Journal of Power Sources 71 (1998) 150–155

Advanced PEFC development for fuel cell powered vehicles

Shigeyuki Kawatsu

Higashifuji Technical Center, Toyota Motor Corporation. 1200, Mishuku, Susono, Shizuoka 410-11, Japan

Abstract

Vehicles equipped with fuel cells have been developed with much progress. Outcomes of such development efforts include a Toyota fuel cell electric vehicle (FCEV) using hydrogen as the fuel which was developed and introduced in 1996, followed by another Toyota FCEV using methanol as the fuel, developed and introduced in 1997. In those Toyota FCEVs, a fuel cell system is installed under the floor of each RAV4L, to sports utility vehicle. It has been found that the CO concentration in the reformed gas of methanol reformer can be reduced to 100 ppm in wide ranges of catalyst temperature and gas flow rate, by using the ruthenium (Ru) catalyst as the CO selective oxidizer, instead of the platinum (Pt) catalyst known from some time ago. It has been also found that a fuel cell performance equivalent to that with pure hydrogen can be ensured even in the reformed gas with the carbon monoxide (CO) concentration of 100 ppm, by using the Pt–Ru (platinum ruthenium alloy) electrocatalyst as the anode electrocatalyst of a polymer electrolyte fuel cell (PEFC), instead of the Pt electrocatalyst known from some time ago. Published by Elsevier Science S.A.

Keywords: Fuel cells; Electric vehicles; Hydrogen; Methanol; Reformer

1. Introduction

The problem of global warming caused by the greenhouse effect of carbon dioxide (CO_2) contained in the atmosphere was noticed and regarded as a serious environmental issue in the latter half of the 1980s. CO_2 being emitted out of various sources, such as industrial and transport systems and even from ordinary homes may give a critical effect on the future of the earth. It is a fact that some aspects of the global warming mechanism still remain unclear, causing much controversy. However, one thing is positive—that is, maintaining a sound environment for the earth is an important responsibility of people who are engaged in automobile industry.

Efforts are being made at Toyota to develop various technologies simultaneously, including those on further enhancements of gasoline and diesel engines for the reduction of CO_2 in the atmosphere, as well as innovative technologies for hybrid vehicles, fuel cell powered vehicles etc. which are noticed as new power trains. In other words, Toyota's philosophy is to develop technologies with multifaceted approaches while exploring all possibilities/potentials to attain an 'ultimate ecology vehicle'. Fig. 1 shows the Toyota's image for CO_2 reduction.

Needless to say, a prerequisite of such an ecology vehicle is to become a vehicle that is gentle to environment, but 'being gentle to environment' alone cannot satisfy all of its requirements. The same as for any other vehicle introduced into markets, an ecology vehicle must be safe, convenient and comfortable.

Having noticed the high energy conversion efficiency of polymer electrolyte fuel cells (PEFCs), aggressive research and development efforts are being made at Toyota for the practical use of electric vehicles equipped with (PEFCs) – FCEVs – as the most promising candidates for the 'ultimate ecology vehicle'. The estimated values of CO_2 emissions of individual power sources are shown in Fig. 2.

2. Toyota FCEV (hydrogen-fueled)

Toyota developed and introduced a fuel cell electric vehicle (FCEV) in October 1996, as a near future generation vehicle. [1,2] Owing to the development of this Toyota FCEV, it became possible to install a fuel cell system under the floor of RAV4L, sports utility vehicle, by combining unique components developed by Toyota, such as the PEFC stack, metal hydride tank and synchronous permanent-magnet motor. Fig. 3 is a photograph showing the appearance of the hydrogen-fueled FCEV, while Fig. 4 shows the system structure. Table 1 shows the main specifications of the hydrogen-fueled FCEV.

0378-7753/98/$19.00 Published by Elsevier Science S.A.
PII S0378-7753(97)02740-7

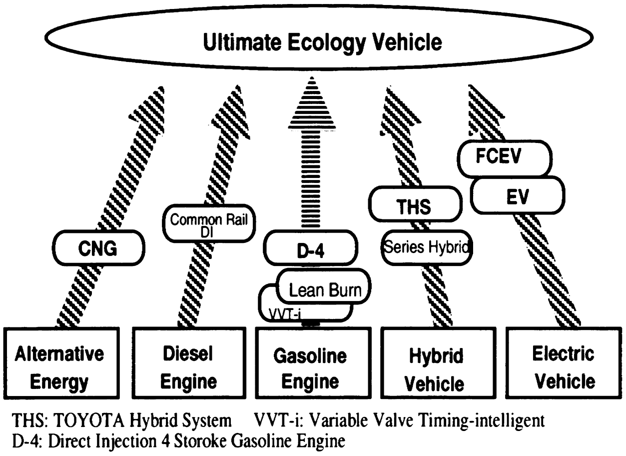

Fig. 1. Toyota's strategy for CO_2 reduction.

The Toyota FECV is provided with a hybrid electric vehicle system consisting of a PEFC and a secondary battery. The secondary battery plays multiple roles—load leveling against the load fluctuation, and storage of the electric energy regenerated by braking. The PEFC hybrid EV system with this structure is capable of operating the PEFC in a high energy conversion efficiency region, and attaining a higher fuel economy and a lower CO_2 emission level than those of conventional vehicles equipped with internal combustion gasoline engines.

3. Fuel supply method for PEFC

Toyota developed a high performance metal hydride capable of absorbing twice as much hydrogen than the conventional metal hydride [3,4]. It has become possible to store approximately 2 kg of hydrogen onboard, with the use of the new metal hydride by 100 kg. This is equivalent to the hydrogen storage capacity of 20 000 l or so at room temperature under ordinary pressure.

When considering the supply of hydrogen to the FCEV, however, the infrastructure for manufacture, transport and storage of hydrogen has not been adequately provided for. Hence, it will be necessary to wait until such an infrastructure is improved in future.

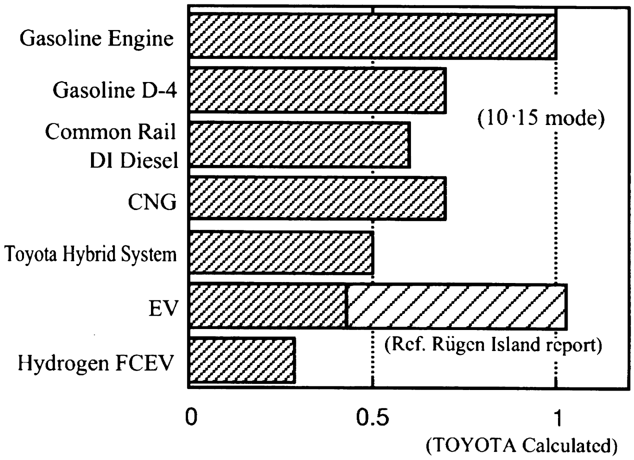

Fig. 2. CO_2 emission of each power source.

Fig. 3. Photograph of hydrogen-fueled FCEV.

Taking account of the problems when supplying hydrogen to the FCEV, the most promising option at present is to store methanol in the onboard tank as the hydrogen source for the FCEV, and to reform the methanol onboard, then to supply the hydrogen-rich reformed gas to the PEFC. This steam reforming method using methanol has several merits as described below.

1. a relatively low reforming temperature and a low energy consumption for reforming;
2. small amounts of by-products to be generated during the reforming process;
3. the capability to refuel in a short period of time, as in the case of gasoline;
4. existence of a relatively well established refueling infrastructure, with current markets for methanol engine vehicles;
5. availability of methanol handling technologies accumulated in the process of methanol engine vehicle development; and
6. independence from crude oil resources, as methanol is made from natural gas.

This steam reforming method is inconvenient in terms of a short vehicle running distance that can be covered per fueling when it is used in an existing internal combustion engine, since the calorific value of methanol is only a half that of gasoline as compared in the same volume. However, it does not become a problem in a system combined with a PEFC, since the fuel cell has a high energy conversion efficiency.

Considering the foregoing features, Toyota is also striving for the development of another type of FCEV using methanol as the fuel, which is considered as a step forward from the hydrogen-fueled FCEV.

Table 1

Specification of hydrogen-fueled FCEV

Vehicle	Based on	RAV4, 5-door
	Length/width/height (mm)	3975/1695/1635
Performance	Maximum speed	Over 100 km/h
	Range per hydrogen charge	250 km
Drive	Type	Front motor, front wheel drive
Drive motor	Type	Permanent-magnet, synchronous
	Maximum power	45 kW
	Maximum torque	165 Nm
Fuel cell	Type	Polymer electrolyte
	Length/width/height (mm)	1050/500/230
	Weight	120 kg
	Rated output	20 kW
Hydrogen storage device	Type	Metal hydride
	Lenth/width/height (mm)	700/450/170
	Weight	About 100 kg
	Hydrogen storage capacity	About 2 kg

4. Toyota FCEV (methanol-fueled)

Toyota developed and introduced a methanol-fueled FCEV in September 1997. This Toyota FCEV was developed based on the hydrogen-fueled FCEV developed in 1996, with further enhancements of performances of the components. By combining such features with a unique methanol reformer developed anew at Toyota, it became possible to install a methanol reformer and a fuel cell system under the floor of RAV4L, sports utility vehicle. Fig. 5 is a photograph showing the appearance of the methanol-fueled FCEV, while Fig. 6 shows the system structure. Table 2 shows the main specifications of the methanol-fueled FCEV.

5. PEFC operation with reformed gas

When reforming methanol onboard and generating a hydrogen rich reformed gas, then operating a PEFC with the reformed gas, it must be recognized that the reformed gas obtained by the methanol steam reforming is not hydrogen itself (i.e. pure hydrogen) but a mixed gas containing hydrogen as the main component.

There are a number of reports on effects of non-hydrogen components in the reformed gas. Take, for example, CO contained in the reformed gas, with a well-known adverse effect on PEFCs. It is confirmed that the PEFC performance deteriorates markedly where a Pt electrocatalyst is used with the reformed gas, even if the CO concentration is as extremely low as 20 ppm [5].

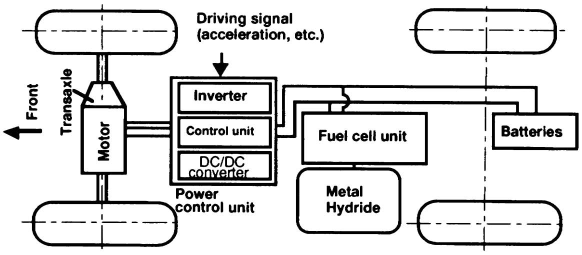

Fig. 4. System structure of hydrogen-fueled FCEV.

Fig. 5. Photograph of methanol-fueled FCEV.

It is necessary to overcome the adverse effects of non-hydrogen components contained in the reformed gas, in order to manufacture fuel cell powered vehicles equipped with the methanol reformer. Three approaches may be considered to solve the problems.

The first approach is to provide a gas cleaning mechanism for the methanol reformer, in order to eliminate all of the non-hydrogen components, so that pure hydrogen can be supplied to the PEFC stack.

The second approach is to provide proper durability that will not be affected by the PEFC output even if non-hydrogen components (e.g. CO, CO_2 and N_2) flow into the stack.

Upon application of PEFC to electric vehicles, the size and weight of PEFC must be so suppressed that the PEFC can be accommodated within a limited space, and the cost

Table 2

Specification of methanol-fueled FCEV

Vehicle	Based on	RAV4, 5-door
	Length/width/height (mm)	3980/1695/1635
Performance	Maximum speed	Over 125 km/h
	Range on full tank	500 km
Drive	Type	Front motor, front wheel drive
Drive motor	Type	Permanent-magnet, synchronous
	Maximum power	50 kW
	Maximum torque	190 Nm
Fuel cell	Type	Polymer electrolyte
	Length/width/height (mm)	1080/500/240
	Rated output	25 kW
Methanol reformer	Diameter/length (mm)	300/600
Fuel		Methanol

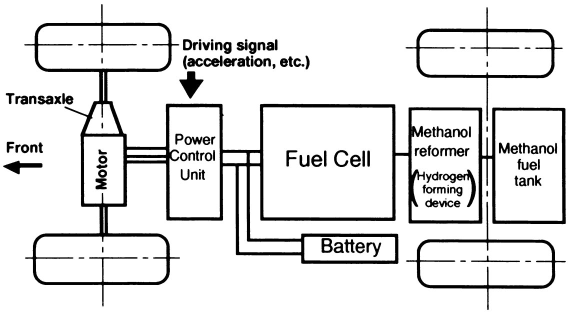

Fig. 6. System structure of methanol-fueled FCEV.

must be low enough to allow mass production, while maintaining the high energy conversion efficiency. In such regards, the first and the second approaches described above are not practical.

Thus the third approach was selected, namely, the installation of a shifter and/or CO selective oxidizer to the methanol reformer in order to reduce the CO concentration in the reformed gas to an allowable level, while providing an adequate level of CO tolerance in the PEFC anode electrocatalyst as well. Although this approach is most practical, it is vital to make well-balanced R&D efforts for both the methanol reformer and the PEFC itself.

Some technological outcomes gained with the third approach in the R&D process for the methanol-fueled FCEV will be described in the following, covering both the methanol reformer and the PEFC in detail.

6. Investigation results

6.1. CO reduction in the CO selective oxidizer

Using a model gas corresponding to that of reformed methanol, the CO selective oxidation performance of various catalysts was evaluated. As shown in Fig. 7, the Ru catalyst was found to be capable of reducing CO concentration in a wider operating temperature range and in a wider range of gas flow rates than that of the well-known Pt catalyst widely used for the CO selective oxidizer. These results indicate that, by using the Ru catalyst for the CO selective oxidizer, it is possible to supply reformed gas with a stably low CO concentration, continuously, against the load variations imperative for automobile operation [6].

Side reactions that occur in the CO selective oxidizer were studied to help to elucidate the reason for the excellent CO selective oxidation characteristics shown by the Ru catalyst. It is known that CO is generated by the reverse shift reaction, as expressed in Eq. (1), which occurs in the CO selective oxidizer [7].

$$H_2 + CO_2 \rightarrow CO + H_2O \tag{1}$$

In order to check the influence of reverse shift reaction, a model gas ($CO_2 = 25\%$, $H_2 = 75\%$) not containing CO was humidified and fed, without air, into a CO selective oxidizer. The CO concentration in the out going gas was then measured. It was clearly found that the amount of CO generated with the Ru catalyst was smaller than that with the Pt catalyst, as shown in Fig. 8.

Also known to occur in the CO selective oxidizer, where a noble metal catalyst is used, are the methanation reactions expressed in Eq. (2) and Eq. (3).

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{2}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{3}$$

To check the relationship between the CO and CH_4 concentrations formed, another model gas ($CO = 0.1\%$, $CO_2 = 25\%$, $H_2 =$ balance) containing CO was humidified and fed, without air, into a CO selective oxidizer. As the results in Fig. 9 indicate, as the catalyst temperature rose, the CH_4 concentration tended to increase while the CO concentration tended to decrease. Additional investigations indicated that these reactions occurred more readily when the Ru catalyst was utilized for CO selective oxidation [8].

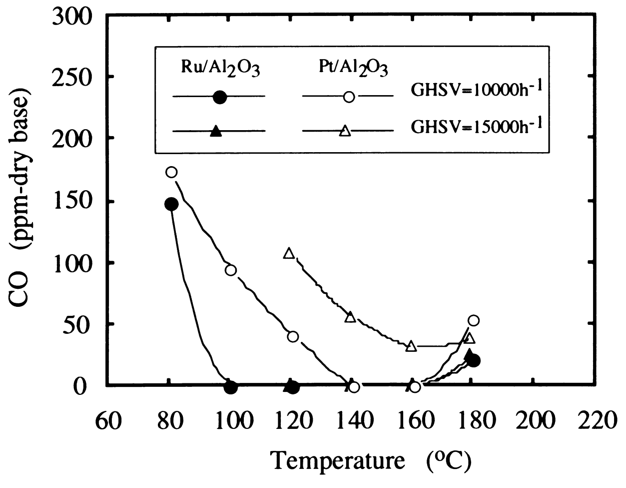

Fig. 7. CO oxidation performance of Ru and Pt catalysts.

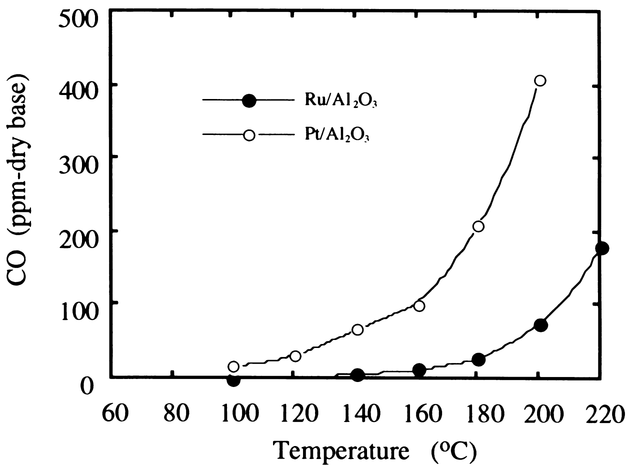

Fig. 8. Reverse shift reaction of Ru and Pt catalysts.

Detailed analysis produced further insight into the reverse shift reaction and methanation reactions, as well as the benefits of Ru utilization. In the case of an oxidizer using the Pt catalyst, CO is oxidized into CO_2, but then a portion reverts back to CO via the reverse shift reaction. Though this reversal also occurs where the Ru catalyst is used, it is to a lesser extent. In addition, with Ru, a portion of the CO generated by reverse shift reaction is converted to CH_4 as methanation reaction occurs. Consequently, the Ru catalyst is capable of producing lower levels of CO at the oxidizer outlet, owing, not only to reduced reverse shift reaction, but also to this CO to CH_4 conversion. Thus, in view of these results, as well as obvious cost advantage over Pt a compact, low cost methanol reformer, suitable for automotive use, can be devised by the application of Ru to the CO selective oxidizer. Another vital requirement is to make the price of Ru electrocatalyst drastically below the price of Pt electrocatalyst.

6.2. Prevention of CO poisoning with alloy electrocatalyst

In order to enhance the CO tolerance of the PEFC anode electrocatalysts, the CO tolerances of several Pt based alloy electrocatalysts were evaluated. Proper alloying of the experimental catalysts were confirmed by means of X-ray diffraction prior to evaluation. Utilizing a Pt cathode electrocatalyst and anode gas containing 100 ppm CO the samples were evaluated. Fig. 10 shows a comparison of the cell voltage measurements obtained at a current density of 0.4 A/cm^2. Only the Pt–Ru electrocatalyst exhibited a higher CO tolerance than the unalloyed Pt electrocatalyst.

Once the Pt–Ru electrocatalyst was identified as superior in CO performance, the alloy ratio was then optimized, as was the active layer thickness and supporting process of the Pt–Ru electrocatalysts. Using the knowledge obtained by these optimization efforts, a new type of Pt–Ru electrocatalyst was prepared, and its performance in the PEFC was evaluated. As shown in Fig. 11, cell performance equivalent to that of a Pt electrocatalyst was obtained, and performance similar to that in pure hydrogen was obtained, even with gas containing CO concentrations of 100 ppm [9,10].

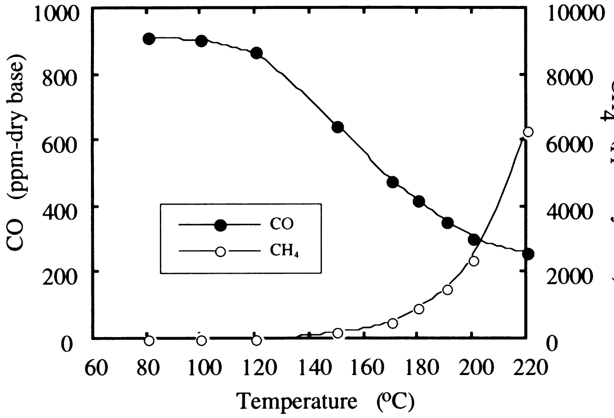

Fig. 9. CO methanation reaction of Ru catalyst.

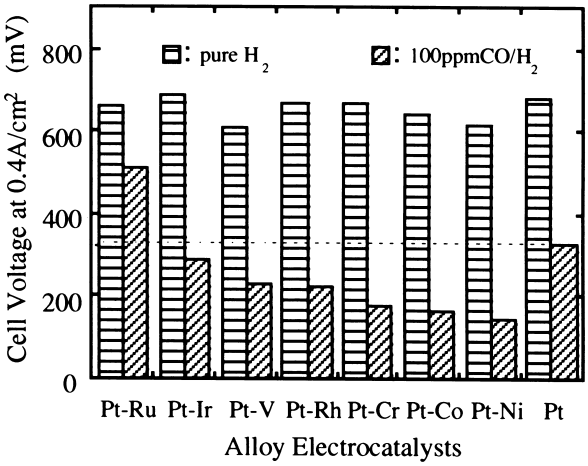

Fig. 10. CO tolerance of alloy electrocatalysts.

Regarding the prevention of the adverse effect of CO on PEFCs, the method to inject the air into the anode, the method to increase the fuel cell operating temperature to 100°C or higher, etc. have been proposed. However, the method to enhance the CO tolerance by using the Pt–Ru electrocatalyst has advantages of a simple PEFC system structure that can be controlled easily.

6.3. Prevention of the effects of CO_2

In addition to CO, reformed gas also contains CO_2. The probable detrimental effects on the PEFC, anticipated by the presence of CO_2, were investigated. As a result, two phenomena were found, namely, CO poisoning and CO_2 barrier effect. CO generated from the CO_2 contained in the reformed gas was found to poison the electrocatalyst [11]. Additionally, the CO_2 was found to stagnate around the anode. Due to the greater specific gravity of the CO_2, this stagnation impeded the diffusion of H_2 over the electrode's active layer and lowered performance.

As indicated earlier, the poisoning caused by CO can be successfully averted by the application of a Pt–Ru alloyed

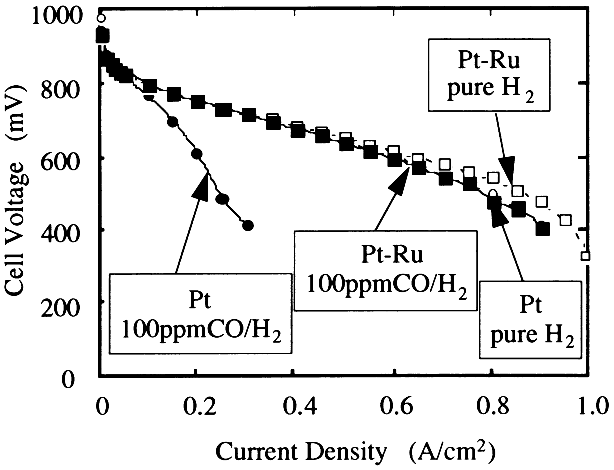

Fig. 11. CO tolerance of developed Pt–Ru electrocatalyst.

anode electrocatalyst to the PEFC. Regarding the control of the CO_2 barrier effect, optimization of the gas flow field shape was found to be the most effective. In other words, by combining the knowledge of electrocatalysts and gas flow fields, it is possible to prevent the adverse effects of CO_2 contained in the reformed gas [12].

6.4. Prevention of the effects of residual methanol

Because reformed gas was also found to contain some residual methanol, its effects on cell performance needed to be clarified. Cell performance was measured using a model reformed gas containing various concentrations of methanol. It was found that as methanol concentrations increased cell performance decreased. As expected, Pt electrocatalyst poisoning was one of the sources of the deteriorating performance. This poisoning was caused by the dissolution of methanol in the anode, resulting in the formation of poisonous aldehyde. The occurrence of another phenomenon was also confirmed, methanol crossover. Methanol contained in the anode gas permeated into the electrolyte membrane, reaching the cathode and reacting with oxygen contained in the air, thus, lowering the potential of the cathode.

Nevertheless, it was concluded that these adverse effects of residual methanol can be reduced to an acceptable level with the employment of both a Pt–Ru anode electrocatalyst, and optimization of PEFC operating conditions [13].

7. Conclusions

As described, extensive knowledge has been gained on electrocatalysts, electrode structures, gas flow fields, PEFC operating conditions, catalysts for CO selective oxidizer, etc. Through the application of this knowledge to the methanol reformer and PEFC, it has become possible to attain cell performance equivalent to that in pure hydrogen when utilizing a methanol reformer and reformed gas in the PEFC system.

FCEVs cannot be developed with the fuel cell related technologies alone. Such vehicles can be created only if technologies in various fields accumulated for conventional internal combustion engines vehicles, electric vehicles, hybrid vehicles, alternative fuels vehicles and so on are combined with the fuel cell technologies.

As mentioned at the beginning of this paper, Toyota is engaged in simultaneous developments of extensive technologies in various fields. There is a firm belief that such a comprehensive approach is a key to the practical applications of the ‘ultimate ecology vehicle’ which is gentle to environment, safe, convenient and comfortable to drive.

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