Induced AlF_3 segregation for the generation of reciprocal Al_2O_3 and LiF coating layer on self-generated $LiMn_2O_4$ surface of over-lithiated oxide based Li-ion battery

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Abstract

For Li-ion batteries, AlF_3 coating has been known to modify the over-lithiated layered oxide (OLO) cathodes to produce stable cathodes, but during synthesis procedure, the environment of excess amount of Li metal and free-exposed oxygen may cause the formation of Al_2O_3 and LiF materials, separately. We investigated the possibility of separated coating formation of Al as Al_2O_3 and F as LiF from AlF_3 using density functional theory calculation, which suggests a favorable binding affinity of both Al_2O_3 and LiF phases to the OLO surface to support the preferable formation of coating layer of Al_2O_3 and LiF. Meanwhile, we found the well-distributed surface modification with the coating layers and a small amount of AlF_3 (< ~11 vol%) throughout various surface analyses using the well-known coating process of AlF_3 formation. Importantly, during the coating process LiF led to the transformation of OLO surface from Li_2MnO_3 to a self-generated structure of spinel-like $LiMn_2O_4$ phase, which enhances electronic conductivity. In addition, Al_2O_3 plays a key role in suppressing reactions between cathode and electrolyte, leading to stable cyclability. Experimental findings suggest that the well-distributed coating layer of two materials leads to a synergic effect on the enhanced electrochemical performance for high voltage operating Li-ion batteries.