CR

CATALYST RESEARCH CORPORATION

TEST EVALUATION OF FUEL CELL CATALYSTS

by

H. J. Goldsmith
J. R. Moser
T. Webb

Final Report

February 15, 1968

Contract NASW-1577

National Aeronautics and Space Administration
NASA Headquarters, Washington, D. C. 20546

TABLE OF CONTENTS

TABLE OF CONTENTS

LIST OF TABLES

SUMMARY

The objective of this work was to test materials prepared by the Pittsburgh Coal Research Center for NASA as anodic catalysts for ammonia in alkaline electrolytes and carbon monoxide in acidic and aqueons carbonate fuel cell electrolytes.

A total of fifty-four samples consisting of carbides, nitrides, borides, nitrocarbides, carbonitrides and Raney alloys of iron, cobalt, and nickel were tested. Corrosion potentials were run to determine usable electrolyte and catalyst combinations. Surface areas measured by double layer capacitance ranged from 27.1 Cm^2/gm to 117,000 Cm^2/gm. In general the areas were found to be: carbides > nitrocarbides > metals > borides and for the metallic moiety: silver > nickel $\cong$ cobalt >> iron.

Voltammograms at 25°C under approximately steady-state conditions were run in electrolytes compatible with the materials. Results showed the best materials were less than 2% of the activity obtainable with platinum for the same fuel. When ammonia was the fuel, activity followed the trend: carbides $\cong$ nitrocarbides >> metals and nickel >> cobalt $\cong$ silver >> iron. Carbon monoxide activity was generally nitrocarbides >> metals > carbides > borides with silver > nickel > cobalt > iron. With only one exception the sixteen best materials of the twenty-nine tested in acetate buffer contained nickel.

This work was carried out for the National Aeronautics and Space Administration with Mr. E. M. Cohn as Technical Monitor. Principal investigators were T. Webb and J. R. Moser.

I. INTRODUCTION

The high cost and scarcity of the noble metals prompted a search for cheaper, more abundant fuel cell catalysts. Initial results with Hagg carbide (Fe_2C) indicated that iron group interstitial carbides might be the answer. Consequently, a total of fifty-four carbides, nitrides, nitrocarbides, carbonitrides, borides and Raney alloys synthesized by Bureau of Mines were tested in this laboratory. Nineteen iron compounds including four carbides, six nitrides, five carbonitrides and four nitrocarbides were tested for corrosion at 25°C in 30% KOH, saturated K_2CO_3, acetate buffer, 2N H_2SO_4 and 85% H_3PO_4. Thirty-five cobalt and nickel materials consisting of nine metallic alloys, eleven carbides, ten nitrocarbides, and five borides were tested for corrosion at 25°C in 30% KOH, acetate buffer and 2N H_2SO_4. The surface area of each material was determined by double layer capacitance measurements (1).

Compatible catalyst-electrolyte combinations were further tested for anodic activity toward the oxidation of either ammonia or carbon monoxide. Equipment, testing procedures, treatment of catalysts and floating electrode preparation have all been previously described (2-4). All materials were tested during the first three quarters of this contract. No additional materials were received during the fourth quarter.

II. RESULTS

Surface area measurements and the identity of each material tested are given in Table I. Voltammetric data for the oxidation of ammonia are shown in Tables II and III. Results for carbon monoxide oxidation are listed in Tables IV through VII.

III. DISCUSSION

III.-1 Surface Areas

Double layer capacitance measurements on the 54 materials tested gave values for surface areas from 27.1 Cm^2/gm to 117,000 Cm^2/gm. Our platinum black measured was 210,000 Cm^2/gm.

As a group, the iron compounds exhibited the lowest area. The remaining materials which contained silver generally showed the largest areas. Surface areas according to type of non-ferrous material were usually in the order carbides> nitrocarbides> metals> borides.

III.-2 Ammonia Oxidation

Voltammograms for the oxidation of ammonia were run in 30% KOH for all materials stable in that electrolyte. Additionally the iron compounds which were stable in saturated K_2CO_3 were tested in that electrolyte.

In 30% KOH the half-cell potential for the reaction was between 0.54 and 0.58 V vs DHF for most catalysts. This corresponds to the calculated value. Five of those tested, however, had lower half-cell potentials; one was higher. All six of these anomalies were due to corrosion of the electrode upon addition of ammonia. This was evidenced by the discolored electrolyte accompanying high exchange currents. The tafel slope for the oxidation with platinum is 0.04 volt while that for most of the other materials is around 0.12 volt. This may be explained by the mechanism of Owen and Salomon (5) who calculated Tafel slopes for the four steps in the reaction:

III. DISCUSSION (Cont'd)

			Calculated Tafel Slope
(i)	$NH_3 + M + OH^- \rightarrow$	$M\text{-}NH_2 + H_2O + e^-$	0.118 volt
(ii)	$M\text{-}NH_2$ to $H^- \rightarrow$	$M{=}NH + H_2O + e^-$	0.039 volt
(iii)	$M{=}NH + OH^- \rightarrow$	$M{=}N + H_2O + e^-$	0.024 volt
(iv)	$2\ M{=}N \rightarrow$	$2M + N_2$	0.010 volt or ∞

Reaction (ii) is the rate determining step for platinum but reaction (i), the initial dissociative adsorption, seems to be the rate determining step for the other materials.

When saturated potassium carbonate was the electrolyte much lower currents, high Tafel slopes and variable half-cell potentials were obtained. These results were not readily interpreted. This electrolyte was abandoned after the first group of materials was tested.

In general for the oxidation of ammonia all of the materials tested were greatly inferior to platinum. However, those interstitial compounds containing carbon and/or nitrogen were much better catalysts than the pure metals or alloys. The order found for the catalysts activity of metallic constituents was Nickel >> Cobalt $\cong$ Silver >> Iron.

III. DISCUSSION (Cont'd)

III.-3 Carbon Monoxide Oxidation

Four electrolytes were used in this study. Currents were very low in 85% H_3PO_4 and saturated K_2CO_3; consequently, these systems were abandoned after the first group of materials was tested. The maximum current was obtained with platinum in $2\underline{N}$ H_2SO_4. All other materials gave currents less than 2% of this value.

The oxidation reaction mechanism for carbon monoxide has not been well established. It is known that for platinum a reaction occurs around 0.26 volt versus DHE during which the electrode is poisoned by a reaction product. The major reaction occurs around 0.96 volt vs DHE where the product is carbon dioxide. For most of the catalysts tested the first reaction is predominant in 85% H_3PO_4 and acetate buffer while the second reaction is the major one in $2\underline{N}$ H_2SO_4. In K_2CO_3 the potentials are well scattered. Three Tafel slopes were observed in the acidic electrolytes: 0.040, 0.080 and 0.140 volt. However, the second was absent in H_3PO_4 while the third was absent in H_2SO_4. The overall reactions seem to be:

$$\text{(v)} \qquad M + CO + OH^- \rightarrow MCO_2H + e^-$$

$$\text{(vi)} \qquad MCO_2H + OH^-_{dl} \rightarrow M + CO_2 + H_2O + e^-$$

$$\text{(vii)} \qquad CO_{ad} + 2OH^-_{dl} \rightarrow CO_2 + H_2O + 2e^-$$

III. DISCUSSION (Cont'd)

III.-3 Carbon Monoxide Oxidation (Cont'd)

The nitrocarbides were much better catalysts than the pure metals or alloys while lowest in activity were the carbides and finally the borides.

The trend in catalytic activity was Silver > Nickel > Cobalt > Iron. Silver is known to strongly adsorb hydroxy ions; unoxidized nickel forms a carbonyl at room temperature -- nickel must catalyze reaction (v) since in acetate buffer with only one exception the sixteen best materials of the twenty-nine tested contained nickel. Two containing nickel and silver were actually better than platinum in this electrolyte although much lower than platinum in 2N H_2SO_4.

IV. CONCLUSIONS

The catalytic activity of all the materials tested was greatly inferior to the best results that could be obtained with platinum. For ammonia and carbon monoxide oxidation none of these proved to be a good platinum substitute. The results indicate that catalytic activity was limited by failure of these materials to adsorb the fuels. The reason is in some cases undoubtedly due to the presence of surface oxide (passivation) which also prevents corrosion of the metal by the electrolyte.

V. RECOMMENDATIONS

Since all of these materials were originally prepared for possible use as oxygen electrodes in alkaline electrolytes it would be fortuitous if any were found to be suitable as anodes in acid solutions. A thorough understanding of the fuel cell reaction mechanisms would be an extremely desirable asset in selecting potential catalysts. With this knowledge and a systematic approach as used by Bond (6), it should be possible to arrive at the optimum catalyst for a particular reaction under a fixed set of conditions.

VI. REFERENCES

(1) McCallum, J. R., R. W. Hardy and R. F. Redmond, "Measurement of True Surface Area in Electrodes" Technical Report APAPL-TR-66-31 Battelle Memorial Institute, Columbus, Ohio, 1966.

(2) Goldsmith, H. J., J. R. Moser and T. Webb "Test Evaluation of Fuel Cell Catalysts", Quarterly Report Q-1 May 15, 1967, Contract NASW-1577 Catalyst Research Corporation, Baltimore, Maryland 21209.

(3) Ibid. Q-2 August 15, 1967.

(4) Ibid. Q-3 November 15, 1967.

(5) Oswin, H. G. and M. Salomon, "The Anodic Oxidation of Ammonia at Platinum Black Electrodes in Aqueous KOH Electrolyte", Conad, J. Chem. 41 1686 (1963).

(6) Bond, G. C., "Catalysis by Metals" New York: Academic Press (1962).

TABLE I

Surface Areas (cm^2/gm)

		Raney Metals			
RC-1	Cobalt	5,300	RAL-9	3Co/1Ni	3,090
RN-2	Nickel	5,300	RAL-10	1Ni/1Co/1Ag	6,200
RAL-6	3Ni/1Ag	26,900	RAL-11	1Ni/1Co/1Au	9,700
RAL-8	1Co/1Ag	69,800			
		Reduced Hydroxides			
53R	1Ni/1Ag	32,500	61R	3Ni/1Co	121
		Carbides			
10C	θ-Fe_3C, α-Fe	33.5	39C	1Co/1Ag	20,200
12C	ϵ-Fe_2C, α-Fe	32.9	42C	1Ni/1Co	10,400
15C	θ-Fe_3C	30.0	43C	1Ni/1Ag	13,650
23C	ϵ-Fe_2C, α-Fe	27.1	46C	3Ni/1Ag	4,050
27C	3Ni/1Co	7,060	53C	1Ni/1Ag	1,870
29C	1Ni/3Ag	117,000	60C	1Ni/1Ag/1Au	3,000
33C	Cobalt	4,920	61C	3Ni/1Co	403
35C	Nickel	54,400			
		Carbonitrides			
1CN	ϵ-Fe_2X	46.0	7CN	ϵ-Fe_2X, Ag	90.4
4CN	ϵ-Fe_2X	156	8CN	ϵ-Fe_2X, 3Ag	83.8
5CN	ϵ-Fe_2X	54.2			
		Nitrides			
1N	ϵ-Fe_2N, γ-Fe_4N	51.0	19N	ζ-Fe_2N, -Fe_3N	33.8
10N	ϵ-Fe_3N	27.1	20N	ϵ-Fe_3N	72.0
18N	ζ-Fe_2N, ϵ-Fe_3N	82.6	21N	γ-Fe_4N, -Fe_3N	74.0
		Nitrocarbides			
1NC	ϵ-Fe_2X, Fe_3O_4	97.5	23NC	Nickel	19,800
2NC	χ-Fe_2X, ϵ-Fe_2X	85.6	26NC	1Co/1Ag	45,500
3NC	ϵ-Fe_2X	103	28NC	1Ni/1Co	29,200
4NC	ϵ-Fe_2X	27.6	32NC	3Ni/1Ag	78,400
15NC	3Ni/1Co	6,900	38NC	1Ni/1Ag	37,400
21NC	Cobalt	2,700	44NC	1Ni/1Ag/1Au	48,000
22NC	3Co/1Ag	36,300	45NC	3Ni/1Co	4,900
		Borides			
B6	Nickel	565	B18	1Ni/3Co	6,900
B7	Cobalt	700	B20	3Ni/1Co	2,650
B9	1Ni/1Co	1,100			

X = (C, N)

TABLE II

Activity of Materials Toward NH_3 Oxidation in 30% KOH at 25°C

	io ma/gm	Tafel Slope Volt	E_r Volt		io Ma/gm	Tafel Slope Volt	E_r Volt
Pt	883	0.04	0.58	RAL-6	1.78	0.14	0.54
33C*	106	0.04	0.22	20N	1.66	0.13	0.56
43C*	60.1	0.08	0.68	RAL-8	1.57	0.13	0.54
46C*	42.4	0.08	0.24	RN-2	1.42	0.12	0.54
28NC*	28.3	0.10	0.32	1NC	1.37	0.12	0.54
27C*	14.1	0.12	0.26	RC-1	1.35	0.12	0.54
12C	3.54	0.17	0.55	RAL-11	1.28	0.14	0.54
15NC	3.53	0.23	0.56	5CN	1.13	0.26	0.55
B6*	3.50	0.03	0.33	RAL-9	1.07	0.13	0.54
21N	3.15	0.12	0.56	4CN	0.99	0.11	0.56
61C	2.80	0.11	0.54	RAL-10	0.71	0.07	0.56
18N	2.47	0.12	0.56				

* Dissolves in NH_3

TABLE III

Activity of Materials Toward NH_3 Oxidation in Saturated K_2CO_3 at 25°C

	io ma/gm	Tafel Slope Volt	E_r Volt		io ma/gm	Tafel Slope Volt	E_r Volt
Pt	205	0.20	0.79	19N	1.20	0.26	0.09
1NC	2.40	0.56	0.16	4NC	0.885	0.85	0.13
2NC	1.87	0.27	0.20	21N	0.813	0.17	0.09
1N	1.66	0.70	0.12	5CN	0.777	1.40	0.20
1CN	1.55	0.36	0.17	12C	0.177	0.16	0.14
3NC	1.52	0.65	0.32				

TABLE IV

Activity of Materials Toward CO Oxidation in 85% H_3PO_4 at 25°C

	io ma/gm	Tafel Slope Volt	E_r Volt		io ma/gm	Tafel Slope Volt	E_r Volt
Pt	17.7	0.02	1.00	10C	0.254	0.49	0.04
2NC	1.59	0.11	0.23	15C	0.177	0.07	0.26
3NC	1.34	0.22	0.22	19N	0.177	0.11	0.25
10N	1.17	0.04	0.04	23C	0.152	0.14	0.26
21N	0.849	0.13	0.25	4NC	0.120	0.05	0.29
1N	0.814	0.49	0.98	12C	0.035	0.04	0.29
1CN	0.283	0.50	0.15				

TABLE V

Activity of Materials Toward CO Oxidation in 2 N H_2SO_4 at 25°C

	io ma/gm	Tafel Slope Volt	E_r Volt		io ma/gm	Tafel Slope Volt	E_r Volt
Pt	1.980	0.11	0.89	61C	3.5	0.04	0.05
1CN	36.4	2.20	0.50	B20	2.5	0.07	1.09
45NC	15.0	0.04	0.00	4NC	2.12	0.13	0.67
19N	12.7	0.22	0.96	RN-2	2.12	0.08	0.99
53C	8.8	0.07	0.42	60C	2.1	0.05	0.96
B9	5.7	0.15	1.09	12C	1.87	0.08	0.64
44NC	5.0	0.08	0.85	B7	1.8	0.07	1.02
10N	4.95	0.22	0.88	B18	1.4	0.03	1.07
10C	4.60	0.60	0.58	1NC	1.31	0.30	0.88
61R	4.2	0.10	0.03	B6	1.0	0.05	1.06
20N	3.71	0.49	0.92				

TABLE VI

Activity of Materials Toward CO Oxidation in Acetate Buffer at 25°C

	io ma/gm	Tafel Slope Volt	E_r Volt		io ma/gm	Tafel Slope Volt	E_r Volt
32NC	97.2	0.30	0.67	61R	2.8	0.54	0.46
RAL-10	95.4	0.25	0.58	60C	2.6	0.04	1.03
Pt	47.6	0.17	0.21	B7	2.0	0.05	1.02
RAL-11	25.4	0.70	0.48	18N	1.77	0.12	1.00
23NC	24.7	0.12	0.46	23C	1.76	0.09	0.36
43C	20.5	0.27	0.72	B6	1.2	0.08	1.06
B9	14.	0.02	0.42	1NC	1.13	0.18	0.98
10C	12.4	0.14	0.31	21N	1.13	0.16	1.03
35C	7.42	0.14	0.48	RC-1	1.13	0.12	1.06
46C	6.36	0.07	0.50	B18	1.1	0.07	1.03
61C	4.6	0.15	0.84	B20	0.88	0.04	1.04
RAL-9	4.24	0.16	0.73	4NC	0.85	0.18	1.04
RN-2	3.89	0.08	1.08	4CN	0.81	0.14	1.05
53C	3.5	0.03	0.48	12C	0.56	0.14	1.06
15NC	3.00	0.17	0.46	5CN	0.42	0.15	0.41

TABLE VII

Activity of Materials Toward CO Oxidation in Saturated K_2CO_3 at 25^oC

	io ma/gm	Tafel Slope Volt	Er Volt		io Ma/gm	Tafel Slope Volt	E_r Volt
Pt	40.7	0.04	0.63	1NC	0.233	0.90	0.30
21N	0.530	0.14	0.40	12C	0.223	0.20	0.40
2NC	0.282	0.11	0.40	19N	0.212	0.33	0.18
1N	0.257	0.29	0.23	4NC	0.191	0.45	0.52
1CN	0.247	0.17	0.30	3NC	0.141	0.13	0.48
5CN	0.247	0.90	0.19				

DISTRIBUTION

To:	No. of Copies
Chief, Solar and Chemical Power Systems - Code RNW NASA Headquarters Washington, D. C. 20546	8
Scientific and Technical Information Facilities P.O. Box 33 College Park, Maryland Attention: NASA Representative	1 (reproducible)
New Technology Representative Office of Technology Utilization - Code UT NASA Headquarters Washington, D. C. 20546	1
Mr. Ernest M. Cohn Code RNW NASA Headquarters Washington, D. C. 20546	1
Mr. D. Bienstock Bureau of Mines 4800 Forbes Avenue Pittsburgh, Pennsylvania 15213	1
Dr. A. Makrides TYCO Laboratories Bear Hill Waltham, Massachusetts 02154	1
Dr. D. Pouli Allis-Chalmers Manufacturing Company 1100 South 70th Street Milwaukee, Wisconsin 53214	1
Dr. C. E. Heath Esso Research and Engineering Company P.O. Box 8 Linden, New Jersey 07036	1

DISTRIBUTION (Cont'd)

To:	No. of Copies
Dr. Eugene Weissman Direct Energy Conversion Operation General Electric Company 950 Western Avenue West Lynn, Massachusetts 01905	1
Dr. Seigo Matsuda Monsanto Research Corporation 1101 Seventeenth Street, N.W. Washington, D. C. 20036	1
Dr. George E. Evans Union Carbide Corporation Electronics Division P.O. Box 6116 Cleveland, Ohio 44101	1
Mr. Robert J. Flannery 910 South Michigan Avenue Chicago 80, Illinois	1
Catalyst Research Corporation 6101 Falls Road Baltimore, Maryland 21209	
Attention: Mr. H. J. Goldsmith	1
Mr. T. E. Webb	3
Mr. J. R. Moser	2
Mr. D. Ciganovic	1
Dr. E. S. McKee	1
Mr. A. McDearmon	1