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Improved electrochemical properties of $Li(Ni_{0.6}Mn_{0.2}Co_{0.2})O_2$ by surface coating with $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$

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HIGHLIGHTS

- A Li^+-conductor, $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP), is coated on $LiNi_{0.6}Mn_{0.3}Co_{0.2}O_2$.
- The LATP-coated sample shows higher Li^+-diffusion coefficient than the bare sample.
- The LATP-coated sample shows narrow gap between the redox potentials.
- 0.5 wt% LATP-coating much improves the rate capability and cycling stability.
- Excessive coating of LATP degrades the cell performances of $LiNi_{0.6}Mn_{0.3}Co_{0.2}O_2$.

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ABSTRACT

$LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (C622) is one of the Ni-rich layer-structured cathode materials with a high capacity, but it suffers from a poor cycling stability and rate capability. In this study, $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP), a NASICON-type lithium-conductor, is coated on C622 by a sol–gel process to overcome the shortcomings of C622. We find that a 0.5 wt% coating of LATP on C622 significantly improves the cell performance including the discharge capacity, rate capability, and cycling stability. The pristine and LATP-coated samples were analyzed using X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS). In addition, various electrochemical analyses such as cyclic-voltammetry (CV), galvanostatic intermittent titration technique (GITT), and electrochemical impedance spectroscopy (EIS) are conducted to determine the reason for the improvement of the cell performance.

The cell performance of C622 is enhanced by a coating amount of less than 1.0 wt% and the overall performance degrades with the increase of the coating amount. The electrochemical analyses reveal that a high lithium-ion diffusion coefficient and a low interfacial resistance are the reasons for the improved cell performance; however, our study demonstrates that an excessive coating may degrade the cell performance, thereby acting as a barrier against the movement of lithium ions.

1. Introduction

An increasing demand for lithium rechargeable batteries with high energy and power capabilities has emerged as the market for the battery type continues to expand from the mobile IT-device market to other segments including vehicles such as xEVs and energy storage systems that require large-format batteries; accordingly, electrode materials with high-energy and power-density attributes are required. Major attention has been directed toward $LiNiO_2$-based or Ni-rich cathode materials [$Li(Ni_xCo_yMn_{1-x-y})O_2$, $x > 0.5$] with high contents of nickel due to the higher capacity, lower cost, and enhanced safety compared to $LiCoO_2$ [1,2]. These materials are, however, beset with several shortcomings including a poor rate capability and thermal instability, while numerous studies have been conducted to overcome these problems [3–5]. The substitution of alien elements to suppress the transformation of the crystal structure or surface modifications, so that the interfacial reaction between the electrode and electrolyte are controlled and the contact between them is minimized, can be listed as the major initiative to alleviate the previously mentioned problems. There have been several studies on the correlation to the structure-property relationship of layered cathode materials such as the lithium-rich or nickel-rich one [6–8].

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Yue et al. reported on enhancing the rate capability of C622 by surface modification with reduced graphene oxide [9]. LATP ($Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$) coating has been applied to $LiMn_2O_4$ and it has proven to be effective for the improvement of the cycling stability at high temperatures [10]. A similar approach was tried for $LiCoO_2$ and it resulted in a high discharge capacity and a sound cycling stability due to the electrode/electrolyte interfacial resistance [11]; however, there remains a dearth of the studies that have investigated the effects of the LATP coating on NMC-based cathode materials ($LiNi_xMn_yCo_{1-x-y}O_2$).

In this study, an LATP coating was applied on the promising Ni-rich layered cathode material C622 using a sol–gel process as part of a series of studies on coating technologies wherein solid electrolytes were used to improve the rate capability and cycling stability. LATP is known as one of the materials with a high ionic conductivity of approximately ~10^{-3} S/cm under an ambient temperature. In spite of its high conductivity, though, LATP is not practically used as a solid electrolyte due to its significant electronic conductivity, which may cause a cell leakage current; moreover, LATP is engaged in electrochemical reactions at around 2.5 V vs. Li^+/Li [12]. These drawbacks, however, may not matter when the LATP is applied as a material for the surface coating of the C622-cathode materials because the operating voltage of the cathode is much higher than the potential range. We therefore investigated the possibility of using LATP as a coating material for C622 in this study.

2. Experimental

The positive electrode material C622 was supplied by ENF Technology Ltd., and the starting materials for the LATP-coating layer on the C622—lithium nitrate ($LiNO_3$) aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$), titanium (IV) isopropoxide ($Ti(OCH(CH_3)_2)_4$), and anhydrous phosphoric acid (H_3PO_4)—were purchased from Samchun Chem.

The starting materials for the LATP were first dissolved in anhydrous ethanol. All of the solutions of the LATP starting materials were mixed together according to a stoichiometric ratio to prepare the coating solution ($LiNO_3$, 1.3 M: $Al(NO_3)_3 \cdot 9H_2O$, 0.3 M: $Ti(OCH(CH_3)_2)_4$, 1.7 M: H_3PO_4, 3.0 M) and stirred vigorously for 30 min at 25 °C. The coating solution is equivalent to the coating amount that was transferred to an evaporating flask, followed by the addition of C622 to the flask. The amount of coating was adjusted to 0.5, 1.0, 1.5, and 2.0 wt% of C622. (C622 coated with *x* wt % of LATP is subsequently denoted 'C622L-*x*' in this paper.) A rotating evaporator was used to ensure the application of a homogeneous coating on the surface of the C622 particles. The slurry in the flask was vacuum dried using an aspirator at 80° C, and the dried powder was calcined at 750° C for 4 h in air.

X-ray diffraction (XRD) analyses were carried out using an X-ray diffractometer (Rigaku, ULTIMA VI) over the 2θ range of 10° to 80° with monochromatized Cu-K_α radiation. The morphology of the powder was observed using high-resolution SEM with an energy dispersive spectrometer (HR-SEM/EDS, TESCAN-MIRA LMH).

To measure the electrochemical performances, 2016 coin-type half-cells were assembled in a glovebox wherein the moisture content is below 1 ppm; lithium metal was used as a counter electrode. The cathode was fabricated by casting a slurry with a formulation comprised of 90 wt% active material, 5 wt% acetylene black, and a 5 wt% polyvinylidene-difluoride (PVdF) binder on an aluminum foil. The electrolyte is 1.0 M of $LiPF_6$ solution in a 3:7 (vol %) ethylene carbonate (EC):diethyl carbonate (DEC) ratio. The coin-type cells were subjected to galvanostatic cycling and a galvanostatic-intermittent-titration-technique (GITT) measurement using a cycler (PNE Solution) within the voltage range of 3.0 V–4.3 V. The specific capacity was measured at a 0.1 C-rate and a rate capability test was conducted at a variety of current densities (0.1, 0.5, 1.0, 3.0, 5.0 and 7.0 C-rate). The cells were cycled for 100 cycles at 1.0 C-rate in the voltage range from 3.0 V to 4.3 V to examine the cycling stability.

Cyclic-voltammetry (CV) measurements were carried out in the voltage range from 3.0 V to 4.3 V at a scanning rate of 0.1 mA/s using a potentiostat/galavanostat (France, Bio-Logic, VSP). An impedance analyzer (France, Bio-Logic, VSP) was used to perform AC impedance spectroscopy with a frequency range of 500 μHz to 1 MHz, and an applied voltage of 20 mV.

3. Results and discussion

To compare the crystal structure of the pristine C622 with the LATP-coated C622, an XRD measurement was conducted and the results are shown in Fig. 1. All of the sample diffraction peaks are matched with an R-3m hexagonal layered structure without the presence of impurities. The information regarding the crystal structure is summarized in Table 1. The relative intensity of I(003)/I(104) (= R_w) shows a maximum value for the C622L-0.5 and decreases thereafter. It has been reported that the relative intensity is closely related to the degree of the cationic disorder for the $LiNiO_2$-based cathode materials [13]. In general, those cathode materials with an R_w less than 1.2 are likely to show a poor cell performance because of a severe cationic disorder [13,14]. We expected that the C622L-0.5 would exhibit the best cell performances in terms of the low cationic disorder.

Fig. 2 represents the surface morphologies of the samples. Overall, distinct changes of the particle shape were not observed after the coating process; furthermore, a particle-like film, which is considered an LATP layer, was found on the C622 surface and the coverage of the film increases with increases of the coating amount.

Energy dispersive X-ray spectroscopy (EDS) analyses were carried out on the samples to investigate the uniformity of the coating material. A typical elemental mapping result for C622L-0.5 is shown in Fig. 3. The constituent elements of LATP – Al, Ti, and P – were uniformly dispersed on the surface of C622 particles.

The initial charge and discharge profiles for the samples are displayed in Fig. 4(a); the upper and lower cut-off voltages are 3.0 and 4.3 V, respectively. The charge and discharge capacities that were obtained with the LATP-coated sample are higher than those that were obtained for the pristine sample when the coating amount is 0.5 and 1.0 wt%; however, the capacity decreased thereafter, showing lower values than the pristine for the C622L-1.5 and C622L-2.0. It is common for the reversible capacity to decrease when the electrode material is coated with electrochemically

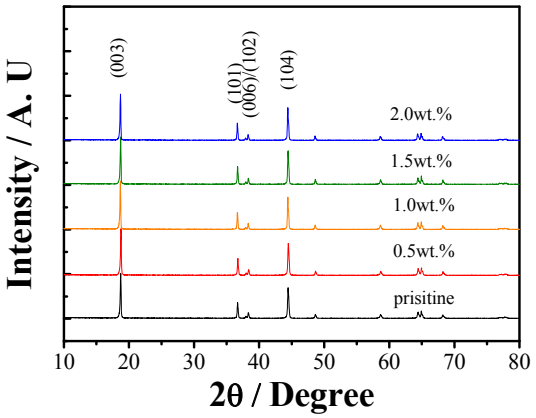

Fig. 1. Powder XRD patterns of the pristine and LATP-coated samples.