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Eric McCalla

# Consequences of Combinatorial Studies of Positive Electrodes for Li-ion Batteries

 Springer

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*A learned blockhead is a greater blockhead than an ignorant one.*

–Benjamin Franklin

*I dedicate this thesis to my mother, Joanne McCalla, who was my first science teacher and helped me become a spectacular blockhead.*

# Foreword for Eric McCalla's Thesis-prepared by Jeff Dahn

Given the large number of attractive and useful materials in the Li–Ni–Mn–O system and given the confusion about the structure and properties of many of them, Eric McCalla decided to undertake a complete determination of the Li–Ni–Mn–O phase diagram as the major portion of his Ph.D. thesis. Eric adopted combinatorial and high throughput materials science methods for the synthesis of these materials and used X-ray diffraction as the main characterization tool. Eric learned how to control lithium loss during heating of the small combinatorial samples and studied the effects of oxygen partial pressure, heating temperature, and cooling rate on the obtained materials.

The phase diagrams presented in this thesis have all been determined with great care. Analysis of multiphase regions using the lever rule gave phase boundaries that agree very well with direct determinations of phase boundaries by inspection of X-ray patterns for single phase or hints of other phases. The dramatic effect of cooling rate on the three phase regions in the phase diagrams was a huge surprise. In addition, the identification of a solid solution phase,  $\text{Li}[\text{Li}_{1/3-x}\square_{x/2}\text{Ni}_{x/2}\text{Mn}_{2/3}]\text{O}_2$ , where Ni and a vacancy ( $\square$ ) replace two Li atoms in  $\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ , showed that lithium-deficient layered materials incorporate vacancies, not  $\text{Mn}^{3+}$ .

The thesis shows that “layered-layered” nanocomposites and the “layered-layered-spinel” three phase composites do exist in certain regions of the phase diagram. However, these materials do not incorporate  $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$  and  $\text{Li}_2\text{MnO}_3$  as the two layered components. Instead, the Mn-rich component contains some Ni and vacancies and the Ni-rich component is not  $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ . Furthermore, Eric shows in the thesis that materials which are “layered-layered” nanocomposites yield inferior electrochemical performance to those which are single-phase solid solutions. The thesis also explains why rock-salt structure so-called “impurity” phases occur in many samples in the literature and that these rock-salt phases are not impurities but are expected based on the Li–Ni–Mn–O phase diagram. There are many more gems in the thesis that the reader can discover.

The thesis was examined and approved by Dr. Shirley Meng of the University of California at San Diego. Dr. Meng was impressed by the gap that Eric's thesis helped fill in the cathode materials research community. Meng believes that Eric's methodology was unique and the information Eric presented in his thesis will be critical to researchers in the future.

It was my pleasure to be involved in this work as Eric's supervisor and to be able to interact with him on a daily basis. Eric was an excellent student who solved many puzzles developing the results in this thesis. The methodology developed by Eric will be used to complete future studies on the entire Li-Ni-Mn-Co-O system.

11 Feb, 2014  
Dalhousie University

Jeff Dahn

# Preface

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  $\text{Li}_2 \text{MnO}_3$  to  $\text{LiNi}_{0.5} \text{Mn}_{0.5} \text{O}_2$  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.



# Acknowledgments

I would like to thank my supervisor, Dr. Jeff Dahn, for guidance, encouragement, and his generous financial support. I have had many interesting and challenging discussions with Dr. Dahn over the last three years and working in his lab has given me access to state of the art research equipment and opportunities to contact world class researchers in industrial and academic fields. I am extremely grateful for the opportunity to have done my doctorate in his research group.

Thanks also go out to the present and former staff in the Department of Physics and Atmospheric Science for their assistance during my time. Thank you to Anne Murphy, Barbara Gauvin, Tanya Timmins, Jennifer Currie, and Heather Anne Jennex in the physics office. I would also like to thank Andy George, Kevin Borgel, Dan Chevalier, and Simon Trussler for their help and advice.

I would like to thank all members of the Dahnlab who, over the past few years, have made this time both very enjoyable and sufficiently insane. A number of students were directly involved in this work, including Aaron Rowe, Colby Brown, Cassandra Lowartz, Cody Watson, John Camardese, Paul Duchesne, and Ramesh Shunmugasundaram and I would to thank them all for working and arguing with me. I would also like to thank Jennifer Romero, Robbie Sanderson, David Stevens, and Trevor Byrne for a lot of help with knowing how to use and fix a variety of equipment. I also thank all the coopians for much needed distractions and useful conversations! Thanks also go to Laura Downie who ensured I survived the writing of this thesis.

I am, as always, thankful to my family and friends who have supported me throughout.

Halifax, December 2013

Eric McCalla

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# List of Symbols and Abbreviations Used

$2\theta$	Scattering angle
$2\theta_k$	Scattering angle for the center of the k-th X-ray diffraction peak
$\alpha, \beta, \gamma$	Angles defined in the Li-Mn-Ni-O Gibbs triangle
$\beta_k$	Integral breadth of the k-th X-ray diffraction peak
$\beta_T$	Constant used to set the temperature scale in Monte Carlo simulations
$\delta$	Ratio of an atom's charge to its oxidation state, used in Monte Carlo simulations
$\epsilon_0$	Permittivity of free space
$\eta$	Lorentzian component in the pseudo-Voigt function
$\lambda$	Wavelength
$\sigma$	Standard deviation
$\mu$	Linear X-ray absorption coefficient
$\sqrt{\langle e \rangle^2}$	Root-mean square micro-strain
AA	Atomic absorption spectroscopy
C	Lorentzian, or Cauchy, function
D	Particle diameter
$F_k$	Sample scattering X-ray diffraction intensity for the k-th peak
FWHM	Full width at half maximum
G	Gaussian function
$H_k$	FWHM of k-th X-ray diffraction peak
ICP	Inductively coupled plasma optical emission spectroscopy
$I_k$	Calculated X-ray diffraction intensity for the k-th peak
$I_k^0$	Integrated peak intensity for the k-th X-ray diffraction peak
IRC	Irreversible capacity
$k_B$	Boltzmann constant
L	Average crystallite size
M	XRD machine peak broadening function
JCPDS	Joint Committee on Powder Diffraction Standards
$n_i$	Oxidation state of i-th atom in Monte Carlo simulations
$Ni_{Li}$	Fraction of sites on the lithium layers occupied by nickel
NN	Nearest neighbor
SEM	Scanning electron microscopy

T	Temperature
TM	Transition metal
TGA	Thermo-gravimetric analysis
XRD	X-ray diffraction
XANES	X-ray absorption near-edge structure

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