

Interfacial characterization and ultrahigh rate performance and long cyclability of high voltage spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$

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Abstract

The electrolyte decomposition, manganese dissolution along with interfacial kinetics and transport properties are needed to be addressed to establish better electrochemical performance of high voltage spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, (LNMO). It is not clearly understood whether the rate performance of the material is limited by bulk transport properties or interfacial charge transfer reaction kinetics. The present investigation elucidates the role of the electrochemical charge transfer kinetics at the electrode/electrolyte interface of $\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ in determining the rate performance of the spinel cathode. The measurements have been carried out on additive free sintered dense plate in order to exclude any extrinsic effect. The exchange current density at the electrode/electrolyte interface is found to be continuously increased with increasing the degree of delithiation for ordered phase ($\sim 0.21\text{--}6.5\text{mA/cm}^2$) at ($x=0.01\text{--}0.60$), in contrast the disordered phase exhibits gradually decrease of exchange current density in the initial delithiation at the 4V plateau regime ($x=0.01\text{--}0.04$) and again monotonously increases ($0.65\text{--}6.8\text{mA/cm}^2$) with further delithiation at ($x=0.04\text{--}0.60$) [4, 5]. The ionic diffusivity of ordered and disordered phase is found to be $\sim 5 \times 10^{-10}\text{cm}^2\text{s}^{-1}$ and $\sim 10^{-9}\text{cm}^2\text{s}^{-1}$, respectively, and does not vary much with the degree of delithiation [5]. On the other hand, since the voltage of LNMO lies beyond the stability window of conventional liquid electrolyte, different coating materials (ZrO_2 and SiO_2) are used to coat the LNMO particle surface in order to protect the electrolyte decomposition and Mn^{3+} dissolution. Coating thickness is optimized in terms of rate capability and cyclability of LNMO at two temperatures ($25\text{ }^\circ\text{C}$ and $55\text{ }^\circ\text{C}$). The electrochemical testing indicates that the particles coated with 1% ZrO_2 (or SiO_2) exhibits better performances both half and full cell configurations. The specific capacity was retained 105 mAh/g at 40C rate at the end of one thousand cycles in the half cell configuration against lithium metal and 118 mAh/g at 1C rate after four hundred cycles in the full cell configuration against LTO. Thermal behavior of Li/LMO and LTO/LMO with and without coating has also been investigated using isothermal calorimeter. The obtained results provide the path way to efficiently engineering of the material in order to achieve high rate capability and long cyclability.

References

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