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Investigation of Al modification as cationic dopants in Ni-rich $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ cathode

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In this paper, we have successfully prepared Al-doped Ni-rich $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ cathodes. The structural properties and electrochemical performances are studied according to Al cationic doping. It can be confirmed that the crystallinity and cation disordering of Ni-rich $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ were improved by Al doping. Based on such excellent structural quality, the electrochemical performance of Al doping $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ was superior to that of pristine $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$. The Al doping Ni-rich NCM has an initial discharge capacity of 209.2 mAh g^{-1}. In addition, it shows superior rate capability by showing capacity retention of 58.5% under a high rate of 6.0 C. Therefore, it can be judged that Al doping $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ can be applied to next-generation cathode for long-distance and fast-charging electric vehicles.

Keywords: Al-doped Ni-rich $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$, Excellent structural quality, Next-generation cathode, Long-distance and fast-charging electric vehicles.

Introduction

Recently, studies on energy storage devices such as lithium ion batteries, fuel cells, supercapacitors, hybrid supercapacitors and power semiconductors are being conducted. Among them, a lithium ion battery having a high energy density is commercialized as a power source for electric vehicles, energy storage devices, and mobile devices, and is the most widely used energy storage device.

Among various applications of lithium-ion battery, the development of lithium-ion battery for electric vehicles is important because the battery market for electric vehicles is predicted to grow the most rapidly. For example, a portable device contains one lithium ion battery, but a hybrid electric vehicle, a plug-in hybrid electric vehicle, and a battery electric vehicle contain 100 to 6000 or more lithium ion batteries.

The one of the most important parameter in lithium-ion battery for electric vehicles is energy density. Among lithium-ion battery components, the cathode determines not only the price due to expensive raw materials such as Li, Ni and Co, but also the energy density of the lithium-ion battery. Therefore, studies on the electrochemical performances of various cathode candidates are being conducted.

One of two widely studied candidates, the Ni-rich NCM (Ni ≥ 80%) has higher energy density under actual operating conditions than Li- and Mn-rich NCM, and it has high economic feasibility due to low content of expensive lithium. One of the fatal disadvantages of Ni-rich NCM is the cycle performance degradation due to side reaction with electrolyte. Therefore, in this paper, we tried to improve the cyclability of Ni-rich $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ through bulk modification using Al.

Experimental

To improve the electrochemical performances of pristine $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$, Al doped $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ powders were fabricated by co-precipitation method. The $Ni_{0.91}Co_{0.06}Mn_{0.03}(OH)_2$ precursor was fabricated via using $NiSO_4{\cdot}6H_2O$, $MnSO_4{\cdot}H_2O$, $CoSO_4{\cdot}7H_2O$, $NH_3{\cdot}H_2O$ and Na_2CO_3 aqueous solution. The NH_4OH and NaOH solution was adapted as a precipitating agent. The spherical $Ni_{0.91}Co_{0.06}Mn_{0.03}(OH)_2$ precursor was mixed with Li sources ($LiOH{\cdot}H_2O$) at the molar ratio of Li sources/$Ni_{0.91}Co_{0.06}Mn_{0.03}(OH)_2$ precursor was 1.05 : 1. Also 0.5 wt% Al_2O_3 powders were added as a cationic dopants. After that, the powders were calcined at 710 °C for 7 h and then sintered 860 °C for 10 h under O_2 atmosphere.

In order to measure the electrochemical performances, the $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ cathode was prepared using $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ powder (96 wt%), polyvinylidene fluoride (2 wt%) as a binder and Super P (2 wt%) as a conductive additive. For making slurry, the mixture was blended with N-methyl-pyrrolidinone (NMP) solvent. Afterward, slurry was coated on aluminum-foil and dried at 100 °C for 24 h in a vacuum oven to eliminate the NMP solvent. The CR 2032 coin cells

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were prepared with lithium foil as an anode in Ar-gas filled glove box. The dimethyl carbonate (DMC), ethyl methyl carbonate (EMC) and ethylene carbonate (EC) (1 : 1 : 1 by volume) with 1M $LiPF_6$ were selected as an electrolyte.

In order to compare the morphologies and structural properties, field emission scanning electron microscopy (FE-SEM, Hitachi S-4800) and X-ray diffraction (XRD, X'pert MPD DY1219) were measured. The initial charge-discharge capacities, rate performances, long-term cycle performances are estimated via electrochemical equipment (TOSCAT-3100, Toyo system).

Results and Discussion

Fig. 1 shows the XRD patterns of Al-doped and pristine $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$. Both samples show typical layered hexagonal α-$NaFeO_2$ structure with R-3m space group. Also, no additional phases were observed for the both samples. Therefore, it can be inferred that both samples are well crystallized. The good separation of (006)/(102) and (108)/(110) peaks means excellent layered structure. It is well known that the I(003)/I(104) ratio is a key parameter to determine the degree of cation disordering, which is one of the negative factor for electrochemical performances of Ni-rich NCM. If the (003)/(104) peak ratio value is lower than 1.2, the cation ordering is considered poor. In case of pristine $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$, the value of I(003)/I(104) value is 1.35, which is also higher than 1.2, indicating good cation ordering. The Al-modified $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ possess a higher I(003)/I(104) value of 1.54 than the pristine sample. Therefore, it can be confirmed that the cation ordering is effectively improved by the Al doping into the pristine $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$.

Fig. 2 shows the microstructures of (a) Al-doped, (b) pristine $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ and (c) EDS mapping of Al-doped $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$. It can be seen that there is no big difference between both samples. Both samples have a similar secondary particle size of 11.5 μm and the same spherical shape with porous structures. The size of primary particle sizes, constituting the secondary particles, are in the range from 100 to 200 nm for both samples. Based on these, it was confirmed that Al doping did not clearly affect particle morphology or size. The significant difference between the both samples is the surface chemistry. In the case of the xx-modified sample, the surface is clean, but in the case of the pristine sample, it can be confirmed that there are impurities such as LiOH and Li_2CO_3 on the surface, as indicated by the yellow circle. These materials are due to the low structural stability of the pristine sample. In many previous papers, it has been reported that

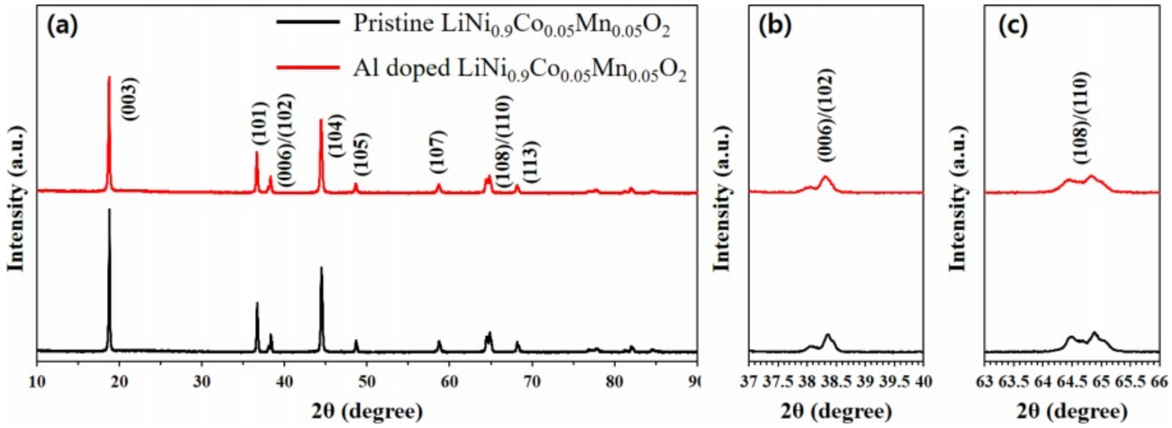

Fig. 1. XRD pattern of Al doped and pristine $LiNi_{0.9}Co_{0.05}Mn_{0.05}O_2$.

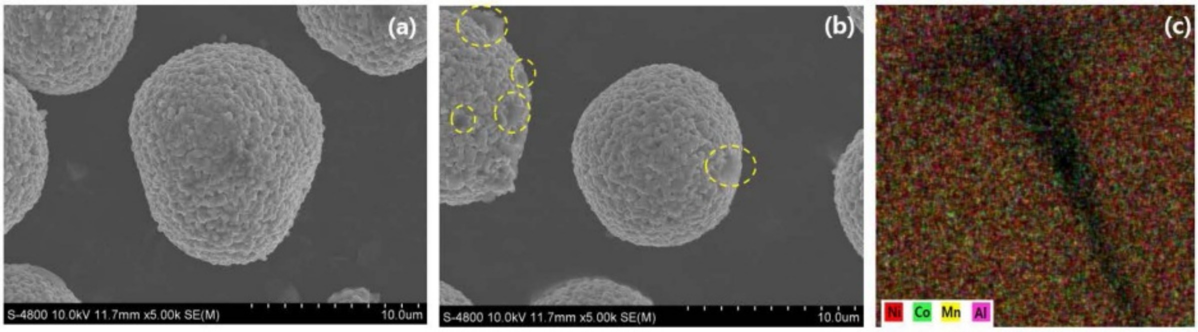

Fig. 2. FESEM images and EDS mapping of Al doped and pristine $LiNi_{0.9}Co_{0.05}Mn_{0.05}O_2$.

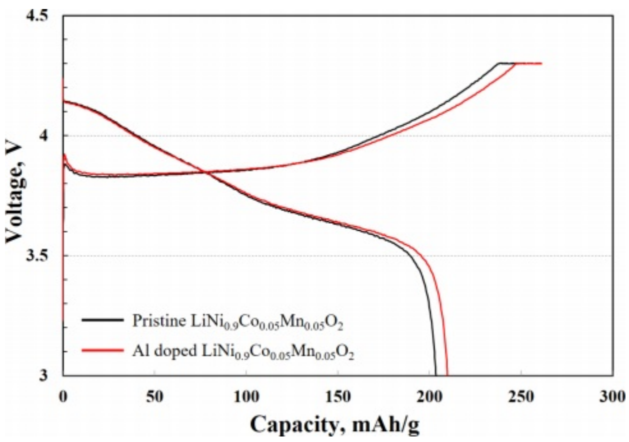

Fig. 3. Initial charge-discharge profiles of Al doped and pristine $LiNi_{0.9}Co_{0.05}Mn_{0.05}O_2$ at 0.5 C (1 C = 210 mAh g^{-1}).

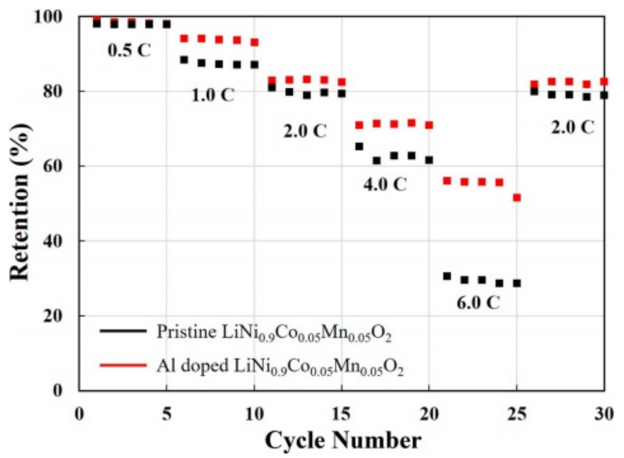

Fig. 4. Rate performance of Al doped and pristine $LiNi_{0.9}Co_{0.05}$-$Mn_{0.05}O_2$.

performance degradation is caused by existence of unwanted lithium compounds on the Ni-rich cathode surface. As shown in Fig. 2(c), the successful Al modification can be confirmed through EDS mapping. In the case of the Al modified sample, the chemical stability of the Ni-rich NCM can be explained by the Al substitution.

To confirm the commercial potential, both samples for measuring the electrochemical performance were prepared to have a high mass loading per are of about 15.4 mg/cm^2. Fig. 3 shows the initial charge-discharge curves of Al-doped and pristine $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ in the voltage range from 3.0 V to 4.3 V at 0.1 C at 25 ^oC. The voltage plateaus, meaning the charge/discharge process, with no significant difference between the both samples, which are the same as that of the typical Ni-rich NCM sample. The specific charge and discharge capacity of Al doped $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ are 251.4 and 209.2 mAh g^{-1}, respectively. Such high charge and discharge capacities of Al doped $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ are because unwanted materials (lithium compounds) are formed on the surface of the pristine $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ by reaction with the electrolyte. These lithium compounds have relatively low lithium ion and electronic conductivity. Therefore, the movement of lithium ions and electrons becomes difficult. As a result, the charge and discharge capacities of pristine $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ are 249.6 and 204.7 mAh g^{-1}, respectively, which are lower than those of Al doped $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$.

Fig. 4 shows the rate performances of Al-doped and pristine $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ in the current density range from 0.5 C to 6.0 C. Under low current densities such as 0.5 C, it can be seen that the capacity retentions of both samples are almost the same. This means that the movement of lithium ions and electrons is possible regardless of the surface chemistry at low current densities. In both samples, capacity retentions are decreased in proportion to current densities from 0.5 C to 6.0 C. However, the pristine sample decreases much faster compared to the Al doped sample. The capacity retentions of Al-doped samples are 99.1, 92.5, 82.5, 72.3 and 58.5% at 0.5 C, 1.0 C, 2.0 C, 4.0 C, and 6.0 C. And when the current density return to 2.0 C again, the recovery of capacity retention is excellent. However, the capacity retentions of the pristine sample are poor than those of the Al-doped sample (99.0, 90.7, 80.4, 64.7 and 31.2% at 0.5 C, 1.0 C, 2.0 C, 4.0 C, and 6.0 C). In addition, it can be seen that the recovery is also lower when the current density returns to 2.0 C. The lithium diffusion coefficients of Al-doped and pristine samples are 5.04×10^{-12} and 3.41×10^{-12}, respectively. The higher value allows for fast and smooth Li-ion movement, resulting in superior rata performance. This is due to the low-conductivity materials created on the surface of the pristine sample, mentioned earlier. Conversely, in the case of the Al modified sample, low conductivity lithium compounds are not generated and the surface is clean due to the stronger bonding force by Al doping into the cathode. Therefore, it is considered that Al modified sample has relatively high capacity even at high current density.

Conclusions

In this paper, we have successfully prepared Al -doped $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$. The Al -doped $LiNi_{0.91}$-$Co_{0.06}Mn_{0.03}O_2$ has a well ordered layered structure compared to the pristine $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$. Based on this, Al -doped $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ exhibits relatively higher electrochemical performances. This can be explained by the fact that the Al dopant can effectively inhibit the unwanted reaction with the electrolyte based on its strong bonding with Ni, Co and Mn. As a result, the structure of the Al -doped $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ does not collapse during charging and discharging process, and the original structure is well maintained. Therefore Al-doped

$LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ can be regarded as a promising way to improve the electrochemical performances of pristine NCM.

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