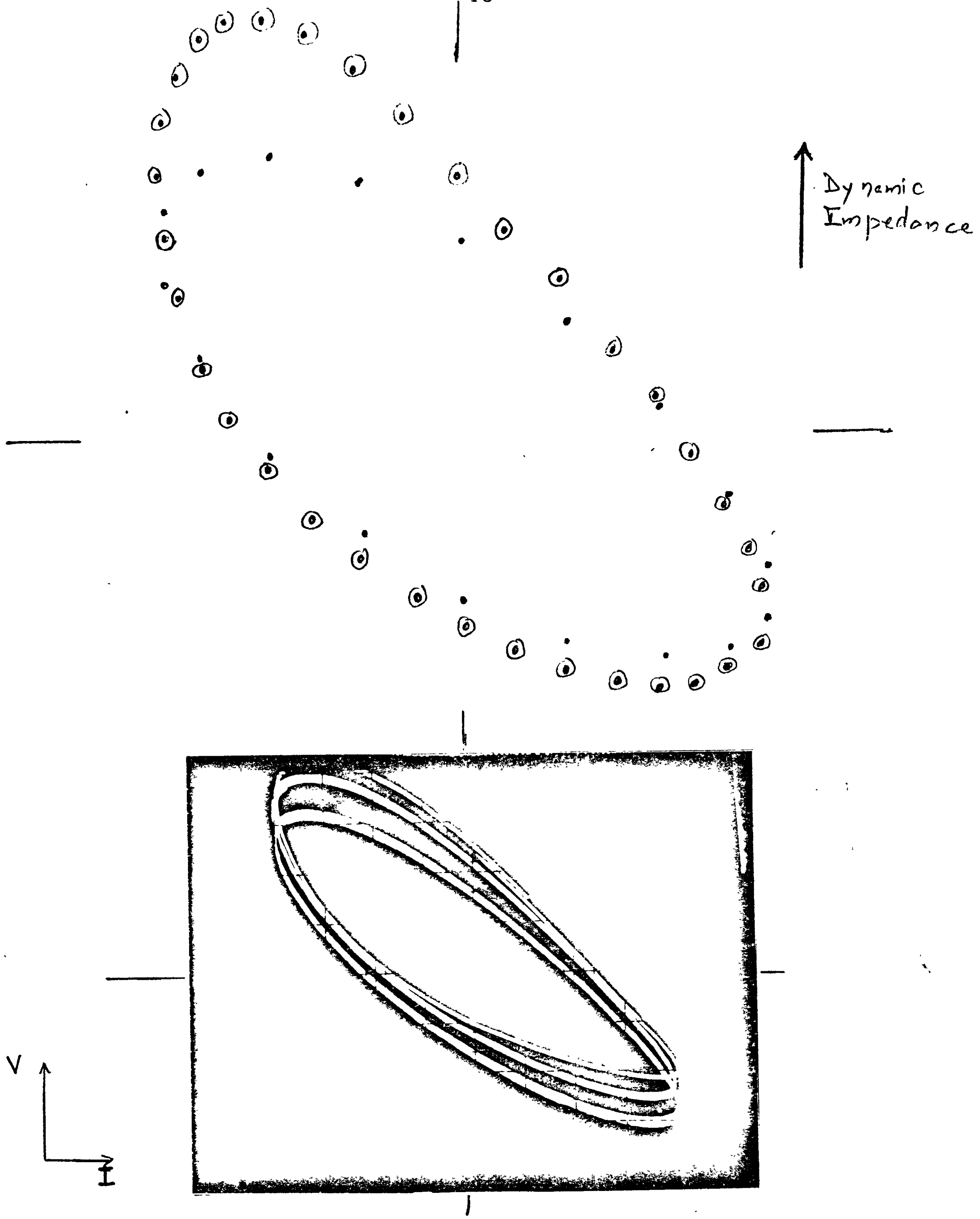


Fig. 3.10(c) Theoretical (top) and observed (bottom) asymmetric Lissajous pattern caused by a diffusing positively charged ion.

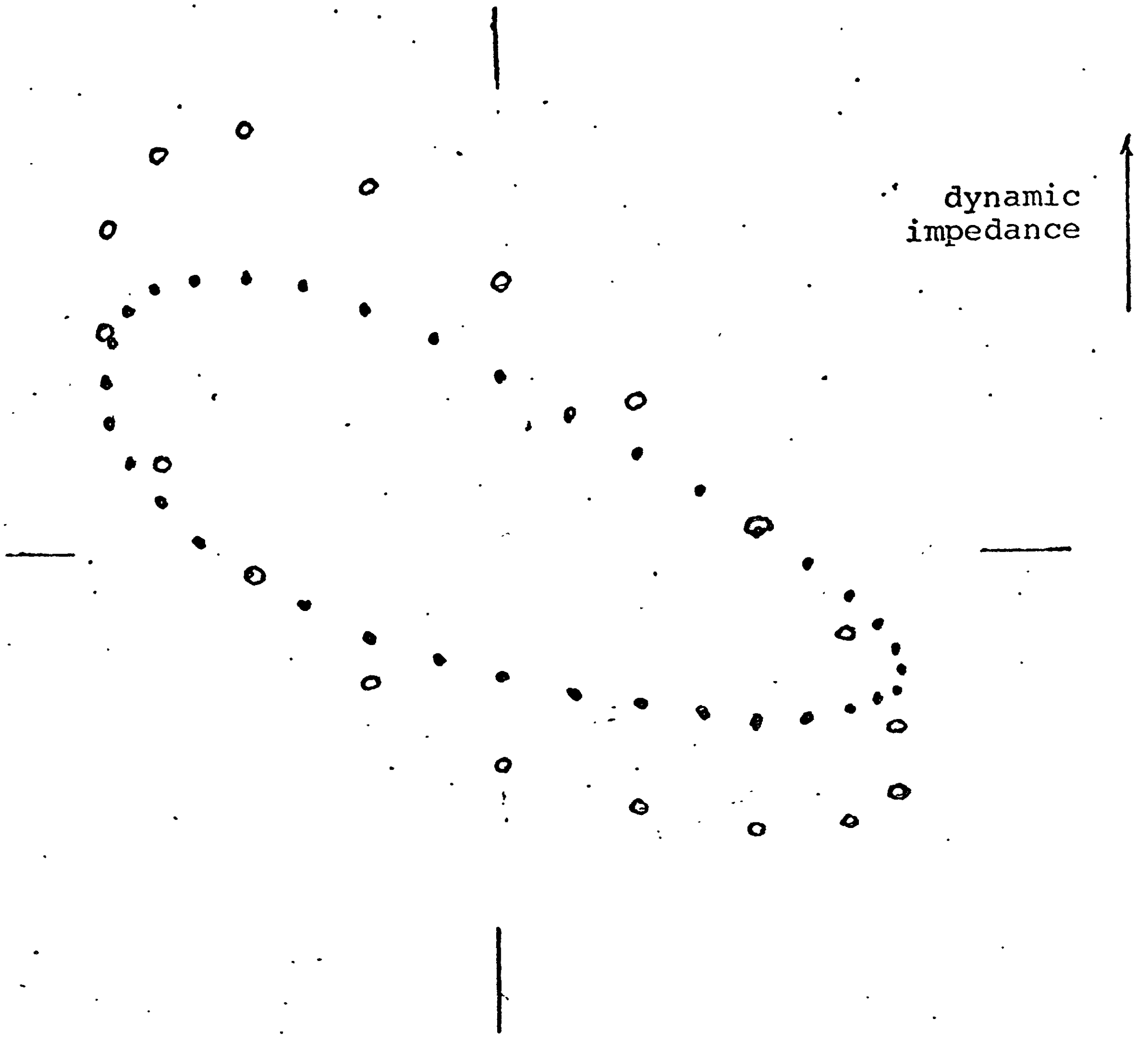


Fig. 3.11 Theoretical dynamic impedance

Legend:

●●● ; $I_p = 10^{-2}$, $\delta = 0.55$, $\vec{\alpha} = 0.5$, Scale: 10^3 ohm/cm

○○○ ; $I_p = 10^{-3}$, $\delta = 0.5$, $\vec{\alpha} = 0.5$, Scale: 10^4 ohm/cm

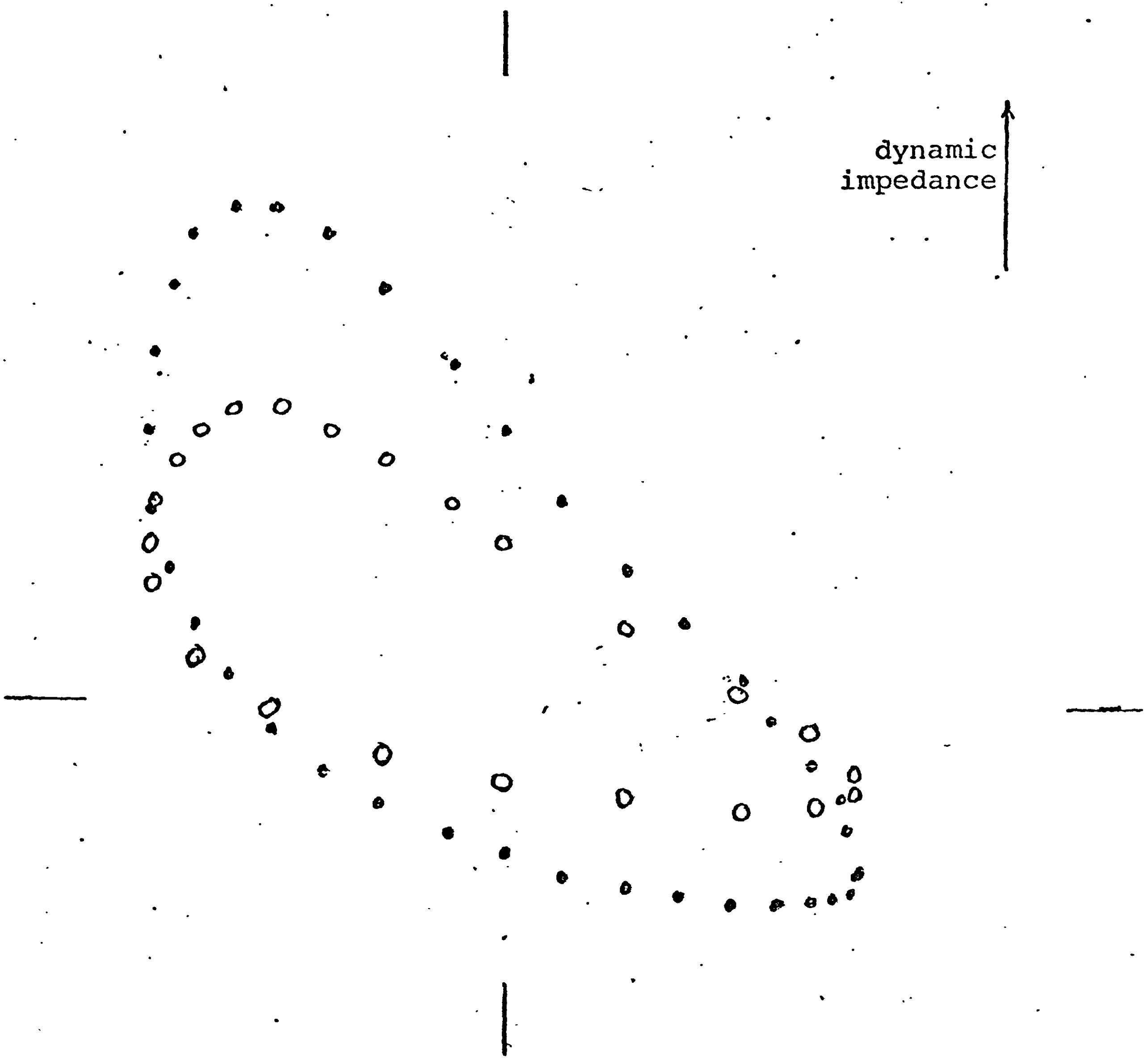


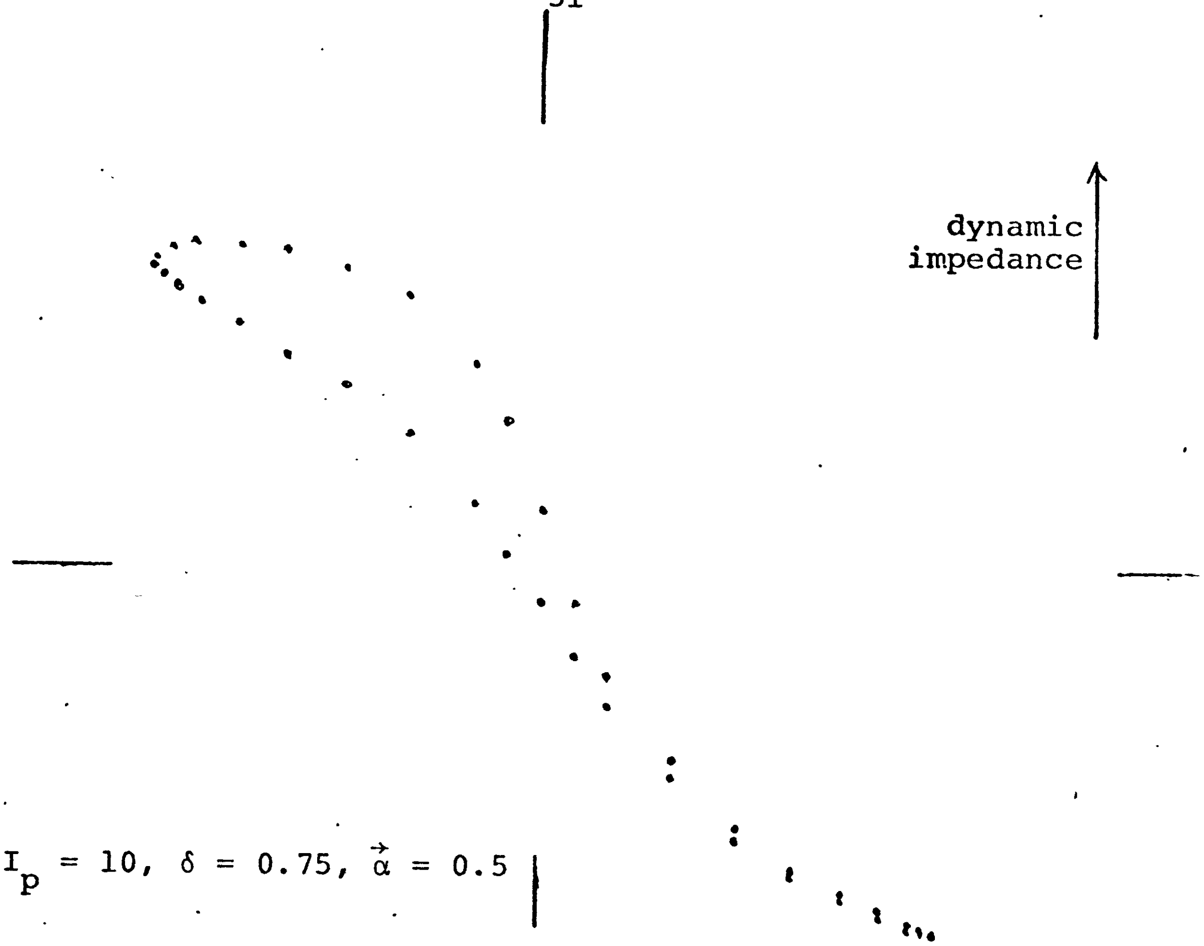
Fig. 3.12 Theoretical dyanmic impedance

<u>Legend</u>:

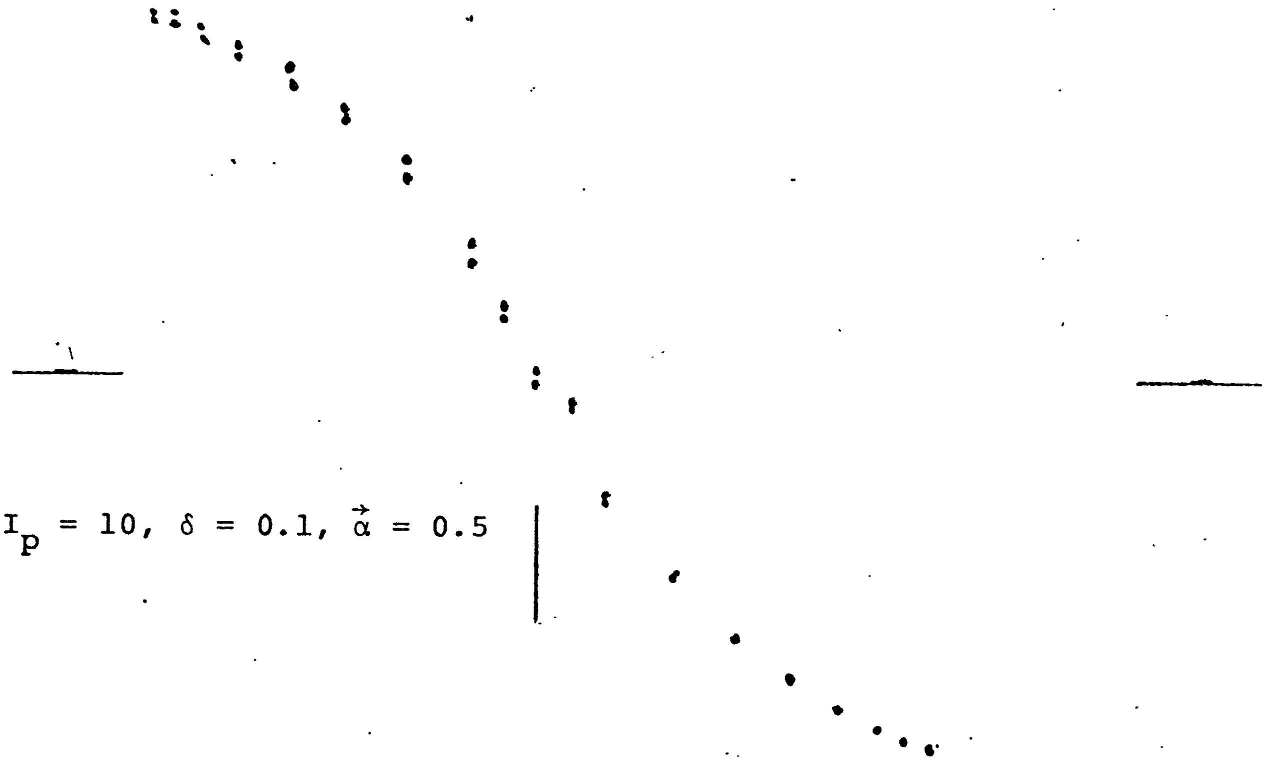
● ● ● ; $I_p = 10^{-3}$, $\delta = 0.75$, $\vec{\alpha} = 0.5$

○ ○ ○ ; $I_p = 2\ 10^{-3}$, $\delta = 0.77$, $\vec{\alpha} = 0.5$

[Scale: 10^4ohm/cm]



(a) $I_p = 10$, $\delta = 0.75$, $\vec{\alpha} = 0.5$



(b) $I_p = 10$, $\delta = 0.1$, $\vec{\alpha} = 0.5$

Fig. 3.13 Theoretical dynamic impedance [Scale: 5 ohm/cm] for pyrite mineral situations, but the reasons for the observed large phase angles in chalcopyrite is still largely not understood. We can hypothesize that there is a competition between diffusion controlled and reaction resistance controlled processes in which neither possesses an overriding effect. But we cannot be very comfortable with this since our models are very simple and a good deal of exploring among more sophisticated ones will still be necessary.

CHAPTER FOUR

4 Conclusions

A lot of new information about the electrodic process can become available, even at just a single frequency, by exploring the non-linear characteristics of the mineral-electrolyte systems. In order to contain this new data "explosion", it will be necessary to limit observations to only the early non-linear regime. This study represents a venture in this direction and has provided some new results which are fundamental to the processes controlling the electrode impedance in sulphide minerals. Some of the results, though, are not well understood and this makes us believe that more work is required in this case.

The present study shows that some minerals are less non-linear than the others. We can list the minerals studied with the most non-linear first: chalcocite (CuS_2), covellite (CuS), chalcopyrite ($CuFeS_2$) and pyrite (FeS_2). This classification refers to potassium chloride solution. The range of the current density required to make the non-linearity observable is about $0.1\text{-}1.0 \mu A\,cm^{-2}$. In copper sulphate solution about 100 times this current is required to drive electrodes observably non-linear.

It has also become evident that different processes do indeed dominate the electrode impedance at different mineral-electrolyte boundaries. This can only be found out from the non-linear characteristics of the minerals. Although the "Warburg impedance" is important, it does not play any universal dominant role under non-linear conditions. There is an indication that ultimate identification of the "mineral-signatures" might be possible from this type of study. Our experiments show that diffusion processes are characterized by wide phase angles and the lack of symmetry in the electrode Lissajous patterns, while reaction controlled processes tend to force an S-type of symmetry on the Lissajous patterns. And specifically, toward nonlinearity, chalcocite electrode impedance is initially dominated by some diffusion process and at current densities of about $0.5 \mu A\,cm^{-2}$, a parallel charge transfer process starts to dominate causing a decrease in the electrode impedance and the phase angles. Such characteristics have not been observed in the other minerals.

Chalcopyrite behavior is notably peculiar and not well understood. The electrode impedance decreases with current but there is no corresponding decrease in the phase even at about $7 \mu A\,cm^{-2}$. The "hysteresis-like" Lissajous patterns characteristic of chalcopyrite might be accounted for by the introduction of the fixed layer effect and a parallel charge transfer process which we have not considered in our models.

We are able to identify the sign of the charge of the diffusing ion in potassium chloride solution as being positive by comparing the observed and theoretical results. This ion appears stable in the potassium chloride environment and could be Cu^{++} impurities.

An obvious extension of this work is the incorporation of more complicated models and more quantitative evaluation of the mechanism of the non-linear electrodic process. This could be accomplished by setting up and solving the inverse problem of the electrode process. Models which are parametrized to quantify the electrodic effects such as the fixed layer capacitance, diffusion process (in solution/surface) and parallel charge transfer steps, can be used to generate dynamic impedance as a function of the phase and then fitted to the entire observed non-linear Lissajous patterns. On the experimental aspect, it might be useful to construct a continuously adjustable electrode spacer to enable optimum determination of the solution resistance for each electrode type or experiment.

APPENDIX A

The effect of the diffuse and diffusion layers in the electrodic process

The behavior of ions diffusing under the influence of external forces can be described by a set of coupled non-linear partial differential equations:

$$\frac{\partial F}{\partial t} = D_p \nabla^2 p - \nabla \cdot (p v_p)$$

$$\frac{\partial \eta}{\partial t} = D_n \nabla^2 n - \nabla \cdot (n v_n)$$

where the drift velocities, v_p and v_n, are given by

$$v_p = \mu_p E, \; v_n = -\mu_n E$$

and

E - electric field

μ - mobility

D - diffusion coefficient

p,n - positively and negatively charged ions respectively.

Therefore the above equation becomes (in one dimension)

$$\frac{\partial p}{\partial t} = D_p \frac{\partial^2 p}{\partial x^2} - \mu_p \frac{\partial (PE)}{\partial x} \tag{A.1a}$$

$$\frac{\partial n}{\partial t} = D_n \frac{\partial^2 n}{\partial x^2} + \mu_n \frac{\partial (nE)}{\partial x} \tag{A.1b}$$

assuming $\mu \neq \mu(x)$.

The Poisson relation is given by

$$\frac{\partial E}{\partial x} = \frac{F}{\varepsilon}(p - n) \tag{A.1c}$$

A relationship between the process of migration in the presence of external force, an electric field, say, and the perpetual haphazard motion of the species in solution is given by the Einstein relation:

$$D = \mu RT/N_o$$

$$= \mu eRT/F \qquad (A.1d)$$

or

$$= \mu kT$$

where

k - Boltzmann constant

N_o - Avogadro's number

e - the electrodic charge

ε - dielectric constant

We can solve the equations A.1(a) - A.1(d) using the method of perturbation by expanding p(x,t) and n(x,t) as power series in ε:

$$p = p_0 + \varepsilon p_1 + \varepsilon^2 p_2 + \varepsilon^3 p_3 + \ldots$$

and

$$n = n_0 + \varepsilon n_1 + \varepsilon^2 n_2 + \varepsilon^3 n_3 + \ldots$$

for some small $\varepsilon > 0$.

If we completely linearize the problem we can neglect all second order and higher terms and need only substitute

$$p = p_o + \delta p \, , \; \delta p = \varepsilon p_1$$

and

$$n = n_o + \delta n \ , \ \delta n = \varepsilon n_1$$

into the differential equations.

If $D_n = D_p = \sigma D$

$$\mu_n = \sigma \mu_p = \sigma \mu$$

$$n_o = p_o = c$$

then we have

$$\frac{\partial p_1}{\partial t} = D \frac{\partial^2 p_1}{\partial x^2} - Q(p_1 - n_1)$$

$$\frac{\partial n_1}{\partial t} = \sigma D \frac{\partial^2 n_1}{\partial x^2} - \sigma Q(n_1 - p_1)$$

where $Q = cF/\varepsilon$ and δn, δp are written as n_1 and p_1 for convenience and in agreement with the original notation used in Madden's theory.

Assuming a time dependence of the form exp $i\omega t$ then the above becomes

$$p_1'' - (\frac{K^2}{2} + \gamma) p_1 + \frac{K^2}{2} n_1 = 0 \tag{A.2a}$$

$$n_1'' - (\frac{K^2}{2} + \frac{\gamma}{\sigma}) n_1 + \frac{K^2}{2} p_1 = 0 \tag{A.2b}$$

using $\mu/D = F/eRT$,

$$K^2 \equiv \frac{2\phi F}{eRT} = \frac{2cF^2}{e\varepsilon RT}$$

and $\gamma \equiv j\omega/D$, $j = \sqrt{-1}$.

These equations are subject to the boundary conditions determined by the Fick-Faraday relation:

$$J_E + J_D = J_F$$

J_E - current density due to forced convection

J_D - current density due to Fickian diffusion

and J_F - faradaic current

Hence,

$$\mu p_o E - D \frac{dp_1}{dx} = \frac{\alpha_p i}{F} \tag{A.3a}$$

and $$\sigma \mu n_o E + \sigma D \frac{dn_1}{dx} = \frac{x_n i}{F} \tag{A.3b}$$

at the electrode surface, x = 0, that is.

α_p, α_n represent the fraction of the faradaic current carried by positive and negative ions respectively and,

$$\alpha_p + \alpha_n \leqslant 1,$$

(equality only if there is no non-faradaic current flowing through the fixed layer capacitance).

We can assume without loss of physical significance that the species have equal mobilities and coefficients of diffusion, hence the solution of the ordinary differential equations A.2(a) and A.2(b) can be put in the form

$$\begin{bmatrix} p_1 \\ n_1 \end{bmatrix} = \begin{bmatrix} A_1 & A_2 \\ -A_1 & A_2 \end{bmatrix} \begin{bmatrix} e^{-r_1 x} \\ e^{-r_2 x} \end{bmatrix} \tag{A.4}$$

This solution automatically removes any singularities at infinity provided r_1, r_2 are non-negative.

Since $n_o = p_o = c$, the Poisson's equation becomes

$$\frac{\partial E}{\partial x} = \frac{F}{\varepsilon}(p_1 - n_1)$$

whose solution is

$$E = E_o - \frac{2F}{\varepsilon r_1} A_1 e^{-r_1 x} \tag{A.5}$$

where,

$$r_1^2 = K^2(1 + \gamma/K^2)$$

and $r_2^2 = \gamma$ for $K^2 = \frac{2cF^2}{e\varepsilon RT} > \frac{\omega}{D}$,

which is valid for low frequencies.

The ionic species in solution can be classified as indifferent or active. They are indifferent if they do not undergo any charge transfer reaction or even if they do, they still remain at unity activity. In either case, such ions do not contribute to the (faradaic) electrode impedance. The active ions will at least take part in the electrochemical charge transfer process but their contribution to the electrode impedance would depend on how they diffuse or are transformed before or after the charge transfer step.

Let,

p_s, n_s be the concentration of the indifferent species

p_a, n_a be the concentration of the active species, then

$$p_s = p_{so} + \varepsilon p_{s1} + \text{HOT}$$

$$n_s = n_{so} + \varepsilon n_{s1} + \text{HOT}, \qquad (\text{HOT} \equiv \text{Higher order terms})$$

The equations of motion for these species are also described by Equations A.2a and A.2b and the additional boundary conditions to those specified in Equations A.3a and A.3b are

$$\mu p_{so} E - \frac{dp_{s1}}{dx} = 0$$

and $$\mu n_{so} E + \frac{dn_{s1}}{dx} = 0$$

in agreement with our definition of indifferent electrolytes. Again $p_{s1} \equiv \varepsilon p_{s1}$ for convenience.

The linearized equation for active species is obtained from Equations A.2a and A.2b as

$$j\omega p_{a1} = Dp''_{a1} - \mu p_{ao} \frac{2F}{\varepsilon} A_1 e^{-r_1 x} + \text{NT}$$

and $$j\omega n_{a1} = Dn''_{a1} - \mu n_{ao} \frac{2F}{\varepsilon} A_1 e^{-r_1 x} + \text{NT} \quad (\text{NT} \equiv \text{negligible terms})$$

The above equations suggest a solution of the form

$$p_{a1} = M \exp(-\delta_2 x) + N \exp(-\delta_1 x)$$

where $\delta_1 = r_1$. By direct substitution into the differential equation and collecting the coefficients of the exponential terms, we have

$$\delta_2^2 = j\omega/D = \gamma = r_2^2$$

and

$$N(j\omega - Dr_1^2) = -\mu p_{ao} \frac{2FA_1}{\varepsilon}$$

Hence

$$N = \frac{2\mu p_{ao} FA_1}{D\varepsilon(r_1^2-\gamma)} = \frac{2\mu p_{ao} FA_1}{D\varepsilon K^2} ,$$

using $r_1^2 = K^2 + \gamma$.

But $K^2 = \frac{2cF^2}{e\varepsilon RT}$, by definition, and $D = \mu kT$ (Einstein's relation).

Therefore,

$$N = \frac{\varepsilon eRT}{FcD} p_{ao} A_1 = \frac{p_{ao}}{c} A_1$$

where c is the undisturbed solution concentration. The solution for the active species is thus,

$$p_{a1} = \frac{p_{ao}}{c} A_1 \exp(-r_1 x) + M \exp(-r_2 x) \qquad (A.6)$$

If we suppose that only the p_a species are active, then the boundary conditions are modified by the fact that the changes in the n_a species do not contribute to any current flow.

We shall restate the formulation of the problem for the sake of clarity:

Active species: $p_a = p_{ao} + p_{a1}$

$$p_{a1} = \frac{p_{ao}}{c} A_1 \exp(-r_1 x) + M \exp(-r_2 x) \qquad \text{(A.7a)}$$

Indifferent species: $p_s = p_{so} + p_{s1}$

$$n_s = n_{so} + n_{s1}$$

$$n_a = n_{ao} + n_{a1}$$

The negative species can add: $n = n_o + n_1$

Using ~~(2.35)~~ equation (A.4)

$$n_1 = -A_1 \exp(-r_1 x) + A_2 \exp(-r_2 x) \qquad \text{(A.7b)}$$

Also $p_1 = A_1 \exp(-r_1 x) + A_2 \exp(-r_2 x)$

where $p \equiv p_s + p_a$

$$= p_o + p_1, \quad [p_o = p_{so} + p_{ao}; \; p_1 = p_{s1} + p_{a1}]$$

Since $p_{s1} = p_1 - p_{a1}$,

$$p_{s1} = A_1 \left(1 - \frac{p_{ao}}{c}\right) \exp(-r_1 x) + (A_2 - M) \exp(-r_2 x) \qquad \text{(A.7c)}$$

Electric field:

$$E = -\frac{2F}{\varepsilon r_1} A_1 \exp(-r_1 x) + E_o \qquad \text{(A.7d)}$$

where E_o is the field in the solution far from the electrode.

Boundary conditions:

Active species: (p_a), $\mu p_{ao}E - D\frac{dp_{al}}{dx} = \frac{\alpha i}{F}$ (A.8a)

Indifferent species: $(n_l = n_{sl} + n_{al})$, $\mu cE - D\frac{dn_l}{dx} = 0$ (A.8b)

$(p_{sl} = p_l - p_{al})$, $\mu(c - p_{ao})E - D\frac{dp_{sl}}{dx} = 0$ (A.8c)

Even though the charge transfer is carried by only one species, $\alpha \neq 1$, since the non-faradaic component is not zero.

Far away from the electrode the electric field controls the drift and the resulting conduction flux, J, is given by

$$J = cv_d$$

where

c - concentration in moles per liter, say
v_d - drift velocity.

Since zeN_o is the molar charge, the net current density i is given by

$$i = JzeN_o$$

$$= cv_d eN_o. \qquad (z = \text{charge valence})$$

But the drift velocity is determined by the electric field,

$$v_d = \mu E,$$

hence, from the last two equations,

$$E = \frac{i}{zFc\mu}$$

We can use the above equation to evaluate the value of E_o in Equation A.8d as

$$E_o = \frac{i}{zFc_a\mu} \tag{A.9}$$

where c_a is the total concentration. (Here, $c_a = 2c$.)

When Equations A.8(a) - A.8(c) are used together with A.7d and A.9, the boundary conditions, Equations A.8(a) - A.8(c) become

$$\begin{bmatrix} \frac{p_{ao}}{c} H & 0 & r_2 \\ \frac{\Delta c}{c} H & r_2 & -r_2 \\ H & -r_2 & r_2 \end{bmatrix} \begin{bmatrix} A_1 \\ A_2 \\ M \end{bmatrix} = T \begin{bmatrix} -\frac{1}{z}(z\alpha - \frac{p_{ao}}{2c}) \\ \frac{\Delta c}{2c} \\ \frac{1}{2z} \end{bmatrix} \tag{A.10}$$

where $\Delta c \equiv c - p_{ao}$,

$$H \equiv r_1\left(1 - \frac{2\mu cF}{D\varepsilon r_1^2}\right)$$

and $T \equiv -\frac{i}{DF}$

But $K^2 = \frac{2cF^2}{e\varepsilon RT}$,

$$\frac{\mu}{D} = \frac{F}{eRT},$$

and $r_1^2 = K^2 + \gamma = K^2(1 + \frac{\gamma}{K^2})$

If $\delta \equiv \frac{\gamma}{K^2}$, then

$$H = r_1 \frac{\delta}{(1 + \delta)} \equiv r_1\delta^*, \quad \delta^* \sim \delta$$

We can solve (A.10) to give

$$\begin{bmatrix} A_1 \\ \\ A_2 \\ \\ M \end{bmatrix} = T \begin{bmatrix} \frac{\alpha - 1}{2r_1\delta^*} \\ \\ \frac{\alpha}{2r_2} \\ \\ \frac{\alpha}{r_2}(1 - \frac{p_{ao}}{2c}) \end{bmatrix} \text{, for univalent species, } z = 1 \qquad \text{(A.11)}$$

Equation (A.11) enables us to compare the effect of the diffuse and diffusion layers since these layers are characterized by the amplitudes A_1 and A_2 respectively. The diffusion layer for the active species is characterized by the amplitude M.

For $\alpha = 0$, that is, no faradaic current, the electrode is said to be ideal polarized, and there is no diffusion zone (see Madden, 1961, p. 20). We would also expect a very weak diffuse zone if all the currents are faradaic in nature.

From Equation (A.11)

$$\frac{A_1}{M} = \frac{\alpha^*}{2\sqrt{\alpha}} (1 + \frac{p_{ao}}{2c})$$

if $\delta = \frac{\gamma}{K^2} \sim \frac{\gamma}{r_1^2}$, $\delta^* \sim \delta$, $\alpha^* = \frac{\alpha - 1}{\alpha}$ and $\frac{p_{ao}}{c} << 1$.

Hence, even for large faradaic current, the diffuse zone due to the active species dominates the diffusion zone, at low frequencies.

If the diffuse layer thickness is less than some L_o, then the voltage drop across the electrode-electrolyte system is

$$V = \int_o^{L_o} E\,dx$$

$$= \frac{2F}{\varepsilon r_1^2} A_1 e^{-r_1 L_o} - \frac{2F}{\varepsilon r_1^2} A_1 + E_o L_o$$

Since $L_o >> 1/r_1$ by requirement,

$$V = - \frac{i(\alpha-1)}{\varepsilon r_1^3 D \delta^*} + V_o$$

But $\delta^* \sim \delta = j\omega/Dr_1^2$,

therefore

$$V = - \frac{i(\alpha-1)}{\varepsilon r_1 j} + V_o$$

$$= - \frac{i(\alpha-1)}{j\omega c_D} + V_o$$

where $c_D = \varepsilon r_1$ represents the capacitance of the diffuse layer for the active species. The effect of the fixed layer capacitance is to act in series with the diffuse layer, hence the above equation is modified as

$$V = \frac{(1-\alpha)i}{j\omega c_F} - \frac{i(\alpha-1)}{j\omega c_D} + V_o$$

The electrode-solution impedance, ignoring any reaction process, is

$$Z = \frac{1-\alpha}{j\omega c_F} - \frac{\alpha-1}{j\omega c_D} + R_o$$

$$= Z_F + Z_D + R_o$$

where

$Z_F = \frac{1-\alpha}{j\omega c_F}$ is the fixed layer impedance

$Z_D = \frac{1-\alpha}{j\omega c_D}$ is the diffuse layer impedance

and R_o = solution resistance.

We can rearrange the equation to obtain the total impedance,

$$Z = Z_F(1 + \frac{Z_D}{Z_F}) + R_o$$

(In practice $Z_F >> Z_D$ and the diffuse layer impedance can be neglected.) This equation does not give the full picture of the electrodic process involving ion exchange and diffusion at the interface. These latter processes lead to a reaction impedance which acts in parallel with the two layers' capacitance. The combination then acts in series with the solution resistance. In order to obtain the equivalent circuit for the electrodic system, the reaction impedance must be evaluated for some particular reaction associated with the current flow.

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Biographical Note

The author was born in September 1948 in the Western State of Nigeria. He was admitted to the Department of Physics, University of Ibadan, Nigeria in 1966 and has since been there. He was awarded the degrees of B.Sc. (1970) and Ph.D. (1974) by the same department and became a member of the faculty in March 1974. He has been teaching Physics and is actively interested in Geophysics research.

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