

*The application of the methods of electrode kinetics, especially the impedance, to the study of gas evolving reactions at electrodes**

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Received 4 October 1984

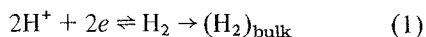
The methods of electrode kinetics, particularly steady state current–potential and impedance–potential measurements, have been successfully applied to the investigation of gas forming reactions, such as chlorine, oxygen and hydrogen evolution. Developments in computer-controlled instrumentation have made these the preferred methods (together with potential pulse methods). The paper discusses the results and suggests how these can be interpreted in terms of the electron transfer reaction and the bubble layer.

Nomenclature

C_A^b	bulk concentration of A	i	current density
C_A^s	surface concentration of A	j	square root of -1
C_{dl}	differential capacity	a	anodic Tafel slope
D_A	diffusion coefficient of A	b	cathodic Tafel slope
E	potential w.r.t SCE electrode	R_ω	ohmic loss resistance
E_0	standard potential w.r.t SCE (1 mol cm ⁻³ concentrations)	R_{ct}	charge transfer resistance
k_A	rate constant w.r.t applied E	$Z(\omega)$	impedance
F	Faraday number	ω	frequency of ac potential
		δ	diffusion layer thickness
		σ	Warburg impedance parameter

1. Introduction

Reactions such as hydrogen, chlorine and oxygen evolution, in which bubbles are formed, are complex. The electron transfer part of the overall reaction



for hydrogen evolution, say, involves more than one electron and this immediately opens up the possibility of reaction intermediates. The stability of intermediates in the hydrogen evolution reaction, for example, is usually

considered by means of the volcano diagram in which the rate of the reaction, measured in some way, is plotted against some characteristic of the metal of the electrode. A reworking of these arguments has been presented [1]. However there is little direct experimental evidence for the participation of intermediates in any of the gas-evolving reactions during gas-evolution. Except, that is, for the well known under-potential deposition of hydrogen atoms in the case of platinum. Because of the unknown effect of the bubble layer the kinetic data used in these correlations is to be viewed with caution. Bubble formation also introduces fluctuations into the

*Paper presented at the International Meeting on Electrolytic Bubbles organized by the Electrochemical Technology Group of the Society of Chemical Industry, and held at Imperial College, London, 13–14 September 1984.

measurements due to bubble initiation, coalescence and departure from the electrode. It probably does this by causing a fluctuation in the free area of the electrode surface which is available to the electron transfer reaction.

The purpose of this paper is to present results obtained by methods of electrode kinetics and attempt to identify those parts of the electrical response which are due predominantly to the electron exchange and those which are due to bubble formation. It will be assumed throughout that at each potential, in the steady state, an average bubble population exists. This means that at each potential a certain fraction of the surface is covered with bubbles.

The methods of electrode kinetics have not been extensively applied to gas-forming reactions. The reason is that the presence of gas bubbles complicates the experimental results and researchers are not agreed on what would be the most appropriate electrochemical methods to apply. In fact the choice of methods is quite critical, and the use of inappropriate or too limited a range of electrochemical methods, usually leads to difficulty in interpreting the results.

The use of computers to control the instrumentation and assess the results has substantially improved the study of electrode kinetics [2]. A great deal of experience has now been accumulated in this group on the application of computer methods to industrial and basic problems in electrochemistry. It is now possible to carry out much longer and more comprehensive experimental investigations and to use the methods of electrode kinetics in a flexible way. Steady state current – potential, impedance – potential, and current – time responses to a potential pulse, have been used in the present work. The reason for the emphasis on the steady state and the impedance is that the theory to process the results is much simpler than for other electrochemical methods. Another important consideration is that technical processes are invariably operated in the stationary state and it is to that that the kinetic measurements should be directed.

As is usual in investigations of electrode kinetics it is necessary to be able to control the other factors which might contribute to the reaction kinetics, in addition to the electrical factors which are controlled, essentially, by the

potential. For the particular case of a gas forming reaction the quantities which could usefully be varied include:

- (a) the concentration of the reactant
- (b) the ions of the electrolyte solution
- (c) the physical structure of the electrode surface
- (d) the bubble population on the electrode.

The last can be achieved in a qualitative manner by using a rotating disc electrode [11]. At least the stream lines created by the hydrodynamic conditions give a mechanism for controlling the bubbles. It is also possible that the rotating cone electrode [4] may be useful in controlling bubble populations. Potential pulse current–time transients, steady state current–potential and impedance–potential measurements at the rotating disc are the most powerful electrochemical techniques which can be applied.

As well as having an experimental capability it is essential to be able to handle a large amount of data and to calculate possible reaction schemes [2]. A number of strategies can be used to interpret the data.

One is to plot the steady state $\log i-E$ curve after correction for the ohmic resistance from the impedance–potential measurements. For gas-forming reactions it is essential to measure the ohmic resistance at each potential as it often depends on potential.

Another is to present the parameter curves $R_{ct}-E$, $C_{dl}-E$, $R_{\omega}-E$, $\sigma-E$ obtained from interpreting the measured impedance–potential measurements by a suitable equivalent circuit.

A third is to interpret the $\log i-E$ and the impedance–potential data by means of a particular reaction mechanisms and test how well the data fit over a wide potential range. The reaction mechanism which has been chosen here is that for a redox reaction and the parameter curves could be $kSH-E$, $C_{dl}-E$, $R_{\omega}-E$.

Of all the parameters which describe the electrical behaviour the double layer capacity–potential curve is worth special mention as it is a sensitive measure of what is happening at and near to the electrode surface. It might be expected that this measured quantity would be sensitive, in systems which produce bubbles, to the bubble layer, i.e. to the area covered by bubbles, and to

the ionic environment. It would be desirable to have a theory for the ionic double layer structure so that purely ionic effects could be accounted for in the data.

2. Experimental aspects

Throughout this work a conventional three-electrode cell has been used. It was operated at ambient temperature and contained a working electrode, a counter electrode separated from the working electrode by a glass frit and a commercial saturated calomel reference electrode (to which all the potentials are referred). The working electrode was either a vertical sheet embedded in plastic (nickel and platinum), a sheet held horizontally in a suitable PTFE holder (ruthenium dioxide) or was a rotating disc (nickel, ruthenium dioxide). In this work the surfaces of the metal electrodes were prepared by polishing with 6/0 carborundum paper or γ -alumina or in some cases by electro-polishing. The ruthenium dioxide electrodes were used as prepared. The double layer capacity-potential curves, available after data processing, for the individual electrodes and their surface treatment was used as an indication of the surface roughness. The HCl solution was Aristar, and the solutions were made up with triply distilled water. The experiments were carried out by a mini computer system, the latest version of which is described in a recent publication [2].

The equipment will implement automatically virtually all the methods of electrode kinetics. In this instance steady state i - E and $Z(\omega)$ - E curves have been measured, with some potentiostatic i - t transients and linear potential sweep curves. The measurement of impedance is particularly useful as it allows the steady state to be split into its components. The operation of the equipment is completely automatic and all the information is permanently stored.

The steady state i - E data were plotted as $\log i$ - E curves (after correction for the measured ohmic loss). The curves could also be analysed in terms of a particular reaction mechanism and the data then interpreted in terms of the parameters which describe that reaction scheme.

A quantitative analysis of the $Z(\omega)$ - E data was carried out by calculating the values of the usual R_{ct} - E , C_{dl} - E , R_{ω} - E , σ - E sets of parameters using

the equation

$$\frac{1}{Z(\omega) - R_{\omega}} = \frac{1}{R_{ct} + (1 - j)\sigma\omega^{-1/2} \tanh [(j\omega/D)^{1/2} \delta]} + j\omega C_{dl} \quad (3)$$

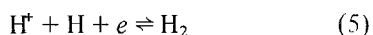
and the usual fitting procedure. If diffusion of reactant or product in the gas evolution reaction plays a role in the impedance then the Warburg coefficient, σ , will be a dominant parameter in determining the impedance data. A second approach is to directly interpret the impedance data over a large potential range in terms of a reaction mechanism and then display the appropriate parameters. This is equivalent to Equation 3; however, reaction parameters, chosen from the list of parameters which control the reaction rate, are used in the fitting procedure. A calculation of the impedance for parallel redox reactions, one of which could be hydrogen evolution, has been carried out [5]. This theory would allow the interpretation of the data in terms of a standard rate constant (as a function of potential to highlight the bubble layer inhibition effects), as has been carried out for the chlorine evolution reaction [6]. An advantage of this method of data assessment is that effects for different metal electrodes can be quantitatively compared.

One further experimental point needs to be emphasized. Because of the inherent fluctuations in the data due to bubble formation and detachment the current and the impedance measurement needed to be averaged over sufficient times. The quoted results then refer to an average state of the bubble layer.

3. Theory for the interfacial rate

Diffusion is responsible for the difference between the interfacial concentrations, $C_{H^+}^s$, and the bulk concentrations, $C_{H^+}^b$. The surface concentrations can be calculated in the usual way and so can be used here directly. The problem is to interpret any i - E or $Z(\omega)$ - E (after removal of the double layer capacity and ohmic loss contributions) data in terms of a reaction mechanism. Consider for simplicity the steady state i - E data only. Assume

that only the electron transfer reaction controls the behaviour. The common gas evolving reactions involve more than one electron and, in principle, intermediates, so the question is how these affect the measured i - E characteristic? Consider the reaction scheme which is usually assumed for the hydrogen evolution reaction (other schemes could be considered in a similar way)



In principle the kinetic rate of the reaction can be written as

$$i_1 = F(k\text{SH})_1 [C_{\text{H}}^{\text{s}} \exp \alpha_1(E - (E_0)_1) - C_{\text{H}^+}^{\text{s}} \exp -\beta_1(E - (E_0)_1)] \quad (6)$$

$$i_2 = F(k\text{SH})_2 [C_{\text{H}_2}^{\text{s}} \exp \alpha_2(E - (E_0)_2) - C_{\text{H}^+}^{\text{s}} C_{\text{H}}^{\text{s}} \exp -\beta_2(E - (E_0)_2)] \quad (7)$$

where a single rate, $k\text{SH}$, and a standard potential, E_0 , is written for each step. Also

$$i = i_1 + i_2 \quad (8)$$

$$\alpha_1 = 2.303/a, \beta_1 = 2.303/b \text{ etc.} \quad (9)$$

The particular properties of Equations 6 and 7 were thoroughly investigated in the 1960s and are clearly reviewed by Vetter [7]. In the steady of H atoms

$$i/2 = i_1 = i_2 \quad (10)$$

and it is easily possible to eliminate C_{H}^{s} from the two equations and produce a complicated equation for the i - E relation. In addition the two equations are consistent with the equilibrium Nernst equation for the overall reaction. The individual standard potentials are unknown, however, they must be related to the observed overall standard potential by

$$2E_0 = (E_0)_1 + (E_0)_2 \quad (11)$$

Making the assumption that coverage with the intermediate is low, then two courses of action seem to be open. The first is to grapple with Equations 6 and 7 and possibly introduce a largely empirical equation for the dependence of intermediate coverage with potential. This brings new parameters into the argument. The second alternative is to write the kinetics in terms of 'observables' only

$$i = 2F[k_{\text{H}_2} C_{\text{H}_2}^{\text{s}} \exp \alpha E - k_{\text{H}^+} (C_{\text{H}^+}^{\text{s}})^2 \exp -\beta E] \quad (12)$$

or

$$i = 2Fk\text{SH}[C_{\text{H}_2}^{\text{s}} \exp \alpha(E - E_0) - (C_{\text{H}^+}^{\text{s}})^2 \exp -\beta(E - E_0)] \quad (13)$$

with

$$k\text{SH} = k_{\text{H}_2} [(C_{\text{H}^+}^{\text{b}})^2 / C_{\text{H}_2}^{\text{b}}]^{-\alpha RT/2F} \exp \alpha E_1 \quad (14)$$

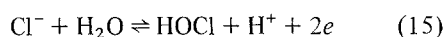
It has never been possible to test any of the kinetic models for the electron exchange reaction with any precision because of the interference by bubbles. As a result of the investigations discussed in this paper it would now be possible, in principle, to carry out an exhaustive investigation.

4. Results

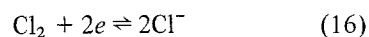
4.1. Chlorine evolution on platinum

This reaction has not been studied in great detail. Only enough data have been assembled to compare with the experiments on the same reaction on ruthenium dioxide electrodes.

1. The i - E results for the oxidation of chloride ions on porous platinum indicate 'reversible' behaviour for the particular experimental configuration. The log i - E plots (corrected for the measured ohmic effects) have a 30 mV Tafel slope and the expected rotation dependence at a rotating disc electrode. A comparison of the experimental i - E curves with the theoretical curves (see the theory section) indicates that the electrode process has standard potential (1 mol cm⁻³ standard concentration) of some 1130 mV SCE. This compares with $E_0 = 1241$ mV SCE estimated for



and $E_0 = 960$ mV SCE estimated for



(see below for chlorine reduction experiments on RuO₂/TiO₂ electrodes).

2. The shape of the $Z(\omega)$ - E plots indicates a reversible electrode reaction. An analysis of the $Z(\omega)$ - E curve indicates $D = 7.4 \times 10^{-6}$ cm² s⁻¹. It

has not proved possible to extract the double layer capacity from the data. It is likely that the species diffusing from the interface is molecular chlorine, as chloride ions are in large excess.

3. The i - E and $Z(\omega)$ - E results for smooth Pt show, using similar methods to those given in the previous paragraph, that the rate of the chlorine formation reaction is slower than on porous platinum and is controlled by the interfacial electron exchange reaction. The double layer capacity value is some $\mu\text{F cm}^{-2}$. Although the results were obtained where the influence of PtO was minimized a small amount may be present. When large amounts of PtO are present the reaction is inhibited.

4.2. Chlorine evolution on ruthenium dioxide

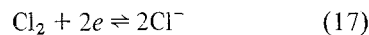
The main features of the data, which have been obtained previously are as follows. The detailed results are presented in the literature [6, 8 and 9 and references therein] and it is intended here to present a summary of the present view

1. The log i - E curve (corrected for ohmic resistance) has two sections. One at low potential with a 40 mV slope and one at higher current densities with a larger slope. The 40 mV slope region seems to be dominated by the electron exchange reaction and the effect of the bubbles is small. The larger slope depends on rotation speed of the electrode and the physical preparation of the electrode and is essentially caused by the bubble layer. The crossover between the two potential regions is approximately as expected from the solubility of chlorine in the electrolyte. An unexpected result is that the i - E curves are first order in the chloride ion concentration under conditions where the effects of bubbles are minimized. This is achieved at high rotation speed of the electrode and when ohmic corrections have been made. Similar remarks apply to the $1/R_{ct}$ curve. This result has been obtained on two separate occasions.

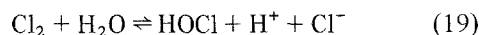
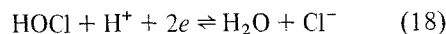
2. The $Z(\omega)$ - E data for the oxidation of chloride ion on $\text{RuO}_2/\text{TiO}_2$ electrodes [6, 8 and 9 and references therein] indicates a slow reaction. In this case the double layer capacity values are some mF cm^{-2} . The C_{dl} value varies greatly with the chemical nature of the electrode and with its

history, and can be used to characterize a particular electrocatalyst.

3. One or two waves are obtained for the chlorine reduction reaction, depending on the pH, suggesting that in the overall reaction scheme



there are two reducible species, HOCl and Cl_2 , as in the reaction kinetic scheme



which are not in rapid equilibrium. Some confirmation of this result has appeared in the literature.

4. The i - E and $Z(\omega)$ - E data can be considered as a whole [6] and the parameter curves C_{dl} - E , k_{SH} - E and R_{ω} - E are extracted. In reference [6] the values of the Tafel slopes consistent with the data were inadvertently switched and are correctly $a = 40$ mV and $b = 120$ mV. The method of outputting parameter curves as the primary data to be considered is essentially equivalent to putting electrode kinetics onto the same basis as spectroscopy.

4.3. Oxygen evolution on ruthenium dioxide

The steady state i - E and $Z(\omega)$ - E data and the derived parameter curves for the evolution of oxygen on various electrocatalytic electrodes in NaClO_4 solution have been given previously [3, 15]. The Tafel slope of the corrected log i - E curve is some 120 mV and a change in slope associated with an increase in size of the bubble layer, as in the case of the chlorine and hydrogen evolution reactions, is not observed. Either the bubble layer is complete at low potentials and is always present, or the oxygen bubbles rapidly leave the electrode and do not affect the electron exchange reaction. The double layer capacity-potential and the ohmic resistance-potential curves suggest that the latter explanation is most likely.

4.4. Hydrogen evolution on platinum

Steady i - E and $Z(\omega)$ - E data have been obtained at a vertical stationary electrode [10]. The bubble layer has a strong effect on the results. On an initially bubble free surface the hydrogen evolution reaction is reversible. The form of the

impedance measurements and the value of the charge transfer resistance show that the bubble layer has the effect of slowing down the electron exchange reaction and eventually inhibiting it. It seems also that as the double layer capacity is reduced, the free area of the electrode decreases. The system has similarities to the active-passive situation found in metal dissolution reactions.

4.5. *Hydrogen evolution on nickel*

A similar experimental philosophy to that used in the case of chlorine evolution has been applied to the evolution of hydrogen from acid solutions at stationary and rotating disc electrodes [11]. Current-time curves at constant potential show oscillations due to bubble growth and departure and the slow approach to a steady state current. So it is necessary experimentally to average the currents and the impedance measurements until a steady state is reached. This system has been used as a model reaction to see if it is possible to assess the extent of the bubble layer quantitatively, as considered in the next section.

5. Use of parameters from impedance to characterize the bubble layer

All the parameter curves $k_{SH}-E$, $C_{dl}-E$ derived from the experimental $i-E$ and $Z(\omega)-E$ data reflect the bubble layer. However, the set which is most closely connected with the surface of the metal is the double layer capacity-potential curve. Unfortunately in spite of much effort by electrochemists to interpret these curves a basic understanding of the factors which contribute to their shape is still not available. The most popular theory involves splitting the double layer capacity into inner and outer layer contributions and invoking a combination of the properties of interfacial water and anion specific adsorption to account for the inner layer values. However, this view has been criticized in a number of papers, of which the most recent are [12, 13]. However, even with this handicap it is possible to investigate gas forming reactions in different ionic environments. In the case of chlorine evolution this would involve changing the cation and investigating, say, NaCl and HCl solutions. In both cases the faradaic reaction would be proceeding. A better example

would be the hydrogen evolution reaction where the electrode could be investigated in NaCl solution, without the hydrogen reaction, and in HCl solution. It would be expected [12, 13] that under these conditions the ionic influence of the solution would not be too different, and therefore the results should only reflect the properties of the bubble layer and any effect of the reaction intermediates (pseudocapacitance). Examples of double layer capacitance curves for NaCl and HCl are given in reference [11]. These depend on rotation speed at a nickel rotating disc electrode so are clearly dependent on the bubble layer. In addition the curves depend on the anion. This is evidence that the curves only depend on the extent of the bubble layer and the ionic environment and do not contain pseudocapacitance information. This conflicts with work reported in the literature [14] in which the properties of the bubble layer are not included. On the arguments presented here the ratio of double layer capacitance in HCl to NaCl at the same potential should be a measure of the electrode surface which, on average, is free of the bubble layer.

6. Conclusions

The main conclusions are;

1. The most suitable methods of investigation are the steady state (averaged) current-potential and impedance-potential data. These can be used up to high current densities without restriction. It is convenient to analyse the data as a set of parameter curves. Potentiostatic pulse measurements are also necessary as a second line technique.
2. The presence of the bubble layer is reflected in all the parameter curves. It will be necessary to have a model for the bubble layer described, if possible by one parameter, so that the effects of the bubble layer on the reaction rate can be quantitatively described. Suitable data to which this could be applied are the rate constant-potential data presented in [6].
3. Of all the descriptive parameter curves the double layer capacity is most directly concerned with the state of the electrode surface. Measurements of the double layer capacity-potential curves for hydrogen evolution on nickel in acid solution in NaCl and HCl and HClO₄ solution

suggest that the differences between the measured curves depend on the bubble layer and the ion distribution in the electrolyte and do not contain a contribution due to intermediate H atoms. The ratio of capacity in HCl and NaCl at a particular potential is probably a measure of the fraction of free metal surface in the presence of the reaction.

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