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MS-14-P-2199 Impact of the nanostructure on the electrochemical performance of Li-rich cathode materials

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In search for high capacity and high energy cathode materials for the next generation Li-ion batteries (LIB), Li-rich cathode materials are promising candidates. This material class is derived from the classical layered cathode ceramics, such as $LiCoO_2$, commonly used in commercial LIBs. In order to improve stability and capacity, these structures have been blended with Li_2MnO_3, which can be considered as Li-rich layered material ($Li[Li_{1/3}Mn_{2/3}]O_2$) that is well mixable with classical layered cathode materials [1-3]. The structures of the rhombohedral $Li(TM)O_2$ (TM = Ni, Co, Mn) and the monoclinic Li_2MnO_3 are depicted in Fig. 1.
It is well known that the synthesis conditions influence the nanostructure and hence the electrochemical performance of Li-rich cathode ceramics [4-6]. In the present study, a molten salt and a coprecipitation synthesis route were chosen in order to prepare two different kinds of samples with the same nominal stoichiometry of $0.5Li_2MnO_3$:$0.5Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$, hereinafter called MS55 and CP55, respectively. Results of the electrochemical characterization are depicted in Fig. 2. The charge-discharge curves show better characteristics concerning energy density for the MS55 sample in the first cycle and after the 70th cycle. The CP55 shows a lower first discharge capacity and a higher voltage drop after the 70th cycle. High resolution transmission electron microscopy (HRTEM) and electron diffraction has been used to investigate the nanostructure of the pristine material blends. The HRTEM micrograph depicted in Fig. 3 shows the nanostructure of the MS55 sample. The HRTEM pattern can be interpreted as intergrowth of Li(TM)O2 and Li2MnO3 on an atomic scale with only short range monoclinic ordering. Fig. 4 shows the HRTEM pattern obtained from a CP55 crystallite. In contrast to the MS55 sample, the nanostructure consists of blocks which can be described exclusively by monoclinic symmetry and parts which show contrast comparable to the MS55 sample.
This experiment shows the impact of the nanostructure of Li-rich cathode ceramics with the same nominal stoichiometry on the electrochemical performance. It is necessary not only to consider the composition but also to analyze the nanostructure in order to compare the electrochemical performances of nominal the same material, which makes TEM an obligatory tool in the field of research for new Li-rich cathode materials.

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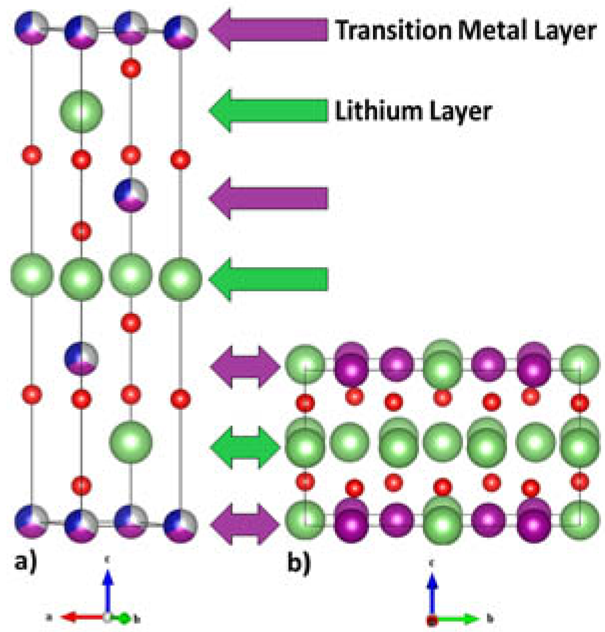

Fig. 1: a) rhombohedral Li(TM)O_2 with R-3m symmetry b) monoclinic Li_2MnO_3 with C2/m symmetry

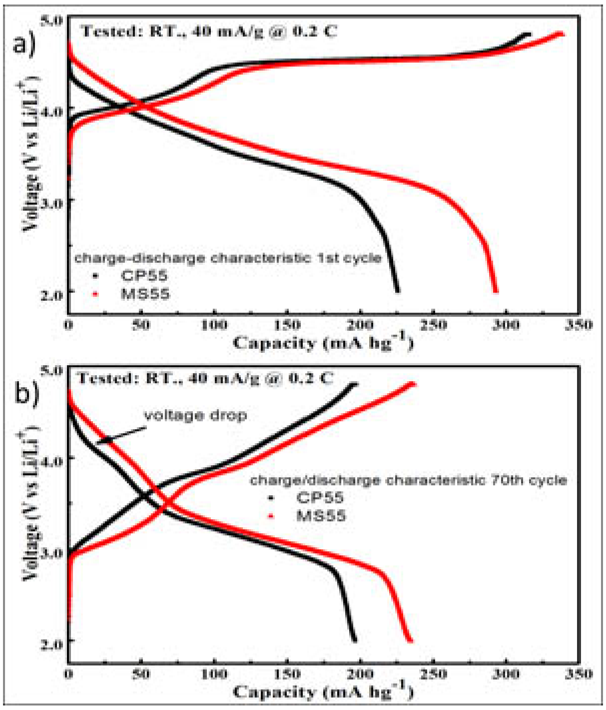

Fig. 2: Charge-discharge characteristic a) for the first and b) after the 70th cycle

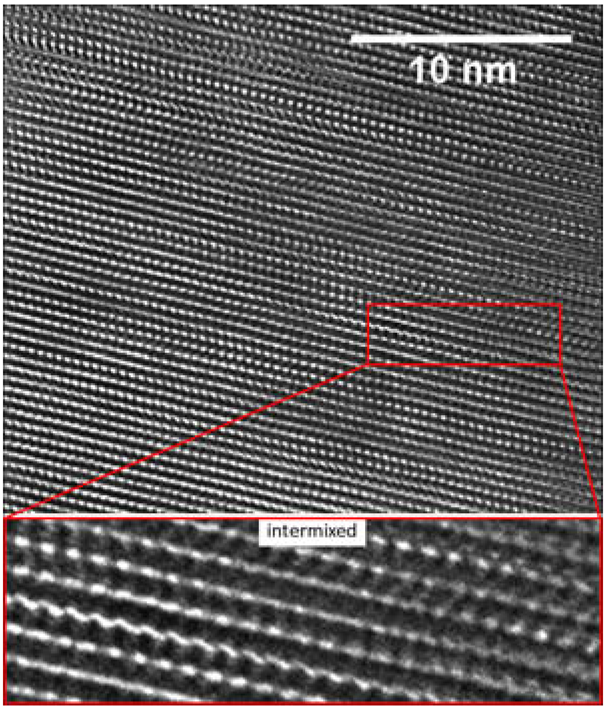

Fig. 3: HRTEM micrograph of the MS55 sample. The pattern can be interpreted as intermixing of Li(TM)O_2 and Li_2MnO_3 on an atomic scale

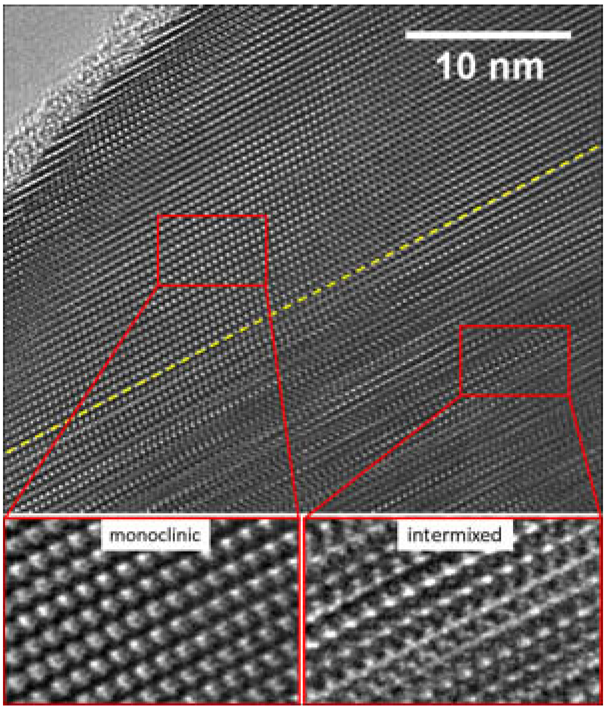

Fig. 4: HRTEM micrograph of the CP55 sample. The particle contains parts which are monoclinic only and parts that are intermixed on the atomic scale