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Publication Date
1985-02-01

LBL-18281

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

Presented at the Philadelphia ACS Meeting
on The New Surface Science in Catalysis,
Philadelphia, PA, August 26-31, 1984;
and to be published in the Proceedings

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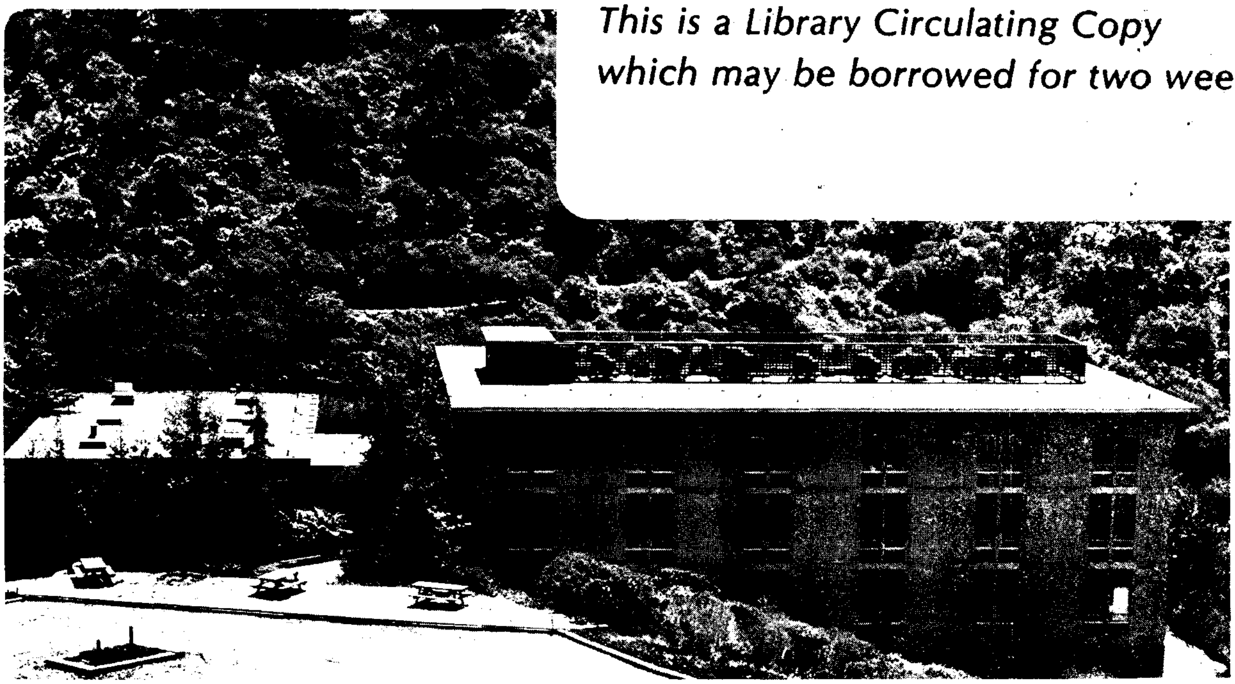
February 1985



Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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This research was supported by the Assistant Secretary for Fossil Energy, Office of Fuel Cells, Advanced Concepts Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098, and by the Electric Power Research Institute under Contract No. RP-1676-2.

New Catalysts and New Electrolytes for Acid Fuel Cells

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Introduction

In the phosphoric acid fuel cell as currently practiced, a premium (hydrogen rich) hydrocarbon (e.g. methane) fuel is steam reformed to produce a hydrogen feedstock to the cell stack for direct (electrochemical) conversion to electrical energy. At the fuel electrode, hydrogen ionization is accomplished by use of a catalytic material (e.g. Pt, Pd, or Ru) to form solvated protons,

$$H_2 + S \rightarrow 2\,[HS^+] + 2e^-$$

At the cathode, air is reduced catalytically by reaction with solvated protons to generate the product water

$$1/2\ O_2 + 2\ [HS^+] + 2e^- \rightarrow H_2O + S$$

In practical cells, the acid concentration is very high (>95%) and the solvated protonic species are not actually known, i.e. H_3O^+ and $H_4PO_4^+$ but probably very little $H_9O_4^+$. In order to maximize waste heat utilization, the cell stack operating temperature has been increased to the maximum value tolerated by the materials in current use, which is presently about 200°C. Catalysis is the key to the commercial viability of fuel cells, particularly the air cathode catalysis, as much more polarization occurs at the cathode than at the anode. Because of the severe operating conditions of the cell stack, the choice of catalytic materials is extremely limited. At present, the emphasis in cathode materials research is to find catalysts that provide improved kinetics over the integrated lifetime of the cell stack (ca. 40,000 hrs.). The baseline cathode material is Pt supported on a graphitized carbon black, usually at a weight loading of 10%, and a crystallite size of ca. 3 ± 0.5 nm (i.e. about 30 percent exposed as measured by hydrogen chemisorption). At the end-of-life, we project that some Pt will be lost from the cathodes, and the crystallite size will have increased considerably, to 10-15 nm or more. The actual end-of-life conditions for the baseline catalyst is not known, since phosphoric acid fuel cell stacks have not yet been operated for the expected lifetime.

Recent testing in phosphoric acid fuel cells has shown improved performance using promoted Pt on carbon catalysts in the air cathode. The promoters are oxides of the base transition metals, e.g. Ti (1), V (2), Cr (3), Zr (1) or Ta (1). The role of these promoters in the air cathode is unclear, and some have suggested that the active catalysts are alloys of the Pt with the transition metal (1,4) which form during heat-treatment of the oxide impregnated precursor. In the first section of this paper, we review the work from the Lawrence Berkeley Laboratory on the study of the mechanism of promotion of air cathode performance by these transition metal additives.

Phosphoric acid does not have all the properties of an ideal fuel cell electrolyte. Because it is chemically stable, relatively non-volatile at temperatures above 200°C, and rejects carbon dioxide, it is useful in electric utility fuel cell power plants that use fuel cell waste heat to raise steam for reforming natural gas and liquid fuels. Although phosphoric acid is the only common acid combining the above properties, it does exhibit a deleterious effect on air electrode kinetics when compared with other electrolytes (5) including such materials as sulfuric and perchloric acids, whose chemical instability at $T > 120^\circ C$ render them unsuitable for utility fuel cell use. In the second part of this paper, we will review progress towards the development of new acid electrolytes for fuel cells.

New Catalysts

All of the preparation procedures for the oxide promoted catalysts (1-4) shared one common feature, heat-treatment of the oxide impregnated Pt on carbon catalysts in an inert atmosphere at elevated temperature, usually around 900°C. If an "alloy" phase of Pt with the metal of the metal oxide is formed by this heat-treatment, thermal reduction would have to occur with carbon as reducing agent, e.g.

$$Pt + TiO_2 + C \rightarrow Pt_3Ti + CO_2$$

This reduction is thermodynamically favorable due to the very exothermic free-energy of formation of Pt_3Ti (6). However, such reduction reactions would require, in principal, the physical contact of three phases, which seems unlikely; it is more likely that the reduction proceeds through a complex pathway involving a series of two-phase reactions. To understand these essential reduction reactions, we conducted a series of model studies of oxide overlayers on Pt surfaces. Because of the difficulty in characterizing supported multi-metallic catalysts, we decided to select just one of the bimetallic systems for detailed study, rather than attempt the characterization of the state of several different metal oxide promoters. We initially selected the Pt/ZrO_2 system because of the very strong intermetallic bonding between Pt and Zr (7). However, following an initial study of the surface chemistry of ZrO_x overlayers on Pt (8), we decided that the Pt/TiO_2 system was a more interesting choice. The Pt/ZrO_2 system had the major disadvantage that very high temperatures (1200°K) were required to cause reactions between the ZrO_x and Pt(Zr) phases to occur, whereas in the Pt/TiO_2 system the analogous reactions occurred at ca. 500°K lower temperatures. We attributed this effect to the smaller metallic radius of Ti vs. Zr, noting that the radii of Ti, V, Cr and Ta are all much smaller than Zr.

Surface Chemistry of TiO_2 Overlayers on Pt

Auger electron spectroscopy (AES) of TiO_2 overlayers on Pt(100) single crystal was used to follow the changes in surface composition with thermal annealing (9) in UHV. Generally, the overlayers were ca. 4 monolayers thick, prepared by electron beam evaporation of Ti metal with simultaneous oxygen dosing. Above an annealing temperature of 600°K, the O/Ti and Ti/Pt AES ratios changed as a function of time, indicating reduction of the oxide overlayer and dissolution of Ti into the Pt bulk. It was not clear where the oxygen in the overlayer went, but since in most UHV systems $[H_2]/[H_2O] >> 1$ and/or $[CO]/[CO_2] >> 1$, it is presumed to have left the surface as H_2O

or CO_2. In the presence of a deliberately introduced reducing gas like H_2 or CO (typically 100 L dose), the O/Ti AES ratio decreased more rapidly than for thermal annealing, but the rate of the Ti/Pt AES ratio change was unaffected, indicating that Ti dissolution (solid state diffusion) was a slower step. Also, at temperatures above $900^{o}K$ the oxygen surface concentration went to essentially zero, indicating that at this temperature (and possibly at lower temperatures as well) titanium was dissolved into Pt as Ti metal, and not as "TiO" as reported by Gorty (10). The difference may be due to the polycrystalline nature of the Pt substrate used in (10) and grain boundary diffusion of "TiO" species. It was clear from the overlayer studies that with thermal annealing in reducing atmpspheres, TiO_2 overlayers on Pt can be completely dissolved, forming Pt-Ti alloy surface phases of nominal composition Pt_xTi ($3 \leq x \leq 8$). Therefore, it seemed reasonable to conclude that similar reactions can occur in the supported TiO_2 impregnated catalysts, and that alloy phases are responsible for the enhanced catalysis.

Surface Chemistry of Pt - Ti Alloys

The most recent work on the structure of the bulk alloys of composition Pt_xTi ($3 \leq x \leq 8$) is by Schryvers et al. (11). They reported that in the composition range between those for the ordered phases Pt_3Ti and Pt_3Ti there exists two long-period antiphase boundary structures based on the face-centered cubic structure. They suggest that due to strong ordering forces extending over several atomic separations (as exhibited by Pt_3Ti) there is no composition in this range in which the alloy phase is a solid-solution (disordered). We have studied the surface properties of the model systems Pt_3Ti extensively, including the surface composition and structure (12), the electronic properties (13), the reactivity of the surface towards oxygen (14), and small molecule adsorption on the surface (15). These studies have shown that while the Pt_3Ti surfaces have very interesting properties for catalysis in reducing atmospheres, which may be related to the SMSI effect in CO/H_2 chemistry on Pt/TiO_2 (16), the reactivity of the Ti in the surface towards oxygen is very high, resulting in the formation of TiO_x overlayers on a Pt enriched (relative to the bulk) surface layer. The stoichiometry and coverage by TiO_x depend on the oxidation conditions. At 350°C in air, which is a common curing (of polymer binder) condition during electrode preparation, the surface becomes covered by a dense, compact multi-layer of TiO_2. Curiously, there is some evidence of proton conduction through this film when the surface is immersed in dilute acid solution. However, under the conditions of use in phosphoric acid fuel cells, very concentrated hot acid, the TiO_2 overlayers are dissolved rapidly, leaving an essentially pure Pt surface. These studies suggest that the electrocatalytic properties of Pt_3Ti in commercial fuel cells would be the same as pure Pt. There is the possibility that the Pt surface left after TiO_2 dissolution is an atomically rough surface, and therefore the comparison to "pure Pt" would have to be made taking into account differences in morphology.

Characterization of TiO_2 Promoted Pt Catalysts

Characterization studies of the oxide impregnated Pt on carbon catalyst are being conducted to determine the chemical state of the admetal as a function of heat treatment. Ultimately one wants to supplement these "dry" characterizations with characterizations of the "wet" state, i.e. as the catalyst exists in the fuel cell cathode. These characterization studies are still in progress, and we have no results published as yet. The techniques of x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), and extended x-ray absorption fine structure spectroscopy (EXAFS) are being used in combination. Each of the techniques "looks at" the catalyst in a different way and each provides a different kind of characterization. We are using XRD to indicate any phases present in crystalline form, XPS to determine the valence states of Ti, and EXAFS to determine the ligand coordination about the Ti atoms. In a supported catalyst both XPS and EXAFS are "integral" techniques, that is they sample all the Ti atoms present. Table I reports the binding energies for Ti (2p) in standard materials that represent the expected possible chemical states of the Ti.

Table I. XPS Binding Energies for Ti 2P3/2 in Different Chemical States.

State	B.E.*	Chemical Shift
Ti	453.8 eV	ref.
TiO	454.6	+0.8
TiC	454.7	+0.9
$TiPt_3$	454.9	+1.1
TiO_2	458.5	+4.7
$TiCl_3$	459.4	+5.6

*Energy scale referenced to carbon 1S at 284.6 eV.

The +4 and +2 states are easily distinguished from the metallic state, but titanium in the ordered alloy Pt_3Ti has the nearly same chemical shift as in TiC which is also a possible reduction product. XPS alone would not be capable of reliably resolving the reduced state of Ti. But the backscattering cross-section of Pt is enormously greater than that of carbon, so the EXAFS coupled with XPS provides a clear discrimination of Ti in TiC and Ti in Pt_3Ti clusters too small to be observed in XRD patterns. A summary of the qualitative characterization heat-treated TiO_2 impregnated Pt on carbon catalyst is given in Table II.

Table II. Characterizations of State of Ti as a Function of Heat-Treatment Temperature

	Method (characterization)		
Sample	XRD(phases)	XPS(valence)	EXAFS(ligands)
TiO_2 impregnated	amorphous	+4	0
HT 700°C	"	+4	0
HT 900°C	TiC, Pt alloy	+4, "+1"‡	0, Pt
HT 1200°C	Pt_3Ti	"+1"	Pt

‡ "+1" is nominal oxidation state of Ti in Pt_3Ti [13] or TiC.

Curiously, very little TiC was observed at any stage of the treatment; it does not appear to be an intermediate to alloy phase formation. A significant amount of alloy phase appears only at 900^{o}C and above. At 1200^{o}C, Pt_3Ti is the predominant Ti phase present.

Fuel cell testing has indicated that the promotional effect of TiO_2 is observed after heat treating at 900^{o}C; at 700^{o}C the heat treatment had a small promotional effect that was not regarded as significant. Therefore, alloying may be essential to the promotional effect. However, a key element we are missing from the characterization mix is knowledge of the physical structure of the phases. Such structural characterization is possible by transmission electron microscopy (TEM) and such studies are in progress.

Current Status of New Catalysts

Based on the characterization studies and the behavior of the model systems, it appears that the promotion effect of oxides of Ti, V, Zr, Ta and Cr is probably not truly catalytic. The most probable mechanisms are changes in physical properties of the Pt catalyst in the "dry" state which result in improved electrode performance due to two effects: 1) a Pt crystallite shape/morphology effort, where the base metal oxide acts to impede Pt crystallite size growth (by coalescence) but allows surface diffusion to occur and equilibrium shapes to form during heat treatment; 2) the oxide acts as a "flux" for improving the wetability of the catalyst when fabricated into a gas diffusion electrode, resulting in higher catalyst layer effectiveness. Both of these effects have been discussed in the literature, but not with respect to how additives or promoters might relate to such effects. The effect of Pt crystallite shape/morphology on oxygen reduction activity has been discussed at length (17), and it is clear that metal oxides can have an indirect effect on oxygen activity via modification of shape/morphology. The effectiveness factor for the catalyst layer is known to be extremely sensitive to physical properties of the carbon, the Teflon dispersion, the use of wetting agents, the hydrophilicity of the SiC matrix, etc., and it is a difficult matter to determine truly catalytic effects from electrode structural effects. Watanabe et al. (18) have recently presented data showing that a novel electrode fabrication method enhanced the performance of "standard" Pt catalyst by ca. 40 mV, which is about the same performance enhancement by metal oxides reported in References 1-4.

New Electrolytes

Recent work has shown that use of concentrated trifluoromethane sulfonic acid (TFMSA) in place of concentrated phosphoric acid enhances the activity of standard Pt electrodes for oxygen reduction by 40 mV (which could improve the heat rate of first-generation fuel cells by 400 Btu/kWh) (19). It shows the real possibility that the catalytic activity of platinum-based catalysts in phosphoric acid can be improved under utility fuel cell conditions by the use of new electrolytes, especially fluorinated sulfonic or phosphoric acids. However, trifluoromethane sulfonic acid is much too volatile for practical use in utility fuel cells. Efforts to synthesize suitable non-volatile, stable fluorinated sulfonic acids to replace phosphonic acid have been moderately successful and are continuing. There has been some doubt about the kinetics of oxygen reduction in non-volatile, higher homologs of TFMSA, and whether the kinetic benefits are retained in the higher molecular weight acids. Recent work (20) has shown that, in the absence of impurities resulting from by-products of the synthesis, the kinetics in the higher acids are identical to those observed in TFMSA (at the same pH and temperature). The result allows some guarded optimism that the search for the optimum acid electrolyte will ultimately prove to be successful.

Acknowledgment

This research was supported by the Assistant Secretary for Fossil Energy, Office of Fuel Cells, Advanced Concepts Division of the U.S. Department of Energy under Contract NO. DE-AC03-76SF00098, and by the Electric Power Research Institute under Contract No. RP-1676-2.

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