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pH changes at near-electrode surfaces

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Anodic or cathodic processes in which protons are released or consumed, respectively, lead to local pH changes at the electrode surface. The phenomenon is important in several branches of metal finishing, in corrosion, electro-organic synthesis and other branches of applied electrochemistry, as well as being a factor which can invalidate mechanistic investigations. The concept of 'pH_s' (near-surface pH) is examined, as are the experimental techniques which have been used to measure it. Many of these are inherently weak. Published results are shown to be largely discrepant, both in respect of the magnitude of the effect and even its incidence. Attempts to treat the phenomenon theoretically are briefly summarized.

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1. Introduction

Most electrochemists, if they pause to consider the matter, will recognize that a pH change can take place in the layer of electrolyte immediately adjacent to the electrode, during electrolysis. This change in pH is almost invariably due to depletion of H_3O^+ ions in the vicinity of the cathode, and OH^- ions at the anode resulting from H_2 and O_2 evolution respectively, although this is by no means the only reason. The methodology of this type of measurement was critically reviewed a number of years ago by Brenner [1]. However, a great deal has been published since that time and moreover, Brenner's criticisms, which are still largely as true today as when they were made, were not tested in any way by a comparative data analysis which is attempted here, apparently for the first time.

In this examination of the subject, an attempt will be made to show that this phenomenon is of very far-reaching importance in virtually all areas of electrochemistry. There are many signs that the implications of near-electrode pH changes have been neglected in both fundamental and applied studies in the literature, and that they exercise an influence which should be taken into account. For some reason which is not apparent, the overwhelming majority of the work in the field comes from the USSR. Many important papers not hitherto available in English have been translated for the first time and their contents are incorporated into this discussion. We shall show firstly how very important the impact of the phenomenon is. Secondly, we shall review the methods by which near-electrode pH has been measured. Thirdly we shall examine the results of measurements in actual systems, after which an examination of the theoretical treatments will be made.

2. Importance of pH changes in the near-electrode layer

It is useful to list some of the most important situations where pH changes take place in the near-electrode layer and where the effect has a finite consequence on the overall situation.

2.1. *Metal finishing*

When a metal is co-deposited with hydrogen a pH increase takes place at the cathode surface which can be so large that precipitation of the hydroxide or even oxide can take place. The latter species are

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incorporated in the deposit. Perhaps the most surprising finding is that such pH changes take place even at open circuit, as discussed subsequently.

Electrocoat painting, or electrophoretic paint deposition, is a totally different process, but here too, local pH changes occur and affect the process [2–4].

2.2. *Corrosion*

During anodic dissolution, when simultaneous oxygen evolution is occurring, the near-electrode layer will become more acidic and the corrosion rate will thus be even faster than might be expected. This phenomenon would seem to be of special importance in the corrosion of the so-called 'permanent anodes' as used in the chlor-alkali industry or in metal winning. Other pH changes would appear to be important in 'free corrosion', where it has long been known that the pH is lower than in the bulk electrolyte either because of O_2 reduction or H_2 evolution. The pH changes that occur at open circuit are also significant in that, by leading to hydroxide formation, they can reduce the rate of corrosion by formation of a passive or semi-passive film, while the role of pH changes in pitting or crevice corrosion is equally important.

2.3. *Cathodic protection*

When an object is cathodically protected in sea water or fresh water, the alkalinity of the near-electrode layer leads to precipitation of magnesium and calcium salts, either hydroxides or carbonates or double carbonates. These will ultimately coat the object and so further decrease the rate of attack [5, 6].

2.4. *Electrode fouling*

Electrodes used for the electrolysis of sea water, notably in undivided hypochlorite cells or in electrodialysis stacks, suffer the same sort of precipitation as cathodically protected items described above. In the present case, such precipitates are not always deleterious, and it has been found that slight coverage of hydroxides etc, lead to increased cell efficiency by reducing the loss of OCl^- at the cathode [7].

2.5. *Electro-organic synthesis*

Many electro-organic reactions are pH rate dependent and changes at the electrode surface will make interpretation difficult.

In the cathodic reduction of glucose, the rate of the first step, an isomerisation from the cyclic to the linear form is pH dependent and is the rate-determining step [8]. The potential dependence of the process on solid electrodes can be quantitatively interpreted using data quoted in this review, in terms of an increasingly alkaline near-electrode layer due to increased hydrogen evolution [9]. There can be no doubt that many other electro-organic reactions will lend themselves to similar interpretation.

2.6. *In polarography*

It has long been recognized [10, 11] in polarography that the uptake of H_3O^+ ions by the species being reduced at the electrode surface will lead to pH changes which cause problems in interpretation.

2.7. *In fundamental studies*

It is possible to locate numerous fundamental studies of hydrogen or oxygen evolution (especially those in which a 'parametric analysis' is attempted) which must have been corrupted by the effects to be discussed here. In particular those studies where relatively high current densities and an intermediate pH (whether buffered or unbuffered) were employed must now be regarded with caution. The work of Bockris *et al.* [12] on the kinetics of Fe deposition and dissolution represents one of the few systematic studies where the effect has been considered.

3. Theoretical treatment

3.1. *The concept of near-electrode pH*

It is clear how the loss of hydrogen or oxygen as a result of a heterogenous process at the electrode surface gives rise to changes in pH_s. For a perfectly smooth metal surface, in a solution where a laminar convective flow regime exists, the concept is easy to envisage. It must be recalled that few metals even approach perfect smoothness, and most have pits or projections. Both metal–solution potentials and convection conditions will greatly differ from point to point, and for all these reasons, 'pH_s' must in reality be some kind of mean value, or one which ignores the most extreme changes of pH which must exist locally in deep pits or crevices. This is the first conceptual restriction on the idea of pH_s. Where hydrogen ion concentration is changed due to release or uptake of species wholly in the solution phase, or possibly across the solution–solid interphase, the traditional Nernstian diffusion conditions prevail and a theoretical solution of the pH_s problem is possible; Winkelmann [13] wrote: (for oxygen reduction in seawater)

$$D_{H^+}\frac{dC_{H^+}}{dx} - D_{OH^-}\frac{dC_{OH^-}}{dx} = -\frac{i}{F} \qquad (1)$$

where x is the distance from the electrode, reflecting the fact that in unit time, the hydrogen ions diffusing in to the electrode surface less the hydroxyl ions moving out equalled the current flowing. The C_{H^+} term is then eliminated, using the expression:

$$K_w = C_{H^+}C_{OH^-} \qquad (2)$$

for the dissociation of water. Equation 1 may be integrated, using the limiting condition that at $x = \delta$ (diffusion layer thickness) $C_{OH^-} = C_{OH^-}$ (bulk), which gives, for OH^- concentration at the surface:

$$C_{OH^-} = -\frac{A}{2} \pm \left[\left(\frac{A}{2}\right)^2 + B\right]^{1/2} \qquad (3)$$

where

$$A = \frac{D_{H^+}}{D_{OH^-}}\frac{K_w}{C_{OH^-}\,(\text{bulk})} - C_{OH^-}\,(\text{bulk}) + \frac{i\delta}{FD_{OH^-}} \qquad (4)$$

and

$$B = \frac{D_{H^+}}{D_{OH^-}}K_w\,. \qquad (5)$$

Engell and Forchammer [14] extended this theory firstly to cater for pH changes due again to oxygen reduction, and also to examine the effects of hydrogen evolution. Their approach was to formulate the condition for limiting oxygen reduction current using Fick's law, and also the diffusion back into the bulk of the OH^- ions so formed. The two terms are of course equal at limiting conditions. Furthermore, oxygen reduction being a four electron reduction, hydroxyl formation being only a single electron reaction,

$$i_{diff,\,O_2} = 0.25\,i_{diff,\,OH^-}\,. \qquad (6)$$

Hence

$$[OH^-]_{surf} = \frac{4\beta_{O_2}}{\beta_{OH^-}}[O_2]_{bulk} \qquad (7)$$

where β is the mass transfer coefficient. Using dimensionless numbers and accepted mass-transfer theory, the authors arrive at the time relationship:

$$[OH^-]_{surf} = 4\left(\frac{D_{O_2}}{D_{OH^-}}\right)^{2/3}[O_2]_{bulk} \qquad (8)$$

from which, using a value for $2.85 \cdot 10^{-4}$ mol dm^{-3} for the solubility of oxygen in seawater at 10° C, and diffusion coefficient $1.98 \times 10^{-5}\,cm^2 s^{-1}$ (O_2) and 5.25×10^{-5} (OH^-) they obtain a pH_s value of 10.9.

There appears to be no reason why a similar approach should not be used to predict pH_s changes due to hydrogen or hydroxyl ion take-up by any dissolved species in solution.

It should be pointed out that even when hydrogen or oxygen evolution are taking place, at current densities below 1–5 mA cm^{-2}, the gas can usually escape as a dissolved species, and what is discussed below may not apply.

Dahms and Croll [15] in a study of the codeposition of Ni and Fe, derived a somewhat different equation, though using the same general approach. They do not appear to have tested it directly.

Bardal [5] presented a modification of Engell's theory [14] and tested it using an Sb microelectrode, finding reasonable agreement. Koura [16] again quotes a very similar equation in his work on pH_s and Ni electrodeposition.

3.2. *Bubble-forming situations*

The analysis of the problem becomes much more difficult, however, when pH_s changes are due to gas evolution. In place of the relatively simple picture of the diffuse layer, we must envisage an electrode, partly covered with bubbles, some of which are continuously detaching themselves and drifting into solution. According to a relationship which is probably complex, involving convective flow in the electrolyte and other factors, there will be a distribution of bubble population density perpendicular to the electrode surface. In addition, there will be other factors such as bubble coalescence. From this follow several consequences. Firstly the idea of a diffuse layer in the Nernstian sense is virtually obsolete. Equally, the concept of pH itself must be questioned. Do we mean by pH, hydrogen ion activity per volume of electrolyte or simply per volume? For as the rate of bubble evolution increases, there will be a tendency for the volume adjacent to the electrode surface to be a two-phase gas–liquid system ever richer in gas. In terms of hydrogen ion activity per volume, each ion will be associated with more gas (which is inert) and less liquid. In trying to predict what will occur, we can envisage (for hydrogen evolution) pH increasing by a double-acting mechanism, in which an increasing flux of OH^- ions is generated in a decreasing volume of liquid. If some sort of pH probe (this will be discussed in Section 5.3), senses the volume adjacent to the electrode surface, it will encounter a two-phase system in which it will ignore the gaseous component and become less an immersed probe and more one periodically 'washed' by droplets of electrolyte. While such pH measurements are 'genuine' in the sense that – for example – a base catalysed reaction in this zone would reflect them, they are extremely difficult to predict. The literature, however, contains studies which give some indication of expected values. Workers in the field of electroflotation have studied the formation of bubbles at electrode surfaces and their size distribution. The subject has been reviewed by one of us [17]. These workers studied bubble size distribution after the bubbles had left the electrode but were only able to provide an indication as to the steady-state residence phenomena on the surface. Presumably larger bubbles will have shorter residence time. But from this work it is clear that bubbles of 100 μm are found. Another body of work, reviewed in [17] is devoted to the electrical resistivity of gas–liquid electrolyte mixtures. From this, one may see one's way to a definitive experiment. If, during a gas-evolving electrochemical process, the ohmic drop at the electrode surface is measured and compared with that at the same electrode in the absence of gas evolution, the resistance of the near-electrode gas rich layer may be obtained and from this, using the data referred to above, its void-fraction. Such a measurement has been made by Hayes [18].

In considering the overall situation at the surface, another factor which merits consideration is the partial pressure of molecular hydrogen. It is known (Kelvin's equation) that the equilibrium concentration of a gas dissolved in water and the internal pressure of gas bubbles present can be related according to:

$$C_r = C_{\mathrm{inf}} \exp\left(\frac{2\sigma V}{RTr}\right) \tag{9}$$

where C_r is the equilibrium concentration of dissolved gas, C_{inf} the same value for a plane gas–liquid boundary, σ is the surface tension, V the molar volume, R the gas constant and r the bubble radius. Panov and Kravchenko [19] have shown that for bubbles formed electrolytically, overpressure could be 1.1 to 1.2 times atmospheric and this might affect a pH probe which is also responsive to molecular hydrogen. (See also Section 5.1.)

Finally, as numerous workers have shown [20], transport of species across the diffuse layer is greatly accelerated in the presence of bubble formation and this might argue for the faster relaxation of pH gradients.

3.3. *Film-forming situations*

When a film, usually a simple or complex hydroxide, is formed at the electrode surface, either wholly from species in solution, as in the case of seawater immersed cathodes, or, as in corrosion, from the metal of the electrode itself, there are further aspects to be considered. At open circuit, the dissociation constant of the hydroxide itself determines pH_s. But under current load, pH_s will revert to the non-film-forming value shown by noble metal electrodes. However the current density leading to pH change is not i_{total} but $i_{\mathrm{total}} - i_{\mathrm{corr}}$. That such films are often semi-permeable membranes should not affect steady-state results, though there may well be two widely different pH values, namely $pH_{\mathrm{metal-film}}$ and $pH_{\mathrm{film-solution}}$ the latter corresponding to pH_s as it is discussed here.

3.4. *Measurements of pH_s*

We may subdivide situations where pH_s has been measured into the following categories:

(1) Gas evolution at 'permanent' electrode

surfaces, where no chemical change takes place in the solid phase.

(2) Gas evolution at electrodes where a surface film is formed.

(3) Open circuit pH_s change at electrodes where surface films are formed.

(4) Miscellaneous situations.

In practice, comparatively little work has been done on the first case, though it represents a simpler situation than the second one. Here (usually when a metal ion capable of forming an insoluble hydroxide is present) the increase in pH leads to formation of this hydroxide and an equilibrium is then set up.

$$M^{n+} + nOH^- \rightleftharpoons M(OH)_n$$

and the pH close to the electrode is determined by the solubility product of the hydroxide $M(OH)_n$. A similar process explains why pH changes can occur close the electrode at open circuit, since if the metal of the electrode dissolves to form a species such as a hydroxide, this will then control the pH.

The fourth category is illustrated by oxygen reduction from seawater, or the deposition of copper from acidic copper sulphate solutions, which, as reported by Brenner [1] leads to local acidity increases. In most of the four cases cited above, there are examples of both buffered and unbuffered electrolytes, with smaller pH changes being reported in the former case.

4. Discussion of results obtained by previous workers

Data relating to pH measurements in the near-electrode region can be subdivided into two categories. In the simpler case, we can consider situations in which no new solid-phase – such as metal hydroxide – is formed on the electrode surface. In the more complex situation, where such films are formed, analysis and comparison is extremely difficult.

4.6. *Discussion of 'simple' situations*

There is surprisingly little data covering situations where no new solid film is formed. Even Chernovyants [21] ostensibly working under these conditions, declares that his results are tainted by the presence of small traces of metallic impurities in the 'CP' grade chemicals he used. Without further details of his work, it is not possible to calculate what total amounts of such impurities were present and what thickness of film they might form, even assuming, unlikely though that be, that all of them were deposited on the electrode surface. These data and other results are reproduced below in tables and figures. There are certain trends evident although there appear to be exceptions to almost all of them.

4.6.1. Effect of current density. Increase in current density increases the difference between solution pH and that at the surface. However some measurements suggest that the increase is a smooth one, others suggest that the effect levels out above a certain current density while at least some workers (Fig. 4) suggest there is an exponential increase in ΔpH as a function of current density.

Thus Fig. 1 suggests that both in dilute sulphuric and hydrochloric acids, there is little change in pH_s over a fourfold range of current density. Figure 2 shows a rather similar picture, with a rate of change of pH_s which decreases and appears to become asymptotic, at a current density of around 10 mA cm^{-2}. Knoedler *et al.* [22] (Fig. 3), show a fairly smooth progression of pH_s with current density up to 400 A m^{-2} (40 mA cm^{-2}). The data of Ives [25] again indicate a progressive increase in surface acidity at the anode, as current density increases, and the current densities he uses

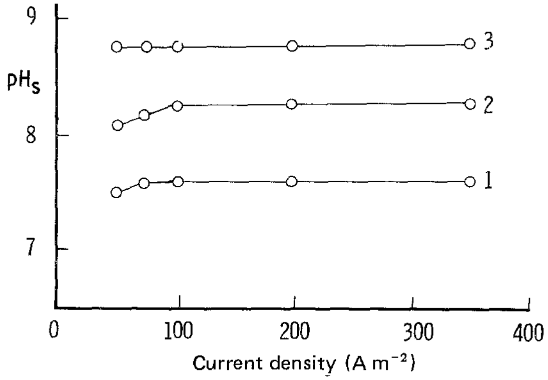


Fig. 1. Dependence of catholyte surface pH (pH_s) on polarizing current density (in A m^{-2} , 18° C. Electrolyte; 1 = 0.0025 mol dm^{-3} sulphuric acid, 2 = 0.995 mol dm^{-3} HCl, 3 = 0.001 mol dm^{-3} HCl. Data (from [21]) obtained with Pt–H_2 electrode.

Table 1. pH_s measurements where no solid film is formed at the electrode

System	*Technique*	*pH_s*	*Temperature (° C)*	*Buffer*	*Workers*	*Comments*
Seawater 10° C, dissolved oxygen	Calculation	10.9	10 or 20	no	[14]	current density not stated, $= i_{lim}$ for O_2 reduction based on erroneous theory
ditto. current density $= 5 i_{lim(O_2)}$		11.6	10 or 20	no	[14]	
Pt/Ti anode 100 g dm^{-3} sulphuric acid (pH = −0.3)	rear Q/HQ reference	−0.84 (100 A m^{-2}) −1.79 (500 A m^{-2}) −2.60 (1000 A m^{-2})	70	no	[23]	see text
Na_2SO_4 pH = 4.8	suck-off	6.2 (400 A m^{-2}) 5.8 (100 A m^{-2}) 5.2 (10 A m^{-2})	20	yes	[22]	
Na_2SO_4 pH = 7	suck-off	11 (400 A m^{-2}) 10.7 (100 A m^{-2}) 10.3 (10 A m^{-2})	20	no	[22]	
$HCOO^-$ pH = 12.3	ring-disc Pt reference	3.0 (?)	20	no	[24]	
HCl pH = 2 pH = 4	potentiometric	2.5 (7500 A m^{-2}) 8.0 (7500 A m^{-2})	20	no	[21]	pH_s independent of *i* from 100 to 350 A m^{-2} pH_s. Effect said to be due to trace metal ion concentration
H_2SO_4 pH = 3.2	potentiom. and glass microelectrodes	8.7* (100–400 A m^{-2})		no	[21]	after correction for diffusion potential
0.5 mol dm^{-3} NaCl pH 2.6 7.2 9.6	glass micro	6.8 (250 A m^{-2}) 11.2 (250 A m^{-2}) 14+ (250 A m^{-2})		yes	[25]	
KCl pH = 4.8	potentiom.	5.9 (1.0 A m^{-2}) 14 (100 A m^{-2})	20	yes	[26]	
K_2SO_4 0.01 N pH = 1.8 2.2 4 etc	Sb microelectrode	2.0 (50 A m^{-2}) 12 (50 A m^{-2}) 12 (50 A m^{-2})	20	yes	[27]	
$(NH_4)_2SO_4$ pH = 3.54		8 (100 A m^{-2}) 9 (1000 A m^{-2})		yes	[27]	

* After correction for diffusion potential. Uncorr. value = 12.5.

Table 2. pH$_s$ changes in the presence of a metal ion or other film-forming species

Solution composition	*Current density* (A m^{-2})	ΔpH_s	*Sources and notes*
NiSO$_4$ 0.5 mol dm^{-3} pH 1.5 to 5.85	nil	0 (pH = 5.85) 2.5 (pH = 1.5)	Slizhis and Matulis [28] also data for brief pulse
NiSO$_4$ 0.5 mol dm^{-3} pH = 1.5	50	4.0	[28]
	100	5.5	
NiSO$_4$ 0.5 mol dm^{-3} + 20 g dm^{-3} H$_3$BO$_3$ buffer pH = 1.5	50	3.8	[28]
	100	4.5	
NiSO$_4$ 0.5 mol dm^{-3} pH = 4.3	50	3.7	[28]
NiSO$_4$; buffer 20 g dm^{-3} pH = 4.3	50	2.5	[28]
NiSO$_4$ pH = 5.1	200	1.5	Gershov and Purin [29]
NiSO$_4$ (buffered) pH = 3.5	200	1.5	range of current densities from 0 to 320 A m^{-2} also cited
NiSO$_4$ pH = 1.4	200	2.5	
NiCl$_2$ pH = 1.65	800	2.55	Ovchinnikova and Rotinyan [30]
NiCl$_2$ pH = 1.65	400	0.7 approx.	
NiCl$_2$ pH = 1.65	400	2.65 (20° C) 2.25 (30° C) 1.45 (40° C)	
NiSO$_4$ pH = 4	200	5.3–5.8	Savel'ev [31, 32] current density 0–400 A m^{-2}
NiSO$_4$ pH = 4.2 (buffered)	200	4.0	current density 0–400 A m^{-2}
MnSO$_4$–(NH$_4$)$_2$SO$_4$ pH $\simeq$ 7	500	2	Bondar [33]
	2000	2.3	also pulse data
CoSO$_4$ + K$_4$P$_2$O$_7$ pH = 9.5, 20° C	200	3	Gershov and Purin [33] current density 0–200 A m^{-2} 20 & 40° C
CoSO$_4$ + NH$_4$Cl pH = 9.5, 40° C	200	0.5	
NiCl$_2$ pH = 4.5	400	1.7	Knoedler [22] current density 0–400 A m^{-2}
NiCl$_2$ (buffered) pH = 4.4	400	0.2	
NiSO$_4$ 1 mol dm^{-3} pH = 4.5	400	2.0	
NiSO$_4$ (buffered) pH = 4.4	400	0.2	Knoedler [22] *
NiCl$_2$ pH = 3	400	3.0	
NiCl$_2$ (buffered) pH = 3	400	0.4	
NiSO$_4$ pH = 3	400	3.5	
NiSO$_4$ (buffered) pH = 3	400	0.1	
K$_4$P$_2$O$_7$ pH = ?	200	1.8	Orekhova [35]; also with additives
Watts bath pH = 4	10	2.4	Ives and Rothwell [36]

Table 2. Continued

Solution composition	*Current density* (A m^{-2})	ΔpH_s	*Sources and notes*
$NiSO_4$ (0.25–2.0 mol dm^{-3}) 20°–55° C pH = 1.25–4.0	0–250	up to 3	microglass and open circuit decay. Shielding effects? [106]
$NiSO_4$ (1 mol dm^{-3}) + NaCl pH 5–5.5	100	1.5–2	Kudrayavstev [26]
$NiSO_4$ + NaCl, buffer pH 5–5.5	100	1	Many other specialized baths and buffers
as above	150	4	
$FeSO_4$	500		Nagirnyi [37]
pH = 2		6.5	
pH = 4		6.5	
pH = 1.5		2.5	
$CoSO_4$	1000		Kublanovskii [38]
pH = 1		2.5	
pH = 2		4	
pH = 3		4	
pH = 5		2.5	
$NiCl_2$ pH = 2	800	4	Ovchinikova and Taran [30]
$NiCl_2$ + NaCl pH = 2	800	4	
as above (at 55° C)		0.3	
$MnSO_4/(NH_4)_2$	500		Schvab [39]
pH 1		3.8	
2		5.5	
4		3.5	
6		2	
8		1	
10		1.5?	

* Further data which broadly say that there is no change with buffers except at highest currents. Also that with unbuffered solutions, maximum deviation is at pH = 2 while at pH = 6, there is virtually no difference.

are higher than those used by any other worker. However since he alone has studied pH$_s$ at an anode, it is not possible to make comparisons and phenomena due to loss of O_2 (at the anode) are unlikely to be identical to those due to H_2 loss (at the cathode). In addition the quinhydone electrode he used is known to be O_2 sensitive. All these contrast sharply with the findings of Varypaev (Fig. 4) on the one hand, and Kudrayavstev (Table 3) on the other. In these two

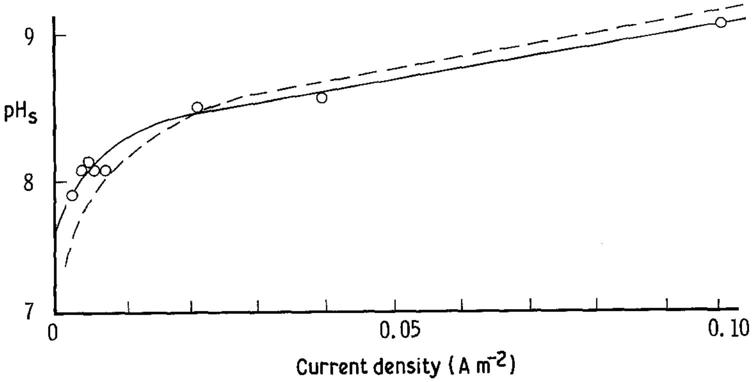


Fig. 2. Dependence of near-cathode pH (pH$_s$) on current density (A m^{-2}) 0.5 mol dm^{-3} ammonium sulphate solution, bulk pH = 3.54, 21.5° C. Solid line is experimental data. Broken line gives calculated values from theory (taken from the work of Kublanowski [27]).

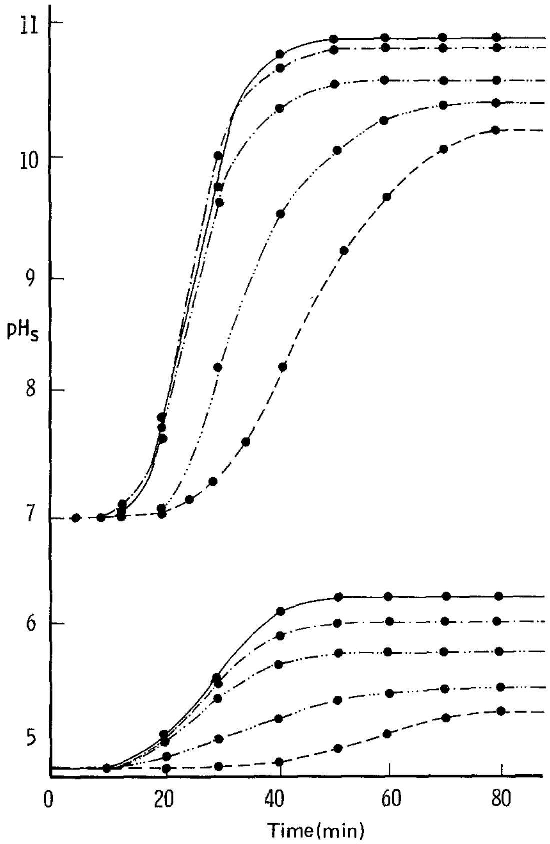


Fig. 3. Change of pH near the cathode surface as a function of time after current imposition. Data (from [22]) obtained using suck-off method. Top group of curves; borate free, lower group of curves; 30 g dm^{-3} borate. Current density, reading from top to bottom in each group: 400, 200, 100, 50 and 10 A m^{-2}.

cases, the rate of change of pH$_s$ *accelerates* as the current density is increased and between 10^{-3} and 10^{-2} A cm^{-2}, there is an exponentially increasing rate of change of pH$_s$. The really big change occurs in the latter case between 50 and 100 A m^{-2}. This is really a very difficult result to explain. The suggestion is that a current increase of 2–5 times, (and let us assume that this implies a corresponding increase in the rate and volume of gas formed), thus appears to change the hydrogen ion concentration by four orders of magnitude. Is this a genuine result or merely some artefact of the measurement system? The reference electrode will, without doubt, be looking at higher current densities in what is a two-phase electrolyte of gas and liquid. To set this into perspective, it should be noted that Slizhis [40] shows that pH$_s$ is constant over the first 100–200 μm from the electrode surface (but not in all cases) and this in a 'filmed electrode' situation. On the other hand it is well known, for example from the work of Matov [41] that bubble size during cathodic hydrogen evolution follows a Gaussian distribution, with a peak

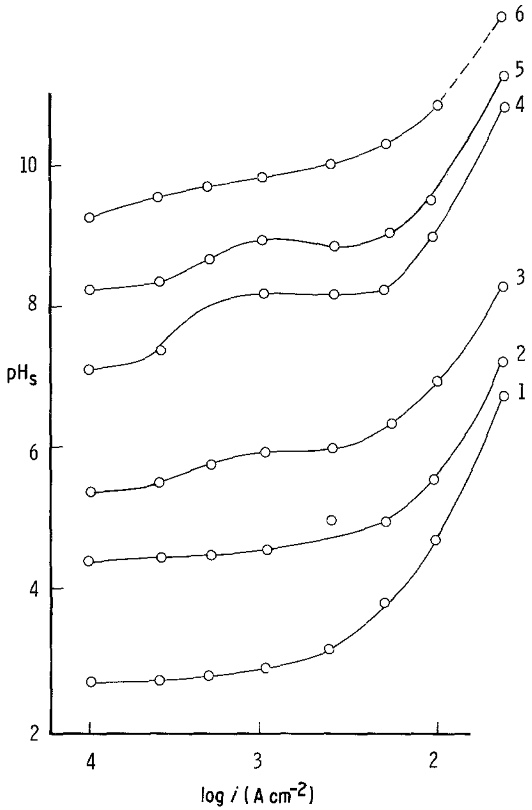


Fig. 4. Near-cathode pH (pH$_s$) as a function of cathodic polarising current density (log A cm^{-2}) obtained with a micro-glass electrode (from [25]). Bulk solution pH was: 1 = 2.6; 2 = 4.3; 3 = 5.4; 4 = 7.1; 5 = 8.2; 6 = 9.3.

Table 3. Near-electrode pH data of Kudrayavstev [26]. Pt cathode in KCl. pH$_0$ = 4.8

Current density (A m^{-2})	*pH$_s$*
0.1	5.9
0.5	7.6
1.0	7.5
2.5	7.5
5	8.3
10	8.85
25	9.5
25	10.1
100	14

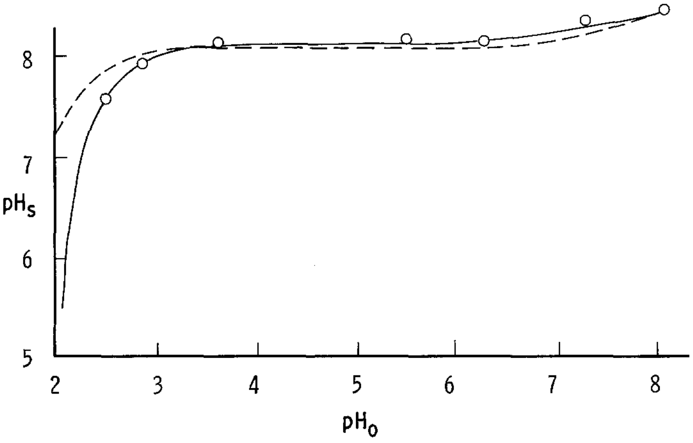


Fig. 5. Effect of bulk pH on near-surface pH (pH$_S$). 0.5 mol dm^{-3} ammonium sulphate solution with additional acid or alkali to produce stated pH. 22.5° C, current density 1.1 × 10^{-2} A cm^{-2} (from work of Kublanowski, [27]).

around 140 μm (for a curved wire cathode) and probably around 250 μm for a flat surface. The two-phase electrolyte would quite likely extend over the entire measurement zone. This in itself should not change the pH. The only explanation that comes to mind is if the most alkaline layer close to the electrode surface, is 'dispersed' by the gassing action, into a somewhat deeper zone, where the reference electrode will record it. If this sort of action is taking place, then why did the other authors not observe it in comparable media and at the same current densities? If the most alkaline layer is that adjacent to the surface, then the rear-suck-off technique (Knoedler) would detect it.

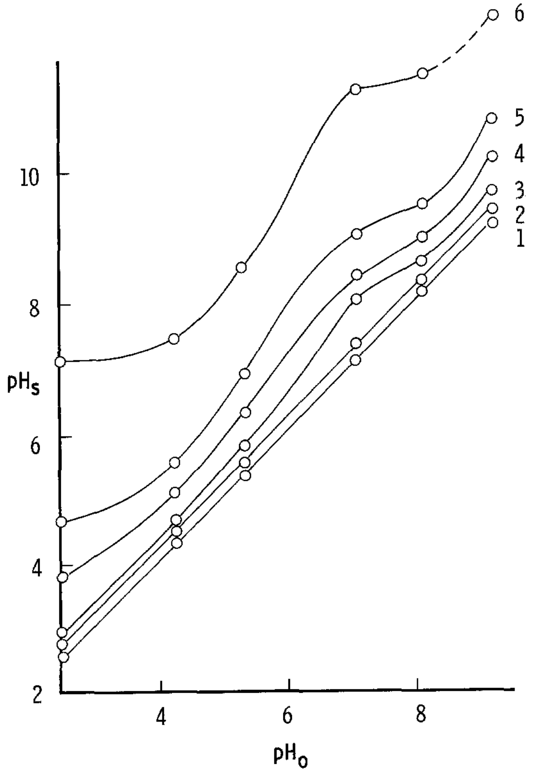


Fig. 6. As Fig. 5 but from Varypaev [25]. Current densities 1 = 0.1; 2 = 0.24; 3 = 0.5; 4 = 5.0; 5 = 10.0; 6 = 25 mA cm^{-2}. Solution was 0.5 mol dm^{-3} NaCl adjusted with universal buffer (0.04 mol dm^{-3} of HAc, H_2BO_3 and H_3PO_4) and NaOH, 20° C.

4.6.2. Correlation between pH$_0$ and pH$_s$. Obviously as the bulk pH becomes less acidic, the difference between it and the surface pH will increase, other factors being equal. However some strange effects are reported. Figure 5 (Kublanowski [27]) suggests that at pH$_0$ values above 2, a 'jump' effect exists, until pH$_0$ = 4, after which no further change in pH$_s$ occurs. This is in total contradiction to Varypaev (Fig. 6), who shows a more or less smooth progression.

An even sharper 'step' is seen in Fig. 7, from the work of Kublanowski.

The medium in Fig. 7 is 0.01 mol dm^{-3} K_2SO_4, at 5 mA cm^{-2}. Once again, common sense suggests that a change in bulk pH of one or two units cannot possibly have such a gross effect on the surface phenomenon, and here again, it seems clear that further investigation is called for.

Summarizing this section it is clear that the overall picture is thoroughly discrepant, and badly in need of further research. Of the factors which could affect the results, it would appear that current density, the presence of buffers and the techniques used for measurement, are all variables which are common throughout. Possible weaknesses of all these are considered later, but it

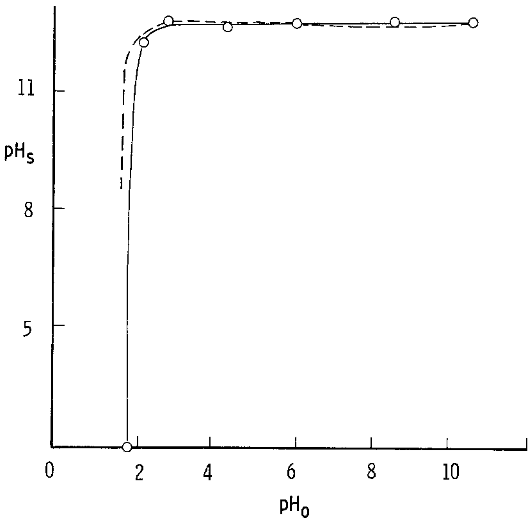


Fig. 7. As Fig. 5 (from [27]). 0.01 mol dm^{-3} K_2SO_4. Current density = 5 mA cm^{-2}. 21° C. Solid line; experimental data. Broken line, calculated data.

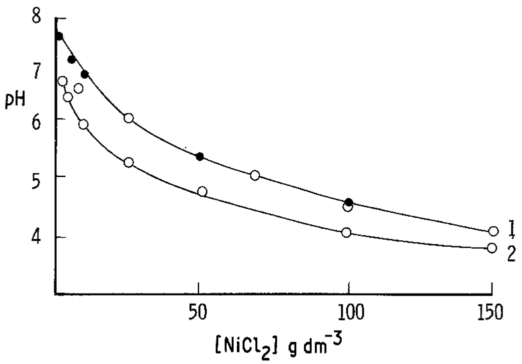


Fig. 8. Dependence of the pH of hydroxide formation on temperature and nickel concentration in $NiCl_2$ solution at: (1) 25°; (2) 55°. The points on the curves represent duplicate experiments. The curves for the $NiCl_2$ solution containing NaCl (120 g dm^{-3}) are similar, but are 0.2 pH unit lower.

should be emphasized that Knoedler *et al.* [22] were well aware of the criticisms of Brenner regarding the suck-off method and went to some lengths to avoid errors due to an excessive removal rate. Likewise Chernovyants [21] recognized the problems inherent in his chosen method. The fact that the authors discuss these problems gives greater confidence in their results, even though the discrepancy remains.

4.2. *Analysis of data in situations where a film is formed*

When either a metal cation or an oxy-metal anion such as chromate, is present in solution, at least two Faradaic reactions are possible at the cathode, namely metal ion discharge and hydrogen evolution. The competition between them depends both on the relative positions of the E_0s and the concentrations of the metal ions and the pH, as well as the exchange current density (i_0). It is recognized that in many instances of practical importance, conditions are such that significant amount of hydrogen evolution can occur with the resulting formation of an alkaline layer close to the electrode. The deposition of iron, cobalt, manganese and nickel are only a few important practical examples where this is known to occur.

In many instances, the problem is only serious when the diffusion limiting current for the metal ion deposition reaction is exceeded. Ovchinnikova and Rotinyan [30] have shown, by simultaneous pH$_S$ measurements and current–voltage plots, that as long as the potential is in the Tafel region, surface alkalinity will not be important. A temperature increase from ambient to 50–60° C was found by several workers to be quite effective in obviating changes in near-surface pH. Bearing in mind the small energies of activation involved in diffusional processes, this is somewhat surprising. Stirring is also said to delay the onset of alkali formation at the electrode surface.

When an alkaline layer is formed, however, it is possible that a metal hydroxide, oxide or double salt will form on the surface of the electrode at the same time as metal deposition is taking place, and the end product will be a metal with severe inclusions of these hydroxides or salts. Ovchinnikova and others [30] have pointed out that the pH at which this phenomenon sets in can be lower than the literature value for the hydroxide of the variables. Figure 8 shows how this works out in the case of nickel.

The film, once formed, by virtue of its ability to dissociate will give rise to a pH$_S$ effect at open circuit, and probably also at lower current densities. The properties of the film will also affect the morphology of the metal electro-deposit. These effects are outside the scope of this paper. Levin and Pushkareva [42], who describe iron deposition, mention that the hydroxide films forming here are colloidal in many cases and can act to regulate crystal growth. Because the micelles are positively charged in this case, they adsorb on the metal surface at potentials cathodic to the point of zero charge (pzc). These colloidal films are also involved where metal deposits in powdery form. However more relevant to the pH distribution, is the 'sieve' effect of such films which itself is partly related to their thickness. Bard [47] shows how hydrogen evolution on Pt is affected by the presence of a tin hydroxide film at the Pt surface, and discusses the pH changes in the film.

It is known that films of hydroxides and other materials can act as ion-selective membrances, and that the transport of hydrogen ions is favoured over that of metal ions. This arises partly due to the superior mobility of hydrogen ions and partly because (in many situations) they are present in higher concentration. Film thickness appears to be determined by an equilibration of growth and destructive processes. The latter are both chemical (dissolution) and mechanical (attrition by the gas bubbles formed on the surface). The same gas bubbles will also induce a porosity in the hydroxide film. A recent study of film thickness, growth rate and composition is due to Hamzah *et al.* [44].

Considering a metal surface covered by a porous film itself in contact with aqueous electrolyte, we can see that there may well be a pH gradient across the film. In such a case, any measurements of pH_s made by the probe technique (one excepts potentiometric methods) can only ascertain the outer pH_s and not that immediately adjacent ot the metal surface. If hydrogen ion transport is largely due to a 'hopping' mechanism, there will be little movement of water molecules or formation of hydroxyl ions, once a given concentration of these has been achieved. Such films are less than perfect, and there will be some transport of water and/or hydroxyl ions into the bulk. However the significant voltage drop reported across these films which can range from 50 mV to 5 V or more will quite probably include a hydrogen ion concentration term, sometimes referred to as a diffusion potential by workers in this field.

In terms of the above analysis, it can be seen that the acidity at the outer surface of the film (pH_f), cannot be less than that resulting from dissociation of the film (at open circuit or low current densities) and may be considerably more alkaline.

The presence and effect of 'indifferent' ions such as sodium, is the subject of debate. Ovchinnikova [30] has argued that by participation in the current carrying process, addition of such will delay the onset of concentration polarization and so pH differences. Other authors have suggested that such ions actually promote alkalization at the cathode surface.

4.2.1. Other trends. Results of Knoedler suggest that in plotting pH_s against pH_0, while an approximately linear relationship between the two exists for buffered solutions (e.g. 30 gm dm^{-3} boric acid buffer in either $NiCl_2$ or Watts bath) a much steeper increase, followed by a plateau at $pH_s = 6$, is found in unbuffered versions of these solutions especially at the highest reported current density 400 A m^{-2}. According to these workers, the limiting value of pH_s observed by them is equal to the value to be expected from the dissociation of the $Ni(OH)_2$. The 0.5 pH unit difference observed in the case of sulphate and chloride is seen to be due to differences in the ionic activity of the two solutions. They also make the point that certain solutions such as $NiCl_2$ do in fact have a buffer action, although this might not be apparent at first sight.

Slizhis [40] is one of very few who actually quote the effect of distance from the electrode surface. Figure 9 shows how pH varies over the first millimetre from the electrode surface. The pH seems constant over the first 200–400 μm and then drops off to the bulk value.

pH_s (at 30 μm from the surface) is shown by him to be current independent from 5–50 mA cm^{-2} for $CoSO_4$ at pH 4.6 while with $NiSO_4$ at pH 4.44, it rises steeply from 5–20 mA cm^{-2} (highest value reported). No explanation is given for the difference. In the paper by Kublanowski and Belinskii [38] on electrodeposition of Co from the same solutions, a plot of pH_s against current density is shown and depending on the pH_0, all types of behaviour are seen. Unfortunately the authors have apparently not reported their pH_0 values in this graph. Knoedler [22] reports $NiSO_4$ pH 4.5 reaching a pH_s that is current density dependent in the range 0.1–4 A dm^{-2}, though with signs of limiting value

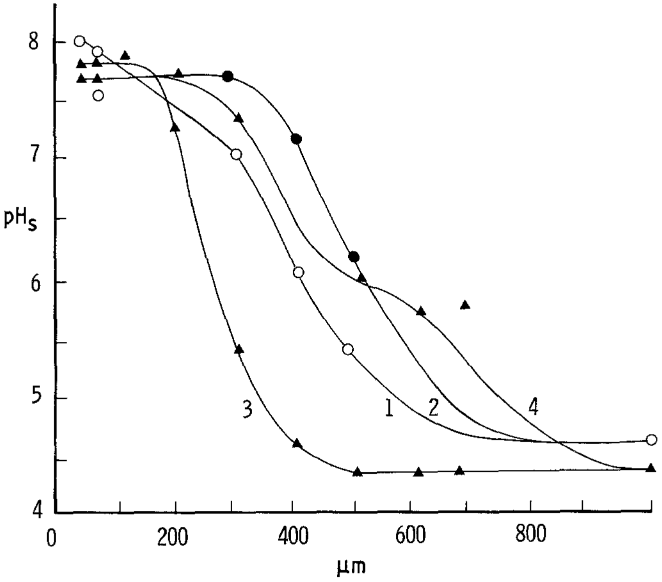


Fig. 9. pH in the diffusion layer (i.e. pH$_s$) as a function of distance from the electrode surface. Curve 1 = 0.5 mol dm^{-3} NiSO$_4$, current density 5 mA cm^{-2}. Curve 2 = Ni electrode at open circuit in same solution. Curve 3 = 0.5 mol dm^{-3} CoSO$_4$ solution, current density 5 mA cm^{-2}. Curve 4 as curve 2, for the cobalt solution (from [40]).

being approached at the higher current density. He thus supports the finding of Slizhis. The paper by Ovchinnikova and Rotinyan [45] bears out the work of Slizhis albeit on a less accurate scale. They report a pH difference in the region 0–1 mm from the electrode surface, falling off sharply in the 1–2 mm zone. Another interesting finding here is that the decay times after current cessation are shortest when no film is formed at the surface (total decay time ca 80 s) and slowest when a film is present. This fits in with the general picture of the film itself regulating the pH$_s$. To what extent the response time of the pH electrode itself enters the former observation is not stated. They are known to have finite response times together with the high impedance circuitry associated with them. In his work with Matulis [46], Slizhis suggests the pH$_s$ effect is measurable from the surface to ca 10^{-2} cm out. These authors also mention the interesting fact that the pH$_s$ is higher after deposition of a fresh Ni deposit. Their explanation is that hydrogen evolution is favoured on the latter with the resulting pH change.

In summary, in spite of being apparently more complex than the 'simple' situation, pH$_s$ measurements in the presence of surface-formed film present a more uniform picture than the cases where they are absent, although once again, there are values which appear outside the generally accepted range.

5. Techniques for the measurement of pH$_s$

There does not appear to be any simple, easy to implement, technique for the measurement of pH$_s$, which is free from criticism. Some of these methods were reviewed by Brenner [1] (and also Ovchinnikova and Rotinyan [47]).

5.1. *Electrometric methods*

A micro pH electrode, placed close to the surface of the working electrode, may be used for pH$_s$ determinations, as may a platinum black reference electrode. If these are used during passage of current, one has to face all the problems of potential gradient between the working and counter electrodes (ohmic drop) as well as shielding effects. Problems of current distribution must render results from the 'mesh electrode wrapped around a glass pH electrode' method [29] open to question, while only a very small ohmic drop (typical nomograms are shown in [18]) would quite overwhelm the potential difference due to a pH change. Hayes *et al.* [18] have reviewed the first of these, Piontelli [48] the second, also showing that rear-entry Luggin capillaries do not avoid these problems. Bondar and Bazdhrey [33] use a calomel side by side with a pH probe to overcome this.

Alternatively, it is possible to break the current

*Table 4. Values found with the aid of platinum–hydrogen electrodes and glass microelectrodes for the pH of the catholyte layer during electrolysis of 0.001 mol dm^{-3} HCl and H_2SO_4 solutions**

Electrolyte	pH	Cathode current density, D_c (A m^{-2})	Platinum–hydrogen electrode		Glass microelectrode		
			pH_s measured after 0.5 s	pH corrected for diffusion potential	pH_s measured after 5 s	pH_s extrapolated to 0.5 s	pH_s corrected for diffusion potential
Hydrochloric acid	3.2	50	12.5	8.7	12.2	12.4	8.7
		62	12.5	8.7	12.2	12.4	8.7
		75	12.5	8.7	12.1	12.3	8.6
		100	12.5	8.7	12.1	12.3	8.6
Sulphuric acid	3.2	50	11.6	8.1	11.1	11.4	8.0
		75	11.8	8.2	11.0	11.3	7.9
		100	11.8	8.2	11.0	11.3	7.9

* Data from [21]

and measure pH_s 'immediately' thereafter. However, here one faces the problem of response times of the pH electrode, and no-one appears to have verified that the former quantity is less than the time required for significant decay of the near-surface pH differential. With the vigorous stirring effects caused by bubble evolution, it might be expected that the near-electrode layer would decay rather rapidly. Newer pH electrodes (Ross-types) are stated to have more rapid response, but these have yet to be adopted for pH_s measurement. The method of open-circuit decay can also be used [40, 49–51] but one factor – again unconsidered – relates to the significant supersaturation of dissolved H_2 close to the electrode, which Vogt [52] has shown to exceed 160 times the saturation concentration. This again would affect the reversible potential, and thus apparent pH_s values. Nor are the problems of capacitative decay taking place in open circuit decays addressed in these studies, though some authors [26, 49–51] do raise doubts and admit [49] the dependence of their results on certain arbitrary procedures. A further variation of this is due to Kadyrov [53] who measures oxide or hydroxide potentials, these being pH dependent.

Among other electrometric techniques for pH_s measurements, we may list the work of Ives and Gilbert [23] who used the Pt-quinhydrone electrode. Apart from a question mark regarding O_2 interference with this system, their reported pH_s values as low as -2.60 are somewhat surprising. Earlier results due to Ives, Eddington and Rothwell [36] with the same system apply to the Ni electrodeposition system, but both these studies should be read with an authoritative description of the quinhydrone electrode [54] in hand.

The antimony–antimony oxide microelectrode has been used by several workers [27, 28, 40, 55] while Kublanowski [27] used both this and the bismuth micro-electrode and once again, a critical appraisal of this type of electrode serves to highlight its limitations [24, 54, 56, 57].

An unusual departure from the stationary near-electrode reference electrode was made by Gunther *et al.* [24] who incorporated a $Pt–H_{ads}$ reference within a rotating disc system, though the limitations of such 'secondary H_2 electrodes' are considered in [54, 57]. Most widely used of all has been the micro glass pH electrode which has been adapted from physiological applications [21, 25, 38, 45, 58–64]. The auto-compensation method based on contiguous placement of the reference [33] is more difficult here. The problems of the effect of electric field [65], diffusion potential contribution [21] and transient phenomena at switch-off time [66] have all been questioned, though Bondar *et al.* [66] by placing a calomel microelectrode adjacent to the glass microelectrode, claim to have overcome most of these.

5.2. *Colorimetric and optical methods*

The presence of a pH indicator at the electrode surface can be used to register pH_s changes. An early attempt by Hendricks [67] was followed by others [68, 69] and quite recently [70] reflectance spectroscopy has been used with an indicator. We believe that such methods are probably the most satisfactory, since the indicator (if correctly chosen), rather than giving a single pH_s value (which as we have seen, is probably mythical) 'integrates' the hydrogen ion excess/deficit in the near-surface layer. A number of optical methods have been used, Schlieren interferometry [71–80] or related methods [81, 82]. The non-specific nature of interferometric data, coupled with changes in refractive index and [83] changes of solution density all bedevil this approach. The presence of gas bubbles would probably render it inapplicable. On the other hand it is a 'non-invasive' method.

5.3. *Sampling techniques*

If the solution close to the electrode surface can be sampled, a chemical analysis of pH_s can be made. A number of workers have tried this [1, 22, 83–90]. The question here is whether the near-surface solution, is so depleted by the drainage, that the influx of bulk solution will affect the measured pH_s. Knoedler *et al.* [22] who are among the more recent protagonists of the method consider this and conclude it is not a problem. An alternative approach [1, 91] is to rapidly freeze the solution surrounding the electrode and then to chemically analyse successive 'slices'. Poor adhesion of the surface frozen layers, together with accretion of frost (condensate), and voidage due to gas bubbles would all introduce problems.

In conclusion, though advances in the technology of micro-electrodes are constantly being reported the problems of pH measurement during current flow, remain. One might have more confidence in results from these methods if two or more had been tried by the same authors on the same system, but apart from recent work by us [92] we are not aware of any such studies. We believe that a simple approach that might yield fruit would be the use of an optically transparent electrode (OTE) used in a spectrophotometer, with a colorimetric indicator, and possibly phase-sensitive detection. Castle *et al.* [7] have used ESCA in conjunction with marker ions to determine pH_s.

6. Theoretical analysis and prediction

We believe the treatment shown earlier in respect of quiescent solutions is probably satisfactory. However where gas evolution is taking place, both because mass-transport rates are enhanced and because of the 'void fraction' effect, we believe that any theory which ignores such effects is very much open to doubt.

An early attempt at prediction of concentration changes near to the electrode surface (though not specifically directed at pH_s) is due to Ibl and Braun [93]. They treated the case of $CuSO_4 + H_2SO_4$ but not with hydrogen evolution. Their paper did not compare predicted with experimental data, and their theory being based on a number of assumptions, is mainly of value as a guideline. However their predicted value using the von Karman method agrees well with the value of $pH_s = -0.81$ obtained by Brenner [84, 85] for the same solution.

Harris [94] provides a purely theoretical treatment, devoid of any comparison with experimental data. While one may criticise his use of the Nernst–Einstein equation for a concentrated solution, and likewise the Nernst–Planck equations, his major omission is not to recognize the effect of gas bubbles. His treatment is further criticized by Kublanowski [95] both because he disregards the migration of ions in the electric field and also because many of his values are arbitrary, not least the sub-division of total current into the fractions going into gas and metal deposition respectively.

Kublanowski [27, 95] has addressed himself at least twice to the problem of pH_s prediction. However in one paper, he does not appear to compare predicted with actual results, and he too neglects bubble effects. Strangely enough, it is his earlier paper where this was done [27] and agreement between theory and experiment are excellent, notwithstanding that he ignores all the factors we have referred to. This paper is difficult to understand. For example a dimensional analysis of 'mobility' as expressed in his Equation 3 gives $cm\,mol^{-1}\,s^{-1}$ whereas ionic mobility should have dimensions $cm^2\,s^{-1}\,V^{-1}$. The quantity U is not defined, its dimensions are not stated nor the provenance of the values used. Both ionic migration in the electric field and convective transport effects are neglected. In his Equation 6, Kublanowski writes:

$$[H^+]_s = \frac{K_h[NH_4^+]_0}{[NH_3]_s}$$

which would lead to:

$$[H^+]_s = \frac{K_h[NH_4^+]_0}{\dfrac{10J_n}{U} + \dfrac{K_h[NH_4^+]_0}{[H^+]_0} - k[H^+]_0} \cdot \quad (10)$$

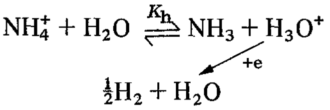
It would be more correct to write:

$$[H^+] = \frac{K_h[NH_4^+]_s}{[NH_3]_s}$$

in which case the final equation would be:

$$[H^+]_s = \frac{K_h[NH_4^+]_0 + k[H^+]_0 - \dfrac{10J_n}{U}}{\left(\dfrac{10J_n}{U} + K_h\dfrac{[NH_4^+]}{[H^+]_0} - K[H^+]_0\right)} \quad (11)$$

where $k = D_{H^+}/D_{OH^-}$. Since, using his own arguments:



$$\begin{array}{c} NH_4^+ + H_2O \overset{K_h}{\rightleftharpoons} NH_3 + H_3O^+ \\ \swarrow{}^{+e} \\ \tfrac{1}{2}H_2 + H_2O \end{array}$$

$$[NH_4^+]_s = [NH_4^+]_0 - \frac{10J_n}{U} + k[H^+]_0 \quad (12)$$

$$[NH_3]_s = \frac{10J_n}{U} + \frac{K_h[NH_4^+]_0}{[H^+]_0} - k[H^+]_0 . \quad (13)$$

Checking the calculated results of Kublanowski, it appears that $[(NH_4)_2SO_4]$ was $1.0\,mol\,dm^{-3}$ and not 1 N as he states, though this may be a translation

Table 5. Reported and calculated values of pH_0 *and* pH_s

pH_0	pH_s (experimental)	pH_s (calculated using 10)	pH_s (calculated using 11)
2.07	5.5	7.30	7.34
2.55	7.57	7.90	7.95
2.85	7.86	7.98	8.03
3.60	8.11	8.03	8.09
5.50	8.15	8.04	8.10
6.30	8.10	8.05	8.11
7.30	8.34	8.11	8.17
8.20	8.45	8.43	8.47

error. Comparison of calculated and experimental results show very poor agreement at lower pH_0 values. Use of Equation 11 above gives slight improvement over his values as shown in Table 5.

Unless parameters U and k are defined, no further comment can be made, and it has been suggested by one of us that these might simply have been 'best-fit' constants. Something should be said here regarding the results of Chernovyants and his correction for 'diffusion potential' (Table 4). We believe he meant the liquid junction potential ϕ_d for the interface:

$$HCl_0 | HCl_s$$

with ϕ_d given by:

$$\phi_d = -\int_s^0 \frac{RT}{F} t_+ d \ln a_{H^+} + \int_s^0 t_- d \ln a_{Cl^-}$$

where $t_{+,-}$ are transport numbers whose sum is unity. The authors presumably assumed anionic and cationic activity coefficients to be equal to one another so that $a_{H^+} = a_{Cl^-} = my_-$ and $\phi_d = (RT/F)(1 - 2t_+) \ln a_{H_0^+}/a_{H^+}$. However their corrections (of ca 3 pH units) imply a liquid junction potential of − 115 mV while Bates [57] quotes a value of 27 mV for the junction 0.1 mol dm^{-3} HCl|0.1 mol dm^{-3} KCl and thus there appears to be a discrepancy here.

The most recent paper by Bek and Borodihina [96] is the first to take into account the effect of bubble evolution on enhanced transport, which they do by solving steady-state diffusion equations. They themselves point out that use of a D_{av} value for all species other than H^+ or OH^- is not strictly correct. They show good agreement with the experimental data of Varypaev [25]. The authors make a number of interesting points. Their calculated pH_s values are not monotonic and in this they reflect corresponding findings of Varypaev and other authors. They comment on the experimental differences obtained using rear-entry microelectrodes and front-located ones. Their treatment still ignores the void fraction effect and while (where $x = 0$, i.e., at the electrode surface) this may not matter, in other circumstances where any sort of 'mean pH_s' is sought, the effect will be important. Looking at their predicted data, it is noticeable that the one feature that is totally absent is the exponential increase in pH_s with increasing current density, which was commented upon earlier. Incorporation of the void factor would largely correct this discrepancy.

6.1. *Other areas of application*

The measurement of pH_s has been conducted in a number of areas. Thus the pH in the tip of a crack has been measured by Kurov and Melekhov [97] and Lukomski [98], and Koichi [99] as well as Turnbull and Gardner [107–108]. Variations in pH_s have been suggested [100] as the reason for potential oscillations in corroding metals. The change in pH_s during anodization of Nb and Al is considered by Bairachnyi [101]. Further implications of pH_s in corrosion (Fe in Na_2SO_4) are raised by Kovalenko and Kovarskii [102] and Lazorenko-Manevich *et al.* [70] who use an updated version of the colorimetric method to study pH_s on iron. pH_s at the cathode of a chromic acid electrolysis all (and the role of the film there) are reported by Inui [103]. Matulis and Slizys [104] consider the problems of pH_s during Ni electrodeposition. Kelsall [105] has suggested that the anodic behaviour of sulphides, in the electrowinning of metals from these ores, could give rise to pH_s changes of major significance in the ensuing chemical/electrochemical reaction sequences.

7. Conclusions

It is strange and unfortunate that so important an area of research should be the subject of so much disagreement, and it is hoped that one effect of the present discussion will be to stimulate research in this area. How might such work be done? First of all, the micro-electrode work must be repeated and extended using the superior electronics that are today available. Use of both glass and non-glass microelectrodes in a comparative study, should eliminate many of the discrepancies reported here. However real advances must come from the use of optical and spectroscopic techniques. One can envisage two approaches. Firstly the use of an optically-transparent electrode in the transmission mode, using an indicator in a UV–visible spectrometer, probably with a modulated potential applied to it. Secondly, the use of reflective studies where a beam can be located to graze the surface or reflect from it in specular mode so that a 'profile' of pH from the surface of the electrode into the bulk.

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