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R&D on metal hydride materials and Ni–MH batteries in Japan

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Abstract

The production of small-sized Ni–MH batteries, which amounts to some 40% of market share for portable appliances, is still growing because of an increase in the energy density per volume and also a reduction in price. Highly efficient electric vehicles (EV) propelled by a large-sized Ni–MH battery have been commercialized and have twice the driving range of a conventional EV with a Pb–acid battery. A hybrid vehicle with a high-powered Ni–MH battery has been brought onto the market, providing twice the gas mileage and half the CO_2 emissions of a gasoline vehicle. A fuel cell electric vehicle with hydrogen tank or methanol reformer, power-assisted by a Ni–MH battery, is under development. The Ni–MH battery will be a key component for the next generation of vehicles in addition to advanced information and telecommunication systems.

Keywords: Metal hydride materials; Ni–MH battery; Review

1. Background and market trend of Ni–MH batteries

Since the discovery of hydrogen storage alloys such as $LaNi_5$ in about 1969, extensive research has been carried out [1,2]. Initially, R&D on the alloys was focused on gas-phase applications such as hydrogen storage tanks, hydrogen purifiers and chemical heat pumps. In Japan, R&D on metal hydrides has been conducted mainly under ‘‘Sun-shine projects’’ sponsored by MITI, which were started just after the oil crisis in 1974. Osumi et al. [3–10] developed low-cost and practical alloys based on $MmNi_5$ (Mm, mischmetal), where properties such as the pulverizing rate and equilibrium hydrogen pressure of the alloys were controlled mainly by the alloy composition and heat treatment, providing a basic composition for battery alloys. Electrochemical applications of metal hydrides such as palladium electrodes was also started around 1970, but it was thought for a long time that the metal hydrides could not be used as a practical electrode material because of their high corrosion rates in alkaline solution, as reviewed by Bittner et al. [11]. What converted this weak functional material into a tough battery material was micro-designing the composition [12], surface structure [13,14] and microstructure [15] of the alloys, as reviewed by Sakai et al. [16].

In 1990, a nickel–metal hydride (Ni–MH) battery was commercialized in Japan using a combination of hydrogen storage alloys and battery technologies [17,18]. The Ni–MH battery has a 1.5–2 times higher energy density, fewer environmental problems and less resource concerns, but is much more expensive than a Ni–Cd battery. As the legal regulations for the disposal of Ni–Cd batteries became very strict, the market for replacing Ni–Cd batteries with Ni–MH batteries in the small rechargeable battery market expanded rapidly. In 1997, the production of Ni–MH batteries reached 570 million cells, as shown in Fig. 1, comprising 40% of the market share for small rechargeable batteries, including Ni–Cd and lithium-ion batteries. Sales reached 100 billion yen, comprising a 25% share for small rechargeable batteries and a 12.5% share of total battery sales (800 billion yen), including various primary cells and Pb–acid batteries in Japan, as shown in Fig. 2. It was estimated that approximately 5000 tons of rare-earth-based hydrogen storage alloys was produced for the Ni–MH battery in 1977.

Since 1990, large-sized Ni–MH batteries (100 Ah) and pure electric vehicles (PEV) propelled by batteries have been developed by many companies [19,20], demonstrating very high performances for EVs. A PEV with a Ni–MH battery has twice the driving distance compared to a conventional PEV with a Pb–acid battery. In 1996, Toyota finally decided to commercialize the very practical PEV ‘‘RAV4L EV’’ [21] using a Ni–MH battery produced by Panasonic EV Energy [22]. In 1977, Honda also started to lease Ni–MH-powered EVs (Honda EV Plus) in Japan and the US. In late 1997, a hybrid electric vehicle (HEV), power-assisted by a high power Ni–MH battery [23], was launched by Toyota [24], as shown in Fig. 3, which

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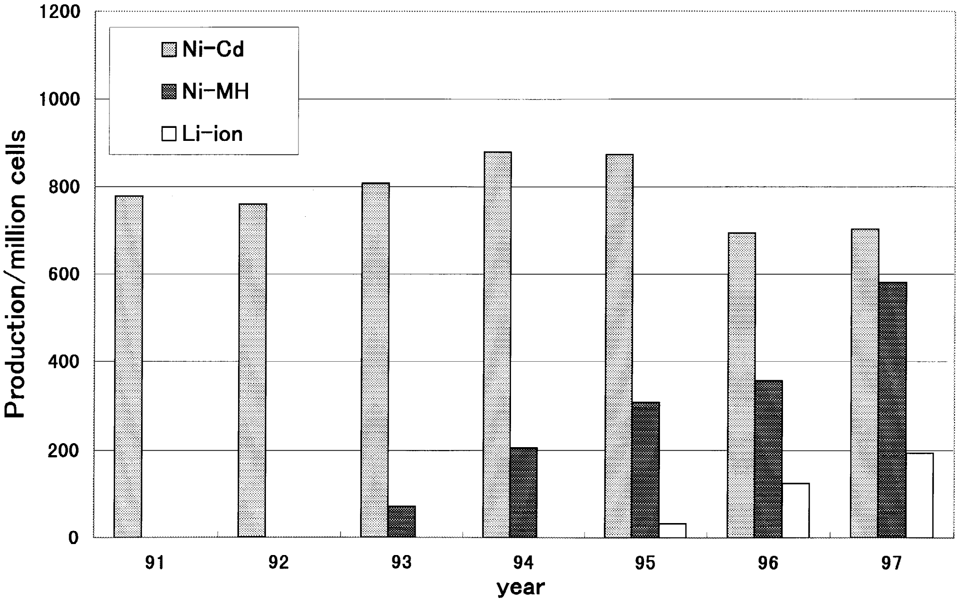


Fig. 1. Change in production of small-sized rechargeable batteries in Japan.

provided twice the gas mileage and half the carbon dioxide emissions of a gasoline car. The HEV market is now expanding rapidly with a production of 2000 units per month, with registration exceeding more than 16,000 units in November 1998.

Since the invention of the Pb–acid battery in 1859 and the Ni–Cd battery in 1899, no successful rechargeable battery has appeared for 90 years. The Ni–MH battery is the third practical secondary battery and is now a key component not only for advanced information and telecommunication systems, but also for the next generation of vehicles in which energy can be used efficiently with low emissions to the environment. The key materials for this high-tech battery would be hydrogen storage alloys.

2. Mechanism and materials for Ni–MH batteries

The charge–discharge mechanism for the Ni–MH battery is very simple, merely the movement of hydrogen between a metal hydride (MH) electrode and a nickel hydroxide (Ni) electrode in an alkaline electrolyte, as shown in Fig. 4. This ‘‘rocking-chair’’ mechanism for the Ni–MH battery is the same as that for a lithium-ion battery, being clearly distinguished from the conventional Ni–Cd and Pb–acid batteries based on the dissolution–precipitation mechanism for Cd or Pb in which a dendrite can be formed with change of electrolyte concentration during the charge–discharge process. This very simple

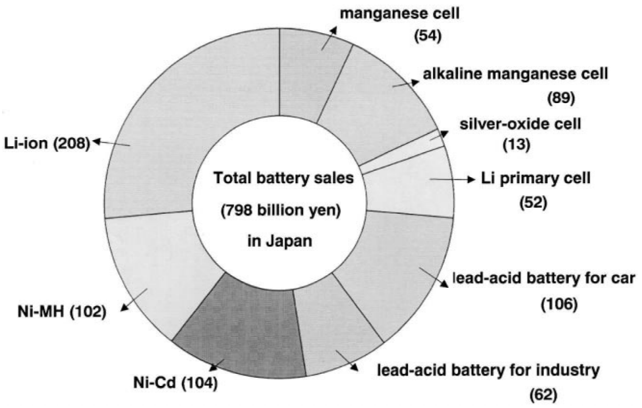


Fig. 2. Sales and market share of various batteries in Japan.

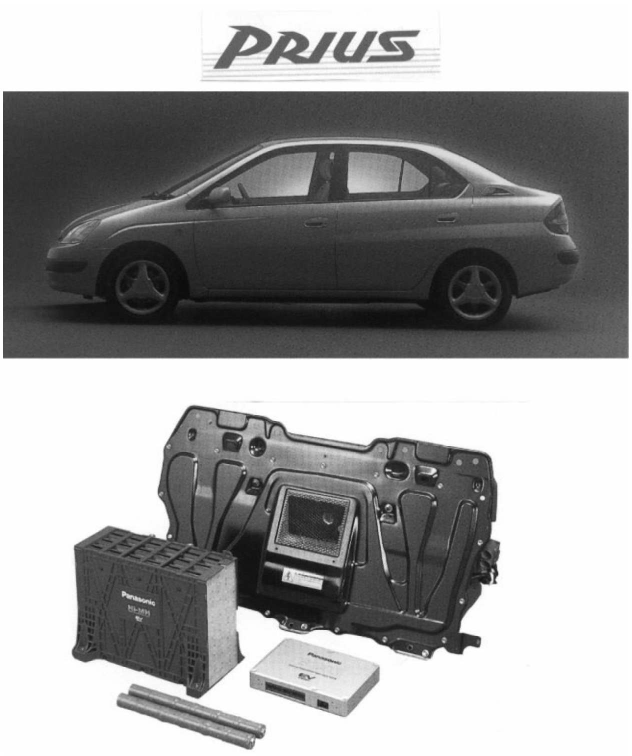
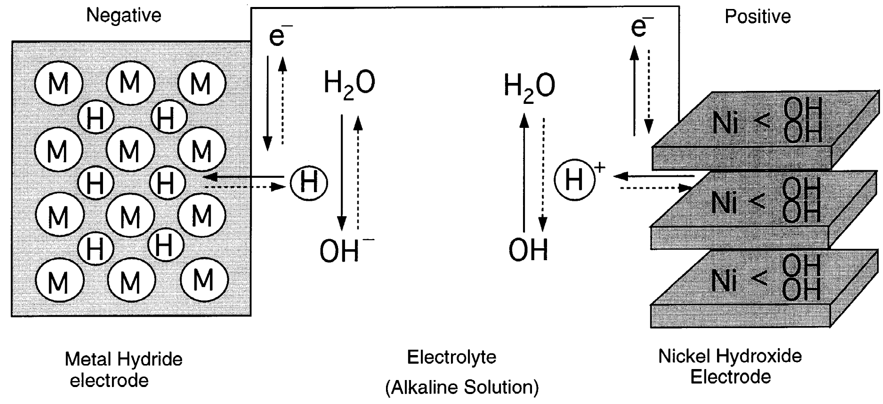


Fig. 3. Hybrid electric vehicle Toyota ‘‘Prius’’ and its battery pack.



Negative $M + H_2O + e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} MH_x + OH^-$

Positive $Ni(OH)_2 + OH^- \rightleftarrows NiOOH + H_2O + e^-$

Total $M + Ni(OH)_2 \rightleftarrows MH_x + NiOOH$

Fig. 4. Charge–discharge mechanism of a Ni–MH battery.

mechanism produces a long battery cycle life of more than 1000 cycles, a high power capability and a dense electrode structure. Both MH and Ni electrodes separated by a separator are spirally rolled for a sealed cylindrical cell or stacked for a prismatic cell. The Ni–MH battery has natural protection against over-charging or over-discharging, and recombining oxygen or hydrogen produced inside the cell to form water.

Battery materials and technologies adopted in commercialized cells are summarized in Fig. 5. The MH electrode is comprised of Mm(Ni,Co,Mn,Al)$_5$-based alloy powder, which is pasted on a nickel-plated punched steel sheet. Some additives such as corrosion prohibitive materials are added to the alloy powder [25]. The MmNi$_5$-based alloy is produced by a rapid solidification process [15], followed by suitable heat treatment for obtaining an homogeneous microstructure. The alloy surface is modified by a chemical and/or physical process in order to form a nickel-rich surface layer and also enlarge the surface area [13,14], improving the reactivity and corrosion resistance. Material design of the battery alloy can be carried out mainly by following three aspects [16]: (1) alloy composition, (2) bulk microstructure and (3) surface structure, as shown in Fig. 6. It is a very important feature of high-tech battery design that the most suitable battery performance for a special purpose can be designed arbitrarily.

MH electrode

1) $Mm(Ni,Co,Mn,Al)_5$
2) Surface modification
3) Rapid solidification process
4) Additives for corrosion protection(Y_2O_3,Yb_2O_3)

Current collector : Nickel-plated punched steel sheet

Ni electrode

1) High-density $(Ni,Co,Zn)(OH)_2$ powder
2) Surface-coating with conductive CoOOH
3) Additives for high temperature charging (CaF_2,$Ca(OH)_2$,Y_2O_3,Yb_2O_3)

Current collector : Foamed nickel or nickel fiber substrate

Separator

1) Polyethylene non-woven cloth surface-modified with SO_3H or COOH
2) Thin & dense cloth with micro-fiber

Fig. 5. Key materials and technologies for Ni–MH batteries.

The Ni electrode is comprised of spherical (Ni,Zn,Co)(OH)$_2$ powder which is packed in a foamed nickel or nickel-fiber mat substrate [26]. The (Ni,Zn,Co)(OH)$_2$ surface is coated with a CoOOH layer as a good electronic conductor. Additives for improving the charging efficiency at 60°C are added to the (Ni,Zn,Co)(OH)$_2$ powder [27]. Both electrodes are separated by a sulphonated or carbonated polypropylene (PP) separator for improving charge retention at high temperature [28].

3. Performance and applications of Ni–MH batteries

The energy density per volume for Ni–MH batteries has doubled from 180 Wh/l in 1990 to 360 Wh/l in 1997, a value comparable to that for the lithium-ion battery, as shown in Fig. 7. The high energy density was achieved by improving the quality of the materials and by increasing the packing density in the cell. Compactness is very important for portable appliances such as cellular phones

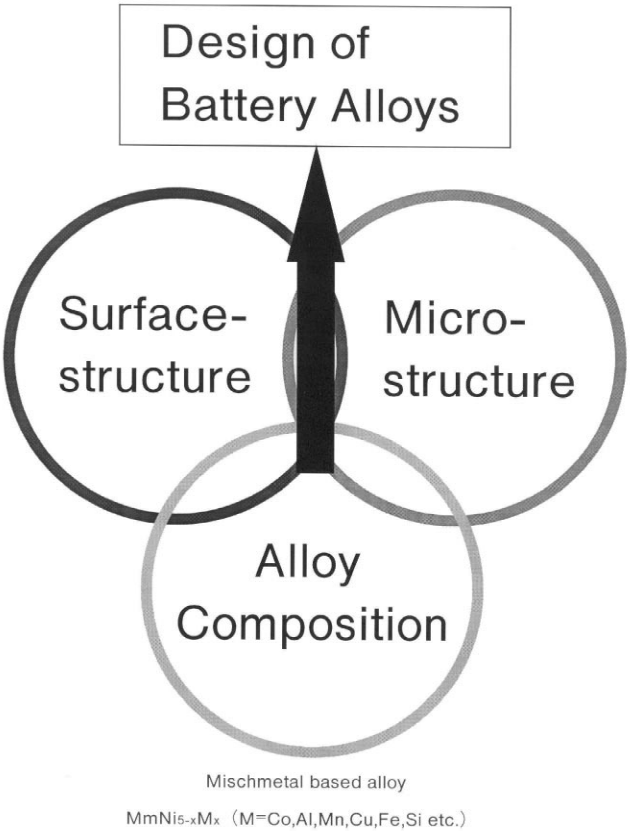


Fig. 6. Concept of material design for battery alloys.

and lap-top computers, making the Ni–MH battery very competitive. The energy density per weight has also improved from the initial 55 to 70 Wh/kg, but the battery weight is still more than 1.5 times heavier than that for the lithium-ion battery. Lighter weight hydrogen storage alloys such as V–Ni-based alloys [29–36] and Mg–Ni-based alloys [37–39] are under development. The cost per cell has greatly decreased to about one-third of the initial value, reaching almost the same level as that of the Ni–Cd battery and less than half of that of the lithium-ion battery.

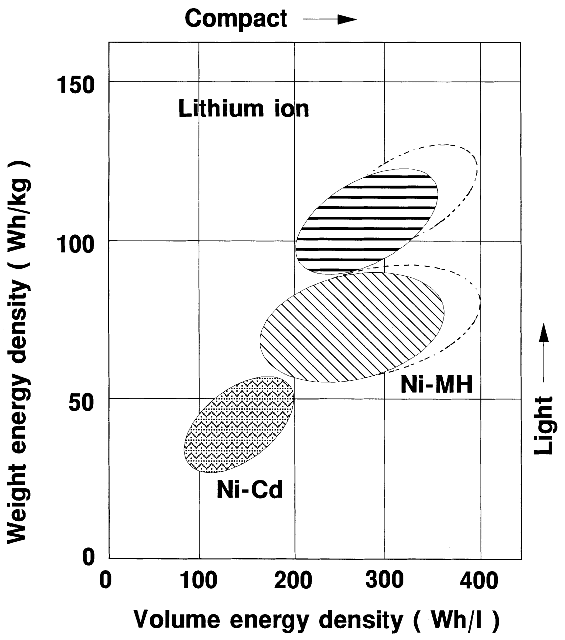


Fig. 7. Energy density per volume and weight for small rechargeable batteries.

The power capability has improved significantly from a 5 C rate (discharging rate at 1/5 h) to a 20 C rate by adopting a multi-tab current collector and by improving the surface conductivity of the electrodes, maintaining a 1.5 times higher energy density than the Ni–Cd battery. Recently, the high power MH battery was been placed on the power-tool market, in which, for a long time, only the Ni–Cd battery has been able to meet the high power demand. The environmental regulations for the Ni–Cd battery provided a good opportunity for the MH battery to enter the power-tool market. The market is estimated to be 500 million cells per year. Further improvement of the power capability is in progress for MmNi$_5$-based alloys. The high-power Ni–MH battery has found growing new markets such as hybrid EVs [23] and power-assisted bicycles.

4. Electric vehicles with a Ni–MH battery

4.1. Pure EVs

Scaling up of the battery has been carried out successfully by improving the high-temperature properties of the materials and also by a heat-management system. A 95 Ah,12 V module (EV-95) was stacked in series to make a battery pack (288 V, 95 Ah) for commercialized Toyota RAV4L EV, as shown in Fig. 8, which provides 50 kW power even in 90% depth of discharge (DOD), giving a top speed of 125 km/h [21,22]. Driving range per charge is 215 km at 10–15 mode. The battery life is more than 1000 cycles, giving a total driving range of 150,000 km. In cities, approximately 20–30% of the energy could be recovered by a regenerative baking system to save energy. The driving characteristics are almost the same as for a gasoline car, but the price of the EV (about 5 million yen) is more than twice that of a gasoline car.

Many automobile companies have developed EVs with Ni–MH batteries (Fig. 8) in addition to conventional Pb–acid batteries [19,20,40]. Since the space for battery storage is limited in passenger vehicles, a driving range of more than 200 km per charge is possible only for the Ni–MH battery and the lithium-ion battery, as shown in Fig. 9. The lithium-ion battery, which is comprised of a carbon-based negative electrode, a lithium cobaltate positive electrode and organic solvent electrolyte is lighter in weight, but it has the same compactness as the Ni–MH battery. The Nissan ‘‘Altra-EV’’ with a lithium-ion battery [41] has the same driving range as vehicles with the

Fig. 8. Pure EVs propelled by a Ni–MH battery.

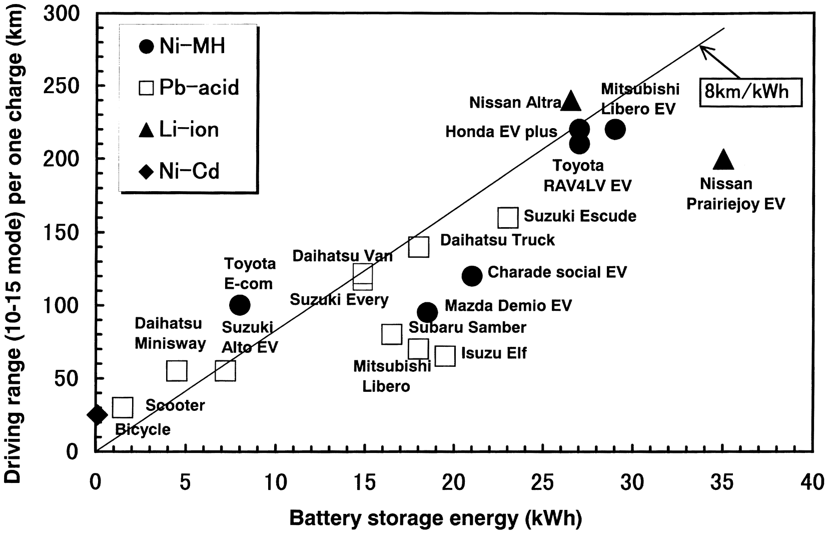


Fig. 9. Driving range vs. battery energy for commercialized and developed PEV in Japan.

Ni–MH battery. The energy density per volume is a more important factor for the PEV battery. The lithium polymer battery [42], which is comprised of a lithium metal negative electrode, a vanadium oxide positive electrode and polymer electrolyte, can provide higher energy densities per weight and volume than the Ni–MH battery.

The EV is expected to reduce the carbon dioxide emissions to less than half that of gasoline cars in Japan, according to a life-cycle assessment. The characteristic features for the EV, such as high cost, limited driving range and long charging time, still prevents widespread use. The small commuter car "Toyota e-com" (Fig. 8), which has a driving range of 100 km, has been developed in order to reduce the cost due to the battery [43]. The loaded battery EV-28 (28 Ah, 288 V) is one-third the size of the EV-95 for the RAV4EV, but still retaining half the driving range. The government has started a program to support half the price difference between the EV and a gasoline car. However, the introduction of the EV on a large scale is required to establish a new social system in which the users are not burdened with the high initial cost.

4.2. Hybrid EVs

The most successful ecological vehicle would be the hybrid EV Toyota "Prius" (Fig. 3), which uses a high-power MH battery [23], and was brought onto the market in December 1997 [24]. The HEV has double the gas mileage and emits half the carbon dioxide gas compared to the same-class gasoline car. The amount of exhaust gas emission is reduced to only one-tenth of the regulated level. The price is 2.15 million yen, only half a million yen higher than that of the same-class gasoline car. Two hundred and forty cells of 6.5 Ah (D size) were connected in series to make a battery pack (6.5 Ah, 288 V) which could provide 20 kW power, as shown in Fig. 10. On starting, the vehicle is propelled only by the battery and then the gasoline engine kicks in automatically for driving and also for charging the battery. During acceleration the battery can assist the power of the engine and during deceleration the battery recovers the regenerative energy. The most suitable operating conditions for the gasoline engine make it possible to obtain a high gas mileage of 28 km per liter of gasoline, which is about twice that for the usual operation of gasoline vehicles. The power capability of the HEV battery has been significantly improved. The peak power vs. storage energy ratio (f) for the HEV battery pack is three times higher than that for the pure EV battery pack (EV-95), as shown in Fig. 11. The high-power lithium-ion battery [44] and ultra-capacitor are expected to become strong competitors in the near future.

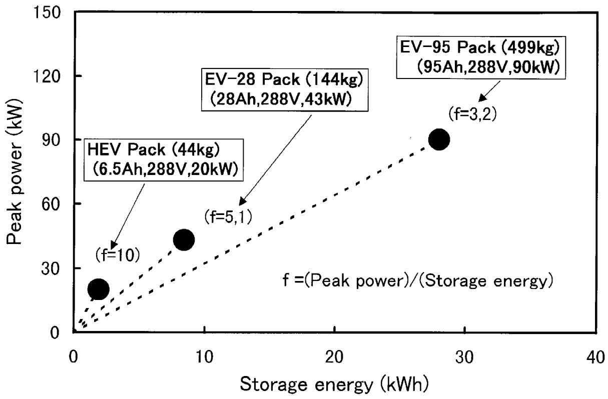


Fig. 11. Peak power vs. storage energy for the battery packs of the PEV, small PEV and HEV.

4.3. Fuel cell EVs

The internal combustion engine loses most energy as wasted heat with a limited efficiency of about 30%, while a fuel cell (FC) system converts the fuel directly into electricity with a doubled efficiency of about 60%. A compact and high-powered fuel cell system in which hydrogen is supplied by a hydrogen storage tank or methanol reformer has been developed for the EV. The FCEV developed by the Daimler-Benz group is propelled

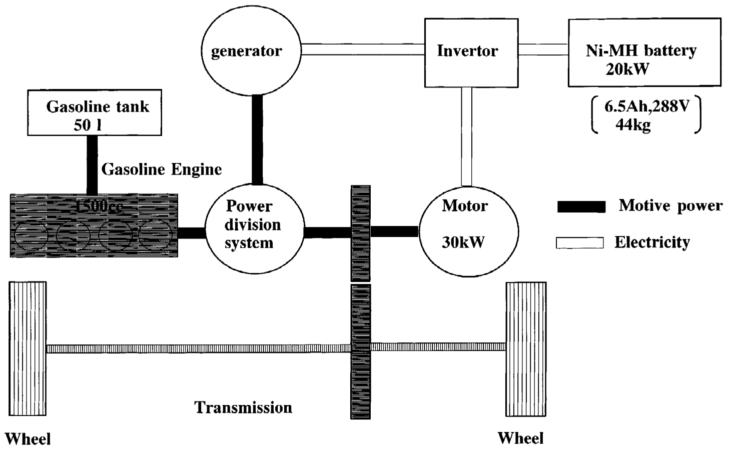


Fig. 10. Hybrid EV system for the Toyota "Prius".

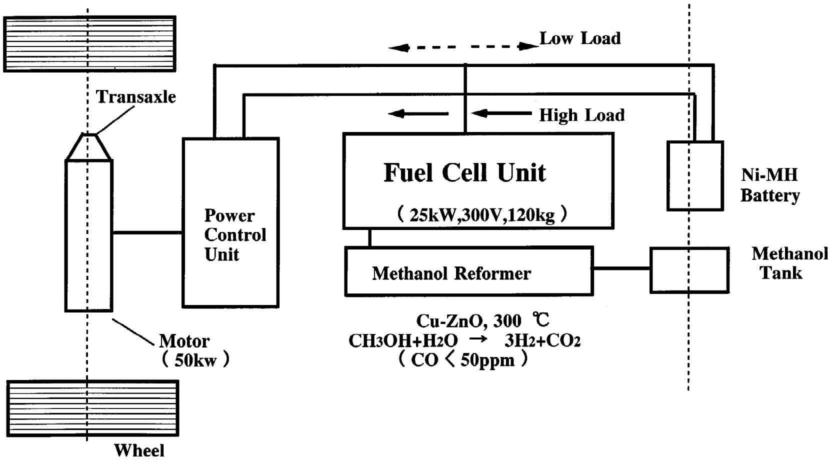


Fig. 12. Fuel cell EV system for the Toyota "FCEV" with methanol reformer.

only by the FC system with 50 kW power [45,46]. On the other hand, the FCEV developed by Toyota [47] adopted a hybrid system comprised of the FC system with 25 kW power and a Ni–MH battery, as shown in Fig. 12. The installed high-power Ni–MH battery is used for starting, for power-assistance during acceleration and for energy recovery through regenerative baking. Mazda [48] also developed a hybrid FCEV using an ultra-capacitor of 20 kW.

Hydrogen engine cars with a metal hydride tank have been developed by Mazda as low emission vehicles, but the gas mileage is estimated to be about 16 km per litter of gasoline, as shown in Fig. 13. A FCEV with the same metal hydride tank achieved more than double the gas mileage, 34 km per liter of gasoline, compared to the hydrogen engine car. The FCEV is expected to be the next generation automobile with the highest energy conversion efficiency. The present cost should be reduced to one-hundredth in order to compete with the gasoline engine of the near future.

A polymer electrolyte membrane (PEM) fuel cell is used for an EV in which a sulphonated ion-exchange membrane has Pt-catalyzed carbon electrodes on both sides. Hydrogen and air are supplied on each side, respectively, generating electricity. Approximately 400 cells are stacked in series, separated by a carbon plate or a Au-coated titanium plate separator, to obtain 300 V for the EV. Pure hydrogen is most favorable for the operation of the fuel cell system with respect to power and durability but, at present, the infrastructure for hydrogen charging does not exist. The methanol reforming system, supplying a mixed gas of 75% hydrogen and 25% CO_2, is one realistic solution, although there are several problems such as contaminated CO poisoning the Pt catalyst, low power

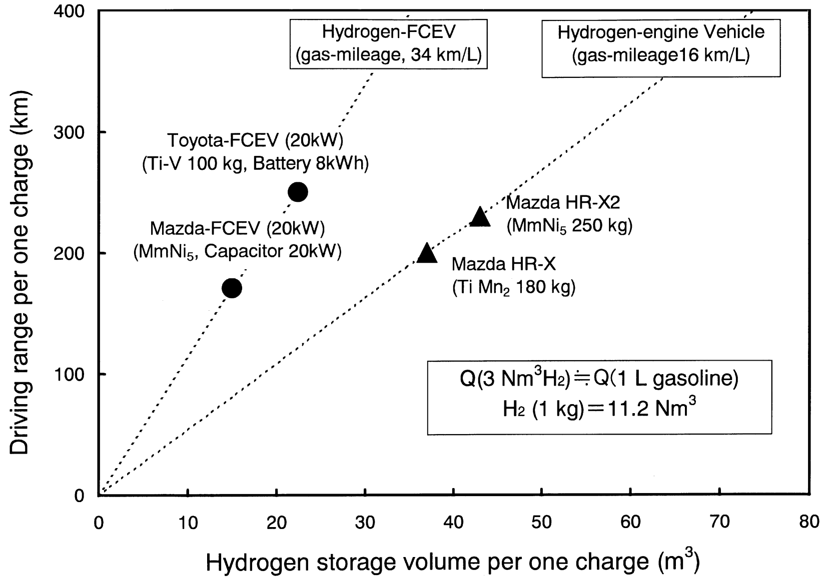


Fig. 13. Driving range vs. storage hydrogen for a hydrogen engine car and fuel cell EV.

capability and electrochemical damage to carbon materials due to a shortage of hydrogen in the ending cells. A hydrogen energy system is under development by the WE-NET project (MITI) to realize a clean energy society. A lighter-weight metal hydride is also needed to store hydrogen in the FCEV.

5. Concluding remarks

Extensive research for more than 20 years in the field of hydrogen storage alloys has combined with advanced battery technology to commercialize the Ni–MH battery. The high-performance battery has become one of the key components in the growing information and telecommunication industries, serving as a compact and light-weight power source that is also environmentally friendly. Sales of so-called eco-vehicles such as pure EV and hybrid EV that use large-sized Ni–MH batteries have begun. FCEV with the Ni–MH battery and metal hydride tank is also under development. It is expected that MH battery technology can contribute to building an ideal society in harmony with the global environment. The heart of the MH battery is the hydrogen storage alloy, the performance of which can be changed by material design, depending on the special purpose of the battery. This high-tech battery has great potential to expand the applicable fields in the future. At present, the most important work would be the creation of lightweight MH materials, which are under development in the WE-NET project supported by MITI and the NEW PROTIUM FUNCTION project supported by the Ministry of Education, Science, Sports and Culture. Recent progress in basic research and applications is reported in the Proceedings of Metal–Hydrogen Systems [49–51] and summarized in a recent book [52].

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