

MS23. Nanoscale structures

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MS23-P1 Nanocrystalline CoMn_2O_4 as anode material for lithium ion batteries: Effect of structure and microstructure

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Rechargeable lithium-ion batteries (LIBs) have found applications in wide range of devices e.g. mobile phones and notebooks but LIBs also possess great potential for utilization in high power applications, such as hybrid electric vehicles¹. The performance of LIBs is greatly determined by the composition, structure and microstructural features of anode and cathode materials. Recent papers point to CoMn_2O_4 as an attractive candidate for alternative LIBs anode material²⁻⁵. The majority of the existing work on battery performance appears to focus on complex morphologies while the studies on the effect of crystal structure on battery performance have been scarce. As-prepared cobalt-dimanganate was prepared by precipitation route. Additionally, samples were thermally treated at $T=300$, 400 and 500°C . Structural investigation using XRPD and Raman spectroscopy have been carried out in order to correlate specific structural features with preparation conditions and furthermore with electrochemical properties. Changes in unit-cell as function of temperature were calculated; observed decrease is inconsistent with simple spinel-type exchange of Co^{2+} by Mn^{3+} on the tetrahedral site, and vice versa on the octahedral site. Based on the Raman spectroscopy an alternative structural model: $^{IV}[\text{Co}^{2+}_{1-x}\text{Mn}^{2+}_x]^{VI}[\text{Co}^{3+}_x\text{Mn}^{3+}_{2-x}]_2\text{O}_4$ has been proposed. Rietveld refinement showed increase of M-O distances within tetrahedra, caused by thermally enhanced substitution of Co^{2+} by larger Mn^{2+} cations at A-site. Consequently, octahedral B-site becomes partially occupied by Co^{3+} on the account of the transferred Mn cations. In all samples, initial capacity drops as commonly observed in high capacity metal oxide materials. However, after a certain number of cycles

specific capacity increases again. Among all samples, thermally treated from 100 - 500°C , highest specific capacities are observed for sample treated at highest temperature (500°C) despite its large particle size. In terms of the particle size, it has been shown that in some metal oxides better capacity retention is obtained for larger particle sizes and it was proposed that there is an optimal size for improved capacity retention⁶.

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