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DEPARTMENT OF PHYSICS AND ATMOSPHERIC SCIENCE

TITLE OF THESIS:	STRUCTURAL AND ELECTROCHEMICAL STUDIES OF THE LI-MN-NI-O AND LI-CO-MN-O PSEUDO-TERNARY SYSTEMS
TIME/DATE:	9:30 am, Monday, December 9, 2013
PLACE:	Room 3107, The Mona Campbell Building, 1459 Lemarchant Street

EXAMINING COMMITTEE:

Dr. Shirley Meng, Department of NanoEngineering, University of California – San Diego (External Examiner)

Dr. Richard Dunlap, Department of Physics and Atmospheric Science, Dalhousie University (Reader)

Dr. Mark Obrovac, Department of Physics and Atmospheric Science and Department of Chemistry, Dalhousie University (Reader)

Dr. Jeff Dahn, Department of Physics and Atmospheric Science, Dalhousie University (Supervisor)

DEPARTMENTAL REPRESENTATIVE:	Dr. Stephen Payne, Department of Physics and Atmospheric Science, Dalhousie University
CHAIR:	TBD, PhD Defence Panel, Faculty of Graduate Studies

ABSTRACT

The improvement of volumetric energy density remains a key area of research to optimize the electrochemistry of Li-ion batteries for such applications 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 ultimately 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 made and analyzed.

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 to slow cooled samples shows that the system transform 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 in this system. The first was Li-Ni-Mn oxide rocksalt structures with vacancies and ordering of manganese which were previously mistakenly identified as $Li_xNi_{2-x}O_2$. The other new structure was a layered oxide with metal site vacancies allowing manganese to order on two $\sqrt{3}$ x $\sqrt{3}$ 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_2MnO_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.