# Supplementary information

## Experimental result and analysis on the high initial columbic efficiency of the prepared spherical hierarchical $LiNi_{0.5}Mn_{1.5}O_4$

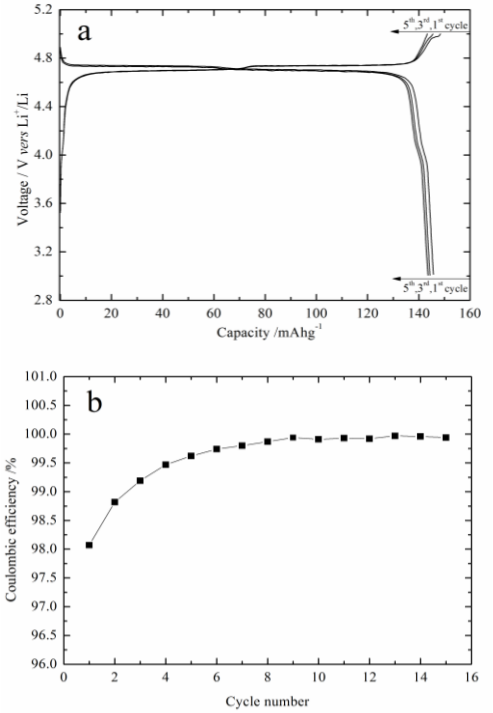


Fig S1. a) The 1st to 5th charging/discharging curves and b) columbic efficiency of the initial 15 cycles of the obtained $LiNi_{0.5}Mn_{1.5}O_4$, 0.05 C, 3.0~5.0 V.

A high initial Columbic efficiency is determined by a low irreversible capacity in the first cycle. Therefore, we have tried to decrease the initial irreversible capacity to improve the columbic efficiency.

Before charging/discharging above 0.3 C, the batteries are charged/discharged at 0.05 C between 3.0~5.0 V. Fig S1 shows the charging/discharging curves and columbic efficiency of the initial cycles. The theoretical capacity of $LiNi_{0.5}Mn_{1.5}O_4$ is 146.7 $mAhg^{-1}$, and the discharging capacity of the obtained spinel reaches 144.9 $mAhg^{-1}$ in this work. Meanwhile, the initial columbic efficiency reaches to above 98%.

These hierarchical spheres manifest a three-dimensional nanoporous structure with high specific surface area. Inspired by the unique structure and inherent short transport length for Li ions, the spinel is supposed to have the ability to reversibly release nearly all the Li ions. Therefore in Fig S1, the obtained $LiNi_{0.5}Mn_{1.5}O_4$ manifests an unusually high Columbic efficiency of 98.07 %, which has seldom been reported.

The formation of SEI would also lead to an irreversible capacity consumption, however, which is the combined reaction of electrode and electrolyte. Thus the stability of the spinel $LiNi_{0.5}Mn_{1.5}O_4$ electrode in this work also favors to form a thin SEI with less Li consumption and hence to result a high columbic efficiency.

It is observed in Fig S1a that there is a tiny voltage plateau near 4.95 V, covering about 2~3 $mAhg^{-1}$, when the cell is charged to 5.0 V in the first cycle. It may be attributed to the passivation of cathode/electrolyte interface, corresponding to some reaction between cathode material and electrolyte. Notably, the capacity gradually decreases during the subsequent three cycles, which can be attributed to the further passivation for the above interface. On the fifth cycle, no voltage plateau can be observed above 4.8 V. It can be concluded here: the formation of passivation process is not rapidly completed in the first cycle, but gradually finished during the initial few cycles. Fig S1b also verifies it that the columbic efficiency increases from the initial 98.1% to above 99.6% after 5 cycles.

We think based on the hierarchical spherical morphology that in the first cycle, the SEI forms prior on the external surface of the spherical particle. As the spherical particle has a smallest specific surface area, it will form a stable uniform thin SEI with a least amount of Li ions consumption. Thus it results in the high initial columbic efficiency of 98.1%.