The improvement of volumetric energy density remains a key area of research to optimize Li-ion batteries for applications such as extending the range of electric vehicles. There is still improvement to be made in the energy density in the positive electrode materials. The current thesis deals with determining the phase diagrams of the Li–Mn–Ni–O and Li–Co–Mn–O systems in order to better understand the structures and the electrochemistry of these materials. The phase diagrams were made through careful analysis of hundreds of X-ray diffraction patterns taken of milligram-scale combinatorial samples. A number of bulk samples were also investigated.

The Li–Mn–Ni–O system is of particular interest as avoiding cobalt lowers the cost of the material. However, this system is very complex: there are two large solid-solution regions separated by three two-phase regions as well as two three-phase regions. Comparing quenched and slow cooled samples shows that the system transforms dramatically when cooled at rates typically used to make commercial materials. The consequences of these results are that much of the system must be avoided in order to guarantee that the materials remain single phase during cooling. This work should therefore impact significantly researchers working on composite electrodes.

Two new structures were found. The first was Li-Ni-Mn oxide rocksalt structures with vacancies and ordering of manganese which were previously mistakenly identified as \( \text{Li}_{x} \text{Ni}_{2-x} \text{O}_{2} \). The other new structure was a layered oxide with metal site vacancies allowing manganese to order on two \( \sqrt{3} \times \sqrt{3} \) superlattices. The electrochemistry of both these materials is presented here.

Finally, the region where layered-layered composites form during cooling has been determined. These materials were long looked for along the composition line from Li\(_2\)MnO\(_3\) to LiNi\(_{0.5}\)Mn\(_{0.5}\)O\(_2\) and the most significant consequence of the actual locations of the end-members is that one of the structures contains a high concentration of nickel on the lithium layer. Layered-layered nano-composites formed in this system are therefore not ideal positive electrode materials and it will be demonstrated that single-phase layered materials lead to better electrochemistry.
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