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INTERSTITIAL COMPOUNDS AS FUEL CELL CATALYSTS:

THEIR PREPARATIVE TECHNIQUES AND ELECTROCHEMICAL TESTING



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By S. Akhtar, C. T. Grein, and D. Bienstock

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CONTENTS

	Page		Page
Abstract	1	Reduction of O ₂ in aqueous KOH	30
Introduction	1	Reduction of O ₂ in aqueous KOH (Tyco Laboratories)	33
Acknowledgments	2	Oxidation of H ₂ in aqueous KOH (Allis Chalmers)	33
Part A.—Preparative techniques	3	Oxidation of H ₂ and C ₃ H ₈ in aqueous K ₂ CO ₃ +KHCO ₃ (American Oil Co.)	37
Interstitial compounds	3	Oxidation of NH ₃ and CO (Catalyst Research Corp.)	39
Interstitial compounds of Fe, Co, and Ni	3	Oxidation of NH ₃	40
Preparation of finely divided metals, mixtures of metals, or alloys	6	Oxidation of CO	41
Raney method	6	Reduction of O ₂ in H ₂ SO ₄ , buffered carbonate and phosphate electrolytes, and molten H ₃ PO ₄ (Esso Research and Engineering Co.)	43
Reduction of coprecipitated hydroxides or carbonates	7	Oxidation of H ₂ and reduction of O ₂ in 3N H ₂ SO ₄ (General Electric Co.)	45
Miscellaneous methods	9	Interstitial compound as cathodes in ammonia battery (Harry Diamond Laboratories and Tracor, Inc.)	45
Decomposition of transition metal salts of organic acids	9	Oxidation of N ₂ H ₄ and dextrose (Monsanto Research Corp.)	47
Reduction of magnetite	9	Oxidation of N ₂ H ₄	47
4Cr-1Mo	9	Oxidation of dextrose	50
Fe ₂ TiO ₃ (iron titanate)	10	Oxidation of N ₂ H ₄ in acid liquid NH ₃ (Naval Weapons Center)	50
Nickel plaque	10	Reduction of O ₂ in KOH containing N ₂ H ₄ (Union Carbide Corp.)	52
Preparation of the carbides, nitrides, nitrocarbides, and carbonitrides of transition metals	10	Reduction of O ₂ in 12M KOH containing N ₂ H ₄	54
Preparation of carbides	18	Conclusions	57
Preparation of nitrides	20	References	59
Preparation of nitrocarbides	22		
Preparation of carbonitrides	25		
Preparation of the borides of cobalt and nickel			
Part B.—Electrochemical testing	29		
Catalysis in fuel cells	29		

ILLUSTRATIONS

	Page
1. Carburization of Ni with CO at several temperatures	4
2. Fe-N phase diagram (in NH ₃)	5
3. Preparation of carbides, nitrides, nitrocarbides, and carbonitrides of transition metals	6
4. Induction furnace for melting alloys	8
5. Preparation of powdered alloy	9
6. Reaction vessel and collection flask for interstitial compounds	18
7. Units for preparing interstitial compounds by gas-solid reactions	19
8. Infrared apparatus for monitoring CO	20
9. Apparatus for reacting reduced metals with pressurized ammonia	20
10. Cross section of a H ₂ -O ₂ fuel cell	29
11. Polarization of a fuel cell	30
12. Floating electrode assembly-electrochemical test cell	31
13. Electrical circuit-electrochemical test cell	31
14. Catalytic activity of Ni-Au mixtures in reduction of O ₂	32
15. Diagram of half cell	34
16. Diagram of mini fuel cell	36
17. Volt-ampere characteristics (3Ni-1Ag series)	36

18. Volt-ampere characteristics (nickel series) -----	36
19. Reproducibility test (84R and Pt black) -----	36
20. Electrode-test apparatus -----	39
21. Cathodic polarization curves in a saturated solution of m-dinitrobenzene in 25.1 pct NH ₃ +57.6 pct CH ₃ OH+17.25 pct NH ₄ SCN at 0° C -----	45
22. Cathodic polarization curves in a saturated solution of m-dinitrobenzene in 25.1 pct NH ₃ +57.6 pct CH ₃ OH+17.25 pct NH ₄ SCN at 0° C -----	45
23. Cathodic polarization curves in a saturated solution of m-dinitrobenzene in 25.1 pct NH ₃ +57.6 pct CH ₃ OH+17.25 pct NH ₄ SCN at 0° C -----	46
24. Cathodic polarization curves in a saturated solution of m-dinitrobenzene in 25.1 pct NH ₃ +57.6 pct CH ₃ OH+17.25 pct NH ₄ SCN at 0° C -----	46
25. Cathodic polarization curves in a saturated solution of m-dinitrobenzene in 25.1 pct NH ₃ +57.6 pct CH ₃ OH+17.25 pct NH ₄ SCN at 0° C -----	46
26. Cathodic polarization curves in a saturated solution of m-dinitrobenzene in 25.1 pct NH ₃ +57.6 pct CH ₃ OH+17.25 pct NH ₄ SCN at 0° C -----	46
27. Cathodic polarization curves in a saturated solution of m-dinitrobenzene in 25.1 pct NH ₃ +57.6 pct CH ₃ OH+17.25 pct NH ₄ SCN at 0° C -----	47
28. Side view of half-cell test unit -----	48
29. Catalytic decomposition of hydrazine -----	53
30. Test cell -----	54
31. Cathodic activity of as received materials in the reduction of O ₂ in 12M KOH containing N ₂ H ₄ -----	55
32. Cathodic activity of homogenized, inducted materials in the reduction of O ₂ in 12M KOH containing N ₂ H ₄ -----	

TABLES

No.	Page
1. Interstitial compounds of refractory type -----	3
2. Interstitial compounds of nonrefractory type -----	3
3. Alloys of the transition metals prepared by Raney method -----	6
4. Mixed metals prepared by the reduction of coprecipitated carbonates -----	10
5. Mixed metals prepared by the reduction of coprecipitated hydroxides -----	10
6. Mixed metals prepared by the reduction of mechanically mixed powders of hydroxides of metals -----	10
7. Preparation of carbides -----	11
8. Preparation of nitrides -----	21
9. Preparation of nitrocarbides -----	22
10. Preparation of carbonitrides -----	26
11. Preparation of borides -----	27
12. Activities of reduced Ni-Au catalysts in the reduction of O ₂ in 35 pct aqueous KOH (ma/cm ²) -----	32
13. Reduction of O ₂ in 35 pct aqueous KOH at 75° C -----	33
14. Oxidation of H ₂ in 35 pct aqueous KOH at 90° C -----	34
15. Oxidation of H ₂ and C ₃ H ₈ in 1.52M K ₂ CO ₃ +1.52M KHCO ₃ at 85° C -----	37
16. Oxidation of NH ₃ in 30 pct KOH at 25° C -----	40
17. Oxidation of NH ₃ in saturated K ₂ CO ₃ at 25° C -----	41
18. Oxidation of CO in 2N H ₂ SO ₄ at 25° C -----	41
19. Oxidation of CO in CH ₃ COOH+CH ₃ COOK buffer of pH 3 -----	42
20. Oxidation of CO in saturated K ₂ CO ₃ at 25° C -----	42
21. Oxidation of CO in 85 pct H ₃ PO ₄ at 25° C -----	42
22. Effect of crushing on the activity of catalysts in the oxidation of CO at 25° C -----	43
23. Reduction of O ₂ -----	44
24. Oxidation of N ₂ H ₄ in 5M KOH -----	48
25. Catalytic decomposition of 2M N ₂ H ₄ in 5M KOH at 70° C -----	51
26. Oxidation of N ₂ H ₄ in NH ₄ SCN+NH ₃ at 25° C -----	52
27. Calculated rate constants for the catalytic decomposition of N ₂ H ₄ -----	53

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THEIR PREPARATIVE TECHNIQUES AND ELECTROCHEMICAL TESTING

by

S. Akhtar,¹ C. T. Grein,² and D. Bienstock³

ABSTRACT

Interstitial compounds of iron, cobalt, and nickel, and their binary and ternary mixtures with silver, gold, palladium, and platinum were prepared and tested as fuel cell catalysts.

The first step in the preparation of the interstitial compounds consisted of preparing finely divided metals. This was done either by the Raney method or by reduction of precipitated hydroxides of the metals. The finely divided reduced metals were then treated with carbon- and/or nitrogen-containing gases to prepare their carbides, nitrides, and nitrocarbides. The materials were tested for cathodic activity towards O_2 and for anodic activity towards H_2 , C_3H_8 , NH_3 , CO , and N_2H_4 in acid and alkaline electrolytes at 25° to 90° C in half-cell assemblies. Samples of carbided and nitrocarbided 1Ni-1Ag-1Au were about one fifth as active as Pt-black in the reduction of O_2 in 35 percent KOH solution, whereas the activities of several interstitial preparations exceeded the activity of Pt-black in the reduction of O_2 in 12M KOH containing N_2H_4 . Nitrocarbides of $x-Fe_2C$, 3Ni-1Au, and 1Ni-3Au were effective catalysts for oxidizing N_2H_4 in liquid NH_3 containing NH_4SCN . Corrosion of the catalysts by electrolytes was severe in many cases.

INTRODUCTION

In March 1966, the Pittsburgh Coal Research Center of the Bureau of Mines, at the suggestion of the National Aeronautics and Space Administration, initiated a study of the interstitial compounds of the transition metals as fuel cell catalysts. The Bureau's interest in the work was generated by a preliminary observation, at Tyco Laboratories, Inc., Waltham, Mass., that the interstitial carbide $x-Fe_2C$ is an active catalyst for the electrochemical reduction of oxygen. The object of the project, Contract W-12,300, funded by the National Aeronautics and Space Administration, was to develop cathode catalysts for alkaline hydrogen-oxygen fuel cells operating at low temperatures. It was a cooperative

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program; catalysts were prepared in the Pittsburgh Coal Research Center laboratory and their cathodic activity was tested at Tyco Laboratories. The scope of the project was later enlarged by cooperative arrangement with 10 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. This report is a consolidated account of the total program with the exception of the work done at Tyco Laboratories. Only a summary of Tyco's findings regarding the activity of the materials has been included in this report since a comprehensive report on their work will appear separately.

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At different stages of the program, we were ably assisted by R. D. Diehl, W. H. Ryback, R. J. Haren, A. P. Dudash, C. C. Kaufman, C. W. DeLeuze, and G. R. Kollar. Chemical analyses were performed by M. Mima and her staff, and X-ray diffraction patterns were prepared by H. W. Swan.

The names of the workers in the cooperating laboratories appear at appropriate places in the text.

PART A.—PREPARATIVE TECHNIQUES

INTERSTITIAL COMPOUNDS

Interstitial compounds, formed by many metals with carbon (C), nitrogen (N), and boron (B), are so-named because the nonmetallic atoms occupy the interstices of the metal lattice. From a consideration of their physical and chemical properties, the interstitial compounds are divided into two categories: refractory and nonrefractory. The refractory type, as listed in table 1, gener-

Table 1.—Interstitial compounds of refractory type

Compound	Melting point, °C	Hardness, Mohs' scale
TiC	3,140	9
HfC	4,160	—
NbC	3,900	—
W ₂ C	2,860	10
TiN	2,950	9
NbN	2,573	—
TaN	3,440	8
TiB ₂	2,900	—
NbB ₂	2,900	—
TaB ₂	3,000	—

ally are alloylike phases and are stable over a range of composition. They are characterized by metallic luster, extraordinary hardness, and very high melting points. Chemically they are inert and, even under strong oxidizing conditions, react only slowly with inorganic acids (30)⁴. In most cases they may be synthesized directly by fusing together the component elements. Examples of the nonrefractory type of interstitial compounds are listed in table 2. The carbides, nitrides, and borides of this category decompose when heated and are not noted for hardness or metallic luster. They ignite in air and react readily with mineral acids. They are prepared by indirect methods; for example by the action of C- or N-containing gases on metals. Interstitial compounds of both categories conduct electricity.

⁴ Italic numbers in parentheses refer to items in the list of references at the end of this report.

⁵ There are some reservations as to the stated chemical formulas of these carbides. The existence of any carbide of composition Fe₂C has been questioned recently (21), the preferred formulations being Fe₃C₂ and Fe₃C₃.

Table 2.—Interstitial compounds of nonrefractory type

Compound	Decomposition temperature, °C
ε-Fe ₂ C	250, to χ-Fe ₂ C.
χ-Fe ₂ C	450, to Fe ₃ C + C
θ-Fe ₃ C	~600, to α-Fe + C
Co ₂ C	~270, to Co + C
Ni ₃ C	~280, to Ni + C
γ'-Fe ₄ N	—
ε-Fe ₃ N-Fe ₂ N	—
ζ-Fe ₂ N	—
Co ₂ N	to Co ₃ N.
Co ₃ N	—
Ni ₃ N	~360, to Ni + N ₂ .
Fe _x B	(¹)x = 2 (?)
Co _x B	
Ni _x B	

The term "x = 2 (?)" indicates that the composition of the compounds Fe_xB, Co_xB, and Ni_xB is not known with certainty. The available evidence is often contradictory, but a critical assessment of the literature leads the author to favor the proposed value 2 for x in these compounds.

A number of the interstitial compounds of the nonrefractory type have been studied as catalysts. Indeed, a large part of the earlier interest in the carbides and nitrides of iron (Fe), cobalt (Co), and nickel (Ni) centered around their value as catalysts in Fischer-Tropsch and ammonia syntheses (1, 15). It is questionable whether the catalytic activity of interstitial compounds is greater than that of the corresponding reduced metals. Nevertheless, some of the compounds do offer certain advantages of practical value over reduced metals. They are less easily oxidized and have great mechanical strength; hence, their useful life is often longer. Some of them also offer advantages of selectivity. Recently, the borides of Fe, Co, and Ni have been demonstrated to catalyze a variety of reactions (3, 22, 24, 29).

Interstitial Compounds of Fe, Co, and Ni

The principal carbides, nitrides, and borides of Fe, Co, and Ni have been listed in table 2. Iron forms three well characterized carbides (14), ε-Fe₂C, χ-Fe₂C,⁵ and θ-Fe₂C, of the nonrefractory type. ε-Fe₂C changes to χ-Fe₂C at 250° C, χ-Fe₂C decomposes to θ-Fe₃C and C at 450° C,

and θ -Fe₃C, the most stable of the three carbides, decomposes on prolonged heating under vacuum at about 600° C. The carbides of Fe have been prepared by the action of CO, CO+H₂, or hydrocarbons, on Fe or oxides of Fe (16-17, 31). When CO+H₂ is employed, Fe is in effect carburized with a mixture of CO and hydrocarbons, since CO reacts with H₂ to form hydrocarbons in the presence of reduced Fe (Fischer-Tropsch synthesis). Hydrocarbons alone do not lead to complete carbiding (31), and CO alone tends to deposit free carbon. The action of CO on Fe is very exothermic and there is a strong tendency for the Fe to become overheated. Best results are obtained by reacting 1CO+3 to 10 H₂ with finely divided and reduced Fe. Reaction temperature should be carefully controlled below that at which the desired carbide decomposes. H₂ in the reacting gas helps remove the excess heat and minimizes the amount of free carbon in the product.

Co₂C is prepared by the action of CO on Co (18), and Ni₃C by the action of CO on Ni (7) at 250° to 280° 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. Free carbon may be distinguished chemically from the combined carbon in that the combined carbon reacts with H₂ at about 200° C., but free carbon does not react with H₂ below 300° C. Some fea-

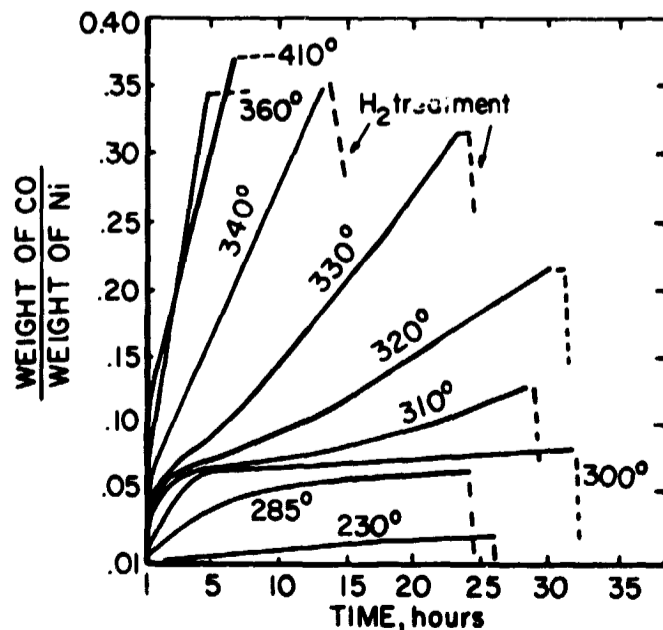
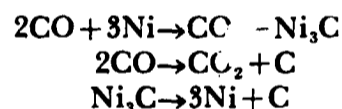


Figure 1.—Carburization of Ni with CO at several temperatures, ° C.

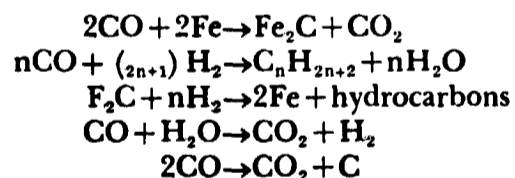
tures of the kinetics of the reaction of CO with Ni are presented in figure 1 from the published results of Eyraud (8). A fixed weight of reduced Ni was carburized with CO at several temperatures. Below 250° C the rate of formation of Ni₃C was very slow, but the product was substantially free from deposited carbon. At 285° C, the reaction was complete in about 30 hrs, but Ni₃C was contaminated with free carbon. At temperatures above 300° C, large quantities of free carbon were deposited.

As with Fe, the reactions of CO with Co and Ni are strongly exothermic. However, H₂ cannot be employed to dilute CO in carburizing Co and Ni; Co₂C and Ni₃C cannot be prepared under conditions of Fischer-Tropsch synthesis. The contrast in this respect with Fe may be noted.

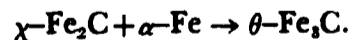
Several reactions occur simultaneously when transition metals are carburized. For the action of CO on Ni, Eyraud (8) suggests the following scheme of three reactions:



For the action of CO+H₂ on Fe, the scheme is probably much more complicated. Any or all of the following reactions may occur:



The list is not exhaustive: The hydrocarbons may react with Fe to give iron carbides (31); Fe₂C may undergo phase changes (table 2) or may react with α -Fe as follows:



The nitrides of Fe, Co, and Ni are prepared by reacting the metals with NH₃. The phase diagram for the nitrides of Fe (fig. 2) does not represent Fe-N system in equilibrium with N₂ at atmospheric pressure; it shows the phases that are in equilibrium with N₂ at the pressures corresponding to the disassociation of NH₃. ϵ -Fe₃N-Fe₂N has the most extended range of existence. The different nitrides of Fe may all be prepared at about 350° C, the composition of the product depending on the space velocity of NH₃ and the duration of nitriding. The nitrides of Co and Ni also have been prepared by the action of Ni₃ on the metals, but their preparation

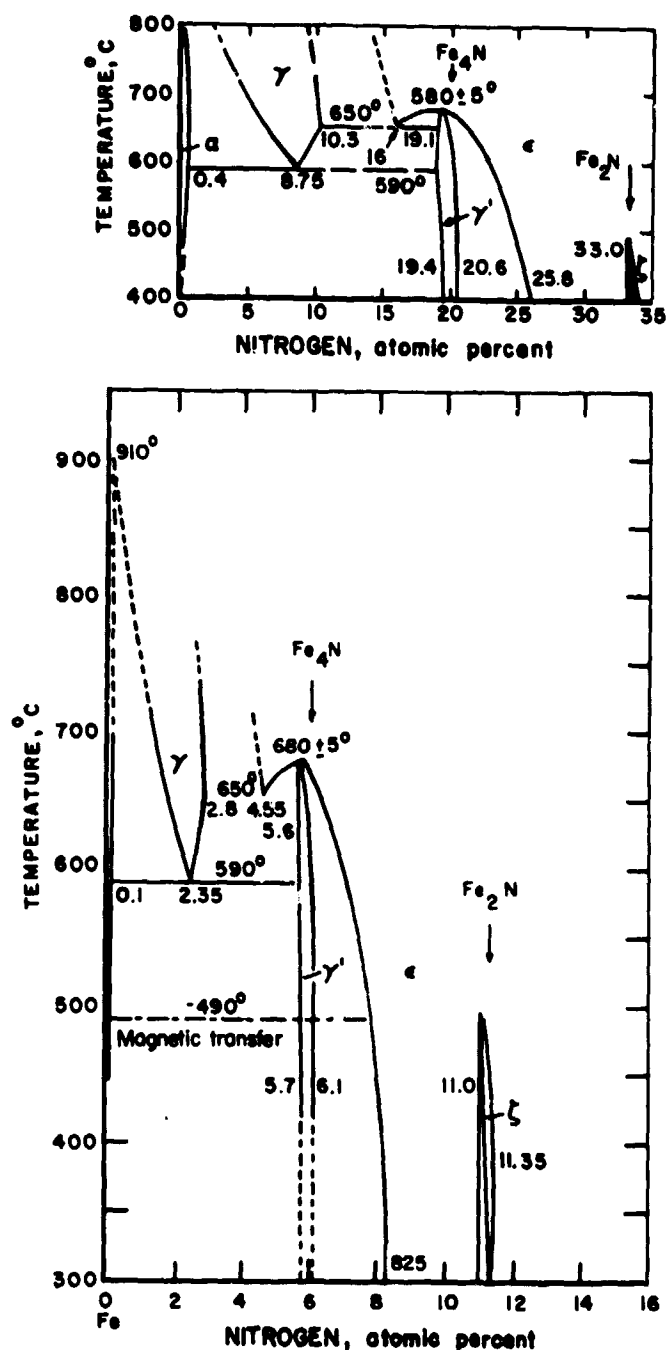


Figure 2.—Fe-N phase diagram (in NH_3).

appears to be attended by unusual difficulties (12, 33); 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.

An interesting group of interstitial compounds of Fe, Co, and Ni consists of those containing both C and N (5, 20, 34). By reacting a carbide of Fe, Co, or Ni with NH_3 at about 260°C , the interstitial carbon may be replaced progres-

sively with nitrogen. Up to a point this will proceed without destroying the structure of the original carbide. However, when sufficient N has replaced the C, the solid will change over to the structure of the corresponding nitride. By continued treatment with ammonia, the interstitial C may be replaced entirely with N and pure nitride obtained. Conversely, by reacting a nitride with CO, the interstitial N may be replaced with C—in part, to obtain a mixed (C,N)-interstitial compound; or in full, to obtain a pure carbide.

The structure of a mixed (C,N)-interstitial compound will thus depend upon whether N has replaced C in a carbide lattice or C has replaced N in a nitride lattice. (C,N)-interstitial compounds are, therefore, accorded two distinctive nomenclatures in this report: a carbide with a portion of its interstitial carbon replaced with nitrogen is referred to as a nitrocarbide, whereas a nitride with a portion of its interstitial nitrogen replaced with carbon is referred to as carbonitride. If the carbide and nitride are isostructural, the distinction is, of course, trivial.

The inclusion of the borides of Fe, Co, and Ni in the list of nonrefractory interstitial compounds is explained as follows: Metal borides may be prepared by a number of methods (10)—direct combination of elements, reduction of metal oxides with boron, reaction of metals or metal oxides with B_2C , electrolysis of fused mixtures of metal oxides and borax, reaction of BCl_3 with metals—all involving high temperatures. The borides prepared by any of these methods are refractory materials. But borides of Fe, Co, and Ni may also be prepared by a low temperature method; namely, interaction of NaBH_4 with metal salts in aqueous solutions (35). The precise composition of the borides prepared by this method has not been established, but they are reactive, pyrophoric in air, and of questionable thermal stability. Accordingly, they belong to the category of nonrefractory type interstitial compounds.

In the present work, electrochemical activities of the interstitial compounds of Fe, Co, and Ni were studied singly, in combination with each other, and in combination with silver (Ag), gold (Au), palladium (Pd), and platinum (Pt). The mixtures were tried for possible synergistic effects. The scheme for preparing the carbides, nitrides, nitrocarbides, and carbonitrides is shown in figure 3, and the details are described in the following sections. The first step consists of preparing finely divided metals and mixtures of

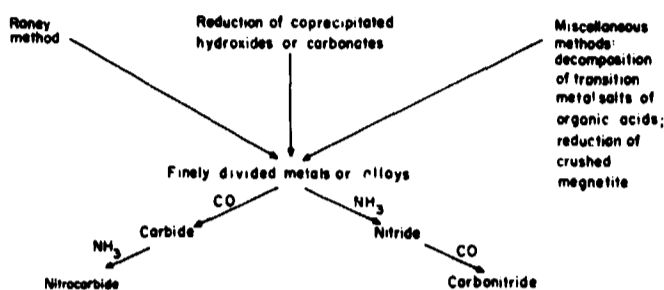


Figure 3.—Preparation of carbides, nitrides, nitrocarbides, and carbonitrides of transition metals.

metals or alloys. 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; hence, for a speedy completion of the reactions 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 figure 3.

The borides were prepared by the wet method, and their preparation is described in the section "Preparation of the Borides of Cobalt and Nickel."

PREPARATION OF FINELY DIVIDED METALS, MIXTURES OF METALS, OR ALLOYS

Raney Method

The classical method developed by Raney (32) for making skeletal nickel catalyst was employed for preparing finely divided alloys of Fe, Co, Ni, Ag, Au, and Pd. The method consisted of the following steps:

Metals + aluminum
 ↓ melt in induction furnace under a helium atmosphere
 Raney alloy
 ↓ crush, sieve
 Raney alloy powder
 ↓ leach with NaOH
 Finely divided alloys
 (Store under ethanol or pyridine)

125- to 150-g charges were melted in fire clay crucibles.

The quantities of the components were so adjusted that the Raney alloys contained 60 pct Al and 40 pct of the other metals. The heating

chamber of the induction furnace (fig. 4) was repeatedly flushed with helium before the furnace was energized. On cooling, most Raney alloys were friable and were crushed to powder in a hammer mill or ball mill. Some of the Raney alloys, however, were malleable and their ingots had to be machined into turnings (fig. 5) before they could be put through a mill. The powders were sieved through standard screens and the desired cut (150 to 250 or 150 to 400 mesh) was leached with NaOH according to the directions of Covert and Adkins (6). The leached materials were washed free of alkalinity and stored under ethanol or pyridine. When alloys containing Co were leached, the leach liquid turned blue, indicating some loss of metal.

The Ag, Au, and Pd used were of more than 99.8 pct purity; commercially available Raney alloys of Fe, Co, and Ni were employed as the source for these metals. Table 3 is a complete list of the alloys prepared by this method. In addition to the alloys, Raney Fe, Raney Co, and Raney Ni also were prepared for carburizing and nitriding.

Chemical analysis of the leached Raney alloys always indicated small amounts of residual aluminum. Generally, it amounts to 1 to 4 pct, but in RAL-7 and RAL-9 (table 3), the residual

Table 3.—Alloys of the transition metals prepared by Raney method

Identification ¹ and nominal composition, (weight ratios)	Composition by chemical analysis, wt pct				
	Raney alloy		Leached alloy		Number of leachings
RA-1 (1Ni-1Co)	Ni 18.68	Ni 43.98	Co 50.26	Al 2.01	
	Co 23.4	Co 2.01	Al 56.0	Na .04	
	Al 56.0	Al .04			
RA-2 (1Ni-3Co)	Ni 9.78	Ni 21.71	Co 67.83	Al 1.55	2
	Co 32.38	Co 1.55	Al 54.54	Na .06	
	Al 54.54	Al .06			
RA-3 (3Ni-1Co)	Ni 29.19	Ni 70.30	Co 23.44	Al 2.31	2
	Co 11.70	Co 2.31	Al 57.22	Na .09	
	Al 57.22	Al .09			
RA-4 ² (1Ni-3Ag)	Ni 13.16	Ni 18.44	Ag 69.97	Al 3.28	3
	Ag 27.32	Ag 1.19	Al 54.9	Na 1.19	
	Al 54.9	Al 1.19			
RA-5 ² (1Ni-1Ag)	Ni 17.55				2
	Ag 21.57				
	Al 53.64				
RA-6 ² (3Ni-Ag)	Ni 20.81	Ni 52.00	Ag 31.1	Al 3.67	2
	Ag 15.00	Ag 1.68	Al 62.27	Na 1.68	
	Al 62.27	Al 1.68			

Table 3.—Alloys of the transition metals prepared by Raney method—Continued

Identification ¹ and nominal composition, (weight ratios)	Composition by chemical analysis, wt pct			Number of leachings ²
	Raney alloy	Leached alloy		
RA-7 ² (1Co-3Ag)	Co 9.81 Ag 29.9 Al 56.30	Co 18.7 Ag 57.1 Al 10.9 Na 17.8		2
RA-8 ² (1Co-1Ag)	Co 11.69 Ag 29.16 Al 56.5	Co 28.3 Ag 60.2 Al 5.54 Na 1.09		2
RA-9 (3Co-1Ag)	Co 24.01 Ag 15.31 Al 57.32	Co 53.4 Ag 21.5 Al 11.0		2
RA-10 ² (1Ni-1Co-1Ag)	Ni 12.49 Co 12.63 Ag 14.57 Al 57.6			2
RA-11 (1Ni-1Co-1Au)				2
RA-12 ² (1Ni-1Ag-1Au)				2
RA-13 ² (1Co-1Ag-1Au)				2
RA-14 (1Ni-1Pd) (150-400 mesh)	Ni 17.8 Pd 17.5 Al 62.61	Ni 41.4 Pd 40.8 Al 1.27		2
RA-15 (1Co-1Pd) (150-400 mesh)		Co 48.00 Pd 44.7 Al 2.54 Na .11		2
RA-16 (1Ni-1Co-1Pd) (150-400 mesh)		Co 30.0 Co 32.2 Pd 30.91 Al 2.4 Na .13		2
RA-17 (1Ni-1Pd-1Au) (150-400 mesh)				3
RA-18 (1Fe-1Pd) (150-400 mesh)	Fe 21.32 Pd 17.40 Al 59.6	Fe 43.7 Pd 30.0 Al 3.89 Na 4		2
RA-19 (1Fe-1Au-1Pd) (150-400 mesh)				2
RA-20 (1Co-1Au-1Pd) (150-400 mesh)				2
RA-21 (1Ni-1Ag-1Pd)	Ni 16.34 Ag 10.1 Pd 14.83 Al 54.11	Ni 25.6 Ag 37.5 Pd 28.74 Al 1.11 Na 16±3		2

¹Letters RA stand for Raney alloy. Leached Raney alloys have the number of the original Raney alloy but are preceded by the letters RAL. Mesh size 150-250 unless otherwise stated.

²Raney alloys machined into turnings before they were crushed.

aluminum was found to be 10.9 pct and 11.0 pct respectively. Total removal of all aluminum from Raney catalysts appears to be unusually difficult (25).

Reduction of Coprecipitated Hydroxides or Carbonates

Fine powders of transition metals were prepared by reducing co-precipitated hydroxides or carbonates of the metals. The following sequence of steps were involved:

Metal salts in aqueous solution

↓ aqueous solution of NaOH or Na₂CO₃, 80° to 90° C

Hydroxides or carbonates

↓ H₂, 250° to 275° C, 85 hr

Reduced metals

The reaction mixture was vigorously stirred during the addition of the precipitant. Stirring and heating was continued until the mass came to a boil, after which the solid was allowed to settle. The precipitate was washed repeatedly by decantation with distilled water, filtered on a Büchner funnel, dried at 90° C, crushed to powder, and redried at 110° C.

The metal salts employed in this work were preferably nitrates, but stock solutions of Au, Pd, and Pt were prepared by dissolving the metals in aqua regia. Accordingly, mixtures containing Ag and Au, Pd, or Pt were precipitated in two steps: The component or components other than Ag were precipitated separately and the precipitate was washed free of chloride ions. The washed precipitate was then suspended in a solution of NaOH, and a solution of AgNO₃ was added with vigorous stirring. Thereafter, the solid was processed as before.

Since Pt is not precipitated from its solution by NaOH, this metal was brought down as Pt-black by reduction with sodium formate. A solution containing Pt and other metals was treated with NaOH in the usual manner and then an excess of sodium formate was added to the hot reaction mixture. Thus, Pt-black was precipitated on the hydroxides of the other metals of the combination. Heating and stirring was continued until the reduction of Pt was complete.

Gold is not precipitated quantitatively from its solution by NaOH since the metal forms a soluble complex with NaOH. The proportion of Au thus remaining in solution appeared to depend not only on the concentration of the free alkali but also on the concentration of the

sodium salts in the reaction mixture. Accordingly, the excess acids from the stock solution of Au in aqua regia were evaporated off, and only a minimum excess of NaOH was employed when the hydroxides of the combinations of metals containing Au were precipitated. Even so, there was visible loss of Au which could be judged from the color of the filtrate. Further, some Au was also lost when the precipitates were washed. Although a number of Au-containing combinations were prepared by co-precipitation, a modified method was subsequently adopted for preparing such combinations. Au(OH)₃ was precipitated alone, washed, and dried; weighed amounts of this powder were mixed mechanically with separately prepared, washed, and dried hydroxides of other metals.

Reduction of the dried hydroxide powders

was carried out in Vycor tubes. It was observed that the powders containing Pt and Pd were reduced with H₂ even at room temperature. As soon as H₂ was brought in contact with these materials, large quantities of water of reduction were released and the temperature of the bed rose rapidly. Precipitated materials containing Pt or Pd were, therefore, reduced with a mixture of He (or, in a few cases, CO₂) and H₂ until the initial phase of high activity had subsided. Thereafter, the temperature was raised slowly to 275° C. and reduction was continued with pure H₂. With this precaution, there was no tendency for overheating. Preparations containing Au also exhibited similar behavior but at a milder level: the reduction could be pursued with pure H₂ even in the initial stages if proper ventilation was provided to conduct the heat of reac-

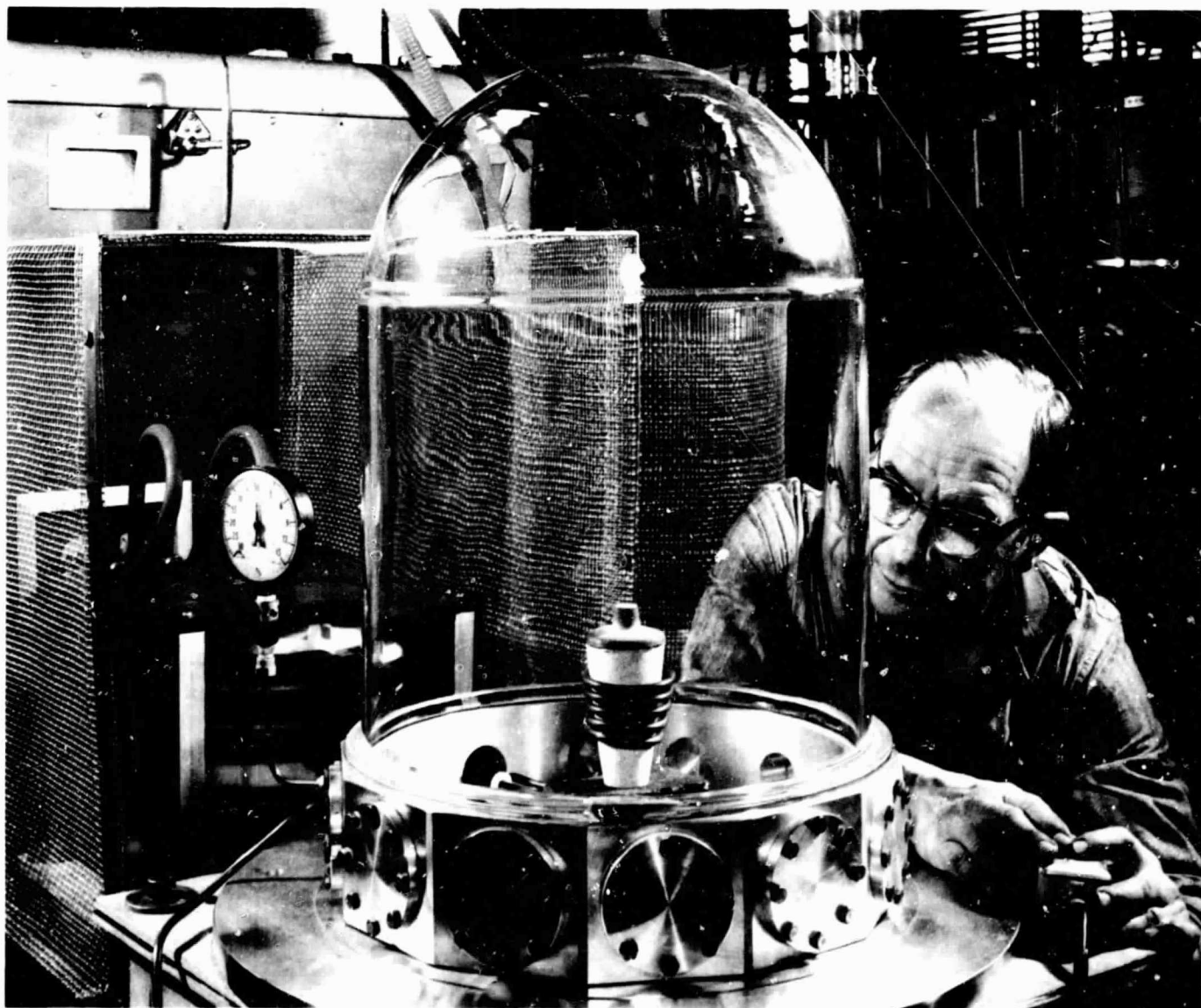


Figure 4.—Induction furnace for melting alloys.

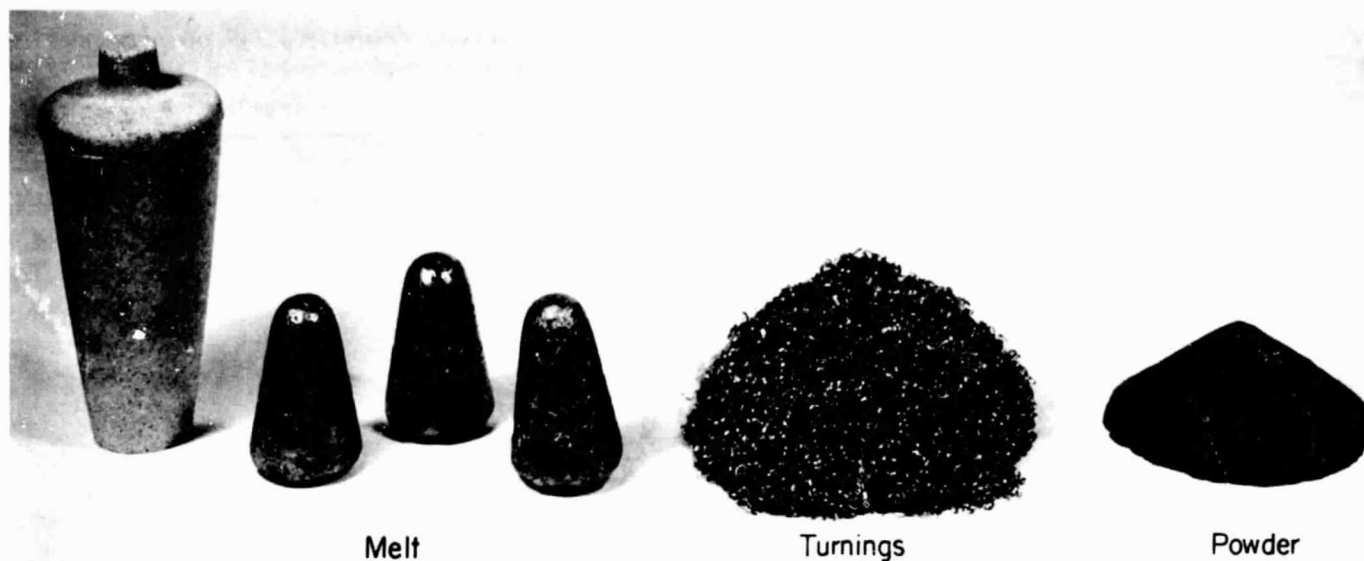


Figure 5.—Preparation of powdered alloy.

tion away from the bed. All reduced powders were protected from air by a blanket of N_2 or CO_2 during handling and were stored in a transfer box filled with CO_2 .

Only a few mixed metal combinations were precipitated as carbonates (table 4); these powders were reduced with H_2 at $450^\circ C$. Table 5 lists mixed metals prepared by the reduction of coprecipitated hydroxides, and table 6 lists mixed metals all containing Au prepared by the reduction of mechanically mixed hydroxides.

There is some evidence in the literature (11) that when coprecipitated carbonates of metals are reduced with H_2 at $350^\circ C$, alloys of metals are obtained. The homogeneity of such alloys depends on the duration of reduction. Coprecipitated carbonates of Ni and Cu reduced at $350^\circ C$ for 16 to 48 hours and subsequently heated under vacuum for "several hours" were found to be perfectly homogeneous. In the present work, the reduction temperature was lower, 250° to $275^\circ C$; nevertheless, X-ray patterns of the preparations 89R, 90R, 94R, 97R, 98R, and 100R (table 5) indicated some alloy formation. Small amounts of alloys, sufficient to affect the surface properties of the powders but insufficient for detection by X-rays, may conceivably have been formed in other tests.

Miscellaneous Methods

Decomposition of Transition Metal Salts of Organic Acids

50R.—A mixture of nickel formate and cobalt

acetate in the weight ratio 3Ni/1Co was prepared by slurring nickel formate in an aqueous solution of cobalt acetate. The slurry was dried at room temperature and the dried mass was homogenized in a mortar. The powder was then heated in an oven at $190^\circ C$ for 17 hr, and reduced with H_2 at $250^\circ C$ for 27 hr at a space velocity of $1,000\text{ hr}^{-1}$. (See runs 50C and 68C-73C in table 7.)

54R.—Nickel formate was decomposed in an oven at $190^\circ C$ and the decomposed powder was reduced with H_2 at $250^\circ C$ for 85 hr at a space velocity of $1,000\text{ hr}^{-1}$. (See run 54C in table 7.)

Reduction of Magnetite—An alkali-promoted magnetite was powdered and reduced with H_2 at $450^\circ C$ for 40 to 44 hr at a space velocity of $2,500\text{ hr}^{-1}$, its composition is as follows, in percent:

Fe ₃ O ₄	93.46
MgO.....	4.61
K ₂ O.....	.57
SiO ₂71
Cr ₂ O ₃65
	100.00

Total iron = 67.40 percent.

The degree of reduction was determined by the amount of water collected in a series of drying tubes. (See runs 8C-11C, 13C, and 14C in Table 7.)

4Cr-1Mo.—Chromium nitrate and ammonium molybdate in the weight ratio 4Cr/1Mo were crushed together and heated on a hotplate under a hood. The mass melted into a liquid which, in time, dried to fluffy solid. It was crushed and

Table 4.—Mixed metals prepared by the reduction of coprecipitated carbonates(Reducing gas: Hydrogen; Temperature: 450° C;
Space velocity: 2,500 hr⁻¹)

Identification ¹	Duration of reduction, hrs	Nominal composition of reduced material, weight ratios
ICP.....	18.0	3Fe-1Ag
IICP.....	7.0	1Fe-1Ag
IIICP.....	3.3	1Fe-3Ag
38CP.....	14.0	3Fe-1Ag
39CP.....	11.0	1Fe-1Ag
40CP.....	13.0	1Fe-3Ag

¹The letters CP stand for coprecipitated material. The precipitated carbonates ICP, IICP, and IIICP were washed with water, acetone, ethanol, and ether, in that order, before reduction.**Table 5.—Mixed metals prepared by the reduction of coprecipitated hydroxides**(Reduction gas: Hydrogen; Space velocity: 1,000 hr⁻¹;
Time: 85 hr.)

Identification ¹	Temperature of reduction, °C	Nominal composition of reduced material, weight ratios
53R.....	275	1Ni-1Ag
56R.....	275	Ni
57R.....	275	1Ni-1Pd
59R.....	275	Co
60R.....	275	1Ni-1Ag-1Au
61R.....	275	3Ni-1Co
62R.....	250	1Ni-3P
63R.....	250	3Ni-1Pd
64R.....	250	1Ni-1Au-1Pd
65R.....	250	1Ni-1Au-1Pt
66R.....	250	1Ni-1Ag-1Pt
67R.....	² 250	1Ni-3Ag
	³ 275	
74R.....	250	3Ni-1Au
75R.....	250	1Ni-1Ag-1Pd
76R.....	250	1Ni-3Au
77R.....	275	1Ni-1Au
78R.....	275	1Ni-4Cr
79R.....	250	1Ag-3Pd
80R.....	250	3Ni-1Pt
81R.....	250	1Ni-1Pt
82R.....	250	1Ni-3Pt
84R.....	275	3Ni-1Ag
85R.....	250	1Ag-1Pd
86R.....	250	3Ag-1Pd
88R.....	250	1Au-3Pd
89R.....	250	1Au-1Pd
90R.....	250	3Au-1Pd
91R.....	250	3Ag-1Pt
92R.....	⁴ 250	1Ag-3Pt
93R.....	⁴ 250	1Ag-1Pt
94R.....	250	1Pt-1Pd
95R.....	250	3Pt-1Pd
96R.....	250	1Pt-3Pd
97R.....	250	1Au-1Pd-1Ag
98R.....	⁵ 250	1Ni-1Pt-1Pd
99R.....	⁵ 250	1Ag-1Au-1Pt
100R.....	250	1Ag-1Pd-1Pt

¹The letter R stands for reduced metals.²11 hr.³74 hr.⁴Space velocity of H₂: 2,500 hr⁻¹.⁵Space velocity of H₂: 2,000 hr⁻¹.**Table 6.—Mixed metals prepared by the reduction of mechanically mixed powders of hydroxides of metals**

(Reducing gas: Hydrogen; Temperature: 250° C)

Identification No ¹	Space velocity, hr ⁻¹	Duration of reduction, hr	Nominal composition of reduced material, weight ratios
101R.....	1,500	89	3Ag-1Au
102R.....	1,500	80	3Au-1Pt
103R.....	3,000	92	1Au-3Pt
104R.....	1,500	82	1Au-1Pt
105R.....	1,000	89	1Ag-3Au
106R.....	1,000	90	1Ag-1Au
107R.....	1,000	86	1Au-1Pt-1Pd
108R.....		91	9Ni-1Au
109R.....		91	8Ni-2Au
110R.....		91	7Ni-3Au
111R.....		91	6Ni-4Au
112R.....		91	Au
113R.....		91	5Ni-5Au
114R.....		91	4Ni-6Au

¹The letter R stands for reduced metals.reduced with H₂ at 275° C for 85 hr at a space velocity of 1,000 hr⁻¹. (See run 87C in table 7.)**Fe₂TiO₃ (Iron Titanate).**—A mechanical mixture of 1 M Fe₂O₃ and 1 M TiO₂ was reduced with H₂ at 450° C for 100 hr at a space velocity of 1,000 hr⁻¹. (See run 83C in table 7.)**Nickel Plaque.**—A 6 inch × 6 inch porous plaque of nickel was cut into strips and reduced with H₂ at 450° C for 10 hr. (See run 28C in table 7.)

PREPARATION OF THE CARBIDES, NITRIDES, NITROCARBIDES, AND CARBONITRIDES OF TRANSITION METALS

This group of interstitial compounds was prepared by gas-solid reactions: the carbides by the action of CO or CO+H₂ on activated metal powders; the nitrides by the action of NH₃ on metal powders; the nitrocarbides by the action of NH₃ on carbides; and the carbonitrides by the action of CO on nitrides. The reactions were carried out in horizontally placed Vycor tubes of 1-inch diameter, shown on the right in figure 6. Each tube was fitted with metallic end pieces which had provisions for gas inlet and outlet. From 50 to 100 grams of solids were processed at a time. Separate thermocouples monitored the temperatures of the front, middle, and rear of the powder beds. Figure 7 shows the complete setup, which included furnaces, thermoregulators, gas flow meters, safety valves, and a 12-point

Table 7.—Preparation of carbides

Run No.	Charge	Carbiding			X-ray analysis	Carbon, chemical analysis, wt pct		Remarks
		Gas (hourly space velocity)	Duration, hr	Temperature, °C		Total	Free	
1C	Raney Fe	1CO+10H ₂ (3,000)	40	230	Fe ₃ O ₄ , α-Fe, χ-Fe ₂ C, ε-Fe ₂ C			
2C	Raney Fe	1CO+10H ₂ (3,000)	45	215	ε-Fe ₂ C, Fe ₃ O ₄	6.60	3.60	
3C	Raney Fe	1CO+10H ₂ (3,000)	48	305	χ-Fe ₂ C, Fe ₃ O ₄	4.90	3.45	
4C	1C	1CO+10H ₂ (3,000)	24	265	χ-Fe ₂ C, Fe ₃ O ₄	7.50	3.34	
5C	Raney Fe	1CO+10H ₂ (3,000)	44	250	χ-Fe ₂ C, α-Fe	7.9	1.7	
6C	Raney Fe	1CO+10H ₂ (3,000)	14 31	230 385	θ-Fe ₂ C, χ-Fe ₂ C	23.2	19.0	
7C	Raney Fe	1CO+10H ₂ He	52 40	250 340	χ-Fe ₂ C, ε-Fe ₂ C χ-Fe ₂ C	7.24	3.05	
8C	Reduced magnetite	CO (100) He	23 3	225 505	θ-Fe ₂ C, ε-Fe ₂ C	9.25	4.39	
9C	Reduced magnetite	CO (100)	16 24 6	190 260 320	χ-Fe ₂ C			
10C	Reduced magnetite	CO (100) He	7 8 3	235 290 500	θ-Fe ₂ C, α-Fe	8.49	5.88	
11C	Reduced magnetite	CO (100)	20 25	205 340	χ-Fe ₂ C	17.31	11.81	
12C	Raney Fe	1CO+10H ₂ (3,000) He	10 14 12	240 240 300	ε-Fe ₂ C, α-Fe χ-Fe ₂ C, ε-Fe ₂ C χ-Fe ₂ C	7.6	2.2	
13C	Reduced magnetite	CO (100)	24 72 72 31 48	160 170 175 190 210	α-Fe α-Fe, ε-Fe ₂ C (trace) α-Fe, ε-Fe ₂ C (small amount) α-Fe, ε-Fe ₂ C (trace) α-Fe, ε-Fe ₂ C (faint)			Pure ε-Fe ₂ C could not be prepared from magnetite.

PREPARATIVE TECHNIQUES

Table 7.—Preparation of carbides—Continued

Run No.	Charge	Carbiding			X-ray analysis	Carbon, chemical analysis, wt pct		Remarks
		Gas (hourly space velocity)	Duration, hr	Temperature, °C		Total	Free	
14C	Reduced magnetite	CO (100)	20	175-325				The temperature was raised slowly from 175 to 325° C in 20 hr under CO, and immediately thereafter the flow gas was changed to He.
		He	3	500	θ -Fe ₃ C	7.98	5.15	
15C	Raney Fe	1CO+10H ₂ (3,000)	24	300				
		He	3	500	θ -Fe ₃ C, χ -Fe ₂ C			
			3	500	θ -Fe ₃ C, χ -Fe ₂ C			
			8	550	θ -Fe ₃ C	6.23	1.63	
16C	Raney Fe	1CO+10H ₂ (3,000)	15	240	α -Fe, ϵ -Fe ₂ C			
			10	240	ϵ -Fe ₂ C, α -Fe			
			8	245	ϵ -Fe ₂ C, χ -Fe ₂ C, α -Fe (small amount).			
17C	Raney Ni	CO (100)	7	160-250				Despite repeated carburization, traces of Ni remained uncarbided, probably because Ni was coarse. Most of the massive amount of free C was deposited during the last leg of carburization when the temperature was raised to 300° C. There was a large gain in the weight of the charge over this period.
			24	250	Ni ₃ C, Ni (trace)			
			48	250	Ni ₃ C, Ni (trace)			
			24	300	Ni ₃ C, Ni (trace)	30.76	27.6	
18C	Raney Co	CO (100)	2	200				
			18	225				
			49	300	Co ₂ C, Co			
19C	Raney Ni	CO (100)	8	200				Twice during carburization the temperature of the bed rose to 420 to 440° C. Hence the large amount of free C.
			18	225				
			48	250	Ni ₃ C, Ni			
			20	250	Ni ₃ C, Ni (trace)	18.07	15.5	
20C	Raney Co	CO (100)	17	210				
			48	250	Co ₂ C, Co			
			27	260	Co ₂ C, Co	5.79	2.46	
21C	38CP (3Fe-1Ag)	CO (100)	42	170-350	Ag, χ -Fe ₂ C	12.25	11.10	
			3	350				
22C	39CP (1Fe-1Ag)	CO (100)	42	170-350	Ag, χ -Fe ₂ C	10.64	9.10	
			3	350				

Table 7.—Preparation of carbides—Continued

Run No.	Charge	Carbiding			X-ray analysis	Carbon, chemical analysis, wt pct		Remarks
		Gas (hourly space velocity)	Duration, hr	Temperature, °C		Total	Free	
23C	Raney Fe	1CO+10H ₂ (3,000)	48	230	ε-Fe ₂ C, α-Fe (trace)	8.06	3.6	
24C	40CP (1Fe-3Ag)	CO (100)	41 4	170-350 350	Ag	5.24	2.75	
25C	RAL-1 (1Ni-1Co)	CO (100)	13 216	170-250 250	Ni (cubic), Ni ₃ C	9.78	6.18	
26C	RAL-2 (1Ni-3Co)	CO (100)	16 144	170-250 250	Co ₂ C, small amounts of Ni ₃ C	8.86	4.86	
27C	RAL-3 (3Ni-1Co)	CO (100)	14 144	170-250 250	Ni ₃ C	9.33	7.48	
28C	Ni plaque	CO (3l/hr)	6 103	160-250 250	Ni (cubic)			Space velocity of CO could not be calculated since the strips of Ni plaque did not form a compact bed in the reaction tube.
29C	RAL-4 (1Ni-3Ag)	CO (100)	6 104	170-250 250	Ag (cubic)	1.21	.7	
30C	RAL-5 (1Ni-1Ag) (60-250 mesh)	CO (100)	6 102	60-250 250	Ag (cubic), Ni ₃ C (faint pattern)	2.31	1.12	
31C	RAL-5 (1Ni-1Ag) (150-250 mesh)	CO (100)	6 100	160-250 250	Ag (cubic), Ni ₃ C	2.04	1.06	Little difference in the quality of the product on account of difference in particle size; cf. 30C.
32C	RAL-6 (3Ni-1Ag)	CO (100)	6 102	160-250 250	Ag (cubic), Ni ₃ C	3.42	.8	
33C	Raney Co	CO (100)	28 72	160-250 250	Co ₂ C, α-Co	3.59	.54	
34C	RAL-9 (3Co-1Ag)	CO (100)	6 105	160-250 250	Ag (cubic), Co ₂ C	4.67	1.75	
35C	Raney Ni	CO (100)	24 72	160-250 250	Ni ₃ C	10.78	6.55	Grace Co. material, no mesh size indicated by company. Very good Ni ₃ C pattern.
36C	Raney Ni (<250 mesh)	CO (100)	12 72	160-250 250	Ni ₃ C	7.32	2.73	Quality of product better with Raney Ni of finer particle size; cf. 35C.

PREPARATIVE TECHNIQUES

Table 7.—Preparation of carbides—Continued

14

Run No.	Charge	Carbiding			X-ray analysis	Carbon, chemical analysis, wt pct		Remarks
		Gas (hourly space velocity)	Duration, hr	Temperature, °C		Total	Free	
37C	Raney Fe	1CO+10H ₂ (3,000)	9 44	160-250 250	χ-Fe ₃ C, ε-Fe ₂ C	7.53	2.86	
38C	RAL-7 (1Co-3Ag)	CO (100)	6 100	160-250 250	Ag (cubic), Co ₂ C	1.82	.72	
39C	RAL-8 (1Co-1Ag)	CO (100)	14 100	160-250 250	Ag, Co ₂ C, α-Co	2.56	.66	
40C	RAL-10 (1Ni-1Co-1Ag)	CO (100)	14 100	160-250 250	Ag, Ni ₃ C, Co ₂ C, Ni, Co	.84	.33	
41C	RAL-11C (1Ni-1Co-1Au)	CO (100)	23 102	160-250 250	α-Co, Au	1.26	.56	
42C	RAL-1 (1Ni-1Co)	CO (100)	22 101	160-250 250	Ni (cubic), α-Co	4.25	1.11	Repeat of 25C.
43C	RAL-5 (1Ni-1Ag)	CO (100)	4 102	160-250 250	Ag (cubic)	2.14	.16	Repeat of 31C.
44C	RAL-12 (1Ni-1Ag-1Au)	CO (100)	4 103	160-250 250	Au, Ag	1.27	.22	
45C	RAL-13 (1Co-1Ag-1Au)	CO (100)	5 104	160-250 250	Au, Co ₂ C (faint)	2.72	.74	
46C	RAL-6 (3Ni-1Ag)	CO (100)	7 104.5	160-250 250	Ag, Ni ₃ C	3.44	.22	Repeat of 32C.
47C	Decomposed Ni-formate (reduced with H ₂ at 450° C, for 4 hr).	CO (100)	8 100 84 36	160-250 250 260 350	Ni Ni, Ni ₃ C Ni, Ni ₃ C Ni	.37 .84 10.38 22.1	.05 .07 8.55 22.37	Rear of the bed. Front of the bed. Very heavy deposition of free carbon, specially in the front of the reaction bed, when the temperature was raised to 350° C.
48C	Coprecipitated hydroxides of 3Ni-1Co, reduced with H ₂ at 350° C for 3.5 hr.	CO (100)	5 101 102	160-250 250 270	Ni Ni	.80 .30	.18 .25	
49C	Ni hydroxide reduced with H ₂ at 350° C for 8.5 hr.	CO (100)	105	250	Ni	.47	.04	

INTERSTITIAL COMPOUNDS AS FUEL CELL CATALYSTS

Table 7.—Preparation of carbides—Continued

Run No.	Charge	Carbiding			X-ray analysis	Carbon, chemical analysis, wt pct		Remarks
		Gas (hourly space velocity)	Duration, hr	Temperature, °C		Total	Free	
50C	3Ni-1Co (Mixture of Ni-formate and Co-acetate decomposed and reduced with H ₂ at 250° C.)	CO (100)						
		CO (100)	6 97	170-270 270	Ni ₃ C, Co ₂ C (faint)	12.77	7.22	
51C	Co-hydroxide reduced with H ₂ at 350° C.	1CO+1CO ₂ (200)	5 140	160-270 270	α-Co	.6	.28	
52C	3Ni-1Ag, coprecipitated hydroxides, reduced with H ₂ at 350° C.							The material was discarded, for in view of the experience gained in runs 47C-51C, it appears that Ni and Co obtained by reducing hydroxides, formates, or acetates at 350° C or higher can not be carbided.
53C	53R (1Ni-1Ag)	CO (100)	5 102 106	160-250 250 260	Ag, Ni ₃ C	1.92	.12	
54C	Decomposed Ni-formate reduced with H ₂ at 250° C for 95 hr.	CO (100)	5 100	160-250 250	Ni ₃ C (standard quality pattern)	6.85	.57	Combined C, by difference 6.28 pct. Calculated value for Ni ₃ C, combined carbon 6.38 pct.
55C	RAL-14 (1Ni-1Pd)	CO (100)	5 106	160-250 250		8.37	7.49	
56C	56R (Ni)	CO (100)	6 102 36	160-250 250 260	Ni ₃ C, Ni Ni ₃ C, Ni	.94 1.25	.20 .23	
57C	57R (1Ni-1Pd)	CO (100)	6 37 103	160-250 250 260		1.19	.95	
58C	3Ni-1Co Mixture of Ni-formate and Co-acetate reduced with H ₂ at 250° C for 27 hr.	CO (100)	5 107	160-260 260	Ni, Ni ₃ C, Co ₂ C	9.40	3.84	See run 50C (second part). In the present run, the carburization temperature is 10° lower than that in 50C (second part).

PREPARATIVE TECHNIQUES

Table 7.—Preparation of carbides—Continued

Run No.	Charge	Gas (hourly space velocity)	Carbiding		X-ray analysis	Carbon, chemical analysis, wt pct		Remarks
			Duration, hr	Temperature, °C		Total	Free	
59C	59R (Co)	CO (100)	6 70 30	160-250 250 260	----- ----- Co ₂ C	----- ----- 10.66	----- ----- 5.09	
60C	60R (1Ni-1Au-1Ag)	CO (100)	5 102	160-250 260	----- Au, Ag, Ni, Ni ₃ C	----- 1.57	----- .39	
61C	61R (3Ni-1Co)	CO (100)	5 102	160-260 260	----- -----	----- .28	----- .17	
62C	62R (1Ni-3Pd)	CO (100)	6 100	160-260 260	----- -----	----- .35	----- .25	
63C	63R (3Ni-1Pd)	CO (100)	5 100	160-260 260	----- Ni ₃ C	----- 2.34	----- 1.93	
64C	64R (1Ni-1Au-1Pd)	CO (100)	5 104	160-260 260	----- Au, Ni ₃ C	----- -----	----- -----	
65C	65R (1Ni-1Au-1Pt)	CO (100)	5 100	160-260 260	----- -----	----- -----	----- -----	
66C	66R (1Ni-1Ag-1Pt)	CO (100)	6 102	160-260 260	----- Ag, Ni ₃ C, Ni	----- -----	----- -----	
67C	67R (1Ni-3Ag)	CO (100)	6 98	160-260 260	----- Ag, Ni, Ni ₃ C	----- .92	----- .21	
68C	3Ni-1Co Nickel formate and Co-acetate mixture reduced with H ₂ at 250° C for 27 hr.	CO (100)	5 120	160-250 260	----- Ni, Ni ₃ C, Co ₂ C(?)	----- -----	----- -----	In the series of runs 68C to 73C, 3Ni-1Co mixtures were carburized at 260° C and 240° C for different lengths of time; see discussions under 6) of "Preparation of the Carbides, Nitrides, Nitrocarbides and Carbonitrides of Transition Metals."
69C	3Ni-1Co	CO (100)	5 120	160-240 240	----- Ni, Ni ₃ C, Co ₂ C(?)	----- -----	----- -----	
70C	3Ni-1Co	CO (100)	4 72	160-260 260	----- Ni, Ni ₃ C, Co ₂ C(?)	----- -----	----- -----	
71C	3Ni-1Co	CO (100)	4 72	160-240 240	----- Ni ₃ C, Ni	----- 4.15	----- .53	
72C	3Ni-1Co	CO (100)	4 24	160-260 260	----- Ni, Ni ₃ C	----- -----	----- -----	

Table 7.—Preparation of carbides—Continued

Run No.	Charge	Carbiding			X-ray analysis	Carbon, chemical analysis, wt pct		Remarks
		Gas (hourly space velocity)	Duration, hr	Temperature, °C		Total	Free	
73C	3Ni-1Co	CO (100)	4 24	160-240 240	Ni, Ni ₃ C	2.13	.26	
74C	74R (3Ni-1Au)	CO (100)	5 100	160-260 260	Au	1.01	.20	
75C	75R (1Ni-1Ag-1Pd)	CO (100)	5 102	160-260 260	Ni, Ni ₃ C	.94	.61	
76C	76R (1Ni-3Au)	CO (100)	4 103	160-260 260	Au, Ni, Ni ₃ C	1.68	.15	
77C	77R (1Ni-1Au)	CO (100)	5 100	160-260 260	Au, Ni	1.15	.21	
78C	78R (1Ni-4Cr)	CO (100)	4 100	160-260 260		4.61	1.67	
79C	79R (1Ag-3Pd)	CO (100)	4 100	160-260 260		.82	.23	
80C	80R (3Ni-1Pt)	CO (100)	4 105	160-260 260	Ni, Ni ₃ C	5.96	3.40	
81C	81R (1Ni-1Pt)	CO (100)	5 100	160-260 260	Ni, Ni ₃ C	3.66	2.57	
82C	82R (1Ni-3Pt)	CO (100)	4 105	160-260 260	Pt, Ni	1.21	.97	
83C	Reduced 1Fe ₂ O ₃ +1TiO ₂ (mechanical mixture reduced with H ₂ at 450° C for 104 hr).				α-Fe, TiO ₂ (X-ray analysis of the reduced material)			For secondary reasons, the reduced powder was not carburized.
84C	84R (3Ni-1Ag)	CO (100)	4 103	160-260 260	Ni ₃ C (excellent pattern), Ag	5.75	.35	
85C	85R (1Ag-1Pd)	CO (100)	5 104	160-260 260	Ag, Pd	.29	.10	
86C	86R (3Ag-1Pd)	CO (100)	4 105	160-260 260	Ag, Pd	.5	.23	
87C	87R (4Cr-1Mo)	CO (100)	5 103	160-260 260		.96	.19	
88C	88R (1Au-3Pd)	CO (100)	4 104	160-260 260	Pd	.67	.21	

PREPARATIVE TECHNIQUES

recorder for the thermocouples. In some experiments, the concentration of CO in exit gases was followed with the help of a differential type infrared detector shown in figure 8. All pyrophoric solids were handled under a blanket of He, N₂, or CO₂. They were collected in flasks of the kind shown on the left in figure 6, and stored under CO₂ in a transfer box.

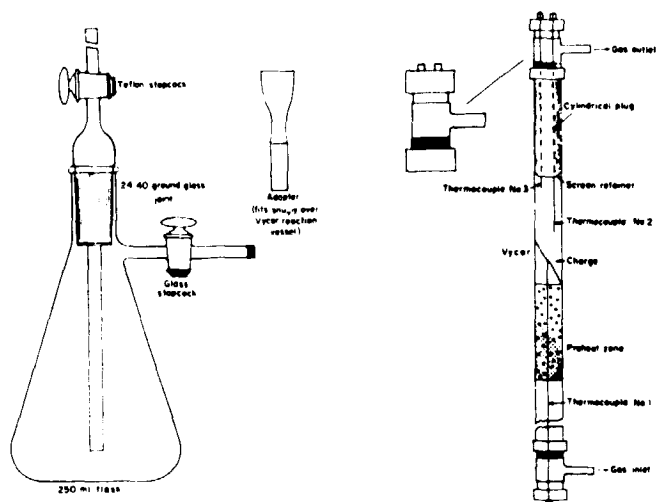


Figure 6.—Reaction vessel and collection flask for interstitial compounds.

The products were identified by qualitative analysis of the X-ray diffraction patterns. A Debye-Scherrer camera of 114.6-mm diameter mounted on a Picker X-ray machine with a Fe target was employed for photographing the patterns on 3.5-cm-wide Kodak no-screen medical films. In most cases, the exposure time was 8 hr; in a few, 12 hr.

Preparation of Carbides

The experimental conditions employed for carburizing metal powders are presented in table 7. All reactions were carried out at ambient pressures. The leached Raney metals were treated with H₂ at 450° C for 10 to 20 hr at hourly space velocities of 1,000 to 2,500 before carburizing. The hydroxides were generally reduced in situ. In all cases, the powders were cooled to at least 160° C before CO or CO+H₂ was introduced. The temperature of the bed was then raised slowly and in steps. Several hours were usually allowed for the temperature to come up to the final level (columns 4 and 5, table 7). Without this precaution the powders tended to overheat and the products showed large quanti-

ties of free carbon. The disproportionation reaction of CO on metals,



is favored by high temperatures. With Co and Ni, the tendency for sudden overheating appears at about 180° to 220° C in the presence of CO. Since the carburization of Co or Ni does not ordinarily proceed at measurable rates below 250° C, the lower temperature represents the point of onset of carbiding of the active spots on the metal powders.

A sample of the exit gas from carburization of Fe (run 3C, table 7) was found to have the following composition, on a dry basis, by volume-percent:

H ₂	89.2
CH ₄	6.0
CO.....	1.7
CO ₂	1.6
C ₂ H ₆8
C ₂ H ₄5
N ₂2

The gas was sampled after the reaction had been in progress for 6 hr and was analyzed by gas chromatography. The feed gas consisted of 1CO+10H₂.

Column 6, table 7, 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 C. As concomitant deposition of some free C is unavoidable, the combined or carbidic C must be distinguished from the free C. In practice, it is simpler to determine the total C and the free C, and to compute the carbidic C by difference. Total C was determined by igniting samples of products 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 C was determined by a two-step process: (1) Samples were digested in dilute (1:3) HCl at 60° to 80° C for one-half hr to drive off carbidic C 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. (2) The crucible was placed in a tube furnace and ignited in excess O₂. As before, CO₂ was scrubbed in ascarite towers. The results for total C and free C are given in columns 7 and 8, table 7.

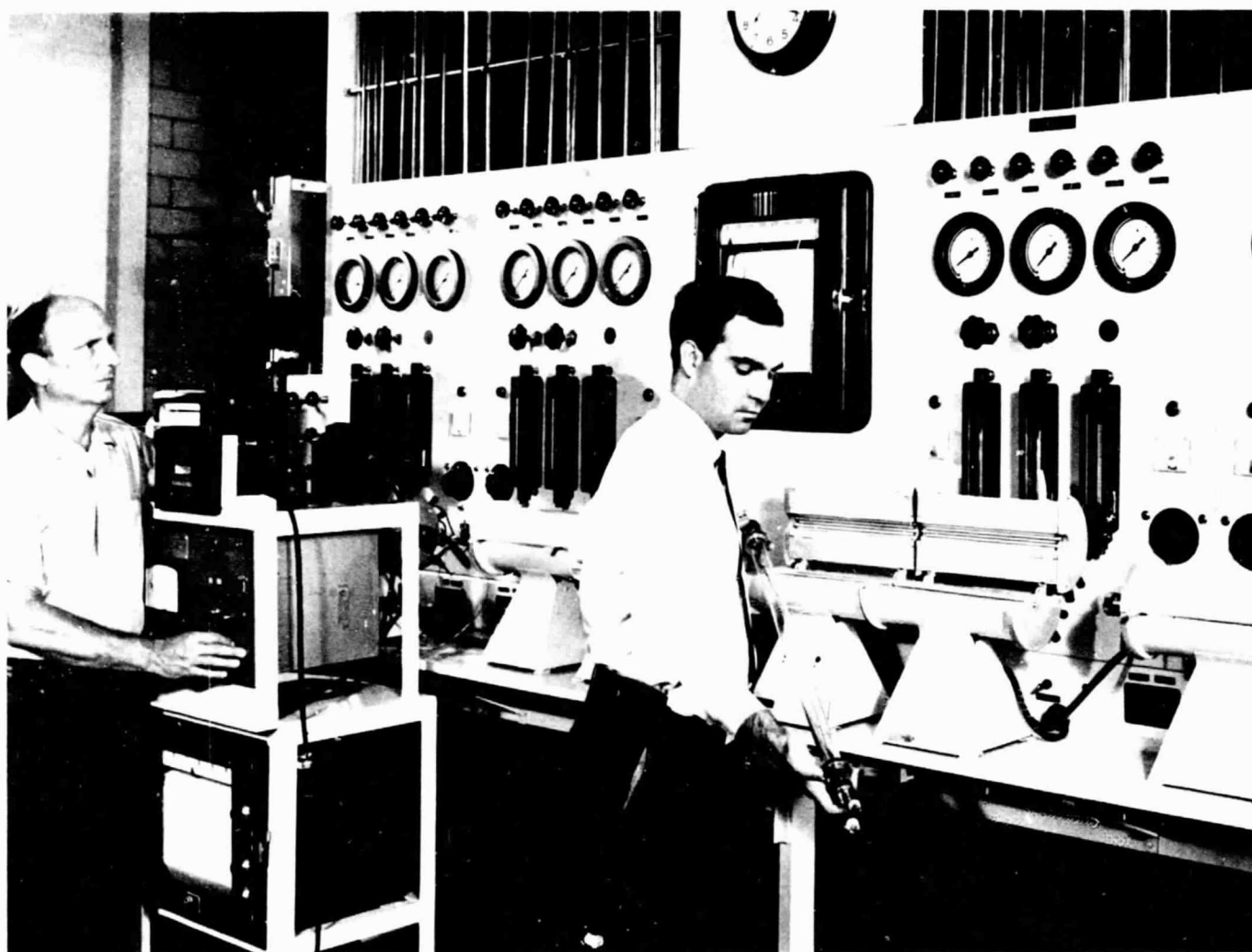


Figure 7.—Units for preparing interstitial compounds by gas-solid reactions.

No extensive study of the hydrocarbons produced by digesting carbides in dilute mineral acids was undertaken, but the gases from acid hydrolysis of one of the carbides, θ -Fe₃C (14C, table 7), were analyzed by mass spectroscopy. The carbide was digested with dilute H₂SO₄ at room temperature in a flask fitted with a dropping funnel and connected to a vacuum manifold. The solid (0.25 g) was placed in the flask under a blanket of CO₂, and the dropping funnel was charged with the acid. The system was flushed with He and evacuated before the acid was run into the flask. The gaseous products were collected with the help of a Töepler pump. The results of analysis, on a dry and airfree basis, are given by volume-percent as follows:

Hydrogen.....	85.93
Methane.....	4.96
Ethane.....	.84
Propane.....	.87
Butane.....	.39
Pentane.....	.28
Ethylene.....	1.04

Propylene.....	1.30
Butene.....	.71
Pentene.....	.55
CO.....	.67
CO ₂	2.47

Over 30 years ago, from his studies on acid hydrolysis of carbides, Schmidt (23) concluded that the primary step in the reaction of the carbides of Fe, Co, and Ni with dilute mineral acids is evolution of active H. The carbidic C then reacts with the active H to form -CH₂ radicals which by hydrogenation and polymerization yield the series of saturated and unsaturated hydrocarbons. The free radical theory was advanced to account for the formation of polynuclear hydrocarbons since there is no evidence for C-C bonds in the carbides of Fe, Co, and Ni. Further, as no acetylenic hydrocarbons are detected in the products of hydrolysis, polymerization must proceed exclusively via -CH₂ radicals. The premises of the mechanism proposed by Schmidt are still valid.



Figure 8.—Infrared apparatus for monitoring CO.

The following comments with respect to preparation of carbides are pertinent:

1) No carbides other than those of Fe, Co, and Ni were formed in any of the experiments.

2) Carbides prepared at 300° C or higher contained more free C than combined C (see 6C, 11C, 17C, 21C, and 22C, table 7).

3) The carbides prepared from Raney metals contained more free C than the carbides prepared from reduced hydroxides at the same temperature.

4) Ni or Co prepared by reducing hydroxides, formates, or acetates at 350° C or higher could not be carbided (47C-52C, table 7).

5) Since direct carburization of Fe to θ -Fe₃C at 500° C yields a product contaminated with intolerable amounts of free C, this carbide of Fe was prepared by heating a mixture of ϵ -Fe₂C and χ -Fe₂C at 500° C under He (8C, 10C, 14C, and 15C, table 7). The mixture of ϵ -Fe₂C and χ -Fe₂C was prepared by carburizing Fe at 225 to 300° C.

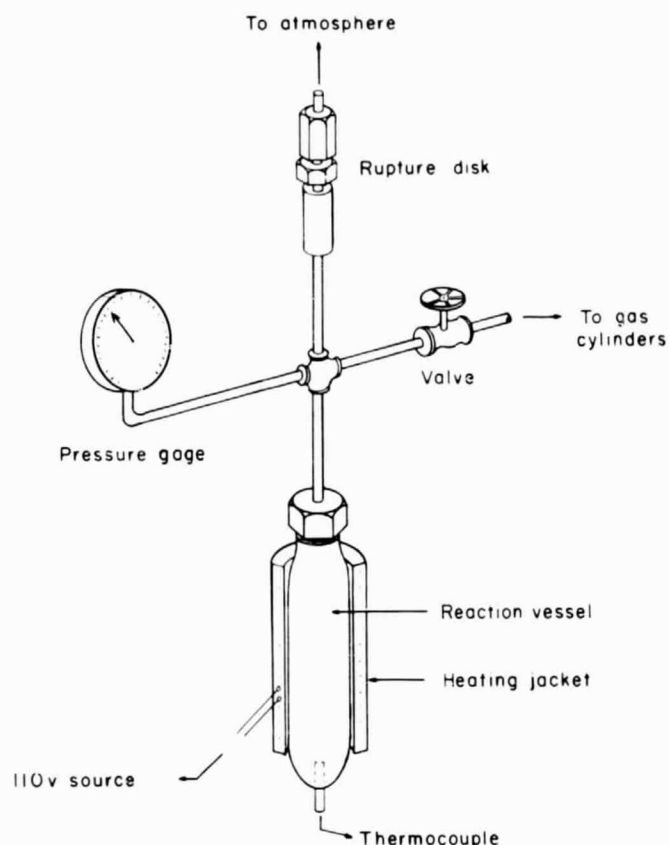


Figure 9.—Apparatus for reacting reduced metals with pressurized ammonia.

6) 68C-73C was a special series of preparations. Samples of a reduced mixture of 3Ni-1Co were carburized at 260° C for 120, 72, and 24 hr. Samples of the same material were also carburized at 240° C for 120, 72, and 24 hr. The six preparations were tested by Two Laboratories, Inc., for cathodic activity in the reduction of O₂ in 6M KOH. The lower the carburization temperature and the shorter the carburization time, the less interstitial C will be incorporated and the less the products will be sintered. The series was prepared to determine if a material of superior catalytic activity may be prepared by minimizing sintering at the expense of complete carbiding, for the activity may be expected to depend mainly on the composition of the catalyst surface.

The results indicated that the loss of activity due to sintering at these temperatures is of far less consequence than complete carbiding; the product obtained by carburization for 120 hr at 260° C was the most active catalyst.

Preparation of Nitrides

The experimental conditions employed for preparing the various nitrides of Fe are given in table 8. Samples of Raney Fe were reduced

Table 8.—Preparation of nitrides

(Nitridding gas, N¹; space velocity, 1,000 hr⁻¹)

Run No.	Charge	Nitridding		X-ray analysis	N, chemical analysis, wt pct
		Duration, hr	Temperature, °C		
1N ¹	Reduced magnetite	6.0	365	ϵ -Fe ₃ N-Fe ₂ N, γ' -Fe ₄ N	5.92
2N ¹	Reduced magnetite	6.0	380	γ' -Fe ₄ N, ϵ -Fe ₃ N-Fe ₂ N	5.47
4N	Reduced magnetite	7.0	350	ϵ -Fe ₃ N-Fe ₂ N, γ' -Fe ₄ N	7.61
5N	Reduced magnetite	7.0	350	ϵ -Fe ₃ N-Fe ₂ N, γ' -Fe ₄ N	6.57
6N	Reduced magnetite	12.0	350	ϵ -Fe ₃ N-Fe ₂ N, ζ -Fe ₂ N, γ' -Fe ₄ N	6.35
7N	Reduced magnetite	6.0	390	γ' -Fe ₄ N, Fe ₃ O ₄	5.04
8N	Raney Fe	7.5	350	γ' -Fe ₄ N, ζ -Fe ₂ N	
9N	Reduced magnetite	24.0	350	ζ -Fe ₂ N	
10N	Reduced magnetite	24.0	350	ϵ -Fe ₃ N-Fe ₂ N	7.94
11N	ICP (3Fe-1Ag)	25.0	355	ϵ -Fe ₃ N-Fe ₂ N, Ag	4.85
13N	Raney Fe	12.0	355	ϵ -Fe ₃ N-Fe ₂ N	9.75
14N	Raney Fe	24.0	355	ϵ -Fe ₃ N-Fe ₂ N	9.61
15N	IICP (1Fe-1Ag)	24.0	350	Ag, ϵ -Fe ₃ N-Fe ₂ N	4.35
16N	IIICP (1Fe-3Ag)	24.0	350	Ag, ϵ -Fe ₃ N-Fe ₂ N	2.81
17N	Raney Fe	12.0	355	ϵ -Fe ₃ N-Fe ₂ N	9.12
18N	Raney Fe	24.0	295	ζ -Fe ₂ N, ϵ -Fe ₃ N-Fe ₂ N, γ' -Fe ₄ N	9.3
19N	Reduced magnetite	24.0	350	ζ -Fe ₂ N, ϵ -Fe ₃ N-Fe ₂ N, γ' -Fe ₄ N	7.77
20N	Raney Fe	7.5	350	ζ -Fe ₂ N, γ' -Fe ₄ N, ϵ -Fe ₃ N-Fe ₂ N	
		48.0	300	ϵ -Fe ₃ N-Fe ₂ N	9.95
21N	Reduced magnetite	5.0	250	γ' -Fe ₄ N, ϵ -Fe ₃ N-Fe ₂ N	5.93

¹ Space velocity of NH₃ 750.

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 nitrided. All efforts to prepare nitrides of Co and Ni were fruitless. Chemical analyses of the solids from these experiments indicated some N (0.03-2.1 pct), but no corroborative evidence for metal nitride was obtained by X-ray analysis. The diffraction patterns indicated only pure metals. A brief review of these experiments, for purposes of record follows:

1) A sample of Raney Ni was treated with NH₃ at an hourly space velocity of 1,000, first at 175° C for 48 hr, then at 300° C for 24 hr, and finally at 380° C for 24 hr. Small samples were withdrawn after each treatment for X-ray analysis. No evidence for Ni₃N was detected. A parallel experiment with Raney Co over 200 to 450° C and hourly space velocities 1,000 to 100,000 of NH₃ failed to produce evidence of Co₂N.

2) Ten g of Ni₃C was stripped of its C by treatment with H₂ at 260° C for 24 hr at an hourly space velocity of 1,000; X-ray analysis of the residual material indicated it was pure Ni. The material was then treated with NH₃ at 350° C for 72 hr at an hourly space velocity of 1,000; X-ray and chemical analysis of the product revealed no evidence for Ni₃N. Nickel obtained by stripping Ni₃C of C was not amenable to nitridding any more than Raney Ni.

3) A sample of Raney Ni was charged in a

pressurized flow system and treated with NH₃ and NH₃ + N₂ at 380°-390° C under 75 psig. No trace of nitride was detected in the highly pyrophoric material discharged after prolonged treatment, extending over several days.

4) Ten grams Raney Ni and 150 to 160 ml of liquid NH₃ were charged in a stainless steel vessel (fig. 9) which, in separate runs, was then—

- kept at room temperature for 72 hr (equilibrium pressure 180 psig);
- heated in a water bath at 100° C for 14 hr (equilibrium pressure 810 psig);
- heated in a water bath at 100° C for 81 hr (equilibrium pressure 830 psig);
- heated in an oil bath at 115°-118° C for 5 hr (equilibrium pressure 780 to 820 psig).

The compressed gases were then released from the vessel and the solid removed under an inert atmosphere. No Ni₃N was detected in the solid from any of the experiments.

5) The stainless steel vessel was charged with 8 g Raney Ni, approximately 150 ml of liquid NH₃, and 120 psig N₂, and heated in a water bath at 97° to 99° C for 21 hr. The equilibrium pressure varied between 950 and 1,030 psig. The compressed gases were released and the solid discharged and tested as before. No Ni₃N was detected.

6) The vessel was charged with 10 g Raney Ni and 1,180 psig N₂ at room temperature. It was then heated by an electric tape, wound extern-

ally, to 300°–320° C for 28 hr. No Ni₃N was detected in the discharged solid.

7) The charge consisted of 10 g Raney Ni, 150 to 160 ml liquid NH₃, and 125 psig N₂. The vessel was maintained at about 135° C for 13 hr (equilibrium pressure 2,100 to 2,300 psig). No Ni₃N was detected.

8) The charge was 10 g Raney Ni, liquid NH₃, and 300 psig N₂ (at room temperature), and was heated at 250° C for 13½ hr (equilibrium pressure 1,470 to 1,500 psig). No Ni₃N was detected.

Preparation of Nitrocarbides

The nitrocarbides were prepared by nitriding carbides with NH₃. The experimental conditions employed for preparing the nitrocarbides along with the X-ray and chemical analyses of the products are given in table 9. Co₂C and Ni₃C were nitrided at 260° C since these carbides are unstable above this temperature. χ -Fe₂C and θ -Fe₃C were nitrided at 300° to 350° C since these carbides are stable at far higher temperatures (table 2). Of course, longer reaction times

Table 9.—Preparation of nitrocarbides

Run No.	Charge	Carbide nitriding			X-ray analysis	Chemical analysis, weight percent		
		Gas (space velocity, hr ⁻¹)	Duration, hr	Temperature, ° C		N	C	
						Total	Free	
1NC	3C (χ -Fe ₂ C, Fe ₃ O ₄)	NH ₃ (1,000)	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)	NH ₃ (1,000)	24	355	χ -Fe ₂ X(C,N), ϵ -Fe ₃ X- Fe ₂ X(C,N).	2.26	11.76	5.93
3NC	8C (θ -Fe ₃ C, ϵ -Fe ₂ C)	NH ₃ (1,000)	24	350	ϵ -Fe ₃ X-Fe ₂ X(C,N), ζ -Fe ₂ N, θ -Fe ₃ C.	4.14	7.50	3.99
4NC	5C (χ -Fe ₂ C, α -Fe)	NH ₃ (1,000)	20	355	ϵ -Fe ₃ X-Fe ₂ X(C,N)	6.64	3.84	1.09
5NC	14C (θ -Fe ₃ C)	NH ₃ (1,000)	6	305	θ -Fe ₃ X(C,N)	.78	8.13	3.53
6NC	7C (χ -Fe ₂ C)	NH ₃ (1,000)	15	300	χ -Fe ₂ X(C,N)	1.13	7.35	6.0
7NC	15C (θ -Fe ₃ C)	NH ₃ (1,000)	6	300	θ -Fe ₃ X(C,N)	1.23	6.19	4.34
8NC	21C (Ag, χ -Fe ₂ C)	NH ₃ (1,000)	14	270	-----	-----	-----	-----
			5	280	Ag, χ -Fe ₂ X(C,N)	.65	12.16	9.90
9NC	22C (Ag, χ -Fe ₂ C)	NH ₃ (1,000)	15	280	Ag, χ -Fe ₂ X(C,N)	.48	10.55	8.82
10NC	24C (carbided 1Fe-3Ag)	NH ₃	15	280	Ag	.37	5.25	3.81
11NC	19C (Ni ₃ C, trace Ni)	NH ₃ (1,000)	15	260	Ni ₃ X(C,N), trace Ni	1.08	-----	-----
12NC	20C (Co ₂ C, Co)	NH ₃ (1,000)	39	260	Co ₂ X(C,N)	.90	5.33	2.50
13NC	26C (carbided 1Ni-3Co)	NH ₃ (1,000)	48	260	Co ₂ X(C,N), Ni ₃ X(C,N).	.92	8.88	4.50
15NC	27C (carbided 3Ni-1Co)	NH ₃ (1,000)	48	260	Ni ₃ X(C,N)	1.01	9.30	6.38
16NC	25C (carbided 1Ni-1Co)	NH ₃ (1,000)	48	260	Ni, Co, Ni ₃ X(C,N)? Co ₂ X(C,N)?	.87	9.45	6.46
17NC	29C (carbided 1Ni-3Ag)	NH ₃ (1,000)	48	260	Ag	.48	1.06	.16
18NC	30C (carbided 1Ni-1Ag, 60-250 mesh)	NH ₃ (1,000)	48	260	Ag, Ni ₃ X(C,N)	.77	1.93	.49

Table 9.—Preparation of nitrocarbides—Continued

Run No.	Charge	Carbide nitriding			X-ray analysis	Chemical analysis, wt pct		
		Gas (space velocity, hr ⁻¹)	Duration, hr	Temperature, °C		N	C	
						Total	Free	
19NC	31C (carbided 1Ni-1Ag, 150-250 mesh)	NH ₃ (1,000)	48	260	Ag, Ni ₃ X(C,N)	.65	1.73	.45
20NC	32C (carbided 3Ni-1Ag)	NH ₃ (1,000)	48	260	Ag, Ni ₃ X(C,N)	.91	2.91	.60
21NC	33C (Co ₂ C, α-Co)	NH ₃ (1,000)	48	260	Co ₂ X(C,N)	.51	3.50	.52
22NC	34C (carbided 3Co-1Ag)	NH ₃ (1,000)	48	260	Ag, Co ₂ X(C,N)	.43	4.60	.90
23NC	35C (Ni ₃ C)	NH ₃ (1,000)	48	260	Ni ₃ X(C,N)	1.32	10.35	6.00
24NC	36C (Ni ₃ C, <250 mesh)	NH ₃ (1,000)	48	260	Ni ₃ X(C,N)	1.12	7.13	2.78
25NC	38C (carbided 1Co-3Ag)	NH ₃ (1,000)	48	260	Ag, Co ₂ X(C,N)	.27	1.85	.52
26NC	39C (carbided 1Co-1Ag)	NH ₃ (1,000)	48	260	Ag, α-Co, Co ₂ X(C,N)	.33	2.52	.45
27NC	40C (carbided 1Ni-1Co-1Ag)	NH ₃ (1,000)	48	260	Ag, Ni, Co	.74	.48	.37
28NC	42C (carbided 1Ni-1Co)	NH ₃ (1,000)	48	260	α-Co, Ni	1.01	3.84	1.11
29NC	41C (carbided 1Ni-1Co-1Au)	NH ₃ (1,000)	48	260	α-Co, Au	.65	.91	.16
30NC	44C (carbided 1Ni-1Ag-1Au)	NH ₃ (1,000)	48	260	Au, Ag	.79	.91	.17
31NC	43C (carbided 1Ni-1Ag)	NH ₃ (1,000)	48	260	Ag	1.06	1.51	0.20
32NC	46C (carbided 3Ni-1Ag)	NH ₃ (1,000)	48	260	Ag, Ni ₃ X(C,N)	1.54	2.44	.22
33NC	45C (carbided 1Co-1Ag-1Au)	NH ₃ (1,000)	48	260	Au, Co ₂ X(C,N)	.51	2.46	.69
36NC	50C (carbided 3Ni-1Co)	NH ₃ (1,000)	48	260	Ni ₃ X(C,N), Co ₂ X(C,N)	1.02		
37NC	58C (carbided 3Ni-1Co)	NH ₃ (1,000)	48	260	Ni ₃ X(C,N), Ni, Co ₂ X(C,N)	.96	8.98	4.03
38NC	53C (carbided 1Ni-1Ag)	NH ₃ (1,000)	48	260	Ag, Ni ₃ X(C,N)	1.31	1.93	.31
39NC	54C (Ni ₃ C)	NH ₃ (1,000)	48	250	Ni ₃ X(C,N) (stan- dard quality pat- tern).	.47	6.63	.41
40NC	55C (carbided 1Ni-1Pd)	NH ₃ (1,000)	48	260	A pattern of Ni-Pd alloy.	1.69	7.65	6.91

Table 9.—Preparation of nitrocarbides—Continued

Run No.	Charge	Carbide nitriding			X-ray analysis	Chemical analysis, wt pct		
		Gas (space velocity, hr ⁻¹)	Duration, hr	Temperature, °C		N	C	
						Total	Free	
41NC	56C (Ni ₃ C, Ni)	NH ₃ (1,000)	48	260	Ni ₃ X(C,N)	.84	1.07	.17
42NC	57C (carbided 1Ni-1Pd)	NH ₃ (1,000)	48	260	A pattern of Ni-Pd alloy.	2.21	.60	.48
43NC	59C (Co ₂ C)	NH ₃ (1,000)	48	260	Co ₂ X(C,N) (excellent pattern).	.58	10.36	4.92
44NC	60C (carbided 1Ni-1Au-1Ag)	NH ₃ (1,000)	48	260	Au, Ag	1.41	1.37	.40
45NC	61C (carbided 3Ni-1Co)	NH ₃ (1,000)	48	260	Ni, Ni ₃ X(C,N)	.65	.37	.24
46NC	62C (carbided 1Ni-3Pd)	NH ₃ (1,000)	48	260	A pattern of Ni-Pd alloy.	.38	.29	.24
47NC	63C (carbided 3Ni-1Pd)	NH ₃ (1,000)	48	260	Ni ₃ X(C,N)	2.45	2.14	1.40
48NC	64C (carbided 1Ni-1Au-1Pd)	NH ₃ (1,000)	48	260	Au			
49NC	65C (carbided 1Ni-1Au-1Pt)	NH ₃ (1,000)	48	260				
50NC	66C (carbided 1Ni-1Ag-1Pt)	NH ₃ (1,000)	48	260	Ag, Ni ₃ X(C,N), Ni	.15	.50	.32
51NC	67C (carbided 1Ni-3Ag)	NH ₃ (1,000)	48	260	Ag, Ni ₃ X(C,N)	.94	.56	.15
52NC	75C (carbided 1Ni-1Ag-1Pd)	NH ₃ (1,000)	48	260	Pd, Ag	2.84	.83	.38
53NC	76C (carbided 1Ni-3Au)	NH ₃ (1,000)	48	260	Au, Ni ₃ X(C,N)	2.07	1.19	.19
54NC	74C (carbided 3Ni-1Au)	NH ₃ (1,000)	48	260	Au, Ni ₃ X(C,N)	2.36	.90	.15
55NC	77C (carbided 1Ni-1Au)	NH ₃ (1,000)	48	260	Au, Ni	1.81	1.23	.50
56NC	78C (carbided 1Ni-4Cr)	NH ₃ (1,000)	48	260		4.00	3.64	1.43
57NC	79C (carbided 1Ag-3Pd)	NH ₃ (1,000)	48	260		.03	.25	.26
58NC	80C (carbided 3Ni-1Pt)	NH ₃ (1,000)	48	260	Ni-Pt alloy, Ni ₃ X(C,N).	.47	5.36	2.37
59NC	81C (carbided 1Ni-1Pt)	NH ₃ (1,500)	48	260	Ni-Pt alloy pattern	.26	3.57	2.86
60NC	82C (carbided 1Ni-3Pt)	NH ₃ (1,000)	48	260	Pt, Ni	.24	1.11	.88

Table 9.—Preparation of nitrocarbides—Continued

Run No.	Charge	Carbide nitriding			X-ray analysis	Chemical analysis, wt pct		
		Gas (space velocity, hr ⁻¹)	Duration, hr	Temperature, °C		N	C	
						Total	Free	
61NC	84C (carbided 3Ni-1Ag)	NH ₃ (1,000)	48	260	Ni ₃ X(C,N), Ag	.57	5.42	.34
62NC	85C (carbided 1Ag-1Pd)	NH ₃ (1,000)	48	260	Ag, Pd	.03	.30	.20
63NC	86C (carbided 3Ag-1Pd)	NH ₃ (1,000)	48	260	Ag, Pd	.03	.32	.22
64NC	88C (carbided 1Au-3Pd)	NH ₃ (1,500)	48	260	Pd	.07	.55	.19

had to be allowed at lower temperatures. ϵ -Fe₂C could not be nitrided because it decomposes at 250° C.

When NH₃ is passed over heated carbides the interstitial C is gradually replaced by N, and the structure of the product depends on the extent of this replacement. In the runs 5NC–9NC, for example, only small amounts of N entered into the carbides and the products retained the structures of the original carbides. In the runs 1NC, 3NC, and 4NC, large quantities of N entered into the carbides and the products acquired the structures of the corresponding nitrides. In run 2NC, sufficient N entered into the carbide for a portion of the material to change over to the nitride structure, but the bulk of the material retained the structure of the original carbide. As in the tables for carbides and nitrides, the major identifiable phase from X-ray diffraction is stated first in table 10.

Analysis of the nitrocarbides for N and C indicates that in the nitriding of carbides, the replacement of carbidic C by N is not atom for atom; more N is gained than C is lost. The net gain for N is most pronounced in the nitrocarbides of Fe.

Preparation of Carbonitrides

The carbonitrides were prepared by carburizing nitrides with CO. Only carbonitrides of Fe could be prepared since there were no nitrides of Co and Ni available. The experimental conditions employed for carburizing the various nitrides of Fe are given in table 10. The remarks made earlier in connection with nitrocarbides are also valid for carbonitrides. The structure of the products depends on the relative proportion of

C and N in them. All the carbonitrides reported in table 10 retained the structure of their original nitrides because the relative proportion of interstitial C to N in the products was insufficient to induce instability in the parent nitride structure. The results of chemical analysis for C and N are included in the table. It will be noted that the replacement of interstitial N by C does not proceed atom for atom; more C is added than N is removed when nitrides are carburized.

PREPARATION OF THE BORIDES OF COBALT AND NICKEL

Borides of Co and Ni were prepared by the action of NaBH₄ on CoSO₄ and NiSO₄ in aqueous solution. The reaction may be represented by the following equation (36):



where M is Co or Ni. Chlorides or acetates of Co and Ni may be interchanged for the sulfates but nitrates should be avoided: NaBH₄ reduces NO₃⁻ to NH₃ which forms amine complexes with Co and Ni. Preparation of Fe₂B also has been reported by the method (24), but confirmation is lacking. Our own efforts to prepare Fe₂B by the action of NaBH₄ on FeSO₄ in solution were unsuccessful; the reaction yielded metallic Fe.

The manner of reacting NaBH₄ with metal salt solutions is of some consequence. The borides of Co and Ni catalyze the decomposition of NaBH₄ in water to sodium metaborate and H₂ (35):



Table 10.—Preparation of carbonitrides

Run No.	Charge	Carbide nitriding				X-ray analysis	Chemical analysis, wt pct		
		Gas (space velocity, hr ⁻¹)	Duration, hr	Temperature, °C	N		C		
							Total	Free	
1CN	4N (ϵ -Fe ₂ N-Fe ₂ N, γ' -Fe ₄ N)	CO(100)	110.0	350	ϵ -Fe ₂ X-Fe ₂ X(C,N)				
2CN	7N (γ' -Fe ₄ N, Fe ₃ O ₄)	CO(100)	4.0 9.0	¹ 210-295 295-345	ϵ -Fe ₂ X-Fe ₂ X(C,N)	4.68	4.50	1.40	
3CN	14N (ϵ -Fe ₂ N-Fe ₂ N)	CO(100)	3.0 7.5	180-350 350	ϵ -Fe ₂ X-Fe ₂ X(C,N)	8.49	4.02	.88	
4CN	18N (ζ -Fe ₂ N, ϵ -Fe ₂ N-Fe ₂ N, γ' -Fe ₄ N)	CO(100)	11.0	¹ 175-350	ϵ -Fe ₂ X-Fe ₂ X(C,N)	9.25	3.23	.81	
5CN	19N (ζ -Fe ₂ N, ϵ -Fe ₂ N-Fe ₂ N, γ' -Fe ₄ N)	CO(100)	11.0	¹ 190-350	ϵ -Fe ₂ X-Fe ₂ X(C,N)	7.43	2.74	3.20	
6CN	11N (ϵ -Fe ₂ N-Fe ₂ N, Ag)	CO(100)	3.0 7.0	225-350 350	ϵ -Fe ₂ X-Fe ₂ X(C,N), Ag				
7CN	15N (Ag, ϵ -Fe ₂ N-Fe ₂ N)	CO(100)	5.0 5.0	180-350 350	Ag, ϵ -Fe ₂ X-Fe ₂ X(C,N)				
8CN	16N (Ag, ϵ -Fe ₂ N-Fe ₂ N)	CO(100)	4.0 6.0	200-350 350	Ag, ϵ -Fe ₂ X-Fe ₂ X(C,N)				
9CN	21N (γ' -Fe ₄ N, ϵ -Fe ₂ N-Fe ₂ N)	CO(100)	0.5 3.5	200-250 250	γ' -Fe ₄ X(C,N)				
10CN	8N (γ' -Fe ₄ N)	CO(100)	1.0 3.0	100-250 250	γ' -Fe ₄ X(C,N)	6.16	1.03	1.14	

¹ In these runs, the temperature of the bed was raised slowly to the maximum indicated temperature in the indicated length of time and then heat supply was cut off.

Thus, when NaBH₄ is reacted with CoSO₄ or Ni SO₄, a portion of the borohydride reagent is always decomposed wastefully. But, for kinetic reasons, the proportion of the reagent consumed in the side reaction will be far larger if the metal salt solution is added to the borohydride solution rather than the other way around. Accordingly, in preparing the metal borides, the borohydride solution is added to the metal salt solutions dropwise and with vigorous agitation of the reaction mixture. Even so, quantitative precipitation of metal borides by stoichiometric amounts of NaBH₄ is not practicable.

The precipitated borides of Co and Ni decompose slowly in water and are sensitive to air even when wet. They should not, therefore, be left in contact with water any longer than is essential and should be blanketed with an inert gas during precipitation, washing, and drying. The dry borides are pyrophoric and must be handled under an inert gas.

The composition of washed and dried nickel

boride does not correspond to Ni₂B by chemical analysis. Ni and B together account for only 90 percent of the solid and Ni to B ratio suggests the formula Ni_{2.5}B (19, 29). Crystallographically, the powder is amorphous and its X-ray diffraction pattern is not identifiable, but if heated under an inert gas at 250° to 400° C, it crystallizes and yields a diffraction pattern identical to that of Ni₃B prepared by other methods (19, 37). The accuracy of equation 1 for Ni is, therefore, questionable. The composition of washed and dried cobalt boride corresponds to Co₂B (35).

Table 11 is a list of the boride catalysts prepared. The mixed borides of Ni and Co and the mixtures of nickel boride with Pt, Au, and Pd were prepared by coprecipitation: NaBH₄ reduces the salts of Pt, Au, and Pd to the metals. Solutions of the noble metals in aqua regia were fumed free of HNO₃ before use. Since Pt also catalyzes the decomposition of NaBH₄ (equation 2), a far larger excess of the borohydride reagent had to be employed to precipitate nickel boride

Table 11.—Preparation of borides

Run No.	Metal or metals, weight ratios	Chemical analysis, B in dried precipitate, wt pct	Metal borides, Ni ₂ B or Co ₂ B, in dried precipitates wt pct (calculated)	X-ray analysis
B-6	Ni	5.20	61.2	Amorphous.
B-7	Co	8.66	100.0	Do.
B-8	1Ni-1Co			Do.
B-8A	1Ni-1Co	6.72	79.1	Ni ₃ B (after the sample was inadvertently exposed to air).
B-9	3Ni-1Co	6.50	76.5	Amorphous.
B-18	1Ni-1Co	4.35	51.1	
B-20	1Ni-3Co	3.75	44.0	
B-24	1Ni-1Pt			Pt + broad halo.
B-26	1Ni-3Pt			Do.
B-28	3Ni-1Pt			Do.
B-31	1Ni-1Au			Au pattern only.
B-32	3Ni-1Pd			Pd + broad halo.
B-33	1Ni-3Pd			Do.

in the presence of this metal. The reactions were carried out at room temperature in a three-necked flask under a continuous flow of N₂. During the addition of NaBH₄ solution, the temperature of the reaction mixture rose to about 60° C. Stirring of the reaction mixture was continued for about 20 minutes after all the borohydride reagent had been added. The supernatant liquid was then drawn off through a filter stick of fine porosity, and the solids were washed four times with distilled water and twice with ethanol. Residual alcohol was removed by distillation under vacuum at 100° C, and then the dry powders were stored under CO₂. The borides of Co and 3Co-1Ni were extraordinarily fine and tended to plug the filter stick. They were, therefore, filtered through a plastic filter covered with a paper mat. The device was not completely

retentive, but most of the solids were retained. During filtration, the liquid level was never allowed to fall below the surface of the precipitate.

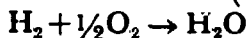
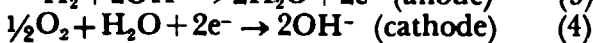
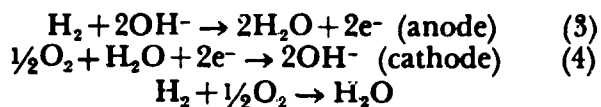
Chemical analysis of the dried powders for B indicated the cobalt boride to be Co₂B, and Co and B together accounted for all the solid if the small amounts lost in filtration were disregarded. The recovery of the precipitates containing nickel boride, however, was always far in excess of the stoichiometric expectation, and large fractions of the total solids remained unaccounted for if all Ni was assumed to be present as Ni₂B. (See column 4, table 11.) X-ray analysis indicated all products were amorphous. One of the preparations, B-8A, gave diffraction pattern of Ni₃B after the dry solid was inadvertently exposed to air and had turned hot.

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PART B.—ELECTROCHEMICAL TESTING

CATALYSIS IN FUEL CELLS

The fuel cell is a device for converting part of the energy of a chemical reaction directly into electrical energy. The direct conversion of energy implies that a heat cycle is not involved. The basic features of the device may be illustrated with the help of figure 10 which represents a fuel cell operating on the reaction of H_2 and O_2 to form water. The cell, on the left of the figure, consists of an electrolyte chamber filled with a solution of KOH, two porous electrodes, a chamber for H_2 on the anode side, and a chamber for O_2 on the cathode side. An enlarged cross-section of a portion of the cell is shown on the right in the figure. H_2 and O_2 diffuse through the respective electrodes to the electrode-electrolyte interfaces where the following reactions occur:



On closing the circuit, the electrons liberated at the anode in equation 3 travel to the cathode through the external circuit and the internal circuit is completed by the migration of OH^- ions from the cathode to the anode. The flow of electrons in the external circuit constitutes electric current.

In a hydrogen-oxygen fuel cell, hydrogen is

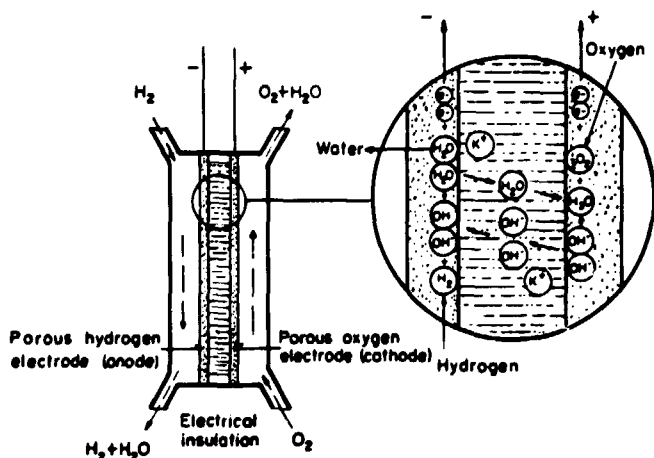


Figure 10.—Cross section of a H_2 - O_2 fuel cell.

referred to as the fuel and oxygen as the oxidant. Other types of fuel cells may have hydrazine, ammonia, carbon monoxide, hydrocarbons, or aldehydes as fuels, and air, hydrogen peroxide, or nitric acid as oxidants. The structural features of the cell must, of course, be modified for liquid fuels and oxidants. In principle, any redox reaction may be employed to construct a fuel cell, and numerous such reactions have been screened for the purpose (2). The electrolyte, in turn, may be alkaline or acidic in nature and may consist of an aqueous solution or a molten solid. The fundamental electron transfer processes, however, are similar in all cases: anions are produced at the cathode and discharged at the anode.

The ideal open circuit potential of a fuel cell may be calculated from the changes in free energy of the reactions at the two electrodes. The individual electrode potential, E , for a change of free energy ΔG is given by the following relationship:

$$E = - \frac{\Delta G}{nF}$$

where n is the number of electrons exchanged in the reaction and F is the Faraday. The open circuit potential of the cell will be equal to the sum of the two electrode potentials. The potential so calculated represents, of course, the theoretical maximum; practical fuel cells generally have lower open-circuit potentials.

It will be seen immediately that a steady flow of electrons in the external circuit of a fuel cell will depend on the efficiency of the reactions at the two electrodes. If the reactions proceed too slowly to keep up the flow of electrons when current is drawn, the potential of a cell falls. The phenomenon of decrease in the potential of a cell under load is known as "polarization" of a cell and is illustrated in figure 11.⁶ A good cell should suffer minimum polarization. The mechanism of reactions in equations 3 and 4, and of the analogous reactions for other types of fuel cells, are not completely known, but, for

⁶ Many other causes may exist for the polarization of a cell (18) which are equally important in the development of fuel cells, but do not form part of the present discussion.

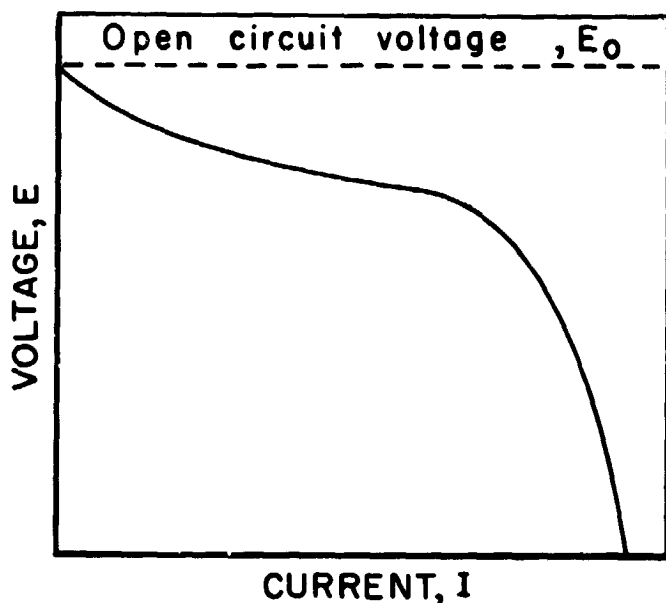


Figure 11.—Polarization of a fuel cell.

heuristic purposes, the following sequence of events may be visualized to occur at the two electrodes:

1. The reactants are adsorbed on the electrodes with dissociation into atoms or radicals.
2. The dissociated reactants form an activated complex on the electrodes.
3. The activated complex breaks up into the products and, in the process, either gives up electrons to the substrate (anode), or draws electrons from the substrate (cathode).
4. The products desorb away from the electrodes.

There is, thus, a close parallel between the role of electrodes in the electrochemical reactions in a fuel cell and the role of heterogeneous catalysts in ordinary chemical reactions. Indeed, most low-temperature fuel cell reactions are activated processes and will not advance without catalytic assistance. The electrodes catalyze the cathodic and the anodic reactions, and the greater the catalytic activity of the electrodes, the less the polarization of the cell when current is drawn from it. Development of suitable electrode catalysts is a key problem in fuel cell technology.

Since the ability to catalyze a reaction is a specific property of a substance, the choice of materials for the electrodes of a fuel cell is determined by cell reaction. The lessons from experience in heterogeneous catalysis of ordinary chemical reactions are helpful but not infallible guides in the selection of electrochemical catalysts. In view of the circumstances of their use, fuel cell catalysts must meet certain additional

requirements which are not relevant to heterogeneous catalysts for ordinary reactions: (1) Fuel cell catalysts should be electronic conductors. (2) They must not react with the electrolyte, or decompose otherwise under the operating conditions of the fuel cell.

Other than metals and alloys, very few materials have good electronic conductivity, and research on fuel cell catalysts has, therefore, mostly been concerned with metals and alloys. Certain metal oxides acquire good electronic conductivity at elevated temperatures ($\geq 500^\circ\text{C}$); they have been investigated as catalysts in fuel cells designed to operate with molten salt electrolytes at 500° to 700°C . Among all the materials investigated, Pt is unique in its versatility; it catalyzes a variety of fuel cell reactions and does so better than any other material. However, cost considerations work out unfavorably for this precious metal, and the search for cheaper substitutes has continued. Reported in the following sections are the results of activity tests with the preparations described in part A in an assortment of electrochemical systems. The names of the cooperating laboratories are indicated at appropriate places in the text. Samples of selected materials were also sent to Peter R. Gray of Phillips Petroleum Co., Bartlesville, Okla., and L. J. E. Hofer of Carnegie-Mellon University, Pittsburgh, Pa., for Mossbauer and magnetic studies. No report is available on the results of these studies for inclusion in this review.

REDUCTION OF O_2 IN AQUEOUS KOH

Teflon-bonded electrodes of finely divided catalysts were tested for cathodic activity in the reduction of O_2 in aqueous KOH. Electrodes were prepared by bonding catalysts to Ni screen by the following method.

A catalyst powder (250 mg) was kneaded with a few drops of water and a measured volume of a Teflon suspension (E. I. du Pont de Nemours & Co., Wilmington, Del.; product type 30).⁷ The doughlike kneaded mass was spread uniformly on a 3- to 4-cm² of a tightly stretched 100-mesh screen of 0.002-inch-diameter nickel wire. The loaded screen was dried at 100°C for 15 minutes and then sintered at 275°C for 5 minutes in a stream of N_2 . It was allowed to cool to room temperature in N_2 and was then cut into circular disks of 1 cm² with a sharp cork-borer. The catalyst loading for each disk was calculated from the

⁷ Reference to brand names is made for identification only and does not imply endorsement by the Bureau of Mines.

weight of the finished disk, the weight of a square centimeter of the blank screen, and the weight of the residue obtained by drying and sintering a unit volume of the Teflon suspension in a separate experiment.

The activities of the electrodes were tested potentiostatically by a floating electrode technique in the cell shown in figure 12.⁸ The cell

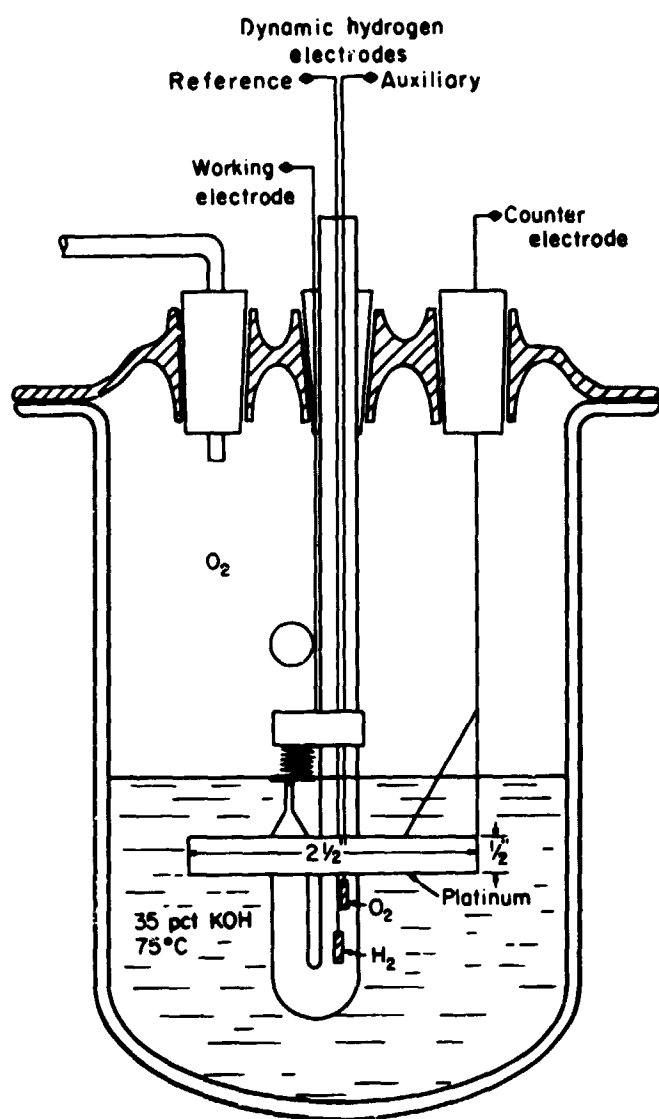


Figure 12.—Floating electrode assembly, electrochemical test cell.

consisted of a 500-ml resin kettle charged with 400 ml of 35-percent KOH solution in conductivity water. The vessel was immersed in a bath of white oil thermostated at $75^{\circ} \pm 0.1^{\circ} \text{C}$. A four-hole cover on the resin kettle provided entry for electrical leads and for a supply of O_2 presaturated with moisture by bubbling through con-

ductivity water at 58°C . The vapor pressure of pure water at 58°C is the same as the vapor pressure of 35 pct aqueous KOH solution at 75°C . All glass to glass contacts were avoided by the use of Teflon gaskets and plugs.

The catalyst disk was placed on a platinum ring hinged to a glass tubing. A spring of platinum wire pressed on the disk to hold it in place. By vertical adjustment of the tubing, the disk was positioned at the surface of the electrolyte. The tubing also served as an isolated chamber for a reference electrode. A dynamic hydrogen electrode (DHE) of the type proposed by Giner (9) was employed as the reference electrode. The DHE was connected to the outside electrolyte through a Luggin capillary. The counter electrode was made of a smooth platinum ring.

The cell operated as a double oxygen half-cell; oxygen was reduced to OH^- ions at the working electrode, and an equivalent amount of the gas was liberated at the counter electrode by the reverse reaction. Hence, current-potential curves could be obtained by grounding the working electrode and measuring the current required to maintain the counter electrode at different potentials. The complete electrical circuitry is shown in figure 13. The applied potential difference must be corrected for the fall of potential due to the internal resistance of the cell (R_c). The latter was determined by a relaxation technique: A known current was applied to the cell, then suddenly interrupted, and the transient potential change was photographed off the screen of an oscilloscope. The instantaneous response was attributed to resistive loss and the rest to capacitive decay. Thus, $R_c = \Delta E_{\text{inst.}} / I_{\text{app}}$ where

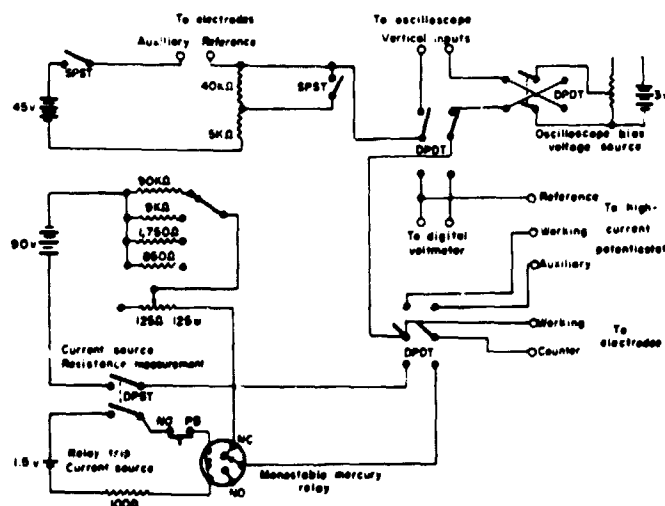


Figure 13.—Electrical circuit, electrochemical test cell.

⁸ We are indebted to Tyco Laboratories, Inc., Waltham, Mass., for their help in setting up the test facilities.

$\Delta E_{inst.}$ is the instantaneous change in potential and $I_{app.}$ is the applied current.

The Teflon-bonded electrodes required about 2 hours to arrive at stable resting potentials. The potential sweep was conducted at 25- or 50-mv intervals, and 3 to 5 minutes were allowed at each interval for the current to stabilize. Corrosion currents were detected by conducting identical potential sweeps under nitrogen.

An exhaustive screening of the preparations described in part A as cathodic catalysts in the reduction of O_2 in KOH solution was carried out by Tyco Laboratories, Inc. A summary of their principal results is presented in the next section. Only a few selected preparations were tested in our own laboratory. The results were in qualitative agreement with those of Tyco Laboratories and will not be duplicated here.

The results of a special series of Ni-Au preparations are presented in table 12 and figure 14.

Table 12.—Activities of reduced Ni-Au catalysts in the reduction of O_2 in 35-percent aqueous KOH, ma/cm²

Weight ratio	Activity, ma/cm ²		
	800 mv	600 mv	400 mv
Ni.....	0.16	2.2	6.5
9Ni-1Au.....	3.8	13.0	15.5
8Ni-2Au.....	32.0	72.0	108.0
7Ni-3Au.....	53.0	121.0	164.0
6Ni-4Au.....	16.3	31.0	40.0
5Ni-5Au.....	3.8	9.0	12.0

The series containing 50 to 90 weight-pct Ni and the balance Au was prepared by mixing powders of nickel hydroxide and gold hydroxide which had previously been assayed for their precise metal contents. The intimately mixed powders were reduced with H_2 at 250° C for 90 hr under identical conditions of gas flow. The reduced powders, on cooling, were washed free of residual alkalinity and chloride contamination with distilled water and dried over anhydrous $CaSO_4$ in an atmosphere of CO_2 . Test electrodes of comparable loading (40 to 50 mg/cm²) containing 30-percent Teflon were prepared from each of the materials and tested under standardized conditions. It will be seen that the activity passes through a peak as the composition of the mixture is varied: the most active preparation contained 70 pct Ni and 30 pct Au which corresponds approximately to 89-atomic pct Ni and 11-atomic pct Au. Reduction of coprecipitated hydroxides of metals has been reported (4, 11, 26) to yield the same substitutional type

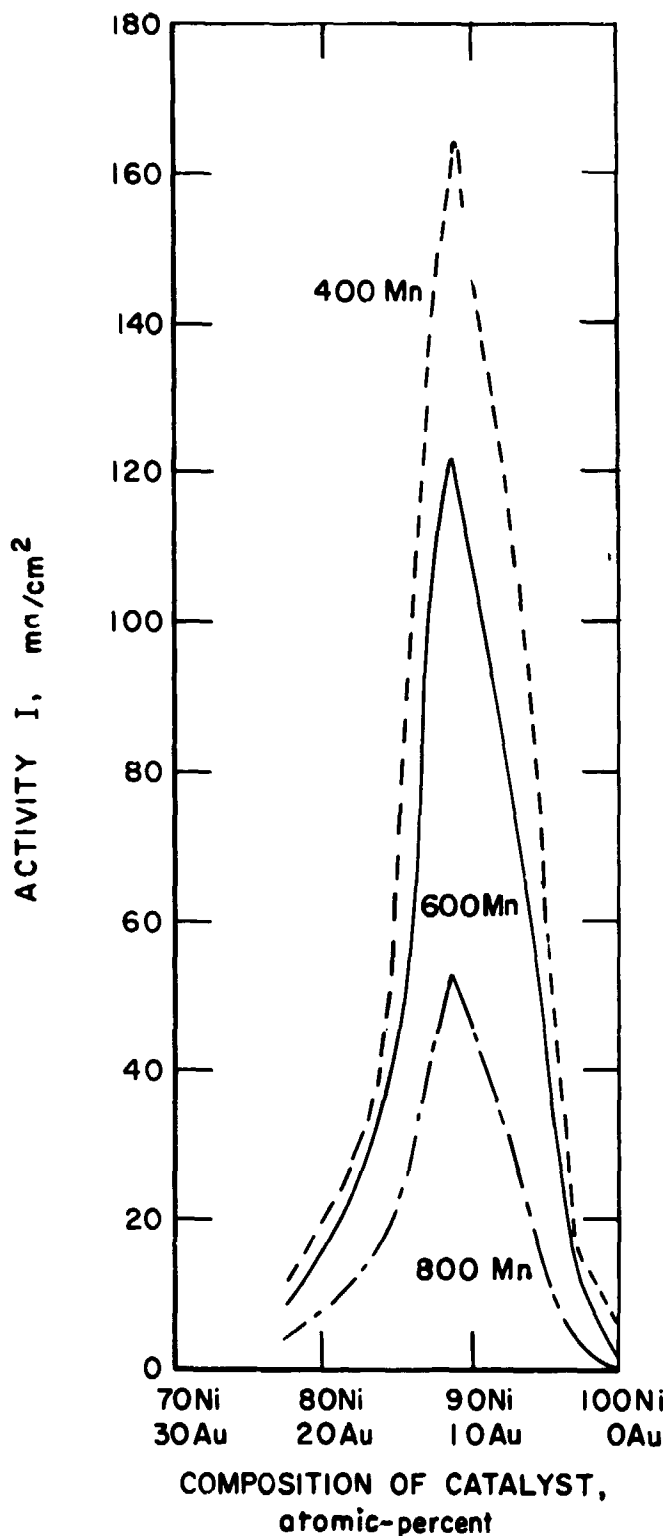


Figure 14.—Catalytic activity of Ni-Au mixtures in reduction of O_2 .

alloys as may be obtained by melting together the component metals. In the present study, although no evidence for alloy formation was detected from the X-ray patterns, the possibility of the formation of small amounts of surface alloys may not be ruled out since their existence will not be detected by the method.

REDUCTION OF O₂ IN AQUEOUS KOH(Tyco Laboratories, Inc.⁹ Waltham, Mass.)

The preparations described in part A of this report were screened for their catalytic activity in the reduction of O₂ in 35 pct aqueous KOH at 75° C by the technique described in the preceding section. For purposes of comparison, Pt-black electrodes also were prepared and tested under identical conditions. The pyrophoric preparations were subjected to a process of "induction" before exposure to air. Induction of a pyrophoric powder essentially consists of oxidizing the surface layer of its particles by exposing the powder to mildly oxidizing conditions. Since the molar volumes of most metal oxides are larger than the molar volumes of the metals, the oxides provide a protective coating for the solid against further attack from oxygen. When pyrophoric powders are ordinarily exposed to air, the conditions are too drastic for the oxidation to stop at the surface layer. In the present work, the metal powders and their interstitial compounds were inducted either by treatment with a mixture of N₂ and 0.1 to 1.0 pct O₂, or by gentle stirring under organic solvents (petroleum ether, acetone, methanol) in air. The powders so treated were found to develop far less heat on subsequent exposure to air, and the electrodes prepared from them were more active than the electrodes prepared from the corresponding uninducted materials.

The activities of the 12 most active preparations are given in table 13. Under comparable

⁹ For a comprehensive report, see the following: Giner, J., J. Parry, L. Swette, and R. Cattabriga. Development of Cathodic Electrocatalysts for Use in Low Temperature H₂-O₂ Fuel Cells With an Alkaline Electrolyte. Final Report Contract No. NASW-1233, Tyco Laboratories, Inc., Waltham, Mass., June 30, 1968, 254 pp. (Available from Clearinghouse for Federal Scientific and Technical Information, Springfield, Va., under the reference number, N69-10585.)

conditions, Pt-black electrodes, of about 10-mg/cm² loading typically supported a current of about 250 ma/cm² at 900 mv. Thus, even the most active preparations—44C, 30NC, and RAL-17—are only about one-fifth as active as Pt-black with twice the catalyst loading. Ternary alloys of Pt with Ni and Ag had surprisingly low activities: the activities of the alloys were far less than the expected activities due to the Pt content alone. It should be pointed out that Ag and Ag-Pt alloys prepared by other methods do show activity comparable to that of Pt. The low activity of the alloys discussed here can probably be ascribed to a far from optimum microstructure in the catalyst particles (low internal porosity). High internal porosity is essential for efficient mass transport in the operation of plastic bonded electrodes. In general, the leached Raney alloys and the reduced mixed metals were slightly more active than the interstitial compounds prepared from them. Preparations containing Co and Fe suffered severe corrosion under test conditions.

Although not comparable to Pt-black in activity, some of the catalysts listed in table 13 may be worthy of investigation in depth, particularly from the point of view of structure optimization. Economics of 44C and 30NC would compare favorably with that of the Pt-group metals.

OXIDATION OF H₂ IN AQUEOUS KOH(Allis Chalmers, Research Division,¹⁰ Milwaukee, Wisc.)

Forty selected preparations were tested for anodic activity in the oxidation of H₂ in 35 pct aqueous KOH at 90° C. One gram of each pow-

¹⁰ Principal investigators: J. A. Magerl, J. N. Murray, and D. Pouli.

Table 13.—Reduction of O₂ in 35-percent aqueous KOH at 75° C

Catalyst	Composition	Loading, mg/cm ²	Teflon, percent	Current, ^{1, 2} ma/cm ² , at		
				900 mv	750 mv	600 mv
44C	Carbided 1Ni-1Ag-1Au	20.0	30	48.0/48.0	355/355	-----
30NC	Nitrocarbided 1Ni-1Ag-1Au	23.0	30	49.0/49.0	340/340	-----
RAL-17	1Ni-1Au-1Pd	18.0	30	45.0/65.0	300/315	-----
79R	1Ag-3Pd	57.0	30	3.5/ 5.0	275/307	-----
86R	3Ag-1Pd	48.0	20	9.0/18.0	205	-----
RAL-21	1Ni-1Ag-1Pd	20.0	30	15.0/48.0	132/232	-----
RAL-5	1Ni-1Ag	31.0	20	11.5/27.5	96/168	-----
57C	Carbided 1Ni-1Pd	40.0	30	-----	100/137	215/230
53R	1Ni-1Ag	16.3	30	-----	100/105	200/210
33NC	Nitrocarbided 1Co-1Ag-1Au	20.0	30	-----	70/90	200/225
54R	Ni	22.7	30	-----	83/92	150/160
RAL-4	1Ni-3Ag	31.0	20	10.0/11.0	39/44	39/44

¹ N.B. All potentials were measured with reference to a dynamic hydrogen electrode.

² The 2 figures refer to the values of observed current during sweepup and sweepdown, respectively.

der was milled with an equal weight of Ni "B" powder¹¹ and an appropriate quantity of a Teflon suspension. The dough was pressed against a Ni screen at 2,100 psi and electrodes of $\frac{5}{8}$ inch diameter were cut from the plaques of 0.025- to 0.035-inch thickness so obtained. The anodic activities of the electrodes were determined by a potentiostatic method in the half cell shown in figure 15. The body of the cell was made of lucite and had threaded ends for compacting together a Teflon component which held the test electrode and a glass component which held a counter electrode. The components were held tightly together by a stainless steel tube which also served as the current collector. The portion of the stainless steel tube that contacted the electrode was gold plated. Potentials were measured with reference to an Hg/HgO electrode, and corrosion currents were measured under N₂.

The results of the activity studies are presented in table 14. Activity data for a sample of Pt-black and a proprietary catalyst "A" are also included in the table. An electrode prepared from the Ni "B" powder alone showed no ac-

¹¹ A commercially available nickel powder Type 287, from International Nickel Co.

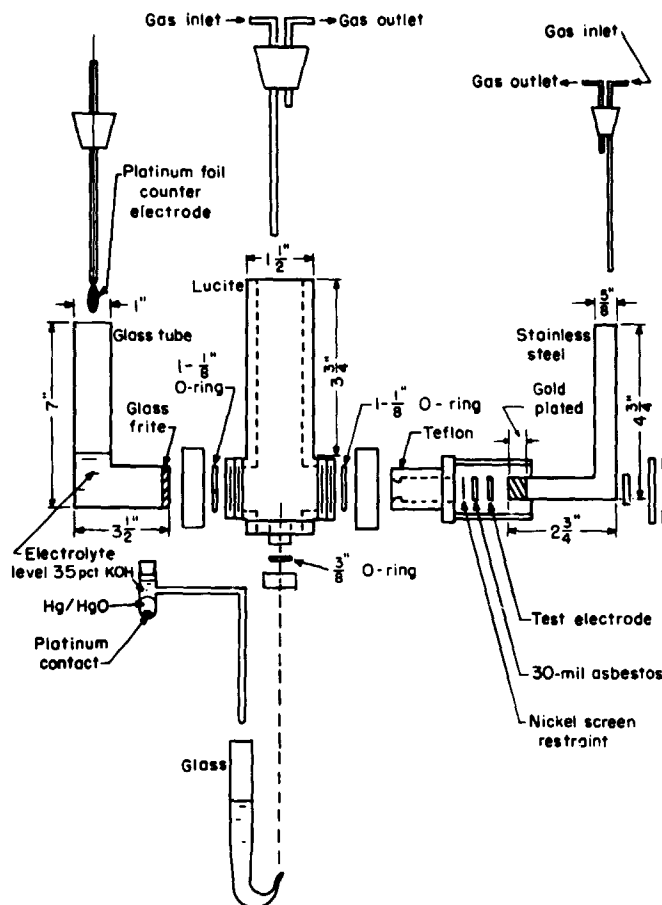


Figure 15.—Diagram of half cell.

Table 14.—Oxidation of H₂ in 35 percent aqueous KOH at 90° C

Catalyst	Composition	Rest potential, v	Current, ² ma/cm ²					
			-0.9v	-0.8v	-0.7v	-0.6v	-0.5v	-0.4v
Pt	-----	-0.93	27.8	75.4	101.0	95.5	93.5	92.5
"A"	(Proprietary)	-.92	7.1	18.7	18.9	2.0	3.1	4.2
84R	3Ni-1Ag	-.92	1.0	20.7	37.1	31.8	8.3	7.6
84C	Carbided 3Ni-1Ag	-.93	24.0	88.4	113.7	79.3	45.5	23.7
61NC	Nitrocarbided 3Ni-1Ag	-.93	4.0	12.6	19.7	19.5	9.6	-----
74R	3Ni-1Au	-.91	1.5	7.6	25	17.2	5.3	3.3
74C	Carbided 3Ni-1Au	-.92	1.3	6.1	23.7	28.9	24.2	6.1
54NC	Nitrocarbided 3Ni-1Au	-.93	4.2	10.5	21.5	23.7	21.2	10.1
56R	Ni	-.875	-----	44.5	39.9	7.9	7.8	8.7
2C	ϵ -Fe ₃ C, Fe ₃ O ₄	(²)	(---)	30	37.5	2.8	2.5	2.2
4C	χ -Fe ₃ C, Fe ₃ O ₄	(²)	(17.2)	36.0	37.5	2.8	2.5	2.2
6C	χ -Fe ₃ C, θ -Fe ₃ C	(²)	(25.6)	55.6	31.2	1.9	1.2	1.2
7C	χ -Fe ₃ C	(²)	(5.6)	44.4	51.8	13.1	2.5	1.2
10C	θ -Fe ₃ C, α -Fe	-.97	31.8	49.4	9.7	3.4	2.5	1.9
11C	χ -Fe ₃ C	(²)	(7.2)	40.0	68.7	27.5	3.7	3.1
			(1.9)	51.2	66.9	9.4	4.4	3.7

Table 14.—Oxidation of H₂ in 35 percent aqueous KOH at 90°C—Con inued

Catalyst	Composition	Rest potential ¹ , v	Current, ² ma/cm ²					
			-0.9v	-0.8v	-0.7v	-0.6v	-0.5v	-0.4v
12C	ϵ -Fe ₂ C, α -Fe		8.1 (.9)	45.2 (30.6)	50.6 (62.3)	11.2 (34.4)	2.2 (3.1)	2.5 (1.9)
4CN	ϵ -Fe ₂ X(C,N)	-1.04	46.8 (23.4)	15.0 (47.5)	1.9 (3.1)	1.9 (.6)	1.2 (.6)	1.2 (.6)
5CN	ϵ -Fe ₂ X(C,N)	-0.94	15.9 (8.4)	39.3 (44.4)	21.8 (44.4)	7.5 (8.4)	3.7 (2.5)	3.4 (1.9)
56C	Carbided Ni	-.92	3.4	18.7 (—)	26.4 (6.1)	4.8 (8.9)	9.3 (5.1)	6.5 (2.7)
41NC	Nitrocarbided Ni	-.925	4.5	18.1 (—)	25.4 (5.2)	4.8 (3.8)	6.2 (2.1)	3.7 (1.2)
59R	Co	-.82	—	8.5 (5.0)	16.8 (.5)	.9 (—)	.7 (—)	— (—)
59C	Carbided Co	-.83	—	5.5 (—)	28.0 (22.6)	8.3 (3.9)	26.4 (24.1)	7.8 (8.3)
43NC	Nitrocarbided Co	-.80	—	— (—)	11.6 (10.1)	8.1 (4.3)	10.9 (10.4)	7.0 (27.2)
61R	3Ni-1Co	-.85	—	18.9 (—)	36.3 (8.6)	39.6 (15.3)	6.0 (—)	2.7 (—)
61C	Carbided 3Ni-1Co	-.88	—	24.3 (—)	47.1 (35.3)	58.6 (51.3)	33.7 (39.9)	1.3 (1.4)
45NC	Nitrocarbided 3Ni-1Co	-.81	—	4.1 (—)	17.6 (14.0)	23.8 (24.9)	6.2 (3.0)	2.7 (.8)
78R	1Ni-4Cr	-.71	—	— (—)	— (—)	— (—)	— (—)	— (—)
78C	Carbided 1Ni-4Cr	-.77	—	— (—)	— (—)	— (—)	— (—)	— (—)
56NC	Nitrocarbided 1Ni-4Cr	-.84	—	— (—)	— (—)	— (—)	— (—)	— (—)
9CN	γ' -Fe ₂ X(C,N)	-.96	31.2 (24.4)	35.6 (36.8)	24.4 (30.0)	12.5 (6.2)	2.8 (2.5)	2.5 (2.5)
1NC	ϵ -Fe ₂ X(C,N), Fe ₃ O ₄	-.97	6.6 (14.7)	4.1 (8.7)	3.1 (16.9)	1.2 (1.2)	— (1.2)	— (1.2)
2NC	χ -Fe ₂ X(C,N), ϵ -Fe ₂ X(C,N)	-.91	<1.0 (1.0)	4.7 (40.6)	11.2 (61.8)	2.5 (35.6)	.9 (3.1)	.8 (2.5)
3NC	ϵ -Fe ₂ X(C,N)	-.96	5.9 (5.0)	24.8 (38.1)	25.6 (48.1)	1.6 (7.5)	— (2.5)	— (—)
4NC	ϵ -Fe ₂ X(C,N)	-.94	3.4 (20.0)	9.4 (42.1)	5.6 (34.4)	1.1 (6.9)	— (3.1)	— (—)
5NC	θ -Fe ₂ X(C,N)	-.94	2.2 (—)	26.2 (22.8)	33.1 (63.1)	4.4 (24.7)	.8 (2.5)	2.5 (2.5)
1N	ϵ -Fe ₂ N, γ' -Fe ₂ N	—	25.9 (13.4)	24 (15.3)	21.8 (15.6)	3.7 (4.4)	1.5 (2.5)	1.1 (1.9)
9N	ζ -Fe ₂ N	—	11.2 (6.2)	19.4 (19.9)	33.7 (25.0)	9.0 (13.7)	2.7 (3.1)	2.2 (1.9)
10N	ϵ -Fe ₂ N	—	5.0 (1.9)	16.2 (13.7)	21.8 (20.6)	7.5 (6.2)	3.2 (2.5)	2.1 (1.9)
18N	ζ -Fe ₂ N, ϵ -Fe ₂ N	—	29.4 (35.0)	2.1 (1.2)	1.6 (1.2)	2.6 (3.1)	1.5 (1.2)	— (1.2)
19N	ζ -Fe ₂ N, ϵ -Fe ₂ N	-1.00	7.5 (3.4)	16.5 (15.3)	6.6 (20.0)	3.4 (11.4)	2.2 (4.4)	1.6 (3.1)
20N	ϵ -Fe ₂ N	-1.02	33.7 (35.0)	1.0 (3.7)	.6 (1.2)	— (1.9)	— (.6)	— (.6)
21N	γ' -Fe ₂ N, ϵ -Fe ₂ N	—	8.1 (6.2)	15.0 (10.6)	17.8 (19.4)	9.4 (5.0)	5.3 (3.1)	— (2.2)

¹ All potentials were measured with reference to an Hg/HgO electrode.

² The figures in parentheses refer to corrosion currents. For a number of catalysts the corrosion currents at -0.9v and -0.8v could not be measured because their rest potentials in N₂ were more positive than -0.8v, (—) indicates that current was measured but was found to be essentially zero.

³ Between -0.90 and -0.86.

tivity. The figures in parentheses refer to corrosion currents. Both the activity currents and the corrosion currents show maxima at about -0.8v to -0.6v. The maxima at an intermediate potential appear to indicate that the catalysts (including Pt-black and the proprietary catalyst "A") become passive at more positive potentials.

Preparation 84C is comparable in activity to Pt-black, and quite a few of the preparations (84R, 74R, 56R, 61R) compare very favorably with the proprietary catalyst "A". With the exception of 84C, the carbides and nitrocarbides are less active and, in some cases, more susceptible to corrosion than the corresponding plain

reduced metals (compare 59C and 59R; 61C and 61R). All Fe-preparations suffered severe corrosion: in several instances the corrosion currents were larger than the currents obtained with H_2 —an observation that may indicate that H_2 inhibits corrosion.

At the conclusion of screening by the half-cell method, six selected preparations—84R, 84C, 61NC, 56R, 56C, and 41NC—were tested in an asbestos matrix H_2 - O_2 minicell (figure 16). The electrolyte consisted of 45 pct aqueous KOH supported on 30-mil-thick asbestos, and the cathode was fabricated from a commercial silver catalyst. The cell was thermostated at $90^\circ C$, and a potential of 1.05v was imposed between the electrodes with a potentiostat. The potentiostat was set to scan continuously at a rate of 50 mv/sec between 1.05v and 0.7v, and the current produced by the cell was recorded. For purposes of comparison, electrodes of Pt-black and of two proprietary catalysts also were tested by the minicell method. The results of the minicell experiments are presented in figures 17, 18, and 19. It will be seen that 84R and 84C are about equally efficient, and the efficiency is comparable to that of the proprietary catalyst "A" (figure

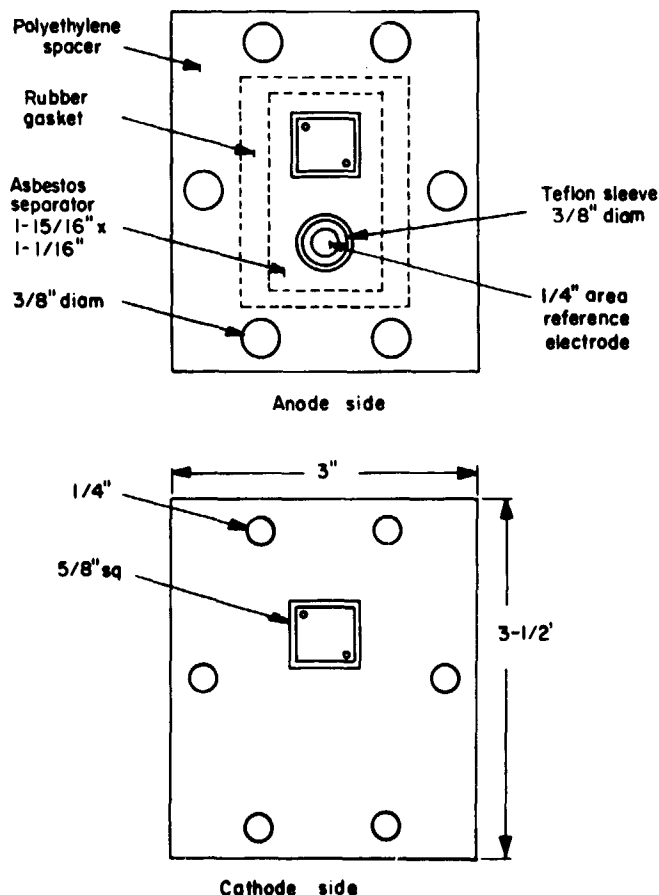


Figure 16.—Diagram of mini fuel cell.

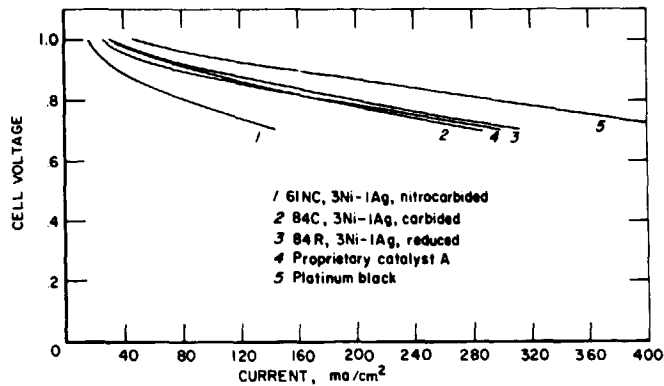


Figure 17.—Volt-ampere characteristics (3Ni-IAg series).

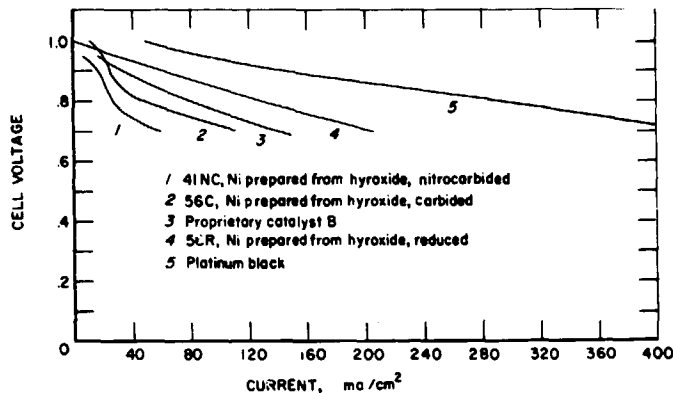


Figure 18.—Volt-ampere characteristics (nickel series).

17). The nitrocarbide of the series, 61NC, is less efficient. Likewise, 56R and 56C are comparable in activity to the proprietary catalyst "B" (figure 18), but 41NC, the nitrocarbide of the series, is less active. The activity data were found to be reproducible within ± 15 pct (figure 19).

The absence of any maxima in the current-potential data from the minicell experiments is conspicuous; compare current-potential data

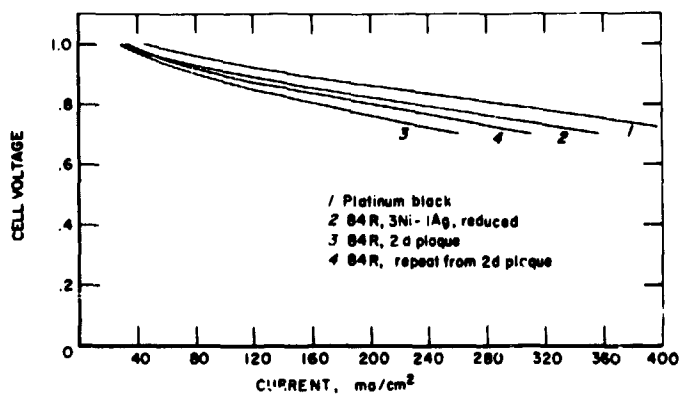


Figure 19.—Reproducibility test (84R and Pt black).

Table 15.—Oxidation of H₂ and C₃H₈ in 1.52M K₂CO₃ + 1.52M KHCO₃ at 85° C—Continued

Catalyst	Corrosion test	Test gas	Limiting current, ma/cm ²	Volts ¹ polarized at, ma/cm ²					
				0	2.5	7.5	17.5	25	50
56C(Ni ₃ C, Ni)	do	A	7.5	.20	.31	.50			
		H ₂	2.5	.19	.43				
		C ₃ H ₈							
59C(Co ₂ C)	Fail								
60C(carbided 1Ni-1Au-1Ag)	No visible corrosion.	A	0	.39					
		H ₂	0	.39					
		C ₃ H ₈							
61C(carbided 3Ni-1Co)	Fail								
38NC(nitrocarbided 1Ni-1Ag)	Pass	A	7.5	.25	.47	.58			
		H ₂	5.0	.10	.17				
		C ₃ H ₈							
39NC[nitrocarbided Ni, Ni ₃ X(C,N)]	do	A	7.5	.28	.40	.46			
		H ₂	25.0	.07	.08	.11	.22	.38	
		C ₃ H ₈	5.0	.29	.47				
41NC[Ni ₃ X(C,N)]	do	A	5.0	.22	.36				
		H ₂	50.0	.03	.05	.08	.14	.19	0.63
		C ₃ H ₈	7.5	.17	.32	.50			
43NC[Co ₂ X(C,N)]	Fail								
44NC(nitrocarbided 1Ni-1Au-1Ag)	Pass	A	0	.42					
		H ₂	0	.16					
		C ₃ H ₈							
45NC(nitrocarbided 3Ni-1Co)	do	A	2.5	.19	.41				
		H ₂	17.5	.04	.07	.14	.36		
		C ₃ H ₈							
74C(carbided 3Ni-1Au)	No visible corrosion.	A	7.5	.29	.38	.48			
		H ₂	25.0	.10	.12	.18	.38	.52	
		C ₃ H ₈	5.0	.30	.57				
78C(carbided 1Ni-4Cr)	Fail								
84C(carbided 3Ni-1Ag)	No visible corrosion.	A	7.5	.37	.57	.84			
		H ₂	25.0	.10	.12	.19	.40	.76	
		C ₃ H ₈	5.0	.31	.57				
51NC(nitrocarbided 1Ni-3Ag)	do	A	2.5	.39	.72				
		H ₂	7.5	.04	.20	.56			
		C ₃ H ₈							
54NC(nitrocarbided 3Ni-1Au)	do	A	7.5	.24	.38	.48			
		H ₂	17.5	.08	.11	.18	.49		
		C ₃ H ₈	.5	.40					
56NC(nitrocarbided 1Ni-4Cr)	Fail								
61NC(nitrocarbided 3Ni-1Ag)	Pass	A	7.5	.29	.47	.56			
		H ₂	17.5	.06	.09	.15	.36		
		C ₃ H ₈	2.5	.20	.52				

¹ All potentials were measured with reference to a hydrogen electrode.

Electrodes were prepared by pressing vacuum-dried mixtures of each catalyst and a Teflon emulsion to a gold-plated Ta screen at 160 psi. Anodic activities and corrosion currents of the electrodes were measured galvanostatically in a half-cell arrangement shown in figure 20. A gold-plated Ta ring was placed in peripheral contact with the circular electrodes to promote efficient distribution and collection of current. The lead and the potential probe also were made of Ta. The fuel gases and Ar were introduced to the inside surface of the electrode and the exit for the gases was set below the

electrolyte at the same level as the electrode. This insured a balance of pressures on the two sides of the porous electrodes and prevented leakage of the electrolyte. The cell was provided with a He bubbler to stir the electrolyte and to sweep away O₂. The counter electrode was made of platinized Pt and a dynamic H₂ electrode was employed as the reference electrode. Limiting currents and polarizations were first determined in Ar and H₂. If an electrode was sufficiently active in H₂, it was also tested in C₃HH₈. For the polarization measurements, regulated currents were supplied to the cell from a 12-volt storage

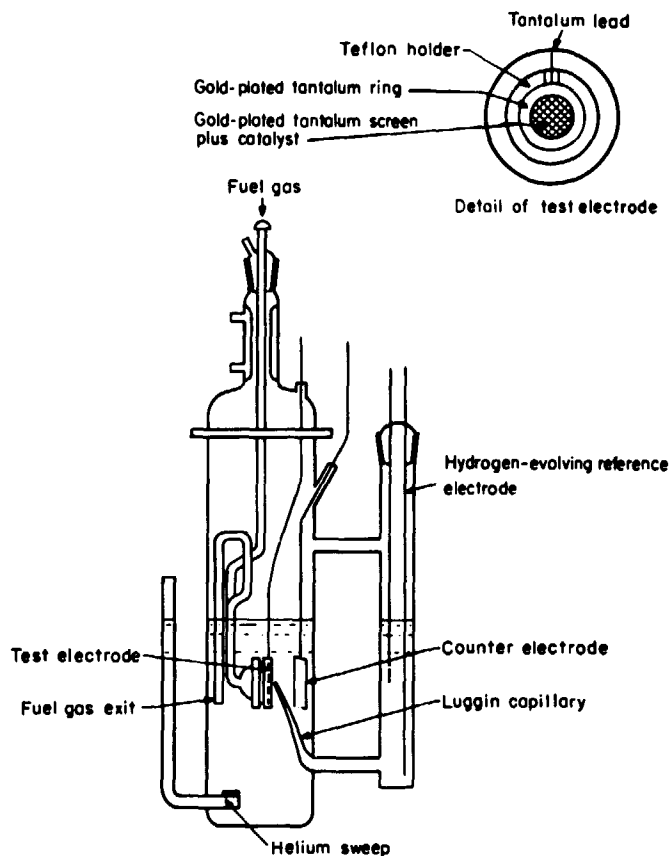


Figure 20.—Electrode-test apparatus.

battery with the help of a decade resistance box of 100 megohms total resistance. Potentials were measured with a vacuum tube voltmeter.

From the results presented in table 15, it will be seen that eight preparations—54C, 39NC, 41NC, 45NC, 74C, 84C, 54NC, and 61NC—are active in the oxidation of H_2 ; 41NC, a nitrocarbide of Ni, is by far the most active catalyst. This nitrocarbide was prepared from Ni obtained by reducing Ni hydroxide. 39NC, also a nitrocarbide of Ni, is less active than 41NC. 39NC was prepared from Ni obtained by decomposing Ni formate. 54C (Ni_3C), 74C (carbided 3Ni-1Au), and 84C (carbided 3Ni-1Ag) are each about one-half as active as 41NC. Preparations containing Fe or Co are all poor catalysts. With the exception of 44NC and 60C all preparations gave significant corrosion currents. Both 44NC and 60C were inactive in the oxidation of H_2 .

The eight catalysts that were active in oxidizing H_2 were tested with C_3H_8 . Only 41NC gave a current that was nominally larger than the corrosion current. Further study of 41NC and, possibly, of 54C, 74C, and 84C may be profitable.

OXIDATION OF NH_3 AND CO

(Catalyst Research Corp.,¹³ Baltimore, Md.)

Anodic activity of selected preparations were tested in the following aqueous systems at 25° C.

- (1) Oxidation of NH_3 in 30 pct KOH;
- (2) Oxidation of NH_3 in saturated K_2CO_3 ;
- (3) Oxidation of CO in 2N H_2SO_4 ;
- (4) Oxidation of CO in $CH_3COOH + CH_3COOK$ buffer of pH 3;
- (5) Oxidation of CO in saturated K_2CO_3 ; and
- (6) Oxidation of CO in 85 pct H_3PO_4 .

Before exposure to air, the preparations were inducted with heptane, acetone, methanol, and water.¹⁴ A few preparations required further induction with H_2O_2 . After drying in air, 28.3 mg of each inducted powder was mixed with an aqueous emulsion of 5 mg PTFE and the mixture was spread on a 1.5-cm by 1.5-cm Pt screen. The screen, with the spread, was dried in vacuum at 85° C for one-half hour and then pressed at 100 psi for 2 minutes at 250° C. For purposes of comparison, identically prepared electrodes of Pt-black also were tested in each system. Anodic activities and corrosion currents were determined potentiostatically by the floating electrode technique described in the section "Reduction of O_2 in Aqueous KOH." The dynamic hydrogen electrode was contained in a separate glass chamber which commuted with the working electrode via a polypropylene Luggin capillary. Corrosion currents were measured in N_2 . The potentiostat was programed for continuous scanning from 0v to 1.2v, and the current-voltage curves were traced directly on an X-Y recorder. Corrosion currents were scanned at the rate of 0.150 v/min and the activities were scanned at the rate of 0.018 v/min. If an electrode gave a corrosion current of more than 1 ma in an electrolyte, 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 (27). The areas were determined in the least corrosive electrolyte and the measured areas were multiplied by an electrolyte factor to compensate for the differences in the resistance of the different elec-

¹³ Principal investigators: H. J. Goldsmith, J. R. Moser, and T. Webb.

¹⁴ The principle and practice of induction are discussed under "Reduction of O_2 in Aqueous KOH (Tyco Laboratories)."

trolites. The following values of electrolyte factor were employed:

Electrolytes	Electrolyte factor
30 pct KOH	1.07
2N H ₂ SO ₄	1.13
Saturated K ₂ CO ₃	1.33
85 pct H ₃ PO ₄	1.76

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 low. The results are presented in tables 16-21.

Oxidation of NH₃

Twenty-two preparations were tested for activity in the oxidation of NH₃ in 30-pct KOH (table 16). Sixteen of the preparations were stable but the remaining six corroded visibly on the addition of NH₃. The stable electrodes gave half-cell potentials of 0.54-0.56v (compare 0.58v for Pt) and Tafel slopes of about 0.12v (compare 0.04v for Pt). The half-cell potentials and Tafel slopes for the unstable materials were widely scattered.

Oswin and Salomon (28) have suggested a four-step mechanism for the anodic oxidation of NH₃. Their scheme and calculated values for the Tafel slopes of the intermediate steps are as follows:

Reactions	Calculated Tafel slope, v
(1) NH ₃ + M + OH ⁻ →	0.118.
(2) M-NH ₂ + OH ⁻ →	0.039.
(3) M=NH ⁺ + OH ⁻ →	0.024.
(4) 2M=N	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 NH₃ is reaction 2, but on the stable catalysts of table 16, the rate-determining step for the oxidation of NH₃ is reaction 1.

From a practical point of view, the anodic activities of the 16 stable catalysts were disappointingly low (table 16, column 3). The carbides and nitrides were nominally more active than the reduced metals and alloys, but none of the materials held out any promise as a useful anode for ammonia fuel cells.

It may be noted that the activity per unit of surface area for some of the preparations is surprisingly high (table 16, column 4). We shall return to this point later in the text.

Ten preparations were tested for activity in the oxidation of NH₃ in a saturated solution of K₂CO₃ (table 17). All gave low currents, high Tafel slopes, and variable half-cell potentials. The results are not amenable to any interpretation, but the following inference is clear: as an

Table 16.—Oxidation of NH₃ in 30 percent KOH at 25° C

Catalyst	Composition	Exchange current		Tafel slope, v	Equilibrium potential, v
		ma/g	μa/cm ²		
Pt		883	4.24	.04	0.58
33C ¹	Co ₂ C, α-Co	106	21.6	.04	.22
43C ¹	Carbided 1Ni-1Ag	60.1	4.40	.08	.68
46C ¹	Ag, Ni ₃ C	42.4	10.5	.08	.24
28NC ¹	Nitrocarbided 1Ni-1Co	28.3	.968	.10	.32
27C ¹	Carbided 3Ni-1Co	14.1	2.0	.12	.26
12C	χ-Fe ₃ C	3.54	107	.17	.55
15NC	Nitrocarbided 3Ni-1Co	3.53	.507	.23	.56
B6 ¹	Ni ₃ B	3.50	6.2	.03	.33
21N	γ'-Fe ₂ N, ε-Fe ₂ N-Fe ₂ N	3.15	42.6	.12	.56
61C	Carbided 3Ni-1Co	2.80	7.0	.11	.54
18N	ζ-Fe ₂ N, ε-Fe ₂ N-Fe ₂ N, γ'-Fe ₂ N	2.47	29.9	.12	.56
RAL-6	3Ni-1Ag	1.78	.0225	.14	.54
20N	ζ-Fe ₂ N, γ'-Fe ₂ N, ε-Fe ₂ N-Fe ₂ N	1.66	23.2	.13	.56
RAL-8	1Co-1Ag	1.57	.0225	.13	.54
RN-2	Raney Ni	1.42	.269	.12	.54
1NC	ε-Fe ₂ X-Fe ₂ X(C,N), Fe ₃ O ₄	1.37	14.3	.12	.54
RC-1	Raney Co	1.35	.225	.12	.54
RAL-11	1Ni-1Co-1Au	1.28	.132	.14	.54
5CN	ε-Fe ₂ X-Fe ₂ X(C,N)	1.13	20.7	.26	.55
RAL-9	3Co-1Ag	1.07	.346	.13	.54
4CN	ε-Fe ₂ X-Fe ₂ X(C,N)	.99	6.45	.11	.56
RAL-10	1Ni-1Co-1Ag	.71	.115	.07	.56

¹ Dissolved in NH₃.

Table 17.—Oxidation of NH₃ in saturated K₂CO₃ at 25° C

Catalyst	Composition	Exchange current		Tafel slope, v	Equilibrium potential, v
		ma/g	μa/cm ²		
Pt		205	0.97	0.20	0.79
1NC	ε-Fe ₂ X-Fe ₂ X(C,N), Fe ₃ O ₄	2.40	25.0	.56	.16
2NC	χ-Fe ₂ X(C,N), ε-Fe ₂ X-Fe ₂ X(C,N)	1.87	21.8	.27	.20
1N	ε-Fe ₂ N-Fe ₂ N, γ'-Fe ₂ N	1.66	32.7	.70	.12
1CN	ε-Fe ₂ X-Fe ₂ X(C,N)	1.55	33.6	.36	.17
3NC	ε-Fe ₂ X-Fe ₂ X(C,N), Fe ₂ N, θ-Fe ₃ C	1.52	15.0	.65	.32
19N	ζ-Fe ₂ N, ε-Fe ₂ N-Fe ₂ N, γ'-Fe ₂ N	1.20	35.6	.26	.09
4NC	ε-Fe ₂ X-Fe ₂ X(C,N)	.885	31.9	.85	.13
21N	γ'-Fe ₂ N, ε-Fe ₂ N-Fe ₂ N	.813	11.0	.17	.09
5CN	ε-Fe ₂ X-Fe ₂ X(C,N)	.777	14.3	1.40	.20
12C	χ-Fe ₂ C	.177	5.37	.16	.14

electrolyte for the oxidation of NH₃, a saturated solution of K₂CO₃ is inferior to a solution of 30 pct KOH.

Oxidation of CO

Of the four electrolytes employed in the oxidation of CO (tables 18–21), 2N H₂SO₄ and an acetate buffer of pH 3 were the best. The largest current was obtained with Pt in 2N H₂SO₄. In the acetate buffer electrolyte, 32NC and RAL 10 gave larger currents than Pt (table 19). By and large, nitrocarbides were more active than metals and alloys; carbides and borides were least active.

Studies on Pt electrodes have revealed that the oxidation of CO may proceed by two different reactions: first, around 0.26v (versus DHE)

by a reaction the unidentified products of which poison the electrode; second, around 0.96v (versus DHE) by a reaction in which CO₂ is formed. The half-cell potentials in 85 pct H₃PO₄ (table 21) indicate that the oxidation of CO in that electrolyte proceeds, on most catalysts, by the first reaction. By the same criterion, the oxidation of CO in 2N H₂SO₄ and in acetate buffer (tables 18 and 19, respectively) appear to proceed, generally, by the second reaction. The data for the half-cell potentials in saturated K₂CO₃ (table 20) are too scattered for a conclusion.

It will be noted again that the activity per unit of surface area for some of the catalysts is surprisingly high (tables 18–21, column 4). As an example, 10C gave an exchange current den-

Table 18.—Oxidation of CO in 2N H₂SO₄ at 25° C

Catalyst	Composition	Exchange current		Tafel slope, v	Equilibrium potential, v
		ma/g	μa/cm ²		
Pt		1980	9.46	0.20	0.89
1CN	ε-Fe ₂ X-Fe ₂ X(C,N)	36.4	790	2.20	.50
45NC	Nitrocarbided 3Ni-1Co	15.0	3.1	.04	.00
19N	ζ-Fe ₂ N, ε-Fe ₂ N-Fe ₂ N, γ'-Fe ₂ N	12.7	378	.22	.96
53C	Ag-Ni ₃ C	8.8	4.7	.07	.42
B9	Coprecipitated boride of 3Ni-1Co	5.7	5.2	.15	1.09
44NC	Nitrocarbided 1Ni-1Au-1Ag	5.0	.10	.08	.85
10N	ε-Fe ₂ N-Fe ₂ N	4.95	182	.22	.88
10C	θ-Fe ₃ C, α-Fe	4.60	138	.60	.58
61R	Reduced 3Ni-1Co	4.2	35	.10	.03
20N	ζ-Fe ₂ N, γ'-Fe ₂ N, ε-Fe ₂ N-Fe ₂ N	3.71	51.9	.49	.92
61C	Carbided 3Ni-1Co	3.5	8.7	.04	.05
B20	Coprecipitated boride of 1Ni-3Co	2.5	.94	.07	1.09
4NC	ε-Fe ₂ X-Fe ₂ X(C,N)	2.12	76.5	.13	.67
RN-2	Raney Ni	2.12	.40	.08	.99
60C	Au, Ag, Ni, Ni ₃ C	2.1	.66	.05	.96
12C	χ-Fe ₂ C	1.87	57.0	.08	.64
B7	Co ₂ B	1.8	2.6	.07	1.02
B18	Coprecipitated boride of 1Ni-1Co	1.4	.20	.03	1.07
1NC	ε-Fe ₂ X-Fe ₂ X(C,N), Fe ₃ O ₄	1.31	13.6	.30	.88
B6	Ni ₂ B	1.0	1.8	.05	1.06

Table 19.—Oxidation of CO in CH₃COOH + CH₃COOK buffer of pH 3

Catalyst	Composition	Exchange current		Tafel slope, v	Equilibrium potential, v
		ma/g	μa/cm ²		
32NC	Nitrocarbided 3Ni-1Ag	97.2	1.24	0.30	0.67
RAL-10	1Ni-1Co-1Ag	95.4	15.4	.25	.58
Pt		47.6	2.84	.17	.21
RAL-11	1Ni-1Co-1Au	25.4	2.62	.70	.48
23NC	Ni ₃ X(C,N)	24.7	1.25	.12	.46
43C	Carbided 1Ni-1Ag	20.5	1.50	.27	.72
B9	Coprecipitated boride of 3 Ni-1Co	14	13	.02	.42
10C	θ-Fe ₃ C, α-Fe	12.4	369	.14	.31
35C	Ni ₃ C	7.42	.136	.14	.48
46C	Carbided 3Ni-1Ag	6.36	1.57	.07	.50
61C	Carbided 3Ni-1Co	4.6	11	.15	.84
RAL-9	3Co-1Ag	4.24	1.37	.16	.73
RN-2	Raney Ni	3.89	.734	.08	1.08
53C	Carbided 1Ni-1Ag	3.5	1.9	.03	.48
15NC	Nitrocarbided 3Ni-1Co	3.00	.431	.17	.46
61R	Reduced 3Ni-1Co	2.8	23	.54	.46
60C	Carbided 1Ni-1Au-1Ag	2.6	.86	.04	1.03
B7	Co ₂ B	1.4	2.0	.05	1.02
18N	ζ-Fe ₂ N, ε-Fe ₂ N-Fe ₂ N, γ'-Fe ₄ N	1.77	21.4	.12	1.00
23C	ε-Fe ₃ C, α-Fe(trace)	1.76	65	.09	.36
B6	Ni ₂ B	1.2	2.1	.08	1.06
1NC	ε-Fe ₂ X-Fe ₂ X(C,N), Fe ₃ O ₄	1.13	11.6	.18	.98
21N	γ'-Fe ₄ N, ε-Fe ₂ N-Fe ₂ N	1.13	15.3	.16	1.03
RC-1	Raney Co	1.13	.213	.12	1.06
B18	Coprecipitated boride of 1Ni-1Co	1.1	.16	.07	1.03
B20	Coprecipitated boride of 1Ni-3Co	.88	.33	.04	1.04
4NC	ε-Fe ₂ X-Fe ₂ X(C,N)	.85	30.7	.18	1.04
4CN	ε-Fe ₂ X-Fe ₂ X(C,N)	.81	5.21	.14	1.05
12C	χ-Fe ₃ C	.56	17.2	.14	1.06
5CN	ε-Fe ₂ X-Fe ₂ X(C,N)	.42	7.82	.15	.41

Table 20.—Oxidation of CO in saturated K₂CO₃ at 25° C

Catalyst	Composition	Exchange current		Tafel slope, v	Equilibrium potential, v
		ma/g	μa/cm ²		
Pt		40.7	0.195	0.04	0.63
21N	γ'-Fe ₄ N, ε-Fe ₂ N-Fe ₂ N	.530	7.2	.14	.40
2NC	χ-Fe ₂ X(C,N), ε-Fe ₂ X-Fe ₂ X(C,N)	.282	3.28	.11	.40
1N	ε-Fe ₂ N-Fe ₂ N, γ'-Fe ₄ N	.257	4.86	.29	.23
1CN	ε-Fe ₂ X-Fe ₂ X(C,N)	.247	5.35	.17	.30
5CN	ε-Fe ₂ X-Fe ₂ X(C,N)	.247	4.54	.90	.19
1NC	ε-Fe ₂ X-Fe ₂ X(C,N), Fe ₃ O ₄	.233	2.42	1.15	.30
12C	χ-Fe ₃ C	.223	6.76	.20	.40
19N	ζ-Fe ₂ N, ε-Fe ₂ N-Fe ₂ N, γ'-Fe ₄ N	.212	6.30	.33	.18
4NC	ε-Fe ₂ X-Fe ₂ X(C,N)	.191	6.87	.45	.52
3NC	ε-Fe ₂ X-Fe ₂ X(C,N), θ-Fe ₃ C	.141	1.40	.13	.48

Table 21.—Oxidation of CO in 85 percent H₂PO₄ at 25° C

Catalyst	Composition	Exchange current		Tafel slope, v	Equilibrium potential, v
		ma/g	μa/cm ²		
Pt		17.7	0.0847	0.02	1.00
2NC	χ-Fe ₂ X(C,N), ε-Fe ₂ X-Fe ₂ X(C,N)	1.59	18.5	.11	.23
3NC	ε-Fe ₂ X-Fe ₂ X(C,N), ζ-Fe ₂ N, θ-Fe ₃ C	1.34	13.2	.22	.22
10N	ε-Fe ₂ N-Fe ₂ N	1.17	42.9	.04	.04
21N	γ'-Fe ₄ N, ε-Fe ₂ N-Fe ₂ N	.849	11.5	.13	.25
1N	ε-Fe ₂ N-Fe ₂ N, γ'-Fe ₄ N	.814	16.0	.49	.98
1CN	ε-Fe ₂ X-Fe ₂ X(C,N)	.283	6.12	.50	.15
10C	θ-Fe ₃ C, α-Fe	.254	7.62	.49	.04
15C	θ-Fe ₃ C	.177	5.92	.07	.26
19N	ζ-Fe ₂ N, ε-Fe ₂ N-Fe ₂ N, γ'-Fe ₄ N	.177	5.23	.11	.25
23C	ε-Fe ₃ C, α-Fe (trace)	.152	5.59	.14	.26
4NC	ε-Fe ₂ X-Fe ₂ X(C,N)	.120	4.34	.05	.29
12C	χ-Fe ₃ C	.035	1.07	.04	.29

sity of 369 $\mu\text{a}/\text{cm}^2$ in the oxidation of CO in an acetate buffer of pH 3 (table 19, column 4) when the exchange current density on Pt-black under the same conditions was only 2.84 $\mu\text{a}/\text{cm}^2$. By contrast, the catalyst utilization (exchange current per unit weight of catalyst) for 10C is only 12.4 ma/g compared to 47.6 ma/g for Pt (table 19, column 3). Likewise, 23C (table 19) and 1CN (table 18) have high exchange current density though very poor catalyst utilization. On a priori considerations it would appear that the utilization of a catalyst may be improved by reducing its particle size. Accordingly, 10C, 23C, and 1CN were crushed in a mortar and their activities redetermined. The results are presented in table 22. The utilization of 10C and 23C improved by crushing, though not in the same proportion as the increase in their surface area. 1CN gave anomalous result. The exchange current density of the three materials, however, suffered sharp decrease by crushing. Thus, the surface exposed by crushing appears to be less active than the original surface of the uncrushed material. Alternatively, the observed exchange current density of the crushed materials were low because the electrodes prepared from them were flooded during activity test; qualitative experience indicates that electrodes prepared from finer materials tend to get flooded more easily than electrodes prepared from coarser materials.

Further investigation of the catalysts with high exchange current density may be profitable. Materials finer by synthesis may give better catalyst utilization, and flooding of the electrodes prepared from the finer materials may possibly be prevented by increasing the teflon-to-catalyst ratio in the binder, or by adding some inert material to the catalyst before fabricating the electrodes.

REDUCTION OF O_2 IN H_2SO_4 , BUFFERED CARBONATE AND PHOSPHATE ELECTROLYTES, AND MOLTEN H_3PO_4

(Esso Research and Engineering Co., Government Research, Linden, N.J.¹⁵)

Sixty preparations were selected for cathodic activity test in the reduction of O_2 in the following electrolytes:

- (1) 3.7M H_2SO_4 ,
- (2) 1M KHCO_3 + 1M K_2CO_3 buffer of pH 10.2,
- (3) 1M KH_2PO_4 + 1M K_2HPO_4 buffer of pH 7, and
- (4) molten H_3PO_4 .

Preliminary corrosion tests,¹⁶ however, revealed that most of the materials were too unstable in the electrolytes for profitable electrochemical investigation. Nearly all preparations corroded in 3.7M H_2SO_4 . The acid decomposed the interstitial compounds of Fe and the borides of Ni and Co with rapid evolution of gas. The corrosion of the carbides and the nitrocarbides of Ni and 1Ni-1Ag-1Au was less rapid but severe. Only 53C, a sample of carbided 1Ni-1Ag, was judged stable enough for electrochemical investigation in the acid. In the carbonate and phosphate buffers, corrosion was less severe than in 3.7M H_2SO_4 and several preparations were passed for activity test. Surprisingly, a number of iron carbides, nitrides, and nitrocarbides were stable in molten H_3PO_4 at 220° C.

The stable materials were fabricated into electrodes by hand pressing mixtures of catalyst powders and Teflon X42 emulsion to Ta or Monel

¹⁵ Principal investigators: J. S. Batsold and M. Beltzer.

¹⁶ The corrosion tests were conducted by the method described in "Oxidation of H_2 and C_2H_2 in Aqueous $\text{K}_2\text{C}_2\text{O}_4$ - KHCO_3 ". In electrolytes (1 to 3), the corrosion tests were conducted at room temperature; in H_3PO_4 , at 22° C.

Table 22.—Effect of crushing on the activity of catalysts in the oxidation of CO at 25° C

Catalyst	10C ¹		23C ¹		1CN ¹	
	Uncrushed	Crushed	Uncrushed	Crushed	Uncrushed	Crushed
Surface area (cm^2/g)	33.5	14,680	27.1	7,950	46.0	809
Exchange current (ma/g)	12.4	18.7	1.76	3.24	36.4	9.88
Exchange current ($\mu\text{a}/\text{cm}^2$)	369	1.27	65.0	.407	790	12.2
Tafel slope, v	.14	.08	.09	.20	2.20	.18
Equilibrium potential, v	.81	.80	.86	.40	.50	.68

¹ Tested in CH_3COOH + CH_3COOK buffer of pH 3.

² Tested in 2N H_2SO_4 .

screens in the cold. Tantalum screens were employed for the electrodes to be tested in 3.7M H₂SO₄, and Monel screens were employed for the electrodes to be tested in the buffer electrolytes. The electrodes were prepared and mounted in the cell inside a dry box filled with N₂, and the cell was removed from the dry box only after the electrolyte had been added and a blanket of N₂ applied to the gas side. Trace quantities of O₂ were then added to the N₂ blanket to passivate the electrode and, after about 15 minutes, pure O₂ was introduced.

The results of galvanostatic measurements on the activity of the electrodes in the reduction of O₂ are presented in table 23. 11C, 74C, and 77C are good catalysts in the carbonate buffer; 11C was tested at 80° C, and 74C and 77C were tested

at 25° C. However, each of these materials gave significant corrosion current in the electrolyte at room temperature. 74C and 77C were also tested for cathodic activity and corrosion in the carbonate buffer at 55° C. The activity was about the same as at 25° C (table 23), but the corrosion current was larger at the higher temperature. This may indicate that 74C and 77C are heterogeneous materials in which the component responsible for cathodic activity is different from the component responsible for corrosion current. If so, the cathodic performance of these materials may possibly be improved by exhaustively leaching out the corrodible component before activity test.

Comparable measurements in carbonate and phosphate buffers indicated that corrosion of

Table 23.—Reduction of O₂

Catalyst	Electrolyte	Temp., ° C	Volts ¹ polarized, from theoretical O ₂ , at ma/cm ²							
			0	1	5	10	15	20	30	50
7C(χ -Fe ₂ C)-----	1M KHCO ₃ +1M K ₂ CO ₃	80	0.50	0.52	0.69	-----	Visible corrosion.			
11C(χ -Fe ₂ C)-----	1M KHCO ₃ +1M K ₂ CO ₃	80	.41	.47	.59	0.71	0.79	0.84	1.00	-----
15C(θ -Fe ₂ C)-----	1M KHCO ₃ +1M K ₂ CO ₃	80	.55	.61	.74	.84	.91	.93	-----	-----
23C(ϵ -Fe ₂ C, α -Fe)-----	1M KHCO ₃ +1M K ₂ CO ₃	80	.56	.62	.83	-----	Visible corrosion.			
33C(Co ₂ C, α -Co)-----	1M KHCO ₃ +1M K ₂ CO ₃	80	1.13	-----	-----	-----	-----	-----	-----	-----
35C(Ni ₃ C)-----	1M KHCO ₃ +1M K ₂ CO ₃	80	.865	.865	.91	.99	-----	-----	-----	-----
44C-----	1M KHCO ₃ +1M K ₂ CO ₃	80	.92	.95	-----	-----	-----	-----	-----	-----
(carbided 1Ni-1Au-1Ag)										
46C(carbided 3Ni-1Ag)	1M KHCO ₃ +1M K ₂ CO ₃	80	.95	.98	-----	-----	-----	-----	-----	-----
54C(Ni ₃ C)-----	1M KHCO ₃ +1M K ₂ CO ₃	80	.98	1.01	1.18	-----	-----	-----	-----	-----
56C(Ni ₃ C, Ni)-----	1M KHCO ₃ +1M K ₂ CO ₃	80	1.01	1.05	-----	-----	-----	-----	-----	-----
74C(carbided 3Ni-1Au)	1M KHCO ₃ +1M K ₂ CO ₃	25	.40	.44	.50	.54	-----	-----	-----	0.90
77C(carbided 1Ni-1Au)	1M KHCO ₃ +1M K ₂ CO ₃	25	.37	.39	.44	.49	-----	-----	-----	.67
74C(carbided 3Ni-1Au)	1M KH ₂ PO ₄ +1M K ₂ HPO ₄	25	.55	-----	.63	.69	-----	-----	-----	.91
77C(carbided 1Ni-1Au)	1M KH ₂ PO ₄ +1M K ₂ HPO ₄	25	.60	-----	.78	.91	-----	-----	-----	-----
53C(carbided 1Ni-1Ag)	3.7M H ₂ SO ₄	25	-----	.77	.80	.87	-----	-----	-----	-----
53C(carbided 1Ni-1Ag)	H ₃ PO ₄	25	-----	.97	-----	-----	-----	-----	-----	-----
53C(carbided 1Ni-1Ag)	H ₃ PO ₄	85	-----	.90	.93	1.00	-----	-----	-----	-----
53C(carbided 1Ni-1Ag)	H ₃ PO ₄	120	-----	.86	.91	-----	-----	-----	-----	-----
Ag-----	H ₃ PO ₄	25	-----	.80	.85	.88	-----	-----	-----	-----
(Silpowder 130-3C, Handy & Harman.)										
Ag-----	H ₃ PO ₄	150	-----	.68	.73	.78	-----	.95	0.88	-----
(Silpowder 130-3C, Handy & Harman.)										

¹ Potentials were measured versus a saturated calomel electrode.

74C and 77C was more severe in the latter electrolyte.

74C and 77C were also tested for anodic activity in the oxidation of H_2 in the carbonate and phosphate buffers at room temperature; the performance was poor.

It was stated earlier that several interstitial compounds of iron were found to be stable in H_3PO_4 at $220^\circ C$. One such material, 11C, a sample of $\chi-Fe_2C$, was tested for cathodic activity in the reduction of O_2 in molten H_3PO_4 at $200^\circ C$ and was found to be completely inactive.

OXIDATION OF H_2 AND REDUCTION OF O_2 IN 3N H_2SO_4

(General Electric Co., Direct Energy Conversion Operation,¹⁷ Lynn, Mass.)

Seventy-three preparations were selected for investigation. Before electrochemical examination, the materials were tested for stability in the electrolyte at room temperature by the procedure described under "Oxidation of H_2 in Aqueous KOH". Samples were kept under intermittent observation for 17 hr. All leached Raney alloys and most of the interstitial compounds of Fe reacted with the acid instantly. The interstitial compounds of Ni and Co and the mixed interstitial preparations of the alloys of Ni and Co with Ag and Au gave visible signs of reaction within 5 minutes. Only two preparations, 76C (carbided 1Ni-3Au) and 78C (carbided 1Ni-4Cr), appeared to stay unaffected after 17 hr. When tested electrochemically, both 76C and 78C catalyzed the oxidation of H_2 and reduction of O_2 in 3N H_2SO_4 , and corrosion currents were low. However, the level of activity was too low for the catalysts to be of practical use.

INTERSTITIAL COMPOUNDS AS CATHODES IN AMMONIA BATTERY

(Department of the Army, Harry Diamond Laboratories,¹⁸ Washington, D.C., and Tracor, Inc.,¹⁹ Austin, Tex.)

Twenty-three interstitial compounds were tested for cathodic activity in a saturated solution of *m*-dinitrobenzene in 25.1 pct NH_3 + 57.65 pct CH_3OH + 17.25 pct NH_4SCN as part of a program to develop ammonia batteries for fuse power requirements.²⁰ Electrodes were prepared

¹⁷ Principal investigators: M. E. Nolan, R. A. Sanford, E. Y. Weissman, A. Kuchar, A. B. LaConti, I. F. Danzig, and J. Amore.

¹⁸ Principal investigator: Raymond H. Comyn.

¹⁹ Principal investigator: P. E. Hudson.

²⁰ Separate considerations had indicated that an electrolyte of the stated composition was most appropriate for the required battery.

by pressing mixtures of interstitial compounds and a wax into standardized pellets of approximately 0.026-square-inch surface. Cathodic efficiency was determined potentiostatically at $0^\circ C$. A saturated calomel electrode was employed as the reference electrode. The polarization curves are presented in figures 21-27.

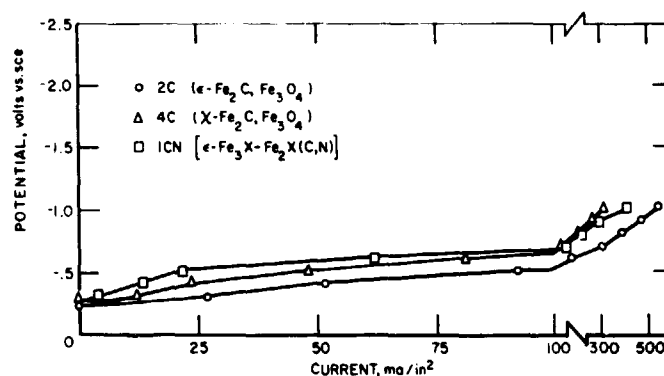


Figure 21.—Cathodic polarization curves in a saturated solution of *m*-dinitrobenzene in 25.1 pct NH_3 + 57.6 pct CH_3OH + 17.25 pct NH_4SCN at $0^\circ C$.

2C, 4C, and 1CN showed mainly resistance polarization (fig. 21). With 2C, the current had not reached its limit even at 530 ma/inch^2 .

TiC and TiN showed activation polarization; they polarized rapidly at very low current densities (fig. 22). 6N also showed mainly resistance polarization but was not as efficient as 2C.

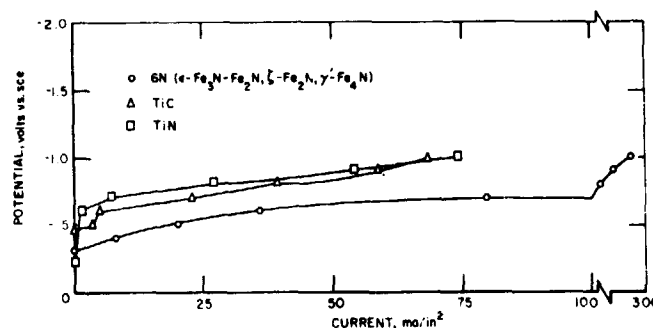


Figure 22.—Cathodic polarization curves in a saturated solution of *m*-dinitrobenzene in 25.1 pct NH_3 + 57.6 pct CH_3OH + 17.25 pct NH_4SCN at $0^\circ C$.

2N and 5N showed chiefly resistance polarization, but with 8N the current leveled off to a limiting value at about 380 ma/inch^2 (fig. 23).

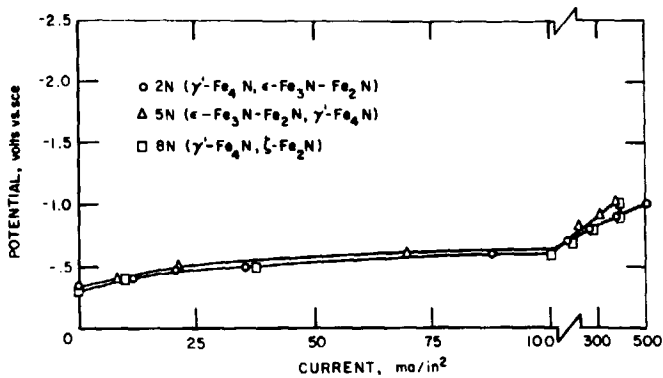


Figure 23.—Cathodic polarization curves in a saturated solution of *m*-dinitrobenzene in 25.1 pct NH_3 + 57.6 pct CH_3OH + 17.25 pct NH_4SCN at 0°C .

2NC showed activation polarization; the electrode polarized badly at low current densities (fig. 24). 9N gave a limiting current at about 440 ma/inch^2 , and the curve for 1NC appears to indicate a limiting current at about 250 ma/inch^2 .

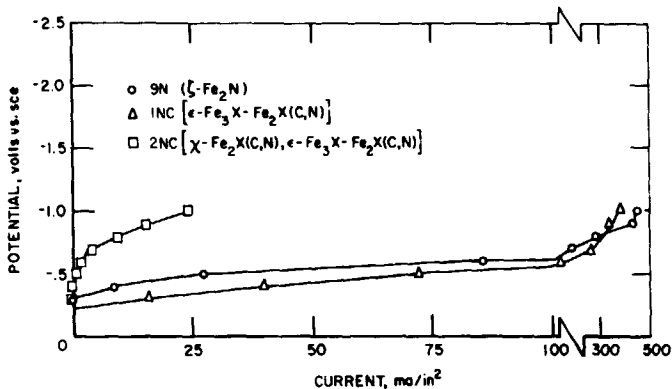


Figure 24.—Cathodic polarization curves in a saturated solution of *m*-dinitrobenzene in 25.1 pct NH_3 + 27.6 pct CH_3OH + 17.6 pct NH_4SCN at 0°C .

Each of the three curves in fig. 25 shows a high degree of polarization at low current densities.

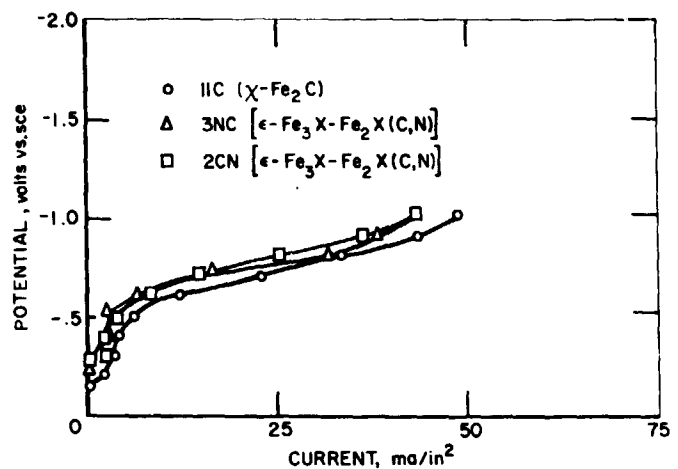


Figure 25.—Cathodic polarization curves in a saturated solution of *m*-dinitrobenzene in 25.1 pct NH_3 + 57.6 pct CH_3OH + 17.25 pct NH_4SCN at 0°C .

Ni_3C has only resistance polarization (fig. 26). The curve for 9CN indicates a slight activation polarization at low current densities, but once over the barrier, the curve indicates only resistance polarization up to 400 ma/inch^2 . 3CN gave a limiting current at 370 ma/inch^2 , but 10CN showed chiefly resistance polarization.

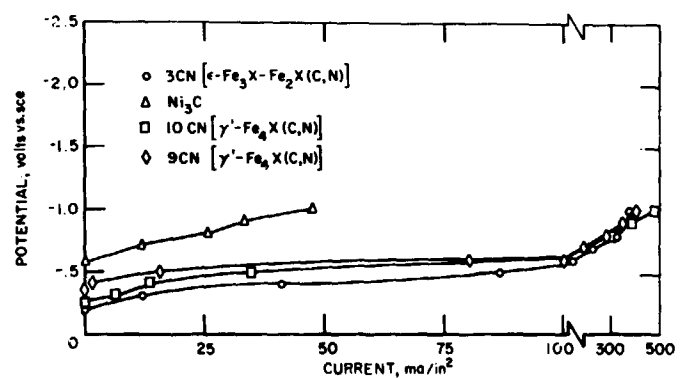


Figure 26.—Cathodic polarization curves in a saturated solution of *m*-dinitrobenzene in 25.1 pct NH_3 + 57.6 pct CH_3OH + 17.25 pct NH_4SCN at 0°C .

6NC gave a limiting current at a low current density but 4NC, 5NC, and 7NC showed mainly resistance polarization (fig. 27).

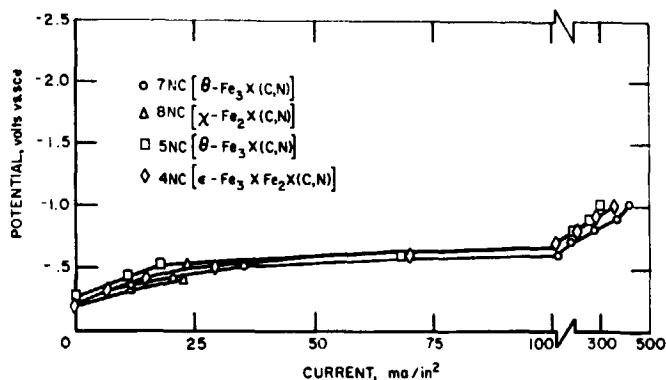


Figure 27.—Cathodic polarization curves in saturated solution of *m*-dinitrobenzene in 25.1 pct NH_3 + 57.6 pct CH_3OH + 17.25 pct NH_4SCN at 0° C.

To sum up, 2C and 2N gave the best cathodic performance of the materials tested. However, it was suspected that the reduction products of *m*-dinitrobenzene tend to stay adsorbed on the cathode and produce a counter emf, presumably by reoxidation of the adsorbed molecular species. The following experiment confirmed the suspicion. A cell of Zn(anode)/saturated solution of *m*-dinitrobenzene in



was discharged through a 100-ohm resistor for 15 minutes at 0° C. The initial voltage of 1.2v had dropped to 0.90v during the time. The zinc anode of the cell was then replaced by the pellet of 2C from the cathode, and a fresh pellet of 2C was introduced as cathode. The cell, "used 2C" (anode)/"fresh 2C" (cathode), had an emf of 0.2v, and even after it had been discharged for an hour through a 100-ohm resistor, an emf of 0.1v was registered.

OXIDATION OF N_2H_4 AND DEXTROSE

(Monsanto Research Corp., Boston Laboratory,²¹ Everett, Mass.)

Selected preparations were tested galvanostatically for anodic activity in the following aqueous systems: (1) Oxidation of N_2H_4 in 5M KOH at 30°, 50°, and 70° C; and (2) oxidation of dextrose in a solution containing 0.5M NaCl,

1M phosphate buffer of pH 7.4, and 0.5M dextrose, at 37° C.

Preliminary tests revealed that all catalysts corroded in KOH. Samples of the materials (0.5g) were soaked overnight in 5M KOH at 70° C. The following day the solids were filtered out, dried in vacuum, and reweighed. All samples had gained weight. Separate tests to determine the stability of the materials in a mixture of 5M KOH and 2M N_2H_4 were inconclusive: the evolution of gaseous products from the decomposition of N_2H_4 was so vigorous that portions of catalysts were lost physically and the change in sample weights due to corrosion could not be computed. In 0.1M HCl, all materials lost weight.

Electrodes were prepared by two methods, both proprietary to Monsanto Research Corp. We will call the products of the two methods type A and type B electrodes. They differ in structural characteristics and, consequently, in certain physical properties. Type A electrodes contain uniform micropores, whereas type B electrodes contain a network of macropores in a matrix of micropores. Hence, type A electrodes have a higher material density and are more hydrophobic than type B electrodes. Some of the catalyst powders were too coarse for the fabrication of electrodes by these proprietary methods. Such powders were, therefore, first ground and sieved to -400 mesh. Before exposure to air, all catalysts were induced²² with a mixture of argon and traces of air in a dry box. Most of the electrochemical tests were conducted in the half cell shown in figure 28. Type A electrodes were sealed directly with O-rings as shown in the figure, but type B electrodes were placed in a leakproof Teflon holder. Some of the earlier experiments were conducted with a simple H-type cell; only type B electrodes were employed in these experiments, and they were completely immersed in one leg of the cell. I-R drop was determined with a Kordes-Marko bridge. All potentials were measured with reference to a saturated calomel electrode.

Oxidation of N_2H_4

N_2H_4 is a very reactive compound and, to no surprise, practically all the materials tested in this program decomposed N_2H_4 readily. From the results presented in table 24, it will be seen

²¹ Principal investigators: R. F. Drake, S. Matsuda, B. P. Sullivan, and S. Polansky.

²² The principles and practice of induction are discussed in the section "Reduction of O_2 in Aqueous KOH (Tyco Laboratories, Inc., Waltham, Mass.)."

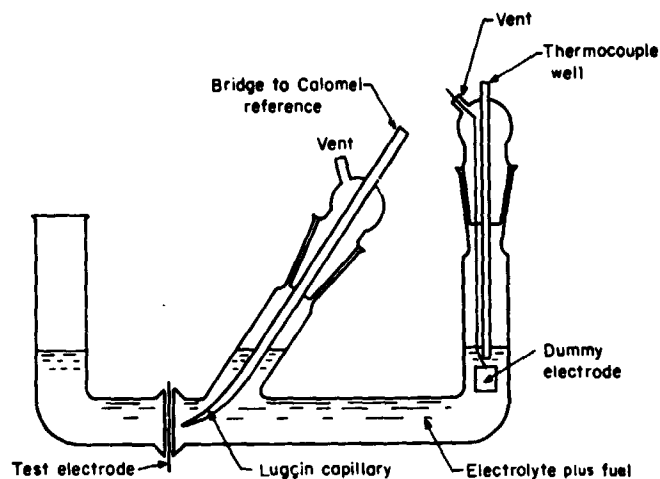


Figure 28.—Side view of half-cell test unit.

that most of the materials were just as active in electrochemical oxidation of N_2H_4 . The open cell potentials corresponded to those of hydra-

zine and, in the range 10 ma/cm^2 to 100 ma/cm^2 , polarization from the open cell potentials was surprisingly small. However, the corrosion problem was extremely serious in a number of cases, and serious enough in others to preclude practical utilization of the materials.

Eight catalysts were selected for some supplementary investigation. The rates of evolution of gaseous products with these catalysts at open circuit and under polarization at 100 ma/cm^2 were determined, and the evolved gases were analyzed for their quantitative composition. Information on these points is needed for designing operational N_2H_4 -air fuel cells; the results are presented in table 25. The NH_3 content of the evolved gases was found to be 100- to 1,000-times higher than the NH_3 content of the gases evolved with a proprietary catalyst of Monsanto Research Corp. for hydrazine electrode.

Table 24.—Oxidation of N_2H_4 in 5M KOH

Catalyst	Composition	Electrode type	Temp., °C	Open cell potential, v	Potentials, v, at ma/cm^2			
					10	20	50	100
(Catalyst loading: 0.7 g/inch ²)								
10C	$\theta\text{-Fe}_2\text{C}$, $\alpha\text{-Fe}$	A	70	-1.13	-1.13	-1.10	-1.09	-1.03
		B	70	-1.18	-1.18	-1.17	-1.13	-1.08
11C	$\chi\text{-Fe}_2\text{C}$	A	70	-1.15	-1.15	-1.14	-1.13	-1.11
14C	$\theta\text{-Fe}_2\text{C}$	A	70	-1.13	-1.13	-1.11	-1.08	-1.01
1N	$\epsilon\text{-Fe}_2\text{N-Fe}_2\text{N}$, $\gamma'\text{-Fe}_4\text{N}$	A	70	-1.16	-1.15	-1.13	-1.11	-1.07
6N	$\epsilon\text{-Fe}_2\text{N-Fe}_2\text{N}$, $\zeta\text{-Fe}_2\text{N}$, $\gamma'\text{-Fe}_4\text{N}$	A	70		Electrode decomposed.			
9N	$\zeta\text{-Fe}_2\text{N}$	A	70	-1.17	-1.16	-1.15	-1.13	-1.12
10N	$\epsilon\text{-Fe}_2\text{N-Fe}_2\text{N}$	A	70	-1.20	-1.17	-1.16	-1.05	-.97
		A	50	-1.16	-1.15	-1.13	-1.08	-.97
		A	30	-.92	-.78	-.74	-.68	-.62
19N	$\zeta\text{-Fe}_2\text{N}$, $\epsilon\text{-Fe}_2\text{N-Fe}_2\text{N}$, $\gamma'\text{-Fe}_4\text{N}$	B	50	-1.20	-1.15	-1.13	-1.11	-1.07
		A	70	-1.21	-1.19	-1.16	-1.10	-1.05
		A	50	-1.20	-1.19	-1.16	-1.10	-1.08
		A	30	-1.13	-1.11	-1.11	-1.04	-.92
21N	$\gamma'\text{-Fe}_4\text{N}$, $\epsilon\text{-Fe}_2\text{N-Fe}_2\text{N}$	A	50	-1.20	-1.17	-1.15	-1.11	-1.06
		A	70	-1.22	-1.21	-1.20	-1.19	-1.12
		A	50	-1.02	-1.07	-1.13	-1.12	-1.10
		A	30	-.86	-.76	-.70	-.62	-.55
2NC	$\chi\text{-Fe}_2\text{X(C,N)}$, $\epsilon\text{-Fe}_2\text{X-Fe}_2\text{X(C,N)}$	B	50	-1.22	-1.17	-1.17	-1.15	-1.15
		A	70	-1.18	-1.17	-1.16	-1.16	-1.15
		A	50	-1.17	-1.17	-1.16	-1.13	-1.12
		A	30	-1.16	-1.15	-1.09	-1.07	-1.03
3NC	$\epsilon\text{-Fe}_2\text{X-Fe}_2\text{X(C,N)}$, $\zeta\text{-Fe}_2\text{N}$	B	70	-1.18	-1.19	-1.18	-1.17	-1.14
		A	70	-1.19	-1.19	-1.18	-1.15	-1.12
		A	50	-1.14	-1.15	-1.14	-1.11	-1.07
		A	30	-1.03	-1.07	-1.03	-.99	-.99
5NC	$\theta\text{-Fe}_2\text{X(C,N)}$	B	70	-1.20	-1.08	-1.05	-.96	-.86
1CN	$\epsilon\text{-Fe}_2\text{X-Fe}_2\text{X(C,N)}$	A	70	-1.15	-1.13	-1.13	-1.10	-1.10
		A	70	-1.19	-1.19	-1.18	-1.15	-1.12
		A	50	-1.15	-1.15	-1.15	-1.14	-1.12
		A	30	-.86	-.65	-.58	-.47	-.33
2CN	$\epsilon\text{-Fe}_2\text{X-Fe}_2\text{X(C,N)}$	A	70	-1.10	-1.10	-1.09	-1.07	-1.03
5CN	$\epsilon\text{-Fe}_2\text{X-Fe}_2\text{X(C,N)}$	A	70	-1.10	-1.11	-1.10	-1.08	-1.05
9CN	$\gamma'\text{-Fe}_4\text{X(C,N)}$	A	70	-1.19	-1.16	-1.14	-1.14	-1.10
		A	50	-1.14	-1.18	-1.16	-1.14	-.98
		A	30	-.99	-.96	-.78	-.64	-.60
		B	50	-1.22	-1.15	-1.13	-1.10	-1.07
2C	$\epsilon\text{-Fe}_2\text{C}$, Fe_3O_4	A	70		Electrode decomposed.			
4C	$\chi\text{-Fe}_2\text{C}$, Fe_3O_4	A	70		Electrode decomposed.			
7C	$\chi\text{-Fe}_2\text{C}$	A	70	-1.17	-1.15	-1.15		Electrode decomposed.

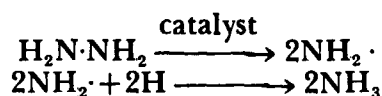
Table 24.—Oxidation of N_2H_4 in 5M KOH—Continued

Catalyst	Composition	(Catalyst loading: 0.7 g/inch ²)		Open cell potential, v	Potentials, v, at ma/cm ²			
		Electrode type	Temp., °C		10	20	50	100
12C	ϵ -Fe ₂ C, α -Fe	A	70	-1.13	-1.13	-1.13	-1.10	Electrode decomposed.
		B	70	-1.08	-1.10	-1.10	-1.08	-1.06
15C	θ -Fe ₂ C	A	70	-1.11	-1.09	-1.09		Electrode decomposed.
23C	ϵ -Fe ₂ C, α -Fe (trace)	A	70	-1.13	-1.14	-1.16		Electrode decomposed.
13N	ϵ -Fe ₃ N-Fe ₂ N	A	70	-1.16	-1.16	-1.12	-1.10	Electrode decomposed.
		A	50	-.90	-.78	-.73	-.62	-.61
		B	50	-1.18	-1.15	-1.14	-1.11	-1.09
17N	ϵ -Fe ₃ N-Fe ₂ N	A	70	-1.15				Electrode decomposed.
18N	ζ -Fe ₂ N, ϵ -Fe ₃ N-Fe ₂ N, γ '-Fe ₄ N	A	70	-1.10	-1.02	-1.02	-.98	Electrode decomposed.
1NC	ϵ -Fe ₃ X-Fe ₂ X(C,N), Fe ₃ O ₄	A	70	-1.17				Electrode decomposed.
4NC	ϵ -Fe ₃ X-Fe ₂ X(C,N)	A	70					Electrode decomposed rapidly.
7NC	θ -Fe ₃ X(C,N)	A	70	-1.05	-1.08	-1.12		Electrode decomposed.
3CN	ϵ -Fe ₃ X-Fe ₂ X(C,N)	A	70	-1.20	-1.18	-1.17		Electrode decomposed.
		A	50	-1.19	-1.17	-1.15	-1.12	-1.08
		A	30	-1.16	-1.12	-1.10	-1.09	-1.05
		B	50	-1.16	-1.12	-1.10	-1.07	-.98
4CN	ϵ -Fe ₃ X-Fe ₂ X(C,N)	A	30					Electrode decomposed.
		B	50	-1.15	-1.10	-1.08	-1.04	-.98
6CN	ϵ -Fe ₃ X-Fe ₂ X(C,N)	A	70	-1.17	-1.14	-1.13	-1.12	-1.11
7CN	Ag, ϵ -Fe ₃ X-Fe ₂ X(C,N)	A	70	-1.15	-1.15	-1.14	-1.13	-1.11
8CN	Ag, ϵ -Fe ₃ X-Fe ₂ X(C,N)	A	70	-1.25	-1.20	-1.20	-1.16	-1.15
33C	Co ₂ C, α -Co	B	70	-1.22	-1.22	-1.21	-1.21	-1.19
35C	Ni ₃ C	B	70	-1.19	-1.18	-1.16	-1.14	-1.12
38C	Ag, Co ₂ C	B	70	-1.17	-1.16	-1.16	-1.15	-1.09
39C	Ag, Co ₂ C, α -Co	B	70	-1.22	-1.22	-1.22	-1.21	-1.21
42C	Carbided 1Ni-1Co	B	70					
43C	Carbided 1Ni-1Ag	B	70	-1.21	-1.21	-1.19	-1.19	-1.19
46C	Ag, Ni ₃ C	B	70	-1.23	-1.21	-1.20	-1.18	-1.18
21NC	Co ₂ X(C,N)	B	70	-1.23	-1.23	-1.20	-1.20	-1.19
23NC	Ni ₃ X(C,N)	B	70	-1.16	-1.13	-1.10	-1.09	-1.07
28NC	Nitrocarbided 1Ni-Co	B	70	-1.16	-1.11	-1.09	-1.03	-.85
31NC	Nitrocarbided 1Ni-1Ag	B	70	-1.25	-1.25	-1.25	-1.21	-1.21
32NC	Ag, Ni ₃ X(C,N)	B	70	-1.19	-1.13	-1.12	-1.12	-1.12
RAL-2	1Ni-3Co	B	70	-1.12	-1.12	-1.10	-1.10	-1.05
RAL-3	3Ni-1Co	B	70	-1.25	-1.25	-1.25	-1.23	-1.23
RAL-4	1Ni-3Ag	B	70	-1.20	-1.19	-1.19	-1.14	-1.12
RAL-5	1Ni-1Ag	B	70	-1.15	-1.15	-1.12	-1.12	-1.12
RAL-6	3Ni-1Ag	B	70	-1.15	-1.15	-1.15	-1.13	-1.10
RAL-7	1Co-3Ag	B	70	-1.24	-1.23	-1.22	-1.20	-1.16
RAL-8	1Co-1Ag	B	70	-1.23	-1.23	-1.20	-1.18	-1.17
RAL-9	3Co-1Ag	B	70	-1.25	-1.25	-1.25	-1.25	-1.25
RAL-10	1Ni-1Co-1Ag	B	70	-1.23	-1.23	-1.23	-1.20	-1.20
RAL-11	1Ni-1Co-1Au	B	70	-1.23	-1.23	-1.23	-1.23	-1.23
RAL-12	1Ni-1Ag-1Au	B	70	-1.20	-1.19	-1.19	-1.19	-1.18
RAL-13	1Co-1Ag-1Au	B	70	-1.24	-1.23	-1.23	-1.22	-1.22
RC-1	Co	B	70	-1.25	-1.25	-1.25	-1.24	-1.19
RN-2	Ni	B	70	-1.16	-1.16	-1.16	-1.15	-1.15
54R	Reduced Ni	B	70	-1.17	-1.17	-1.17	-1.17	-1.16
								Electrolyte turned blue; electrode disintegrated.
54C	Ni ₃ C	B	70	-1.24	-1.22	-1.22	-1.22	-1.21
39NC	Ni ₃ X(C,N)	B	70	-1.15	-1.15	-1.15	-1.15	-1.12
								Electrode disintegrated.
56R	Reduced Ni	B	70	-1.20	-1.20	-1.20	-1.20	-1.20
56C	Ni ₃ C, Ni	B	70	-1.22	-1.22	-1.22	-1.22	-1.20
41NC	Ni ₃ X(C,N)	B	70	-1.20	-1.20	-1.18	-1.18	-1.18
59R	Reduced Co	B	70	-1.25	-1.25	-1.25	-1.25	-1.25
59C	Co ₂ C	B	70	-1.25	-1.25	-1.21	-1.21	-1.21
48NC	Co ₂ X(C,N)	B	70	-1.16	-1.15	-1.15	-1.15	-1.15
								Electrode disintegrated.

Table 24.—Oxidation of N_2H_4 in 5M KOH—Continued

Catalyst	Composition	Electrode type	Temp., °C	Open cell potential, v	(Catalyst loading: 0.7 g/inch ²) Potentials, v, at ma/cm ²			
					10	20	50	100
61R	Reduced 3Ni-1Co	B	70	-1.22	-1.22	-1.22	-1.21	-1.20
61C	Carbided 3Ni-1Co	B	70	-1.22	-1.22	-1.21	-1.21	-1.20
45NC	Nitrocarbided 3Ni-1Co	B	70	-1.17	-1.17	-1.17	-1.17	-1.17
58C	Ni, Ni ₃ C, Co ₂ C	B	70	-1.20	-1.20	-1.20	-1.19	-1.18
36NC	Ni ₃ X(C,N), Co ₂ X(C,N)	B	70	-1.18	-1.18	-1.18	-1.18	-1.18
53R	Reduced 1Ni-1Ag	B	70	-1.20	-1.20	-1.20	-1.20	-1.17
53C	Ag, Ni ₃ C	B	70	-1.21	-1.20	-1.20	-1.20	-1.20
38NC	Ag, Ni ₃ X(C,N)	B	70	-1.20	-1.20	-1.20	-1.20	-1.18
60C	Au, Ag, Ni, Ni ₃ C	B	70	-1.21	-1.20	-1.20	-1.19	-1.18
44NC	Nitrocarbided 1Ni-1Au-1Ag	B	70	-1.18	-1.17	-1.16	-1.16	-1.16
B-6	Ni ₃ B	B	70	-1.25	-1.25	-1.25	-1.25	-1.24
B-7	Co ₂ B	B	70	-1.29	-1.28	-1.28	-1.28	-1.28
B-18	Coprecipitated borides of 1Ni-1Co	B	70	-1.26	-1.26	-1.26	-1.26	-1.26
B-20	Coprecipitated borides of 1Ni-3Co	B	70	-1.28	-1.28	-1.28	-1.28	-1.28
B-9	Coprecipitated borides of 3Ni-1Co	B	70	-1.26	-1.26	-1.26	-1.26	-1.26

It is suggested that the interstitial compounds of the transition metals catalyze the formation of NH_3 from N_2H_4 by the following mechanism:



Hydrogen is supplied by local cathodic reaction on the anode.

Oxidation of Dextrose

This part of the program was sponsored by the National Heart Institute, and the object of the project was to develop an implantable fuel cell for an artificial heart. Since contamination of blood stream with corrosion products is not permissible, electrode materials must be absolutely stable in the electrolyte. Although the materials did not meet the strict criterion of stability, the first 36 compounds listed in table 24 were, nevertheless, tested as glucose anodes. The catalysts were made into 1 x 1 inch type B electrodes which were tested as anodes in deaerated solutions of 0.5M NaCl, 1M phosphate buffer of pH 7.4, and 0.5M dextrose at 37° C. Steady open-circuit potentials were reached in 30 to 60 minutes, but the potentials were 0.2 to 0.4 v less than the potential of a reversible hydrogen electrode in the same electrolyte—Pt-metals and certain chelate catalysts give open circuit potentials very close to the potential of a reversible hydrogen electrode. Potential-time curves

were determined at an anodic current of 1 ma/cm². An instantaneous polarization of 0.5 v or more was noted. The materials were evidently inactive in the oxidation of dextrose. 19N sustained a relatively active potential when current was passed, but analysis of the electrolyte revealed that the current was consumed in dissolving the electrode.

OXIDATION OF N_2H_4 IN ACID LIQUID NH_3

(Naval Weapons Center, Corona Laboratories, Corona Calif.)²³

Twenty-four preparations were tested for anodic activity in the oxidation of N_2H_4 in $NH_4SCN + NH_3$ at 25° C. Electrodes were prepared from 1-cm² pieces of a silver screen. The screen pieces were spot welded to Ni leads and were coated with a conductive silver epoxy. They were then transferred to a dry box filled with Ar where the epoxy coatings were covered with catalyst powders and the finished electrodes were sealed into glass tubings with Bipax epoxy (BA-2112). The electrolyte was prepared by condensing NH_3 on vacuum-dried NH_4SCN . The tests were conducted in a glass cell in which the compartments for the working and counter electrodes were separated by a fritted disk. The reference electrode consisted of a Pb-saturated $PbNO_3$ electrode; NH_3-LiNO_3 was employed as

²³ Principal investigators: M. H. Miles and P. M. Kelleff.

Table 25.—Catalytic decomposition of 2M N₂H₄ in 5M KOH at 70° C

Electrode: type B, 2 x 2; (Loading: 0.7 g/inch²)

Catalyst (composition)	Open circuit potential, v	Evolved gas				Potential, v, at 100 ma/cm ² ¹	Evolved gas			
		Volume, at OCP, cc/min/inch ²	Composition, percent				Volume, at 100 ma/cm ² , cc/min/inch ²	Composition, percent		
			NH ₃	H ₂	N ₂			NH ₃	H ₂	N ₂
1NC ε-Fe ₂ X-Fe ₂ X(C,N), Fe ₂ O ₄	-1.26	7.7	14.4	41.5	44.1	-0.85	24.6	8.5	43.7	47.7
2NC χ-Fe ₂ X(C,N), ε-Fe ₂ X-Fe ₂ X(C,N)	-1.20	4.7	10.2	55.0	34.8	-1.07	11.8	19.8	36.1	44.1
3NC ε-Fe ₂ X-Fe ₂ X(C,N), ζ-Fe ₂ N, θ-Fe ₂ C	-1.30	9.0	13.8	34.0	52.2	-1.17	16.2	13.8	25.0	61.1
5NC θ-Fe ₂ X(C,N)	-1.27	6.25	23.8	31.4	44.8	-1.10	15.6	17.2	23.4	59.4
6CN ε-Fe ₂ X-Fe ₂ X(C,N), Ag	-1.19	1.3	9.0	39.9	51.0	-.84	1.3	3.9	7.8	88.3
7CN Ag, ε-Fe ₂ X-Fe ₂ X(C,N)	-1.30	2.01	7.0	46.2	46.8	-1.19	2.01	3.5	12.2	84.2
8CN Ag, ε-Fe ₂ X-Fe ₂ X(C,N)	-1.29	.85	3.2	45.7	51.1	-1.20	.85	15.7	7.1	77.2
9CN γ'-Fe ₂ X(C,N)	-1.21	6.75	3.0	57.1	39.9	-.93	11.5	1.1	34.0	64.8

¹ All potentials were measured versus a saturated calomel electrode.

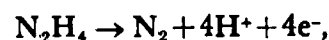
² The area of only one side of electrodes was taken into account in computing current densities since the electrodes were very porous.

salt bridge. The glass partitions between the reference electrode, the salt bridge, and the electrolyte were provided with microcracks. In view of the high impedance of the reference electrode (10^8 ohms), the circuit for measuring potentials was equipped with a unity-gain follower of 10^{12} ohms input impedance. The electrodes were tested by a triangular potential scan method. The solution of $\text{NH}_4\text{SCN} + \text{NH}_3$ was scanned with and without N_2H_4 between 0.2 and 0.7 v at a rate of 50 mv/sec. Hydrazine was added in the ratio of 1 ml $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ to 50 ml $\text{NH}_4\text{SCN} + \text{NH}_3$ solution. The solutions were kept agitated during scanning.

From the results presented in table 26, it will be seen that a nitrocarbide of 3 Ni-1Au is the most active catalyst in the oxidation of N_2H_4 . For purposes of comparison, activity data for bright Pt and 5-pct-Pt-black/C are also included in the table. Using the geometrical areas, the electrode prepared from nitrocarbided 3Ni-1Au was more active than the electrodes prepared from bright

Pt and 5 pct Pt-black/C. However, using estimated real areas, Pt was more active. The significant activity of two other nitrocarbides, a nitride, and three carbides may also be noted. The carbides, on the whole, were less active than the nitrocarbides. Reduced metal preparations were totally inactive.

The net reaction involved in the oxidation of N_2H_4 may be represented as follows:



where H^+ is normally ammoniated. The interstitial compounds containing N evidently promote the formation and evolution of N_2 .

REDUCTION OF O_2 IN KOH CONTAINING N_2H_4

(Union Carbide Corporation Fuel Cell Department,
Parma, Ohio)²⁴

Thirteen interstitial compounds were tested for cathodic activity in the reduction of O_2 in

* Project coordinator: G. E. Evans.

Table 26.—Oxidation of N_2H_4 in $\text{NH}_4\text{SCN} + \text{NH}_3$ at 25° C

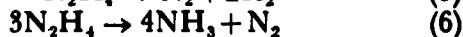
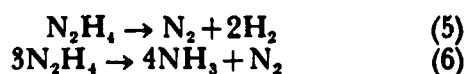
Catalyst	Composition	Geometrical surface area of test electrodes: 2 cm ² Current, ma								
		0.2v			0.5v			0.7v		
		Without N_2H_4	With N_2H_4	Difference due to N_2H_4	Without N_2H_4	With N_2H_4	Difference due to N_2H_4	Without N_2H_4	With N_2H_4	Difference due to N_2H_4
Pt, bright		- 0.1	0.3	0.4	0.1	25	25	0.3	100	100
Pt- black, 5 pct on C.		-35.0	-35.0		55.0	65	10	30.0	110	80
54NC	Nitrocarbided 3Ni-1Au	-25.0	50.0	75.0	100.0	210	110	170.0	320	?
53NC	Nitrocarbided 1Ni-3Au	0	25.0	25.0	40.0	115	75	80.0	200	120
2NC	α - $\text{Fe}_2\text{X}(\text{C,N})$, ϵ - Fe_2X - $\text{Fe}_2\text{X}(\text{C,N})$	-30.0	5.0	35.0	75.0	125	50	75.0	190	115
44NC	Nitrocarbided 1Ni- 1Ag-1Au	-15.0	-15.0		35.0	40	5	15.0	40	25
56NC	Nitrocarbided 1Ni-4Cr	- 4.0	-15.0		7.0	12	5	3.0	8	5
51NC	Nitrocarbided 1Ni-3Ag	-50.0	-50.0		20.0	20		75.0	75	
1N	ϵ - Fe_2N - Fe_2N , γ '- Fe_2N	0	30.0	30.0	50.0	110	60	80.0	170	90
11C	α - Fe_2C	- 5.0	-15.0		15.0	40	25	10.0	90	80
59C	Co_2C	-60.0	-20.0	40.0	60.0	100	40	90.0	160	70
74C	Carbided 3Ni-1Au	5.0	5.0		50.0	70	20	50.0	100	50
76C	Carbided 1Ni-3Au	-10.0	-10.0		45.0	45		50.0	80	30
78C	Carbided 1Ni-4Cr	-40.0	-60.0		80	90	10	25.0	35	10
60C	Carbided 1Ni-1Ag-1Au	-50.0	-25.0	25.0	60	40		30.0	30	
54C	Ni_2C	-20.0	- 5.0	15.0	34	20		25.0	25	
61C	Carbided 3Ni-1Co	-30.0	-30.0		50	40		75.0	50	
67C	Carbided 1Ni-3Ag	-10.0	-10.0		60	50		50.0	50	
77R	Reduced 1Ni-1Au	-40.0	-40.0		30	30		60.0	60	
78R	Reduced 1Ni-4Cr	-16.0	-36.0		44	44		40.0	40	
74R	Reduced 3Ni-1Au	10.0	10.0		60	60		50.0	50	
54R	Reduced 3Ni-1Ag	-60.0	-60.0		80	70		40.0	40	
67R	Reduced 1Ni-3Ag	0	0		40	40		75.0	75	
B18	Coprecipitated boride of 1Ni-1Co.	-20	-20.0		16	16		25.0	25	

12M KOH containing N_2H_4 at room temperatures. In addition, the kinetics of the decomposition of N_2H_4 by the catalytic action of these materials were investigated in 9M KOH at 60° C. We shall consider the results of the kinetic studies first.

Samples of the catalysts (0.1g) were brushed into test tubes containing 25 ml of deaerated 9M KOH inside a dry box filled with N_2 . The test tubes were then removed from the dry box, thermostated at 60° C, and charged with 1 ml of 60 pct N_2H_4 . The rate of decomposition of N_2H_4 was followed by iodometric titration of 0.5-ml samples of the reaction mixture at appropriate intervals. The results are presented in figure 29. The residual concentration of N_2H_4 in the reaction mixture has been plotted against time for each of the catalysts. Comparable results for a sample of Pt-black are also included. The interstitial compounds decomposed N_2H_4 more readily than did Pt-black. The decomposition of N_2H_4 by Pt-black was preceded by a long period of induction whereas only 6CN from amongst the interstitial compounds required an induction period. 14C and 12C were by far the most active catalysts—several times more active than Pt-black. 9CN, 5CN, 11C, 2NC, 3CN, and 1N also

were more active than Pt-black and did not require any induction period. The slopes of 18N, 1NC, 17N, 10N, and 6CN are comparable to the slope of Pt-black, but the first five interstitial compounds did not require induction period. A blank run gave a negligible rate of decomposition for N_2H_4 over the test period.

Not considering complicated mechanisms, the decomposition of N_2H_4 may be represented by either of the following two simple equations:



Equation 5 points to a first order rate constant for the decomposition of N_2H_4 , whereas equation 6 points to a third-order rate constant for the reaction. Both first and third order rate constants were calculated from the data presented in figure 29. The rate constants for the reaction with the four most active catalysts, namely 14C, 12C, 9CN, and 5CN, are presented in table 27. The constancy of the first order rate constants indicates that N_2H_4 decomposes according to equation 5 in the presence of these catalysts. The results of similar calculations from the data obtained with less active catalysts were not conclusive.

There is, however, a serious reservation to the foregoing conclusion derived from the rate constant calculations. Equation 5 does not provide for evolution of NH_3 , but the decomposition products had a strong smell of NH_3 in all experiments. Equation 5 is undoubtedly an oversimplified representation of the reaction.

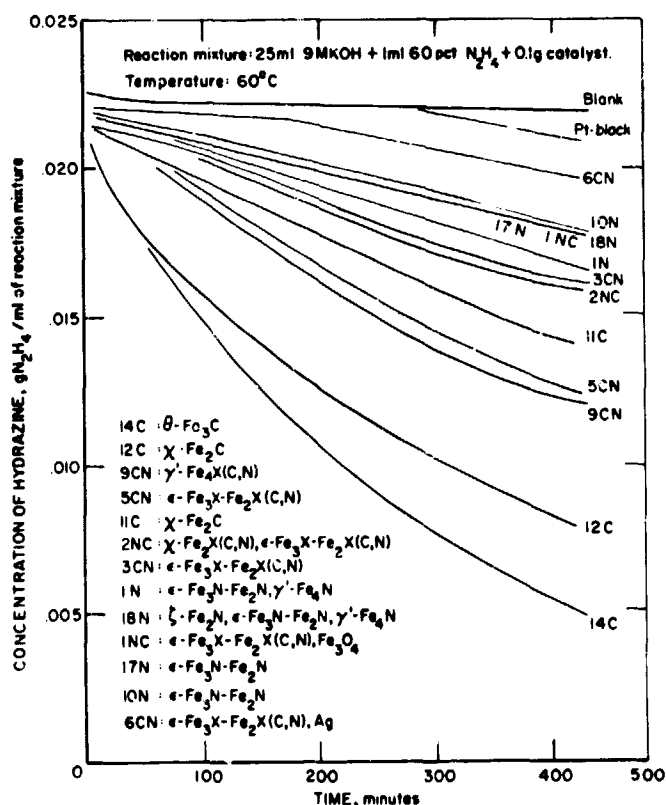


Figure 29.—Catalytic decomposition of hydrazine.

Table 27.—Calculated rate constants for the catalytic decomposition of N_2H_4 .

Reaction rate constants		Time intervals from start of test, minutes
1st order	3d order	
	14C	
3.9×10^{-3}	10.8	2 to 68.
3.5×10^{-3}	18.4	68 to 171.
3.3×10^{-3}	37.8	171 to 297.
3.1×10^{-3}	81.8	297 to 429.
	12C	
2.9×10^{-3}	8.3	2 to 78.
2.3×10^{-3}	12.6	78 to 267.
2.1×10^{-3}	23.8	267 to 422.
	9CN	
1.2×10^{-3}	2.8	2 to 89.
1.6×10^{-3}	5.8	89 to 278.
1.1×10^{-3}	6.1	278 to 434.
	5CN	
1.3×10^{-3}	3.0	2 to 83.
1.4×10^{-3}	4.6	83 to 273.
1.3×10^{-3}	6.7	273 to 428.

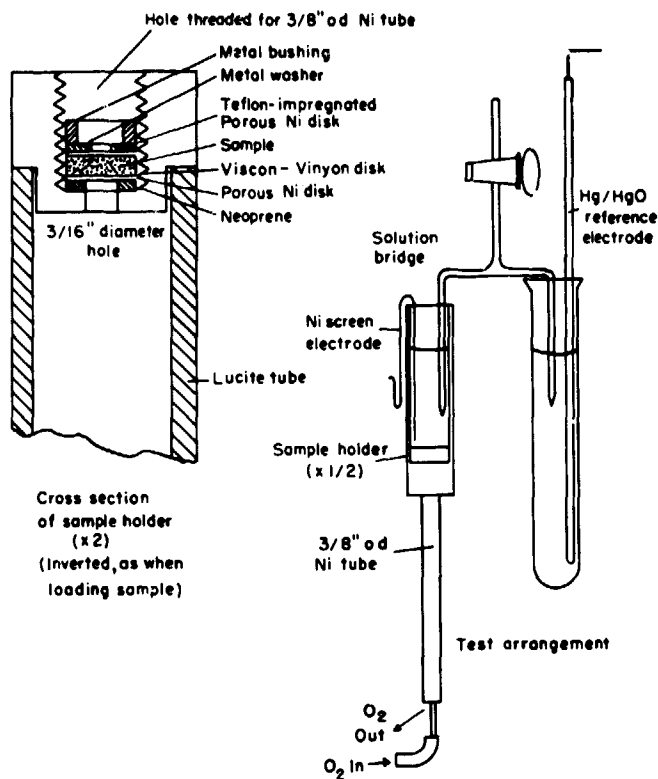


Figure 30.—Test cell

Reduction of O_2 in 12M KOH Containing N_2H_4

Cathodic activity of the interstitial compounds in the reduction of O_2 in 12M KOH containing N_2H_4 was tested galvanostatically in the apparatus shown in figure 30. Two series of tests were conducted: (1) electrodes were prepared from the materials as received; (2) electrodes were prepared from homogenized and induced materials. The former group of electrodes was prepared by mixing 0.1 g of each catalyst with an equal weight of a graphite powder that had previously been wetproofed with a paraffin solution, and packing the mixture in the sample holder shown in figure 30. The weighing, mixing, and packing operations were conducted in a dry box filled with N_2 , and the electrode was covered with 10 ml of 12M KOH containing 0.2 ml of 60 pct N_2H_4 , before removal from the dry box.

For preparing the latter group of electrodes, the interstitial compounds were first ground and sieved to 325 mesh in the N_2 -filled dry box and covered with petroleum ether. They were then brought out in the open and induced²⁸ with diethyl ether, acetone, and ethanol—in that

²⁸ The principles and practice of induction are discussed in the section "Reduction of O_2 in Aqueous KOH (Tyco Laboratories, Inc., Walham, Mass.)."

order. Samples of the induced materials of 0.1g 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. The electrolyte was the same as before.

All polarization measurements were made with a Kordes-Marko bridge. A Hg/HgO electrode served as the reference electrode.

The electrodes prepared from as received materials were tested by polarization at 10 amperes per square foot (ASF) against an inert Ni screen

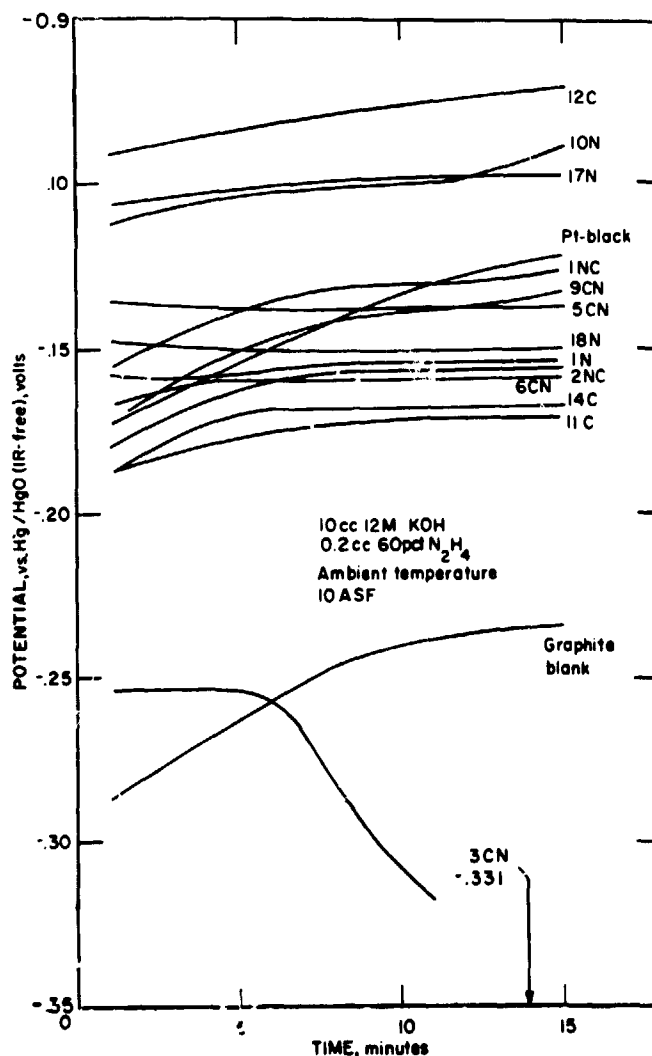


Figure 31.—Cathodic activity of "as received" materials in the reduction of O_2 in 12M KOH containing N_2H_4 .

for 15 minutes, the results are presented in figure 31. The performance of 12C, 10N, and 17N was superior to that of a sample of Pt-black tested under comparable conditions. However, when samples were tested in duplicate, reproducibility was poor.

The electrodes prepared from homogenized and induced materials were tested by polarization, first at 10 ASF for 15 minutes, then at 20, 30, and 40 ASF for 5 minute periods, and finally again at 10 ASF for 5 minutes. Duplicate experiments gave reproducible results. The average values of the potentials are plotted against the apparent current densities in figure 32. 17N, 3CN, and 1NC are about as active as Pt-black.

The homogenized and induced materials were undoubtedly more uniform, and gave reproducible results. However, the relative activity of the materials in figures 31 and 32 are very different. Several catalysts suffered partial loss of activity in homogenization and induction. Further investigation of processing methods may be fruitful.

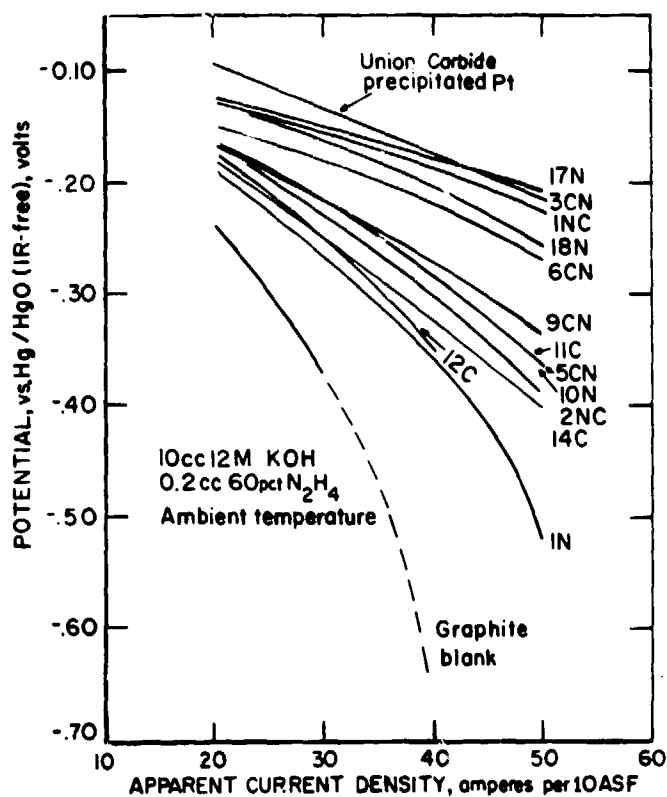


Figure 32.—Cathodic activity of homogenized, induced materials in the reduction of O_2 in 12M KOH containing N_2H_4 .

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CONCLUSIONS

The following groups of materials were prepared and tested for activity as fuel cell catalysts:

- (1) Carbides of Fe, Co, and Ni and their binary and ternary mixtures.
- (2) Binary and ternary mixtures of the carbides of Fe, Co, and Ni with Ag, Au, Pd, and Pt.
- (3) Nitrides of Fe.
- (4) Binary mixtures of nitrides of Fe with Ag.
- (5) Nitrocarbides from the carbides prepared in (1) and (2).
- (6) Carbonitrides from the nitrides prepared in (3) and (4).
- (7) Borides of Ni and Co and their mixtures.
- (8) Binary mixtures of nickel boride with Au, Pd, and Pt.
- (9) Binary and ternary mixtures of reduced Fe, Co, Ni, Ag, Au, Pd, and Pt.

By cooperative arrangement with other laboratories engaged in fuel cell work, the preparations were tested for electrocatalytic activity in the following systems:

(1) Reduction of O_2 in 35 pct KOH at 75° C (Tyco Laboratories, Inc.). Reduced metals were generally more active than their interstitial compounds. However, the two most active materials were samples of carbided and nitrocarbided 1Ni-1Ag-1Au. They were each about one-fifth as active as Pt-black. Corrosion was a serious problem; most of the materials gave large corrosion currents, and the preparations containing Fe or Co disintegrated visibly in the electrolyte. None of the materials held out promise as a practical fuel cell catalyst.

(2) Oxidation of H_2 in 35 pct KOH at 90° C (Allis Chalmers, Research Division). Although electrolyte was the same as in the preceding system, the materials appeared to be less susceptible to corrosion as anode catalysts than as cathode catalysts. Screening for anodic activity by half-cell technique revealed about half a dozen materials of good activity. These were then tested as anodes in a mini H_2 - O_2 fuel cell. Although not as active as Pt-black, samples of reduced and carbided 3Ni-1Ag gave very good performance.

(3) Oxidation of H_2 and C_3H_8 in aqueous 1.52M K_2CO_3 + 1.52M $KHCO_3$ at 80° C (Ameri-

can Oil Co.). Preparations were first tested qualitatively for stability in the electrolyte. This was done visually by noting evolution of gases and changes in the appearance of the solution. The materials suffering visibly severe corrosion were rejected from further consideration. The relatively stable materials were tested for anodic activity with H_2 and C_3H_8 in a half cell and the corrosion currents from them were measured in argon. Although a total of eight materials were found to catalyze the oxidation of H_2 , seven of them gave large corrosion currents. Only one material, a nitrocarbide of Ni, appeared to hold promise as a practical catalyst.

None of the materials catalyzed the oxidation of C_3H_8 .

(4) Oxidation of NH_3 and CO in alkaline and acidic electrolytes (Catalyst Research Corp.). Oxidation of NH_3 was studied in 30-percent KOH and saturated K_2CO_3 at 25° C. Exchange current and Tafel slope were computed for each catalyst from the current-potential data, and the effective surface area of each electrode was determined by a double layer capacitance method. For purposes of comparison, activity of catalysts was computed both in terms of the exchange current per unit weight of the catalytic material in electrodes, and the exchange current per unit of the effective area of the electrodes. The former is a measure of catalyst utilization while the latter represents the intrinsic activity of a heterogeneous catalyst. Compared to catalyst utilization of Pt-black, the catalyst utilization of the interstitial compounds was very low, but the intrinsic activity of a number of the interstitial compounds was surprisingly high. The values of Tafel slope indicated that dissociative adsorption of NH_3 on the interstitial compounds was the rate determining step in the oxidation of NH_3 in 30 pct KOH. The corresponding data for the oxidation of NH_3 in saturated K_2CO_3 were inconclusive.

Oxidation of CO was studied in 2N H_2SO_4 , an acetate buffer of pH 3, saturated K_2CO_3 , and 85 pct H_3PO_4 . The half-cell potentials indicated that CO oxidizes by at least two different reactions: in 2N H_2SO_4 and the acetate buffer by one reaction, and in 85 pct H_3PO_4 by another reaction. The data for half-cell potentials

in saturated K_2CO_3 were too scattered for a conclusion. As for the catalytic efficiency of the interstitial compounds, once again their utilization was poor but the intrinsic activity of several materials was higher than that of Pt-black. To secure better catalyst utilization, two interstitial compounds of high intrinsic activity were crushed to a finer state of subdivision and retested in the oxidation of CO. Their utilization improved, but their intrinsic activity deteriorated. Evidently, the surface exposed by crushing was less active than the original surface.

(5) Reduction of O_2 in $3.7M$ H_2SO_4 , buffered carbonate of pH 10.2, buffered phosphate of pH 7, and molten H_3PO_4 . (Esso Research and Engineering Co.). Only one interstitial preparation, a sample of carbided 1Ni-1Ag, was stable in $3.7M$ H_2SO_4 for electrochemical investigation. In the buffered carbonate and phosphate solutions and in molten H_3PO_4 , corrosion of the interstitial compounds was less widespread but still a serious problem. Samples of γ - Fe_2C , carbided 3Ni-1Au, and carbided 1Ni-1Au were good catalysts for the reduction of O_2 in the carbonate buffer. However, each of them gave large corrosion current. No catalyst of any promise for the reduction of O_2 in $3.7M$ H_2SO_4 , phosphate buffer of pH 7, or 84 pct H_3PO_4 was discovered.

(6) Oxidation of H_2 and reduction of O_2 in $3N$ H_2SO_4 (General Electric Co.) Only two interstitial preparations, carbided 1Ni-3Au and carbided 1Ni-4Cr, were stable in $3N$ H_2SO_4 . Neither of them showed promise as practical fuel cell catalysts for the oxidation of H_2 or the reduction of O_2 in that electrolyte.

(7) Interstitial compounds as cathodes in ammonia battery (Harry Diamond Laboratory of the Department of Army and Tracor, Inc.) This part of the program was concerned with the development of ammonia battery for fuse power supply. The electrolyte consisted of a

saturated solution of *m*-dinitrobenzene in 25.1 pct NH_3 + 57.65 pct CH_3OH + 17.25 pct NH_4SCN . Several interstitial compounds gave good cathodic performance. However, the reduction products of *m*-dinitrobenzene tended to stay adsorbed on the cathode and their reoxidation produced a counter emf.

(8) (a) Oxidation of N_2H_4 in $5M$ KOH.

(b) Oxidation of dextrose in a solution containing $0.5M$ NaCl, $1M$ phosphate buffer of pH 7.4, and $0.5M$ dextrose (Monsanto Research Corp.) Most interstitial compounds decomposed N_2H_4 readily and suffered little polarization at current densities of 100 ma/cm² in $5M$ KOH. However, almost all the materials were found to corrode severely in the electrolyte.

No interstitial preparation showed any activity in the oxidation of dextrose.

(9) Oxidation of N_2H_4 in acid liquid ammonia (Naval Weapons Center, Corona Laboratory.) Three interstitial preparations, χ - Fe_2X (C,N), nitrocarbided 3Ni-1Au, and nitrocarbided 1Ni-3Au, were good catalysts for oxidizing N_2H_4 in a solution of NH_4SCN in liquid NH_3 at 25° C. Carbides, on the whole, were less active than nitrocarbides, and reduced metals were inactive.

(10) Reduction of O_2 in KOH containing N_2H_4 . (Union Carbide Corp.) Preliminary to electrochemical investigation, the kinetics of the decomposition of N_2H_4 by interstitial compounds were studied in $9M$ KOH. The interstitial compounds decomposed N_2H_4 more readily than did Pt-black, and give first order rate constants.

The electrochemical activity of several interstitial compounds in the reduction of O_2 in $12M$ KOH containing N_2H_4 compared very favorably with the activity of Pt-black. However, the results often could not be duplicated. Reproducibility of the results improved when the catalysts were homogenized and inducted before fabricating electrodes, but most materials suffered partial loss of activity by the pretreatment.

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