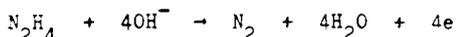


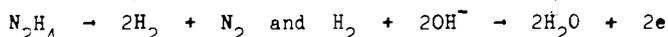
## REACTION MECHANISMS OF THE HYDRAZINE ELECTRODE

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Manchester, England.1. Introduction

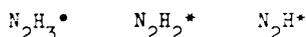
The overall reaction at the hydrazine electrode is:-



Pavela<sup>(1)</sup> suggested that the mechanism involves the anodic oxidation of hydrogen derived from the decomposition of hydrazine, i.e.

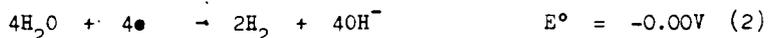
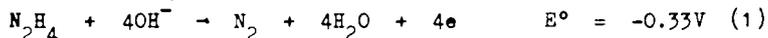


Alternatively, Szpak<sup>(2)</sup> et al concluded that at the hydrazine electrode the hydrazine molecule is systematically degraded through various radicals, e.g.



to finally produce nitrogen gas.

The reversible electrode potentials calculated from Gibbs Free Energy data for the Pavela and Szpak mechanisms are respectively 0.000V and -0.33V, against a hydrogen electrode in the same solution. The reported values for the open circuit potential of the hydrazine electrode are in the range -0.03V + -0.16V<sup>(3)(4)(5)</sup>. Consequently it has been suggested<sup>(6)</sup> that the observed open circuit potential of the hydrazine electrode is a consequence of the oxidation of hydrazine(1) proposed by Szpak<sup>(2)</sup> and the electrolysis of water (2).



No conclusive data has been published however, on the nature of the reactions occurring on hydrazine electrodes working under the conditions encountered in fuel cells. A study was therefore made of the reactions occurring on the hydrazine electrode by investigating the reaction products and the discharge curves associated with a typical working electrode. This paper describes the results obtained on an uncatalysed sintered nickel electrode, worked under conditions where the fuel concentration was strictly controlled with respect to the current being drawn from the system.

2. Experimental2.1 Apparatus

The apparatus is shown schematically in Fig. 1. The electrode A, diameter 5.7 cm was secured in the wall of the electrolyte cell B, by the Acrylic cover C. The gaseous reaction products were removed from the cell by the ports D and E. Ammonia which was produced at high current densities was removed from the effluent gas by a standard solution of hydrochloric acid in the scrubber F. The flow rate and the composition of the gas passing from the scrubber were respectively measured on the bubble flow meter G and a gas chromatograph.

The fuel mixture of hydrazine hydrate in 7M potassium hydroxide solution was contained in the reservoir H. The fuel mixture was forced from the reservoir H through the capillary J to the chamber K at the rear of the electrode. The fuel flow was controlled by varying the nitrogen gas pressure applied to the tank H and its flow rate was determined from the differential pressure L developed across the capillary J. The fuel mixture flowed through the test electrode into the cell B, and the excess liquid that accumulated in the cell was drained away via the tube N. The cell B was contained in a water jacket maintained at 60°C. The current flowing between the test electrode A and the auxiliary electrode P was controlled by the resistance Q and measured by the ammeter R. The potential of the electrode A was measured against a mercury mercurous oxide half cell S on the valve voltameter T then the results were transposed to the potential against a hydrogen electrode in the same electrolyte.

## 2.2 Procedure

An electrode 5.7 cm diameter was cut from 70% porous, 0.08 cm thick, sintered nickel plaque. The electrode was cathodised for five minutes in 10% sulphuric acid solution and thoroughly washed in distilled water. After securing the electrode in the cell wall, the interior of the box was filled with a 7M solution of potassium hydroxide containing various concentrations of hydrazine hydrate.

When the cell electrolyte attained a constant temperature of 60°C the fuel mixture was fed to the electrode at a predetermined flow rate. The working potential of the electrode and the analysis of the effluent gas were determined for current densities between 0 and 500 mA.cm<sup>-2</sup> at various flow rates and concentration of fuel.

## 3. Results

### 3.1 Gaseous Evolution from a Working Hydrazine Electrode

The gases evolved from a working hydrazine electrode were analysed and the results are shown in Table 1 where the respective flow rates of nitrogen and hydrogen are quoted at various current densities when the fuel concentration was 1.5M and its flow rate was 30 ml.min<sup>-1</sup>.

Table 1

Gas Evolution for a Working Hydrazine Electrode

Working Potential	Current Density	Nitrogen	Hydrogen	Nitrogen Calculated from the Current + H <sub>2</sub> Evolved
V	mA.cm <sup>-2</sup>	ml.min <sup>-1</sup>	ml.min <sup>-1</sup>	ml.min <sup>-1</sup>
-0.075	50	6.46	4.78	5.03
-0.066	100	5.7	2.0	6.29
-0.050	150	7.6	0.2	8.0
-0.035	200	11.4	0.1	10.65
-0.025	250	15.5	0	13.2
+0.030	300	20.25	0.25	16.1
+0.038	350	20.3	0.4	18.7
+0.045	400	23.8	0.73	22.56
+0.050	450	30.5	1.80	24.7
+0.055	500	29.2	3.4	28.1

A graph of the increase in working potential with current density is shown in Fig. 2. Similarly, Fig. 3 shows the working electrode potential plotted against hydrogen evolution expressed for convenience as  $\log_{10} H_2$  evolved on closed circuit.

The experimental technique used for quantitative measurements of hydrogen evolution was not capable of detecting the small amounts of gas evolved within the potential range  $-0.035V$  to  $+0.030V$ . The observed results plotted in Fig. 3 however, appear to suggest a relationship between the  $\log_{10} H_2$  evolved on closed circuit and the working potential, which graphically follows a parabolic curve. This curve, shown in Fig. 3, was therefore extrapolated to pass through a minimum, and it is interesting to note that the potential of the minimum coincided with current density inflexion  $x$  shown in Fig. 2.

### 3.2 Effect of Fuel Flow Rate on a Hydrazine Electrode

When the flow rate of 0.5M fuel through the electrode was varied, the inflexion in the discharge characteristic shown in Fig. 2 was found to be dependent upon the rate at which fuel mixture passed through the system. Table 2 shows the correlation between fuel flow rate and the inflexion current density.

Table 2

<u>The Effect of Fuel Flow Rate</u>	
<u>Fuel Flow Rate</u>	<u>Inflexion Current Density</u>
ml.min <sup>-1</sup>	mA.cm <sup>-2</sup>
37	140
56	200
78	250
140	385
220	550

### 3.3 Effect of Fuel Concentration on a Hydrazine Electrode

At 30 ml.min<sup>-1</sup> the concentration of the fuel passing through a working hydrazine electrode was varied between 0.5M and 4.0M. The inflexion in the discharge characteristics observed in previous experiments was found to be dependent upon the fuel concentration as shown in Table 3.

Table 3

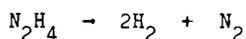
<u>The Effect of Fuel Concentration</u>	
<u>Hydrazine Concentration</u>	<u>Inflexion Current Density</u>
M	mA.cm <sup>-2</sup>
0.5	90
1.0	190
2.0	390
4.0	>500

## 4 Discussion

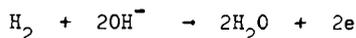
All the experiments on working hydrazine electrodes produced an inflexion in the discharge characteristic as the potential of the electrode passed through zero on the hydrogen scale (Fig. 2). The points of inflexion were shown to depend upon the availability of fuel, either in terms of concentration or flow rate. If the polarisation curve in Fig. 2 is plotted in terms of potential against  $\log_{10}$  (current density) shown in Fig. 4, then it can be seen that the graph displays two distinct

straight Tafel lines A and B. These lines together with the inflexion observed in Tables 2 and 3 suggest that the electrode can work via two mechanisms. As the theoretical and observed nitrogen evolution rates agree within experimental error it was concluded that the measured evolutions of hydrogen and nitrogen were faradaically consistent with the currents drawn from the working electrode. This justifies the conclusions drawn from Fig. 3 which shows that the evolution of hydrogen was at a minimum in the region of zero potential and it is probable that the mechanism changed at this point.

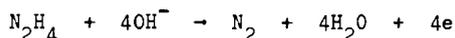
Susbielles and Bloch<sup>(e)</sup> have suggested that the observed open circuit potential of the hydrazine electrode is a mixed potential arising from the direct oxidation of hydrazine and the electrolysis of water. In this case the hydrogen evolution should increase as the potential of the hydrazine electrode becomes more negative relative to the hydrogen electrode. Conversely when the hydrazine electrode is at zero volts on the hydrogen scale there should be no nett evolution of hydrogen. The results in Fig. 3 show that at zero potential the hydrogen evolution appears to pass through a minimum, and that it increases directly with increases in the negative potential. This would suggest that the potential is a consequence of two simultaneous reactions which occur in the region negative to the hydrogen electrode. The negative potentials however, exclude the possibility of the hydrazine electrode working via the thermochemical reaction



and the electrochemical reaction



This leaves the more probable mechanism involving the direct oxidation of hydrazine



associated with the simultaneous evolution of hydrogen by the electrolysis of water



The rate equation for electrochemical processes is

$$i = i_0 \exp \left[ -\frac{nF}{RT} a \eta \right]$$

where  $i$  = Current density ( $\text{A.cm}^{-2}$ ) supporting an overpotential  $\eta$  (V)

$i_0$  = Exchange current ( $\text{A.cm}^{-2}$ )

$n$  = Number of electrons passed

$F$  = Faradaic equivalent

$R$  = Gas Constant

$T$  = Temperature ( $^{\circ}\text{K}$ )

$a$  = Exchange coefficient

The terms  $i_0$ ,  $n$ ,  $F$ ,  $R$ ,  $T$  and  $a$  are constants provided the concentration of reactants remain constant. Under these circumstances the rate equation is simplified to,

$$i = K_1 \exp [-K_2 \eta]$$

where  $K_1$  and  $K_2$  are constants. The relationship between the current  $i_N$  and the overpotential  $\eta_N$  associated with the direct oxidation of hydrazine becomes,

$$i_N = K_{1N} \exp [-K_{2N} \eta_N]$$

Similarly the current  $i_H$  associated with the electrolysis of water is,

$$i_H = K_{1H} \exp \left[ -K_{2H} \eta_H \right]$$

The ratio of the currents for both the reactions can be expressed as

$$\log \frac{i_N}{i_H} = A + K_{2H} \eta_H - K_{2N} \eta_N \quad (3)$$

but the relationship between  $\eta_N$  and  $\eta_H$  is

$$\eta_N = 0.33 - \eta_H$$

Therefore the expression (3) above becomes of the form

$$\log \frac{i_N}{i_H} = B + C \eta_H$$

where B and C are constants.

It can be seen that if at negative potentials on the hydrogen scale, the reaction involving the direct electrochemical oxidation of hydrazine occurs simultaneously with the electrolysis of water on a working hydrazine electrode, then the ratio

$\log \frac{i_N}{i_H}$  should be proportional to the overpotential  $\eta_H$ . Values of  $i_N$ ,  $i_H$  and  $\eta_H$

were therefore evaluated from the negative region of Table 1 and the results are shown in Fig. 5. It can be seen that the overpotential  $\eta_H$  was proportional to  $\log \frac{i_N}{i_H}$  indicating that the hydrogen evolution was an electrochemical process arising from the electrolytic decomposition of water.

As the evolution of hydrogen at negative potentials is an electrochemical process governed by the rate equation

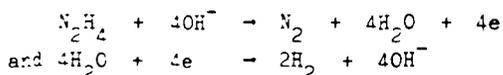
$$i_H = i_0 \exp \left[ \frac{nF}{RT} c_H \eta_H \right]$$

it can be seen that at zero overpotential the hydrogen evolved would be equivalent to the exchange current  $i_0$ . Now Fig. 3 shows that the term  $\log_{10} H_2$  evolved at closed circuit would pass through a minimum value as the potential passes through zero. It was therefore possible to calculate the hydrogen evolution at zero potential and this was found to be  $0.616 \text{ ml. min}^{-1}$ , which is equivalent to a current  $I = 8.85 \times 10^{-3} \text{ A}$ . The exchange current for this reaction was estimated<sup>(7)</sup> at  $i_0 = 4 \times 10^{-7} \text{ A. cm}^{-2}$ . The active area of the hydrazine electrode was therefore calculated from the ratio

$$\frac{I}{i_0} = 2.21 \text{ m}^2$$

A typical hydrazine electrode with a superficial area of  $16 \text{ m}^2$  would weigh  $3.2 \text{ g}$ . The active area to weight ratio would therefore be  $0.7 \text{ m}^2 \cdot \text{g}^{-1}$ . This result agrees closely with the value of  $0.66 \text{ m}^2 \cdot \text{g}^{-1}$  calculated from porosity measurements on sintered nickel plaques.

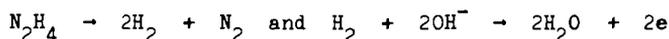
Thus the application of the rate equation to the electrochemical reactions



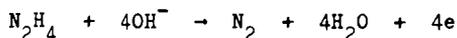
produces a result that theoretically correlates with the observed values of electrode

active area, and the proportional relationship between  $\log \frac{i_N}{i_H}$  and the overpotential  $\eta_H$  at negative potentials below 0.0V. It was concluded therefore that the working potential of a hydrazine electrode in the region negative to zero on the hydrogen scale, is a consequence of two competing electrochemical reactions, the oxidation of hydrazine and the decomposition of water.

The reactions occurring in the region positive to zero on the hydrogen scale on a working hydrazine electrode were far more complex. Fig. 3 shows that as the working potential of the hydrazine electrode increased above zero, there was a net increase in hydrogen evolution. This phenomena was associated with the straight line Tafel plot B shown in Fig. 4. The results show that it is not possible to correlate this increase in the hydrogen evolution with the reactions proposed by either Pavela<sup>(1)</sup> i.e.



or Szpak<sup>(a)</sup> i.e.



The evolution of ammonia in this region has been detected on many occasions and it is probable that a number of partial oxidation processes are involved. The dependence of the inflexion current density on the mass transfer of hydrazine to the reaction interface would suggest that diffusion processes were occurring (Tables 2 and 3) but further work will be required to identify these reactions.

#### References

1. Pavela, Suomen Kemistilehti, 30B, 240, 1957.
2. Szpak, Stonehart and Katan, *Electrochimic Acta* 10, 563, 1965
3. Gillibrand and Lomax, 'Batteries', Ed. Collins, D.H. Pergamon Press, 1963.
4. Baker and Eisenberg, Abstract 45, Extended Abstracts Electrochem. Soc., Boston, September, 1964
5. Jasinski, *Electrochem. Technology*, May-June, 1965, p. 129-132
6. Susbielles and Bloch, *Compt. Rend Acad. Sci. Paris*, 252, 685, 1962.
7. Bockris, *Modern Aspects of Electrochemistry*, Butterworths, 1954, p. 199.

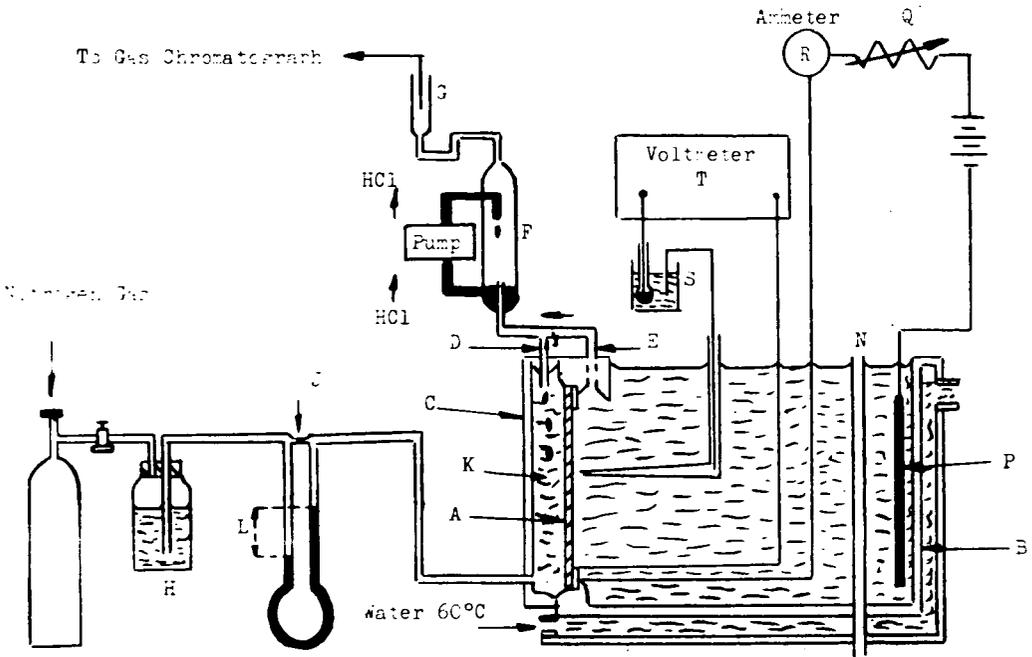


Fig. 1. Apparatus for Investigation on Single Electrodes

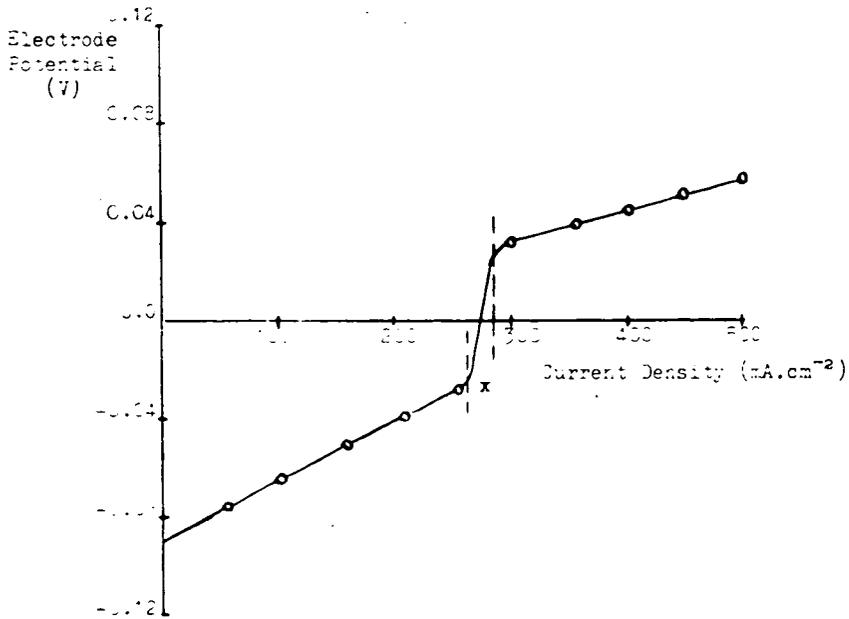


Fig. 2. Typical Discharge of a Hydrazine Electrode

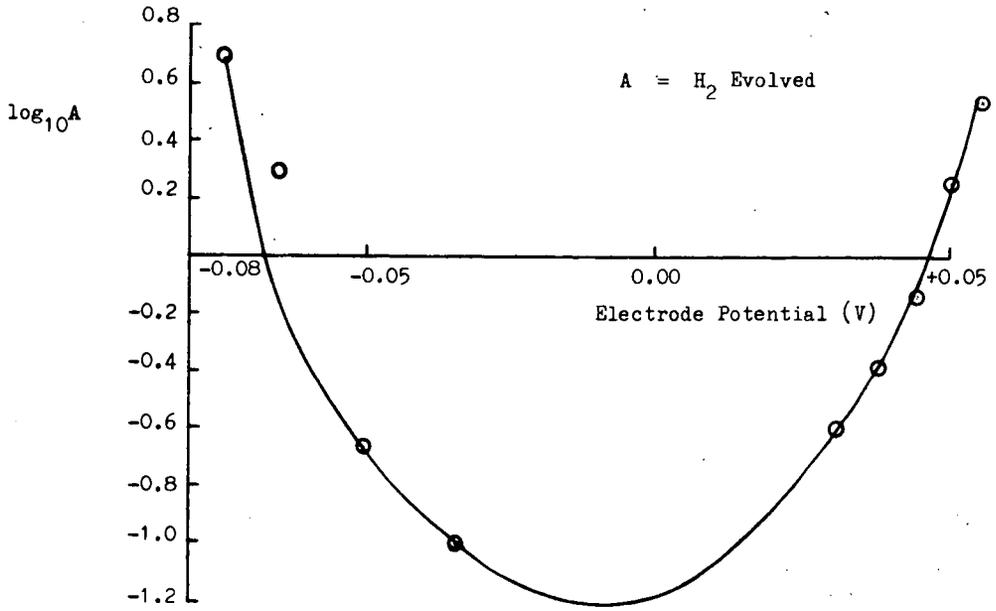


Fig. 3 Hydrogen Evolution from a Hydrazine Electrode

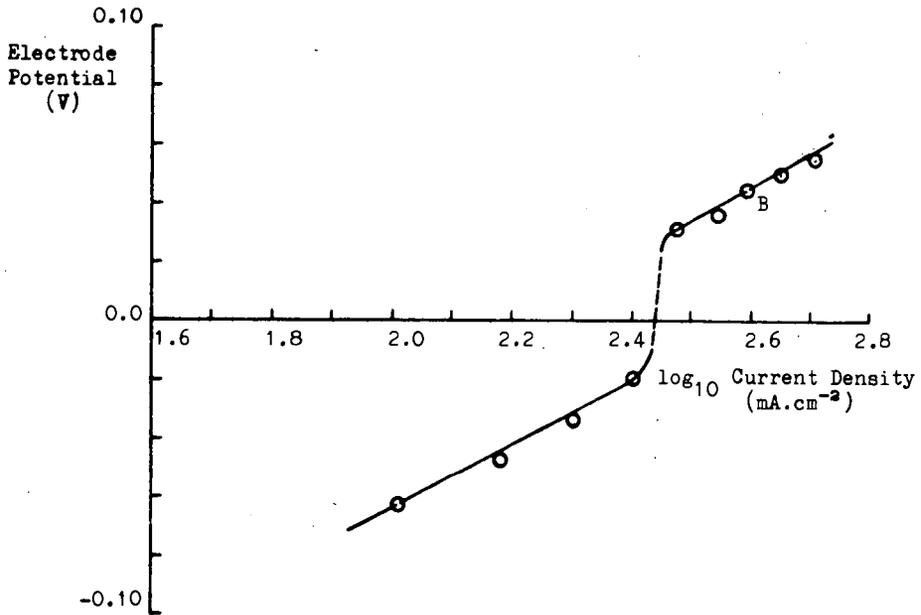


Fig. 4 Tafel Plot for a Working Hydrazine Electrode

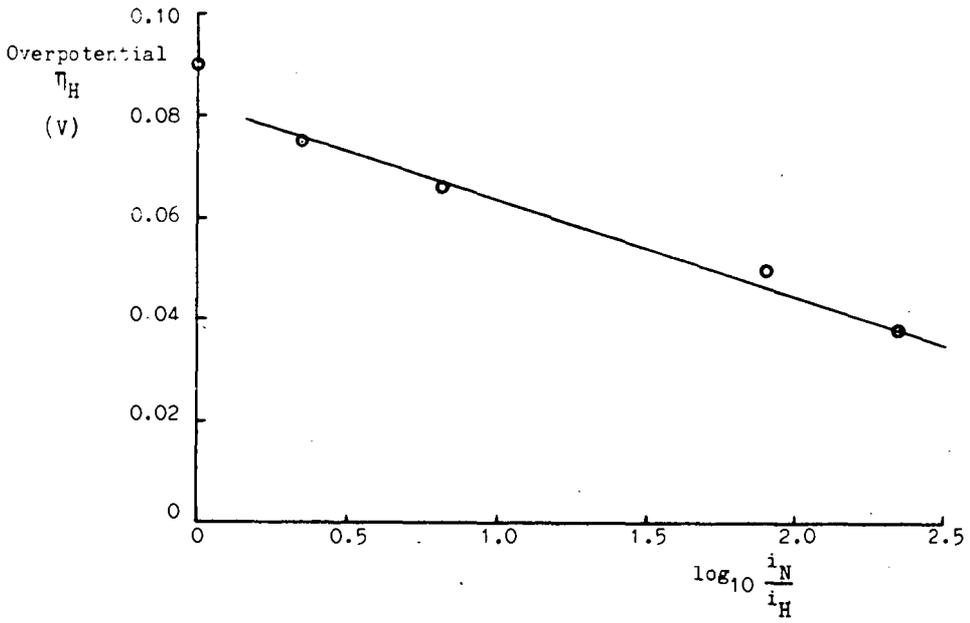


Fig. 5 Relationship Between Overpotential,  $\eta_H$  and  $\log_{10} \frac{i_N}{i_H}$