



Improved electrochemical properties of BiOF-coated 5 V spinel $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ for rechargeable lithium batteries

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ABSTRACT

The electrochemical properties of BiOF-coated 5 V spinel $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ were investigated at elevated temperatures (55 °C). As observed by scanning and transmission electron microscopy, BiOF nanolayers with ~10 nm thickness were coated on the surface of $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$. The BiOF coating layer protected the surface of the active materials from HF generated by the decomposition of LiPF_6 in the electrolyte during electrochemical cycling. The dissolution of transition metal elements was also suppressed upon cycling. Therefore, the capacity retention of the BiOF-coated $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ was obviously improved compared to the pristine $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ at 55 °C.

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1. Introduction

Advances in science and technology that have spurred sophisticated applications ranging from portable devices to hybrid electric vehicles are accompanied by the need for ever increasing power sources. Among the positive electrode materials used for high power applications, spinel-type LiMn_2O_4 compounds are considered to be the most promising due to their economical viability, eco-benign nature, and simple synthetic conditions [1]. However, serious issues regarding the capacity and cycle life of LiMn_2O_4 stemming from Mn dissolution make it less favorable for lithium battery applications [2–4]. To overcome these drawbacks, numerous attempts have been made to improve the capacity and cycle life of the material. For example, the stabilization of the spinel LiMn_2O_4 structure via partial substitution of lithium ions at the 8a tetrahedral site, 16d octahedral site, and 32e oxygen sites with S and F anion species has been attempted [5–12].

Partial substitution or doping of appropriate transition metals into the spinel matrix ($\text{Li}_x\text{M}_y\text{Mn}_{2-x-y}\text{O}_4$, M = Cr, Co, Fe, Ni, Cu,

etc.) has resulted in potential plateaus at around 5 V [13–19]. The capacity and voltage plateau in $\text{Li}/\text{Li}_x\text{M}_y\text{Mn}_{2-x-y}\text{O}_4$ cells strongly depends on the type of transition metal (M) utilized and its concentration. A high operation voltage is attractive from the viewpoint of a high specific energy. Thus, the structural and chemical stability of the electrode are very important issues to retain capacity at high voltage. Recently, we reported that the surface modification of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ by ZnO significantly improved the cyclability at elevated temperature [20,21]. The ZnO coating layer scavenged fluorine anions from HF generated from the decomposition of LiPF_6 salt in the electrolyte by transforming HF to ZnF_2 . At the same time, protection of the active material from HF attack is also important to keep the original particle morphology, reducing an increase in interfacial impedance between cathode and electrolyte.

For this purpose, we suggested a dual-functioned coating medium, BiOF, where the oxygen component may allow fluorine anions from HF and fluorine-containing moieties to protect the active materials [22]. As a result, the BiOF-coated spinel $\text{Li}[\text{Li}_{0.1}\text{Al}_{0.05}\text{Mn}_{1.85}]\text{O}_4$ exhibited excellent electrochemical cycling performances at 55 °C in the 4 V region. In this study, we applied the dual function BiOF coating nanolayer for 5 V class spinel $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ and evaluated the functionalities in the high voltage region in which oxidation of the electrolyte readily occurs. Here, we report the electrochemical properties of BiOF-coated $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ operated at 55 °C.

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2. Experimental

To synthesize BiOF-coated $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$, spherical precursor $[\text{Ni}_{0.25}\text{Mn}_{0.75}](\text{OH})_2$ was first prepared by a co-precipitation method [23]. The appropriate amounts of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ were used as the starting materials for the co-precipitation of $[\text{Ni}_{0.25}\text{Mn}_{0.75}](\text{OH})_2$. An aqueous solution of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ at a concentration of 2.4 mol L^{-1} was pumped into a continuously stirred tank reactor (CSTR, 4L) under a N_2 atmosphere. At the same time, a NaOH solution (aq.) of 4.8 mol L^{-1} and the desired amount of a NH_4OH solution (aq.) as a chelating agent were also separately pumped into the reactor. The obtained $[\text{Ni}_{0.25}\text{Mn}_{0.75}](\text{OH})_2$ was thoroughly mixed with an appropriate amount of $\text{LiOH} \cdot \text{H}_2\text{O}$ (molar ratio of Li/transition metals = 1.03) and calcined at 870°C for 20 h in air. To prepare the BiOF coating precursor, bismuth nitrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, Kanto) was dissolved in distilled water containing nitric acid. Details of the synthetic process and BiOF chemistry are described in our previous study [22]. Next, ammonium fluoride (NH_4F , Aldrich) was dissolved in distilled water, into which the prepared $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ powder was immersed. Then, the bismuth nitrate solution was slowly added to the mixture simultaneously with the appropriate amount of the NH_4OH solution. After continuous mixing for 1 h, the BiOF (might be $\text{BiO}_{0.5}\text{F}_2$) coated $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ powders were filtered and washed with distilled water. The resulting powders were dried at 110°C to remove residual water and then heated at 450°C for 5 h under air, bringing about BiOF-coated $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$.

The crystalline phase was analyzed by powder X-ray diffraction (XRD, Rigaku, Rint-2000) using $\text{Cu K}\alpha$ radiation. The morphology of the prepared powders was investigated by scanning electron microscopy (SEM, JSM-6340F, JEOL). The surface of the BiOF-coated powder was examined by means of transmission electron microscopy (TEM, JEOL 2010).

Electrochemical testing was performed in R2032 coin-type cells. The positive electrodes were fabricated by blending the prepared powders, Super P carbon black, and polyvinylidene fluoride (85:7.5:7.5) in *N*-methyl-2-pyrrolidone. The slurry was then cast on aluminum foil and dried at 110°C for 10 h in a vacuum oven. The negative electrode was lithium foil and the electrolyte was a 1 M LiPF_6 solution in an ethylene carbonate (EC)–diethyl carbonate (DEC) mixture (3:7 ratio by volume, Cheil Industries). The positive and negative electrodes were separated by a porous polypropylene film. Cycling tests were carried out in the voltage range of 3.5–5 V at 55°C .

AC impedance measurements were performed with cycling using a Zahner Elektrik IM6 impedance analyzer over the frequency range of 1 MHz to 5 mHz with an amplitude of $10 \text{ mV}_{\text{rms}}$. To measure the dissolved Ni and Mn contents, the fully charged positive electrodes (ca, 10 mg) were stored in fresh electrolytes (10 ml) for 4 weeks at 55°C . Using an atomic absorption spectroscope (AAS,

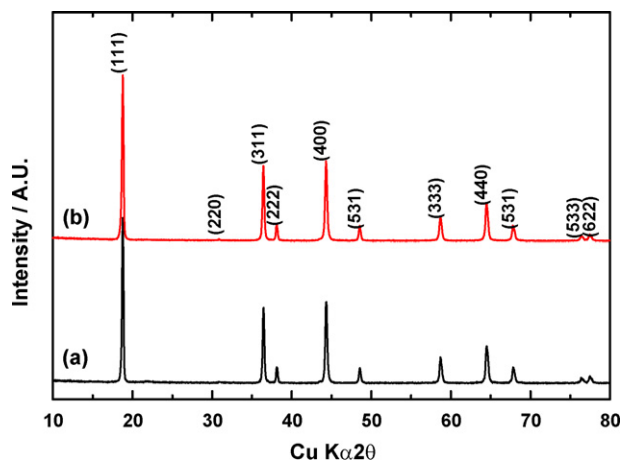


Fig. 1. XRD patterns of the (a) pristine $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ and (b) BiOF-coated $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$.

Vario 6, Analytikjena), the dissolved Ni and Mn amounts were quantified as a function of storage time. HF contents in the electrolyte were measured by a neutralization titration method. The acid–base indicator used was bromothymol blue (BTB, Aldrich).

3. Results and discussion

XRD patterns of the as-prepared $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ and BiOF-coated $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ powders are shown in Fig. 1. The existence of a well-defined spinel phase with a $Fd\bar{3}m$ space group was confirmed from the XRD patterns. No significant differences between the XRD patterns of the BiOF-coated $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ and pristine sample materials were observed. The lattice parameters were calculated by a least square method from Fig. 1. The calculated lattice parameters of the pristine and the BiOF-coated $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ are $a = 8.1678(1) \text{ \AA}$ and $a = 8.1675(1) \text{ \AA}$, respectively. These measured values are close to those previously reported [24,25]. This indicates that the BiOF coating medium was not incorporated into the $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ structure.

Figs. 2–4 show SEM, SEM-EDX and TEM images, respectively, of the pristine and BiOF-coated $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ particles. Smooth planes and well-defined edges are observed for the pristine particles in Figs 2a and 4a. Alternatively, fine and uniformly distributed BiOF particles are visible on the surface of the $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ particles in Fig. 2b. EDX elemental mappings exhibit the presence of Bi and F elements on the surface of $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ in Fig. 3d and e. TEM bright-field images further confirm the existence of the foreign coating layer on the surface of $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ in Fig. 4b. The BiOF coating layer has a thickness of approximately 20 nm and the

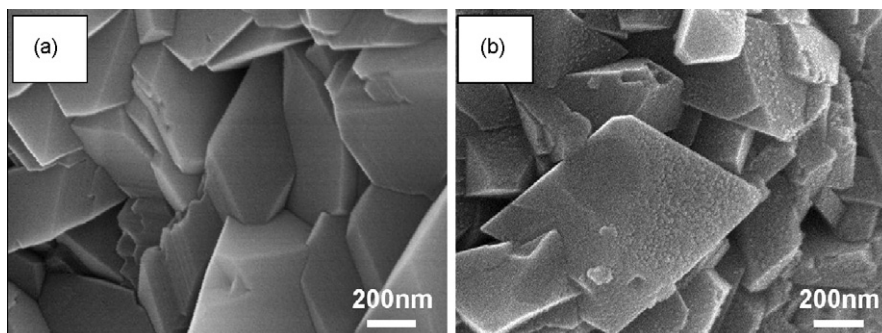


Fig. 2. SEM images of (a) pristine $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ and (b) BiOF-coated $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$.

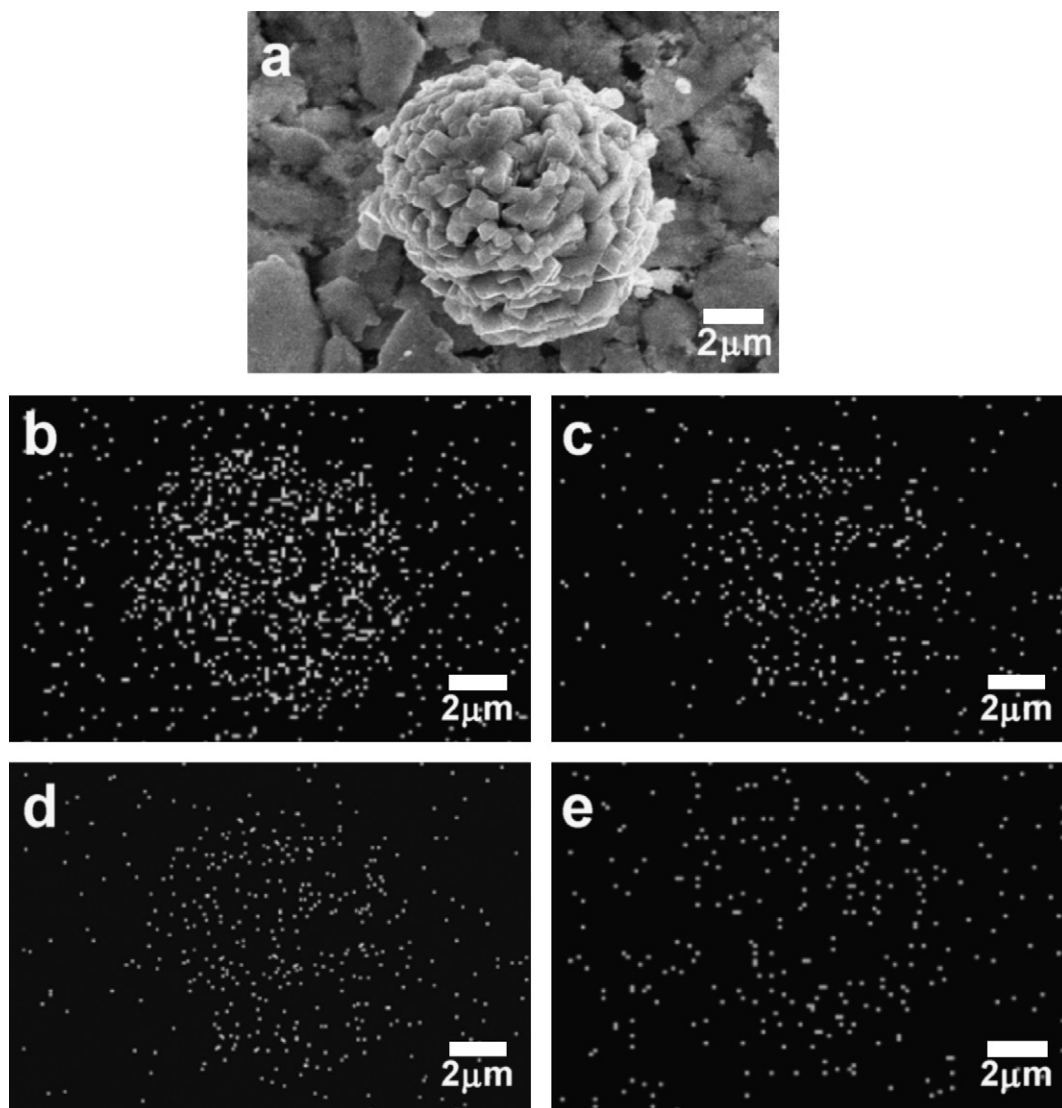


Fig. 3. EDX mappings of (a) BiOF-coated $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$, (b) Mn, (c) Ni, (d) Bi, and (e) F. The spherical BiOF-coated $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ particle was loaded on the silver paste for the measurement.

uniform contrast of the BiOF layer implies that the BiOF coating layer is thin and uniform.

Continuous charge and discharge curves of Li/pristine $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ and Li/BiOF-coated $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ cells operated at 55°C are shown in Fig. 5. The pristine and the BiOF-coated

$\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ cells had similar initial discharge capacities of around 130 mA h g^{-1} . However, the pristine $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ suffered from severe capacity fading and had a discharge capacity of only 41.4 mA h g^{-1} after 70 cycles (Fig. 5a). The resulting operation voltage also decayed drastically with cycling. On the other hand,

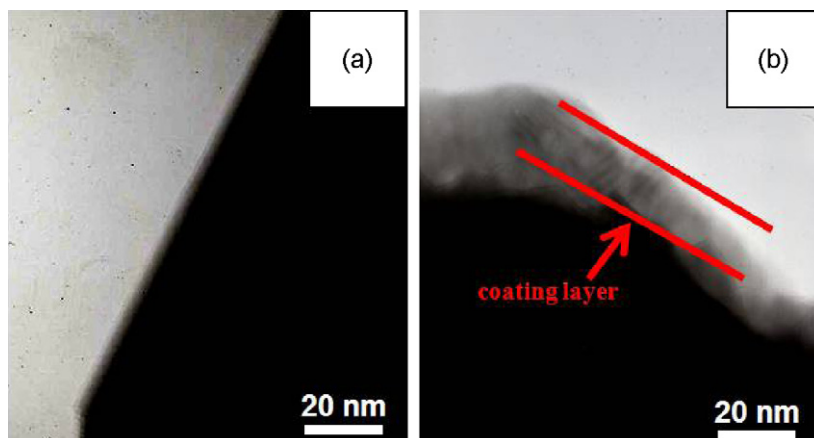


Fig. 4. TEM bright-field images of (a) pristine $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ and (b) BiOF-coated $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$.

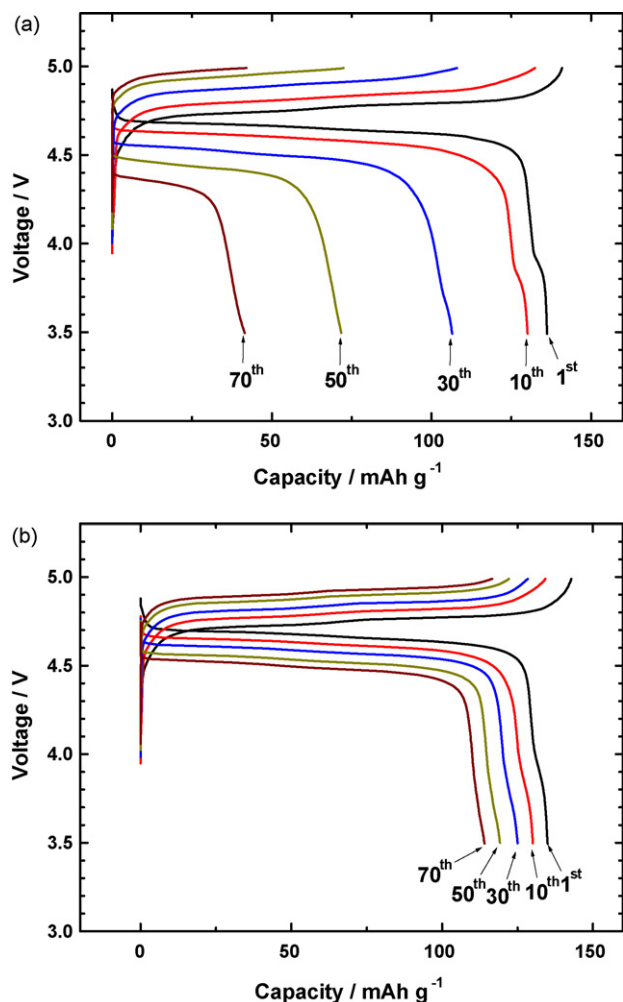


Fig. 5. Continuous charge and discharge curves of (a) Li/pristine $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ and (b) Li/BiOF-coated $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ cells at 55°C .

the discharge capacity of the BiOF-coated $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ after 70 cycles was $114.1 \text{ mA h g}^{-1}$, showing an average operation voltage as high as 4.5 V with two potential plateaus. The cycling stability with the BiOF coating was greatly enhanced, even up to the 5 V cut-off voltage limit.

The rate capability behavior also demonstrates the effect of the BiOF coating. Fig. 6 shows the discharge capacities for the Li/pristine $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ and BiOF-coated $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ cells as a function of current ($27\text{--}1350 \text{ mA g}^{-1}$) between 3.5 and 5 V vs. Li at 30°C . The cells were charged galvanostatically at a constant current of 0.2C (27 mA g^{-1}) before each discharge test. Although the pristine electrode showed abrupt capacity deterioration at currents above 5C (675 mA g^{-1}), the BiOF-coated electrode demonstrated much enhanced capacity retention, especially at higher currents. At 10C (1350 mA g^{-1}), the obtained capacity of the BiOF-coated electrode was about 65% (85.5 mA h g^{-1}) of the capacity of 133 mA h g^{-1} at 0.2C (27 mA g^{-1}) in Fig. 6b, whereas the capacity of the pristine electrode was only 35% (48.2 mA h g^{-1}) at the same current utilized in Fig. 6a. We believe that the surface modification of $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ with a BiOF nanolayer is beneficial to improve the capacity retention and rate capability especially at a higher operation voltage.

We speculated that the enhanced electrochemical properties resulted from the reduced interfacial resistance between cathode and electrolyte due to the BiOF coating. Thus, electrochemical impedance spectroscopy (EIS) for the pristine $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ and

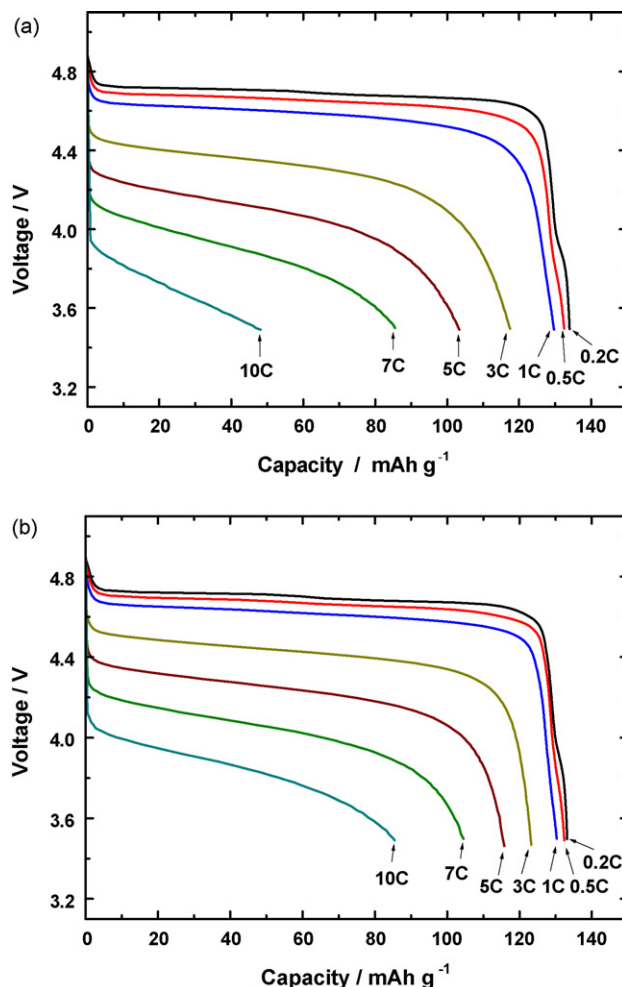


Fig. 6. Rate capabilities of (a) pristine $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ and (b) BiOF-coated $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ between 3.5 and 5 V at 0.2C, 0.5C, 1C, 3C, 5C, 7C, 10C at 30°C .

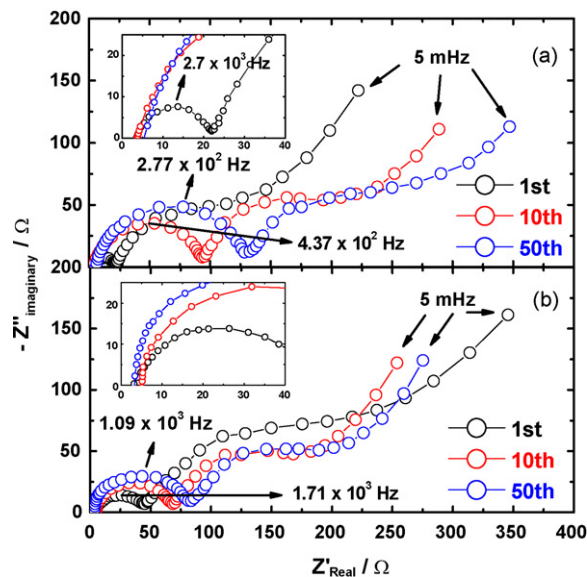


Fig. 7. Cole-Cole plots (a) pristine $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ and (b) BiOF-coated $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ between 3.5 and 5 V at 0.5C (30°C).

Table 1Comparison of lattice parameters of the extensively cycled electrodes at 55 °C for the pristine Li[Ni_{0.5}Mn_{1.5}]O₄ and BiOF-coated Li[Ni_{0.5}Mn_{1.5}]O₄.

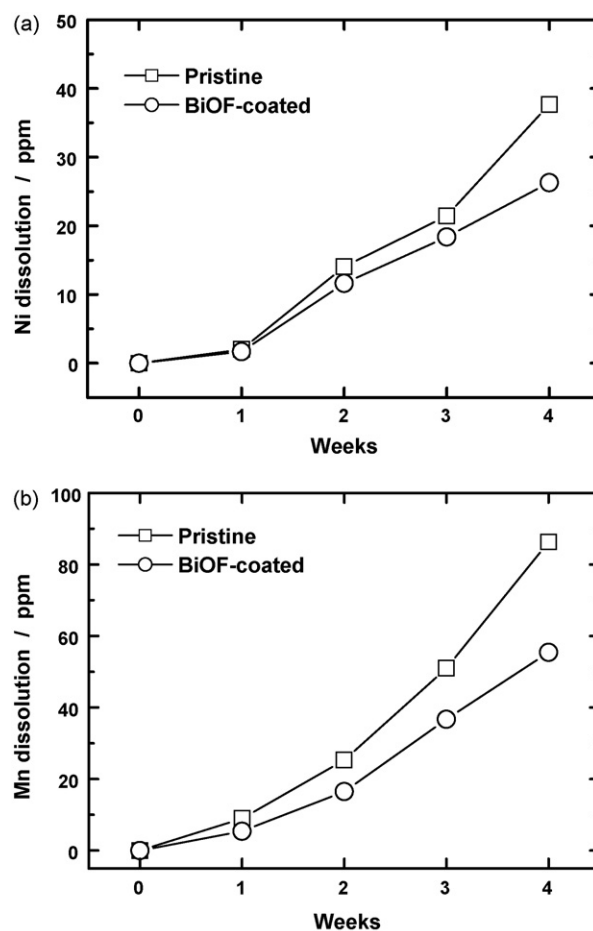
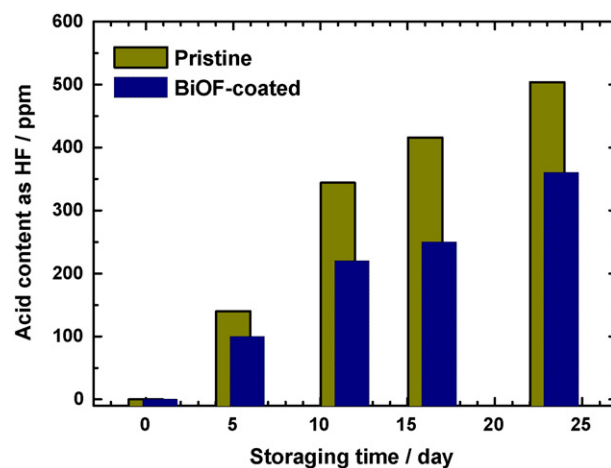
| Composition | Lattice parameter (Å) | | |
|--|-----------------------|-------------------|-----------------------------|
| | Before cycling | After 100 cycling | Difference in lattice value |
| Pristine Li[Ni _{0.5} Mn _{1.5}]O ₄ | 8.1678(1) | 8.1464(2) | 0.0214 |
| BiOF-coated Li[Ni _{0.5} Mn _{1.5}]O ₄ | 8.1675(1) | 8.1669(2) | 0.0006 |

BiOF-coated Li[Ni_{0.5}Mn_{1.5}]O₄ electrodes was performed at the fully charged state (Fig. 7). The semicircle observed at the high frequency is attributed to the contact resistance among oxide particles, and the second arc reflects charge transfer resistance accumulated on the surface of the electrode [26]. At the first charge, the contact resistance of the BiOF-coated electrode was almost twice that of the pristine electrode in the insets of Fig. 6a and b. This is reasonable because the electrically insulating BiOF nanolayer present on the surface of the active material works as an electric resistor. At the 10th charge, the contact resistance increased by a factor of almost 6 compared with the first charge for the pristine sample (Fig. 6a). In addition, the resistance value constantly increased at the 50th charge. The BiOF-coated electrode showed slight increases in the contact resistance and charge transfer resistances throughout the electrochemical cycling shown in Fig. 6b, compared with the results of the first charge. The increase in contact and charge transfer resistances for the pristine electrode implies that the interface is disturbed by other factors. This tendency indicates that the surface modification of the active material by the BiOF nanolayer is effective for reducing interfacial resistance between the electrode and electrolyte during cycling.

Extensively cycled electrodes were examined to find possible clues for the increase in the impedance by XRD. Table 1 shows the difference of lattice parameter of pristine Li[Ni_{0.5}Mn_{1.5}]O₄ and BiOF-coated Li[Ni_{0.5}Mn_{1.5}]O₄ before and after 100 cycles at 55 °C. The lattice parameter was calculated by a least square method. The lattice parameter, *a*, for the BiOF-coated Li[Ni_{0.5}Mn_{1.5}]O₄ after the extensive cycling was almost similar to that before cycling. However, the pristine Li[Ni_{0.5}Mn_{1.5}]O₄ after cycling had a slightly smaller *a* value in Table 1.

Changes in the structure are usually derived from the dissolution of active materials [22]. Thus, the fully charged electrodes were stored in fresh electrolytes for 4 weeks at 55 °C, and the dissolved amounts of transition metal elements were then measured by AAS, as shown in Fig. 8. The dissolved amounts of Ni and Mn for the pristine Li[Ni_{0.5}Mn_{1.5}]O₄ were approximately 3 and 11 ppm, respectively, during the first week, while the BiOF-coated Li[Ni_{0.5}Mn_{1.5}]O₄ exhibited smaller Ni and Mn dissolutions of 1.5 and 6 ppm, respectively. The dissolved contents of Ni and Mn increased monotonously with time. After 4 weeks, the dissolved Ni and Mn for the pristine and BiOF-coated Li[Ni_{0.5}Mn_{1.5}]O₄ were 37.7 and 84 ppm, 26.3 and 56 ppm, respectively. Based on the dissolution results, it is likely that the reduced dissolution of transition metals may partially affect the variation in the cell impedance with cycling.

As shown in Fig. 5, the voltage plateaus of the pristine and BiOF-coated Li[Ni_{0.5}Mn_{1.5}]O₄ are in the voltage range of 4.5–5.0 V, where oxidation of the electrolyte readily takes place. This reaction facilitates the decomposition of the electrolytic salt LiPF₆, which generates HF as a byproduct in the electrolyte. Fig. 9 shows the HF titration results for the electrolyte of the fully charged Li/pristine Li[Ni_{0.5}Mn_{1.5}]O₄ and Li/BiOF-coated Li[Ni_{0.5}Mn_{1.5}]O₄ cells taken over 4 weeks at 55 °C. The amount of HF obviously increased as a function of time. The HF concentration for the pristine Li[Ni_{0.5}Mn_{1.5}]O₄ was around 550 ppm after 4 weeks, while that of the electrolyte of the BiOF-coated Li[Ni_{0.5}Mn_{1.5}]O₄ was

**Fig. 8.** Ni and Mn dissolution for the electrolyte of the fully charged (to 5 V) Li/pristine Li[Ni_{0.5}Mn_{1.5}]O₄ and Li/BiOF-coated Li[Ni_{0.5}Mn_{1.5}]O₄ cells during 4 weeks at 55 °C.**Fig. 9.** HF titration results for the electrolyte of the fully charged (to 5 V) Li/pristine Li[Ni_{0.5}Mn_{1.5}]O₄ and Li/BiOF-coated Li[Ni_{0.5}Mn_{1.5}]O₄ cells during 4 weeks at 55 °C.

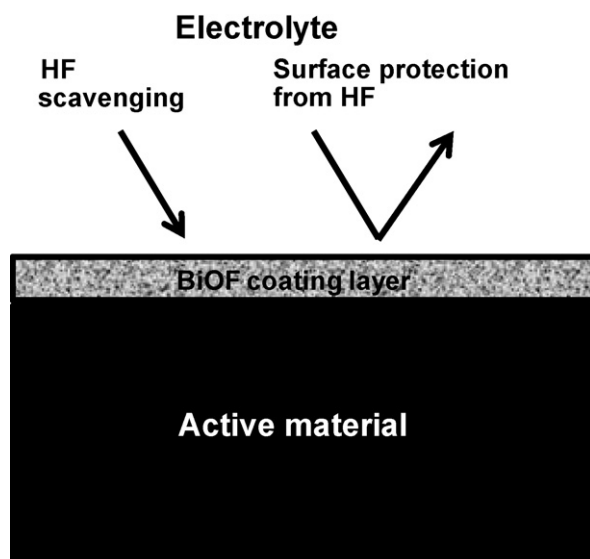


Fig. 10. Schematic drawing of interface between positive electrode and electrolyte. The BiOF coating layer performs dual functions: HF scavenging and surface protection from HF attack into the electrolyte.

approximately 325 ppm. This result indicates that the BiOF coating provides an effective means to suppress HF propagation. In our prior report, we suggested that the BiOF works as a HF scavenger, particularly for F^- ions, so that the propagated amount of HF was significantly reduced for the BiOF-coated $Li[Li_{0.1}Al_{0.05}Mn_{1.85}]O_4$ [22]. In a similar way, the BiOF nanolayer present on the surface of $Li[Ni_{0.5}Mn_{1.5}]O_4$ scavenges the HF resulting from the decomposition of the electrolytic salt in the electrolyte. Therefore, it is believed that the amount of HF was quite reduced for the case of the BiOF-coated active material.

In the electrolyte decomposition process which generates HF, ethylene carbonate, LiF, Li_xPF_y -type, and $Li_xPF_yO_z$ -type compounds are concurrently formed as byproducts [27–29]. Then, the byproducts are able to adhere on the surface of the positive electrode. As shown in the impedance results (Fig. 7a), the large increases in the contact and charge transfer resistances for pristine $Li[Ni_{0.5}Mn_{1.5}]O_4$ can be ascribed to the adherence of these byproducts on the electrode surface. LiF, which is highly resistive to Li ion transport, covering the electrode surface would delay the Li^+ kinetics so that the pristine $Li[Ni_{0.5}Mn_{1.5}]O_4$ demonstrated a poor rate capability [30], as seen in Fig. 6a. Partial surface degradation of the active material by the Lewis acid HF gives rise to an increase in interfacial resistance, which results in a capacity fading and poor rate capability, as seen in Figs. 5a and 6a. Again, the BiOF coating layer on $Li[Ni_{0.5}Mn_{1.5}]O_4$ scavenges HF into the electrolyte during cycling. Hence, the formation of ethylene carbonate, LiF, Li_xPF_y , and $Li_xPF_yO_z$ byproducts may be suppressed on the surface of BiOF-coated $Li[Ni_{0.5}Mn_{1.5}]O_4$. As a result, the interfacial resistance became smaller during cycling (Fig. 7b), and the rate capability and cycling performances were improved by the successful protection of the active material from HF due to the HF scavenging ability of the BiOF coating layer in the 5V region, as schemed in Fig. 10.

4. Conclusions

Spinel $Li[Ni_{0.5}Mn_{1.5}]O_4$ powders were coated with BiOF to improve their electrochemical performances. The BiOF-coated $Li[Ni_{0.5}Mn_{1.5}]O_4$ showed a significantly improved capacity retention of 84.5% for 70 cycles at 55 °C, while the pristine exhibited a capacity retention of only 31.3%. Furthermore, the rate capability of the BiOF-coated $Li[Ni_{0.5}Mn_{1.5}]O_4$ was remarkably enhanced. The improved electrochemical performance is attributed to the BiOF nanolayer scavenging HF in the electrolyte. In addition, the decreased dissolution of transition metals with the BiOF coating was not a major factor for the enhanced battery performances. Therefore, the BiOF coating was found to have positive effects on the improvement of electrochemical properties with the 5V $Li[Ni_{0.5}Mn_{1.5}]O_4$ spinel compound.

Acknowledgements

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