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DEACTIVATION AND POISONING OF FUEL CELL CATALYSTS

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A fuel cell is an electrochemical energy conversion device which converts chemical to electrical energy without the use of an intermediate mechanical (or Carnot) cycle. At present, all fuel cell devices approaching real practice convert only hydrogen directly, and not any form of hydrocarbon. This is not a fundamental limitation but a practical limitation due to the absence of a catalyst which provides direct conversion of hydrocarbons at a practical rate (and cell potential). With the exception of special purpose fuel cells that use pure hydrogen as fuel, e.g. space and deep-sea vehicles, fuel cells have a fuel conditioning (steam reforming and water gas shifting) unit that converts a hydrocarbon fuel into a hydrogen rich gas that is fed to the electrical generating unit. Typical hydrocarbon fuels in use are natural gas, naphtha, and methanol. Heavier fuels or coal gases are problematic and are the subject of research and development designed to broaden the fuel range for future fuel cell technology. In this paper, we will not discuss the problems of catalyst deactivation in the fuel conditioning unit, since these are conventional catalysts and reactors that are covered by other papers in this symposium. The discussion here will be restricted to the unique aspects of catalysts in the electrical generating unit of fuel cells.

Fuel cell catalysts suffer from deactivation and poisoning phenomena

that are either identical to or strongly analogous to the processes which occur in heterogeneous catalysis. As in conventional catalytic reactors, fuel cell performance is degraded by poisoning from impurities, loss of surface area of noble metal, and physical deterioration of the catalyst structure. Unlike conventional catalytic reactors, where some catalyst regeneration capability is usually designed into the system, the fuel cell catalyst is an integral part of the physical structure of the electrical generator, and there are at present no designs which are able to employ catalyst regeneration. Therefore, catalyst deactivation and poisoning phenomena are even more serious technological problems in fuel cells than in conventional reactors.

The deactivation and poisoning phenomena to be reviewed in detail in this paper are: the poisoning of anode (fuel electrode) catalyst by carbon monoxide and hydrogen sulfide; the deactivation of the cathode (air electrode) catalyst by sintering; the deactivation of the cathode by corrosion of the support. The fuel cell technology discussed in the context of these phenomena is the phosphoric acid fuel cell. The operating conditions for this technology are typically 180-210 C, 95-99% acid, and in pressurized versions 50-120 psig.

The anode catalyst is Pt supported on a conductive, high area carbon black, usually at a loading of 10 w/o. This catalyst is tolerant to some level of carbon monoxide or hydrogen sulfide or both in combination, the level depending on temperature and pressure. Carbon monoxide poisoning has been studied extensively, including detailed adsorption studies at various temperatures and pressures. Based on these studies, predictive models have been developed that effectively predict anode tolerance to

carbon monoxide. Much less is known about hydrogen sulfide poisoning, and at present the tolerance levels can only be described parametrically. Typical tolerance levels are 2% CO, and 10 ppm H₂S.

The cathode catalyst is typically Pt supported on a graphitic carbon black, usually a furnace black heat-treated to 2700⁰ C. The Pt loading is typically 10 w/o, and the dispersion (or percent exposed) as-prepared is typically 30%. The loss of dispersion in use depends on the operational parameters, most especially the cathode potential history, i.e. higher potentials cause more rapid decrease in dispersion. Relatively few fundamental studies of this phenomenon have been published, and what are available are contradictory; the mechanism of loss of dispersion is not well known. The graphitic carbon support corrodes at a finite rate that is also potential dependent. Support corrosion causes thickening of the electrolyte film between the gas pores and the catalyst particles, which in turn causes increased diffusional resistance and performance loss. In addition, support corrosion may also cause loss of Pt into the separator. Support corrosion appears to be the life limiting factor for phosphoric acid fuel cells.

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