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COMMUNICATION

LiFePO₄ modified Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄ cathodes with improved lithium storage propertiesI. C. Jang,^a C. G. Son,^a S. M. G. Yang,^a J. W. Lee,^a A. R. Cho,^a V. Aravindan,^{ab} G. J. Park,^c K. S. Kang,^d W. S. Kim,^e W. I. Cho^f and Y. S. Lee^{*a}

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LiCoPO₄ and Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄ were prepared by conventional solid state reactions. The surface modification of Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄ particulates by LiFePO₄ was successfully carried out by a dry coating procedure. TEM analysis confirmed the presence of a LiFePO₄ coating layer of about 20 nm on the surface of the Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄ particles. All three cells delivered high initial discharge capacities of 122, 130 and 128 mA h g⁻¹ for LiCoPO₄, Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄, and LiFePO₄ modified Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄, respectively. However, these cells presented quite different cycle retention rates after 20 cycles, 21, 22 and 70% for LiCoPO₄, Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄, and LiFePO₄ modified Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄, respectively. The improved cycle retention of the LiFePO₄-modified Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄ resulted from its reduced reactivity towards the electrolyte and the effective prevention of resistive layer formation on the LiCoPO₄ surface during high voltage cycling.

Introduction

The research interests into lithium cobalt phosphate, LiCoPO₄ have recently attracted scientists due to their overwhelming advantages, such as, a high theoretical energy density (800 W h kg⁻¹), a high and flat operating potential ~4.8 V vs. Li/Li⁺, which ensures high thermal stability owing to the presence of a strong P–O covalent bond, and the ease of preparation on the industrial scale. However, due to poor conductivity (~10⁻⁹ S cm⁻¹) the high voltage redox couple located at ~4.8 V vs. Li makes the practical application doubtful in conventional solutions.^{1–5} Several research efforts are focused on developing high voltage candidates for practical applications. Amine *et al.*¹

originally demonstrated the electrochemical activity of LiCoPO₄ in sulfolane based electrolytes and found that 0.42 moles of Li-ions could be reversibly inserted. Yang *et al.*⁶ attempted to employ an *in-situ* carbon coating technique to improve the conductivity, like LiFePO₄, and revealed that it is very difficult to carbon coat its surface. Li *et al.*⁷ successfully prepared LiCoPO₄ core-shell nanoparticles with pronounced carbon coating by introducing acetylene black during synthesis. Conversely, a Li/LiCoPO₄ cell experienced severe capacity fade during cycling due to poor compatibility with the electrolyte. The conductivity improvement observed in the above system was not due to the presence of carbon coating but originated from the appearance of Co₂P, as confirmed by Wolfenstine.⁸ This secondary phase appeared when heat treating the material in an inert atmosphere with carbon. Later Han *et al.*⁹ successfully adopted isovalent (Fe) doping for Co sites with carbon coating by microwave heating in the presence of activated carbon to improve the conductivity. This approach improved the cell performance of LiCoPO₄, however, no cycling profiles were reported. Another approach to improve the electrochemical property is to create rich or deficient phases in the lithium sites, which reveals a drastic improvement in the electronic conductivity and was well established by Herle *et al.*,¹⁰ Kim *et al.*¹¹ and our group¹² for the LiFePO₄ system. In this line, we adopted the same strategy for the LiCoPO₄ system, which means creating a lithium rich phase along with the isovalent substitution of the cobalt site by Fe via a solid state method to improve the electrochemical performance of LiCoPO₄. Furthermore, to reduce the reactivity towards conventional electrolytes, the LiFePO₄ coating was made through a dry coating procedure.¹³ The obtained result was compared with LiCoPO₄ and Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄ prepared by a similar solid-state route.

Experimental section

Stoichiometric ratios of LiOH·H₂O (Junsei, Japan), Co₃O₄ (Aldrich, USA), adipic acid (Aldrich, USA) and (NH₄)₂PO₄ (Sigma-Aldrich, USA) were used for the solid state synthesis of LiCoPO₄. The starting materials were finely ground, formed into pellets, and heated at 400 °C for 10 h to decompose the hydroxyl and ammonia moieties. The resulting intermediate was finely ground, made into a pellet and fired in a tubular furnace at 800 °C for 10 h. After placing the pellets into the tubular furnace, which was purged with Ar gas until the temperature reached 800 °C when the flow of Ar was stopped.

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The presence of available carbon (derived from the carbonization of adipic acid) will reduce the oxidation states from Co^{3+} to Co^{2+} . A similar technique was adopted for the doping of Li and Fe into lithium and cobalt sites, respectively, forming $\text{Li}_{1.02}(\text{Co}_{0.9}\text{Fe}_{0.1})_{0.98}\text{PO}_4$. The exact proportions of the prepared materials are calculated based on the inductively coupled plasma (ICP) and Rietveld analysis. Stoichiometric ratios of Li_2CO_3 (Wako, Japan), $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (Junsei, Japan) and $(\text{NH}_4)_2\text{PO}_4$ (Sigma-Aldrich, USA) were used as source materials for the preparation of nano-crystalline LiFePO_4 . In a typical solid-state synthesis, the starting materials were finely ground and heated at 400°C for 1.5 h to decompose any moieties present in the material. The intermediate was re-ground and heated at 660°C for 2.5 h under Ar to yield LiFePO_4 .¹⁴ For surface modification, an appropriate amount of (1.5 wt.%) LiFePO_4 was coated on the $\text{Li}_{1.02}(\text{Co}_{0.9}\text{Fe}_{0.1})_{0.98}\text{PO}_4$ surface using a dry coating system (NOB-130, Hosokawa micron Ltd., Japan) with a rotation rate of 2700 rpm for 3 min.^{13,15} This product was again subjected to heat treatment at 500°C for 4 h to ensure LiFePO_4 coating on $\text{Li}_{1.02}(\text{Co}_{0.9}\text{Fe}_{0.1})_{0.98}\text{PO}_4$ particles. All the electrochemical studies were performed using a CR2032 coin cell. The cathodes were fabricated with 20 mg of accurately weighed active material, 3 mg of ketjen black, and 3 mg of teflonized acetylene black (TAB) which was pressed onto a 200 mm^2 stainless steel mesh and dried at 130°C for 5 h in a vacuum oven. 1 M LiPF_6 in an ethylene carbonate (EC)/dimethyl carbonate (DMC) (1 : 1 v/v, Techno Semichem Co., Ltd, Korea) mixture was used as the electrolyte. Electrochemical impedance spectroscopy (EIS) was performed using a Bio-Logic electrochemical work station (SP-150, Biologic, France) with a three electrode cell configuration. The charge/discharge current density was 0.1 mA cm^{-2} with a cut-off voltage of 3.5 to 5.2 V. The detailed information about characterizations and electrode fabrications are given in our previous publications.^{12,14}

Results and discussion

X-ray diffraction (XRD) patterns of pristine LiCoPO_4 , $\text{Li}_{1.02}(\text{Co}_{0.9}\text{Fe}_{0.1})_{0.98}\text{PO}_4$ and LiFePO_4 modified $\text{Li}_{1.02}(\text{Co}_{0.9}\text{Fe}_{0.1})_{0.98}\text{PO}_4$ are presented in Fig. 1(a). The XRD pattern revealed the formation of an olivine phase without any secondary phases like Co_2P and Li_3PO_4 . However, the trace amount of the Co_3O_4 phase was observed in the XPS analysis (not shown in here), which is below the detectable limitations of an X-ray diffractometer. The sharp, intense reflections correspond to the highly ordered crystalline nature of the materials prepared. The observed patterns are consistent with JCPDS card (No. 89-6192) and the Bragg reflections were indexed according to their orthorhombic structure with $Pnma$ space group. It is well known that, to detect the Fe doping or LiFePO_4 coating through XRD is too complicated, because the substance used for doping or coating is too small.^{13,15,16} Moreover, the coating substance, LiFePO_4 also belongs to the same orthorhombic structure, which makes it more difficult to distinguish against the parent LiCoPO_4 material. Therefore, a TEM was recorded for both $\text{Li}_{1.02}(\text{Co}_{0.9}\text{Fe}_{0.1})_{0.98}\text{PO}_4$ and LiFePO_4 modified $\text{Li}_{1.02}(\text{Co}_{0.9}\text{Fe}_{0.1})_{0.98}\text{PO}_4$ powders to ensure the coating over the particulates, and the recorded images are presented in Fig. 1(b and c). It is very obvious that there is a pronounced coating of the LiFePO_4 layer on the surface of $\text{Li}_{1.02}(\text{Co}_{0.9}\text{Fe}_{0.1})_{0.98}\text{PO}_4$ particles when compared to the $\text{Li}_{1.02}(\text{Co}_{0.9}\text{Fe}_{0.1})_{0.98}\text{PO}_4$ powders.

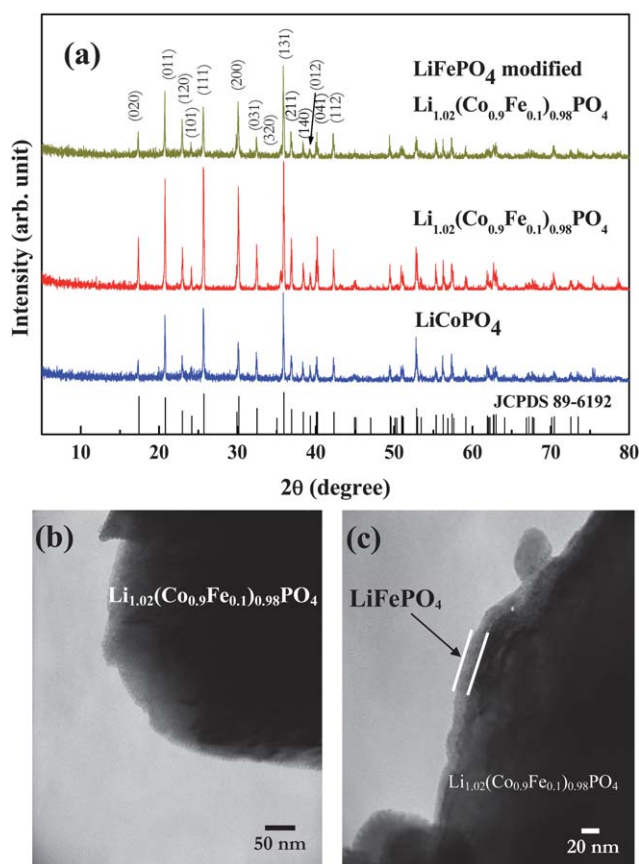


Fig. 1 (a) X-ray diffraction patterns of synthesized olivine phosphates, (b) TEM images of $\text{Li}_{1.02}(\text{Co}_{0.9}\text{Fe}_{0.1})_{0.98}\text{PO}_4$, and (c) LiFePO_4 modified $\text{Li}_{1.02}(\text{Co}_{0.9}\text{Fe}_{0.1})_{0.98}\text{PO}_4$.

Fig. 2 shows the typical galvanostatic cycling profiles of different cobalt phosphates which were cycled at a current density of 0.1 mA cm^{-2} between 3.5–5.2 V at room temperature. All three,

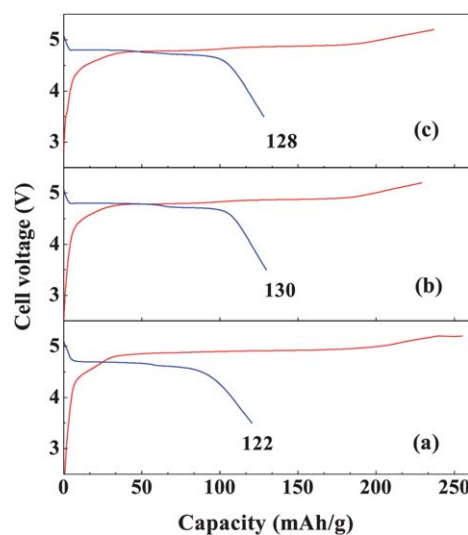


Fig. 2 Initial charge/discharge curves of various cobalt phosphates recorded between 3.5–5.2 V. (a) LiCoPO_4 , (b) $\text{Li}_{1.02}(\text{Co}_{0.9}\text{Fe}_{0.1})_{0.98}\text{PO}_4$, and (c) LiFePO_4 modified $\text{Li}_{1.02}(\text{Co}_{0.9}\text{Fe}_{0.1})_{0.98}\text{PO}_4$.

LiCoPO₄, Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄ and LiFePO₄ modified Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄ electrodes exhibited a long, distinct plateau around ~4.8 V vs. Li, which is attributed to the oxidation of Co²⁺ to Co³⁺. The cells delivered initial discharge capacities of 122, 130 and 128 mA h g⁻¹ for LiCoPO₄, Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄ and LiFePO₄ modified Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄, respectively against a theoretical capacity of 167 mA h g⁻¹. During charging, all three cells showed decomposition of the electrolyte, which is observable in the charge curves of Fig. 2. This is due to the higher oxidation potential of the Co^{3+/2+} redox couple, which exceeds safe operation limits of conventional electrolyte solutions. As expected, Fe and Li substitution certainly improved the electronic conductivity of LiCoPO₄⁹⁻¹² and it was well reflected in the electrochemical studies. The substituted electrodes are able to reversibly insert a slightly greater amount of lithium ions (0.79 and 0.77 moles Li⁺ ions per formula unit for Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄ and LiFePO₄ modified Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄ respectively) than LiCoPO₄ (0.72 moles) during the first cycle. It could be seen that there was no obvious difference in the electrochemical performances of Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄ and LiFePO₄ modified Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄ when compared with LiCoPO₄.

The cycling profiles of the three cells are presented in Fig. 3. It is apparent that, during the initial cycling that both the LiFePO₄ modified and Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄ electrodes showed good performance up to the 5th cycle. Thereafter, the Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄ electrode experiences capacity fade and it finally coincides with the profiles of LiCoPO₄ at the 19th cycle. As shown in the figure, LiCoPO₄ faces a continuous capacity fade which was also noticed by other researchers.^{3,9} After 20 cycles, 21 and 22% of the initial discharge capacities were respectively retained by the cells employing LiCoPO₄ and Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄. The LiFePO₄-modified Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄ retained 70% of the initial capacity after 20 cycles, which is one of the best cycling results reported for a LiCoPO₄-based material. Generally, there are two reasons attributed to the fade, (i) inherent electronic conductivity of the materials and (ii) poor compatibility with conventional electrolytes or higher reactivity towards them. The conductivity issue can be circumvented by substituting transition metal elements to either the lithium or cobalt sites,^{3,9,10,12} but reducing the reactivity towards electrolytes is challenging. The surface modification with carbon (*in-situ*) is not possible and also leads to the formation of Co₂P.^{6,8}

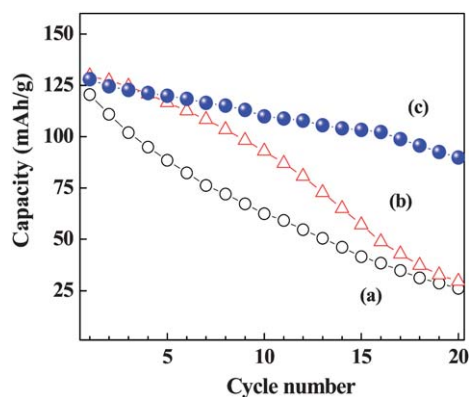


Fig. 3 Cycle performance of various cobalt phosphates recorded between 3.5–5.2 V. (a) LiCoPO₄, (b) Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄, and (c) LiFePO₄ modified Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄.

Ex-situ carbon coating also failed to provide the expected improvement during cycling.^{7,9} Hence, the LiFePO₄ coating of the Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄ particles was tested because it can render good thermal stability at elevated temperatures, provide long-term capacity retention and reduce reactivity towards electrolytes at high voltages. This was convincingly proven by Wang *et al.*¹⁶ for LiCoO₂ and our group^{13,15} for Li(Ni_{0.5}Co_{0.2}Mn_{0.3})O₂. The same strategy was applied to improve the cycling profiles of cobalt phosphates in the high voltage region for the first time. Further studies are underway to improve the cycling performance even further.

To understand the LiFePO₄ modified Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄ effect in depth, AC impedance measurements were carried out using the cells containing the bare LiCoPO₄ and Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄.

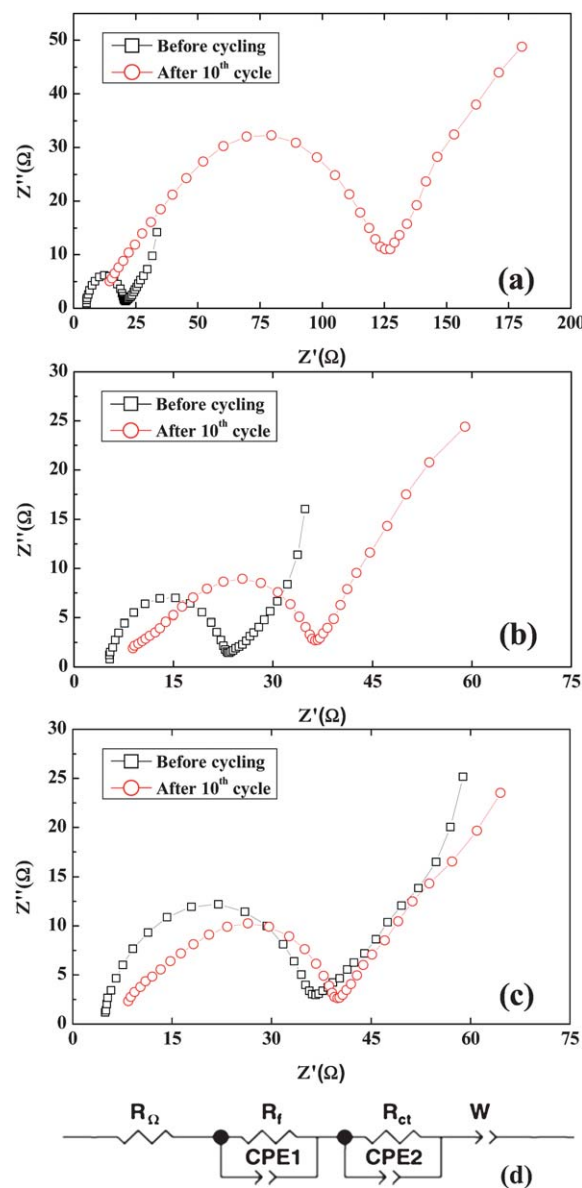


Fig. 4 Electrochemical impedance spectroscopic traces of (a) LiCoPO₄, (b) Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄ (c) LiFePO₄ modified Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄ before cycling and after 10 cycles, and (d) equivalent circuit used for the EIS analysis.

To ensure solid electrolyte interphase (SEI) film formation and the percolation of the electrolyte through the electrode particles, impedance measurements were carried out after 10 cycles. Fig. 4 shows Nyquist plots obtained from the bare LiCoPO₄ and Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄ electrodes after the 10th cycles. The cycle behavior of the three materials rapidly changes from this point, already shown in Fig. 3. Generally, an intercept at the Z_{real} axis at a high frequency corresponds to the ohmic resistance (R_s), which represents the total resistance of the electrolyte, separator, and electrical contacts. The depressed semicircle in the high frequency range is related to the Li-ion migration resistance (R_f) through the SEI film formed on the electrode or another coating layer. The second semicircle in the middle frequency range indicates the charge transfer resistance (R_{ct}). The inclined line in the lower frequency range represents the Warburg impedance, the inclined line at an approximate 45° angle to the real axis corresponds to the lithium diffusion kinetics towards the electrodes. Simplified equivalent circuit models were constructed to analyze the impedance spectra (Fig. 4d).

In particular, the charge transfer resistance of the bare LiCoPO₄ electrode increased drastically after 10 cycles, while the R_{ct} of the LiFePO₄ modified Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄ electrode did not change much. The R_f values were decreased for the LiFePO₄ modified Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄, suggesting that the resistance of the Li-ion migration was decreased. It showed that the values of R_f and R_{ct} of the LiFePO₄ modified Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄ electrode were reduced compared to the bare LiCoPO₄ and Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄ electrodes, which explains the good compatibility towards electrolyte solutions. The total interfacial resistance can be derived from the resistance of the semi-circle within the curves. It can be seen that the interfacial resistance of the bare LiCoPO₄ increased drastically, indicating a shift in the impedance spectra from 18 to 120 Ω after 10 cycles, while the interfacial resistance of the bare Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄ cell shifts from 15 to 32 Ω after 10 cycles. For the LiFePO₄ modified Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄, the interfacial resistance is observed to shift slightly from 30 to 35 Ω after 10 cycles, indicating the synergic effects of the LiFePO₄ modification over Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄ particles.^{17,18} Recently, Park *et al.*¹⁹ reported the useful approach to surface modification of polyimide gel polymers on LiCoO₂ for the high voltage region. This trial was very effective at suppressing the undesirable interfacial reaction between the charged LiCoO₂ surface and the liquid electrolyte. LiFePO₄ modification on the Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄ can be considered to be a very similar concept which prevents unnecessary reactions between active materials and the electrolyte at high voltages. This holds good agreement with the charge curves of LiCoPO₄ (Fig. 2a) which exceeds 250 mA h g⁻¹ and compares to other electrodes. This decomposed mass on the surface hinders Li⁺ ion migration and increases capacity fade during cycling. Whereas for the LiFePO₄ modified Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄, the rate of change of the CT impedance is found to be very small (it was even decreased when compared with before cycling) compared with LiCoPO₄ and Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄. A more detailed coating mechanism of the LiFePO₄ layer onto Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄ is undergoing and will be discussed in other reports. We concluded that the improved cycle retention of LiFePO₄ modified Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄ resulted from the reduced reactivity towards the electrolyte components and the effective suppression of resistive layer formation compared to LiCoPO₄ and Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄ surface during cycling.

Conclusion

The effect of LiFePO₄ surface modification on the electrochemical properties of Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄ was studied. Isovalent doping certainly improves the cell performance of LiCoPO₄ for the initial cycle, however, it also experiences severe capacity fade during cycling, similar to the parent compound due to poor compatibility with the electrolyte. LiFePO₄ modified Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄ yielded better capacity retention than other compounds. Especially after 20 cycles, 21, 22 and 70% of initial discharge capacities were retained for LiCoPO₄, Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄ and LiFePO₄ modified Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄, respectively. These results suggest that the surface modification with LiFePO₄ on Li_{1.02}(Co_{0.9}Fe_{0.1})_{0.98}PO₄ particle strongly prevented vigorous reactivity towards the electrolyte and effectively suppresses the resistive layer formation, which leads to improved cell performance of high voltage materials.

Acknowledgements

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