

Development of Fuel Cell Stack Durability based on Actual Vehicle Test Data: Current Status and Future Work

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ABSTRACT

Nissan began developing a fuel cell vehicle (FCV) in 1996 and has participated in fleet programs in the USA (CaFCP) and in Japan (JHFC) since 2001 to promote FCV development and to educate the public on the benefits of FCVs. The X-TRAIL FCV (latest model) is equipped with various new technologies, including a fuel cell stack that was engineered in-house. The X-TRAIL FCV has evolved from a test vehicle in 2002 to today's model, which provides the utility and conventional conveniences consumers would demand. The cruising range, acceleration performance and maximum speed are competitive with existing gasoline vehicles. However, to enable commercialization of FCVs, further improvements in performance and durability as well as reduction in costs will be necessary. Therefore, Nissan is investigating several different approaches for reducing cost and improving durability and performance.

This paper describes the durability of the fuel cell stack on the X-TRAIL FCV. Stack durability was estimated from the results of durability tests conducted with power train test benches. Stack performance degradation is considered in terms of three factors--start-stop, load cycling and high potential (idling)--which might be the main causes of the performance decline. Each degradation ratio is discussed in detail. The accuracy of the stack life estimation is also described on the basis of a comparison of FCV test data obtained on public roads, including proving ground and durability test data. A new fuel cell stack is now being developed, aimed at achieving lower cost, higher performance and greater durability. The measures taken to improve the durability of the new stack are also described.

INTRODUCTION

There are growing expectations that hydrogen-powered fuel cell vehicles (FCVs) will be an effective means of reducing the environmental impact associated with vehicle use, specifically by reducing atmospheric emissions of greenhouse gases like carbon dioxide (CO₂). Vehicle manufacturers are moving ahead with R&D programs to develop FCVs. For example, Nissan is vigorously pushing forward with the development of FCVs as part of the development of various technologies for reducing vehicle emissions of CO₂ under the Nissan Green Program 2010 (NGP2010) announced in 2006.

Aoyama (et al.) described the present status of FCV development at Nissan in detail.⁽¹⁾ It was shown that the latest model of the X-TRAIL FCV provides power performance equal to that of ordinary internal combustion engine (ICE) vehicles. However, a wide range of issues, including reduction of cost, weight reductions through performance improvements, and FC stack durability, must still be addressed in order to promote widespread use of FCVs.

In this study concerning FC stack durability, an investigation was made of the degradation condition of the FC stack used on the latest X-TRAIL FCV model. The results were compared with preliminary estimations of stack degradation in order to verify the accuracy of the method proposed here for estimating FC stack performance degradation. The contributions of this stack degradation estimation method to the improvement of the durability of the next-generation FC stack are also described.

Table 1 Fuel cell operating modes and major types of degradation

Operating mode	Degradation	Main causes
Start-up	Cathode catalyst surface area loss Cathodic reactant gas diffusion deterioration	Cathode carbon support corrosion by high potential
Load cycling	Cathode catalyst surface area loss	Cathode catalyst dissolution by potential cycling
Idling (low current)	Cathode catalyst surface area loss Membrane proton conductivity loss	Cathode catalyst dissolution by high potential Chemical decomposition by peroxide (radical) attack Cathode catalyst poisoning by membrane fragments

METHOD OF ESTIMATING FC STACK PERFORMANCE DEGRADATION

This section outlines the method used to estimate the performance degradation of the FC stack on the X-TRAIL FCV. This method of estimating performance degradation was developed before an actual vehicle was built in order to make necessary estimates of stack durability and improve durability efficiently. Trying to investigate FC stack durability by building physical models and conducting durability tests and studies over a number of years would be time-consuming and costly. That approach was deemed to be an inefficient way of developing FC stack durability for FCVs.

MAIN CAUSES OF FC STACK PERFORMANCE DEGRADATION

The main causes of FC stack degradation in vehicle use are thought to be carbon corrosion at start-up, platinum (Pt) dissolution during load cycling and Pt dissolution and electrolyte membrane degradation during low current densities (high potential) such as when a vehicle is idling (Table 1). These causes have been reported in the literature and discussed in conference presentations.⁽¹⁾⁻⁽²⁾ There are other possible causes of stack degradation besides those listed in the table, but the results of analyses done to date have not shown substantial degradation, so it is presumed that the influence of other factors is minimal.

Carbon Corrosion

At start-up, both the anode gas channels and the cathode gas channels in the stack are filled with air (oxygen). When hydrogen is supplied to the anode in this condition, electromotive force occurs in the areas receiving hydrogen, but in the areas that do not receive hydrogen, the electromotive force produces a high electric potential on the cathode side. As shown in Fig. 1, this mechanism gives rise to degradation in the form of carbon corrosion.⁽²⁾⁻⁽⁴⁾ Carbon corrosion causes the catalyst layer to collapse, and simultaneously the supported Pt particles aggregate, resulting in a decline in performance.

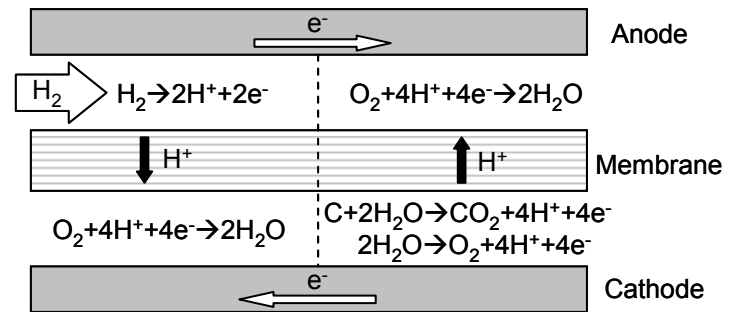


Fig. 1 Degradation mechanism at FC stack start-up

Pt Dissolution

During load cycling and idling operation, changes in the electric potential and the holding of a high potential oxidize and reduce Pt. As a result, the surface of some Pt particles dissolves to produce an ion state (Fig. 2). The dissolution of Pt reduces the Pt surface area compared with the initial condition, which causes performance to decline.^{(2),(5)-(12)}

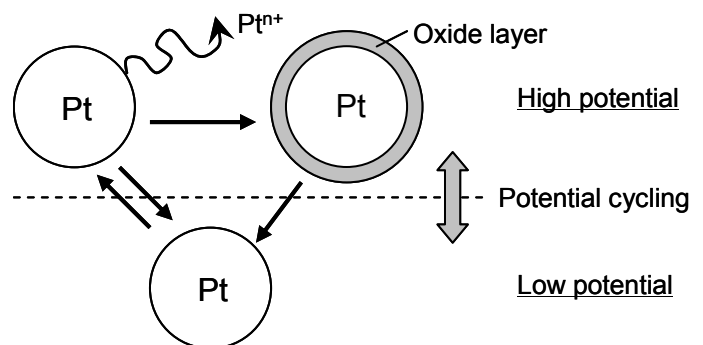


Fig. 2 Mechanism of Pt dissolution during load cycling

Electrolyte Membrane Degradation

It has been estimated that electrolyte membrane degradation during low-current densities (high potential) causes performance to decline through the following mechanism.^{(2),(13)-(16)} Hydrogen peroxides produced inside the electrolyte membrane decompose to form radicals that attack the membrane, thereby worsening the proton conductivity of the membrane, resulting in degradation of performance. However, it is known that serious degradation occurs under the harsh conditions

of high temperature and low humidity.⁽¹³⁾⁻⁽²⁰⁾ It is also known that FC stack performance declines due to catalyst poisoning by the decomposition products resulting from electrolyte membrane degradation.⁽²¹⁾ Under ordinary vehicle control conditions, the influence on performance degradation is not so large, as will be explained later.

SEPARATE ESTIMATION OF DEGRADATION UNDER EACH OPERATING MODE

Estimation of Degradation for Start/Stop Mode

Degradation that occurs during FC stack start-up and shut-down can be divided between these two processes. At start-up, the composition of the gases in the anode and cathode and the start-up control procedure cause the electric potential in the corroded part of the cathode to change, which varies the severity of the degradation that occurs. Assuming that the same start-up control procedure is applied every time, the oxygen concentration in the anode and cathode probably causes a pronounced difference in the degree of degradation. Even if all the oxygen in the cathode has been consumed at the time of shut-down, air permeates and diffuses from the gas seals of the FC stack and the piping at the inlet and outlet of the cathode. As a result, the inside of the cathode gradually changes to an air atmosphere. The inside of the anode also becomes an air atmosphere before long owing to the permeation of air (oxygen) from the cathode through the electrolyte membrane. In other words, degradation at start-up increases in proportion to the length of elapsed time since the last shut-down. For that reason, when estimating degradation at start-up in vehicle applications, it is necessary to ascertain the oxygen concentration in the FC stack at the time a vehicle is started.

The oxygen concentration in the anode and cathode was found in this study using the length of time between shut-down and start-up (referred to here as standing time) as the parameter. A test rig was used to conduct a start-up durability test under a condition with an air atmosphere in the anode and cathode. The amount of component degradation that occurred under various oxygen concentrations (0-21%) was also found in separate tests. The data thus obtained were used to estimate degradation sensitivity to the oxygen concentration. A frequency distribution of the standing time (from stop to start) for ordinary ICE vehicles was found and used in estimating start-up degradation.

The rate of degradation at shut-down was calculated in repeated start-stop cycles conducted with a test rig. It was assumed that loading cycles are applied to the FC stack when it is shut down under the same conditions every time.

In line with the preceding discussion, the following data are needed to estimate the degradation of FC stack performance at start-up and shut-down.

- Durability bench test data for repeated start/stop operation during a short period of time
- Durability bench test data for repeated cycles in which the FC stack is completely changed to an air atmosphere in the interval from shut-down to start-up
- The degree of start-up degradation relative to the oxygen concentration in the stack
- The oxygen concentration in the FC stack relative to the standing time (from shut-down to start-up)
- A frequency distribution of the standing time of ICE vehicles

Degradation Estimation for Load Cycling Mode

During FCV operation, the output of the FC stack changes every time the driver depresses or lets up on the accelerator pedal, causing the current and voltage of the stack to change. This produces potential cycling in the cathode catalyst layer that gives rise to degradation of performance. Three load patterns were defined for the FC stack--low load, medium load and high load cycles--as shown in Fig. 3, and durability bench tests were conducted under each load pattern. Degradation that occurs under load cycling was then estimated taking into account the number of times and the duration frequency of the three load patterns, based on the output frequency of ICE vehicles.

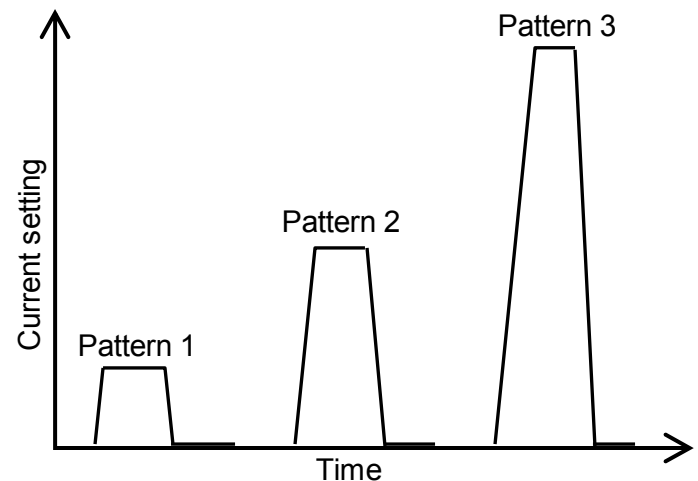


Fig. 3 Durability patterns defined for load cycling

To recapitulate the preceding analysis, the following data are needed to estimate the degradation of FC stack performance during load cycling.

- Durability bench test data for low, medium and high load cycles
- The distribution of the output frequency of ICE vehicles

Degradation Estimation for Idling (Low Current) Mode

As noted earlier, electrolyte membrane degradation and dissolution of the Pt catalyst layer are assumed to be the two principal causes of FC stack performance degradation during idling operation. It is thought that Pt dissolution causes a larger decline in performance than electrolyte membrane degradation. This is attributed to the fact that the FC stack on FCVs does not constantly operate at high temperature nor does it constantly operate under a low current condition. Accordingly, in estimating degradation of performance for idling operation, bench tests were conducted under a condition where a low current density was continued for a certain length of time, followed by a larger current so as to change the electric potential. Degradation during idling was then estimated by taking into account the idling time of ordinary ICE vehicles based on their output frequency.

To recapitulate the preceding discussion, the following data are needed to estimate the degradation of FC stack performance under idling operation.

- Durability bench test data for load cycling that includes low current densities
- The distribution of the output frequency of ICE vehicles

DURABILITY OF ONBOARD FC STACK ESTIMATED FROM DURABILITY BENCH TEST DATA

As explained in the preceding section, the loads imposed on an FCV during real-world driving were estimated from the manner in which ordinary ICE vehicles are operated. Degradation of performance under each operating mode was then simply summed to estimate FC stack degradation. Figure 4 shows the ratio of the estimated degradation among the three operating modes.

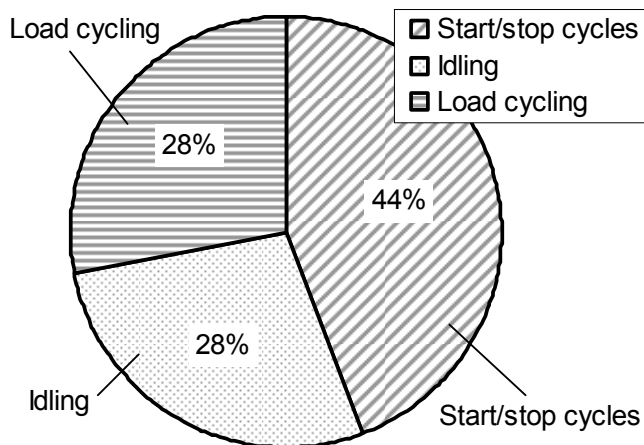


Fig. 4 Ratio of estimated FC stack degradation by operating mode

The results in the graph show that the start-stop mode accounted for 44% of the total degradation, representing an exceptionally large proportion. Both the load cycling mode and the idling mode showed approximately the same degree of degradation at around 28%. While degradation in the load cycling mode is large per unit of time, cumulative idling time is longer, which is probably why the two modes showed approximately the same values. Degradation can also be divided between that which occurs during start-up/shut-down and that which occurs during power generation (load cycling + idling). Degradation during start-up/shut-down accounted for 44% of the total and degradation during power generation accounted for 56%, indicating approximately the same relative degree of degradation.

While these results were estimated for the FC stack used on the X-TRAIL FCV, this method of estimating performance degradation can also be applied to other FC stacks by taking into account the control procedure at start-up/shut-down, the control procedure during power generation and other relevant conditions.

STACK PERFORMANCE DEGRADATION CALCULATED FROM VEHICLE DATA

TREND FOR DECLINE IN VEHICLE PERFORMANCE

To date, the latest model of the X-TRAIL FCV has been driven on public roads for over two years, or in some cases, for three years in Japan and overseas combined, including use at numerous events in North America and Europe. The vehicle system and the FC stack both continue to display high levels of reliability.

Figure 5 shows the change in FC stack performance as a function of the stack operating time for one vehicle that has a long cumulative operating time in Japan. FC stack voltage is shown along the vertical axis in relation to the FC stack operating time along the horizontal axis. These FC stack voltage data were extracted only for high load conditions above a certain specified current value. It is seen that FC stack voltage, i.e., performance, has gradually decreased as the cumulative operating time has increased. In order to quantify the degradation of each FC stack performance parameter, the FC stack voltage was averaged for every 100 hours of operating time. The values were then plotted to eliminate the influences of different operating environments, and linear approximations were made to calculate the performance degradation. In making the linear approximations, data that singularly deviated from a straight line was omitted. This method was used to express the levels of degradation for various FC stacks.