

TEST EVALUATION OF FUEL CELL CATALYSTS

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I. SUMMARY

During the third quarter of the contract, the third group of compounds supplied by the U. S. Bureau of Mines was tested for catalytic activity in the oxidation of N_2H_4 . All compounds showed relatively high activities for the reaction. Among the catalysts, a group of borides was significantly more active than the others, reduced metals, alloys and their carbides and nitrocarbides. However, all compounds showed severe corrosion in 5M KOH solution, and less, but apparent, corrosion in 5M KOH added with 2M N_2H_4 .

II. INTRODUCTION

The objective of this contract is to determine certain essential properties of non-noble metal compounds as electrode catalysts for fuel cells. Properties of major interest include: polarization characteristics of the electrodes containing these compounds; and the chemical stability of these electrodes in prescribed test environments.

The work originally undertaken at Monsanto Research Corporation is to investigate the electrocatalytic activity of the compounds for oxidation of dextrose and hydrazine. However, tests for dextrose oxidation were waived after the first quarter, because of the relatively poor chemical stability of these compounds in the specific testing environment for the dextrose oxidation. Since the dextrose electrode is to be used in an implantable fuel cell for an artificial heart, even the slightest contamination of the electrolyte system is not permissible.

During the first two quarters, interstitial compounds of iron, namely, carbide, nitride, carbonitride and nitrocarbide leached Raney alloys of Ni, Co and Ag, and their carbides and nitrocarbides were tested for N_2H_4 oxidation, although the majority of these compounds were badly corroded in 5M KOH electrolyte and less, but still significantly attacked by KOH solution with N_2H_4 .

During this quarter, the third batch of catalysts prepared by the U. S. Bureau of Mines was examined. These catalysts were Ni, Co and their alloys prepared from various compounds by reduction and the Ni and Co carbides, nitrocarbides and borides, shown in Table 1.

Table 1

SAMPLE NUMBERS FOR CATALYSTS TESTED DURING THE THIRD QUARTER

<u>Ni</u>	<u>Reduced</u>	<u>Carbide</u>	<u>Nitrocarbide</u>
prepared from the formate	54R	54C	39NC
prepared from the hydroxide	56R	56C	41NC
<u>Co</u>			
prepared from the hydroxide	59R	59C	43NC
<u>3Ni:1Co</u>			
prepared from the hydroxides	61R	61C	45NC
prepared from the nickel formate, cobalt acetate		58C	36NC
<u>1Ni:1Ag</u>			
prepared from the hydroxides	53R	53C	38NC
<u>1Ni:1Ag:1Au</u>			
prepared from the hydroxides		60C	44NC

Borides

(prepared from the reaction of NaBH_4 and the sulfate of the transitional metals)

Ni	B-6
Co	B-7
1Ni:1Co	B-18
1Ni:3Co	B-20
3Ni:1Co	B-9

III. PREPARATION OF ELECTRODES

All catalysts were preconditioned according to the procedure described in the first quarterly report.

All catalysts were ground and sieved to -400 mesh in a chemically pure argon atmosphere prior to the final preconditioning process.

All electrodes prepared were type B*. These electrodes contain a network of macropores in a micro-porous matrix and are considered very suitable for the present study.

Catalyst loading was approximately 0.7 g/inch².

*The method for preparing this type electrode is Monsanto Research Proprietary.

IV. TEST RESULTS

A. CORROSION TESTING

Weighed samples (about 0.5 gram each) were soaked overnight in 50 cc of 5M KOH in a constant temperature bath at 70°C. All catalysts showed corrosion, as indicated by significant discoloration of the test solution. Since formation of hydroxides was also obvious, no weight determination was made after the tests. Addition of N₂H₄ to the KOH solution did not stop the corrosion. The appearance of the various test solutions are shown in Table 2.

B. N₂H₄ ELECTRODE TESTING

Although the corrosion tests revealed that all catalysts in the third group were attacked in some degree by the test electrolyte (5M KOH + 2M N₂H₄), the polarization data for N₂H₄ oxidation was taken in the manner described in the previous report.

IR free electrode potentials vs the saturated calomel electrode at various current densities above 10 mA/cm² (apparent densities) are given in Table 3.

Results indicate that the electrode potentials of these catalysts are more active even at 100 mA/cm² than that of the reversible hydrogen electrode in the same electrolyte. Among the catalysts, a group of borides are significantly more active than the others. The very strong odor of NH₃ was detected in exhaust gas only from the electrodes made of the borides.

Table 2

CORROSION TESTS

Testing Solution: 5M KOH at 70°C

<u>Sample No.</u>	<u>Appearance</u>
54R	blue color
54C	blue color
39NC	green color
56R	brown color and deposit
56C	brown color and deposit
41NC	brown color and deposit
59R	blue color and brownish deposit
59C	brownish color and deposit
43NC	brownish color and deposit
61R	blue color
61C	blue color
45NC	brown color and deposit
58C	brown color and deposit
36NC	brown color and deposit
53R	blue color
53C	blue color
38NC	brown color and deposit
60C	brown color and deposit
44NC	green color
B-6	blue color
B-7	blue color
B-18	brown color and deposit
B-20	blue color
B-9	blue color

Table 3

N₂H₄ ELECTRODE TESTING -
ELECTRODE POTENTIAL VS. THE SATURATED CALOMEL ELECTRODE

Catalyst	Current Density, mA/cm ²						Remarks
	OCF	10	20	50	100		
54R	-1.17	-1.17	-1.17	-1.17	-1.16	-1.16	Electrolyte colored blue. Electrode disintegrated.
54C	-1.24	-1.24	-1.22	-1.22	-1.21	-1.21	
39NC	-1.15	-1.15	-1.15	-1.15	-1.12	-1.12	
56R	-1.20	-1.20	-1.20	-1.20	-1.20	-1.20	Electrode disintegrated.
56C	-1.22	-1.22	-1.22	-1.22	-1.20	-1.20	
41NC	-1.20	-1.20	-1.18	-1.18	-1.18	-1.18	
59R	-1.25	-1.25	-1.25	-1.25	-1.25	-1.25	
59C	-1.25	-1.25	-1.21	-1.21	-1.21	-1.21	
43NC	-1.16	-1.15	-1.15	-1.15	-1.15	-1.15	Electrode disintegrated.
61R	-1.22	-1.22	-1.22	-1.21	-1.20	-1.20	
61C	-1.22	-1.22	-1.21	-1.21	-1.20	-1.20	
45NC	-1.17	-1.17	-1.17	-1.17	-1.17	-1.17	
58C	-1.20	-1.20	-1.20	-1.19	-1.18	-1.18	Electrode disintegrated.
36NC	-1.18	-1.18	-1.18	-1.18	-1.18	-1.18	Electrode disintegrated.
53R	-1.20	-1.20	-1.20	-1.20	-1.17	-1.17	
53C	-1.21	-1.20	-1.20	-1.20	-1.20	-1.20	
38NC	-1.20	-1.20	-1.20	-1.20	-1.18	-1.18	Electrode disintegrated.
60C	-1.21	-1.20	-1.20	-1.19	-1.18	-1.18	
44NC	-1.18	-1.17	-1.16	-1.16	-1.16	-1.16	Electrode disintegrated.
B-6	-1.25	-1.25	-1.25	-1.25	-1.24	-1.24	
B-7	-1.29	-1.28	-1.28	-1.28	-1.28	-1.28	Strong NH ₃ odor.
B-18	-1.26	-1.26	-1.26	-1.26	-1.26	-1.26	Strong NH ₃ odor.
B-20	-1.28	-1.28	-1.28	-1.28	-1.28	-1.28	Strong NH ₃ odor.
B-9	-1.26	-1.26	-1.26	-1.26	-1.26	-1.26	

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