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Li-ion batteries are promising candidates for electrical energy storage in applications ranging from portable electronics to hybrid and electric vehicles. In this context, layered compounds in the $Li_{1+\delta}(TM_xMn_{1-x})_{1-\delta}O_2$ family (TM=transition metal) have received much attention due to their high capacity and stability. In this Research News article we describe recent advances on structural characterization of Li-ion electrode materials using state-of-the-art electron microscopy. Direct evidence of the monoclinic nature of Li_2MnO_3 has been provided. It has been demonstrated that differences in Z-contrast imaging between Li_2MnO_3 and $LiTMO_2$ may be used to screen samples for phase separation in the 10–100 nm scale.