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ABSTRACT

Fuel cells are the most promising power sources for electric vehicles and do not suffer from the inherent limitations of efficiency, energy density, and lifetime, as encountered with all types of batteries considered for this application. The projected performance of fuel-cell-powered vehicles is comparable to that of the internal combustion and diesel engine vehicles but with the additional advantages of higher fuel efficiency, particularly with synfuels from coal. The ideal fuel for a fuel cell power plant for electric vehicles is methanol. This fuel is reformed to hydrogen, which combines with oxygen from the air in an acid electrolyte (phosphoric, solid polymer, or superacid) fuel cell to produce electricity. Though the phosphoric acid fuel cell is in the most advanced state of development (mainly for power generation applications), the solid polymer and superacid electrolyte fuel cells are more promising for the transportation application because of the faster oxygen reduction kinetics (and hence potential for higher power densities) and shorter start-up times. Alkaline electrolyte fuel cells can be used only with pure hydrogen (which causes a weight or energy penalty for any of the methods it can be carried on board the vehicle), but have the best potential for minimizing or eliminating noble metal requirements. The paper summarizes needed areas of research (i.e., reduction or elimination of noble metal loading, finding CO tolerant electrocatalysts, finding less expensive solid polymer electrolytes, synthesis of and elucidation of higher molecular weight superacids) to advance fuel cell technology for vehicular applications.

KEYWORDS

Fuel cells, power sources for electric vehicles; electrolytes [phosphoric acid, solid polymer (Nafion), superacid (e.g., $CF_3SO_3H_2$)]; electrocatalysis; CO poisoning; sintering of platinum; oxygen reduction kinetics; double layer; adsorption.

RATIONALE AND ELECTROCHEMICAL REQUIREMENTS

The energy crisis after the oil embargo in 1973 stimulated research and development of power plants for electric vehicles. Vehicles with batteries face serious problems such as the need for long periods of recharging, low energy density, and poor cycle life. In the 1970s, concentrated efforts were made to develop advanced batteries with performance characteristics superior to those of lead-acid batteries. Though many of these battery systems showed promise initially, the research and development programs demonstrated difficulties in overcoming the above problems. If electric vehicles are to approach the performance characteristics of diesel-engine- and internal-combustion-powered vehicles in respect to range and acceleration but with more efficient fuel utilization, the most promising source appears to be a fuel cell using reformed methanol. In order to advance fuel cell technology for vehicular applications, several electrochemical considerations are essential. This paper focuses on these aspects in an analysis of the potential fuel cells as power sources for electric vehicles.

In establishing the needs in terms of performance of fuel cells for transportation, the first parameter that has to be defined is the type of fuel. One of the most promising fuels is methanol, (McCormick and coworkers, 1979), which can be obtained from coal, natural gas, or biomass and can easily be converted to H_2 in a reformer.

It is possible that in the future, an abundance of H_2 fuel will be produced because of the development of nuclear and fusion reactors. However, efficient and safe ways to store, transport, and handle this fuel will have to be devised.

From the computer simulation studies of Lynn (1980), it is possible to list the electrochemical requirements of fuel cells for transportation, and these are presented in Table 1. Parameters such as the current density, cell potential, noble metal loading, and internal resistance are related to the kinetics of the electrode processes and the conductivity of the electrolyte. Also, the performance and the life of the cell are related to CO chemisorption on the electrocatalyst particles, the sintering of these particles, and electrochemical corrosion of the support materials.

TABLE 1 Background - Essential Electrochemical Requirements of Fuel Cells for Electric Vehicles

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- High Power Density (>130 mW/cm^2)
- High Efficiency (>30%)
- Low Oxygen Overpotential (<400 mV)
- Fast Start-up Time (<5 min)
- Fast Response Transients
- Lifetime of 5,000-6,000 h with Operation Under Simulated Vehicle Operating Conditions
- Stability of Cell Component Materials at Close to Open Circuit Potentials
- Optimize Systems Engineering of Methanol Reformer and Fuel Cell
- Reduction in Noble Metal Loading; Finding Noble Metal Substitutes; Low Cost of Other Cell Components
- Minimal Poisoning of Anode by Impurities

Table 2 shows the main characteristics of the promising types of fuel cells for electric vehicles. The electrochemistry of each of these systems will be presented in the following sections.

TABLE 2 Promising Types of Fuel Cells for Electric Vehicles

Fuel	Electrolyte	Operating Temperature	Electrocatalysts
Methanol	85-100% H_3PO_4	150-225°C	Pt; intermetallics; alloys; nonmetals (Organic, inorganic)
Methanol	SPE-Nafion	80-150°C	Same as above
Methanol	Superacids-TFMSA, Higher Homologs	60-150°C	Same as above
Hydrogen	25-50% KOH	60-90°C	Same as above and nonnoble metals, e.g., Ag with and without additives

Phosphoric Acid Electrolyte Fuel Cell

The phosphoric acid fuel cell is in the most advanced state of development, and its potential for vehicular application is currently under investigation at Los Alamos. The cell needs a relatively high temperature of operation (~200 C) to overcome the low conductivity of the electrolyte and the slow kinetics of the oxygen reduction reaction. Recently a study of the interfacial characteristics between mercury electrodes and 95% phosphoric acid using thiourea as a probe species was carried out in our laboratory (Gonzalez, Hsueh, and Srinivasan, 1981). The results showed that the double layer is thicker in phosphoric acid (6Å) than in aqueous media (4Å). This means that the electron transfer during oxygen reduction at the electrode-phosphoric acid interface occurs over a wider barrier than at an electrode-aqueous electrolyte interface and hence can be expected to be considerably slower in the former case. Also, it was found that H_3PO_4 is more strongly adsorbed than water. Thus, the adsorption of reactants and intermediates, which leads to faster reaction rates, will be more difficult in concentrated phosphoric acid than in aqueous electrolytes. This is confirmed by the experimental results that the oxygen reduction kinetics is two orders of magnitude faster in dilute H_3PO_4 than in the concentrated acid (Hsueh and others, 1982).

In the phosphoric acid fuel cell, the electrocatalyst consists of platinum particles on a conducting carbon substrate. The platinum can be poisoned by chemisorption of CO contained as impurity (~1%) in reformate fuels. At temperatures exceeding 180°C, this effect is not too serious, and about 1% CO can be tolerated. Also, it has been observed that via an electrocrystallization process the Pt particles tend to sinter (Kinoshita, 1979) with the consequent loss of active area. A third problem presented by the electrocatalyst is the loss of platinum on the electrolyte side. This could be related to corrosion processes of the platinum and of the carbon support when close to the open circuit potentials. This shows the need for electrochemical research oriented toward finding suitable substitutes for noble metal electrocatalysts and carbon supports. Some metal-organic complexes show good performance (Walsh, 1980) at temperatures up to 120°C but are unstable in the phosphoric acid environment above this temperature.

Alkaline Electrolyte Fuel Cell

The alkaline electrolyte was the first to be developed, but progress has not been too evident because of the stringent limitation imposed that the inlet gases must not contain even trace amounts of CO_2. The electrochemistry of these cells is highly satisfactory because at relatively low temperatures (<100°C) the oxygen reduction kinetics even with non-noble metal catalysts (Ag) is sufficiently fast (Mund, Richter, and von Sturm, 1[illegible]; McBreen and others, 1980). These cells need to operate with a circulating electrolyte. Because of this, internal resistances tend to be relatively high, making it difficult to attain high current densities. Thus, for transportation applications, the power output from cells for start-up and acceleration is very limited (McBreen and others, 1980), requiring hybrid configurations involving secondary batteries. These problems could certainly be improved, but the development of the alkaline electrolyte fuel cells is tied to the availability of pure H_2 as well as to the advancement of ways of storing and handling this fuel.

Solid Polymer Electrolyte Fuel Cell

At present, solid polymer electrolyte fuel cells use Nafion as the electrolyte (McElroy, 1968). This membrane is quite expensive; it is predicted to have a lifetime in fuel cells (100,000 h) that far exceeds the needs for transportation applications (5,000 h). Enhanced oxygen reduction kinetics on platinum in this medium and low internal resistances make it possible to achieve higher power densities than with other types of fuel cells. Further electrochemical research, systems design, and engineering are still needed prior to the development of power plants for vehicular applications. The main problem with this type of cell has been water management when operated above 100°C because the drying out of Nafion makes it nonconducting. Several methods are being explored to keep the membrane wet. The present platinum loading is about 10 times higher than that for the phosphoric acid fuel cell. However, power densities in the solid polymer electrolyte fuel cells are about three times higher than in the phosphoric acid fuel cell. Efforts to lower noble metal loadings by use of supported electrocatalysts are still necessary. The solid polymer electrolyte fuel cell has in common with alkaline and superacid electrolyte fuel cells a low temperature of operation (<100°C), which means a faster start-up time, a very important factor in transportation applications. On the other hand, the problem of CO chemisorption at these temperatures may be enhanced, which again points to the need for more electrochemical research leading to electrocatalysts that are tolerant to CO.

Superacid Electrolyte Fuel Cells

At present, the only superacid commercially available is trifluoromethane sulfonic acid (CF_3SO_3H, TFMSA). Interest in this acid is based on the fact that the oxygen reduction reaction in aqueous TFMSA is much faster than in concentrated phosphoric acid (Appleby and Baker, 1978; Srinivasan and Olender, 1977). As discussed above, this can be explained partly by a reduced thickness of the double layer in the aqueous medium. Recently, the authors investigated the double layer properties of mercury electrodes in solutions containing $CF_3SO_3^-$ anions (Gonzalez and Srinivasan, 1981). It was determined that $CF_3SO_3^-$ adsorbs very weakly on electrodes and even desorbs at sufficiently anodic potentials. Thus, the presence of these anions in the electrolyte should not interfere with the adsorption of reactants or intermediates for the oxygen reduction reaction.

Early work with TFMSA involved the use of the monohydrate in systems similar to those using phosphoric acid. Because the monohydrate wets Teflon, research on this acid as the electrolyte was steered in the direction of aqueous solutions (George, 1981). TFMSA has a relatively high vapor pressure. Consequently, efforts are being focused on the synthesis of higher homologs such as tetrafluoroethanedisulfonic acid (Walsh and Eynon, 1980). This acid does not wet Teflon so readily because of a higher sulfonic group/fluorine atom ratio.

Because of the enhanced oxygen reduction kinetics in these superacids, it is expected that fuel cell power densities will be twice as high as those obtained in PAFCs. This means that there is room for electrochemical research toward reducing the noble metal loading or the use of nonnoble metal catalysts.

CONCLUSIONS

Electrochemical considerations are essential in determining the suitability of particular fuel cell systems for transportation applications. Fundamental research is needed on all four types of fuel cells in areas such as the effects of electrode materials and electrolyte composition on the oxygen reduction kinetics, electrosorption of CO on noble metals and alloys, electrocrystallization processes leading to the sintering of catalyst particles, and the development of nonnoble metal catalysts. Needed areas of research are listed for each type of fuel cell in Table 3.

TABLE 3 Needed Areas of Electrochemical Research on Fuel Cells for Electric Vehicles

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- o Phosphoric Acid Fuel Cells
  - Improvements in Oxygen Reduction Kinetics
  - Evaluation of Performance of Cell Under Simulated Vehicle Operating Conditions
  - Reduction in Noble Metal Loading
- o Alkaline Fuel Cells
  - Efficient CO_2 Removal Membrane for Operation With Reformed Methanol
  - Lower Internal Resistance of Cell
  - Substitutes for Noble Metals
- o Solid Polymer Electrolyte Fuel Cells
  - Low Cost Ion Exchange Membrane
  - Efficient Water Management
  - Reduction in Noble Metal Loading
- o Superacid Fuel Cells
  - Selection and Synthesis of Higher Molecular Weight Acids
  - Acid Concentration Management With TFMSA
  - Substitutes for Noble Metals

At the same time, it must be kept in mind that the performance and lifetime of a fuel cell system are dependent on the operational characteristics. Until the present time, most studies have been carried out under continuous operation at nearly constant power levels for power generation applications. For this reason, investigations are under way at Los Alamos National Laboratory to examine the variation of performance of fuel cells when subjected to simulated drive cycles and to elucidate the mechanism of performance degradation.

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