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Effects of Na doping on $Li_{1.2}Mn_{0.53}Ni_{0.13}Co_{0.13}O_2$ prepared via spray pyrolysis

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Li_xMO_2 (M= Mn, Ni, Co) materials with layered structures have received attention as high-capacity, low cost and safer cathode materials for lithium-ion batteries [1]. Various synthesis methods have been developed for the production of these materials, including co-precipitation, solid state synthesis and ball milling [2-4]. Recently a spray pyrolysis synthesis method has been developed by this group for producing cathode materials with porous morphologies [5]. Spray pyrolysis has certain advantages compared to other methods: the short residence time in the reactor allows large throughput; the process is scalable, no further post-synthesis purification steps are required, the product is inherently purified throughout the synthesis and due to the one-droplet-one-particle reaction mechanism each particle is synthesized according to the desired stoichiometry. This allows for accurate control of dopant levels in the product.

The layered lithium/manganese rich oxides, such as $Li_{1.2}Mn_{0.53}Ni_{0.13}Co_{0.13}O_2$ have been shown to exhibit voltage fade over cycling. This effect is presently associated with a layered-spinel transformation inside the material and has received significant attention recently [6-7]. Most of the studies conclude that the voltage fade can potentially be eliminated via doping. Therefore the present research will focus on doping $Li_{1.2}Mn_{0.53}Ni_{0.13}Co_{0.13}O_2$ with trace levels of Na and other elements to explore their effect on voltage fade.

Figure 1 shows the initial cycling profile of $Li_{1.2-x}Na_xMn_{0.53}Ni_{0.13}Co_{0.13}O_2$ materials annealed at 900°C for 2 hours and containing x=0.01, 0.025, 0.05 and 0.1 levels of Na. For x=0.05 and 0.1 the shape of the charge curves change, resulting in lower capacities. Figure 2 compares the XRD patterns of the materials with different Na dopant levels. It is clear that for x=0.05 and 0.1 an additional phase forms, which is apparently responsible for the lower charge and discharge capacity of the material. Figure 3 compares the dQ/dV curves for the x=0, 0.01 and 0.1 materials. It seems that for x=0.01 there is some improvement compared to the Na-free material, but for x=0.1 additional peaks occur during cycling. Results related to other dopants and their effect on the voltage fade of the material will also be discussed.

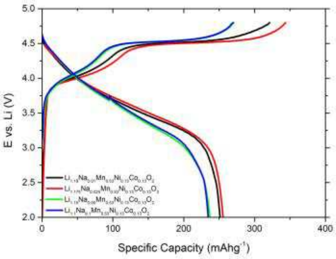

Figure 1. Initial charge and discharge profile of $Li_{1.2-x}Na_xMn_{0.53}Ni_{0.13}Co_{0.13}O_2$ where x=0.01, 0.025, 0.05 and 0.1

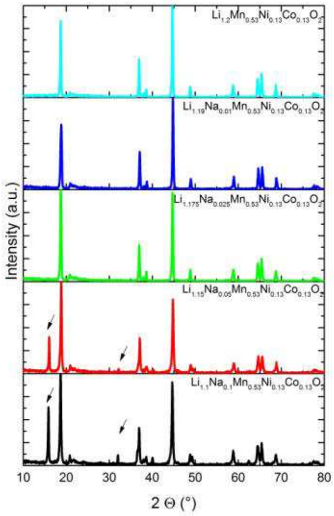

Figure 2. XRD spectra of $Li_{1.2-x}Na_xMn_{0.53}Ni_{0.13}Co_{0.13}O_2$ where x=0, 0.01, 0.025, 0.05 and 0.1

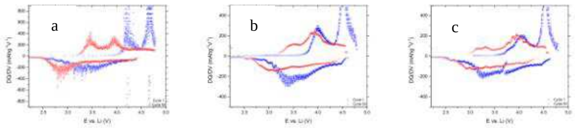

Figure 3. dQ/dV curves of $Li_{1.2-x}Na_xMn_{0.53}Ni_{0.13}Co_{0.13}O_2$ where (a) x=0, (b) 0.01 and (c) 0.1 half cells for the 1st cycle and the 50th cycle.

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