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CORROSIVE DEGRADATION IN BATTERIES AND FUEL CELLS

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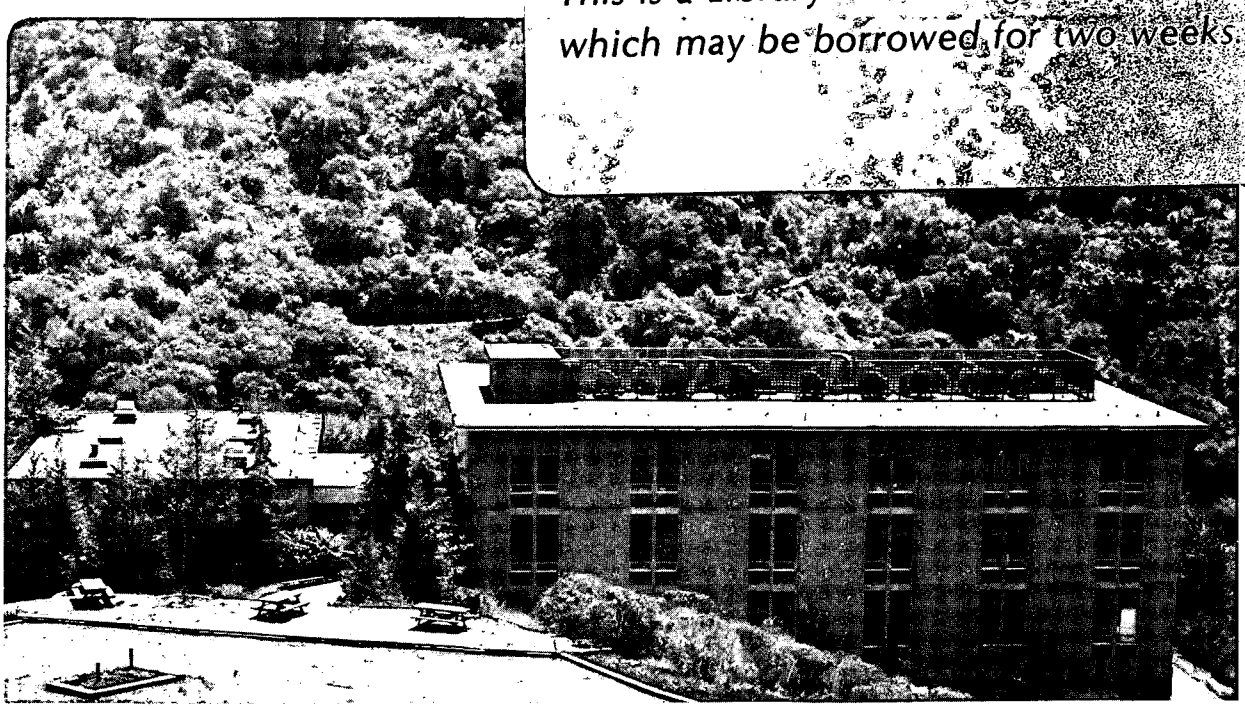

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CORROSIVE DEGRADATION IN BATTERIES AND FUEL CELLS

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There are two types of fuel cell technology whose state of development has advanced to the stage where reliability and lifetime are important issues in the evolution to a commercial product. Corrosive degradation of the components is now known to be a key factor in both reliability and lifetime of these power plants. Because the two types of fuel cells employ different families of materials to form the basic components, the two technologies will be discussed separately. The discussion will concern only corrosive degradation of the electrochemical energy conversion section of the power plant, omitting the fuel conditioning, thermal management (heat exchangers), and power conditioning sections.

PHOSPHORIC ACID FUEL CELLS (PAFC)

The basic repeating elements in the electrochemical energy conversion section of the fuel cell are shown schematically in Figure 1. The repeating elements forming a single electrochemical cell are literally "stacked" to form a multi-cell module connected electrically in-series. With the exception of the catalyst in the electrodes, the materials in the repeating elements are non-metallic, and are primarily allotropic forms of elemental carbon. The basic structural component in the PAFC stack is the bipolar plate, which channels the gas flows across the backsides of the anode and cathode and also carries the electrical current from one cell to the next. The bipolar plate is a graphite-carbon composite fabricated by heat-treating a graphite powder impregnated with hydrocarbon resin (1). It is generally

the case that pyrolysis of the resin produces a glassy carbon second phase as opposed to a graphitic second phase (2) characteristic of synthetic graphite produced from coke-pitch (3) processing. The electrodes have a bi-layer composite structure, with a porous, gas-supplying substrate layer fabricated from graphite fibers supporting the catalyst layer, a high area carbon black impregnated with microcystallites (2 - 10 nm) of platinum (4). A fluorocarbon elastomer, like polytetrafluoroethylene, is used as a binder and wet-proofing agent in the electrode structure. The electrolyte, very concentrated phosphoric acid (95 - 99 wt. % H_3PO_4), is retained in a matrix of silicon carbide powder. The operating conditions for PAFCs vary depending on the application and the size of the unit, from 478 K at 300 - 500 kPa to 433 K at ambient pressure. The pressurized operating conditions are more corrosive, due both to the higher temperature and higher water activity.

At the anode, hydrogen is electrochemically converted to solvated protons by the reaction

$$H_2 + 2S \rightarrow 2(HS)^+ + 2e^-, \; S = H_2O, H_3PO_4 \qquad [1]$$

and oxygen is consumed by reaction with solvated protons to form water by the reaction

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

The primary corrosion reactions are the anodic oxidation of the various allotropic forms of carbon, which can be represented by the generic cell reaction

$$C + 2\ H_2O + 4S \rightarrow CO_2 + 4(HS)^+ + 4e^- \qquad [3]$$

and the dissolution of platinum probably to form complexed Pt^{2+} ion in solution. Graphite is the most corrosion resistant allotropic form of carbon. It is easily shown that the galvanic corrosion of graphite in oxygen saturated acid is limited by the kinetics of the cathodic half-reaction, the oxygen reduction reaction on the graphite surface. However, if the surface of the graphite is both electronically and ionically coupled to a oxygen reduction catalyst (like platinum), then the kinetics of the anodic half-reaction are controlling. This latter condition is clearly seen to be the case in the fuel cell cathode, as all components are in electrical contact and at some points of physical contact the components are wetted with electrolyte and share ionic pathways with the platinum crystallites. Extensive post-mortem analysis has been conducted and the regions subject to corrosion are well-known. Material loss, as a fraction of the material initially present, is greatest in the catalyst layer, followed by the losses in the substrate and then loss from the bipolar plate. This ranking is what would be expected based on relative surface area and extent of electrolyte wetting of the different components, assuming the intrinsic corrosion resistance of each component was the same.

Reasonably extensive comparative studies of the kinetics of anodic

oxidation of the various allotropic forms of carbon have been conducted. Stonehart and co-workers (5) have reported a fairly extensive study of the corrosion of candidate high area carbon blacks for use in the catalyst layer. They report a correlation between corrosion rate (on a unit area basis) and c-axis layer plane spacing determined from x-ray powder diffraction analysis of heat-treated furnace blacks. Furnace blacks graphitized by heat-treatment at 3000 K appear to be the material of choice for this component. They also compared corrosion rates for graphite fiber materials to graphitized furnace blacks, and found that on a unit area basis the rates were comparable (same order of magnitude). Christner and co-workers (6) have reported extensive studies of corrosion of various types of carbon composite materials used in the bipolar plate, and followed the progressive development of corrosion resistance in the resin phase with thermal treatment. Ross (7) has reported the only fundamental study of the kinetic parameters of the corrosion reaction using single phase materials such as glassy carbon and single crystal graphite. This study confirms the suggestions from previous work that graphite is the most corrosion resistant form of carbon (with the possible exception of diamond and diamond-like forms which are electrically non-conductive and generally considered to be unsuitable), that the basel plane of graphite has much higher corrosion resistance than the edge-plane, and also reports for the first time that the corrosion rate is first-order in water activity.

Pt corrosion (dissolution to solvated ions) is also a serious problem in phosphoric acid fuel cells. Bindra et al. (8) measured the solubility of bulk Pt in concentrated H_3PO_4 at 443 and 463 K. The potential dependence of

the solubility was found to be RT/2F, consistent with the Nernst equation for Pt/Pt^{2+} (as opposed to Pt/Pt^{4+}). Using these data, Ross (9) was able to show that Pt dissolution becomes rapid for cell voltages above 0.8V and will result in loss of Pt from the cathode and reprecipitation at the anode. Pt corrosion is a phenomenon for which there appears to be no "fix" other than operating the fuel cell in such a way as to avoid cathode potentials above ca. 0.8V for extended periods of time.

MOLTEN CARBONATE FUEL CELL (MCFC)

The MCFC component assembly follows the bipolar principle of the PAFC stack, but employs completely different materials. A schematic diagram of the basic repeating elements in an MCFC stack are shown in Figure 2. The electrolyte is a molten form a a mixture of lithium- potassium- and/or sodium carbonates, with the most commonly chosen composition being 62% Li_2CO_3 - 38% K_2CO_3 (usually referred to as a "tile" as the carbonate salts and the aluminate powder are hot-pressed to form a solid piece) at 923 K. The ionic current in the cell is carried by the carbonate ion, so the half-cell reactions at the anode and cathode are different from their PAFC counterpart. In this case, the cathode reaction is the reduction of oxygen by reaction with carbon dioxide to form carbonate ion,

$$1/2\ O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-} \qquad [4]$$

and at the anode hydrogen reacts with the carbonate ion to form carbon

dioxide and water,

$$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^- \qquad [5]$$

To maintain invariance in electrolyte composition with time, it is necessary to recycle carbon dioxide from the anode gas to the cathode gas streams continuously. The current collector material is typically a high chromium stainless steel, and the electrodes are nickel-based materials, a metallic porous nickel at the anode and a porous nickel oxide at the cathode.

The components subject to corrosion and the nature of the corrosion processes is reasonably well inderstood from post-mortem analyses of tested cells. With 316 stainless as current collector, after a few thousand hours of operation moderate to severe attack of the anode current collector was observed (10), with much less attack observed at the cathode. The region of the current collector most severely attacked was the point of contact with the anode material, and thus in contact with the carbonate melt, and areas near the point on contact, probably owing to creep of carbonate onto the current collector. Early cells showed severe attack in the wet-seal region (10). The wet-seal is a component that seals the anode from the external ambient gas. The wet-seal corrosion problem appears to have been solved by use of an aluminum coating on the collector housing that forms a dense insulating layer of Al_2O_3 that breaks the ionic path between the housing surface and the electrolyte and prevents galvanic corrosion (11). A more serious and as yet unsolved corrosion process is the finding of significant

solubility of NiO in the carbonate melts in use. The early theoretical analysis of metal corrosion in molten alkali carbonates by Ingram and Janz (12) presumed that NiO dissolution occurred by the reaction

$$NiO + CO_2 \rightarrow Ni^{2+} + CO_3^{2-} \qquad [6]$$

and predicted that NiO solubility would increase in proportion to CO_2 pressure. In the early period of MCFC technology development, it was felt that the CO_2 partial pressure at the cathode would be within a range where NiO would not be significant. A more recent theoretical analysis of NiO dissolution by Shores et. al. (13) and experimental results from Orfield and Shores (14) have shown the importance of other dissolution reactions for NiO, particularly those involving the formation of soluble anions according to

$$NiO + 1/2\ Li_2CO_3 + 1/2\ O_2 \rightarrow NiO_2^- + 1/2\ CO_2 + Li^+ \qquad [7]$$

$$NiO + Li_2CO_3 \rightarrow NiO_2^{2-} + 2\ Li^+ + CO_2 \qquad [8]$$

Reaction 6 predicts an oxygen partial pressure dependance for NiO solubility that would enhance solubility with pressurization of the reactant gases. Recent measurements of NiO solubility and transport in the electrolyte tile have been reported by Baumgartner (15). NiO solubility is now recognized as a serious technical problem for MCFC technology (16) and alternative cathode materials are being sought.

General corrosion studies of simple metals and selected alloys in molten carbonate melts date back to the earliest time of interest in MCFC technology. A relatively recent bibliography on molten salt corrosion was compiled by Janz (17) which covers several types of molten salts in addition to carbonates and provides a useful index to the literature prior to about 1976. The review article by Selman and Maru (18) contains a section on carbonates and includes references from the Russian literature. Work addressing corrosion phenomena specific to MCFC technology is much less plentiful. Rapp (19) presented an excellent theoretical overview of the requirements for corrosion resistance in MCFC applications which has served as a quide for much of the recent work.

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FIGURE CAPTIONS

1. Schematic diagram of the repeating components of the phosphoric acid fuel cell power generation section.

2. Schematic diagram of the repeating components of the molten carbonate fuel cell power generation section.

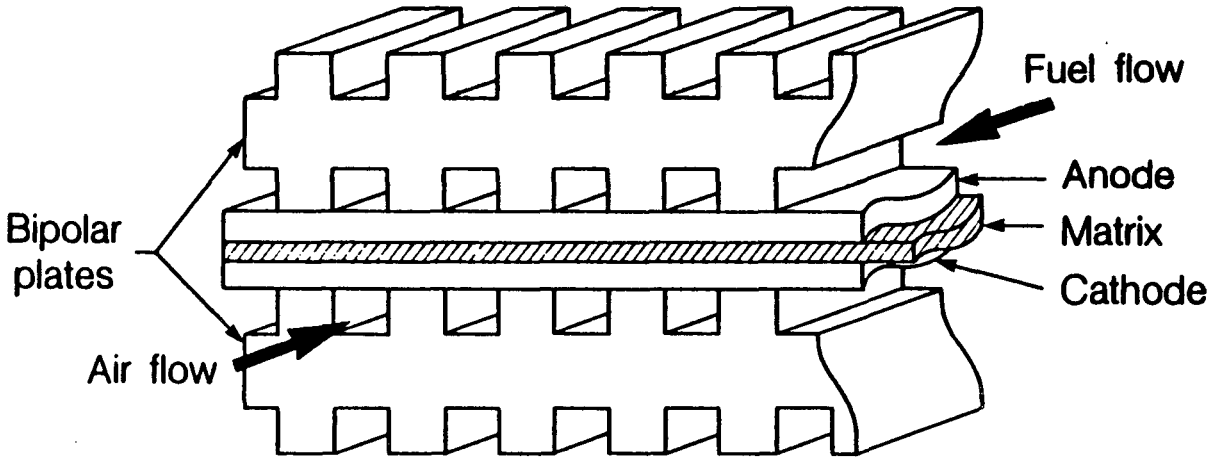

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Fig. 1

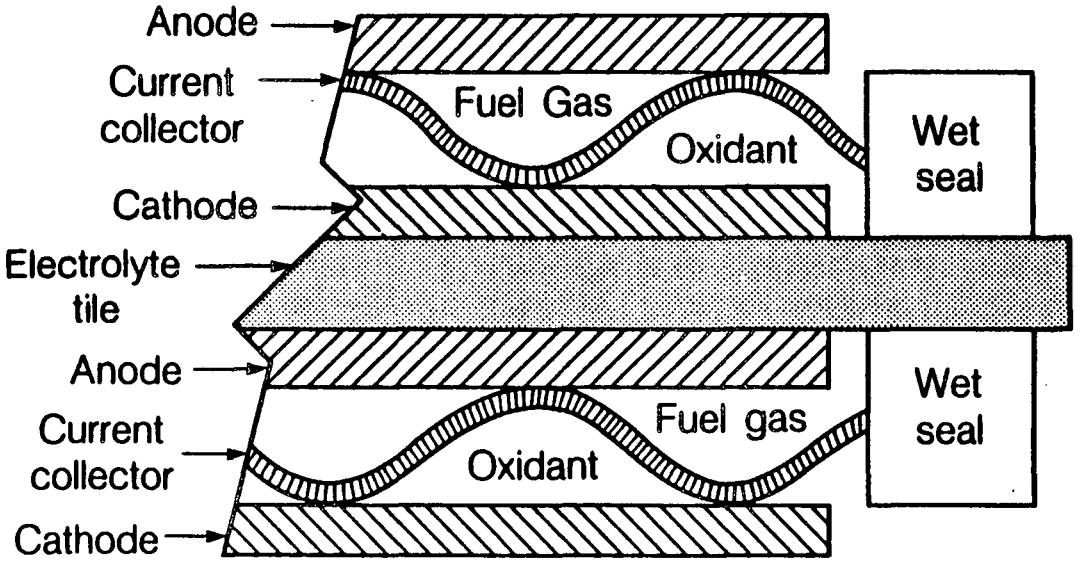

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Fig. 2

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