

## EXTRACTION AND EXAMINATION OF ANODIC DIFFUSION LAYER

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**Abstract.** An attempt has been made to extract the anodic diffusion layer by the porous electrode technique. The diffusion layer extracted under static conditions on porous nickel in sodium chloride reveals the existence of a sort of supersaturated metal chloride solution. The pH value of the layer ranges between 5.1-5.4. The rate of extraction is to be controlled carefully to ensure the quality of diffusion layer. The technique can be used successfully for the extraction of the diffusion layer.

In order to understand the mechanism of the chemical reactions taking place during electrochemical machining it is important to have a complete knowledge of the changes that take place in the composition of the anolyte. A type of viscous layer called the diffusion layer exists on the anode during ECM in the polishing plateau region. A determination of the composition and other properties such as pH and viscosity could produce some useful information about the electrochemical changes in the inter-electrode gap. Therefore, it is essential to devise a method for extracting the diffusion layer in the purest form.

The various attempts made in the past to collect any diffusion layer have been made on the cathode during electrodeposition process. The methods used are optical methods,<sup>1,2,3</sup> based on Schlieren interferometry. These have the disadvantage of being nonspecific and dependent on the shift in the index of refraction. It is, therefore, difficult to use it for analysis of several different ions in the solution.<sup>2</sup> Sampling methods consists of drainage, pinhole, and freezing techniques. The drainage methods<sup>3,4</sup> has been used for analysing the concentration of solution at the cathodes and pH determination at the cathode-solution interphase of nickel baths. The method is rather crude and consists of removing the cathode while the current is still on. The solution is drained and the diffusion layer is removed with a squeeze and collected for investigation.

The pinhole method<sup>5</sup> based on withdrawing the diffusion layer through a capillary tube mounted on the back side of the cathode over a hole, but is very unreliable as regards the purity of the sample, since the bulk electrolyte may become mixed with that of the layer.

The freezing method developed by Brenner used deposition on the outer surface of a hollow cylindrical electrode. Partially frozen isopentane is poured into the cylinder causing the diffusion layer to be frozen on the cylinder. The switching off of the current and the pouring of the frozen isopentane is done simultaneously. The method suffers from poor adhesion of the layer to the metal electrode and the collection of frost during the turning operations, required to sample the layer, but it gives a good estimate of the concentration profile and possibly the thickness of the diffusion layer.

**Experimental**

**Porous Electrode Method.** The porous electrode method has been used previously for extraction of the cathode-diffusion layer by Yannakopoulos and Brenner,<sup>6</sup> who collected the diffusion layer using porous stainless steel cathode in a copper plating bath.

The present method of extracting the anolyte is based on the porous electrode method. Since the diffusion layer is very much dependent on the flow rate and could be as thin as 0.003-0.005 in under static conditions, it was considered more appropriate to extract diffusion layer under static conditions. The technique used, employed a porous nickel sheet which had pores of a few microns in diameter and was about 40% porous and 1.5 mm thick. An approximate area of about 4 cm<sup>2</sup> of anode with a working area of 1 cm<sup>2</sup> was cemented by a resinous material on the open side of a small hollow metallic cube. Such a cube had a conical top with a small tube fitted at the top to open into a graduated pipette. (Fig. 1). The cubical chamber used had an inner dimension of about 2.5 cm each side. The graduated pipette was to note the rate of collection of the diffusion layer extracted. Thin copper wire was soldered to the nickel specimen, while chloroform, which is immiscible with water, but denser, was injected through the small hole to completely fill the chamber. The purpose of using such denser liquid was to let the diffusion layer rise immediately after it is extracted in the chamber and thus the rate of extraction was controlled.

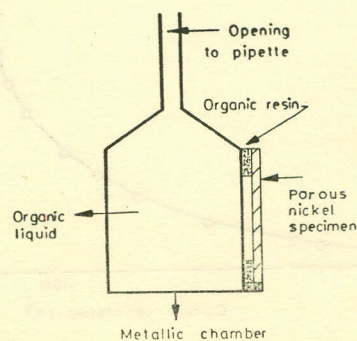


Fig. 1. Vertical section through middle of the extraction chamber.

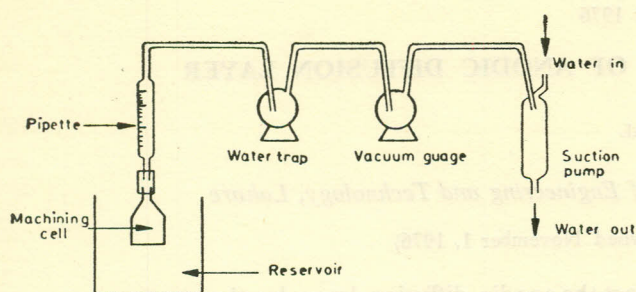


Fig. 2. The set-up for the extraction of anodic diffusion layer.

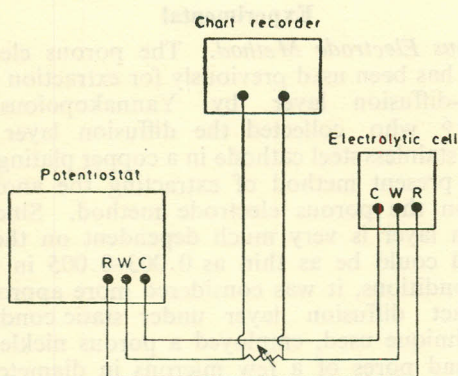


Fig. 3. Electrical circuit diagram for the extraction of anodic diffusion layer.

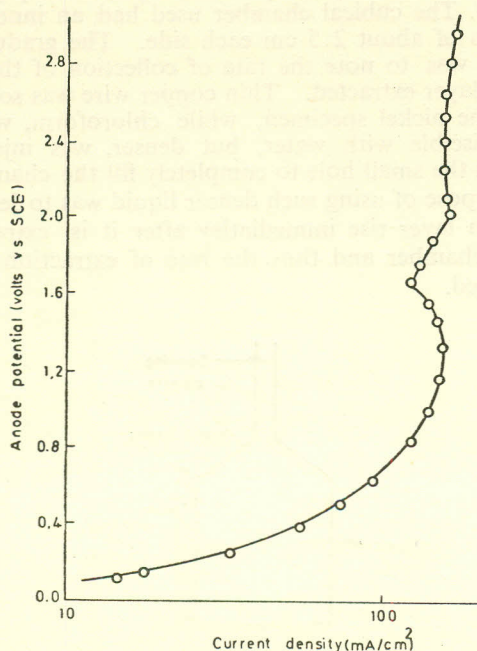
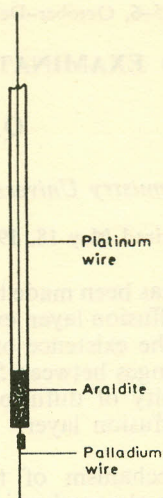


Fig. 4. Anodic polarization of nickel in 20% NaCl solution under static condition.



Figs. 5. Palladium hydrogen electrode.

The measuring pipette which was connected to the extraction chamber, was connected by a rubber tubing into a vacuum pump via a water tap and finally to a suction pump run by water (Fig. 2). A vacuum of about 10–15 mm Hg was found to be most suitable for most of the arrangements.

**Rate of Extraction.** The rate of extraction was easily controlled and kept usually in the range of 0.02–0.05 ml/min. The greater rate would extract the bulk electrolyte while a lesser rate would need more sampling.

After the electrical connection were (Fig. 3), made the chamber containing the specimen was dipped into the bulk solution to soak and then filled with chloroform and finally the potentiostat switched on at the anode potential between 1.5–2.0 V to obtain a polishing region. Although it is difficult to state the exact current density, a comparison was made between the porous nickel sheet and an ordinary sheet, and the area in the case of porous nickel sheet was about 15% higher with a current density of 400 mA/cm<sup>2</sup>. (Fig. 4). The first few drops collected were discarded. The electropolishing was continued for about 20–25 min and about 0.5–1 ml of the diffusion layer was collected and finally separated from the chloroform.

**Electrolytes Used.** The solutions were made of 10, 20, 30% w/v of sodium chloride (AR grade). The temperature of the solution was maintained at 15°. The electrolyte was discarded after each run.

**pH Measurements.** Since the amount of the diffusion layer collected was only 0.5 ml, a palladium hydrogen indicator electrode (Fig. 5) was used in place of the glass electrode for pH determinations. The electrode was made from a thin palladium wire of about 1 mm thickness and about 2 cm long, which was soldered to copper wire and then sealed in a glass tube. The palladium was anodically polarised at 30 mA for 10 min to clean the surface and then cathodically polarised for 30 min at 30 mA to saturate it with hydrogen.

**Analyses of Cl<sup>-</sup> and Ni<sup>2+</sup> ions.** Unicam spectrometer No. 300 was used to analyse the concentration of chloride and nickel ions after drawing the standard graphs from each ion respectively and the values of  $\Delta Ni$  and  $\Delta Cl$  are given in Table 1.

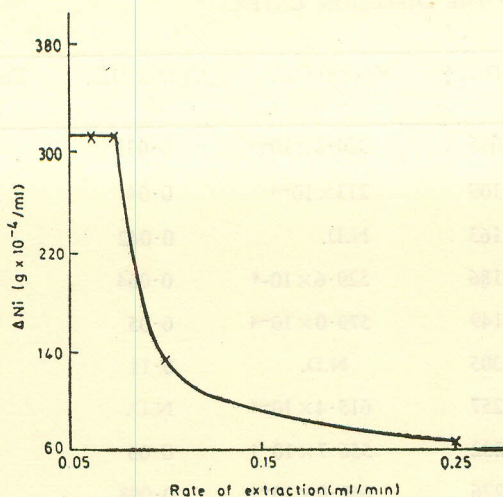


Fig. 6. Curve showing change in  $\Delta Ni$  vs rate of extraction on porous nickel in 10% sodium chloride solution (w/v).

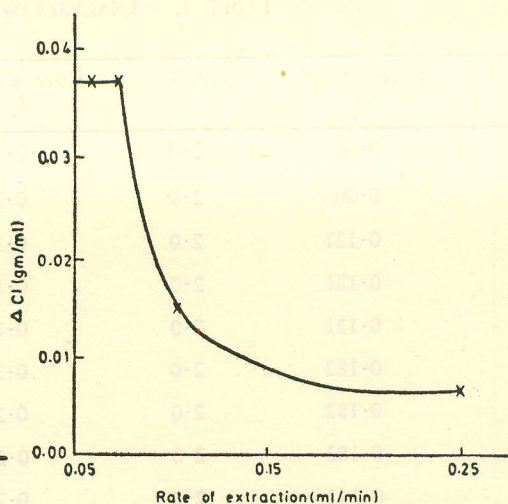


Fig. 7. Curve showing change in  $\Delta Cl$  vs rate of extraction on porous nickel in 10% sodium chloride solution.

### Results and Discussion

Anodic polarisations for the porous electrode (Fig 8.) show the very small effects of concentration, but there is a small effect, i.e. limiting current density is reduced with increasing concentration. The enrichment of the diffusion layer with more nickel ions in the case of more concentrated sodium chloride solution, i.e. in 30 and 20 than 10% solution, is perhaps due to the greater availability of chloride ions which behave as acceptors at the electrode/solution interface. During the electropolishing of nickel in hydrochloric acid Higgins<sup>7</sup> found that there was a decrease in the limiting current density as the solution became more concentrated. The explanation for such a decrease in limiting current density on electropolishing of copper in different concentrations of phosphoric acid has been given by Hoar.<sup>8</sup> According to him the decrease in limiting current density with increase of acid concentration is caused by an increase of solution resistance within the pores of the loose layer of corrosion product in the more concentrated solution.

*Effect of Rate of Collection on  $\Delta Ni$  and  $\Delta Cl$  in Diffusion Layer.* The analysis of the different diffusion layer samples obtained employing the different collection rate is shown in Table 1. The value of  $\Delta Ni$  decreases with the increase of extraction rate greater than 0.07 ml/min (Fig. 6). It shows that when the rate of collection is increased, some amount of the bulk solution is also drawn along with the diffusion layer and thus results in a decrease in  $\Delta Ni$ . The decrease in  $\Delta Ni$  is very dependent on the rate of collection but is constant, however, below the value of 0.05 ml/min. A similar decrease in  $\Delta Cl$  in the diffusion layer samples at different rates of collection is shown in Fig. 7. Subsequently the collection rate was kept at 0.07 ml/min.

It appears that the accumulation of chloride in the diffusion layer is dependent upon the nickel atoms removed from the metal lattice and their existence in the diffusion layer. As the concentration of nickel ions in the diffusion layer increases, so does

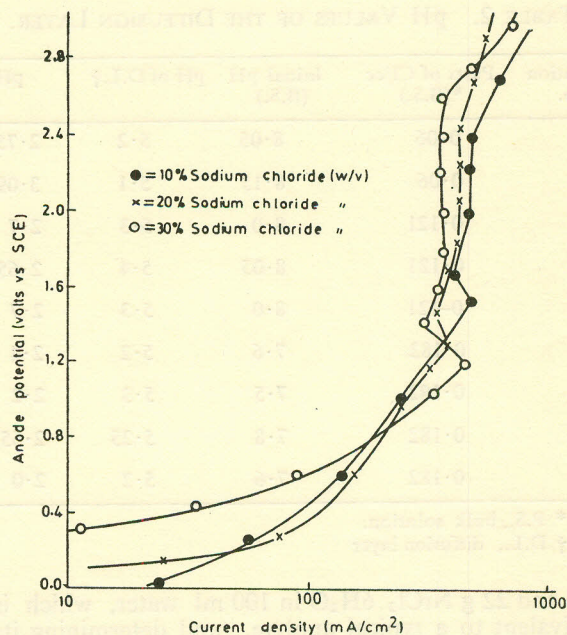


Fig. 8. Anodic polarization curves of porous nickel in sodium chloride solutions in static conditions.

the chloride ion concentration.

*pH Value of the Diffusion Layer.* From the Table 2 it appears that in all cases, pH value showed a decrease as compared to the pH value of bulk electrolyte. The change in pH is independent of the electrolyte concentration and of the current density. The difference in pH value varies from 2 to 2.8. The reasons for such a decrease is the depletion of OH ions in the diffusion layer. The consumption of OH probably takes place in the precipitation of nickel ions at the diffusion layer-bulk solution interface. Thus the hydrogen ions are increased in the diffusion layer resulting in a decrease of pH. A similar decrease in pH at the aluminium anode in sodium chloride has been found by Edeleanu.<sup>9</sup>

A comparison was made of the pH value of sample solution prepared from dissolving 30 g sodium chlo-

TABLE 1. ANALYSES OF THE DIFFUSION LAYER.

Solution No.	Cl/cc (B.S.)* (g)	A.P. (V)	Cl/cc in D.L. † (g)	Ni/cc in D.L. (g)	$\Delta$ Cl/cc in D.L. (g)	Theoretical $\Delta$ Cl (g)
1	0.06	2.0	0.095	$320.8 \times 10^{-4}$	0.035	0.0357
2	0.06	2.0	0.109	$213 \times 10^{-4}$	0.04	0.0357
3	0.121	2.0	0.163	N.D.	0.042	0.059
4	0.121	2.0	0.186	$529.6 \times 10^{-4}$	0.064	0.059
5	0.121	2.0	0.149	$579.0 \times 10^{-4}$	0.05	0.059
6	0.182	2.0	0.305	N.D.	0.11	0.078
7	0.182	2.0	0.257	$615.4 \times 10^{-4}$	N.D.	0.078
8	0.182	2.0	0.232	$556.7 \times 10^{-4}$	0.06	0.078
9	0.182	2.0	0.276	$662.0 \times 10^{-4}$	0.098	0.078

\*B.S., bulk solution  
†D.L., diffusion layer

TABLE 2. pH VALUES OF THE DIFFUSION LAYER.

Solution No.	Parts of Cl/cc *(B.S.)	Initial pH (B.S.)	pH of D.L.†	pH
1	0.06	8.05	5.2	2.75
2	0.06	8.15	5.1	3.09
3	0.121	8.0	5.3	2.7
4	0.121	8.05	5.4	2.65
5	0.121	8.0	5.3	2.7
6	0.182	7.6	5.2	2.4
7	0.182	7.5	5.3	2.2
8	0.182	7.8	5.25	2.55
9	0.182	7.6	5.2	2.0

\* P.S., bulk solution.  
† D.L., diffusion layer

ride and 22 g  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  in 100 ml water, which is equivalent to a typical anolyte, and determining its pH value after the addition of small amount of sodium hydroxide solution. The precipitation starts by the appearance of turbidity at a pH value of 6, which is completed after the pH has reached a value of 6.5. The value of the pure specimen anolyte artificially prepared was 5.1. Since the value of the diffusion layer collected lies below 5.5, it suggests that the nickel does not exist in a precipitate form but in some sort of solution.

It is probable from the above discussion that nickel atoms from the metal lattice dissolve and become concentrated in the diffusion layer and elevated in some sort of chloride of nickel. So the concentration of chloride ions of the bulk solution. Saubester<sup>10</sup> has tried to explain such a possibility while explaining the anodic dissolution of nickel in a plating bath of the Watts type. According to him it is probable that the electrode potential for the formation of  $\text{NiCl}_4^{++}$  is less negative than for  $\text{Ni}^{++}$  formation. Since nickel

TABLE 3.

Solution concn (w/v)	10%	20%	30%
Current density	450 mA/cm <sup>2</sup>	415 mA/cm <sup>2</sup>	350 mA/cm <sup>2</sup>
Current efficiency (%)	60.85	57.85	66.9

can exist as  $\text{Ni}(\text{H}_2\text{O})_4^{++}$  it may exist as a chloride complex. Hence some intermediate chloride ion complexes such as  $\text{NiCl}(\text{H}_2\text{O})_3$ ,  $\text{NiCl}_2(\text{H}_2\text{O})_2$  or  $\text{NiCl}_3(\text{H}_2\text{O})^-$  may exist. The greater concentration of nickel ions and the additional chloride ion needed to satisfy the charges for nickel ions in the anodic diffusion layer may become depleted of water molecules resulting in the increase of viscosity of the diffusion layer.

Greene<sup>11</sup> obtained a much higher corrosion rate on stainless steel specimens under the potential-controlled than under chemical-controlled conditions, and suggested that this may be due to increased chloride concentration on or near the anode.

From the Table 1,  $\Delta\text{Cl}$  in diffusion layer and theoretical  $\Delta\text{Cl}$  based on  $\text{NiCl}_2$  basis shows that the decrease in the value of  $\Delta\text{Ni}$  is proportional to a decrease in  $\Delta\text{Cl}$  in the diffusion layer, which further suggests the probable nickel chloride formation in the diffusion layer. Thus at the metal-diffusion layer interface, the probable reaction is between the chloride ions and the metal cations which form some sort of chloride depending upon the stability of the compound formed. It may be in this solvated form that it exists in the diffusion layer while at the diffusion layer-bulk solution interface, probably the chloride of nickel hydrolyses to form  $\text{Ni}(\text{OH})$  thus consuming most of the hydroxide ions. Moreover, its increase in the bulk solution, i.e. the enrichment of hydroxide ions, shows that the major existence of hydroxide ions is in the bulk solution.

**Conclusions**

(i) The diffusion layer can be extracted in a relatively pure form employing suitable conditions by using a porous anode material. (ii) pH value of the diffusion layer is lower than the bulk solution to keep the nickel ion in soluble form. (iii) Accumulation of chloride ions in the diffusion layer is proportional to the concentration of nickel ions dissolved from the anode.

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