

Raney Type Transition Metals as Fuel Electrode Catalysts

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ABSTRACT

Porous metal electrodes incorporating Raney catalysts are prepared by powder techniques from transition metals of the first and eighth groups. Half-cell and fuel cell measurements are taken in various aqueous electrolytes at temperatures from 20° to 100°C. At 80°C in either 5N KOH or 5N H₂SO₄ electrolyte, both hydrogen and methanol yield current densities beyond 300 ma/cm². In 5N K₂CO₃ electrolyte, there are limiting current densities of the order of 10 ma/cm². Neither hexane nor methylcyclohexane display appreciable electrochemical oxidation under the conditions of this report. The methanol reaction appears to approach complete oxidation; this conclusion applies in both acid (CO₂-formation) and alkaline (carbonate formation) electrolyte as well as for both half-cell and fuel cell operation.

There is so far no satisfactory low-temperature hydrocarbon fuel electrode. On the other hand, electrochemical conversion at an appreciable rate of partially oxidized hydrocarbons such as methanol and glycol seems to be possible, but only in the case of methanol was complete oxidation reported (1). At least some of the reactions involved in the stepwise oxidation at the anode must be accelerated catalytically in order to achieve a sufficient reaction rate at low temperatures (below 200°C). The electrode must, therefore, contain catalysts accelerating, above all, the acceptance of electrons from the fuel by the anode.

The activity of a catalyst seems to be related to the number of crystallographically disoriented surface atoms. Defect structures are attained by several processes which are not discussed here. In the present investigations it was decided to use Raney catalysts because, on the one hand, they can be produced at room temperature so that recrystallization enhanced by elevated temperatures is avoided, and because, on the other hand, a relatively simple method of Raney electrode preparation was described by Justi (2-4). Raney catalysts are made by alloying the catalyst material with a base metal, for instance aluminum, which is subsequently dissolved from this alloy leaving the catalyst metal in a highly active state.

Justi has used Raney nickel electrodes, especially as hydrogen electrodes, with outstanding success. He also mentioned work with Raney electrodes based on copper, tungsten, molybdenum (for carbon monoxide oxidation), and palladium (as a pH electrode), but he did not discuss his results with these metals in detail. The present work must be regarded as an application, and possibly an extension, of Justi's technique.

The preparation of fuel electrodes from Raney copper, cobalt, nickel, rhodium, palladium, and platinum is described in the following along with the re-

sults obtained from tests with hydrogen, methanol, and hydrocarbon fuels.

Experimental Procedure

All electrode specimens were prepared in the form of porous disks by compressing a mixture of skeleton metal powder with powdered Raney alloy and subsequent dissolution of the base metal of the Raney alloy. In all cases the skeleton material and the catalytic substance of the Raney alloy were identical. The diameter of the disks was 1.2 cm. They were glued around the circumference into an electrode support ring made of Plexiglas. The projected surface area of the active part of the disk was 0.65 cm².

The Raney alloys were prepared by alloying the catalyst metal with aluminum. In order to achieve a high alloying rate without melting the components beforehand, the two metals were mixed in the form of powders and compressed into disks. The disks contained in individual crucibles were heated in an electric furnace until the alloying reaction started with conflagration at about 700°C. Owing to the heat of reaction, the temperature increased, causing the mixture to melt and to form a homogeneous alloy. Immediately after this reaction was completed, the alloy solidified; it was then removed from the furnace. It would not be possible, at least under mild conditions, to eliminate the aluminum from, in particular, the XAl compound where the catalyst metal X is compounded with aluminum at an atomic ratio of 1:1. The percentage of the catalytically active metal in the alloy, therefore, must be lower than the stoichiometric ratio of 1:1. It must, however, be above, say, 20 at. % because the alloy becomes too ductile for powdering below this limit.

For the preparation of the electrode disks, one part by volume of a pure metal powder, the skeleton material, was mixed with one part by volume of powdered Raney alloy. The mixture was subsequently compacted by pressing it into disks. Justi's

technique to achieve homoporosity by fractionation of the powders was not applied at this research stage.

The copper, cobalt, and nickel electrodes were prepared by compacting the powders at a pressure of 3,000 kg/cm², and sintering them at 400°C (Cu) and 600°C (Co, Ni). The platinum, palladium, and rhodium electrodes were left unsintered in order to prevent the formation of the stable compound XAl from the Raney alloy and the skeleton metal during the heat treatment. The unsintered electrodes were compacted at a pressure of 10,000 kg/cm², and at the same time two platinum screens were included with a view to increase the mechanical stability.

After cementation of the disks into a Plexiglas ring, the aluminum of the Raney alloy was dissolved by treating the electrode first with a dilute and then with a concentrated KOH solution, finally at a temperature of 80°C. The aluminum is not completely eliminated by this process. Further aluminum was dissolved anodically. A KOH solution was employed irrespective of whether the disks were used in alkaline or acid electrolytes because the dissolution rate of aluminum in acids is too large.

The electrodes were tested by taking current-potential plots using the half-cell system depicted in Fig. 1.

The test electrodes (porous disk cemented into a Plexiglas ring) were fixed in a Plexiglas holder providing a gas inlet. The electrical contact with the disk was established by two spring-type platinum wires to insure good contact. A platinum wire served as counter electrode. The electrode potential was measured against a calomel electrode using a Luggin capillary placed at a distance of 5 mm from the electrode surface, which gave a maximum measuring error of 50 mv. The ohmic polarization due to the ohmic resistances in the electrode and the electrolyte was not measured and consequently is still included in the potential values as reported. The measured potentials were not corrected for the diffusion potential between the electrolyte contained in the liquid junction (5N) and that at the reference electrode (0.1N); the involved error would not exceed 30 mv. The current was adjusted by means of a galvanostat. The measured amperages were converted into current densities by taking the projected surface area of the electrode to be 0.65 cm².

All electrodes were tested with gaseous hydrogen and methanol and some, in addition, with methylcyclohexane and hexane. The latter three fuels were

admitted to the electrodes using nitrogen as a carrier gas. The electrode gas excess pressures totalled 0.5-1 atm. Reference runs were made using pure nitrogen.

In addition to the gaseous fuels, the tests included formaldehyde, formic acid, and methanol, dissolved in the electrolyte.

Alkaline, acid, and carbonate electrolytes have been employed as 5N solutions in water. The majority of the tests performed to date have been run at 80°C.

After the described chemical dissolution of aluminum, further aluminum was dissolved in the half-cell anodically. To this end the electrode was used as a hydrogen electrode. The electrode potential was increased stepwise to about 200 mv below the reversible oxygen potential. Although mainly hydrogen is oxidized during this process, part of the current is due to dissolving aluminum.

In the case of nickel, the electrode activity was much greater when electrochemical activation was used. For example a Raney nickel electrode using hydrogen in a half cell at -650 mv yielded current densities of 12 and 80 ma/cm², respectively, when the electrode was activated chemically in 5N KOH at 40°C for 24 hr or activated electrochemically for ½ hr in 5N KOH at 40°C with an electrode potential of +150 mv. Electrochemical activation was not necessary with the other metals of the eighth group tested.

The amount of hydrogen dissolved in the electrode was reduced substantially prior to tests with methanol or hexane by passing a nitrogen stream through the electrode. To accelerate this process, a potential was applied which was about 200 mv below the standard reversible oxidation potential of the corresponding electrode metal:

Current Density-Potential Plots

Most of the results are plotted in the form of current density-potential characteristics.

All reported potential values were obtained within a few minutes after adjustment of the current and remained constant during the measuring period up to several hours. Figure 2 depicts the results with hydrogen in KOH solution.

With all electrodes the open-circuit potential reached the reversible hydrogen potential. Deviations within ±30 mv are due to variations of the potential of the calomel reference electrode. The nickel electrode shows a distinct limiting current density beyond which the polarization as a function of the current deviates strongly from linearity. As the diagram shows, the platinum electrode has

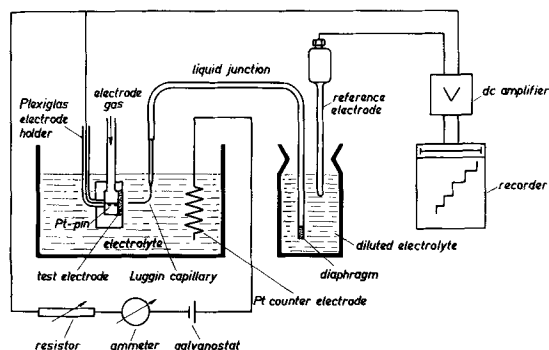


Fig. 1. Diagram of test stand for measuring current-potential plots.

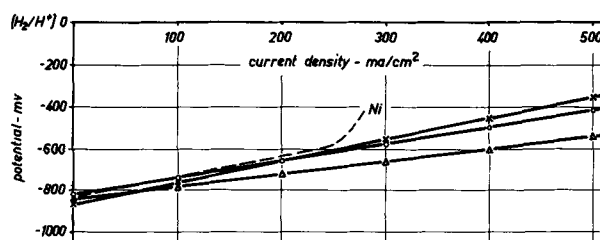


Fig. 2. Current density-potential plots of Raney electrodes with H₂ in 5N KOH at 80°C.

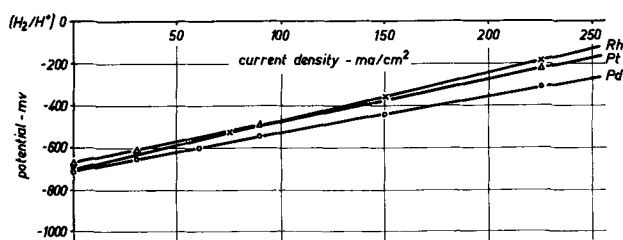


Fig. 3. Current density-potential plots of Raney electrodes with CH_3OH in 5N KOH at 80°C.

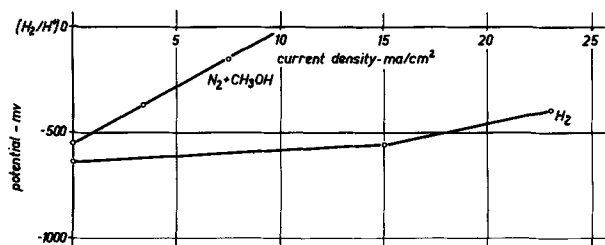


Fig. 4. Current density-potential plots of Raney palladium electrode with H_2 and CH_3OH in 5N K_2CO_3 at 80°C.

the smallest polarization. With palladium, platinum, and rhodium as hydrogen and methanol electrodes, the tests were not extended beyond current densities of about 500 ma/cm^2 and 300 ma/cm^2 , respectively, so that the respective limiting current densities were not ascertained.

The results obtained with the sintered nickel electrode, using hydrogen as fuel were inferior to those reported by Justi, presumably because of the much smaller number of active pores. It is thus assumed that all electrodes investigated may be improved by employment of better techniques of powder metallurgy.

Figure 3 shows the results with methanol fuel in KOH solution.

Again the polarization increased linearly with the current. The open-circuit potential was about 100-150 mv smaller than that with hydrogen. Here palladium furnished the best results.

If the KOH electrolyte is replaced by K_2CO_3 , very large polarizations are obtained both with hydrogen and methanol as fuels (see Fig. 4).

Large current densities were obtained not only

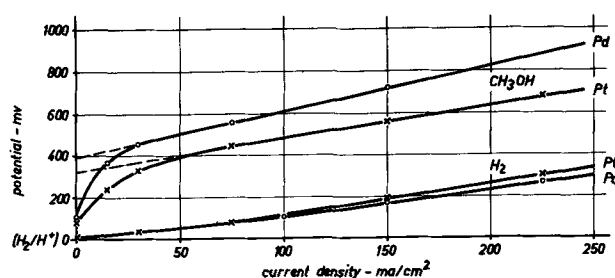


Fig. 5. Current density-potential plots of Raney electrodes in 5N H_2SO_4 at 100°C.

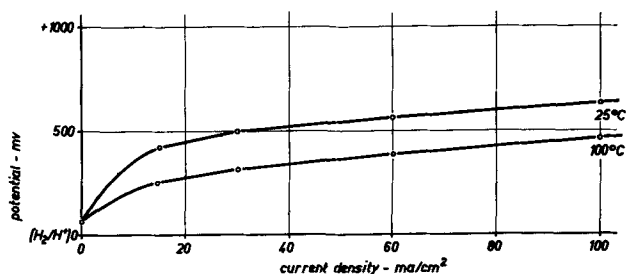


Fig. 6. Current density-potential plots of a Raney platinum electrode with CH_3OH in 5N H_2SO_4 as a function of temperature.

in KOH solution but also in H_2SO_4 solution with hydrogen and methanol as fuel (see Fig. 5 and 6).

With methanol, the polarization shows a peculiar nonlinearity at small current densities. With methanol in an acid solution, platinum proves to be superior to palladium as a catalyst. The open-circuit potential exceeds that of hydrogen by about 100 mv.

Figure 6 shows the temperature dependence of methanol oxidation as a function of the temperature between 25° and 100°C.

The above results are summarized in Table I together with results not illustrated so far. "Specific polarization" is defined as the slope of the curve potential *vs.* current density. For methanol in acid electrolyte, the slope is taken from the linear portion of the curve at large currents; in these cases the value of the open-circuit potential is complemented by the interception of the extrapolated linear part of the polarization curve with the ordinate. Copper and cobalt turned out to be unsatisfactory catalysts for methanol or hydrogen electrodes.

Table I. Open-circuit potential, specific polarization, and limiting current density with hydrogen and methanol, respectively, at 80°C

Catalyst	Electrolyte	H_2			CH_3OH		
		Open-circ. pot., mv	Spec. polar., ohm·cm ²	Limit. curr. den., ma/cm ²	Open-circ. pot., mv	Spec. polar., ohm·cm ²	Limit. curr. den., ma/cm ²
Cu	KOH	-780	3	10	—	—	zero
Cu	H_2SO_4	+20	24	10	—	not tested	—
Co	KOH	-850	4	50	—	—	zero
Ni	KOH	-820	0.9	240	—	—	small
Pd	KOH	-820	0.8	>500	-710	1.8	>300
Pd	K_2CO_3	-640	5	15	-550	55	10
Pd	H_2SO_4	+10	1.1	>300	+100	2.3	>300
					(+380)*		
Rh	KOH	-860	1.0	>500	-700	2.3	>300
Pt	KOH	-840	0.6	>500	-670	2.0	>300
Pt	H_2SO_4	+10	1.2	>300	+80	1.5	>300
					(+320)*		

* Basis for calculation of the specific polarization.

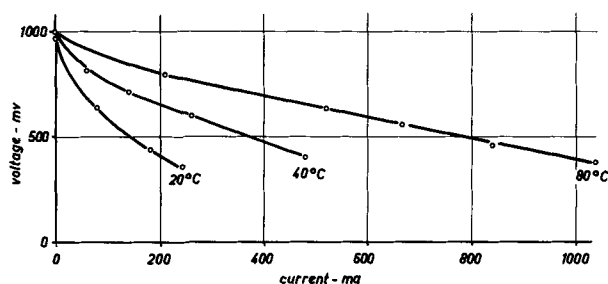


Fig. 7. Current-voltage plots of a fuel cell in 5N KOH as a function of temperature with methanol fuel (electrode area 12 cm²).

In addition, the following remarks may be made: (A) There was no appreciable electrochemical oxidation of hexane or methylcyclohexane with the described types of electrodes and under the described conditions. (B) Sintering of the noble metal electrodes destroys their activity with methanol and seriously affects their activity with hydrogen. (C) The current-potential plots with methanol are independent of whether the fuel is admitted as a vapor or dissolved in the electrolyte in excess concentrations. (D) In both KOH and H₂SO₄ solutions, formaldehyde and formic acid, dissolved in the electrolyte, are converted with current densities similar to those achieved with methanol.

Experiments with a Laboratory-Stage Alkaline Methanol Fuel Cell

A laboratory-stage methanol fuel cell was set up, using a palladium fuel electrode and a silver oxygen electrode of a projected surface area of 12 cm² each. The electrodes were spaced at 1 cm in an aqueous 5N KOH electrolyte to which methanol was added in amounts of 1 mole/l as a liquid admixture.

The current-voltage characteristic of the cell was plotted at 20°, 40°, and 80°C (Fig. 7).

It is apparent that, at the same voltage, the cell output rises about fourfold on increasing the temperature from 20° to 80°C. The characteristic does not change even after continuous operation for several weeks; the electrolyte had to be replaced several times during this period owing to the KOH consumption. The cell was used to examine the degree of conversion of, alternatively, methanol, formaldehyde, and formic acid.

Tests were run which showed that there was negligible activity of the methanol at the oxygen electrode.

A known amount of methanol was added to a cell, and the cell was operated until completely discharged. The total amount of current withdrawn was measured and compared to the calculated total current for complete oxidation to carbonate. The measured current corresponded to about 95% of the calculated current.

Methanol Oxidation Reactions

Various experimenters (1, 5-9) have found different reaction end products in methanol fuel cells. During the present program, several avenues have been followed in an attempt to investigate the course and the completeness of the methanol conversion.

In order to test their electrochemical activity, the supposed intermediates of the methanol oxidation were anodically oxidized in a half-cell arrangement. With formaldehyde as well as with formic acid large current densities were obtained at polarizations comparable to those observed with methanol. This holds for both an alkaline and an acid medium.

Another approach to the problem of the degree of oxidation is the chemical analysis of the electrolyte after extended operation. Therefore, the amounts of formaldehyde and formic acid were determined that were formed after a cell had been operated for 2 hr at, alternatively, 20° and 80°C from methanol owing to incomplete oxidation. The applied analytical procedure was based on the formation of an intensely colored complex of formaldehyde and chromotropic acid which was determined colorimetrically. Formic acid is reduced to formaldehyde by magnesium and sulfuric acid before its determination. Such a procedure was carried out for half-cells after 5000 coulombs had been withdrawn. In the case of alkaline electrolyte with a palladium electrode, the amounts of formaldehyde and formic acid totalled 5% of the converted electricity. With a rhodium electrode, they were about 10% thereof. In the case of an acid electrolyte, using a platinum electrode, the amount of formaldehyde was about 1%, and that of formic acid smaller than 0.1% of the converted electricity. There was no appreciable temperature effect.

The same analyses were conducted for the alkaline methanol fuel cell with a palladium electrode after 8000 coulombs had been withdrawn. The amounts of formaldehyde and formic acid corresponded to 1 and 3%, respectively, of the converted electricity.

Finally, at 20°C the laboratory stage alkaline fuel cell was operated on defined amounts of formaldehyde and formic acid in separate runs. Total current withdrawal was measured for each fuel and was found to be about 95% of the calculated current for complete oxidation in each case. This was in agreement with the tests run to determine fuel activity with methanol as the fuel.

These various findings lead to the conclusion that even at room temperatures methanol oxidation proceeds almost completely to carbonate or carbon dioxide on the Raney electrodes of the present study. This result appears to be independent of the electrolyte and of the half-cell *vs.* fuel cell operation.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1963 JOURNAL.

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Determination of the Internal Resistance of Leclanche Cells by Square-Wave Method

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ABSTRACT

The internal resistance of Leclanché dry cells was studied on shelf and during discharge by means of a square-wave technique. A constant-current square-wave signal was passed through the cell on test, and the potential variation across the cell displayed on a high-sensitivity oscilloscope with differential input. The instantaneous voltage drop in the oscilloscope pattern, caused by the leading edge of the constant current square wave, indicated the internal resistance of the Leclanché cells. The internal resistance is independent of the amplitude and frequency of the applied square-wave current and of the momentary d-c current. The type of manganese dioxide used in the cathode mix and the composition of the electrolyte influenced the internal resistance of D-size Leclanché cells, both undischarged and during 4-ohm continuous discharge.

In the past, both steady-state and transient measuring methods using either alternating or direct current were investigated for determining the internal resistance of dry cells. Results obtained by these methods were inconsistent. One of the simplest and least accurate methods is the d-c steady-state method in which the resistance is calculated from the potential drop at a certain current drain (1-4). Several d-c transient methods were developed (5-8). Generally, the a-c steady-state methods use various types of impedance bridges to separate the resistive (real) and reactive (imaginary) part of the impedance. Various arrangements were used by the several authors (9-18). The a-c transient method is represented by Brodd's (19) current pulse method.

Impedance of an electrical circuit consists of two parts: resistive and reactive. The resistive part is frequency independent while the reactive part varies with the frequency. The reactive part can include inductance or capacitance or both. In the case of Leclanché cells with relatively short leads, the inductance is negligible, and only the capacitive reactance and the pure resistive component have a role in the impedance.

In general, the separation of the resistive and reactive components of the impedance by the a-c bridge methods is a fairly lengthy operation or complicated instrumentation is involved, *e.g.*, the use of double-servo-controlled a-c bridge (20). During the changes taking place in the discharge and storage of cells, not only the resistive part can change but also the reactive part. Brodd's pulse method (19) yielded

only the resistive part of the impedance, whereas the square-wave current method gives information concerning the reactive part of the impedance as well as the resistive part. Very recently however, a pulse method was described (21) to measure parameters of the electrical double layer, namely, the reactive part of the impedance. Various square-wave techniques have been utilized previously for electrochemical studies (22-25).

In this modification of the method developed at this laboratory (25), a constant-current square-wave signal was passed through the test cell and the potential variation across the cell displayed on an oscilloscope. The instantaneous voltage drop in the oscilloscope pattern, caused by the leading edge of the constant-current square wave, represents the internal resistance of the Leclanché cell. Results concerning the reactive part of the impedance will be described in a later article.

Experimental

The block diagram of the circuit used to measure the internal resistance of Leclanché cells is shown in Fig. 1. The Leclanché cell A, was connected in series with a noninductive resistor B. This converted the constant-voltage output of the square-wave generator C, to constant current, since the value of resistor B is much larger than the sum of the impedances in the constant-current circuit loop (C-A-G-F). The voltage response of the square-wave current across the Leclanché cell was measured through oscilloscope probes (5X)D, with a high-