# An Approach for Enhancing the Stability of Bipolar Plate Materials Through Application of a Glassy Carbon Coating

by

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## Introduction

In some instances, the stability of the bipolar plate has been identified as a limiting factor in attaining long life in hot phosphoric acid fuel cells. In the operating fuel cell, the bipolar plate, made of a graphite-resin composite, serves to separate the individual galvanic cells and to conduct the electrical current from cell to cell.

The stability of the bipolar plate under hot phosphoric acid fuel cell conditions has been studied by several companies. Both chemical resistivity to hot phosphoric acid and plate mechanical strength have been cited as obstacles to achieving the long-term service life goal. The dominant corrosion process on the cathode side of the plate is electrochemical corrosion, which is significantly high at the cathode potential. The porosity of the plate material can be a contributing factor; bipolar plates were reported to soften and to swell around the edges when in contact with phosphoric acid in a fuel cell.

In the work described herein, the program was directed initially toward the development of new low-temperature treatments (900°C) and/or compositions of bipolar plate materials to give improved corrosion resistance. The heat-treatment temperature was later extended to 1700°C. This approach involves the use of glassy carbon, either as a protective, impermeable, corrosion-resistant coating or as a constituent of the composite plate material.

Doping with boron to make the glassy carbon approach yet more effective was also investigated. In previous work, the authors correlated differences in the electrochemical behavior of samples of heat-treated Vulcan XC-72R with the structural properties of the carbon produced, as reflected by lattice parameters.[1] Doping of Vulcan XC-72R with boron proved to have a beneficial effect; samples of heat-treated boron-doped Vulcan XC-72R were shown to have enhanced resistance to corrosion compared with undoped Vulcan heat-treated at the same temperatures. Changes in BET surface areas and lattice parameters as well as in electrochemical behavior showed evidence that the addition of boron resulted in "graphitization" that was not achieved by heat-treatment alone. Boron-doping may enable the production of a bipolar plate that is at least as corrosion-resistant as is allowed by present technology, at a lower fabrication cost.

## Results and Discussions

The corrosion characteristics were determined for commercial glassy carbons, in order to evaluate the corrosion resistances of these materials in comparison to those of materials which were at that time utilized in bipolar plates. Glassy carbon samples received from Carbone Lorraine were tested for corrosion properties at 0.9V in 200°C phosphoric acid; their corrosion characteristics were most encouraging.

There are two distinct aspects of the effort involved in covering a carbon plate with a glassy carbon layer, both of which were addressed. The first is the production of the glassy carbon itself from a suitable precursor; the second is the application of an adherent, cohesive coating of the glassy carbon to the carbon plate. In pursuit of the former, the following parameters were examined to determine their effect on the corrosion and physical properties of the glassy carbon produced, the polymeric precursor, the final heat-treatment temperature, the duration of hold at final temperature, the temperature ramp, and the addition of a possible graphitization catalyst, boron.

The polymers investigated to determine their suitability as precursors were: polyfurfuryl alcohol phenolic, polyfurfural phenolic, modified furfuryl alcohol, phenolic, and polyvinyl chloride. The possibility that boron acts as a catalyst for carbonization of the resin was also investigated. Efforts were focused on Varcum 29-703 (a two-stage phenolic resin from Reichhold) as the precursor for the glassy carbon coating to be applied to the bipolar plate material, since that is the resin employed by Westinghouse in the fabrication of the composite bipolar plates.

Small "chip" samples of glassy carbons prepared from the polymeric precursors served as samples for measuring the corrosion characteristics of the glassy carbons thus produced. Glassy carbons were produced which possess great tolerance to hot phosphoric acid at the potentials of test. Heat-treatment to 1200°C was found to be more effective than to 900°C. The time of hold at final temperature did not appear to have an effect on either the weight losses or the corrosion characteristics of the glassy carbon produced.

Difficulties were encountered with the application of a glassy carbon coating to the plate material, perhaps due in part to the warping and shrinking of the resin during carbonization. It was theorized that a coating prepared from a glassy carbon constituent intimately mixed with a carbon black would not have the problems associated with dimensional stability during carbonization to the extent that glassy carbons do.

Such a coating was prepared from Consel (steam-activated acetylene black) and Varcum 29-703 on a sample of flat bipolar plate received from Westinghouse. The coating is cohesive and adhesive. Particularly significant is the fact that the application of the coating was successful without a pretreatment of the plate material.

As stated above, there are two separate aspects involved in covering a carbon plate with a glassy carbon layer. The second, the application of an adherent, cohesive coating of the glassy carbon to the carbon plate, may require pretreatment of the plate material. Much work has been done with the pretreatment of the carbon fibers to form composites of graphite/carbon fibers bound with resins, particularly epoxies. Several methods involved some means of oxidation of the fiber surface. It was felt that certain of these techniques may be applicable or adaptable to the present work. Dry oxidation was chosen for initial experiments. An adherent coating of glassy carbon was applied to bipolar plate material which had been oxidized in air. The precursor used was polyfurfuryl alcohol phenolic; attempts to coat the untreated plate material with glassy carbon prepared from this resin had previously proved unsuccessful.

Glassy carbon coatings based on degraded polyvinyl chloride were successfully applied to both as-pressed and heat-treated (900°C) Westinghouse bipolar plate material. Vygen 65, a highly cross-linked, unstabilized polyvinyl chloride resin (General Tire) was utilized as the precursor. the method of applying the coating to an as-pressed plate has two advantages: the aforementioned success in applying the coating without pretreatment of the plate material; additionally, one heat-treatment step is eliminated.

Work was begun on the approach of doping the resin-graphite composite material itself with boron. Westinghouse provided samples of their bipolar plate composite mixes, which were doped with boron, and returned to Westinghouse to be formed into plates according to their procedure and then heat-treated to various temperatures. Initial testing indicates that the boron has a beneficial effect on the corrosion resistance of the plate material.

## Experimental

With the exception of polyvinyl chloride, the glassy carbon precursors were polymerized according to recommendations or information supplied by the vendors. For polyvinyl chloride, the patent by Rossi served as a guide.[2] In the case of the boron-doped samples, boron was added in the form of boric acid. The method of addition depended on the resin. The polymerized resins were carbonized in Lindberg tube furnaces, with maximum heating capabilities of 900°C, 1200°C and 1700°C. The furnaces were computer-controlled to give the desired heating rate and hold times.

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## References

1. Proceedings of the Workshop on the Electrochemistry of Carbon, S. Sarangapani, J. R. Akridge and B. Schumm, eds. The Electrochemical Society Inc. PV 84-5

2. Ronald C. Rossi, U. S. Patent 3,854,979 (1974)