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Electrochemical properties of FeF_3-coated $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ cathode material

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ABSTRACT

The electrochemical properties of the $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ cathode, both in the pristine form and after the application of a coating, were characterized. FeF_3 was used as a new coating material in order to improve the electrochemical performance of $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$. It was observed that the capacity, rate capability, and cyclic performance of $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ consequently improved, in addition to improvements in thermal stability and resistance of the surface of the cathode to reactive electrolytes. The optimum amount of coating needed to produce enhanced electrochemical properties was 0.5 or 1.0 wt.% of the pristine powder.

1. Introduction

Since the introduction of the lithium ion batteries in the early 1990s, their development have been quite rapid, and they have been widely applied as power sources for electronics, in vehicles, and in energy storage systems as a result of their significant advantages over traditional rechargeable battery systems [1–7]. Recently, the structural features on the surface of the components have been the focus of many research projects, as it has been demonstrated that these features have a significant impact on the electrochemical performance of lithium ion batteries [8–11]. In particular, the safety and cyclic performance of the lithium ion batteries are primarily related to the surface reactions between the cathode and the electrolyte. Therefore, one promising approach to improve the electrochemical properties of the lithium ion batteries is to modify the surface of the cathode using stable materials in order to protect them from reactive electrolytes [12–18]. In this investigation, FeF_3 was introduced as a new coating material in order to enhance the electrochemical properties of $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$, which is a promising cathode material. Previously, fluorides have been successfully employed as coating materials [17,19,20]. FeF_3 is a stable 3D transition metal compound composed of inexpensive elements. It can react with Li reversibly through conversion reaction. Moreover, it has also been utilized as cathode materials with high voltage [21–24]. So, it is expected that the FeF_3 may act as suitable coating materials for cathode materials. In this report, FeF_3-coated $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ was characterized, and its capacity, rate capability, cyclic performance, and thermal stability were compared to those of the pristine cathode.

2. Experimental

For the pristine cathode, commercially available $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ (ECOPRO) was employed. In order to prepare the FeF_3-coated $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$, ammonium fluoride ($NH_4F$, Aldrich, USA) and aluminum nitrate nonahydrate ($FeN_3O_9{\cdot}9H_2O$, Aldrich, USA) were first dissolved in distilled water. This solution was then slowly added to the NH_4OH solution, and adjusted to a pH of 9. $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ powder, which was used without any additional purification, was mixed thoroughly with the abovementioned coating solution and dried at 80 °C. The coated powder was then annealed at 400 °C for 3 h in a flowing nitrogen atmosphere. The surface morphologies of the samples were analyzed using a field emission scanning electron microscope (FE-SEM, Nova Nano 200). The electrode used for the electrochemical testing was composed of a prepared sample containing carbon black (Super P) and poly(vinylidene) fluoride (PVDF), in a weight ratio of 80:12:8. The half cells employing the coated/pristine electrodes were then subjected to galvanostatic cycling using a WonATech system. The electrolyte was a solution of 1 M $LiPF_6$ dissolved in ethylene carbonate/dimethyl carbonate (EC/DMC) (50:50 vol.%). Differential

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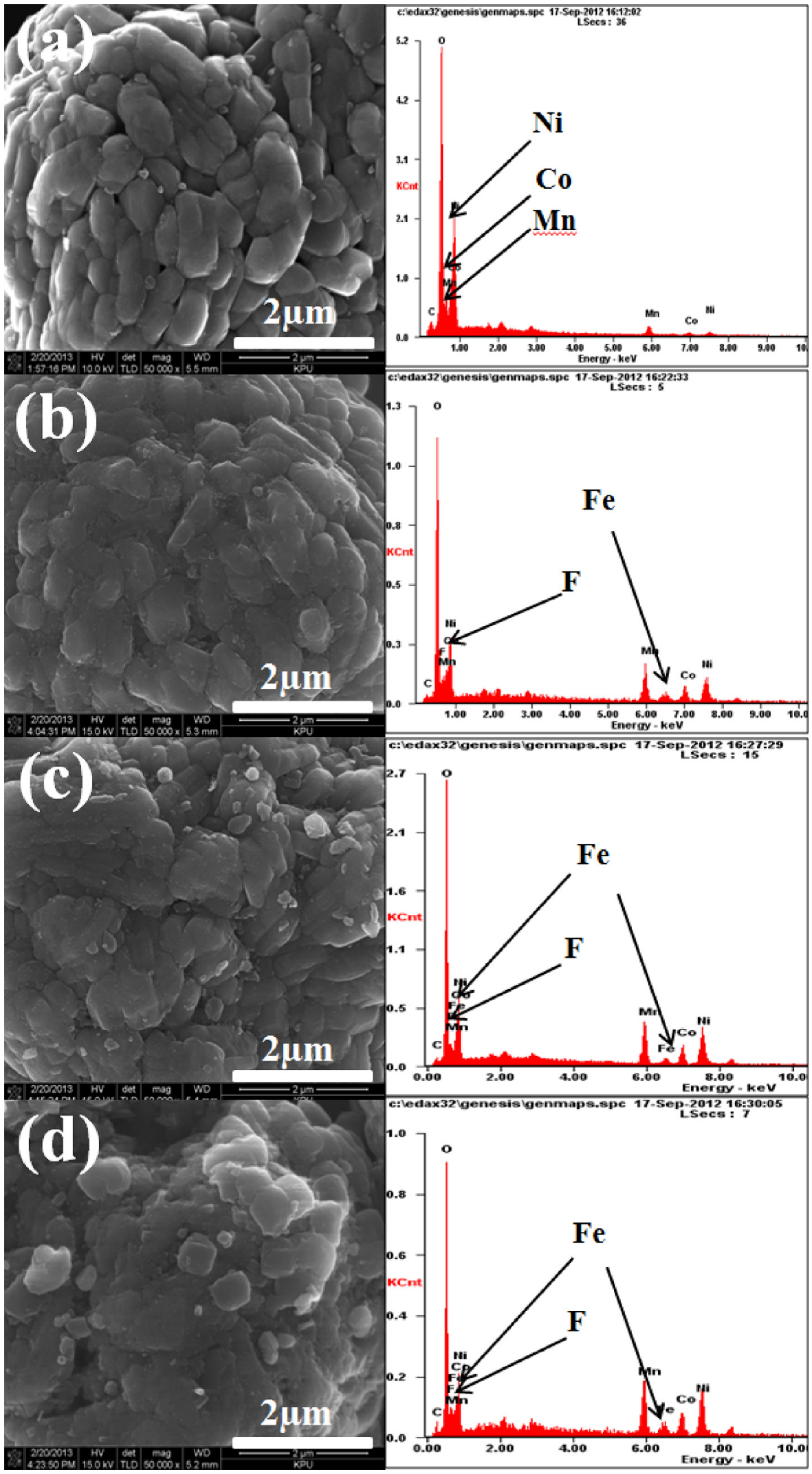

Fig. 1. SEM images of the Li[$Ni_{1/3}Co_{1/3}Mn_{1/3}$]O_2 powders; (a) pristine powder; (b) 0.25 wt.% FeF_3-coated sample; (c) 0.5 wt.% FeF_3-coated sample; and (d) 1.0 wt.% FeF_3-coated sample. The panels on the right side display the EDS results of the samples.