Development of positive electrode materials for low-cost and high-performance lithium-ion secondary batteries

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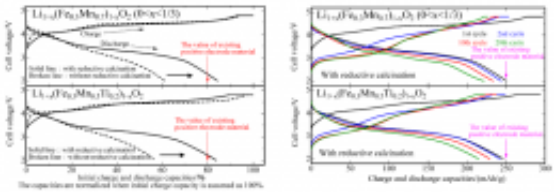

Comparison of initial charge/discharge characteristics of two types of newly developed positive electrode material (left)and charge/discharge cycle characteristics for up to 20 cycles (right)

Mitsuharu Tabuchi (Senior Researcher), Ionics Research Group, the Research Institute for Ubiquitous Energy Devices (Director: Tetsuhiko Kobayashi) of the National Institute of Advanced Industrial Science and Technology (AIST; President: Tamotsu Nomakuchi), has developed two types of new oxide material (namely, $Li_{1+x}(Fe_{0.3}Mn_{0.7})_{1-x}O_2$ and $Li_{1+x}(Fe_{0.3}Mn_{0.5}Ti_{0.2})_{1-x}O_2$) for the positive electrode of lithium-ion secondary batteries in collaboration with Junji Akimoto (Leader), Crystal and Materials Processes Group, the Advanced Manufacturing Research Institute (Director: Nobumitsu Murayama) of AIST and Junichi Imaizumi (Manager), Technology Development Team 5, Technology Development Department of Tanaka Chemical Corporation (Tanaka Chemical; President: Tamotsu Tanaka). Approximately 30 % of the total amount of transition metals in these newly developed oxide

materials is made up of iron, which is a low-cost and resource-wise abundant metal.

The researchers have produced these positive electrode materials by optimizing their chemical composition and using a wet chemical method that includes a reductive calcination process. The initial cycle efficiency at room temperature (normalized discharging capacity value at the lower limit voltage of 2.0 V in the left side graph) has been improved drastically to approximately 80 %; this is equivalent to the performance of conventional positive electrode materials.

These newly developed materials assure high initial charge and discharge capacities of approximately 250 mAh/g or higher (right side graph). They offer a performance equivalent to that of conventional positive electrode materials and yet do not contain rare metals, cobalt and nickel. Therefore, the new materials are expected to contribute to resource saving and cost reduction for lithium-ion secondary batteries used in electric vehicles etc.

Details of this technology will be presented at the "52nd Battery Symposium in Japan" to be held in Edogawa Ward, Tokyo from October 17 to 20, 2011. This research has been conducted as part of "Development of High-performance Battery Systems for Next-generation Vehicles (Li-EAD project) - R&D of novel and high-capacity positive electrode material consists of low-cost constituent oxides (FY2007 - FY2011)" project commissioned by the New Energy and Industrial Technology Development Organization.

With growing awareness of energy savings and resource conservation in recent years, electrical vehicles and hybrid vehicles are drawing attention and the use of these vehicles is becoming more widespread. The amount of electrical power stored and discharged per unit weight of a battery (energy density) of lithium-ion secondary batteries is much superior to

that of other secondary battery systems. Therefore, a lithium-ion secondary battery is one of key storage devices with high potential for vehicle applications. Studies are also being conducted on the applications that require large-size storage batteries, such as stationary energy storage systems in combination with renewable energy, for example wind power and solar power generation systems.

Improved performance and cost reduction without compromising safety are required for lithium-ion secondary batteries for vehicles. To reduce cost, the constituent materials of the battery must be replaced with less expensive materials. Among the constituents, the positive electrode material that serves as the lithium ion supply source is the most expensive constituent. Furthermore, the positive electrode material is the key constituent that determines battery capacity and operating voltage. Hence, there is a strong demand for the development of low-cost and high-performance positive electrode materials.

For lithium batteries, AIST has been researching positive electrode materials that contain iron, the most inexpensive and abundant metal, and titanium, which were previously considered difficult to use. Through that research, AIST has developed lithium manganese-based oxide materials for positive electrodes. The basis of the materials is lithium manganese oxide (Li_2MnO_3) that contains a large quantity of lithium (AIST press releases on October 21, 2004 and November 6, 2006). In order to bring the discharge voltage (3 V) of these materials closer to that of existing positive electrode materials (4 V), AIST and Tanaka Chemical have jointly developed an iron- and nickel-substituted lithium manganese-based (FNM-based) oxide material for positive electrodes ($Li_{1+x}(Fe_{0.2}Ni_{0.2}Mn_{0.6})_{1-x}O_2$; average discharge voltage of 3.5 V) (joint press release of AIST and Tanaka Chemical on August 17, 2009).

To achieve further cost reduction and higher performance, it is desirable to develop a positive electrode material that does not contain nickel,

which is the most expensive material among all the constituent metals. For that reason, the researchers have developed positive electrode materials such as iron-substituted lithium manganese oxide (FM-based) and iron- and titanium-substituted lithium manganese oxide (FMT-based).

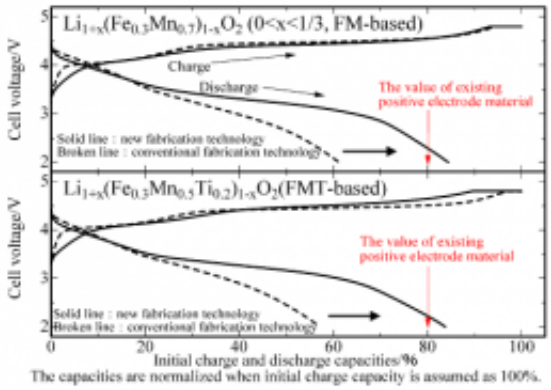

Figure 1 : Comparison of initial charge and discharge characteristics of two types of newly developed positive electrode material (Metallic lithium is used as the negative electrode material; potential range: 2.0 V to 4.8 V)

The initial cycle efficiency at room temperature is particularly important for positive electrode materials and an efficiency of at least 80 % is required for commercial use in the potential range of a conventional positive electrode of 2.0 V to 4.8 V. The researchers applied the new fabrication technology to develop two types of positive electrode material (FM-based and FMT-based materials) in order to realize higher capacity, high initial cycle efficiency, and reduction of cycle degradation for lithium-ion secondary batteries. This technology can optimize the metallic element composition ratio and chemical composition.

Regarding the metallic element composition ratio, both FM-based and FMT-based materials have an iron content of 30 % among metallic

elements other than lithium, because it is the optimal amount of iron from the standpoint of charge and discharge characteristics, and $Li_{1+x}(Fe_{0.3}Mn_{0.7})_{1-x}O_2$ (0