



Short communication

Eliminating the irreversible capacity loss of high capacity layered $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ cathode by blending with other lithium insertion hosts

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ABSTRACT

The large irreversible capacity loss generally encountered with the high capacity layered oxide solid solutions between layered $\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ and LiMO_2 ($M = \text{Mn}, \text{Ni}, \text{and Co}$) has been reduced by blending layered $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$, which is a solid solution between $\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ and $\text{Li}[\text{Mn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}]\text{O}_2$, with spinel $\text{Li}_4\text{Mn}_5\text{O}_{12}$ or LiV_3O_8 . The irreversible capacity loss decreases from 68 to 0 mAh g^{-1} as the $\text{Li}_4\text{Mn}_5\text{O}_{12}$ content increases to 30 wt.% in the $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ – $\text{Li}_4\text{Mn}_5\text{O}_{12}$ composite and the LiV_3O_8 content increases to 18 wt.% in the $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ – LiV_3O_8 composite. The decrease in irreversible capacity loss is due to the ability of $\text{Li}_4\text{Mn}_5\text{O}_{12}$ or LiV_3O_8 to insert the extracted lithium that could not be inserted back into the layered $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ during the first cycle. The $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ – LiV_3O_8 composite with ~18 wt.% LiV_3O_8 exhibits a high capacity of ~280 mAh g^{-1} with little or no irreversible capacity loss and good cyclability.

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1. Introduction

Lithium ion batteries have become the choice of power source for portable devices, and the limited capacity of the currently used cathodes has created enormous interest in developing high capacity cathodes. In this regard, solid solutions between layered $\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ (i.e. Li_2MnO_3) and LiMO_2 ($M = \text{Mn}, \text{Ni}, \text{and Co}$) [1–7] are becoming appealing recently as they exhibit high capacities of ~250 mAh g^{-1} while lowering the cost and improving the safety compared to LiCoO_2 cathode. One of the drawbacks, however, with these high capacity cathodes is the large irreversible capacity loss C_{irr} (40–100 mAh g^{-1}) in the first cycle [8,9], i.e. a large difference between the first charge and discharge capacity values. The irreversible capacity loss is due to the oxidation of O^{2-} ions (following the initial oxidation of transition metal ions), which involves the extraction of lithium as Li_2O during first charge, and the inability to insert part of the extracted lithium back into the lattice during first discharge. This inability is due to the elimination of oxide ion vacancies formed at the end of first charge [9] and a reduction in a corresponding number of lithium sites after the first charge.

Attempts like surface treatments or modifications have been pursued to lower the irreversible capacity loss. For example, mild acid treatment of $0.3\text{Li}_2\text{MnO}_3$ – $0.7\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ has been found to

reduce the irreversible capacity loss [10,11], but could not increase the discharge capacity. We reported recently that surface modification of the cathodes by other inert materials like Al_2O_3 and AlPO_4 reduces the irreversible capacity loss significantly and increases the discharge capacity values to as high as 285 mAh g^{-1} [12–14]. Reduction in irreversible capacity loss was also observed subsequently by Zheng et al. [15] on surface modifying with TiO_2 . We attributed the decrease in irreversible capacity loss on surface modification to a suppression of the elimination oxide ion vacancies at the end of first charge [13,14]. In other words, surface modification helps to retain more number of oxide ion vacancies in the layered lattice at the end of first charge compared to the pristine sample, resulting in the availability of more number of lithium sites in the lattice during first discharge and a consequent increase in discharge capacity. However, the surface modification could not eliminate the irreversible capacity loss completely.

We reported recently a novel strategy to eliminate the irreversible capacity by blending the layered oxide $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$, which belongs to the solid solution series $(1-z)\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ – $z\text{Li}[\text{Mn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}]\text{O}_2$ with $z = 0.4$, with a lithium-free insertion host V_2O_5 [16]. V_2O_5 acts as a host to insert back the extracted lithium ions (from the layered lattice) that could not be inserted back into the layered lattice and thereby eliminates the irreversible capacity loss. However, the $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ – V_2O_5 composite exhibited some capacity fade during cycling. With an aim to improve the cyclability, we present here, following a similar strategy, the electrochemical

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characterization of the $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ – $\text{Li}_4\text{Mn}_5\text{O}_{12}$ and $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ – LiV_3O_8 composites. Spinel $\text{Li}_4\text{Mn}_5\text{O}_{12}$ and LiV_3O_8 without much extractable lithium due to Mn^{4+} and V^{5+} can serve as a host to insert the extracted lithium that could not be inserted back into the layered $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ and thereby lower the irreversible capacity loss C_{irr} . Mixtures consisting of the layered oxides and other oxides are also being pursued by Thackeray's group [17].

2. Experimental

$\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ was prepared by firing the coprecipitated hydroxides of Mn, Ni, and Co with LiOH at 900°C for 24 h in air, followed by quenching into liquid nitrogen [18]. The spinel $\text{Li}_4\text{Mn}_5\text{O}_{12}$ sample was prepared by a solid state reaction of Li_2CO_3 and MnCO_3 at 400°C for 48 h [19]. LiV_3O_8 was prepared by a solution dispersion method, followed by firing at 500°C in air for 6 h [20]. The $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ – $\text{Li}_4\text{Mn}_5\text{O}_{12}$ and $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ – LiV_3O_8 composites were prepared by grinding required amount of $\text{Li}_4\text{Mn}_5\text{O}_{12}$ or LiV_3O_8 with $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ without further heating.

The samples were characterized by X-ray diffraction (XRD) with Cu $K\alpha$ radiation. Electrochemical performance evaluations were carried out with CR2032 coin cells in the voltage range of 2.0–4.8 V, employing metallic lithium anode, 1 M LiPF_6 in ethylene carbonate/diethyl carbonate (1:1) electrolyte, and Celgard polypropylene separator. The electrodes were fabricated by mixing 75 wt.% active material with 12.5 wt.% acetylene black and 12.5 wt.% teflonized acetylene black binder, rolling into thin sheets, and cutting into circular electrodes of 0.64 cm^2 area. The charge–discharge profiles and cyclability data were collected at 12.5 mA g^{-1} ($\sim 0.05\text{ C}$ rate) between 4.8 and 2.0 V.

3. Results and discussion

Fig. 1 shows the XRD patterns of layered $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$, spinel $\text{Li}_4\text{Mn}_5\text{O}_{12}$, LiV_3O_8 , 70 wt.% $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ –30 wt.% $\text{Li}_4\text{Mn}_5\text{O}_{12}$ composite, and 83 wt.% $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ –17 wt.% LiV_3O_8 composite. The reflections of the $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$, $\text{Li}_4\text{Mn}_5\text{O}_{12}$, and LiV_3O_8 samples could be indexed on the basis of layered α - NaFeO_2 -type structure (space group $R\bar{3}m$), cubic spinel structure (space group $Fd\bar{3}m$) [21], and a layered monoclinic structure (space group $P21/m$) [20], respectively. A few weak superstructure reflections around $2\theta = 20$ – 25° correspond to the ordering of the Li^+ , Ni^{2+} , and Mn^{4+} ions in the transition metal planes of $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ [2,8]. The XRD patterns of the $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ – $\text{Li}_4\text{Mn}_5\text{O}_{12}$ and $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ – LiV_3O_8 composites show reflections corresponding to the two components as they represent a physically blended mixture without any heating. However, it is hard to distinguish the reflections of $\text{Li}_4\text{Mn}_5\text{O}_{12}$ as they overlap with those of $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ due to a common face centered cubic arrangement of the oxide ions in both the materials.

Fig. 2 compares the first charge–discharge profiles of $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$, $\text{Li}_4\text{Mn}_5\text{O}_{12}$, and the $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ – $\text{Li}_4\text{Mn}_5\text{O}_{12}$ composites with various $\text{Li}_4\text{Mn}_5\text{O}_{12}$ contents (15–60 wt.%) in the range of 4.8–2.0 V. The layered $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ exhibits charge and discharge capacity values of, respectively, 330 and 262 mAh g^{-1} with a large irreversible capacity loss C_{irr} of 68 mAh g^{-1} as normally observed with these materials [8–13]. $\text{Li}_4\text{Mn}_5\text{O}_{12}$, on the other hand, exhibits a small first charge capacity ($\sim 70\text{ mAh g}^{-1}$) as the oxidation state of Mn is slightly lower than 4+ and a first discharge capacity of $\sim 200\text{ mAh g}^{-1}$ in the range of 4.8–2.0 V.

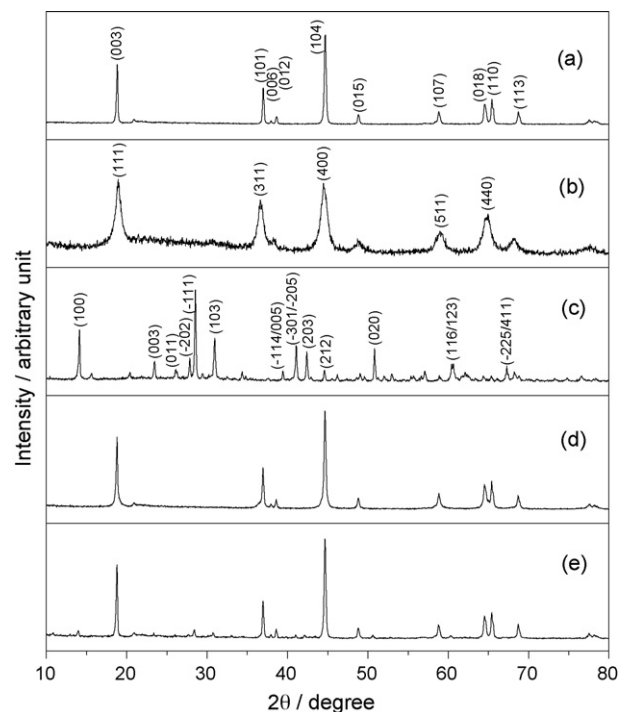


Fig. 1. XRD patterns of (a) layered $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$, (b) spinel $\text{Li}_4\text{Mn}_5\text{O}_{12}$, (c) LiV_3O_8 , (d) 70 wt.% $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ –30 wt.% $\text{Li}_4\text{Mn}_5\text{O}_{12}$ composite, and (e) 83 wt.% $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ –17 wt.% LiV_3O_8 composite.

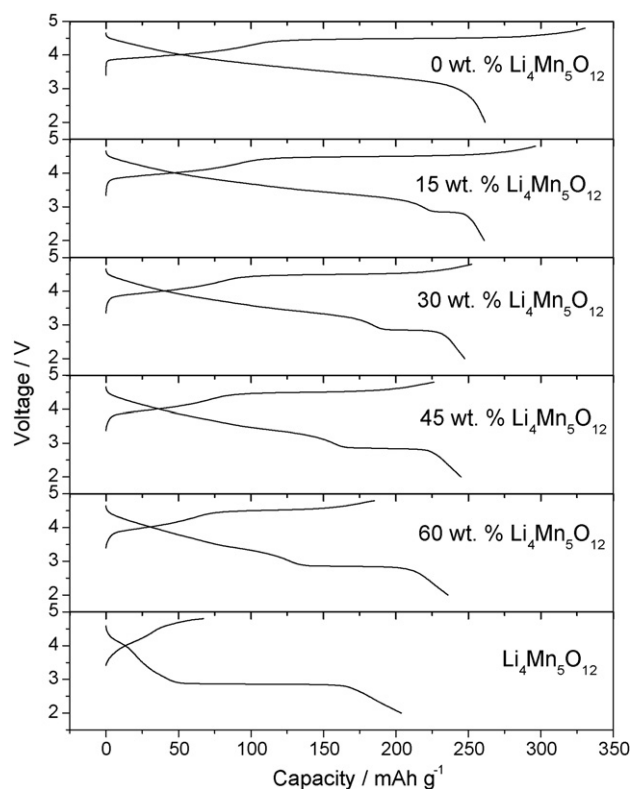


Fig. 2. First charge–discharge profiles of layered $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$, $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ – $\text{Li}_4\text{Mn}_5\text{O}_{12}$ composite with various $\text{Li}_4\text{Mn}_5\text{O}_{12}$ contents, and $\text{Li}_4\text{Mn}_5\text{O}_{12}$.

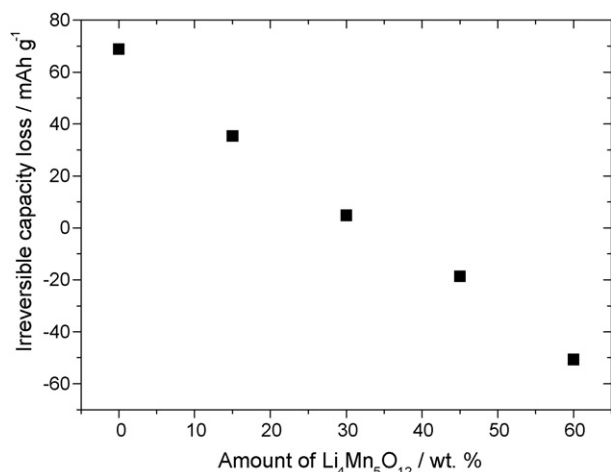


Fig. 3. Variation of the irreversible capacity loss with Li₄Mn₅O₁₂ content in the Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂-Li₄Mn₅O₁₂ composite.

In the case of the Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂-Li₄Mn₅O₁₂ composite, the first charge capacity decreases significantly with increasing Li₄Mn₅O₁₂ content as Li₄Mn₅O₁₂ has much lower charge capacity than Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂. However, the first discharge capacity decreases only slightly with increasing Li₄Mn₅O₁₂ content as Li₄Mn₅O₁₂ serves as a host to insert the extracted lithium that could not be inserted back into the layered oxide lattice. As a result, the irreversible capacity loss in the first cycle decreases significantly with increasing Li₄Mn₅O₁₂ content in the Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂-Li₄Mn₅O₁₂ composite as seen in Fig. 3, which is similar to that found before by us with the Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂-V₂O₅ composite. The irreversible capacity loss decreases from 68 to 0 mAh g⁻¹ as the Li₄Mn₅O₁₂ content increases from 0 to 30 wt.%. The irreversible capacity loss value (C_{irr} = first charge capacity - first discharge capacity) appears negative above about 30 wt.% Li₄Mn₅O₁₂ in Fig. 3 as the first discharge capacity (~200 mAh g⁻¹) of Li₄Mn₅O₁₂ is much larger than its first charge capacity (~70 mAh g⁻¹). In other words, with a metallic lithium anode employed in our experiments, the amount of lithium that could be inserted into the Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂-Li₄Mn₅O₁₂ composite with >30 wt.% Li₄Mn₅O₁₂ is more than the amount of lithium extracted from the composite in the first charge-discharge cycle, which results in a negative irreversible capacity loss for >30 wt.% Li₄Mn₅O₁₂.

Fig. 4 compares the first charge-discharge profiles of the Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂-LiV₃O₈ composites with various LiV₃O₈ contents (10–30 wt.%) along with those of Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂ and LiV₃O₈ in the range of 4.8–2.0 V. In contrast to Li₄Mn₅O₁₂, LiV₃O₈ exhibits much smaller first charge capacity (~20 mAh g⁻¹) as vanadium exists as V⁵⁺, but a much higher first discharge capacity of ~280 mAh g⁻¹ in the range of 4.8–2.0 V. The first charge capacity of the Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂-LiV₃O₈ composite decreases significantly with increasing LiV₃O₈ content as LiV₃O₈ has much lower charge capacity, similar to that found with the Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂-Li₄Mn₅O₁₂ composite. However, the first discharge capacity of the Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂-LiV₃O₈ composite increases slightly with increasing LiV₃O₈ content as LiV₃O₈ serves as a host to insert the extracted lithium that could not be inserted back into the layered oxide lattice and LiV₃O₈ has much higher discharge capacity than Li₄Mn₅O₁₂. Consequently, the irreversible capacity loss decreases with increasing LiV₃O₈ content and reaches zero at 18 wt.% LiV₃O₈ as seen in Fig. 5. The irreversible capacity loss value becomes negative above about 18 wt.% LiV₃O₈ in Fig. 5 as the first discharge

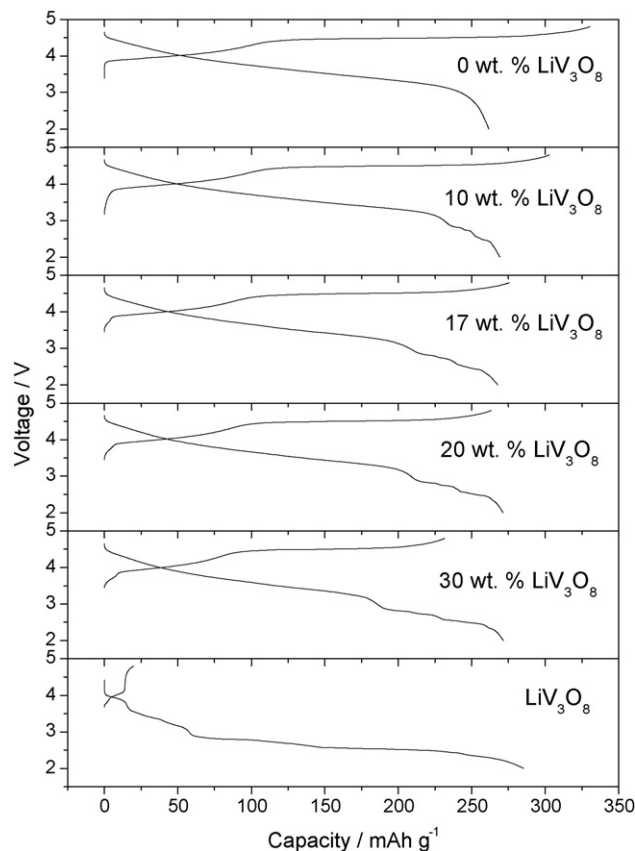


Fig. 4. First charge-discharge profiles of layered Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂, Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂-LiV₃O₈ composite with various LiV₃O₈ contents, and LiV₃O₈.

capacity (~280 mAh g⁻¹) of LiV₃O₈ is much larger than its first charge capacity (~20 mAh g⁻¹), similar to that discussed above with the Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂-Li₄Mn₅O₁₂ composite. The decrease in the irreversible capacity loss is much faster in the Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂-LiV₃O₈ system (Fig. 5) compared to that in the Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂-Li₄Mn₅O₁₂ system (Fig. 3) as LiV₃O₈ has higher discharge capacity than Li₄Mn₅O₁₂. Accordingly, while 30 wt.% Li₄Mn₅O₁₂ is needed to eliminate the irreversible capacity loss completely, only 18 wt.% is needed in the case of LiV₃O₈. Thus, from a practical point of view, the

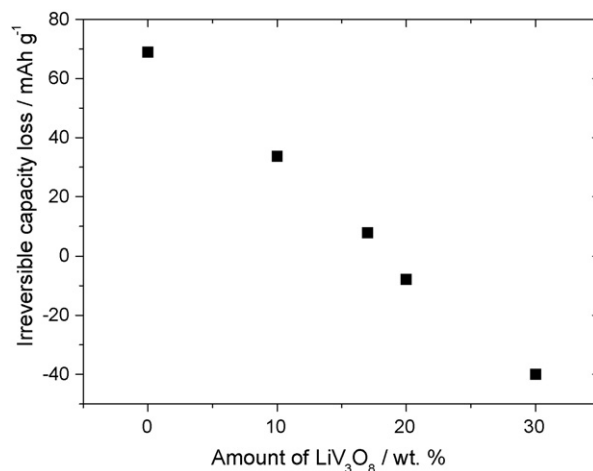


Fig. 5. Variation of the irreversible capacity loss with LiV₃O₈ content in the Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂-LiV₃O₈ composite.

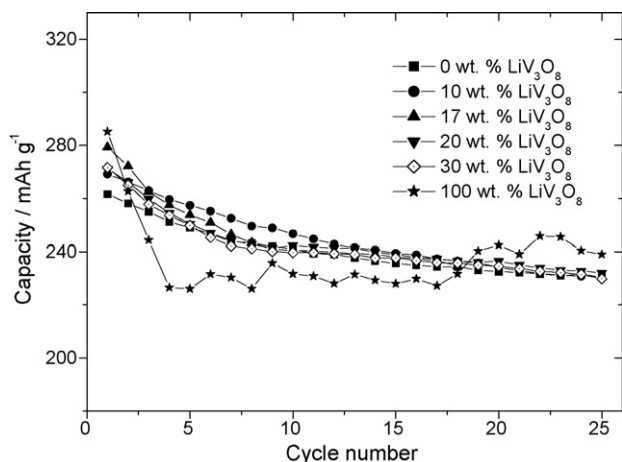


Fig. 6. Comparison of the cyclabilities of layered $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$, LiV_3O_8 , and $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2\text{-LiV}_3\text{O}_8$ composites with various LiV_3O_8 contents.

$\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2\text{-LiV}_3\text{O}_8$ system may be preferred to maximize the discharge capacity values.

Fig. 6 compares the cyclability of the layered $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$, LiV_3O_8 , and $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2\text{-LiV}_3\text{O}_8$ composites with various (10–30 wt.%) LiV_3O_8 contents. The $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2\text{-LiV}_3\text{O}_8$ composites exhibit cycling stability similar to the pristine layered $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ sample, in contrast to the $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2\text{-V}_2\text{O}_5$ composite [16] that exhibits larger capacity fade than the pristine $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$. The better cyclability is due to the stable cycling of LiV_3O_8 itself as seen in Fig. 6 compared to that found with V_2O_5 [16]. The results indicate that incorporation of LiV_3O_8 into the layered oxide $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ offers a combination of high capacity with low or little irreversible capacity loss and good cycling stability.

4. Conclusions

The blending of spinel $\text{Li}_4\text{Mn}_5\text{O}_{12}$ or LiV_3O_8 with the high capacity layered $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ eliminates the irreversible capacity loss completely at 30 wt.% $\text{Li}_4\text{Mn}_5\text{O}_{12}$ and 18 wt.% LiV_3O_8 . The elimination is due to the ability of $\text{Li}_4\text{Mn}_5\text{O}_{12}$

and LiV_3O_8 to insert the extracted lithium that could not be inserted back into the layered $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$. The $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2\text{-LiV}_3\text{O}_8$ composite with an optimum LiV_3O_8 content of 18 wt.% exhibits a high discharge capacity of $\sim 280 \text{ mAh g}^{-1}$ with little or no irreversible capacity loss and good cyclability. The composite strategy presented here offers an attractive approach to increase the energy density of lithium ion batteries. However, realizing the high capacity involves charging to 4.8 V, and development of more robust electrolytes that can withstand such high voltages is needed to tap their full potential for next generation lithium ion cells.

Acknowledgments

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