



# Domain formation in lithium-rich manganese-nickel-cobalt-oxide epitaxial thin films and implications for interpretation of electrochemical behavior



Aaron C. Johnston-Peck<sup>\*,1</sup>, Saya Takeuchi<sup>1,2,3</sup>, K. Kamala Bharathi<sup>4</sup>, Andrew A. Herzing, Leonid A. Bendersky<sup>\*</sup>

Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899, United States

## ARTICLE INFO

### Keywords:

Electrochemistry  
Li ion battery  
Thin film  
Transmission electron microscopy

## ABSTRACT

Due to the directional dependence of physical properties, it is advantageous to grow and then study materials in specific orientations. Films of battery materials grown in epitaxy offers the possibility to gain new insight into the role of physical structure on electrochemical behaviors. Here we demonstrate the growth, testing, and characterization of monoclinic-phase (space group  $C2/m$ ) Li-Mn-Ni-Co-O epitaxial films. The monoclinic phase is a layered structure and as such lithium diffusion is favored along specific crystallographic directions. Films were grown by pulsed laser deposition onto SrRuO<sub>3</sub>/SrTiO<sub>3</sub> substrates with (001) and (111) orientations. Cyclic voltammetry measured the response of these positive electrode materials, while the film structure was characterized using scanning transmission electron microscopy. A combination of imaging and diffraction identifies the presence of orientational variants. Variants disrupt the orientation anisotropy expected of these layered materials when grown in epitaxy, thereby masking differences in electrochemical behavior as a function of substrate orientation. Learning to control the domain structure now presents itself as a challenge to realize the potential of low symmetry battery materials grown in epitaxy on high symmetry substrates.

## 1. Introduction

Battery electrode materials are often studied in powder form, which is a limited approach for establishing fundamental structure-property relationships due to sample heterogeneity. Variation in crystal structure, size, morphology, and composition will result in changes in performance. Global measurements reflect an ensemble average while site specific measurements can suffer from sampling bias. By contrast, binder-free thin films in direct contact with the electrolyte provide a material platform with well-defined structural characteristics which mitigates issues related to structural heterogeneity and the limitations associated with global or local characterization techniques. Thin film properties can be systemically engineered (e.g., through adjustment of the substrate orientation) to probe changes in behavior as a function of microstructure. Thus, epitaxial films provide the possibility to increase our understanding of the fundamental behavior of these materials.

Research on heteroepitaxial films of lithium ion battery materials has comprised of a number of positive electrode and electrolyte

materials, including LiCoO<sub>2</sub> (LCO) [1–7], LiMn<sub>2</sub>O<sub>4</sub> [8–13], LiTi<sub>x</sub>O<sub>y</sub> [14,15], Li(Ni, Mn)O<sub>2</sub> [16], Li(Ni, Co)O [17], Li<sub>2</sub>MnO<sub>3</sub> [18], and (Li, La)TiO<sub>3</sub> [19–21]. To the best of our knowledge monoclinic-phase films grown in epitaxy with transition metal ions of Mn-Ni-Co have not been reported. Layered lithium-rich transition metal oxides – Li<sub>1+x</sub>M<sub>1-x</sub>O<sub>2</sub> (M=Co, Ni, Mn) – are attractive due to their high discharge capacities in excess of 200 mAh/g [22–28]. These materials are structurally complex and can benefit from improved understanding of structure-property relationships. Beyond simply acting as a platform for the study of structure-property relationships of positive electrodes, such films can be utilized for all solid-state batteries that are of current interest for improved performance and safety, as well as, for miniaturization [29]. Therefore, understanding and controlling the growth of these films will be important in the development of all solid-state batteries.

We grow heteroepitaxial films by pulsed laser deposition (PLD) using a target made from powder with the composition Li<sub>1.2</sub>Mn<sub>0.55</sub>Ni<sub>0.15</sub>Co<sub>0.1</sub>O<sub>2</sub> (forthwith referred as MNC). This material by its stoichiometry has a theoretical capacity 377 mAh/g and discharge

\* Corresponding authors.

E-mail addresses: [aaron.johnston-peck@nist.gov](mailto:aaron.johnston-peck@nist.gov) (A.C. Johnston-Peck), [leonid.bendersky@nist.gov](mailto:leonid.bendersky@nist.gov) (L.A. Bendersky).

<sup>1</sup> A.C.J.-P and S.T. contributed equally to this work.

<sup>2</sup> Current address: Theiss Research, La Jolla, California 92037, United States.

<sup>3</sup> Current address: Physical Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, United States.

<sup>4</sup> Current address: Department of Physics and Nanotechnology, SRM University, Kattankulathur, Chennai-603 203, India.

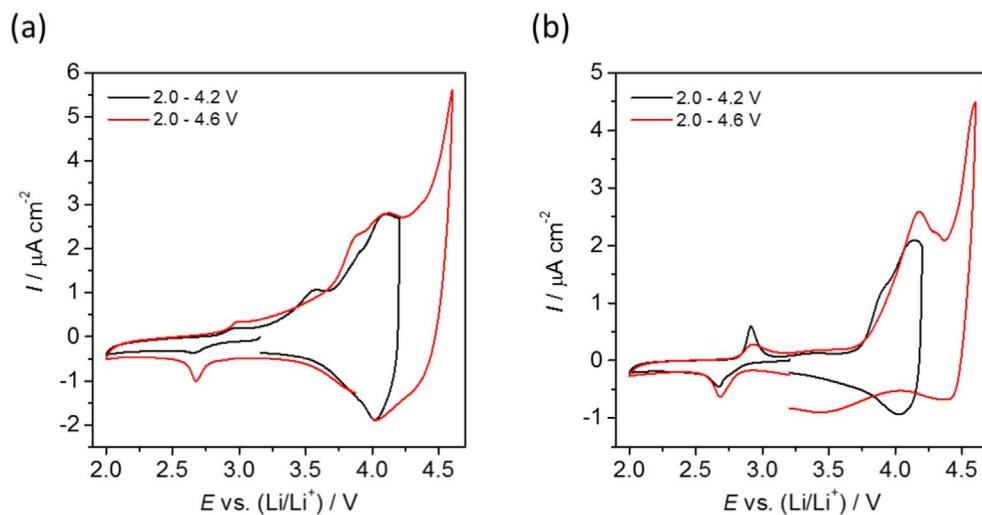


Fig. 1. Cyclic voltammograms of MNC/SRO/STO (a) (111) and (b) (001) in 1 mol/dm<sup>3</sup> LiClO<sub>4</sub>/PC. The sweep rate was 0.1 mV/s and the voltage range was 2.0 V to 4.2 V and 2.0 V to 4.6 V.

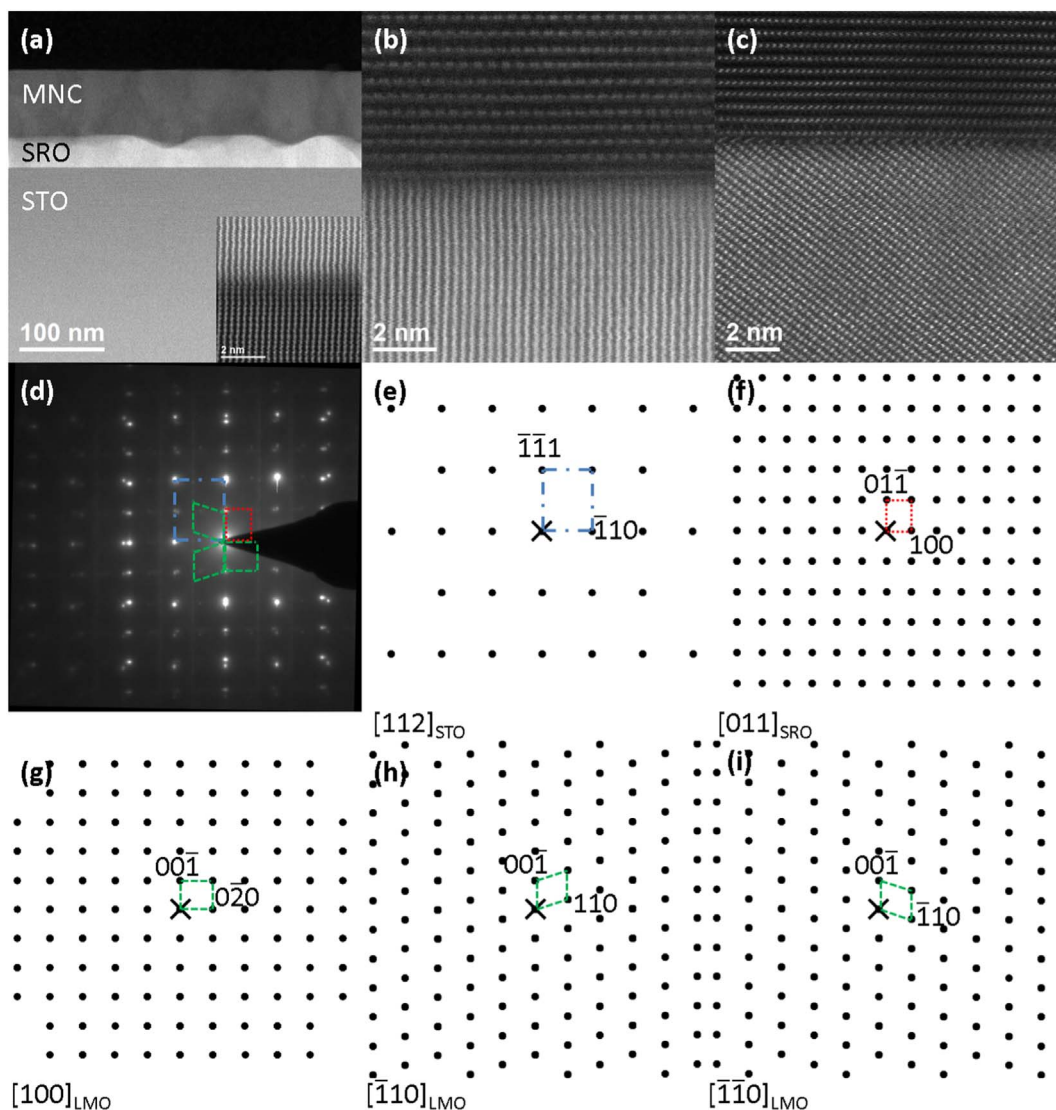


Fig. 2. Cross-sectional HAADF-STEM image (a) of the film grown on SRO/STO (111) and the MNC/SRO interface with the substrate oriented along [112]<sub>STO</sub> (b) and [101]<sub>STO</sub> (c). The inset in (a) depicts the SRO/STO interface. A selected area diffraction pattern (d) and simulated diffraction patterns of [112]<sub>STO</sub>, [011]<sub>SRO</sub>, [100]<sub>Li<sub>2</sub>MnO<sub>3</sub></sub>, [110]<sub>Li<sub>2</sub>MnO<sub>3</sub></sub>, and [110]<sub>Li<sub>2</sub>MnO<sub>3</sub></sub> (e-i).

Download English Version:

<https://daneshyari.com/en/article/8033034>

Download Persian Version:

<https://daneshyari.com/article/8033034>

[Daneshyari.com](https://daneshyari.com)