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Non-Noble Catalysts and Catalyst Supports For Phosphoric Acid Fuel Cells

1st Quarterly Report

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Introduction

Under this contract, work is being carried out on three tasks:

I. Anode catalysts resistant to CO poisoning

II. Cathode supports for Pt catalysts

III. W-Ti carbide catalysts.

Under Task I, work has been principally directed toward the possibility that by supporting highly active, CO sensitive Pt upon weakly active, CO tolerant WC, an anode catalyst with intermediate activity and CO tolerance might be achieved. This possibility was suggested by observation by Bockris and McHardy [1] of enhanced specific activity of cathodic reduction of O_2 supported on sodium tungsten bronze, and by the likelihood [Hamilton, 2] that Pt will segregate to the WC surface, perhaps forming monolayer or sub-monolayer coverage. Evidence that very highly dispersed Pt can be prepared on WC was presented in our Oct. '79-July '80 progress report. Improved CO tolerance was indicated, but interpretation was not definitive because, (a) the basis of comparison was Pt sheet, not finely dispersed Pt, and (b) the Pt/WC electrodes obviously contained both a very highly dispersed and a more coarsely dispersed fraction of Pt, and only the overall reduction in activity due to CO poisoning could be ascertained. Immediate objectives in this task will be to prepare Pt/WC samples in which the highly dispersed fraction only is achieved, or at least maximized, and to study them in concentrated H_3PO_4 at elevated temperature. In connection with the objectives of this task, it is of interest to note that the $W_{1-x}Ti_xC$ cubic alloys currently under study in Task III display apparently complete tolerance to poisoning by 3 percent CO included in the H_2 gas feed in measurements made in 1M H_3PO_4 at 23°C.

Task II was motivated by our past observation [3] of exceptional stability of several refractory hard metals, notably TaN and TaB, at high overpotential in H_3PO_4. These offer the possibility of corrosion free performance as O_2 reduction catalyst supports in acid fuel cells.

In Task III, the cubic alloys $W_{1-x}Ti_xC$ are being studied as anode catalysts over the range of solubility of W in cubic TiC. TiC itself is inactive [4,5], while the alloys with W have been found in the present investigation to be active and CO tolerant. Work is in progress to determine the rate constants as function of composition from polararization studies performed on thin pororous electrodes. The work is of interest from the standpoint of the catalysts themselves, as well as the opportunity to observe the behavior of W in a different crystalline environment (cubic as opposed to the hexagonal structure of WC) and to correlate the activity with the titration of surface sites with Ti.

Progress During the Reporting Period

Task I – Two preparations of Pt/WC were carried out by precipitation and reduction of chloroplatinic acid. Loadings were 0.053×10^{-6} and 0.013×10^{-6} gm. Pt per cm^2 of WC BET area. The WC support was of low specific area ($0.38 m^2/gm$ BET) and activity ($i_o = 0.6 \times 10^{-6}$ A/cm^2 at 23° in 1M H_3PO_4). The aim here is to increase the fraction of Pt residing in the highly dispersed form. Thin porous electrodes of each preparation were prepared in the manner described in our Oct. '79 – July '80 progress report, where the precipitation/reduction procedure is also described.

Task II – An attempt was made to prepare dispersed Pt on TaN by precipitation and reduction of chloroplatinic acid. Upon removal of the sample from the reduction chamber, it was found that the H_2 distribution tube had failed, and that the internal residue normally found in the cool area adjacent to the furnace was missing. A porous electrode of this material was prepared and examined by linear sweep voltammetry and H_2 stripping in 1M H_3PO_4; indicated Pt content was nil. The reduction apparatus has been repaired, and further preparative attempts will be carried out.

Task III – Thin porous electrodes of four different samples of the cubic alloy $W_{1-x}Ti_xC$ were prepared and examined in N_2, H_2, and 3 percent CO/H_2 saturated 1M H_3PO_4 by linear sweep voltammetry, at a sweep rate of 2.5 mV/sec. The compositions of the alloys are listed in Table 1. All of the alloys were active for H_2 oxidation and, within the reproducibility of the measurements, unaffected by CO.

An attempt was made, within the framework of the thin porous electrode model [6], assuming reaction control and Tafel kinetics, to obtain the transfer coefficient and total exchange current for each sample. Anomalous results were obtained which, in the light of re-examination of the raw data which showed high surface impedances, were in all likelihood due to transient effects during the dynamic measurements. Steady state measurements were then undertaken (and seriously impeded by a sudden break down in our electronically controlled data aquisition system). At the present time, steady state polarization measurements have been made on three of the four samples. Hydrogen oxidation and evolution have been studied in the cell described in our Oct. '79-July '80 Progess Report. The rate parameters reported for $W_{.24}Ti_{.76}C$ in our July Monthly Narrative were based on the dynamic measurements and should, of course, be disregarded. Transfer coefficients for H_2 evolution and oxidation for the three samples now studied are listed in Table 1, as is the exchange current density for the $W_{.24}Ti_{.76}C$ sample (the only one of the four for which BET measurements are currently available. Other samples have been sent to a commercial laboratory for BET studies, and the results should be available soon.) Fig. 1 shows the results of the polarization studies on $W_{.24}Ti_{.76}C$; the data on the other two samples are comparable. Studies in 3 percent CO/H_2 have beeen carried out in the steady state on two of the samples, and the CO tolerance noted in the dynamic studies confirmed.

The assumption of Tafel kinetics is rather well born out by Fig. 1. The assumption of reaction control, on the other hand, has not been adequately justified. We are confident, however, that these electrodes are operating under reaction control, and will outline our reasons for our confidence, as well as measures now being undertaken to place this belief on firmer ground.

Our assumption of reaction control is based largely on long experience with electrodes of this type [7], fabricated of relatively coarse powders of low activity catalysts lightly bonded wth PTFE. We have had good success in modelling such electrodes, using gross electrode densities and reasonable estimates of the product of the H_2 diffusion coefficient and solubility. Moreover, pore volumes inferred fom the difference between gross electrode density and bulk catalyst density have been found in reasonable agreement with those inferred from mass increase with acid pickup. Given the low oxidation currents obtained in the present work, something very strange would have to occur if our electrodes were not reaction limited. We will of course explore the question further. Much thicker electrodes will be prepared, and activation energy measurements made, looking for diagnostic slope and activation energy reductions.

It is of some interest to compare i_o determined for the $1-x = 0.24$ sample with that measured for a stoichiometric, "oxygen free" WC sample studied under the same conditions. For the WC, α_{ox} = ~~0.18~~ .32 and $i_o = 0.6 \times 10^{-7}$ A/cm^2. Assuming approximately equal metal site surface densities on the two materials and no depletion or enrichment of W on the WTiC surface, multiplication of the WC i_o value by the simple dilution factor of .24 yields $i_o = 0.1 \times 10^{-7}$ A/cm^2, while multiplication by the probability of adjacent W sites, $(.24)^2$, yields $i_o = 0.3 \times 10^{-8}$, quite close to the observed 0.6×10^{-8} for the WTiC sample, and suggesting similar active sites on the two materials. It will be of considerable interest to see if this relation holds over the entire range of W concentration in WTiC.

Current Problems

In this reporting period, two equipmnt failures (the above mentioned electronic data aquisition system and reduction system glassware problems) caused significant delays. Repairs have now been made and no further problems of this type are foreseen. More seriously, a family illness has curtailed the investigator's efforts during most of November. This situation appears to have stabilized and it is hoped that work can now be fully resumed.

Work Planned

Task I - Characterization of the new Pt/WC preparation by H_2 stripping and plating, and measurement of H_2 and 3 percent CO/H_2 isotherms on these preparations will be carried out as soon as possible.

Task II - Preparation of TaN and TaB supported Pt catalysts has begun, and preliminary evaluation of these catalysts will be the main object of the next quarter's work.

Task III - Steady state measurements will be carried out on the remaining WTiC sample, and the measures outlined above for ascertaining whether the thin porous electrodes are in fact truly reaction controlled pursued.

References

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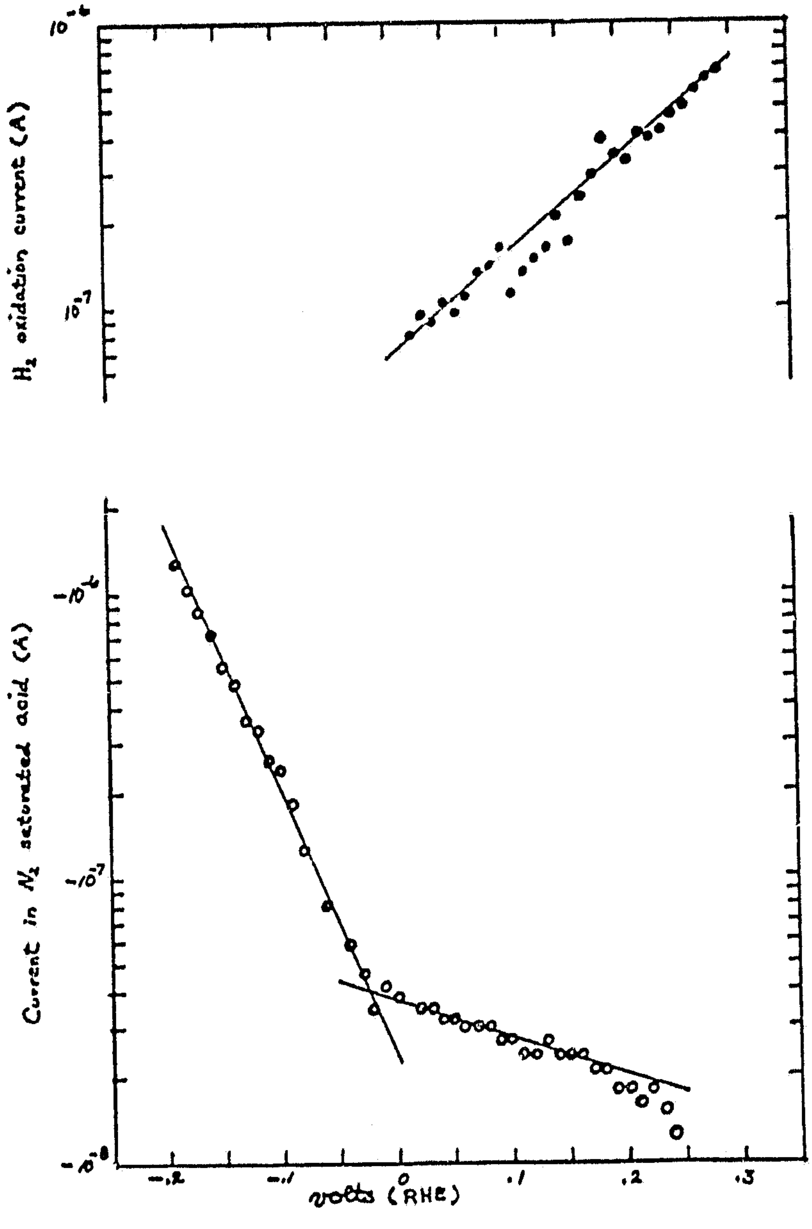
Table 1

Composition and apparent rate constants for H_2 oxidation and evolution on $W_{1-x}Ti_xC$ alloys in 1M H_3PO_4 at 23°C.

1-x	x	α_{ox}	α_{evol}	i_o (A/cm^2)
.24	.76	.20	.57	0.6×10^{-8}
.31	.69	.15	.36	-
.45	.55	.11	.59	-
.47	.53	-	-	-

Figure Captions

Fig. 1. Current density (normalized to total electrode BET area) for $W_{.24}Ti_{.76}C$ in N_2 saturated 1M H_3PO_4 at 23°C, open circles; and the H_2 oxidation current obtained as the difference between the current densities obtained in H_2 and N_2 saturated acid at positive overpotential (vs. a dynamic Pt reference electrode), filled circles.



10^-6
10^-7
H2 oxidation current (A)
-10^-6
-10^-7
-10^-8
Current in N2 saturated acid (A)
-.2
-.1
0
.1
.2
.3
volts (RHE)

Fig. 1