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Research and Development Work on Lithium-ion Batteries for Enviromental Vehicles

Takaaki Abe, Kazuki Miyatake,
Yoshio Shimoida and Hideaki Horie
EV Energy Energy Development Department, Nissan Motor Co., Ltd.,
1, Natsushima-cho, Yokosuka, 237-8523 Japan, takaaki-abe@mail.nissan.co.jp

Abstract

In the first stage of our research and development work on high-performance lithium-ion batteries from the early to the mid-1990s, a high-energy-capacity battery was investigated with the aim of applying it to electric vehicles (EVs). The second stage of our program concerned studies of a lithium-ion battery for application to series hybrid electric vehicles (SHEVs), and the third stage was mainly focused on a high-power lithium-ion battery for use on parallel hybrids (PHEVs). The results of those studies demonstrated that lithium-ion batteries are the best battery systems for use on these environmental vehicles. A battery simulation program was also constructed concurrently with those investigations for use as a tool in verifying the superiority of lithium-ion batteries. This simulation program takes into account the electrochemical phenomena that occur inside the battery, especially the effect of lithium-ion diffusion on power output characteristics. In the present study, battery simulations were performed to quantify the flow of ions inside the battery. This paper presents the results of sensitivity analyses concerning the electrode structural parameters influencing the long-duration power output characteristic that is required of batteries for use on EVs and SHEVs.

Keywords: battery, battery model, simulation

1   Introduction

The tightening of energy supplies and concerns about global warming resulting from the continued increase in massive energy consumption make it imperative to develop and promote the widespread use of high-performance environmental vehicles. Research and development work on electric vehicles (EVs) and hybrid electric vehicles (HEVs) has been under way for many years, as they have long been seen as the most promising candidates for environmentally friendly vehicles.

At Nissan, we began a feasibility study of lithium-ion batteries in 1990, focusing on the intrinsic capabilities of this battery technology for constructing future power supply systems for environmental vehicles. The results of roughly two years of preliminary studies indicated that lithium-ion batteries, which were just beginning to show their true prospects for consumer applications at that time, were also very promising for the development of high-performance environmental vehicles. That finding convinced us that lithium-ion batteries possessed the latent potential to dramatically transform battery systems for vehicle use. Consequently, we launched a full-scale program of vigorous activities in 1992 to research and develop lithium-ion batteries for application to environmental vehicles.

As outlined in Fig. 1, the first result of that program was the development of a cylindrical lithium-ion battery for EV use in 1995. That battery was used to build well over 100 EVs in the latter half of the 1990s, such as the R'nessa EV introduced in the U.S. and the Prairie EV introduced in Japan. Subsequently, the Hypermini EV was also put on the Japanese market in 2000. As described here, our R&D activities have consistently been aimed at improving the performance of lithium-ion batteries. Along with proposing new concepts for high-performance power supply systems based on the use of lithium-ion batteries, we have also worked to open new avenues for applying these batteries to various types of environmental vehicles.

In the process of analyzing the scope of vehicle applicability of lithium-ion batteries, we focused attention on increasing the power output of the battery. When considering application to HEVs, for example, higher battery power is necessarily required. However, the global electrochemical community and the battery industry sector were of the belief that lithium-ion batteries were inherently incapable of delivering high specific power. That view stemmed from the necessity of using an organic solvent as the electrolyte with lithium, inasmuch as water would decompose if a water-based electrolyte were used. Given that the ion conduction rate in an organic electrolyte is approximately two orders of magnitude lower than the rate in water, it was firmly believed that lithium-ion batteries were intrinsically unable to produce high power, regardless of how the battery was configured.

However, our fundamental doubts about the validity of that view prompted us to devise a method for analyzing battery performance theoretically. Not only did we disprove the conventional notion about the inferior power performance of lithium-ion batteries, we demonstrated to the contrary that this type of battery possessed the potential for exceptionally high specific power. We were the first researchers anywhere in the world to advocate that potential and to substantiate it experimentally as well.
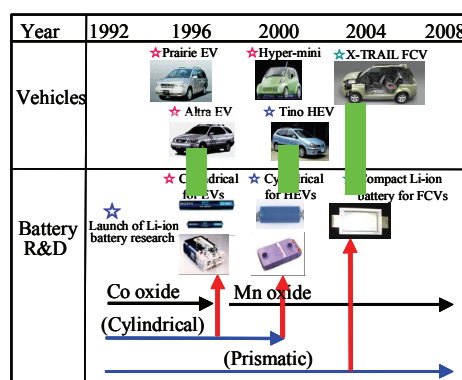

Fig. 1 R&D of advanced Li-ion batteries
for EVs/HEVs at Nissan (1990-2008)

2 Battery performance required by environmental vehicles

Since 1995, we have been researching and developing lithium-ion batteries for application to environmental vehicles such as EVs, series hybrids (SHEVs) and parallel hybrids (PHEVs). The battery performance required by these vehicles is plotted in Fig. 2 in terms of specific energy and specific power. Battery power is expressed here as short-duration output. Since PHEVs seldom travel in the EV mode, the battery is mainly used to provide a power assist for accelerating the vehicle and to accept regenerative energy during vehicle deceleration. This type of environmental vehicle requires a battery with outstanding power

performance. Pure EVs require a battery with excellent energy storage capacity in order to ensure the required driving range. Batteries for SHEVs must provide power for propelling the vehicle, while the EV-mode driving range is maintained to a certain extent because the vehicle is fitted with a generator. This type of vehicle requires a battery with outstanding power performance, though the energy storage capacity can be less than that required of EV batteries. Since batteries for SHEVs and EVs must provide both power performance and energy storage capacity, it is essential to improve both of these attributes and to ensure sustained power output over long periods of time.

The power performance shown in Fig. 2 is sufficient for PHEVs, as these vehicles require battery power for short periods of time. However, batteries for SHEV and EV use must demonstrate that they are capable of providing sustained power output over a long period of time in order to continue to propel the vehicle. When continuous output is required of a battery, there is concern that battery power might decline owing to the phenomena related to lithium-ion diffusion inside the battery. Therefore, experiments were conducted under actual driving conditions to determine how many seconds of continuous battery discharge were required by SHEVs and EVs. Battery electrodes must be designed to meet that discharge requirement.

Figure 3 shows the required battery power and continuous discharge time for propelling a vehicle on battery power alone under different driving modes. The required battery performance was found first for city driving and highway driving under the LA4 mode, representing typical driving patterns. Since the vehicle's maximum power output was not reached in the LA4 driving mode, this driving cycle alone was not sufficient for determining the battery performance design. Accordingly, we specified our own flat highway and sloped highway conditions and the results obtained are also plotted in Fig. 3. In order to facilitate vehicle operation under all of these driving modes, the results in the figure indicate that maximum battery power would be continuously required for 5 sec at the longest. It is seen that battery power decreases as the required discharge interval becomes longer and that approximately one-half of the maximum battery power would have to be output continuously for approximately 30 sec. The effects of the parameters of the battery electrode structure on this required power performance

were then estimated using a battery reaction simulation model that takes into account lithium-ion transport inside the battery. The simulation model and results are described in the following section.
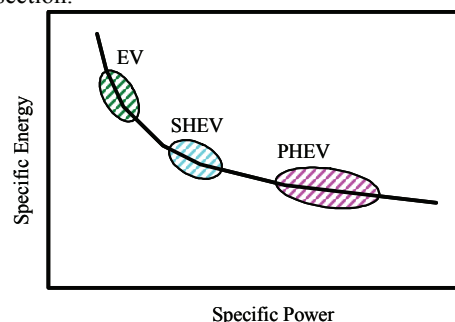

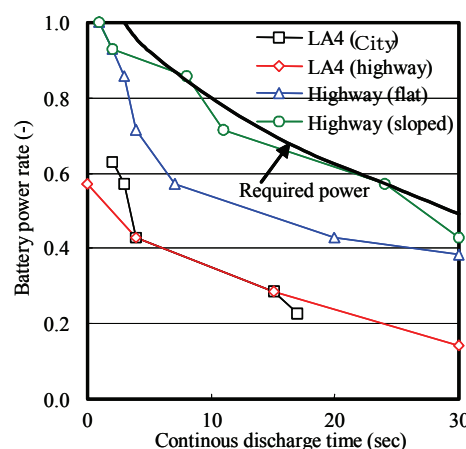
Fig. 2 Specific energy vs specific power

Fig. 3 Dischargable time vs battery power

3 Battery reaction simulation model

Because EVs and various types of HEVs are built with different motive power sources and vehicle systems, the relationship between optimal battery power and energy storage capacity differs for each kind of vehicle. Therefore, the battery electrodes must be optimally designed to match the requirements of each type of vehicle. There are two basic indices for expressing battery characteristics:

(1) Specific energy: How much energy can a battery store?

(2) Specific power: How much power can a battery produce?

Energy consumption inside a battery can be broadly considered in terms of the portion attributable to battery reactions and the portion due to energy losses accompanying the transport of electrons or ions. As these consumption components become smaller, energy dissipation

inside a battery decreases, which means that internal resistance is reduced and voltage drops across the battery terminals during operation are avoided. With respect to the electrode structure, if the thickness of the active material layers is reduced, there is less resistance to the flow of both lithium ions and electrons through these layers. However, in terms of specific energy, it would incrementally increase the relative proportion of the battery components such as the current collectors, separator, excess electrolyte and others that are not directly involved in energy storage. As a result, the battery's specific energy would decline.

What approach can be taken to ascertain internal resistance, i.e., energy dissipation, in a battery more accurately? Because of the complex nature of the reaction processes in a battery, accurate predictions can never be obtained with simplistic formulas. In order to determine the internal resistance values intrinsic to a battery, it is necessary to probe the fundamental causes of resistance, understand thoroughly the various mechanisms involved, posit valid hypotheses of the phenomena and formulate quantitative equations accordingly. Accurate predictions of the transport and reaction processes can only be obtained by going through these steps. These processes are mutually dependent on the electrode material properties, geometrical parameters of the electrode structure, variables such as the ion concentration and electron conductivity, and also on external control variables like the current value. Accordingly, they can only be obtained by solving a set of equations consisting of many related physical quantities. Based on this conceptual approach, we constructed a simulation model of battery reactions and charge transport processes, as shown in Fig. 4.

This battery simulation model consists of schemas for calculating two different transport phenomena:

Lithium-ion diffusion equations for lithium-ion transport in the active materials and in the electrolyte

Electron conduction equations.
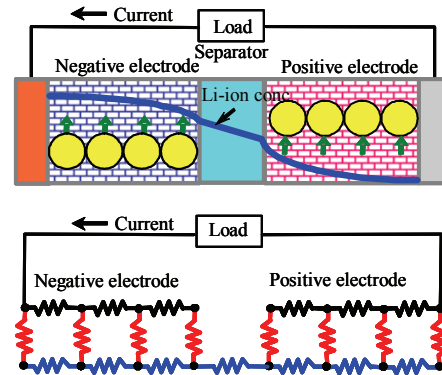
·Lithium ion diffusion in active materials

$$\frac{\partial C_S}{\partial t} = D_S \nabla_r^2 \cdot C_S \qquad (1)$$

·Lithium ion diffusion in electrolyte

$$\varepsilon \frac{\partial C_e}{\partial t} = \varepsilon D_e \nabla_X^2 \cdot C_e + \frac{(1-t_+)}{F} a i_n \quad (2)$$

·Electron transport in active materials

$$\sigma_S \nabla_X^2 \cdot \phi_S - a i_n = 0 \qquad (3)$$

·Ion transport in electrolyte

$$\sigma_e \nabla_X^2 \cdot \phi_e + a i_n$$
$$- \sigma_e \nabla_X^2 \cdot (\ln C_e) \cdot 2RT(1-t) = 0 \qquad (4)$$

$$i_n = k C_e^{\alpha a} (C_t - C_S)^{\alpha a} C_S^{\alpha c}$$
$$\times \left\{ \exp\left(\frac{\alpha F}{RT}\eta\right) - \exp\left(-\frac{\alpha F}{RT}\eta\right) \right\} \qquad (5)$$

$$\eta = \phi_S - \phi_e - U(C_S) \qquad (6)$$

Fig.4 Battery simulation model

4 Battery simulation results
4.1 Parameters influencing continuous power output

There are various parameters that change with time during continuous battery discharge and lead to a decline in power output. Specifically, these parameters are (A) an increase in resistance due to the electrode thickness, (B) an open-circuit voltage drop ascribable to lithium-ion diffusion in the active materials, and (C) an increase in internal resistance due to lithium-ion diffusion in the electrolyte. Figure 5 shows the change in voltage during continuous battery discharge. Line (1) is for a case without any effects of parameters (A)-(C) above. Line (2) is for a case influenced by the current distribution in the electrodes (parameter A). Line (3) is for a case that adds the effect of

lithium-ion diffusion in the active materials (parameter B). Line (4) is for a case that adds the effect of lithium-ion diffusion in the electrolyte (parameter C). The following discussion presents the results of simulations that examined the respective effects of these three parameters.
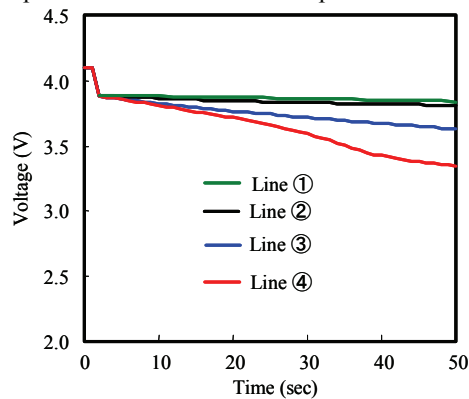

Fig. 5 Discharge characteristics

4.2 Effect of current distribution in electrodes

The internal resistances that occur in a battery are shown in Fig. 6. The total internal resistance value of a battery consists of electron resistance in the active materials, reaction resistance between the active material surface and the electrolyte and ionic resistance in the electrolyte. Because electron resistance in the active materials is approximately three orders of magnitude smaller than the reaction resistance and ionic resistance, many lithium ions flow through the part of the electrode near the separator in the initial period of discharge (line (1) in Fig. 6). As discharge continues, the charge in the part of the electrode near the separator is depleted and lithium ions also begin to flow from the active materials inside the electrode (line (2) in Fig. 6).

Figure 7 shows the current distribution in the electrodes at a 3C discharge rate for a negative electrode thickness of 90 μm and a positive electrode thickness of 80 μm. It is seen that a large current flows at the electrode surface near the separator in the initial discharge period and that current also begins to flow inside the electrodes as discharge proceeds.

In order to examine the effect of the electrode thickness in more detail, the power output characteristic was calculated for different electrode thicknesses. Figure 8 shows the amount of change in power output for three short-duration discharges as a function of the electrode thickness. The conditions used in the calculation

were a 3C discharge rate, removal of the effect of lithium-ion diffusion in the active materials and in the electrolyte, and a discharge duration up to 30 sec, as required in Fig. 3. The results indicate that battery power decreases in proportion to the electrode thickness. Accordingly, care must be taken when designing electrodes in this thickness range.
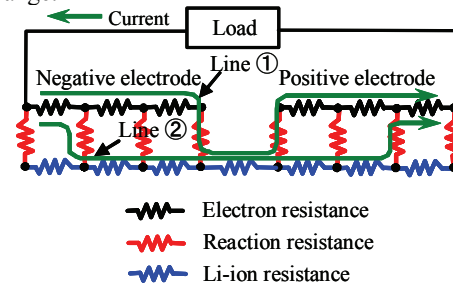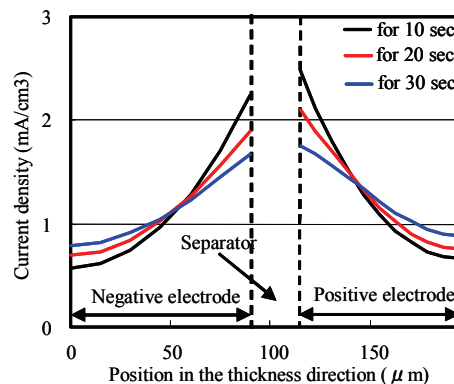

Fig. 6 Current paths in electrodes
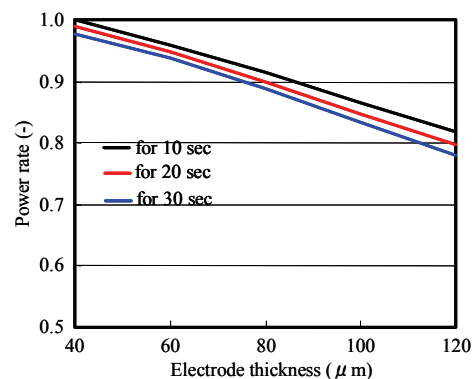

Fig. 7 Current distribution in electrodes

Fig. 8 Effect of electrode thickness

4.3 Effect of lithium-ion diffusion in electrode active materials

At the negative electrode during discharge, lithium ions reach the electrolyte from the active material surface, after which they diffuse from the interior of the active materials toward the surface. At the positive electrode, on the other hand, lithium ions reach the active material surface from the electrolyte and subsequently diffuse from the surface into the center of the active materials. The detected battery voltage, representing the difference in electric potential at the active material surface of the two electrodes, reflects the lithium-ion concentration at the surface of the active materials. If a lithium-ion concentration distribution occurs owing to a slow rate of diffusion in the active materials, it gives rise to a voltage drop, causing battery power to decline.

Figure 9 shows the lithium-ion concentration in the active materials during discharge at a 3C discharge rate for an active particle diameter of 10 μm, a negative electrode thickness of 90 μm and a positive electrode thickness of 80 μm. The results indicate that a lithium-ion concentration distribution develops owing to the influence of the diffusion rate in the active materials.

In order to examine the effect of lithium-ion diffusion in the active materials on battery power in more detail, the change in power output was measured for different active material particle diameters. The results are shown in Fig. 10 for three discharge durations. The influence of lithium-ion diffusion in the electrolyte was removed. This influence was removed in order to investigate only the effect of lithium-ion diffusion in the active materials. The conditions used in the calculations were a 3C discharge rate, an electrode thickness of 80 μm and a discharge duration as long as 30 sec, as required in Fig. 3. The results indicate that battery power decreases in proportion to the particle diameter of the active materials. The active materials used in lithium-ion batteries generally have a particle diameter of 10 μm. For particles of that size, the decline in battery power due to lithium-ion diffusion in the active materials remains at a maximum of 8%.
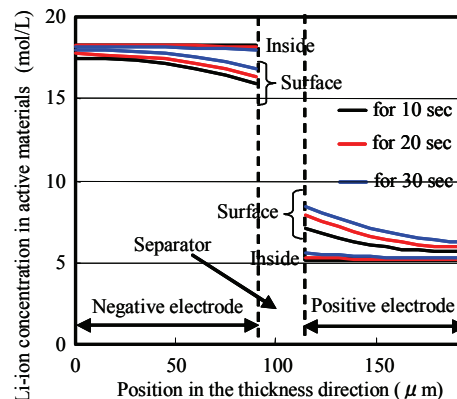

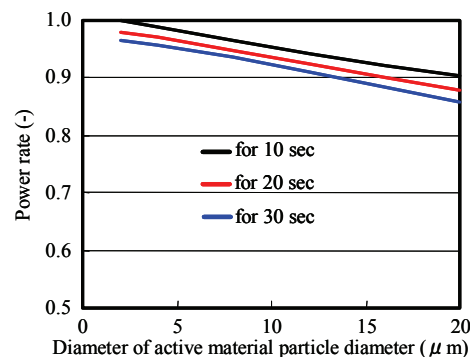Fig. 9 Li-ion concentration distribution in active materials

Fig. 10 Effect of Li-ion diffusion in active materials

4.4 Effect of lithium-ion diffusion in the electrolyte

Prior to the onset of discharge, the lithium-ion concentration in the electrolyte is in a uniform state. Once discharge begins, lithium ions travel from the negative electrode active material to the electrolyte and from the electrolyte to the positive electrode active material, thereby producing a lithium-ion concentration distribution in the electrolyte. As shown in Fig. 11, this distribution is characterized by a high concentration of lithium ions in the negative electrode and a low concentration in the positive electrode. The lithium-ion concentration in the electrolyte influences the ion diffusion coefficient in the electrolyte and ionic resistance. Lithium ions diffuse most easily at a concentration of 1 mol/L, and an electrolyte concentration of 1 mol/L allows ions to pass through it easily. When the lithium-ion concentration in the electrolyte is 1 mol/L, discharge proceeds and battery voltage declines.

In order to investigate the effect of lithium-ion diffusion in the electrolyte in more detail, the change in battery power output was measured for

different electrode porosities (i.e., the proportion accounted for by the electrolyte). The results are shown in Fig. 12 for three discharge durations. The conditions used in the calculations were a 3C discharge rate, an electrode thickness of 80 μm and a discharge duration up to 30 sec, as required in Fig. 3. The results suggest that the effect of lithium-ion diffusion on the decline in power output increases at electrode porosities below 0.4. That is attributed to the increased influence of the smaller area for lithium-ion diffusion in the electrolyte. For EVs and SHEVs that require large energy storage capacity, it is necessary to increase the specific energy of the battery by reducing the porosity of the electrodes. Although increasing the porosity of the electrodes would be difficult, it can be reduced to a minimal level by accurately estimating the battery power and continuous discharge time required by the vehicle.
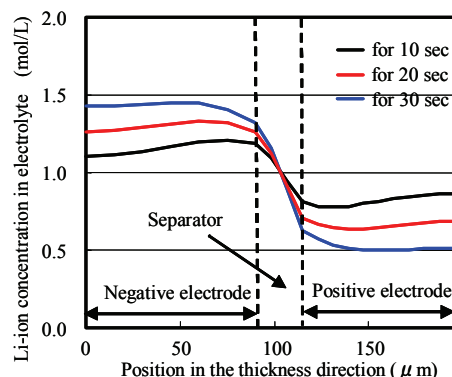

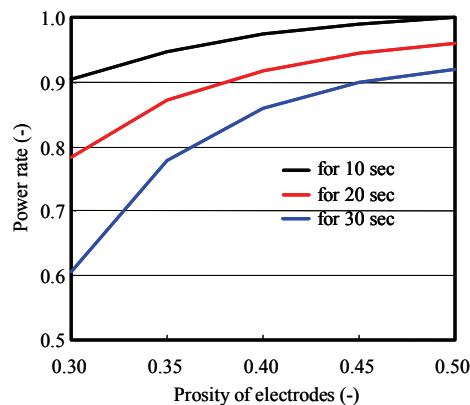Fig. 11 Li-ion concentration distribution in electrolyte

Fig. 12 Effect of electrode porosities

4.5   Long-duration   power   output characteristic

  The power output characteristic for long-duration discharges can be estimated on the basis

of calculations that take into account the effects of the three parameters described above. In future work, it is planned to calculate electrode specifications for satisfying the long-duration power output characteristic needed by EVs and SHEVs. Prototype electrodes will then be fabricated and tested to confirm the power output characteristics obtained.

5 Conclusion

  The power output characteristic for long-duration discharges is a key factor in designing lithium-ion batteries for use on environmental vehicles such as electric vehicles (EVs) and series hybrid electric vehicles (SHEVs). The major parameters influencing the long-duration power output characteristic are (1) the electrode thickness, (2) lithium-ion diffusion in the active materials and (3) lithium-ion diffusion in the electrolyte. Focusing on these three parameters, a simulation model of battery reactions was used in this study to estimate their respective effect on battery power. The simulation results confirmed that the battery electrode design can be optimized to attain both power performance and energy storage capacity by accurately reflecting in the battery design the power output and discharge duration required by the vehicle. It is intended to use the results of this study concerning battery power output characteristics to design the optimal batteries for environmental vehicles in future work. In addition to power output, efforts will also be made to construct a battery management system, including thermal management, in order to obtain the best battery system for vehicle application.

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Authors

Takaaki Abe
1989 – Present Nissan Motor Company Co., Ltd.
Developed Lithium-ion battery for EVs, SHEVs and PHEVs.