Electrochemical issues in impedance tomography

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Abstract

Linear ramp cyclic voltammetry and ac impedance spectroscopy have been used to investigate the electroactivity of Zeneca products and filtration solvents using platinum microelectrodes. Linear ramp cyclic voltammetry has been used to establish appropriate excitation potentials which will minimise electrochemical reactions associated with the product or the solvent during impedance process tomography measurements. Impedance spectroscopy has been used to resolve the electrochemical impedance and the geometric impedance of a small scale test rig. This technique offers a method of establishing the appropriate frequency range of the excitation potential for use in impedance tomography measurements. ©2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Historically the focus of impedance process tomography has been towards industrial applications involving relatively passive materials that exhibit distinctive impedance signatures. However, as this technology progresses into the chemical production arena the issues associated with electrochemical reaction mechanisms present in a chemically active environment must also be considered. Failure to address these issues may lead to sub-optimal imaging, incorrect signal interpretation, accelerated sensing electrode corrosion, and possible corruption of the chemical matrix. The implications of the latter for the pharmaceutical and bio-processing industries are manifold.

This paper is concerned with the characterisation of the electrochemical processes which may occur at the electrode/solution interface when impedance measurements are made in an electrochemically active environment. The methods described in this paper to investigate the electrochemical processes are well established in the electroanalytical field and include voltammetry and ac impedance spectroscopy. The electrochemical processes occurring at the electrode have been modelled and can be used to predict the influence of electrode reactions on the tomographic signal and to allow the optimisation of the impedance measurement sys-

tem. They can also be used to establish the conditions likely to result in product or solvent breakdown or contamination during impedance tomography measurements.

2. Voltammetric techniques

2.1. Voltammetric measurement system

Conventional voltammetric measurement systems use a three-terminal measurement system consisting of a working electrode, counter electrode and reference electrode. A potentiostat is used to drive the current between the working electrode and the counter electrode while ensuring no current passes through the third reference electrode. However, it should be noted that in this investigation a 25 μm diameter inlaid disc microelectrode sensor was used as the working electrode. Due to the very small currents associated with the microelectrode a two-electrode configuration consisting of a working electrode and reference electrode was used. This greatly simplifies the measurement system and the elimination of the potentiostat improves the signal to noise ratio. This approach, which although not yet routinely used by electrochemists, is well documented in the literature.

In analytical applications voltammetric techniques are normally used to measure the concentration of substances in solution and are often the first measurement strategy adopted since they can provide a rapid insight into chemical reactions occurring at an electrode surface. The simplest

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chemical processes at an electrode surface generally involve a loss of electrons from the species to the electrode during an oxidation process or a gain of electrons from the electrode to the species during a reduction process. However, in practice the reactions at the electrode surface are often complex and may include additional processes such as competitive reactions, adsorption of reactants, electrodeposition and electrode corrosion.

Central to all voltammetric techniques is the application of a suitable potential to the working electrode, which increases the rate of the electrochemical reaction, and the subsequent measurement of the Faradaic current associated with the reaction process. A particular variant of voltammetry, linear ramp cyclic voltammetry, requires the application of a linear ramp triangular voltage waveform and the measurement of the subsequent current flow. A graph of the Faradaic current versus the applied potential is generally referred to as a voltammogram.

The magnitude of the current flow will depend on the rate of the slowest step which may be either the mass transport of the analyte to the electrode or the electron transfer process at the electrode surface. If the rate of the reaction can be made sufficiently fast so that the surface concentration approaches zero, then the reaction will become controlled by the rate of mass transport of the analyte to the electrode surface.

The three modes of mass transport to the electrode surface are convection, migration and diffusion. Migration arises from the movement of charges species by the action of an electrostatic force on charged particles in solution when subjected to a potential gradient. It is the mechanism by which charge passes through the solution between two electrodes and without which there would be no electron flow in the external circuit. Convection arises from the action of mechanical forces acting on the solution. This can take the form of natural convection due to thermal gradients or forced convection due to stirring or pumping of the solution. Diffusion arises from the presence of a concentration gradient which results in a flux of material diffusing to and from the electrode surface. In analytical applications migration and convection can generally be controlled to ensure the current flow is limited by diffusion of the species to the electrode surface. At a microelectrode sensor in the presence of excess supporting electrolyte the dominant mode of mass transfer is diffusion. However, in process tomography applications all three modes of mass transport could well be significant.

The current associated with a diffusion limited electrode reaction can generally be related through Fick's laws to the concentration gradient at the electrode surface. At large electrodes with dimensions greater than a few millimetres a non-steady state diffusion limited current will flow. However, at electrodes of micrometre dimensions, commonly referred to as microelectrodes, a steady state diffusion limited current is rapidly established which greatly simplifies the interpretation of the cyclic voltammograms. In this application, cyclic voltammetry has been used to investigate whether pressure filtration products are electroactive and
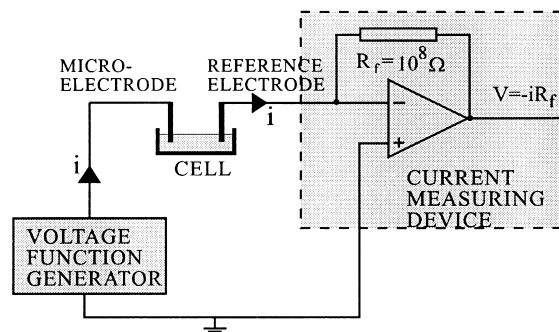

Fig. 1. Cyclic voltammetric measurement system.

also to establish the potentials at which these materials are oxidised or reduced at the electrode surface. Prior knowledge of the oxidation potential of the analyte can be used to select a suitable excitation potential or potential window for the tomographic measurement system which will minimise the influence of electrochemical reactions at the electrode surface.

A block diagram of the cyclic voltammetric measurement system used in this investigation is shown in Fig. 1.

A typical cyclic voltammetric response for a 0.5M potassium chloride solution is shown in Fig. 2.

Region A shows a rapid increase in the current flow due to the evolution of hydrogen. Region B shows a rapid increase in current due to the evolution of oxygen. There is little electroactivity within Region C and this would be the preferred potential window for the excitation potential in an impedance measurement system since the electrolyte is relatively inactive within this region. The hysteresis is due to the charging of the double layer capacitance associated with the electrode/solution interface.

2.2. Double layer capacitance

One of the simplest models, known as the Helmholtz model, that can be used to explain the existence of the double layer capacitance assumes that for a given applied
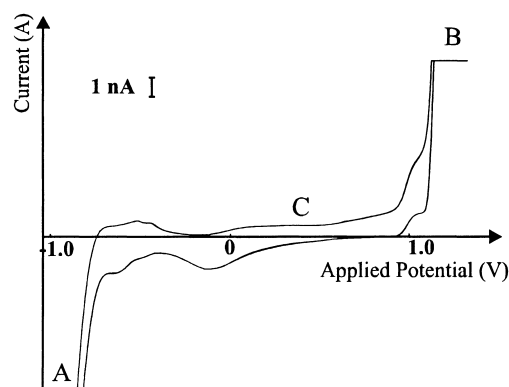

Fig. 2. Cyclic voltammogram: Solution 1 M potassium chloride, Scan range -1 V to $+1$ V, scan rate $20\,\mathrm{mVs^{-1}}$, 25 μm diameter working electrode, Ag/AgCl reference electrode.
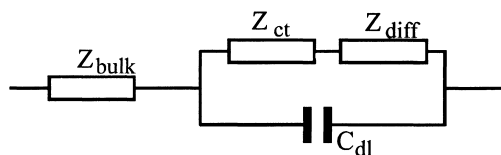
Fig. 3. Equivalent circuit model of electrochemical process at an electrode.

Fig. 4. Block diagram of ac impedance measurement system.

potential to an electrode in solution there will be a segregation of charges arising from the charge on the metal electrode and a charge in the solution due to an excess of ions or cations in the proximity of the electrode [1]. This arrangement of charge is known as the electrical double layer and can be represented as a capacitance which is dependent on the area of the electrode and the potential applied to the electrode. Typical values for the double layer capacitance are in the region of 10 to 100 $\mu F\,cm^{-2}$ and are generally significantly larger than the geometric capacitance measured in an impedance tomography measurement.

2.3. Equivalent circuit model

One of the simplest equivalent circuit models for an electrochemical reaction at an electrode/solution interface which is based on the Randel's equivalent circuit model is shown in Fig. 3.

The electrochemical process is represented by the double layer capacitance C_{dl} in parallel with a charge transfer impedance Z_{ct} or a diffusion impedance Z_{diff}. Under diffusion limited conditions the diffusion impedance will be much larger than the charge transfer impedance. The series impedance Z_{bulk} represents the bulk impedance between the two electrodes and is generally the impedance of interest in tomographic applications. It should be noted that electrode reactions can occur at both sensing electrodes and hence both electrodes will have an electrode/solution interface model. An investigation of the electrode/solution interface has been carried out using impedance spectroscopy.

3. Impedance spectroscopy

3.1. Impedance measurement system

Impedance spectroscopy has been widely recognised as a powerful diagnostic tool for the investigation of the electrical behaviour of an electrochemical system in which various processes proceed at different rates. Equivalent circuit models for electrochemical reactions have been developed and published in the literature and this technique can be used to establish representative values for the magnitudes of the equivalent circuit model components [2,3]. Ac impedance measurements were made using a Solartron 1522 HF frequency response analyser. A block diagram of the impedance measurement system is shown in Fig. 4 and full details of the amplifier design can be found in the literature [3].
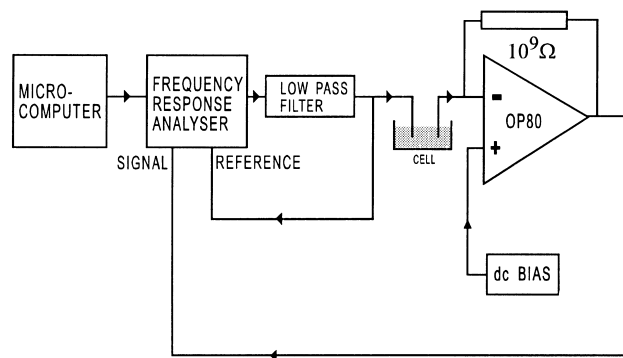
The cell consisted of two parallel $2\,cm^2$ platinum electrodes separated by a distance of 1 cm. Two identical electrodes were used to ensure the similar double layer capacitance characteristics. The cell impedance was measured in the frequency domain by applying a sinusoidal voltage and then measuring the amplitude and phase of the resulting current. The electrode was held at a fixed dc potential at which the electrode process of interest would occur and a small sinusoidal voltage was superimposed on the dc potential. The amplitude of the sinusoidal voltage has to be small to ensure a linear response since the response of an electrochemical cell is essentially non-linear. By repeating the measurement at discrete frequencies the various time dependent components of the model can be resolved. It should be noted that electrochemical processes cannot be represented by ideal resistors, capacitors and inductors. Distributed impedance elements such as a constant phase element or Warburg have been shown to be appropriate elements for use in electrochemical investigations [2]. It is also customary in electrochemical investigations to plot the impedance in the negative imaginary plane versus the real plane, with the negative imaginary components above the axis, since the impedance spectrum normally involves capacitive components rather than inductive component.
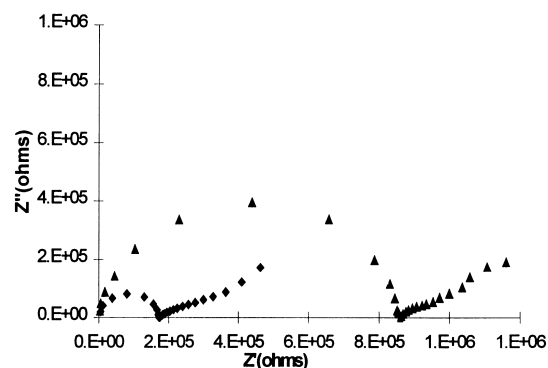

Fig. 5. Nyquist plot of ac impedance response. dc bias 0.15 V, ac amplitude 0.3 V_{p-p}, minimum frequency 10 mHz, maximum frequency 1 MHz, ▲ 20 g Zeneca product A, ◆ 20 g Zeneca product A plus 2 g Mother liquor B.

4. Results

A typical Nyquist plot for Zeneca product A is shown in Fig. 5. The high frequency semicircle is associated with the bulk resistance and geometric capacitance of the sample. The low frequency response is associated with the electrochemical process occurring at the electrode and represents planar diffusion of the electroactive species towards the electrode surface [4]. This is often represented by a Warburg diffusion impedance in the equivalent circuit model [2]. Impedance measurements at low frequencies are therefore dominated by the influence of the chemical reaction while measurements at higher frequencies are dominated by the bulk impedance. Non-linear least squares curve fitting has confirmed a geometric capacitance of 4 pF while the capacitance associated with the low frequency response was found to be 8 μF. This is significantly larger than the geometric capacitance and is in keeping with the typical magnitude of the double layer capacitance of the electrode.

5. Conclusions

Linear ramp cyclic voltammetry can provide a useful insight to the electrochemical processes occurring at the sensing electrodes and can be used to establish appropriate excitation potentials for impedance tomography applica-tions. This information is of considerable importance in or-der to minimise product contamination or breakdown. Pre-liminary investigations using a small scale test rig have shown that ac impedance spectroscopy can be used to re-solve the impedances associated with the electrochemical processes and the bulk impedance associated with the geo-metric capacitance and bulk resistance of the material. This can be used to establish an appropriate frequency range for the tomography measurement system and also offers the possibility of resolving both tomographic information and chemical information simultaneously. Further work on a full scale test rig is required to establish representative values for the equivalent circuit model and also to investigate the influence of convection and migration on the tomographic signal.

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