Suppression of Manganese-ion Dissolution by SiO₂ Aerosol Addition from Spray Pyrolyzed Li₂MnO₃-LiMn_{1/3}Ni_{1/3}Co_{1/3}O₂

Satoshi HASHIGAMI,^{a,b,*} Masayuki KAWANISHI,^b Kei YOSHIMI,^b Satoshi UJIIE,^a Toru INAGAKI,^a Michihiro HASHINOKUCHI,^b Takayuki DOI,^b and Minoru INABA^b

^a R&D Center, The Kansai Electric Power Co., Inc., 11-20 Nakoji 3-Chome, Amagasaki, Hyogo 661-0974, Japan

^b Department of Molecular Chemistry and Biochemistry, Doshisha University, Kyotanabe, Kyoto 610-0321, Japan

* Corresponding author: hashigami.satoshi@c5.kepco.co.jp

ABSTRACT

Layered Li₂MnO₃-LiMn_{1/3}Ni_{1/3}Co_{1/3}O₂ solid-solution cathode materials modified with SiO₂ were prepared by spray pyrolysis and their charge-discharge properties were investigated. Both the capacity and voltage fades of SiO₂-modified Li₂MnO₃-LiMn_{1/3}Ni_{1/3}Co_{1/3}O₂ during charge/discharge cycling were suppressed compared with that of the unmodified sample. It was found that the addition of SiO₂ suppressed the dissolution of manganese ions at 60°C from the results of inductively coupled plasma (ICP) emission spectroscopy. X-ray diffraction (XRD) data indicated that weak reflections corresponding to Li₂SiO₃ appeared as the SiO₂ content increases to 5 wt%. Scanning electron microscope (SEM) studies showed that the microstructure of the particles was significantly changed by SiO₂ addition. As indicated by transmission electron microscope (TEM) analysis, Si-rich regions were seen on the Li₂MnO₃-LiMn_{1/3}Ni_{1/3}Co_{1/3}O₂ primary particles. The suppression of Mn ions and the improved charge and discharge properties were correlated with the microstructural changes.

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1. Introduction

Lithium ion batteries with high energy density have a vital role as power sources, such as portable devices and electric vehicles (EVs). The requirement for high capacity has grown recently for extending the drive range of EVs. High capacity cells are also expected for use in electric power grids with the aim of load frequency control and supply-demand control. Lithium-rich layered solid solution of Li₂MnO₃ and LiMO₂, where *M* denotes at least one 3*d* transition metal, has attracted much attention as a cathode material of lithium ion batteries in recent years because they offer high capacities of around 250 mAh g⁻¹ within the potential range of 2.0 to 4.8 V (versus Li/Li⁺).¹⁻⁴ In the solid solution system, layered *x*Li₂MnO₃-(1 - *x*)LiMn_{0.33}Ni_{0.33}Co_{0.33}O₂ electrodes have been reported to be promising because of their high capacities.⁵ However, the cycle performance of the layered materials is not satisfactory at present. Another critical issue of the materials is the voltage fade during charge and discharge cycling. Croy et al. have reported a correlation between voltage fade and hysteresis in the charge/discharge profiles.^{6,7} The layered electrode materials such as 0.5Li₂MnO₃·0.5LiMn_{0.375}Ni_{0.375}Co_{0.25}O₂ exhibit a significant hysteresis loop, which is considerably different from other traditional lithium insertion electrode materials.⁶ To account for this hysteresis, both the reversible and irreversible migration of transition metal ions were proposed.⁷

Studies in the literature have so far revealed several important factors for the capacity fade of the layered materials, which include the dissolution of Mn ions into electrolytes,⁸ the decomposition of electrolytes through side reactions of LiPF₆ with water molecules,⁹ and structural transformations to, e.g. a spinel-like phase on the surface.¹⁰ One effective approach is to modify the surface with various oxides such as SiO₂,^{8,9} Al₂O₃,¹¹ ZrO₂,¹² TiO₂,¹³ Li₂O·2B₂O₃-glass,¹⁴ etc. They revealed that the surface modification suppresses the dissolution of Mn ions into the electrolytes as well as the decomposition of the electrolytes at high potentials.

Spray pyrolysis is a simple one-step synthesis technique to obtain various kinds of functional oxide powders.^{15,16} As compared with conventional solid-state methods, the particles prepared by spray pyrolysis have some advantages such as small particle size distribution, high purity, and easy control in composition and morphology of multi-component metal oxides. We have developed a synthetic method to prepare core-shell type particles for solid oxide fuel cell anode cermets using spray pyrolysis.¹⁷⁻¹⁹ Such peculiar microstructures of oxide particles obtained by spray pyrolysis may allow unique properties to Li₂MnO₃-LiMn_{1/3}Ni_{1/3}Co_{1/3}O₂ as a cathode in lithium-ion batteries. It has been reported that Li₂MnO₃-LiMn_{1/3}Ni_{1/3}Co_{1/3}O₂ powder prepared by spray pyrolysis exhibited good charge and discharge performance.^{20,21} Furthermore, the powder morphology can be controlled by acid addition to the starting solution of spray pyrolysis.^{18,22}

In this study, Li₂MnO₃-LiMn_{1/3}Ni_{1/3}Co_{1/3}O₂ modified with SiO₂ aerosol were synthesized by simple single-step spray pyrolysis. Li et al. modified LiCoO₂ with SiO₂ by mechano-thermal coating procedure.²³ Arumugam et al. reported that SiO₂-coated LiMn₂O₄ significantly improved the capacity retention compared to the uncoated samples because of the reduction of Mn dissolution.⁸ Furthermore, addition of SiO₂ to organic electrolyte has proved to be effective in trapping impurities.⁹ To the best of our knowledge, SiO₂-modified Li₂MnO₃-LiMn_{1/3}Ni_{1/3}Co_{1/3}O₂ powder has never been prepared by spray pyrolysis yet. We found that a small amount of SiO₂ addition remarkably suppressed the capacity and voltage fade of Li₂MnO₃-LiMn_{1/3}Ni_{1/3}Co_{1/3}O₂ during cycling. We investigated the microstructures of the particles and the dissolution of Mn ions at an elevated temperature of 60°C, which were correlated with the improved charge and discharge properties.

2. Experimental

2.1 Preparation of the cathode materials by spray pyrolysis

Stoichiometric amounts of lithium nitrate (99.9%, Wako Pure Chemical Industries, Ltd.), manganese nitrate hexahydrate (99.9%,

Wako Pure Chemical Industries, Ltd.), nickel nitrate hexahydrate (99.9%, Wako Pure Chemical Industries, Ltd.), cobalt nitrate hexahydrate (99.0%, Wako Pure Chemical Industries, Ltd.) were weighed to prepare 0.2 mol of $\text{Li}_2\text{MnO}_3\text{-LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$, and were dissolved in 500 mL of deionized water. SiO_2 aerosol (Nissan Chemical Industries, Ltd., ST-O type) was added to the solution at a weight ratio of $\text{Li}_2\text{MnO}_3\text{-LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2\text{:SiO}_2 = 100:0, 99:1, 98:2, \text{ or } 95:5$. The solution was stirred for an hour, diluted with deionized water to 1 L, and was used for spray pyrolysis.

$\text{Li}_2\text{MnO}_3\text{-LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$ particles modified with SiO_2 were synthesized with a spray pyrolysis apparatus described elsewhere.¹⁸ The solution was atomized using ultrasonic vibrators with an oscillation frequency of 1.65 MHz in an atomizing vessel. Because the ultrasonic vibrators raise the temperature of the solution during atomizing, cold water was circulated around the atomizing vessel to keep the temperature of the solutions lower than 30°C. This is because atomization at high temperatures tends to give inhomogeneous droplets. The reaction furnace consisted of four independent heating zones, whose temperatures were set at 200, 400, 800, and 800°C from the inlet to the outlet. The atomized mists were flown into the furnace with 1 L min^{-1} of air. The droplets including Li^+ , Mn^{2+} , Co^{2+} , Ni^{2+} and SiO_2 were dried, decomposed, reacted, and sintered when passing through the reaction furnace. The powder was collected using a membrane filter, and was heat-treated at 800°C for 3 h in air.

2.2 Cell fabrication and charge/discharge tests

A cathode slurry was prepared by mixing the oxide powder (80 wt%), an acetylene black conductor (Denka Co., Ltd., 10 wt%), a polyvinylidene fluoride binder (Kureha Corp., 10 wt%) using 1-methyl-2-pyrrolidinone (Wako Pure Chemical Industries, Ltd.) as a solvent. The slurry was coated on an Al foil current collector (20 μm thickness), and dried at 120°C for 24 h under vacuum. The loading of the cathode was typically 1.5 mg cm^{-2} .

Charge and discharge tests were carried out using two-electrode coin-type cells, which were assembled in an Ar-filled glove box (Miwa, MDB-1NKP-DS). Li metal foil (Honjyo Metal) was used as a counter electrode, and a micro-porous monolayer membrane (Celgard® 2400) was used as a separator. The electrolyte solution was 1 M LiPF_6 dissolved in a 1:1 mixture of ethylene carbonate (EC) and dimethylcarbonate (DMC) by volume. The tests were performed galvanostatically at a 0.1 C rate ($1 \text{ C} = 314 \text{ mAh g}^{-1}$) between 2.0 and 4.8 V at 30°C using a BTS2004W-10 battery test system (Nagano Co. Ltd.). Prior to cycling, a stepwise pre-cycling treatment was carried out by increasing the upper potential limit by 0.1 V from 4.5 V every two cycles to 4.8 V according to the procedure proposed by Ito et al.²⁴

2.3 Powder characterization

The crystal structures of the $\text{Li}_2\text{MnO}_3\text{-LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$ powders unmodified and modified with SiO_2 were investigated by X-ray diffraction (XRD, Shimadzu XRD-6000) using $\text{CuK}\alpha$ radiation. The morphology of the oxide particles was observed with a scanning electron microscope (SEM, JSM-7001FD) using a secondary electron detector and with a transmission electron microscope (TEM, JEM-2100F) equipped with an energy dispersive X-ray spectroscopy (EDX). The oxide particles were embedded in a polymer resin, and samples for SEM and TEM observation were prepared by a cross-section polisher (JEOL, SM-09010DM) and a focused ion beam system (Hitachi, FB2000A), respectively. The BET surface area of the powder was measured with a Micromeritics TriStar.

2.4 Analysis of dissolved manganese-ions

In order to evaluate the effect of SiO_2 addition on manganese-ion dissolution, the amount of dissolved Mn ions was analyzed. The cell

was pre-cycled stepwisely to 4.8 V, and stored at 60°C for 3 days under the open-circuit conditions as an accelerated test. After disassembled the cell, the Li metal foil, on which Mn species were deposited, was soaked in ultra-pure water. The solution is acidified to 1 mol L^{-1} with hydrochloric acid, and Mn species were measured by inductively coupled plasma emission spectroscopy (ICP, Thermo Fisher Scientific, iCAP 6000 SERIES).

3. Results and Discussion

3.1 Structure and morphology analysis

XRD patterns of unmodified and SiO_2 -modified $\text{Li}_2\text{MnO}_3\text{-LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$ are shown in Fig. 1. The XRD pattern of each sample was typical of the $\text{Li}_2\text{MnO}_3\text{-LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$ layered structure because the weak superstructure reflections appeared at around $2\theta = 22^\circ$, which originates from the ordering between the Li_2MnO_3 and the LiMO_2 . The intensity ratio of the (003) to the (104) lines is known to be a measure of the cation mixing;²⁵ however, it was not appreciably changed by SiO_2 modification in the present study. The decrease in the (003)/(104) ratio means an increase in cation mixing caused by Li^+/H^+ exchange due to the strong acid such as nitric acid and the migration of transition metal cations into the lithium-ion layer during the annealing (drying) of the electrode, which results in poor cycling stability.²⁶ Before heat-treatment at 800°C for 3 h (not shown), each powder had poor crystallinity and the peaks at around $2\theta = 22^\circ$ were not observed because of a short residence time (<30 s) in the reaction furnaces.

A clearly resolved peak was observed at 36.6° , which is not assigned to the layered oxide, and its intensity increased with SiO_2 content to 5 wt%. This peak is assigned to the spinel LiM_2O_4 phase such as $\text{LiNi}_{0.3}\text{Co}_{0.4}\text{Mn}_{1.3}\text{O}_4$ and $\text{LiNi}_{0.2}\text{Co}_{0.6}\text{Mn}_{1.2}\text{O}_4$. Kang et al. reported that a $0.5\text{Li}_2\text{MnO}_3\text{-}0.5\text{LiNi}_{0.44}\text{Co}_{0.25}\text{Mn}_{0.31}\text{O}_2$ sample after acid-treated for 2 weeks showed a similar doublet peak in the range of $36.0\text{--}39.0^\circ$.²⁷ Besides, a weak reflection appeared at $2\theta = 31.1\text{--}31.2^\circ$ when SiO_2 was added, which is also assigned to the spinel LiM_2O_4 phase. Very weak peaks appeared at $2\theta = 26.94^\circ, 33.00^\circ$, and 38.59° at a SiO_2 content of 5 wt%. These peaks are assigned to Li_2SiO_3 that was formed from SiO_2 during annealing at 800°C. The crystalline and amorphous SiO_2 were not detected by XRD. We prepared the mixture of LiNO_3 and SiO_2 powders ($\text{Li}:\text{Si} = 2:1$), and fired at 800°C for 3 h. Most SiO_2 reacted with Li to give the Li_2SiO_3 phase without any appreciable XRD peaks assigned to crystalline SiO_2 . Although some impurity peaks appeared, the main product was SiO_2 -modified $\text{Li}_2\text{MnO}_3\text{-LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$.

Figure 1. (Color online) X-ray diffraction patterns of $\text{Li}_2\text{MnO}_3\text{-LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$ unmodified and modified with 1, 2, and 5 wt% SiO_2 prepared by spray pyrolysis, followed by calcination at 800°C for 3 h.

Figure 2. SEM images of unmodified $\text{Li}_2\text{MnO}_3\text{-LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$ particles. (a, b) as-synthesized and (c, d) after calcined at 800°C for 3 h.

SEM images of as-synthesized and calcined $\text{Li}_2\text{MnO}_3\text{-LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$ without SiO_2 are shown in Fig. 2. The as-synthesized particles were not agglomerated and had a spherical shape. Their diameter was distributed in the range of 100 nm to 2 μm . The surface of the particles consists of finely-dispersed primary particles of a diameter smaller than 100 nm. After heat-treatment, the particles retained their shape; however, the primary particles on the surface became larger than those of the as-synthesized powder. The interior microstructures of the as-synthesized and the calcined $\text{Li}_2\text{MnO}_3\text{-LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$ particles are shown in Figs. 2(b) and (d), respectively. Before heat-treatment, the interior of the $\text{Li}_2\text{MnO}_3\text{-LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$ particle consisted of finely-dispersed primary particles as was observed on the surface (Fig. 2(a)). After heat treatment, however, the grain growth progressed significantly at the surface of the secondary particles. Bigger particles (1–2 μm) had a hollow structure with a relatively dense shell with a thickness of 0.3 μm and aggregates of smaller primary particles in the interior. On the other hand, smaller particles of less than 1 μm in diameter were almost completely solidified.

Figure 3 shows SEM images of 2 and 5 wt% SiO_2 -modified samples after heat-treatment at 800°C . The interior primary particles were more agglomerated than those of the unmodified particles (Fig. 2(d)). The size of the secondary particle was not appreciably changed by the addition of SiO_2 aerosol. The specific surface area of 0, 1, 2 and 5 wt% SiO_2 -modified samples were 3.44, 3.56, 3.04, and 4.70 m^2g^{-1} respectively. The specific surface area of the unmodified sample was almost the same as that of the 1 wt% SiO_2 -modified sample. However, the specific surface area slightly decreased with SiO_2 content to 2 wt%. Here SiO_2 may have worked as a sintering agent before changing to Li_2SiO_3 . It has been widely recognized that the reduction in surface area improves the stability of cathode oxide materials such as spinel LiMn_2O_4 .^{4,28} The specific surface area increased at a SiO_2 content of 5 wt% and this may be due to the collapsed shape compared with those of other SiO_2 contents. Lengyel et al. reported that the major factor to determine the secondary particle size in spray pyrolysis is the oscillation frequency for atomization.²⁰ Moreover, the spherical shape was partially collapsed by SiO_2 modification. The droplet-to-particle conversion process in spray pyrolysis consists of some complicated transport phenomena such as drying, thermal decomposition, and sintering. The particle morphology is mainly determined by the evaporation rate of the solvent on drying. By the addition of SiO_2 aerosol, the solvent molecules may have evaporated heterogeneously from the

Figure 3. SEM image of (a, b) 2 wt% SiO_2 - and (c, d) 5 wt% SiO_2 -modified $\text{Li}_2\text{MnO}_3\text{-LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$ particles after calcined at 800°C for 3 h.

surface of the atomized droplets. This may be a reason why the SiO_2 -modified particles were slightly collapsed.

TEM-EDX analysis was performed for the $\text{Li}_2\text{MnO}_3\text{-LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$ modified with 2 wt% SiO_2 to evaluate the elementary distribution of Mn, Ni, Co and Si inside the particle (Fig. 4). The distributions of Mn, Ni, Co were uniform throughout the powder as shown in Figs. 4(a)–(c), while the distribution of Si is not uniform as shown in Fig. 4(e). The largest size of the Si regions was about 50 nm, which was larger than the original size of SiO_2 aerosol (10–15 nm). The signal of Si indicates that Si-rich regions were seen on the primary particles, but not in the particles. The line profiles of Mn, Ni, Co and Si are shown in Fig. 4(f). The profiles of Si and the transition metals did not coincide with each other. It seemed that SiO_2 did not cover the surface of the primary particles, but were dispersed between the primary particles.

3.2 Charge and discharge properties

Figure 5 compares the 1st, 10th, and 50th cycle charge-discharge profiles for the unmodified and the SiO_2 -modified $\text{Li}_2\text{MnO}_3\text{-LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$ samples after the stepwise pre-cycling treatment. All samples delivered discharge capacities higher than 220 mAh g^{-1} after activation at ca. 4.8 V on charging (in the pre-cycling treatment) which is inherent to the lithium-rich layered transition-metal oxide cathodes. The unmodified sample gave an initial discharge capacity of 248 mAh g^{-1} . The 1, 2, and 5 wt% SiO_2 -modified samples exhibited initial discharge capacities of 245, 237, and 228 mAh g^{-1} , respectively. The 1 wt% modified sample showed a discharge capacity very close to the pristine sample considering the weight ratio of $\text{Li}_2\text{MnO}_3\text{-LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$ (i.e., 99%). However, the 5 wt% modified sample exhibited a slightly lower discharge capacity than the pristine samples (236 mAh g^{-1} for 95 wt%). In this sample, Li_2SiO_3 was in the XRD pattern (Fig. 1), and part of Li ions in $\text{Li}_2\text{MnO}_3\text{-LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$ was consumed to form Li_2SiO_3 by the addition of SiO_2 . Therefore, the discharge capacity may have decreased with increasing SiO_2 content.

The discharge capacity of the unmodified sample declined rapidly. The capacity retention was improved by SiO_2 modification. For the SiO_2 -modified samples, a new plateau appeared at ca. 2 V on the discharge curve at the 50th cycle. Appearance of a similar plateau at ca. 2 V was reported for Li-rich layered manganese oxide cathodes operated between 2.0 to 5.0 V for 20 cycles.²⁹ The mechanism for the 2-V plateau and its effect on cycleability are not clear at present. It should be noted that even if the capacity at the

Figure 4. (Color online) TEM-EDX elemental maps for (a) Ni, (b) Mn, (c) Co, (d, e) Si in 2 wt% SiO₂-modified Li₂MnO₃-LiMn_{1/3}Ni_{1/3}-Co_{1/3}O₂ particle after calcined at 800°C for 3 h, and (f) line profile for Ni, Mn, Co, and Si. TEM images are superposed in (e) and (f). Arrows indicate SiO₂ particles.

Figure 5. (Color online) Charge and discharge curves of Li₂MnO₃-LiMn_{1/3}Ni_{1/3}Co_{1/3}O₂ cathodes modified with (a) 0, (b) 1, (c) 2, and (d) 5 wt% of SiO₂ in 1 M LiPF₆/EC+DMC (1:1) at C/10 and 30°C.

2-V plateau is ignored, the capacity retention is improved for SiO₂-modified samples. Figure 6 shows the variations of capacity retention for unmodified and SiO₂-modified samples. Here we plotted the discharge capacities between 4.8 and 2.1 V to ignore the capacity for the 2-V plateau in Fig. 5. The capacity of the unmodified sample gradually decreased on cycling. On the other

hand, the capacity fade on cycling was successfully suppressed for all SiO₂-modified samples. The highest capacity retention was obtained for the 2 wt% SiO₂-modified sample.

A close inspection in Fig. 5 revealed that voltage depression was observed on the discharge curve after cycling for each sample, which is another problem for the Li-excess layered oxides called

Figure 6. (Color online) Variations of discharge capacity retention of $\text{Li}_2\text{MnO}_3\text{-LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$ cathodes unmodified and modified with 1, 2, and 5 wt% of SiO_2 in 1 M $\text{LiPF}_6/\text{EC}+\text{DMC}$ (1:1) at C/10 and 30°C . The discharge capacities between 4.8 and 2.1 V were plotted to ignore the capacity for the 2-V plateau in Fig. 5.

Table 1. Average discharge voltages of unmodified and SiO_2 -modified $\text{Li}_2\text{MnO}_3\text{-LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$.

Amount of SiO_2 (wt%)	V_{D1} : Ave. discharge voltage in 1st cycle (V)	V_{D50} : Ave. discharge voltage in 50th cycle (V)	$V_{\text{D1}}-V_{\text{D50}}$ (V)
0	3.48	3.20	0.28
1	3.48	3.23	0.25
2	3.47	3.26	0.21
5	3.43	3.25	0.18

“voltage fade”.²⁴ However, the voltage fade was clearly improved by SiO_2 modification. The average discharge voltages at the 1st and 50th cycles were calculated, and are summarized in Table 1. An excess amount of insulating SiO_2 causes an increase in electrical resistivity, and hence the average discharge voltage at the 1st cycle (V_{D1}) of the 5 wt% modified sample was slightly lower than that of the pristine sample. On the other hand, the average discharge voltages at the 50th cycle (V_{D50}) of the SiO_2 -modified samples were higher than that of the unmodified sample. As a result, the voltage fade during 50 cycles ($V_{\text{D1}}-V_{\text{D50}}$) decreased with increasing SiO_2 content, though it was not completely mitigated by SiO_2 addition. Gallagher et al. reported that irreversible migration of the transition metal ions, which does not lead to the arrangement of a perfect spinel structure, results in the voltage fade.⁷ Taking the morphology and the crystal structure of the SiO_2 -modified samples into account, we note the possibility of lowering the migration of the transition metal ions during charge and discharge because of the presence of the SiO_2 (or Li_2SiO_3) on the primary particles.

3.3 Mechanisms for performance improvements by SiO_2 -modification

As indicated by the TEM-EDX analysis in Fig. 4, SiO_2 was not included in the primary particles, but was present on the primary particles. The SiO_2 (or Li_2SiO_3) particles partially covered the surface of active material particles and prevented the active material surface from direct contact with the electrolyte. Therefore one of the reasons for the observed positive effects of SiO_2 modification is that SiO_2 particles partly suppress electrolyte decomposition and the dissolution of the metal ions from the layered structure into the electrolyte.

Figure 7. (Color online) Amounts of dissolved Mn ions from $\text{Li}_2\text{MnO}_3\text{-LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$ cathodes unmodified and modified with 1, 2, and 5 wt% of SiO_2 in 1 M $\text{LiPF}_6/\text{EC}+\text{DMC}$ (1:1) under the open-circuit conditions at 60°C for after charged to 4.8 V. The amount of dissolved Mn ions is normalized by the total Mn ions contained in each sample before the test.

Borong et al. reported that the capacity fade of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode was suppressed when the electrolyte containing Li_2SiO_3 is reduced.³⁰ They concluded that Mn dissolution and PF_5 -initiated solvent polymerization were mitigated because HF and PF_5 were consumed by Li_2SiO_3 if it precipitated on the cathode surface. In the present study, the suppression of capacity fade may be related to the presence of SiO_2 in the secondary particles. Figure 7 shows the variations of dissolved Mn ions at 60°C with the amount of modified SiO_2 . It is clear that the dissolution of Mn ions were remarkably suppressed by SiO_2 modification, especially at 2 and 5 wt%. One reason is clear because the presence of SiO_2 enhanced the growth of the interior primary particles, which resulted in a reduced surface area. Another reason may be related to the fact that modified SiO_2 particles consumed HF and PF_5 that accelerate Mn dissolution as mentioned above. This suppressed the capacity and voltage fade, and improved the cycle performance of $\text{Li}_2\text{MnO}_3\text{-LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$, though further investigation is needed in the future.

4. Conclusions

SiO_2 modified layered $\text{Li}_2\text{MnO}_3\text{-LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$ particles were prepared by spray pyrolysis and their charge and discharge characteristics as cathodes in lithium-ion batteries were investigated. SiO_2 modification effectively suppressed not only capacity fade, but also voltage fade. ICP measurements showed that Mn dissolution at an elevated temperature was suppressed by SiO_2 addition. SEM analysis revealed that the addition of SiO_2 enhanced the sintering of the primary particles in the spherical secondary particles, while TEM-EDX analysis indicated that SiO_2 particles were not included inside the primary particles, but on the surface of the primary particles. These results demonstrate that SiO_2 modification is an effective way for suppressing the reaction of Mn dissolution and improving the cycle performance of lithium-excess layered lithium manganese oxide cathodes.

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