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SHORT COMMUNICATION

High-rate, high capacity ZrO_2 coated $Li[Li_{1/6}Mn_{1/2}Co_{1/6}Ni_{1/6}]O_2$ for lithium secondary batteries

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Abstract Recently, there have been many reports on efforts to improve the rate capability and discharge capacity of lithium secondary batteries in order to facilitate their use for hybrid electric vehicles and electric power tools. In the present work, we present a ZrO_2-coated $Li[Li_{1/6}Mn_{1/2}Co_{1/6}Ni_{1/6}]O_2$. The bare $Li[Li_{1/6}Mn_{1/2}Co_{1/6}Ni_{1/6}]O_2$ shows a high initial discharge capacity of 224 mAh g^{-1} at a 0.2 C rate. Owing to the stability of ZrO_2, it was possible to enhance the rate capability and cyclability. After 1 wt% ZrO_2 coating, the ZrO_2-coated $Li[Li_{1/6}Mn_{1/2}Co_{1/6}Ni_{1/6}]O_2$ showed a high discharge capacity of 115 mAh g^{-1} after 50 cycles under a 6 C rate, whereas the bare $Li[Li_{1/6}Mn_{1/2}Co_{1/6}Ni_{1/6}]O_2$ showed a discharge capacity of only 40 mAh g^{-1} and very poor cyclability under the same conditions. Based on results of XRD and EIS measurements, it was found that the ZrO_2 suppressed impedance growth at the interface between the electrodes and electrolyte and prevented collapse of the layered hexagonal structure.

Keywords ZrO_2 coating · Rate capability · HEVs · Lithium batteries

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1 Introduction

Since the first commercialization of $LiCoO_2$ by SONY in 1991 [1], there have been outstanding developments in lithium secondary batteries in terms of discharge capacity and electrochemical properties. Lithium secondary batteries have been mainly used as small-scale energy storage sources for laptops, cell phones, and mobile electronic devices. However, with recent development of hybrid electric vehicles (HEVs) and electric power tools, there is a huge demand for application of lithium secondary batteries as large-scale energy storage devices.

In order to use lithium secondary batteries as energy storage devices for HEVs and electric power tools in the future, high-rate capability is an essential property due to the necessity of fast charge/discharge. Accordingly, various methods to improve the high rate capability have recently been proposed. Manthiram et al. reported that high rate capability was obtained by doping Li and Ni ions into $LiMn_2O_4$ [2]. Hatori et al. reported a coprecipitation method to prepare a Mg–Mn hydroxide precursor for optimal synthesis of Mg doped $LiMn_2O_4$ spinel, which showed a very high rate capability [3]. Lee et al. reported that a surface coating with $LiCoO_2$ on $LiMn_2O_4$ and optimization of the amount of conducting agent could improve the rate capability of $LiMn_2O_4$ [4]. In the present work, we adopt the surface coating method to obtain high rate capability. ZrO_2 was used as a coating material because it could suppress additional reactions such as dissolution and corrosion of core powder [5].

In addition to high rate capability, high discharge capacity is also necessary for the practical application of lithium secondary batteries in HEVs and electric power tools. Recently, we have reported a paper on the electrochemical properties of $Li[Li_{1/6}Mn_{1/2}Co_{1/6}Ni_{1/6}]O_2$ [6].

It shows a high discharge capacity of 224 mAh g^{-1} at a 0.2 C rate. Thus, ZrO_2-coated $Li[Li_{1/6}Mn_{1/2}Co_{1/6}Ni_{1/6}]O_2$, which is expected to offer high rate capability and high discharge capacity, has been evaluated in this work. In particular, its physical and electrochemical properties are investigated via XRD, TEM, charge/discharge measurement, and electrochemical impedance spectroscopy (EIS).

2 Experimental

The method of synthesizing $Li[Li_{1/6}Mn_{1/2}Co_{1/6}Ni_{1/6}]O_2$ is sucrose combustion method which is described in detail in our group's recent report [7]. ZrO_2 coated $Li[Li_{1/6}Mn_{1/2}Co_{1/6}Ni_{1/6}]O_2$ was prepared by a wet coating method. The coating solution was prepared by dissolving a proper amount of $Zr(OH)_x(CH_3COO)_y$ $(x + y = 4)$ (Sigma Aldrich) in distilled water and stirring for 24 h at ambient temperature. A proper amount of $Li[Li_{1/6}Mn_{1/2}Co_{1/6}Ni_{1/6}]O_2$ powder was then added into the coating solution such that the weight percent of ZrO_2 was 1 wt%. After ultrasonically agitating the solution for 1 h, the mixture was dried at 50 °C and subsequently heat-treated at 120 °C for 6 h to remove residual moisture at the surface of the precursor powder. The final product was obtained by heat treatment at 500 °C for 6 h in a box furnace. This product was then poured into liquid nitrogen and quenched. X-ray diffraction experiments were performed using an Automated Rigaku X-ray diffractometer in the 2θ range from 10° to 70° with Cu-$K\alpha$ radiation. For transmission electron spectroscopy (TEM) measurements, Phillips CM20 TEM with 200 kV of accelerating voltage was used.

To prepare the positive electrode, the produced powder, carbon black (Vulcan XC-72), which was employed as a conductor, and PVdF (Sigma Aldrich) were mixed in a homogenizer at a mass ratio of 84:8:8, respectively. This viscous slurry was coated on aluminum foil using a doctor blade to a uniform thickness of 20 µm. The coated film was dried in a vacuum oven at 100 °C. Then, a 2032 type coin cell was assembled using a cathode film, a lithium foil (Foote Mineral Co.), a separator (PP, Celgard Inc.), and an electrolyte (1 M $LiPF_6$ solution in a 1:1 volume ratio of EC and DEC) in a glove box filled with Ar gas. Galvanostatic charge/discharge tests were performed using a WBCS3000 system. The current density was 0.2–6 C and the cut-off voltage was 2.0–4.8 V. For the electrochemical impedance measurements, a Solatron 1255 frequency response analyzer was used in conjunction with a Solatron 1286 electrochemical interface. After 50 cycles of charge/discharge measurement at a rate of 6 C between 2.0 and 4.8 V, impedance measurements were carried out by applying an ac voltage of 10 mV over a frequency range from 100 mHz to 100 kHz.

3 Results and discussion

To investigate the crystal structure of bare $Li[Li_{1/6}Mn_{1/2}Co_{1/6}Ni_{1/6}]O_2$ and ZrO_2-coated $Li[Li_{1/6}Mn_{1/2}Co_{1/6}Ni_{1/6}]O_2$, XRD diffraction pattern measurements were performed. XRD patterns of both the bare powder and ZrO_2-coated powder, shown in Fig. 1, are similar to that of $LiCoO_2$ (α-$NaFeO_2$ type, space group R-3m) and can be indexed as hexagonal lattice. The observation of similar XRD patterns for both powders indicates that the coating of ZrO_2 does not affect the layered hexagonal structure of the core powder. In the XRD pattern of the ZrO_2 coated powder, no other secondary phase peak is seen. The reason for this is that there was too little coating material for ZrO_2 to be detected on the surface of the core powder. Also, both XRD patterns show clearly separated (108) and (110) peaks. It is known that a clear splitting of the hexagonal doublet (108)/(110) indicates a high degree of crystallinity and good layered hexagonal ordering [5]. The main peaks of both XRD patterns are not changed significantly, as shown in Fig. 1. However, there are a few differences in XRD results. According to Dahn et al. [8], the intensity ratio of the (006)/(102) to (101) peak can be considered as a criterion for hexagonal ordering, where a lower ratio indicates a high degree of hexagonal ordering. From the present XRD results, the peak ratio of bare powder and ZrO_2-coated powder was determined to be 0.6 and 0.56 respectively, which indicates that the coating of ZrO_2 on the surface of the core powder facilitates hexagonal ordering and high crystallinity.

Figure 2a and b shows TEM images of the bare powder and the 1 wt% ZrO_2-coated powder respectively. The coated powder has 10–20 nm ZrO_2 particles that are inhomogeneously distributed on the surface of the core powder (Fig. 2b), whereas the bare powder has a smooth surface (Fig. 2a). Thus, from the TEM images, it is found

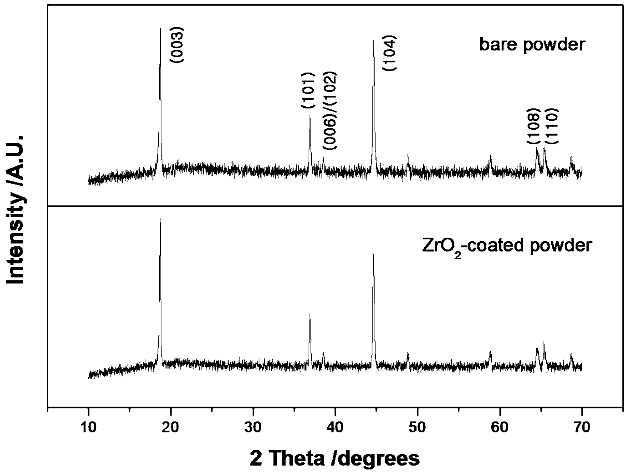

Fig. 1 XRD patterns of bare powder and ZrO_2-coated powder

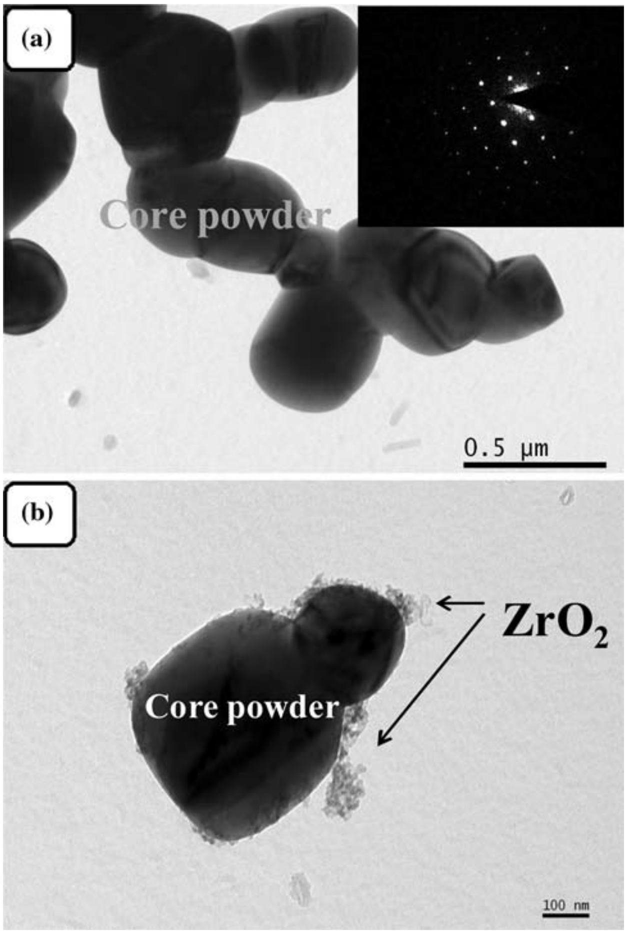

Fig. 2 (**a**) TEM image of bare powder. An inset image is SAD spot of core powder. (**b**) TEM image of ZrO$_2$-coated powder

that the ZrO$_2$ coating remains on the surface layer of the core materials in the form of small particles. Although the ZrO$_2$ particles are not coated homogeneously on the surface, ZrO$_2$ coating on the core powder will influence the electrochemical properties [9]. The inhomogeneous coating of ZrO$_2$ can enable electrons and Li$^+$ ions to transfer more easily from the core powder to the exterior because ZrO$_2$ is an insulating oxide. The inset of Fig. 2a shows a selected area diffraction (SAD) spot of the core material, indicating that the core material is a single crystal with hexagonal ordering.

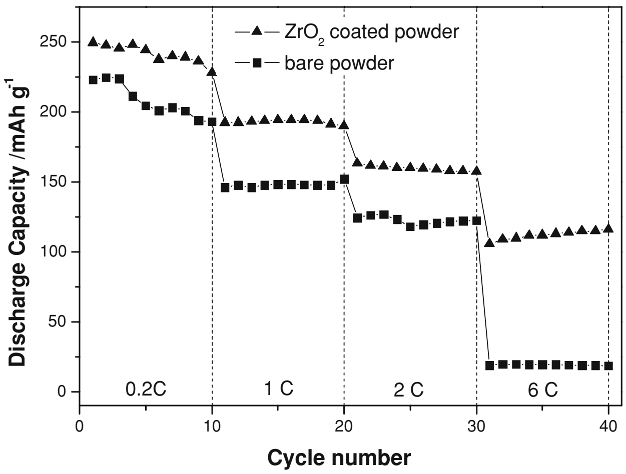

Fig. 3 Rate capability of bare powder and ZrO$_2$-coated powder at 0.2, 1, 2 and 6 C rate in a voltage range of 2.0–4.8 V

The electrochemical properties of the bare powder and ZrO$_2$-coated powder were measured at various current densities. Figure 3 shows the results of the rate capability of the bare powder and the ZrO$_2$-coated powder at rates of 0.2, 1, 2, and 6 C in a range of 2.0–4.8 V, where the samples are cycled 10 times at each current density. As seen in Fig. 3, the discharge capacity is decreased with increasing current density for both powders, but the discharge capacity of the ZrO$_2$-coated powder is decreased more slightly than that of the bare powder. The discharge capacity of the bare powder is significantly decreased from 223 mAh g^{-1} at 0.2 C to 18 mAh g^{-1} at 6 C, whereas the discharge capacity of ZrO$_2$-coated powder is slightly decreased from 249 mAh g^{-1} at 0.2 C to 105 mAh g^{-1} at 6 C. This shows that the ZrO$_2$-coated powder has a significantly enhanced rate capability.

Figure 4 shows the cyclability of the ZrO$_2$-coated powder and bare powder at a rate of 2 C for 50 cycles. The capacity retention of the bare powder after 50 cycles was 75.6%, while it was 89.4% in the case of the ZrO$_2$-coated powder. It is suggested that considerable improvement of the cyclic performance of Li[Li$_{1/6}$Mn$_{1/2}$Co$_{1/6}$Ni$_{1/6}$]O$_2$ was attained by application of the ZrO$_2$ coating. Figure 4 also shows the remarkable cyclability of the ZrO$_2$-coated powder at a rate of 6 C, indicating that a very high discharge capacity of 115 mAh g^{-1} is maintained under a high current density for 50 cycles owing to the ZrO$_2$ coating. An increase in the discharge capacity at a rate of 6 C during the initial cycles is seen; similar trends have been observed in other works on cathode materials with high rate capability [10, 11].

We have also performed cyclability measurement of 1, 2, and 3 wt% ZrO$_2$-coated powder (graph is not shown here). The 1 wt% ZrO$_2$-coated powder showed a discharge capacity of 115 mAh g^{-1} after 50 cycles at a rate of 6 C, while the 2 and 3 wt% ZrO$_2$-coated powder showed discharge capacities of 100 and 33 mAh g^{-1}, respectively, under the same conditions. It is suggested that because ZrO$_2$ is an insulating material, application of an overly high amount of ZrO$_2$ would decrease the electric conductivity. Hence, the rate capability and cyclability of the core powder were worsened. Therefore, only the 1 wt% ZrO$_2$-coated powder was used for subsequent XRD and EIS measurements.

In order to more clearly elucidate effects of ZrO$_2$ coating, we performed XRD measurements of bare powder

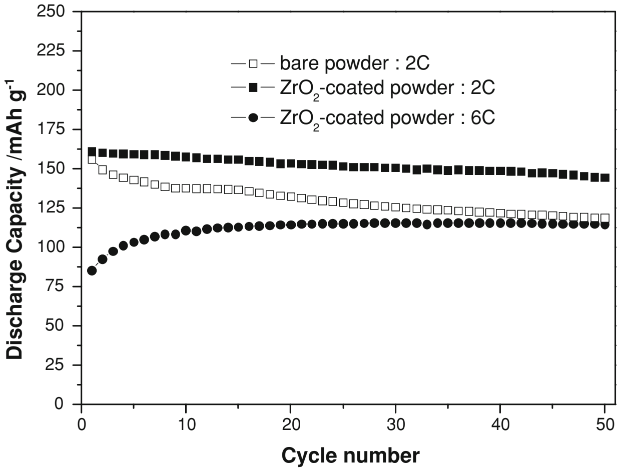

Fig. 4 Cyclic performance of bare powder at 2 C rate and ZrO_2 coated power at 2 and 6 C rate in a voltage range of 2.0–4.8 V

and ZrO_2-coated powder after 50 cycles under high current density (a 6 C rate). These XRD results are shown in Fig. 5. The highest peak at 65° reflects the Al foil current collector of the cathode electrode. As can be seen clearly in Fig. 5, the ZrO_2-coated powder maintains crystallinity with sharp diffraction peaks after 50 cycles, whereas the bare powder shows significant line broadening and loss of crystallinity. Clear separation of the two peaks of (108) and (110) are observed for the ZrO_2-coated powder but not for the bare powder. Based on these results, it is found that the layered hexagonal structure of the bare powder collapsed. Collapse of this structure occurred because strain or defects were generated by a change of volume due to the fast intercalation and extraction process of Li^+ ions during charge/discharge. In contrast, ZrO_2 particles on the surface of the core powder prevented the layered hexagonal structure from collapsing under high current density by stabilizing the layered hexagonal structure of the core powder.

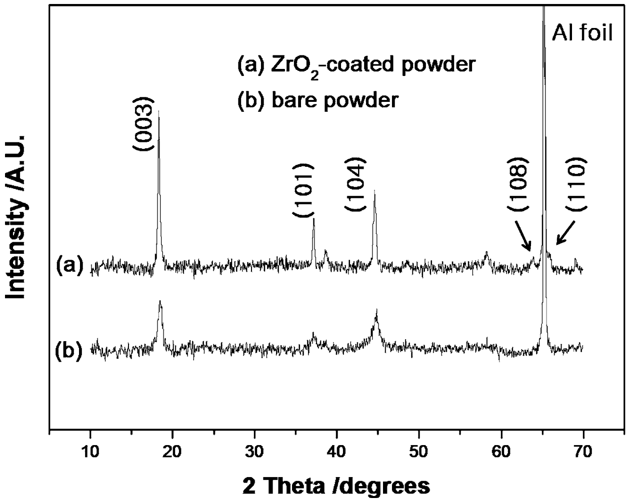

Fig. 5 XRD patterns of bare powder and ZrO_2-coated powder after 50 cycles at 6 C rate in a voltage range of 2.0–4.8 V

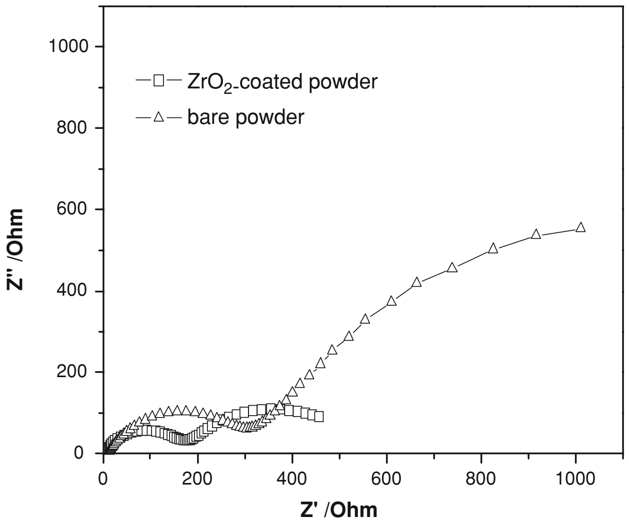

Fig. 6 Nyquist plots of bare powder and ZrO_2-coated powder after 50 cycles at 2 C rate in a voltage range of 2.0–4.8 V

Electrochemical impedance spectroscopy has been also performed to identify the electrochemical characteristics of the bare and ZrO_2-coated powders. Similar EIS studies have also been reported in conjunction with many cathode materials, such as $LiCoO_2$ [12], $Li(Ni_{0.8}Co_{0.2})O_2$ [13, 14], and TiO_2-coated $Li(Ni_{0.8}Co_{0.2})O_2$ [14]. Figure 6 shows the EIS results of the bare and ZrO_2-coated powders after 50 cycles between 2.0 and 4.8 V at a 2 C rate. A high frequency and intermediate frequency semicircle are clearly observable in both cases. In general, it is known that the high frequency semicircle is related to a passivating film that forms on the surface of the cathode electrode, the so-called solid electrolyte interface (SEI), and the intermediate frequency semicircle indicates the charge transfer resistance in the electrode/electrolyte interface [15]. According to Chen et al. [16], the impedance of Li ion batteries is mainly determined by the charge-transfer resistance in the electrode/electrolyte interface on the cathode powder. The size of the semicircle of intermediate frequency observed in the impedance spectrum of the bare powder after 50 cycles is much larger than that of the ZrO_2-coated powder. Furthermore, the size of the high frequency semicircle of the bare powder is larger than that of the ZrO_2-coated powder, indicating that the impedance growth by SEI is suppressed by ZrO_2 during cycling. A SEI is formed by corrosion or dissolution of the cathode material into a liquid electrolyte, and thus it is confirmed that the ZrO_2 coating layer prevents reaction between the electrode and electrolyte. From these EIS results, it was suggested that the lower discharge capacity loss of the ZrO_2-coated powder relative to the bare powder during cycling could be attributed to the inactive ZrO_2 coating layer on the surface of the bare powder. This layer significantly suppressed charge transfer resistance growth and formation of a SEI on the surface of the cathode electrode.

4 Conclusion

We synthesized high rate, high capacity ZrO_2-coated $Li[Li_{1/6}Mn_{1/2}Co_{1/6}Ni_{1/6}]O_2$ as a cathode material for application in lithium batteries for HEVs and electric power tools. From XRD and EIS measurements, it was found that the enhanced cyclability and improved rate capability were related to both suppression of impedance growth and the stabilized layered structure of the cathode. The ZrO_2 coating layer reduced strain and defects in the particles by stabilizing the layered hexagonal structure under high current density. Also, it suppressed charge transfer resistance growth and formation of a SEI on the surface of the cathode electrode by preventing reaction between the electrode and electrolyte during cycling. The proposed cathode material, i.e., ZrO_2-coated $Li[Li_{1/6}Mn_{1/2}Co_{1/6}Ni_{1/6}]O_2$, offers high rate capability and high discharge capacity and is expected to be a good candidate for application in lithium batteries for HEVs and electric power tools in the future.

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References

1. Ozawa K (1994) Solid State Ionics 69:212
2. Shin Y, Manthiram A (2003) Electrochem Solid-State Lett 6:A34
3. Wang X, Tanaike O, Kodama M, Hatori H (2007) J Power Sources 168:282
4. Park SC, Kim YM, Kang YM, Kim KT, Lee PS, Lee JY (2001) J Power Sources 103:86
5. Lee SM, Oh SH, Cho WI, Jang H (2006) Electrochim Acta 52:1507
6. Kim GY, Yi SB, Park YJ, Kim HG (2008) Mater Res Bull. doi: 10.1016/j.materresbull.2008.01.011
7. Yi SB, Chung HT, Kim HG (2007) Electrochem Commun 9:591
8. Reimers JN, Rossen E, Jones CD, Dahn JR (1993) Solid State Ionics 61:335
9. Fey GTK, Muralidharan P, Lu CZ, Cho YD (2006) Electrochim Acta 51:4850
10. Armstrong AR, Dupre N, Paterson AJ, Grey CP, Bruce PG (2004) Chem Mater 16:3106
11. Yun NJ, Ha HW, Jeong KH, Park HY, Kim K (2006) J Power Sources 160:1361
12. Choi YM, Pyun SI (1997) Solid State Ionics 99:173
13. Nobili F, Croce F, Scrosati B, Marassi R (2001) Chem Mater 13:1642
14. Zhang ZR, Liu HS, Gong ZL, Yang Y (2004) J Power Sources 129:101
15. Narayanan SR, Shen DH, Surampudi S, Attia AI, Halpert G (1993) J Electrochem Soc 140:1854
16. Chen CH, Liu J, Amine K (2001) J Power Sources 96:321