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CATALYSIS OF FUEL CELL ELECTRODE REACTIONS

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Research on fuel cells over the past few years has resulted in the development of commercial prototypes of fuel gas cells operating on such gases as hydrogen, carbon monoxide, and hydrocarbons. Several considerations (1,2,3) have dictated the choice of this type of fuel cell (which includes all cells operating directly on fuel gases) over other types. Depending on projected applications and power requirements, fuel gas cells have been designed to operate at low and medium temperatures using aqueous electrolytes (4,5,6) and at higher temperatures using molten salt electrolytes (3,7).

Fuel gas cells, particularly those operating at lower temperatures, are subject to an irreversible free energy process resulting from the interaction of the reactant gases with the electrode surfaces (3,8). The reactant gases are chemisorbed by the electrode catalyst (or the electrode surface, which may act in a similar manner) and the reaction established is between the chemisorbed species and the electrolyte. The potential (free energy) developed by the cell therefore will depend on the equilibrium pressure of the chemisorbed species and has been shown (8) to be inversely proportional to the heat of chemisorption at high coverages. Thus, the catalyst surface can play a dual role in fuel cell electrode reactions - it can enhance the rate of reaction if chemical kinetics are the rate controlling factor, thus playing its usual role as a catalyst, and secondly, it can influence the potential of the cell by minimizing the free energy loss due to chemisorption.

While it is evident that the proper selection of catalysts in the design of fuel cell electrodes is essential for optimum performance, very little systematic work in this area has been published. Our present understanding of catalysis and surface physics, while far from complete, is nevertheless sufficiently comprehensive to enable a general explanation of fuel cell catalysts to be given. The present paper is concerned with a discussion of the activity of a variety of catalysts for both the fuel electrode and oxygen (air) electrode thus giving a guide to the selection of catalysts for specific cell reactions.

FUEL ELECTRODE

The role of the catalyst at the anode in a fuel gas cell is twofold: It must rapidly chemisorb the fuel gas in such a manner as to make it more susceptible to oxidation by the active species of the electrolyte and at the same time it should act to minimize the free energy loss due to chemisorption. Thus, the criteria for an active catalyst generally will be a weak, but rapid chemisorption of the fuel gas. In the selection of a catalyst these conditions must be met in addition to the requirement that the catalyst surface must preferentially

chemisorb the fuel gas species over the reaction products so as to limit self poisoning.

Hydrogen

The chemisorption of hydrogen, particularly on metal surfaces, has been studied more extensively than other fuel gases. At normal temperatures, chemisorption of the type required for high catalytic activity involves a partially covalent surface bond between hydrogen atoms and the d electrons of the metal. Thus, the general requirement for high catalytic activity of a metal in simple gas reactions of hydrogen is that it possesses d band vacancies. This limits the active metal catalysts to the transition elements, although not all of the transition metals are active catalysts even though they chemisorb hydrogen. The early members of the transition series, which have vacancies in both the first and second sub-bands, chemisorb hydrogen strongly and are not particularly good catalysts in hydrogen reactions. The later members of the three transition series, which have vacancies only in the second sub-band, exhibit the lowest heats of chemisorption at the surface coverages involved in heterogeneous reactions, and are recognized as highly active catalysts for hydrogen reactions. Thus, it would appear that the most active metal catalysts for fuel cell electrode reactions where hydrogen is the fuel gas should be selected from those transition metals with d-band vacancies only in the second sub-band- e.g. the group VIII metals.

Confirmation for the views stated above is given by Figure 1 where the open circuit potentials for the hydrogen half-cell are plotted as a function of the approximate number of d-band vacancies of the 5d transition metals and their alloys when used as catalysts at the hydrogen electrode. These data were obtained with a low temperature fuel cell (27°C) employing an aqueous sodium hydroxide electrolyte and porous graphite electrodes which were impregnated with the metal catalysts. In general the catalytic activities of the metals appear to parallel their open circuit potentials e.g. a small free energy loss due to chemisorption generally implies a high catalytic activity. Tungsten and rhenium both have relatively low open circuit potentials and high heats of chemisorption. Tungsten and quite probably rhenium have vacancies in the first d sub-band. The open circuit half cell potential of osmium is intermediate between the latter metals and platinum and iridium. The alloys of platinum-iridium appear to exhibit a maximum in catalytic activity at about one d band vacancy. As the vacancies in the d band of platinum are filled by the s electrons of gold upon alloying, the fuel cell potential decreases sharply until the 60% Au • 40% Pt alloy after which the potential appears to remain relatively constant.

Table I lists the open circuit, hydrogen half-cell potentials for the group VIII transition metals and the neighboring Ib metals. The same trend in catalytic activity is observed in the three transition series, the potential reaching a maximum between the last two transition metals and falling sharply for the following Ib metal. The irreversible free energy loss in chemisorption is larger for the group VIII metals of the first series (Fe, Co, Ni) than for the metals in the second and third series. Also, these metals of the first series are more susceptible to poisoning by impurity gases such as sulfur compounds. Platinum and

Palladium are probably the best catalysts for hydrogen electrodes in fuel gas cells. Although, a maximum in activity is obtained with alloys of certain of these metals the slight increase in potential over the pure metals would probably not justify the difficulties of alloying in commercial practice.

Table I

OPEN CIRCUIT HYDROGEN HALF CELL POTENTIALS FOR GROUP VIII AND Ib METAL CATALYSTS

Fe	Co	Ni	Cu
533	703	693	323
Ru	Rh	Pd	Ag
740	763	743	243
Os	Ir	Pt	Au
603	733	753	263

The results given in Table I for low temperature fuel cells, using aqueous hydroxide electrolyte, in general are paralleled by high temperature cells employing molten salt electrolytes, although the free energy loss on chemisorption often decreases with increasing temperature and consequently is of less importance. For example, palladium and platinum catalysts give higher open circuit potentials with hydrogen as a fuel gas than does nickel, iron, etc. in a variety of molten salt electrolytes. At relatively high temperatures (Ca 500-800°C) the nature of the hydrogen chemisorption changes for several of the group VIII metals. Quite probably, hydrogen forms d s p hybrid bonds with the metal. Indeed, in some cases the catalyst can be poisoned by being heated to a high temperature and then cooled in hydrogen. Presumably, this leaves a strongly bonded form of chemisorbed hydrogen on the surface which is not active in the electrode reaction since the activity of the catalyst can be restored by heating and cooling in helium.

Acetylene and Ethylene

The catalytic activities of the group VIII and Ib metals in the oxidation of ethylene and acetylene in a fuel cell appear to be similar to their activities with hydrogen, i.e. a high catalyst activity is favored by vacancies in the d band of the metal. However, these reaction systems are fundamentally more complex than those of the hydrogen cell. The reactions which occur at the anode are complicated by two factors (i) the nature of the chemisorbed complex, which is in doubt, since either carbon-carbon or carbon-hydrogen bonds may be broken in chemisorption and (ii) the amount of self-hydrogenation at the surface.

The reaction species may be alike in some instances since the fuel cell potentials, for both ethylene and acetylene on certain catalysts, are very similar.

The fuel cell employed for studies of acetylene and ethylene was similar to the cell used for hydrogen except that the electrolyte was a 40% aqueous solution of K_2CO_3. The reactive species in solution may be either the carbonate ion, bicarbonate ion, or the hydroxyl ion. All three ions are present in the solution in reasonable concentrations. Preliminary experiments, however, appear to favor the bicarbonate ion. The products of the reaction at the fuel electrode are in doubt, but first analyses seemed to indicate the presence of aldehydes and carbon dioxide.

The most active catalysts among the metals studied are the group VIII metals of the first transition series along with palladium and iridium as illustrated in Table II.

Table II

Metal	Half Cell Potential (millivolts) Ethylene	Acetylene
Fe	780	790
Co	675	715
Ni	605	595
Cu	410	475
Ru	205	475
Rh	365	535
Pd	710	705
Ag	095	095
W	405	460
Os	425	570
Ir	610	625
Pt	380	570
Au	190	185

The maximum in catalytic activity appears at a different place in each transition series. The group Ib metals, although possessing some activity, are in general poor catalysts for these reactions.

The catalytic activities of these metals in the ethylene and acetylene oxidation reactions at the anode are quite sensitive to the state of the catalyst surface as was the case with hydrogen. This is expecially true for the group VIII and Ib metals of the 2nd and 3rd transition series. If, after reduction, these metals are exposed to the atmosphere only momentarily their catalytic activity is decreased

considerably. This is illustrated in Figure 2 where the lower curves represent catalysts with surface oxides. Although the members of the first transition series are susceptible to oxygen poisoning the effect on catalytic activity is much less accentuated.

The most active catalysts are produced by 'in situ' reductions where the surface, after reduction, is not exposed to the atmosphere but remains constantly under hydrogen until the electrode-electrolyte contact is made.

As in the case for hydrogen, a low heat of chemisorption in either ethylene or acetylene will minimize the irreversible free energy loss at the fuel electrode and, hence, produce a higher potential in the fuel cell. There are two factors which determine the heat of chemisorption of ethylene and acetylene: (i) a geometric factor, i.e., interatomic distances in the catalyst lattice, and (ii) an electronic factor. The most favorable interatomic distance, for ethylene hydrogenation, according to Beeck (9), is 3.75 Å as observed in catalyst activity in ethylene hydrogenation reactions. Our results can neither support nor refute this, since the crystal planes exposed are not known and, thus, the more active spacings cannot be predicted. Probably the more important factor is the electronic character of the catalyst. Our results and the results of other investigators support this view (10). Only transition metals or near transition metals catalyze these reactions. Although surface reactions of acetylene have been investigated only to a limited extent, the results of this paper indicate they follow a pattern similar to that of ethylene.

The slight activity shown by the Ib metals in these reactions can be attributed to either their small d-s electron promotion energies (11), which give rise to vacancies in the d band or σ bonding by the metals to these molecules which can be achieved by a rearrangement of the metallic orbital together with the formation of a bond by overlap of the filled d-orbitals with the antibonding orbitals of the adsorbate(12).

Carbon Monoxide

The same type of fuel cell was used for studies on carbon monoxide as with ethylene and acetylene, the electrolyte being a 40% aqueous K_2CO_3 solution.

The catalytic activities of the transition metals investigated in this cell for the anodic oxidation of carbon monoxide are shown in Table III. The variation in the half cell potential among the transition metal catalysts are small with the exception of Palladium which appears to be the most active catalyst for the reaction. The activities of the Ib metals are low as for the fuel gases previously mentioned. This would indicate the necessity of vacancies in the d band of the metal catalysts for a high activity.

The chemisorption of carbon monoxide may take place by a number of different mechanisms. On certain metals, such as palladium and platinum, it chemisorbs with a one site attachment forming a surface layer similar

Table III

HALF CELL POTENTIALS (MILLIVOLTS) FOR CARBON MONOXIDE

Fe	Co	Ni	Cu
-	440	495	190
Ru	Rh	Pd	Ag
475	540	825	225
Os	Ir	Pt	Au
520	510	545	150

in structure to the metal carbonyls, i.e., M = C = O (13). The second mode of chemisorption is a two site sorption with the carbon monoxide complexes covering two surface sites as indicated in the following diagrams (14).

Two site chemisorption probably takes place on rhodium (13) in this manner. The two types of two site mechanisms cannot be differentiated since the lattice geometry required in the metals for chemisorption falls in quite narrow limits, otherwise, the valence angles would be prohibitive. All of the transition metals studied probably expose crystal planes suitable for both mechanisms.

Again the activities of the Ib metals may be due to the small energies required for d-s electron promotion.

OXYGEN (AIR) ELECTRODE

The general requirements of a catalyst at the oxygen electrode of a fuel gas cell are essentially the same as for the fuel electrode catalyst except that negative ion formation is the process under consideration. In cells employing aqueous hydroxide electrolytes, the oxygen must be chemisorbed in such a manner as to lead to the rapid formation of peroxide and hydroxide ions in the presence of water. A further role of the catalyst in this case is to aid in the decomposition of the peroxide.

The most active catalysts, among those investigated, for the electrode reaction of the oxygen half-cell in aqueous hydroxide electrolytes are the oxides of the group Ib metals: copper, silver, and gold. Copper and silver oxides are known to be active oxidation

catalysts (e.g. they must chemisorb oxygen in a state that will readily take part in oxidation reactions) and their presence presumably also promotes decomposition of peroxide ions formed under current drain. Gold films, however, have been reported to be inert toward the chemisorption of oxygen up to 0°C (15). Possibly O_2^- ions are formed on the gold surface as an intermediate step in the reduction of oxygen. Such a species, if present in small amounts, might not be detected in chemisorption experiments since it would be readily removed from the surface on outgassing. The activities of the Ib metal oxides are in the order: copper silver gold.

Cobalt and nickel oxides possess an activity only slightly greater than unactivated graphite which may indicate that these metals are essentially inactive; while iron oxide has a reasonable activity. The open circuit half-cell potentials for the 3d transition oxides and oxides of cobalt-nickel and nickel-copper alloys are shown in Figure 3. As copper is added to nickel, a slight increase in potential starts after the 60% copper- 40% nickel alloy (oxide) is reached and then a rapid increase is observed as pure copper oxide is approached. A similar behavior is found for palladium-silver alloys (oxides) in the 4d transition series.

The activity of oxides as catalysts at the oxygen electrode may be varied considerably by the introduction of a defect structure. It is well known that heterogeneous reactions proceeding by negative ion formation can be profoundly altered by the defect state of the catalyst surface.

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REFERENCES

(1) Liebhafsky, H.A. and Douglas, D.L., Paper 59-SA-22 published by the Am. Soc. of Mechanical Eng. (1959).

(2) Young, G.J. and Rozelle, R.B., J. Chem. Ed. 36, 68 (1959).

(3) Broers, G.H.J., "High Temperature Galvanic Fuel Cells", Ph.D. Thesis, University of Amsterdam, 1958.

(4) Evans, G.E., Proceedings of the Twelth Annual Battery Conference, p. 4 (1958).

(5) Bacon, F.T., Beama, J. 61, 6 (1954).

(6) Bacon, F.T., British Patent 677,298 (1952).

(7) Gorin, E. and Recht, H.L., Paper 58-A-200 published by the Am. Soc. of Mechanical Eng. (1958).

(8) Rozelle, R.B. and Young, G.J., J. Phys. Chem., in press.

(9) Beeck, O., Rev. Mod. Physi. 17, 61 (1945).

(10) Trapnell, B.M.W., "Chemisorption", p. 228 Butterworths Scientific Pub. London, England 1955.

(11) Ibid. p. 74.

(12) Dowdin, D.A. "Chemisorption" p. 9, Butterworths Scientific Pub. 1957.

(13) Trapnell, B.M.W., "Chemisorption", p. 181, Butterworths Scientific Pub. 1957.

(14) Ibid. p. 182.

(15) Ibid. p. 61.

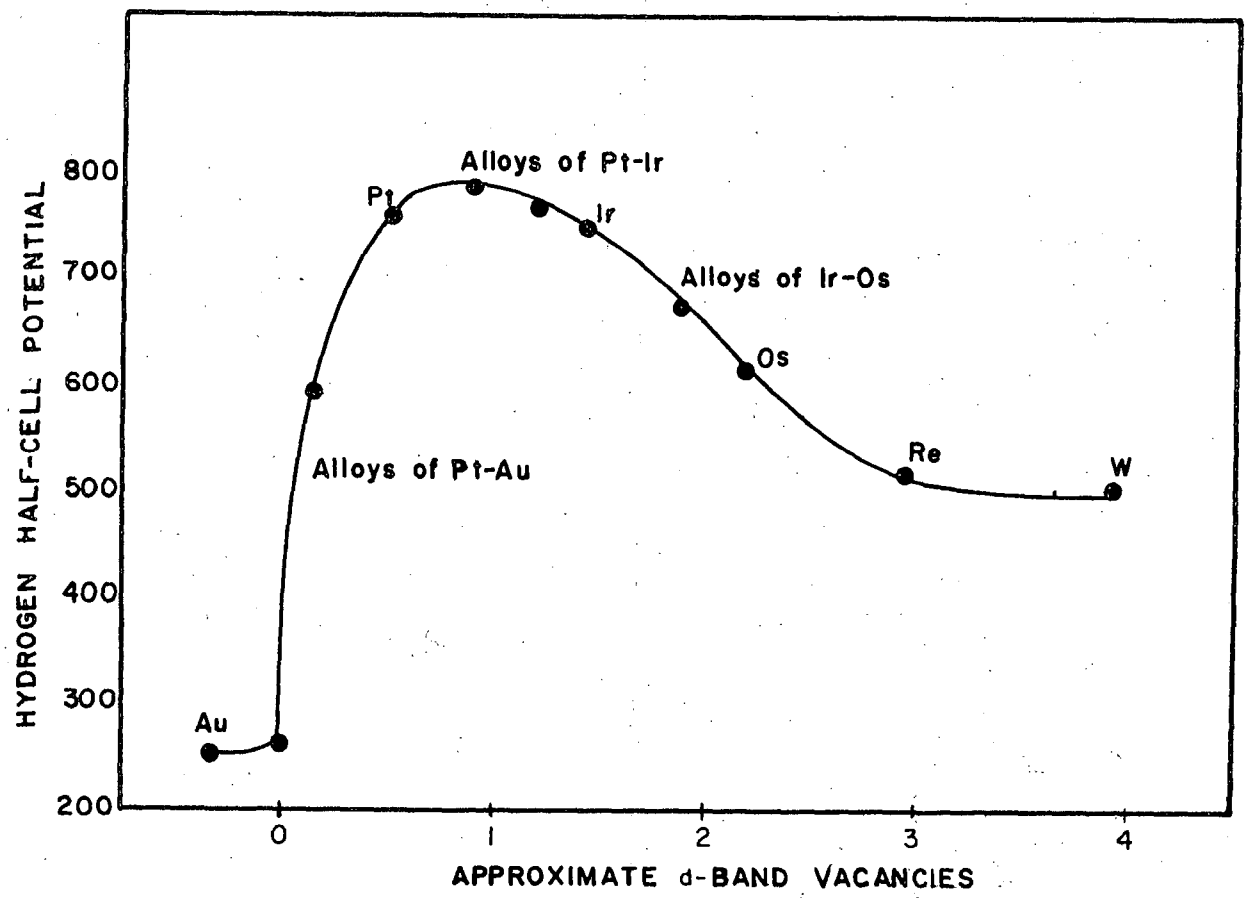

Figure I Hydrogen Half Cell Potentials as a function of d band Vacancies for the 5d Transition

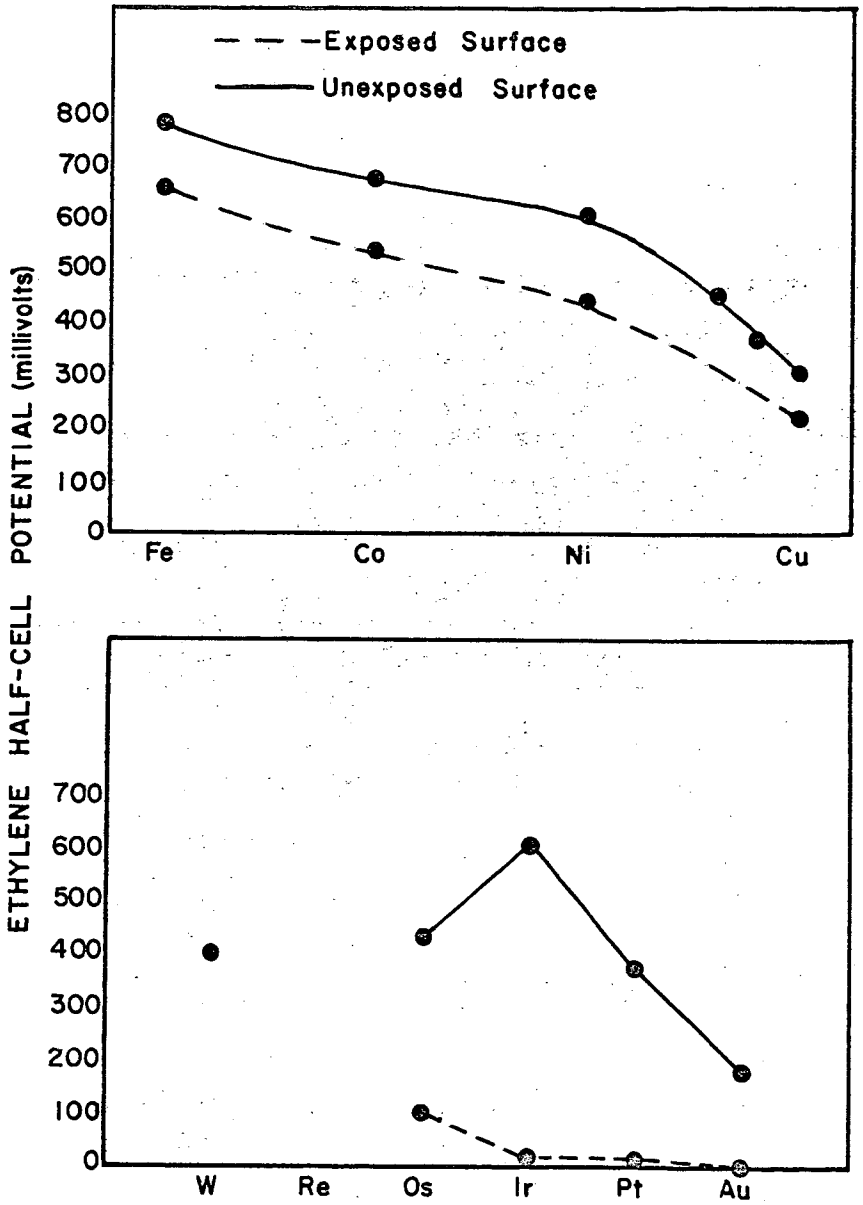

Figure II Ethylene Half Cell Potentials for the 3d and 5d Transition Metals

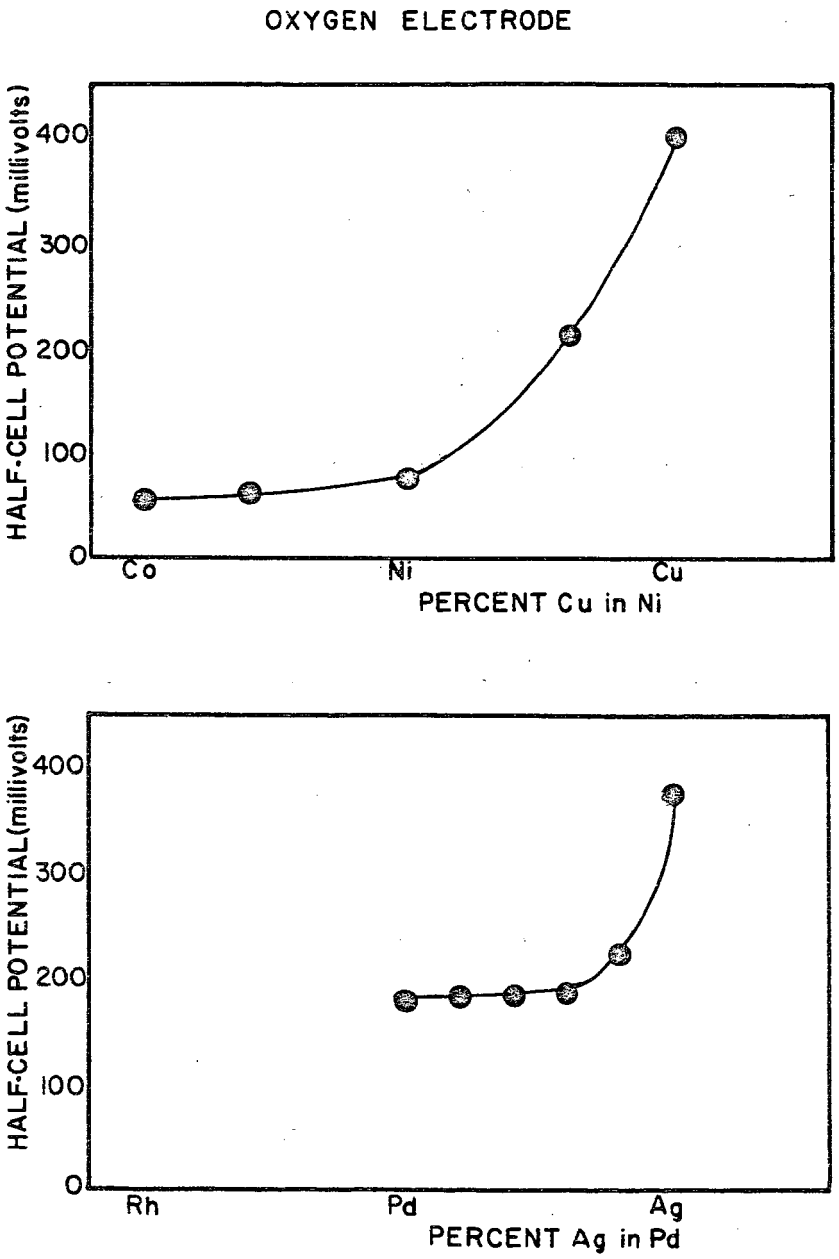

Figure III Oxygen Electrode Half Cell Potentials