A UNIQUE CLASS OF ALTERNATIVE CATALYSTS FOR FUEL CELL APPLICATIONS THAT REPLACE THE NEED FOR PRECIOUS METALS

by

Dr. Patrick G. Bailey
P.O. Box 201
Los Altos, CA 94023-0201

Abstract

A method has been found that allows the replacement of precious metals with non-metal alternative materials for use as the required catalysts in various fuel cell applications. The amount of the precious metal currently used for the catalyst per fuel cell is substantial, and is a significant fraction of the non-variable cost of the entire fuel cell unit. Through the use of a recently developed trade-secret process, a class of non-metal materials can be manufactured into a metal-like polymer that behaves electrically in an identical manner as do the precious metals during normal fuel cell operation. Samples of these alternative catalysts have been manufactured using an inexpensive process developed and protected under trade secret agreements. Actual small-scale fuel cell demonstration tests have been successfully conducted that verify the operational capabilities of these low-cost alternative catalysts in place of platinum and rhodium. The cost savings of using these alternative catalysts within large scale fuel cell power units is economically profound.

Introduction

A method has been found that allows the replacement of precious metals with non-metal alternative materials for use as the required catalysts in

---

* PO Box 201

Los Altos, CA 94023-0201
various fuel cell applications. Specific fuel cells of interest today, such as Permeable Exchange Membrane or PEM Fuel Cells, require the use of precious metal catalysts to provide for the electrical operation of the fuel cell. The amount of the precious metal necessary for commercially feasible lifetimes used for the catalyst per fuel cell is substantial, and will be a significant fraction of the non-variable cost of the entire fuel cell unit. Large systems of such existing fuel cell units are currently being considered for power load-leveling on a large residential scale, especially within the United States and Japan. Through the use of a recently developed trade-secret process, a class of non-metal materials can be manufactured into a metal-like polymer that behaves electrically in an identical manner as do the precious metals during normal fuel cell operation. The theory of the existence of such materials has been recently hinted at and documented in the materials processing and scientific literature. Actual samples of these alternative catalysts have been manufactured using an inexpensive process developed and protected under trade secret agreements. Actual small-scale fuel cell demonstration tests have been successfully conducted under the developer's funding that verify the operational capabilities of these low-cost alternative catalysts in place of platinum and rhodium. Further detailed tests are needed to verify the expected success to medium and large-scale fuel cell units. The cost savings of using these alternative catalysts within large scale fuel cell power units is economically profound.

The process used to manufacture the alternative catalysts is not an expensive process and is covered by a trade secret agreement. The materials produced in this process are very well suited for fuel cell applications for both small and large scale fuel cell energy production applications.

Fuel cells have been traditionally used for small applications, and are now finding more applications in the aerospace industry as energy storage devices, used when other energy may not be available. The capability of a fuel cell to reverse normal operation and covert electricity into stored chemical energy for later use has made their use very attractive in commercial power plant load leveling. Very large fuel cell units, about the size of tennis court complexes, are being considered and built for use in commercial city load leveling applications. Japan has an active interest in this area and has numerous fuel cells in commercial operation at this time. These large fuel cells currently require precious metal catalysts for their operation. Fuel cell industries and the electric utility companies in particular should be very interested in this method of completely replacing these expensive precious metal catalysts with an inexpensive alternative that operates with identical performance characteristics.

Theoretical Considerations

It is well known that science has classified materials into elements by the way that they interact with other elements. The discovery of the protons in the nucleus led to the assumption that each individual element had a specific number of protons, and since atoms are assumed to be electrically neutral, the number of protons would then determine the number of electrons orbiting that nucleus. In chemistry, students are taught that the number of electrons in the electron shell surrounding the nucleus and the number of vacancies in that shell pretty much determine what other elements that nucleus will combine with. So, the product compound then becomes more "stable" from a combined electron band point of view. When the neutron was discovered, it was found that different isotopes of the same element (having different numbers of neutrons and the same number of protons) can and do behave somewhat differently with other different elements and isotopes. Some kind of nuclear shell interaction effect was then included with the electron shell theory to explain this behavior. It is important to note that the experiments have always come first, and the nuclear theories followed - since the proof was there for anyone who was willing to take the time and trouble to see for themselves.

Now it appears that these electron and nuclear shell models are not completely adequate for explaining the behavior of elements under all conditions.

In examining the physics of nuclear fission, the two-center nuclear shell model was proposed in 1969. This model allows the nuclear fission process to be modeled like a large liquid drop model with the ability to change its shape and split into two smaller and more stable isotopes. Since then, it has been recognized that the atoms of elements are not always spherical, and can be better thought of as being prolate spheroids (cigar-shaped) or oblate (disks). The ability of a nucleus to have this deformed shape allows many interesting abilities that cannot be found in earlier classical nuclear theory. "The two-center shell model has provided a precise description of many nuclear phenomena. It has predicted many new fission processes as well as the fusion of light nuclei into superheavy nuclei." It has also led to the prediction of "a nuclear process called superasymmetric fission and the emission of a new type of radioactivity." "...called cluster radioactivity. The cluster is usually several times larger than an alpha particle." Such cluster radioactivity has been predicted "a comprehensive table of various kinds of cluster radioactivity for more than 800 kinds of nuclei." (Greiner and Sandulescu, 1990).

It has also been postulated that small aggregates of atoms in so-called microclusters could constitute a distinct phase of matter, that could have possible application to optics, electronics, and catalysis. "As the number of atoms in the cluster rises, the atomic orbitals combine to form molecular orbitals containing all the cluster's electrons; molecular orbitals then give way gradually to bands, or energy states, akin to solids." "The discovery that small changes in cluster size can produce large differences in adsorbtion behavior strengthens the notion that clusters represent a distinct phase of matter. It also suggests that specifically adsorptive clusters might be chosen by size and deposited on a substrate for industrial catalysis, whereas unreactive clusters might be selectively deposited to form protective coatings. Such a capability would represent a great advance, because most industrial catalysts are still the products of a black art. Now, for the first time, the secrets of catalysis are beginning to yield to the tools of cluster science." (Duncan and Rouvray, 1989).

Previous Funding and Arrangements

Work in this project has been underway since 1977, and over $2 1/2 M in funds have been spent in developing, characterizing, and testing the procedures to produce the alternative catalysts and to apply the results of these findings in small fuel cell demonstration tests. The positive results from these tests have been extremely encouraging. A recent financial downturn has restricted the research group's private funding and their ability to perform the larger fuel cell tests. It is strongly felt that the funding requested will be adequate to provide the test results and data necessary to advance into full scale commercial applications.

Test Results

A great deal of experimental research has been performed to carefully compare the characteristics and operational capabilities of the alternative catalysts with platinum and rhodium catalysts that are currently used in fuel cell operation. This research was privately contracted by the developer with researchers at a recognized independent experimental facility. The results of the two-year research program are documented in detailed proprietary progress reports.

Earlier tests compared the hydrogen oxidation activity in acid solution of electrode structures prepared from the alternative catalysts supplied by the developer with commercially available platinum and rhodium prepared catalysts. Typical polarizations for hydrogen oxidation for these commercial catalysts were 10 to 47 mV at 100 mA/sq.cm and 26 to 80 mV at 200 mA/sq.cm (vs. a dynamic hydrogen electrode). Electrode structures made with the

alternative catalysts exhibited electrode polarizations that were also within these operational ranges.

A major conclusion of this early study was that the alternative catalysts supplied by the developer "all appear to be potentially electrochemically active materials, thus a composition containing mixtures of these materials may not require noble metal separation of these species."

Later experiments included fuel cell tests using a solid polymer electrolyte cell configuration. For these tests anode electrodes were prepared from commercial platinum, commercial rhodium, and the alternative catalyst materials. These anodes were tested with standard anode cathodes as a hydrogen/hydrogen cell (hydrogen pump) and as a hydrogen/oxygen fuel cell. The half-cell performance of the commercial catalysts performed in the range of 20 to 40 mV at 100 mA/sq.cm in both of these cell tests.

A conclusion of that study was: "Promising performance was demonstrated by anodes containing (a mixture of the alternative catalyst) materials. Performance in hydrogen pump and in hydrogen/oxygen fuel cell mode indicated reasonable performance in the range of 100 to 200 mA/sq.cm."

Additional catalyst activation procedures were then investigated to evaluate the electrochemical performance of the alternative catalysts in five specific fuel cell applications in which there is a definite need for a low cost catalyst system:

1. Solid polymer electrolyte fuel cells operating on contaminated hydrogen fuel gas [considered for long range transportation applications in the 20 to 40 kiloWatt (kW) power range]

2. Phosphoric acid fuel cells operating on carbon monoxide contaminated hydrogen fuel gas [considered for dispersed power stations requiring 50 to 250 kW, and major utility applications of 1,000 to 25,000 kW (1 to 25 megaWatts)]

3. Electrowinning of zinc and copper.

4. Chlor-alkali cell processes.

5. Water electrolysis and hydrogen gas production.

The results of these testing programs were very encouraging in some areas and inconclusive in other areas. During the entire testing process, various preparation methods for producing the alternative catalysts and for mounting the fuel cell electrodes were tested and evaluated. Some of the catalysts tested did not function at all, and some functioned at only marginal levels. Certain specific alternative catalysts were found to operate

quite well. From the conclusions of a later report: "Life testing of a (specific alternative) catalyst under hydrogen oxidation conditions in a solid polymer electrolyte cell was performed. The cell voltage at 150 mA/sq.cm was relatively stable over 24 hours of operation at 100 to 150 mV."

Two major conclusions resulted from these testing programs. First that the alternative catalysts did show tolerance to the inclusion of carbon monoxide contamination of the hydrogen gas. {We note that platinum is an excellent hydrogen oxygen catalyst but is poisoned by carbon monoxide gas.) Second: that the alternative catalysts tested "have promise as catalysts for either H2 oxidation or H2 evolution in the solid polymer electrolyte cell; the former mode of operation would be applicable in fuel-cell configurations (medium to long term commercial application), the latter in water electrolysis (very long-range commercial application)."

Specific alternative catalysts were found to give very encouraging and highly positive test results. These alternative catalysts are thus proposed for further testing and upward scaling to commercial applications.

Proposed Research Program

A step-by-step research program is proposed that will repeat the previous test results on a small-scale fuel cell unit, and then scale up the size of the application to medium and large-sized fuel cells. The proposed research will only be concerned with the manufacture of the alternative catalysts and the testing of these three sizes of demonstration units. These tests will provide the proof of application and operation of the alternative catalysts. A follow-on program will apply these techniques to commercial applications, such as within the US and international utility industries.

The proposed research program is two years in duration and consists of the following seven logical project milestones:

- Funding Arrangements and Contractual Terms
- Alternative Catalysts Production in Small Quantity
- Small and Medium Demonstration Fuel Cell Construction
- Small and Medium Demonstration Fuel Cell Testing
- Large Demonstration Fuel Cell Construction
- Large Demonstration Fuel Cell Testing
- Full Scale Implementation Project Proposal and Cost Estimate

The manpower required to perform these tasks and the cost estimate for this two year proposal are defined in detail in the IANS Grant Proposal Questionnaire available during this conference (copies may also be requested by mail to the author). The project team feels that the above milestones are in logical order and can be met within the two years indicated. In the recent past there have not been nor are there envisioned any problems that would interfere with initiating and completing any of these milestones within the project scope and time frame.

Summary

A method has been found that allows the replacement of precious metals with non-metal, non-radioactive alternative materials for use as the required catalysts in various fuel cell applications. It works.

The theory of the existence and operational capabilities of such materials has been recently hinted at and documented in the materials processing and scientific literature. These alternative catalysts have been manufactured using an inexpensive process developed and protected under trade secret agreements. It's use has been demonstrated and tested with small fuel cells and the positive results obtained are extremely encouraging. These successes necessitate the application of these technologies in the large commercial fuel cell industry.

This paper summarizes only a small portion of the information that has been generated experimentally and theoretically to support of the development of these alternative catalysts. This knowledge is proprietary and is covered by trade secrets. Additional information relating to this material is available through the use of existing proprietary information exchange agreements.

References

Greiner, W., and Sandulescu, A. (1990) "New Radioactivities," Scientific American, March 1990, p. 58.

Duncan, M. A., and Rouvray, H. R. (1989) "Microclusters," Scientific American, December 1989, p. 110.