

PREPARATION AND ELECTROCHEMICAL TESTING OF INTERSTITIAL
COMPOUNDS AS FUEL CELL CATALYSTS

by

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INTRODUCTION

In March 1966, the Pittsburgh Coal Research Center of the Bureau of Mines, at the suggestion of E. Cohn of the National Aeronautics and Space Administration and funded by this organization, initiated a study of the interstitial compounds of the transition metals as fuel cell catalysts. The interest in the work was generated by a preliminary observation at Tyco Laboratories, Inc., of Waltham, Mass., that the interstitial carbide $\chi\text{-Fe}_2\text{C}$ is an active catalyst for the electrochemical reduction of oxygen. The Bureau's part in this program was to prepare cathode catalysts for alkaline hydrogen-oxygen fuel cells operating at low temperatures; the cathodic activity of these preparations was to be determined by Tyco Laboratories. The scope of the project was later enlarged by cooperative arrangement with ten other laboratories engaged in fuel cell work. The materials were made available to them for both cathodic and anodic activity tests in a variety of systems. The results obtained in two of these laboratories are presented in this paper.

The carbides of Fe have been prepared by the action CO, CO+H₂, or hydrocarbons on Fe (1,2,3)¹. When CO+H₂ is employed, Fe is in effect carburized with a mixture of CO and hydrocarbons, since CO reacts with

¹

Underlined numbers in parentheses refer to items in the list of references at the end of this report.

H_2 to form hydrocarbons in the presence of reduced Fe (Fischer-Tropsch synthesis). Hydrocarbons alone do not lead to complete carbiding (3), and CO alone tends to deposit unacceptable amounts of free carbon. The action of CO on Fe is very exothermic and there is a strong tendency for the Fe to become overheated. Reaction temperature should be carefully controlled below that at which the desired carbide decomposes. H_2 in the reacting gas helps remove the excess heat and minimizes the amount of free carbon in the product.

Co_2C is prepared by the action of CO on Co (4) and Ni_3C by the action of CO on Ni (5) at $250^\circ-280^\circ C$. In both cases, carbide formation is accompanied by deposition of free carbon, and the higher the reaction temperature, the greater the proportion of free carbon. Some features of the kinetics of the reaction of CO with Ni are presented in Fig. 1 from the published results of Eyraud (6). A fixed weight of reduced Ni was carburized with CO at different temperatures. Below $250^\circ C$, the rate of formation of Ni_3C was very slow but the product was substantially free from deposited carbon. At $285^\circ C$, the reaction was complete in about 30 hours, but Ni_3C was contaminated with free carbon. At temperatures above $300^\circ C$, large quantities of free carbon were deposited.

As with Fe, the reactions of CO with Co and Ni are strongly exothermic. However, H_2 can be employed to dilute CO in carburizing Co and Ni; Co_2C and Ni_3C can not be prepared under conditions of Fischer-Tropsch synthesis. The contrast in this respect with Fe may be noted.

The nitrides of Fe, Co, and Ni are prepared by reacting the metals with NH_3 . The phase diagram for the nitrides of Fe is shown in Fig. 2 (7); it shows the phases that are in equilibrium with N_2 at the pressures corresponding to the dissociation of NH_3 . $\epsilon\text{-Fe}_3\text{N-Fe}_2\text{N}$ has the most extended range of existence. With the exception of the γ -phase, the various nitrides of Fe may all be prepared at about 350°C , the composition of the product depending on the space velocity of NH_3 and the duration of nitriding. The nitrides of Co and Ni also have been prepared by the action of NH_3 on the metals but their preparation appears to be attended by unusual difficulties (8). Temperatures no higher than 350°C and high space velocities of NH_3 are recommended. Even so, the reported successes in the preparation of these nitrides have only been in terms of "milligram" or "up to a gram" quantities.

PREPARATION OF INTERSTITIAL COMPOUNDS

The scheme for preparing the interstitial compounds of Fe, Co, and Ni is shown in Fig. 3. The first step consists of preparing finely divided metals and mixtures of metals, or alloys. Since the rate of formation of carbides and nitrides by gas-solid reactions falls off as successive layers of the products increasingly obstruct the access of the reacting gas to metal substrates, it is important to start with

fine powders of metals. Also, the preparations were intended to be tested as contact catalysts where large specific surface areas are of obvious advantage. The different methods employed for preparing finely divided metals are indicated in the scheme.

The gas-solid reactions were carried out in horizontal vycor tubes of 1-inch diameter shown in Fig. 4. The tubes were fitted with metallic end pieces which had provisions for gas inlet and outlet. Fifty to one hundred grams of solids were processed at a time. Separate thermocouples monitored the temperature of the front end, the middle, and the rear of the powder beds. Fig. 5 is a photograph of the apparatus which included furnaces, thermoregulators, gas flow meters, safety valves, and a 12-point recorder for the thermocouples.

Reactions were carried out at atmospheric pressure. The leached Raney metals were treated with hydrogen at 450°C for 10-20 hours at an hourly space velocity of 1,000-2,500 before carbiding or nitriding. The hydroxides were generally reduced in situ.

The experimental conditions employed in the preparation of the carbides are presented in Table 1. Reduced metals were always allowed to cool down to at least 160°C before CO or CO+H₂ was introduced. When pure CO was employed as the carburizing agent, the concentration of CO in the exit gas was monitored by a differential type infrared detector.

When the concentration of CO in exit gas fell below 80 percent, power supply to the furnace was cut off by an automated arrangement. Higher CO conversions is conducive to run away temperatures and excess carbon deposition. The temperature of the powder bed was raised slowly and in steps. Several hours were usually allowed for the temperature to come up to the final level (see columns 4 and 5 in Table 1). With Co and Ni, the tendency for sudden overheating appears at about 180°-220°C in the presence of CO. Since the carburization of Co or Ni does not ordinarily proceed at measurable rates at temperatures below 250°C, the lower temperature represents the point of onset of carbiding of the active spots on the metal powders. Column 6, Table 1, gives the results of qualitative x-ray analysis of the carburized materials. The major detectable phase is listed first. The findings were further checked by chemical analysis of the products for carbon. As concomitant deposition of some free carbon is unavoidable, the combined or carbidic carbon must be distinguished from the free carbon. In practice, it is simpler to determine the total carbon and the free carbon, and to compute the combined carbon by difference. Total carbon was determined by igniting samples in excess O₂ and scrubbing CO₂ from the stream of combustion gases in towers packed with ascarite. The towers were weighed before and after the absorption of CO₂. The free carbon was determined as follows: Samples were digested in dilute (1:3) HCl at

60°-80°C for $\frac{1}{2}$ hour to drive off carbidic carbon as gaseous hydrocarbons. Free carbon is not affected by digestion with dilute HCl. The insolubles were filtered on a porous crucible, washed with hot water, and dried at 105°C. The crucible was then placed in a tube furnace and ignited in excess O₂. As before, CO₂ was scrubbed in ascarite towers. The results for total carbon and free carbon are given in columns 7 and 8, Table 1.

The experimental conditions employed for preparing the various nitrides of Fe are given in Table 2. Samples of Raney Fe were reduced with H₂ at 450°C before treatment with NH₃. The products were analyzed for nitrogen by the Kjeldahl method. When mixtures of Fe and Ag were treated with NH₃, only Fe was nitrified. All efforts to prepare nitrides of Co and Ni were fruitless.

The experimental conditions employed for the preparation of nitrocarbides and carbonitrides are given in Tables 3 and 4, respectively.

Electrocatalytic Activity of the Interstitial Compounds

As the interstitial compounds of Tables 1-4 are pyrophoric, the preparations were subjected to a process of "induction" before electrochemical investigation. Induction of a pyrophoric powder essentially consists of oxidizing the surface layer of its particles by exposing the powder to mildly oxidizing conditions; the oxide layer then provides a protective coating for the solid against further attack by oxygen. When pyrophoric powders are ordinarily exposed to air, the conditions are too drastic for the oxidation to stop at the surface layer. The powders are inducted by successive treatment with a series of solvents of increasing solubility for O_2 . The powders so treated were found to develop far less heat on subsequent exposure to air and the electrodes prepared from them gave reproducible results.

The catalytic activity of the interstitial compounds were tested in the reduction of O_2 in KOH containing N_2H_4 , and in the oxidation of NH_3 in 30 percent KOH.

(1) Reduction of O_2 in KOH containing N_2H_4 at room temperature²

The interstitial compounds were homogenized by grinding, and sieving through a 325-mesh screen in a dry box filled with nitrogen. The powders were covered with petroleum ether and then brought out in the open, where they were inducted with diethyl ether, acetone, and ethanol. 0.1 gram samples of the inducted materials were waterproofed with a teflon emulsion, cured at 200°C in N_2 , mixed with equal weights of waterproofed graphite, and packed in the sample holder shown in Fig. 6. The electrolyte consisted of 10 ml. of 12 M KOH containing 0.2 ml. of 60 percent N_2H_4 . For activity measurement, the electrodes were polarized against an inert nickel screen at 10 amp/ft² for 15 minutes, then at 20, 30, and 40 amp/ft² for 5 minute periods, and finally again at 10 amp/ft² for 5 minutes. The polarization measurements were made with a Kordes-Marko Bridge, a Hg/HgO electrode serving as the reference electrode. The average values of the potentials are plotted against the apparent current densities in Fig. 7. It will be seen that 17N, 3CN, and 1NC are about as active as Pt-black. Duplicate experiments gave reproducible results.

²

This portion of the work was done in the laboratories of the Union Carbide Corporation, Fuel Cell Department, Parma, Ohio, under the supervision of Dr. G.E. Evans.

(2) Oxidation of NH_3 in 30 percent KOH at 25°C ³

After induction with heptane, acetone, methanol, and water, 28.3 mg of each dried material was mixed with an aqueous emulsion of 5 mg. PTFE and the mixture was spread on a 1.5 cm x 1.5 cm platinum screen. The screen, with the spread, was dried in vacuum at 85°C for half an hour and then pressed at 100 psi for 2 minutes at 250°C . Anodic activities and corrosion currents were determined potentiostatically by a floating electrode technique. A dynamic hydrogen electrode (9) was employed as the reference electrode and corrosion currents were measured in N_2 . The potentiostat was programmed for continuous scanning from 0 v to 1.2 v and the current-voltage curves were traced directly on an x-y recorder. If an electrode gave a corrosion current of more than 1 ma, the electrode material was considered incompatible with the electrolyte. To compare the activities per unit area of the various preparations, the electrochemically effective area of each electrode was determined by a double layer capacitance method (10). The values of equilibrium potential, exchange current, and Tafel slope were computed graphically from the current-potential data. I-R corrections were ignored since the currents were small. The results are presented in Table 5.

3

This part of the work was done in the laboratories of the Catalyst Research Corporation, Baltimore, Md. The principal investigators were H.J. Goldsmith, J.R. Moser, and T. Webb.

Five of the fourteen interstitial preparations tested corroded visibly on addition of NH_3 to the electrolyte. The stable electrodes gave half-cell potentials of 0.54 v-0.56 v compared to 0.58 v for Pt, and Tafel slopes of about 0.12 v compared to 0.04 v for Pt. The half-cell potentials and Tafel slopes for the unstable materials were widely scattered.

Oswin and Salomon (11) have suggested a four-step mechanism for the anodic oxidation of NH_3 . Their scheme and their calculated values for the Tafel slopes of the intermediate steps are as follows:

		<u>Calculated Tafel slope, v</u>
(1)	$\text{NH}_3 + \text{M} + \text{OH}^- \rightarrow \text{M-NH}_2 + \text{H}_2\text{O} + \text{e}^-$	0.118
(2)	$\text{M-NH}_2 + \text{OH}^- \rightarrow \text{M=NH} + \text{H}_2\text{O} + \text{e}^-$	0.039
(3)	$\text{M=NH} + \text{OH}^- \rightarrow \text{M}\equiv\text{N} + \text{H}_2\text{O} + \text{e}^-$	0.024
(4)	$\text{M}\equiv\text{N} \rightarrow 2\text{M} + \text{N}_2$	0.010 (or ∞ at high current densities)

A comparison of the experimental values of the Tafel slope with the calculated values indicates that on Pt the rate-determining step for the oxidation of NH_3 is reaction (2), but on the stable catalysts of Table 5, the rate-determining step for the oxidation of NH_3 is reaction (1).

From a practical point of view, the anodic activities of the nine stable catalysts as measured by the exchange current per unit weight of catalysts were disappointingly low. However, it may be noted that the intrinsic activity of some of the materials, as measured by the activity per unit of surface area, is surprisingly high. If methods for preparing interstitial compounds of specific surface areas comparable to specific surface area of Pt-black could be developed, the interstitial compounds may provide fuel cell catalysts of practical value. The specific surface areas of the interstitial preparations of the present investigation were four orders of magnitude smaller than the specific surface area of Pt-black.

CONCLUSIONS

Interstitial carbides, nitrides, nitrocarbides, and carbonitrides of Fe are active in the reduction of O_2 in KOH containing N_2H_4 at room temperature. The activity of some of these preparations is comparable to that of Pt-black. Further investigation of these compounds with prototype fuel cells appears to be desirable.

None of the preparations tested showed any promise as anode catalysts in the oxidation of NH_3 in KOH.

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TABLE I. - Preparation of carbides

Run no.	Charge	Carbiding gas, (hourly space velocity)	Duration of carbiding, hrs.	Temperature of carbiding, °C	X-ray analysis	Chemical analysis, weight percent	
						Total C	Free C
3C	Raney Fe	1CO+10H ₂ (3,000)	48	305	X-Fe ₂ C, Fe ₃ O ₄	4.90	3.45
9C	Reduced magnetite	CO (100)	16	190			
			24	260			
			6	320	X-Fe ₂ C		
11C	Reduced magnetite	CO (100)	20	205			
			25	340	X-Fe ₂ C	17.31	11.81
12C	Raney Fe	1CO+10H ₂ (3,000)	10	240	ε-Fe ₂ C, α-Fe		
			14	240	X-Fe ₂ C, ε-Fe ₂ C		
		He	12	300	X-Fe ₂ C	7.6	2.2
14C	Reduced magnetite	CO (100)	20	175-325			
27C	Raney 3Ni-1Co	CO (100)	14	170-250	θ-Fe ₃ C	7.98	5.15
			144	250	Ni ₃ C	9.33	7.48
33C	Raney Co	CO (100)	28	160-250	Co ₂ C, α-Co	3.59	0.54
			72	250			
42C	Raney 1Ni-1Co	CO (100)	22	160-250	Ni(cubic), α-Co	4.25	1.11
			101	250			
43C	Raney 1Ni-1Ag	CO (100)	4	160-250	Ag(cubic)	2.14	0.16
			102	250			
46C	Raney 3Ni-1Ag	CO (100)	7	160-250	Ag, Ni ₃ C	3.44	0.22
			104.5	250			
61C	Reduced co-precipitated hydroxides of 3Ni-1Co	CO (100)	5	160-260		0.28	0.17
			102	260			

TABLE 2.- Preparation of nitrides

Nitriding gas: NH_3
Space velocity: 1,000 hr^{-1}

Run no.	Charge	Duration of nitriding, hrs.	Temp., °C	X-ray analysis	Chemical analysis, N, weight percent
1N	Reduced magnetite	6	365	$\epsilon\text{-Fe}_3\text{N-Fe}_2\text{N}$, $\gamma'\text{-Fe}_4\text{N}$	5.92
10N	Reduced magnetite	24	350	$\epsilon\text{-Fe}_3\text{N-Fe}_2\text{N}$	7.94
11N	Reduced, coprecipitated 3Fe-1Ag	25	355	$\epsilon\text{-Fe}_3\text{N-Fe}_2\text{N}$, Ag	4.85
14N	Rancy Fe	24	355	$\epsilon\text{-Fe}_3\text{N-Fe}_2\text{N}$	9.61
17N	Rancy Fe	12	355	$\epsilon\text{-Fe}_3\text{N-Fe}_2\text{N}$	9.12
18N	Rancy Fe	24	295	$\zeta\text{-Fe}_2\text{N}$, $\epsilon\text{-Fe}_3\text{N-Fe}_2\text{N}$, $\gamma'\text{-Fe}_4\text{N}$	9.8
19N	Reduced magnetite	24	350	$\zeta\text{-Fe}_2\text{N}$, $\epsilon\text{-Fe}_3\text{N-Fe}_2\text{N}$, $\gamma'\text{-Fe}_4\text{N}$	7.77
20N	Rancy Fe	7.5 48	350 300	$\zeta\text{-Fe}_2\text{N}$, $\gamma'\text{-Fe}_4\text{N}$, $\epsilon\text{-Fe}_3\text{N-Fe}_2\text{N}$ $\epsilon\text{-Fe}_3\text{N-Fe}_2\text{N}$	9.95
21N	Reduced magnetite	5	250	$\gamma'\text{-Fe}_4\text{N}$, $\epsilon\text{-Fe}_3\text{N-Fe}_2\text{N}$	5.93

TABLE 3.- Preparation of nitrocarbides

Run no.	Charge	Duration of nitriding the carbide, hrs.	Temperature of nitriding the carbide, °C.	Space velocity of NH ₃ : 1,000 hr ⁻¹	X-ray analysis	Chemical analysis, weight percent		
						Total	%rec	
						N	C	
1NC	3C (χ -Fe ₂ C, Fe ₃ O ₄)	28	355		ϵ -Fe ₃ X-Fe ₂ X(C,N), Fe ₃ O ₄	5.65	2.98	2.06
2NC	9C (χ -Fe ₂ C)	24	355		χ -Fe ₂ X(C,N), ϵ -Fe ₃ X-Fe ₂ X(C,N)	2.26	11.76	5.93
15NC	27C (carbided 3Ni-1Co)	48	260		Ni ₃ X(C,N)	1.01	9.30	6.38
28NC	42C (carbided 1Ni-1Co)	48	260		α -Co, Ni	1.01	3.84	1.11

TABLE 4.- Preparation of carbonitrides

Run no.	Charge	Duration of nitride, hrs.	Temperature of carburizing the nitride, °C.	X-ray analysis	Chemical analysis, weight percent																																				
					Total	Free																																			
					N	C																																			
3CN	14N (ϵ -Fe ₃ N-Fe ₂ N)	3	180-350	ϵ -Fe ₃ X-Fe ₂ X(C,N)	8.49	4.02	0.88																																		
		7.5	350					4CN	18N (ζ -Fe ₂ N, ϵ -Fe ₃ N-Fe ₂ N, γ' -Fe ₄ N)	11	175-350	ϵ -Fe ₃ X-Fe ₂ X(C,N)	9.25	3.23	0.81			5CN	19N (ζ -Fe ₂ N, ϵ -Fe ₃ N-Fe ₂ N, γ' -Fe ₄ N)	11	190-350	ϵ -Fe ₃ X-Fe ₂ X(C,N)	7.43	2.74	3.20			6CN	11N (ϵ -Fe ₃ N-Fe ₂ N, Ag)	3	225-350	ϵ -Fe ₃ X-Fe ₂ X(C,N), Ag				7	350	9CN	21N (γ' -Fe ₄ N, ϵ -Fe ₃ N-Fe ₂ N)	0.5	200-250
4CN	18N (ζ -Fe ₂ N, ϵ -Fe ₃ N-Fe ₂ N, γ' -Fe ₄ N)	11	175-350	ϵ -Fe ₃ X-Fe ₂ X(C,N)	9.25	3.23	0.81																																		
								5CN	19N (ζ -Fe ₂ N, ϵ -Fe ₃ N-Fe ₂ N, γ' -Fe ₄ N)	11	190-350	ϵ -Fe ₃ X-Fe ₂ X(C,N)	7.43	2.74	3.20			6CN	11N (ϵ -Fe ₃ N-Fe ₂ N, Ag)	3	225-350	ϵ -Fe ₃ X-Fe ₂ X(C,N), Ag				7	350	9CN	21N (γ' -Fe ₄ N, ϵ -Fe ₃ N-Fe ₂ N)	0.5	200-250	γ' -Fe ₄ X(C,N)				3.5	250				
5CN	19N (ζ -Fe ₂ N, ϵ -Fe ₃ N-Fe ₂ N, γ' -Fe ₄ N)	11	190-350	ϵ -Fe ₃ X-Fe ₂ X(C,N)	7.43	2.74	3.20																																		
								6CN	11N (ϵ -Fe ₃ N-Fe ₂ N, Ag)	3	225-350	ϵ -Fe ₃ X-Fe ₂ X(C,N), Ag				7	350	9CN	21N (γ' -Fe ₄ N, ϵ -Fe ₃ N-Fe ₂ N)	0.5	200-250	γ' -Fe ₄ X(C,N)				3.5	250														
6CN	11N (ϵ -Fe ₃ N-Fe ₂ N, Ag)	3	225-350	ϵ -Fe ₃ X-Fe ₂ X(C,N), Ag																																					
		7	350					9CN	21N (γ' -Fe ₄ N, ϵ -Fe ₃ N-Fe ₂ N)	0.5	200-250	γ' -Fe ₄ X(C,N)				3.5	250																								
9CN	21N (γ' -Fe ₄ N, ϵ -Fe ₃ N-Fe ₂ N)	0.5	200-250	γ' -Fe ₄ X(C,N)																																					
		3.5	250																																						

TABLE 5.- Oxidation of NH_3 in 30% KOH at 25°C

Catalyst (composition)	Exchange current		Tafel slope, V	Equilibrium potential, V
	ma/g	$\mu\text{a}/\text{cm}^2$		
Pt	883	4.24	0.04	0.58
33C* (Co_2C , $\alpha\text{-Co}$)	106	21.6	0.04	0.22
43C (carbided 1Ni-1Ag)	60.1	4.40	0.08	0.68
46C* (Ag, Ni_3C)	42.4	10.5	0.08	0.24
28NC* (nitrocarbided 1Ni-1Co)	28.3	0.968	0.10	0.32
27C* (carbided 3Ni-1Co)	14.1	2.0	0.12	0.26
12C ($\chi\text{-Fe}_2\text{C}$)	3.54	107	0.17	0.55
15NC (nitrocarbided 3Ni-1Co)	3.53	0.507	0.23	0.56
21N ($\gamma'\text{-Fe}_4\text{N}$, $\epsilon\text{-Fe}_3\text{N-Fe}_2\text{N}$)	3.15	42.6	0.12	0.56
61C (carbided 3Ni-1Co)	2.80	7.0	0.11	0.54
18N ($\zeta\text{-Fe}_2\text{N}$, $\epsilon\text{-Fe}_3\text{N-Fe}_2\text{N}$, $\gamma'\text{-Fe}_4\text{N}$)	2.47	29.9	0.12	0.56
20N ($\zeta\text{-Fe}_2\text{N}$, $\epsilon\text{-Fe}_3\text{N-Fe}_2\text{N}$, $\gamma'\text{-Fe}_4\text{N}$)	1.66	23.2	0.13	0.56
1NC [$\epsilon\text{-FeX-Fe}_2\text{X(C,N)}$, Fe_3O_4]	1.37	14.3	0.12	0.54
5CN [$\epsilon\text{-Fe}_3\text{X-Fe}_2\text{X(C,N)}$]	1.13	20.7	0.26	0.55
4CN [$\epsilon\text{-Fe}_3\text{X-Fe}_2\text{X(C,N)}$]	0.99	6.45	0.11	0.56

*The catalysts marked with an asterisk dissolved in the electrolyte when NH_3 was added.

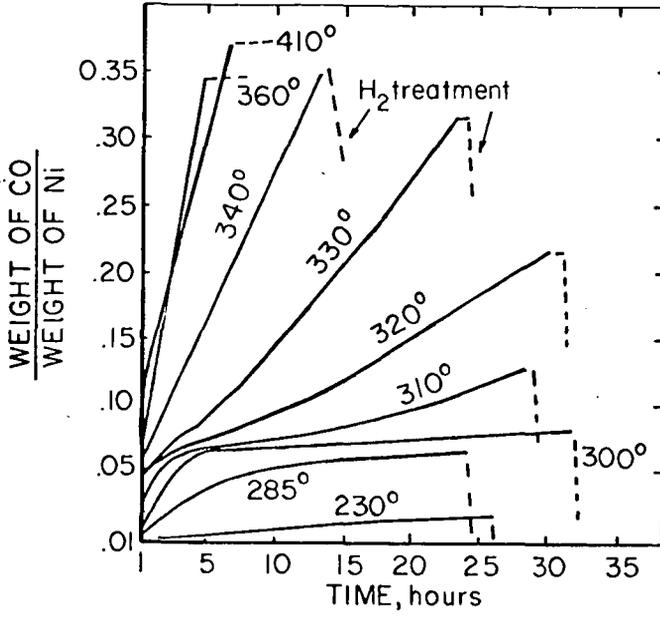
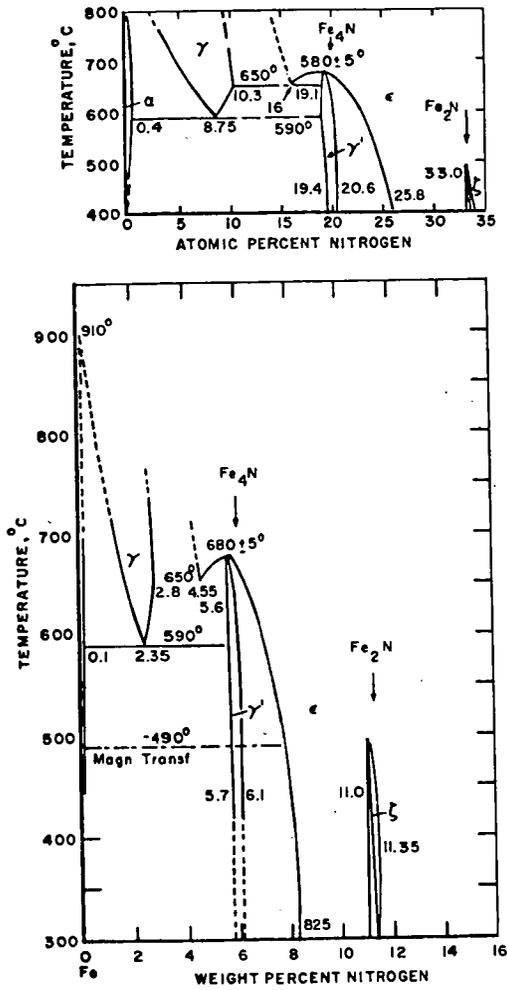


Figure 1.- Carburization of Ni with CO at different temperatures.

Figure 2.- Fe-N system in NH₃ (2).

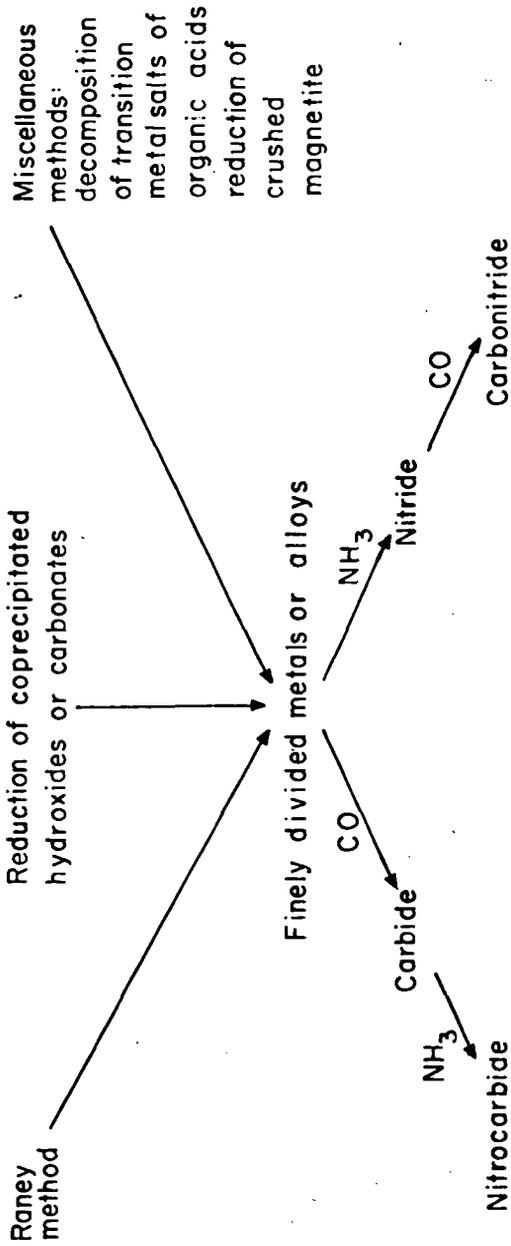


Figure 3.- Preparation of the interstitial compounds.

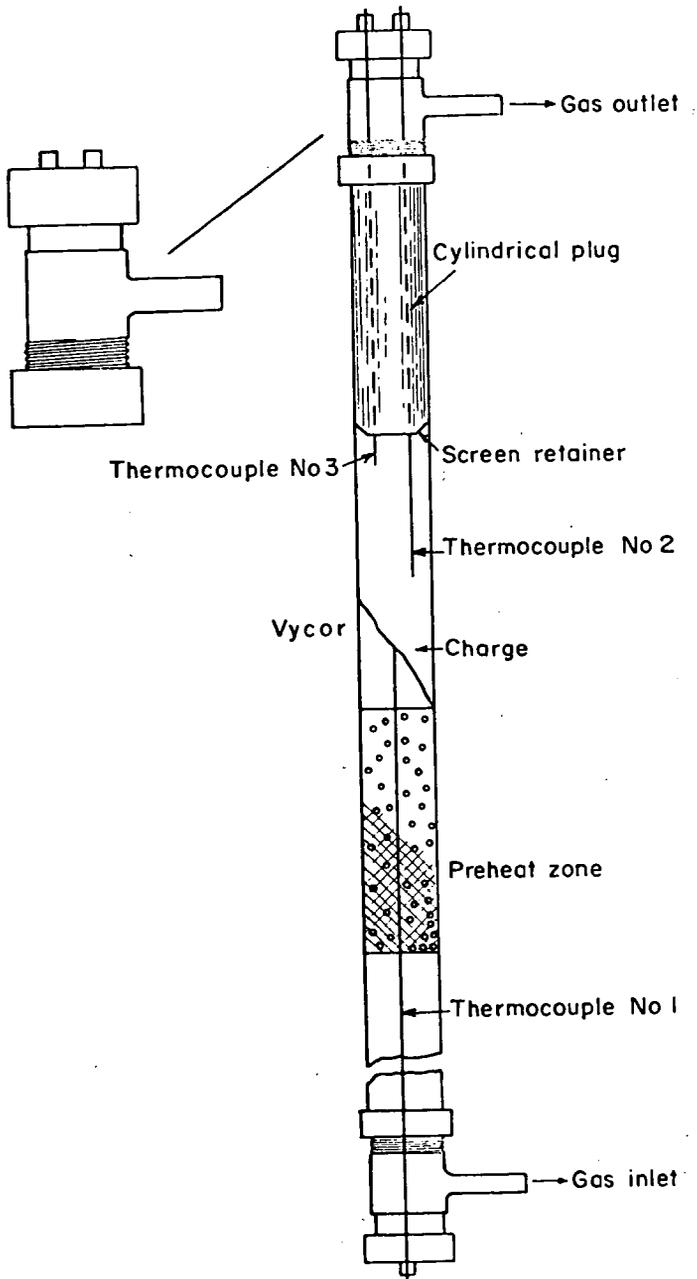


Figure 4.- Vycor reaction vessel.

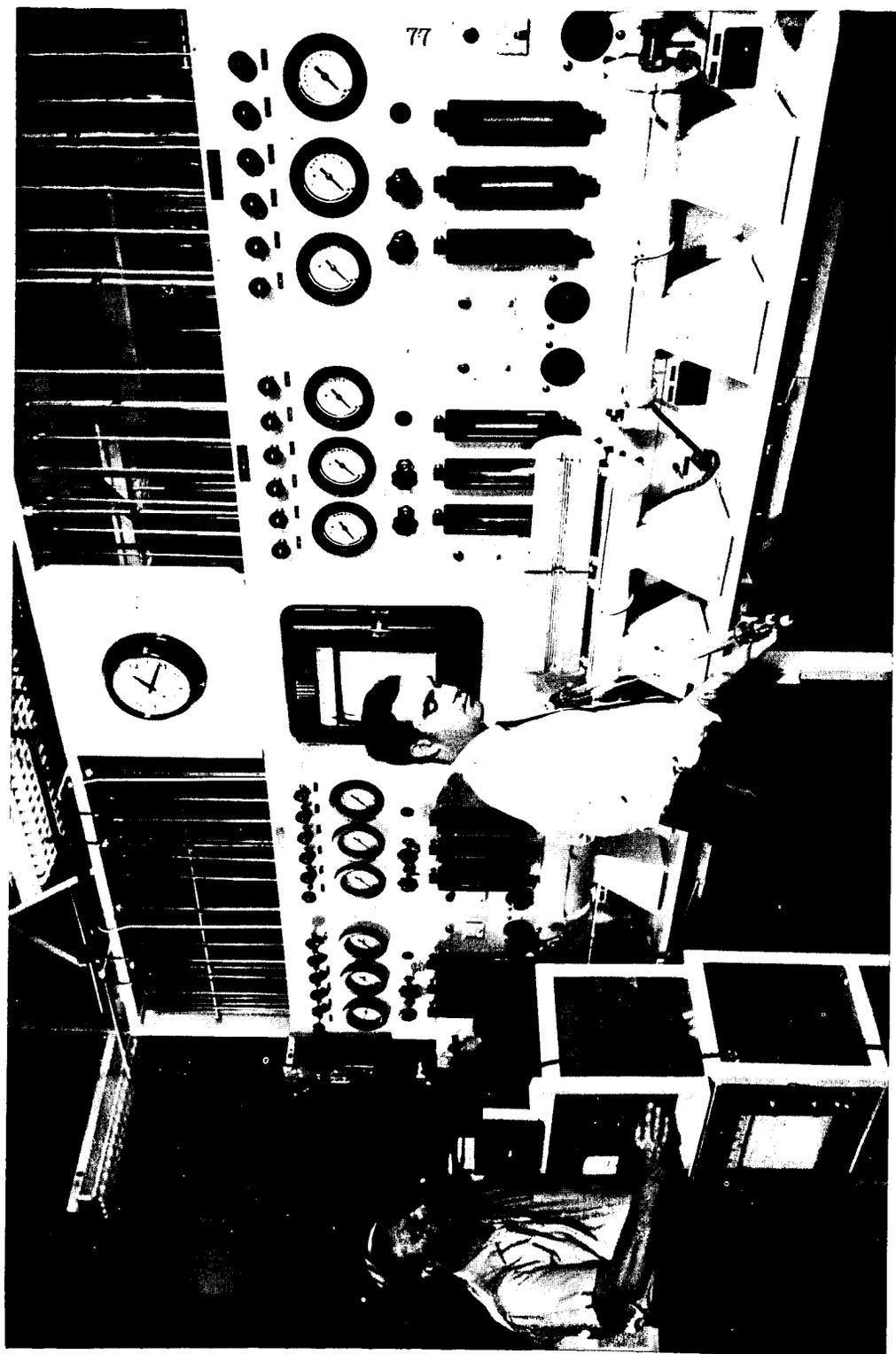


Figure 5.-Units for preparing interstitial compounds by gas-solid reactions

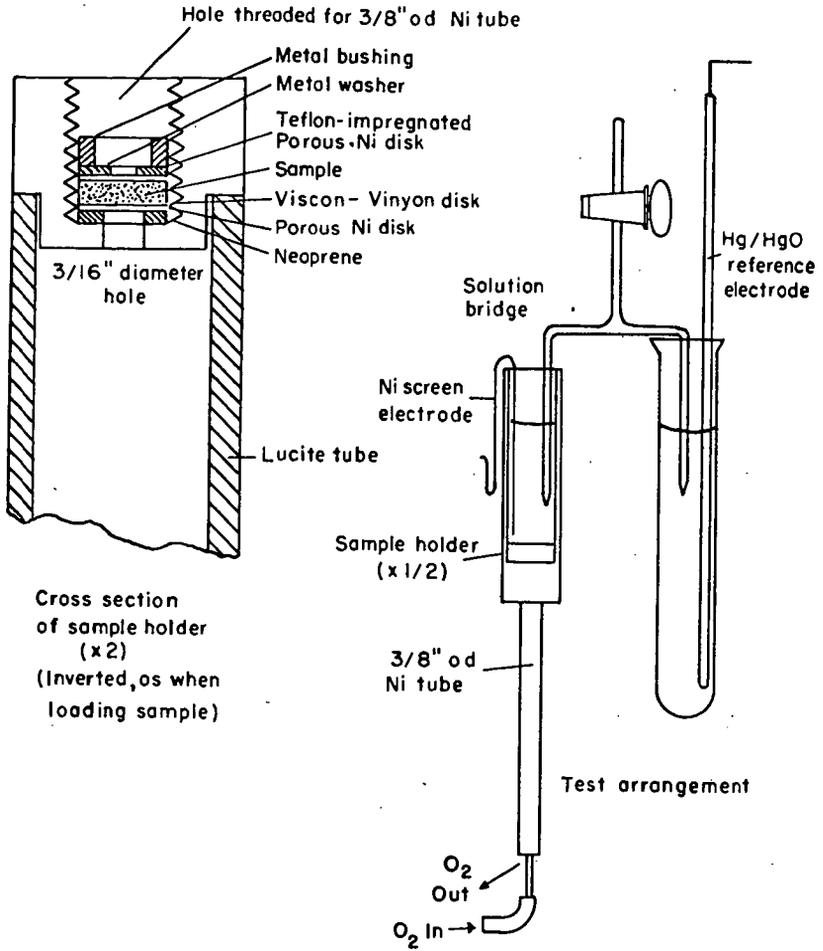


Figure 6.- Test cell.

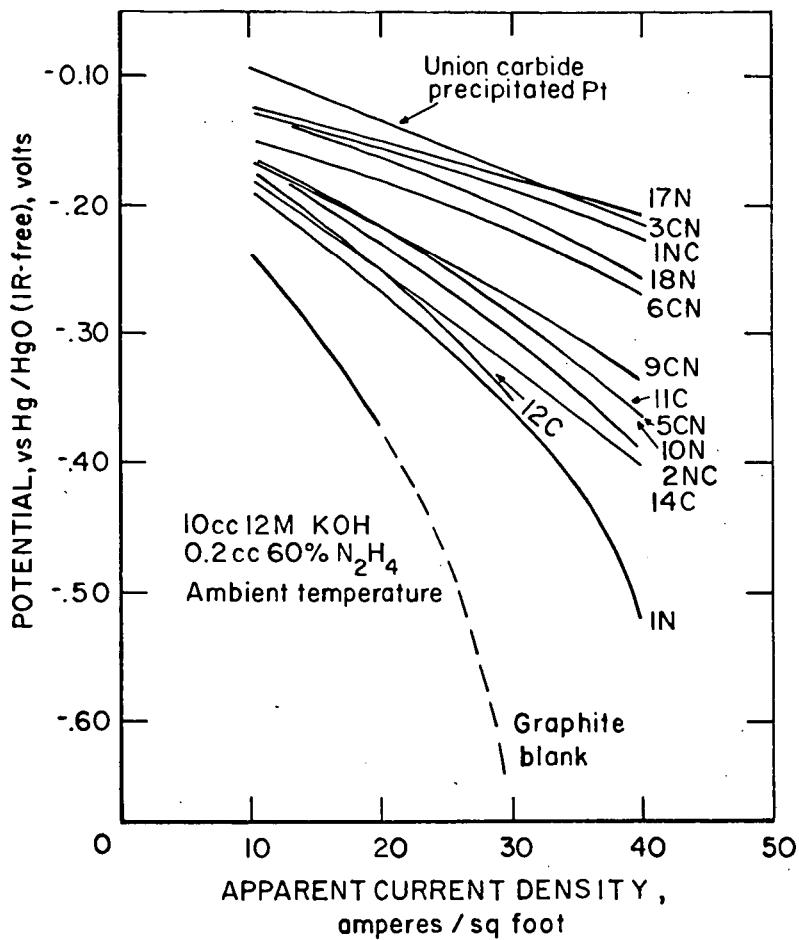


Figure 7.- Cathodic activity of homogenized, inducted materials in the reduction of O₂ in 12M KOH containing N₂H₄.