High-Throughput Electrochemistry of High-Voltage Li-Ion Cathode Materials

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"To achieve great things, two things are needed:

a plan, and not quite enough time."

-Leonard Bernstein

Abstract

In the ongoing search for higher energy Li-ion batteries, the discovery of new cathode materials is of critical importance. Therefore, employing high-throughput methodologies to greatly increase the number of compositions studied is an attractive solution to rapidly screen and optimize next-generation battery materials. While the combinatorial investigation of cathode materials has been reported in the literature, studies have been limited to structural characterization, with electrochemical characterization having only been performed on select compositions. Herein, we adapt a high-throughput electrochemical testing system in order to test 64 different mg-scale cathode compositions simultaneously. As the ∼2 mg samples are synthesized in the same way as commercial materials, the results scale-up very well to that observed in bulk samples. Excellent agreement with literature is observed for both the peak potentials and the capacities obtained for the two test materials: $LiCoO_2$ and $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$. Standard deviations in the 64-cell plate is about 7% for capacity and energy density. This level of precision and accuracy is mostly limited by 5% uncertainty on mass such that the system is considered optimized. We thus have the capability to study important electrochemical performance metrics including energy and voltage fade between cycles. The system is then used to study 192 samples in the Li-Ni-Mn-O ternary system, synthesized and cycled in a one week period, and the results are then correlated to the structural phase diagram. This represents the first application of high-throughput cathode screening on powder electrode materials and enables the development of meaningful structure-property relations that are needed for the rational design of next-generation battery materials.

Résumé

Pour la recherche actuelle de batteries Li-ion à plus haute énergie, la découverte de nouveaux matériaux cathodiques revêt une importance cruciale. Ainsi, l'utilisation de méthodologies à haut débit (combinatoire) pour augmenter considérablement le nombre de compositions étudiées est une solution attrayante pour le criblage et l'optimisation rapides des matériaux de batterie de pointe. Bien que l'étude combinatoire des matériaux de cathode ait été rapportée dans la littérature, les études ont été limitées à la caractérisation structurale, dont la caractérisation électrochimique n'ayant été effectuée que sur des compositions sélectionnées. Ici, nous adaptons un système de test électrochimique à haut débit afin de tester simultanément 64 compositions différentes de cathodes à l'échelle du mg. Étant donné que les échantillons de ∼2 mg sont synthétisés de la même manière que les matériaux commerciaux, les résultats correspondent très bien à ceux observés dans des échantillons échantillons à l'échelle du g et kg. Un excellent accord avec la littérature est observé pour les potentiels de pointe et les capacités obtenues pour les deux matériaux à tester: $LiCoO_2$ et $Li[Ni_{1/3}Li_{1/3}Co_{1/3}]O_2$. Les écarts types dans la plaque à 64 cellules sont d'environ 6% pour la capacité et la densité énergétique. Ce niveau de précision et d'exactitude est généralement limité à 5% d'incertitude sur la masse, de sorte que le système est considéré comme optimisé. Nous avons ainsi la possibilité d'étudier d'importantes mesures de performance électrochimique, notamment la perte d'énergie et de tension entre les cycles. Le système est ensuite utilisé pour étudier 192 échantillons dans le système ternaire Li-Ni-Mn-O, synthétisés et cyclés en une semaine, puis les résultats sont corrélés au diagramme de phase structurel.

Ceci représente la première application du criblage cathodique à haut débit sur des matériaux d'électrode en poudre et permet de développer des relations structure-propriété nécessaires à la conception rationnelle de matériaux de batterie de nouvelle génération.

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List of Abbreviations

Abbreviation	Full Name
1D	One dimensional
2D	Two dimensional
3D	Three dimensional
ccp	Cubic close packed
Combi	Combinatorial
CV	Cyclic voltammetry
DMC	Dimethyl carbonate
EC	Ethylene carbonate
EIS	Electrochemical impedance spectroscopy
EMF	Electromotive force
EV	Electric vehicle
HOMO	Highest occupied molecular orbital
LCO	Lithium colbalt oxide
Li-ion	Lithium ion
LNO	Lithium nickel oxide
$LiPF_6$	Lithium hexafluorophosphate
LSV	Linear sweep voltammetry
LUMO	Lowest unoccupied molecular orbital
MW	Molecular weight
Na-ion	Sodium ion
NMC	Nickel manganese cobalt oxide
NMP	N-methyl-2-pyrrolidone
OCV	Open circuit voltage
PCB	Printed circuit board

Abbreviation	Full Name
PVD	Physical vapor deposition
PVDF	Polyvinylidene fluoride
Redox	Reduction and oxidation
RSD	Relative standard deviation
SEI	Solid electrolyte interphase
TM	Transition metal
XRD	X-ray diffraction

List of Symbols

Symbol	SI Units	Meaning
a	M	Activity
G	kJ	Gibb's free energy
E	J kg^{-1}	Specific energy
E_{eq}	V	Electromotive force
$E°$	V	Standard electromotive force
E_λ	V	Vertex potential
F	C m^{-1}	Faraday's constant
i	A	Current
MW	mol g^{-1}	Molecular weight
n	-	Number of electrons transferred
Q_{exp}	A h kg^{-1}	Specific experimental capacity
Q_{theo}	A h kg^{-1}	Specific theoretical capacity
Q_{irr}	-	Irreversible capacity
R	J mol^{-1} C^{-1}	Gas constant
t	s	Time
T	K	Temperature
μ_A	J mol^{-1}	Chemical potential of anode reductant
μ_C	J mol^{-1}	Chemical potential of cathode reductant
ν	V s^{-1}	Scan rate
V_{avg}	V	Average voltage
V_{OC}	V	Open circuit voltage

Acknowledgments

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Author Contributions

Chapter 2

All experiments were performed by the author, Karlie Potts (KP).

Chapter 3

Materials synthesis was performed jointly by KP and Eloi Grignon (under the supervision of KP). All cell assembly, electrochemical characterization, and data analysis was performed by KP.

Prof. Eric McCalla provided funding and intellectual guidance for all chapters in this thesis.

Chapter 1

Introduction

1.1 Overview of Li-ion Batteries

A secondary battery is a device that converts chemical energy to electrical energy reversibly and describes an individual electrochemical cell or multiple electrochemical cells that are connected to one another in series or parallel. Each cell is comprised of several key components including the positive electrode, negative electrode, and electrolyte.

The positive electrode (referred to hereafter as the cathode) is the electrode which is reduced and accepts electrons from the external circuit during the discharge of a battery, whereas, the negative electrode (referred to hereafter as the anode) is the electrode which is oxidized and donates electrons from the external circuit during the discharge of a battery.

The electrolyte is an ionic conductor that is used to facilitate the movement of ions between the anode and cathode in an electrochemical cell. Whereas in traditional electrochemical cells, electrodes are immersed into a free-flowing electrolytic solution, in a battery, the electrodes are isolated from one another using an electrolyte soaked porous material (separator). As such, it is crucial for electrolytes to be electronically insulating while demonstrating high ionic conductivity under the conditions imposed within the battery. Li-ion batteries utilize a lithium salt, such as $LiPF_6$, dissolved in an organic solvent. The use of an organic solvent is advantageous as the electrochemical stability window (the potential range in which a substance is electrochemically stable) is significantly larger than that of water. It is therefore of high importance for all battery processes to occur within the electrochemical window of the electrolyte to prevent electrolysis of the electrolyte.

It is the combination of these three components that determines the important electrochemical properties of the battery, including cell voltage, energy density, and lifetime.[1]

1.1.1 Operating Principles of a State-of-the-Art Li-ion Battery

The operation of a secondary battery is based upon reversible electrochemical reactions that take place in two half cells. Figure 1.1 depicts the operation of a state-of-the-art Li-ion battery, which commonly uses $LiCoO_2$ (LCO) as the cathode and graphite as the anode. The electrochemical reactions during operation of a battery occur at the electrode-electrolyte

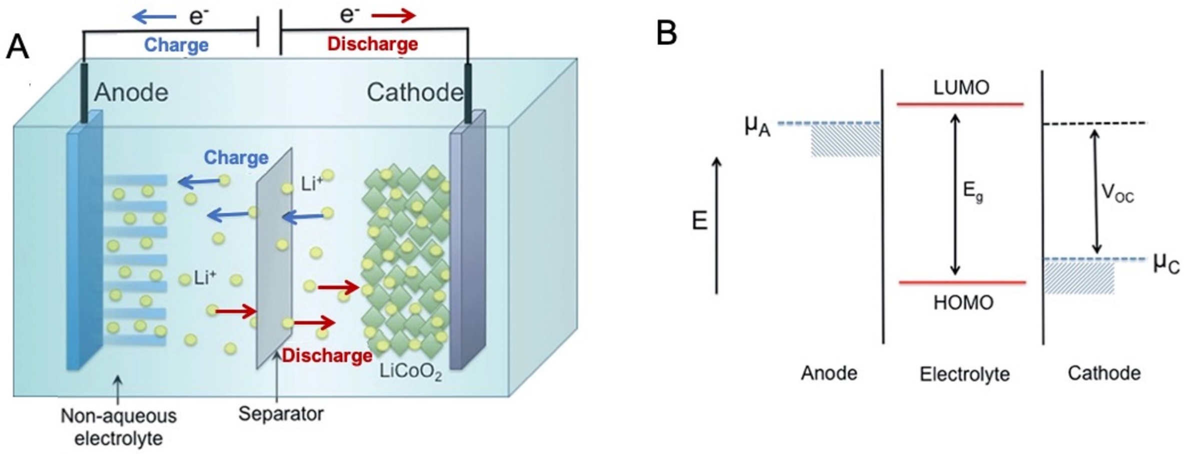

Figure 1.1: (A) Schematic of intercalation and deintercalation processes during the charging and discharging of a battery. (B) Relative energy levels of the electrolyte and electrode chemical potentials in a battery. Reproduced from Ref. [1] with permission from the Royal Society of Chemistry.

interface and are as follows:

$$LiCoO_2 \rightleftharpoons Li_{1-x}CoO_2 + xLi^+ + xe^- \qquad E^\circ = 3.9 \text{ V v}s\text{. Li/Li}^+ \tag{1.1}$$

$$6C + xLi^+ + xe^- \rightleftharpoons Li_xC_6 \qquad E^\circ = 0.1 \text{ V v}s\text{. Li/Li}^+ \tag{1.2}$$

Equations 1.1 and 1.2 represent the electrochemical processes that occur at the cathode and anode in a LCO and graphite battery, respectively. The forward reactions represent the electrochemical processes during charging whereas the reverse reactions represent the electrochemical processes during discharging. The overall electrochemical reaction in the battery may be expressed as the summation of the two half-cell reactions:

$$LiCoO_2 + 6C \rightleftharpoons Li_xC_6 + Li_{1-x}CoO_2 \tag{1.3}$$

The change in standard free energy of this reaction is governed by Gibb's free energy,

$$\Delta G = -nFE^\circ \tag{1.4}$$

where n is the number of electrons, F is Faraday's constant and E° is the standard electromotive force (EMF). When standard conditions are not met, the open circuit voltage (OCV, Eq. 1.5) can be defined by the Nernst equation:

$$E_{eq} = E^\circ - \frac{RT}{F} \ln \frac{a_{Li_xC_6} a_{Li_{1-x}CoO_2}}{a_{LiCoO_2}} \tag{1.5}$$

in which a represents the activity of the species, R is the gas constant, and T is the absolute temperature. Equation 1.5 defines the OCV, when the battery has no current flowing. When a Li-ion battery is first assembled, it is in the discharged state and requires an external electrical stimulus to charge it. A voltage is applied across the cell, such that the transition metal(s) in the cathode are oxidized, thereby compensating the movement of electrons and lithium ions towards the anode through the external circuit and electrolyte, respectively (Fig. 1.1 A). The voltage is continually applied until the desired cutoff voltage is reached. At this point the battery is considered fully charged and is capable of supplying electrical energy through the external circuit. When energy is needed from the battery, the external circuit is completed, causing the reduction of the cathode material. This again causes the migration of lithium ions and electrons back towards the cathode. While returning to their thermodynamic minimum, the electrons are able to perform work on the external circuit. The amount of work that can be performed is proportional to the difference in chemical potential of the anode reductant (μ_A) and cathode oxidant (μ_C) (Fig. 1.1 B). This is equivalent to the OCV (V) of the battery in the charged state and may be expressed as:

$$V = \frac{1}{-nF}(\mu_A - \mu_C) \tag{1.6}$$

The maximum duration (t) that work can be performed is determined by the capacity (Q) of a battery.

$$t = \frac{Q}{i} \tag{1.7}$$

The capacity is defined as the amount of charge that a battery can deliver, and is usually measured at a constant current (i). The theoretical capacity (Q_{theo}) can be determined by way of Faraday's Law and is dependent on the molecular weight (MW) of the electrochemically limiting species. For LCO, where $n = 1$, we obtain:

$$Q_{theo}^{LCO} = \frac{1000 \times nF}{3600 \times MW} = 273\ mAhg^{-1} \tag{1.8}$$

In practice, it is extremely rare for a battery to attain the expected theoretical capacity during discharge. In particular, while LCO presents a high theoretical capacity of 273 mAhg^{-1}, only 170 mAhg^{-1} can be cycled reversibly.[2] The limitation of experimental capacity can be caused by many factors, however the end result is the prevention of reversible intercalation processes in the battery. For example, in the case of LCO, the capacity is limited upon extracting greater than half of the Li ($x_{Li} > 0.5$) on charge, as it introduces irreversible structural transformations, preventing reintercalation during discharge.[2] In addition, charging to higher potentials can often initiate other electrochemical processes, forming parasitic side-products that prevent further intercalation processes. Depending on the severity of these unwanted processes, significant effects may be seen as early as the first cycle and will often be reflected in the irreversible capacity (Q_{irr}). Irreversible capacity is a measure of the reversibility of a battery and considers the difference of capacity attained on charge and discharge:

$$Q_{irr} = \frac{Q_{charge} - Q_{discharge}}{Q_{charge}} \times 100 \tag{1.9}$$

It is important to note that while a loss of capacity may be seen in the first cycle, it is important to consider the trend in irreversible capacity over many cycles. During the initial cycles of a battery, a passivation layer, referred to as the solid electrolyte interphase (SEI), forms on the anode. The SEI layer forms when the voltage at which the anode operates is outside of the electrochemical window of the electrolyte. This contributes to an initial decrease in discharge capacity as the passivation layer traps lithium, preventing it from intercalating into and out of the structure. While the SEI initially serves to stabilize the interface of the electrolyte and anode, it can continually grow causing gradual loss in capacity and occasionally even complete passivation of the anode surface. The rate of the SEI formation is highly dependent on the battery system and is reflected in the irreversible capacity during later cycles.

In addition to capacity, there are several other key performance metrics that may be considered. Specific energy (E), the amount of energy per unit mass, is amongst the most important performance metrics and is of high relevance to electric vehicles, as it determines the range of vehicle. Further, it provides a common reference point to compare various battery materials. The specific energy is determined by considering the specific capacity and average operating voltage (V_{avg}) of a battery and is given by:

$$E = V_{avg}Q \tag{1.10}$$

While the theoretical specific energy may be determined, similar to that of specific capacity, it often differs significantly from that of the experimental specific energy. Over the last thirty years, there has been considerable efforts to improve initially promising battery systems to reach the ultimate goal of attaining their theoretical limits. Along the way, these efforts had to address other and often competing factors affecting the batteries use in applications including their power, safety, and cost. Therefore, tracking multiple metrics is essential in battery development.

1.1.2 Electrochemical Testing of Battery Materials

Various electroanalytical techniques may be used to investigate battery materials, including galvanostatic and voltammetric methods. The difference in these two families of techniques stems from the electrochemical variables that are being controlled and monitored. In particular, galvanostatic techniques measure the voltage across a cell while current is constant, whereas voltammetric techniques measure the current passing through a cell as the voltage is swept.[3] This section will explore the relevance of each technique to the electrochemical testing of battery materials.

1.1.2.1 Galvanostatic Measurements

As seen in Figure 1.2, galvanostatic methods apply a predetermined constant current and measure the corresponding voltage as a function of time. The application of a constant current closely models the operation of a battery, where a constant load is present upon discharging. Therefore, galvanostatic techniques are the most prominent in battery research. The applied current is often described using C-rate notation. C/n represents the current required to charge or discharge the battery in n hours. For example, a rate of $C/2$ corresponds

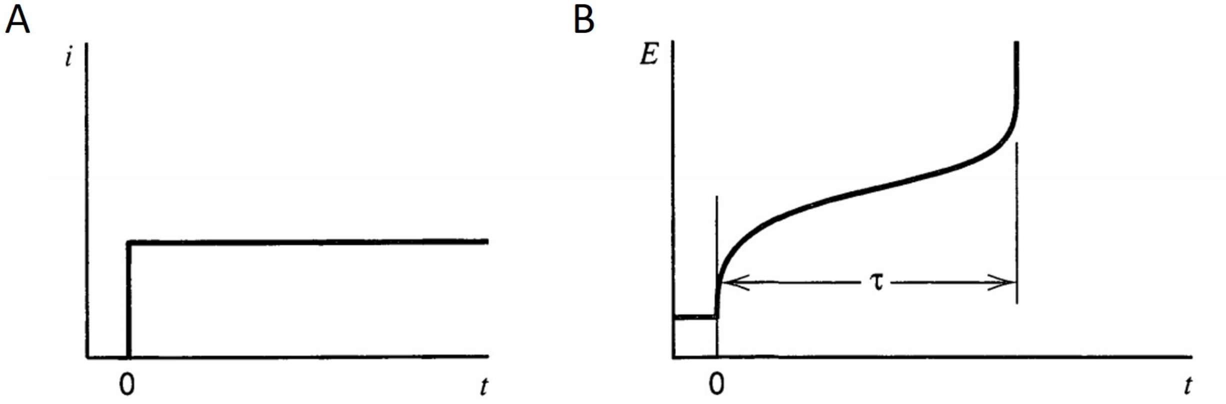

Figure 1.2: Galvanostatic measurement. (A) The applied constant current to a cell as a function of time and (B) the resulting voltage response as a function of time. Reproduced from Ref. [3] with permission from Wiley and Sons.

to the current required to charge or discharge the battery in 2 hours. The potentiostat then dynamically controls the applied voltage to maintain constant current. As a consequence of this, horizontal plateaus, indicative of 2-phase intercalation processes, are often present in voltage-time and voltage-capacity plots.

1.1.2.2 Voltammetric Measurements

In voltammetric-based experiments, a potential waveform governs the potential applied to the cell and the corresponding current is measured as a function of time. Two predominant voltammetric techniques used in battery research include linear sweep voltammetry (LSV) and cyclic voltammetry (CV). Whereas LSV applies a unidirectional potential sweep, CV applies a potential sweep in two directions such that the direction is reversed at a vertex potential (E_λ). The direction reversal in CV results in a cyclic potential waveform, as seen in Figure 1.3 A. While CV is more commonly used to determine the general behavior of a system

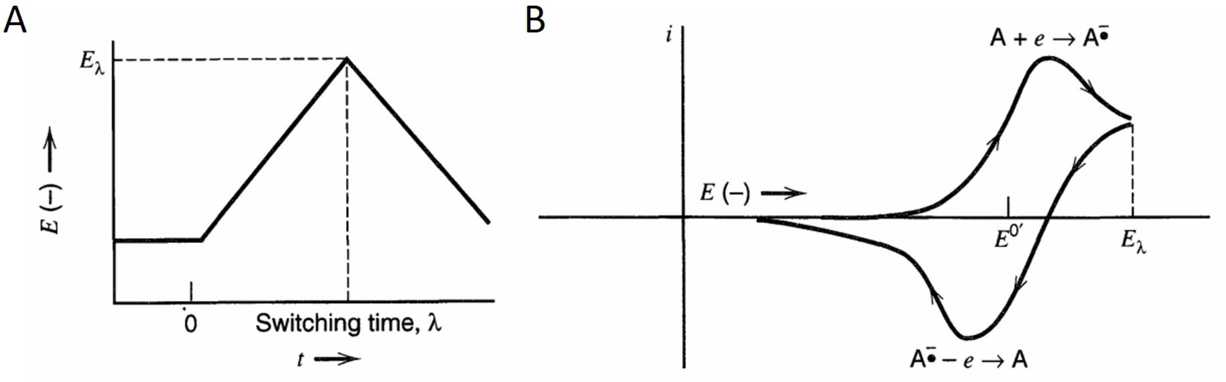

Figure 1.3: Cyclic voltammetry. (A) Characteristic cyclic potential waveform applied during cyclic voltammetry and (B) the corresponding current response as a function of applied potential. Reproduced from Ref. [3] with permission from Wiley and Sons.

(i.e. electrochemical stability window, redox potentials, etc.), it is also possible to convert i vs. V plots obtained with cyclic voltammetry into voltage-capacity plots comparable to those obtained by galvanostatic methods, thereby enabling the determination of relevant battery performance metrics. To do this, the experimental capacity (Q_{exp}) may be determined by the integral of current over the relevant interval of time (e.g. t_0 to t), as seen in Equation 1.11:

$$Q_{exp} = \int_{t_0}^{t} i \cdot dt \tag{1.11}$$

It is important to note that while voltammetric techniques can provide the same electrochemical information as galvanostatic techniques, close attention must be paid to the scan rate. Since intercalation processes can require significant time to occur, it is often necessary to employ an extremely slow scan rate to avoid mass transport effects. If the redox processes are characterized in the system of interest, LSV can be advantageous. Using LSV, a custom potential waveform can be designed to vary the scan rate over different voltage windows to correspond to the separate electrochemical processes occurring. For example, a potential window with no electrochemical processes could employ a much quicker scan rate than a potential window in which redox processes are active. This strategy approaches that of galvanostatic testing and can be employed in situations where constant current techniques may not be permitted (as will be the case in the high-throughput cells in Chapter 3).

1.2 Cathode Materials

1.2.1 Motivation for Cathode Development

The commercialization of Li-ion batteries signified a revolutionary moment for the technology sector. Their inherent high energy density and long lifetime enabled the wide-spread implementation of portable electronic devices, and, more recently, the development of electric vehicles (EVs). Even though the Li-ion batteries of today surpass what is required for small portable electronics, the EV market still needs substantial improvement of several key performance metrics. An exponentially increasing trend, beginning in 2017 with EV sales of US \$25 billion, is expected to reach US \$75 billion by 2025.[4] It is therefore critical to address any performance shortfalls to continue to meet global demand. Figure 1.4 illustrates a radar plot of required improvements to key performance metrics, set by BMW, to enable the wide-spread implementation of EVs by 2025.[5] While certain metrics such as their safety and lifetime for Li-ion batteries are sufficient today, increasing the specific energy by a factor of 4 and decreasing the cost by a factor of 3 are crucial for EVs.[5] These targets currently serve

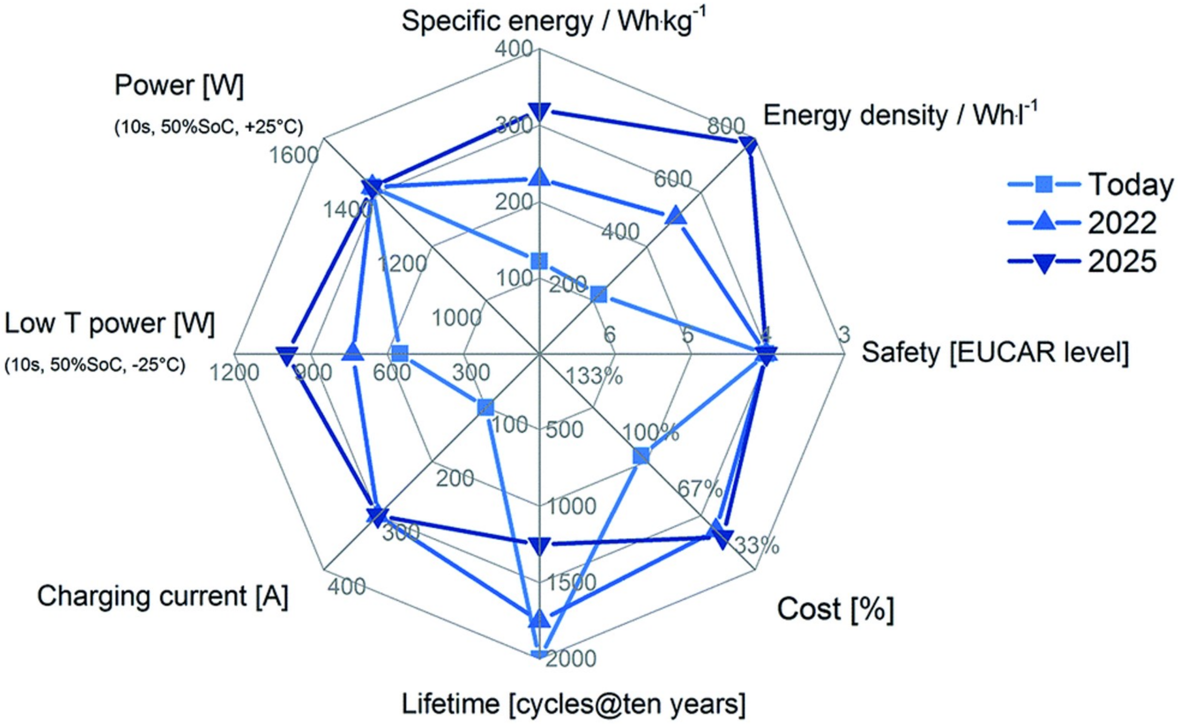

Figure 1.4: Key performance metrics of Li-ion batteries along with automotive industry targets for complete implementation of electric vehicles by 2025. Reproduced from Ref. [5] with permission from the Royal Society of Chemistry.

to direct a significant portion of research and development to focus on cathode materials, as it is the cathode that limits the specific energy of the battery and represents the most expensive component upon manufacturing.[6]

1.2.2 Common Crystal Structures of High-Energy Cathode Materials

In the on-going search for improved materials for high energy density storage devices, the complexity of the materials employed has increased drastically. Whereas the first commercialized Li-ion battery had $LiCoO_2$ (LCO) as the cathode material, cathodes produced today for important applications such as EVs are typically pseudo-quaternary oxides. This has involved making substitutions on the Co sites resulting in $Li[Ni,Mn,Co]O_2$ or $Li[Ni,Al,Co]O_2$. In particular, the cathodes used in state-of-the-art high-energy Li-ion batteries can be divided into two groups of crystal structures: (i) ordered rock salt or layered oxides, and (ii) spinel type structures (Fig. 1.5 A-B).[7,8]

Figure 1.5 A illustrates the crystal structure of a layered oxide cathode. Layered structures ($Li[M]O_2$ where M = Co, Ni, (Ni_x), and ($Ni_xMn_yCo_z$)), present alternating layers of MO_2 slabs and Li sheets. The MO_2 slabs are hexagonal arrays of MO_6 octahedra, such that the M and Li are octahedrally coordinated (1:1 stoichiometric ratio). The oxygen sublattice is cubic close packed (ccp), stacking in an ABCABC (O3) sequence.[7]

Spinel structures ($Li[X]_2O_4$ where X = Mn, ($Mn_{1-\frac{y}{2}}Li_{\frac{y}{2}}$) and ($Mn_{\frac{3}{4}}Ni_{\frac{1}{4}}$)), illustrated in Figure 1.5 B, are similar to that of layered in that they are arranged in a ccp sublattice,

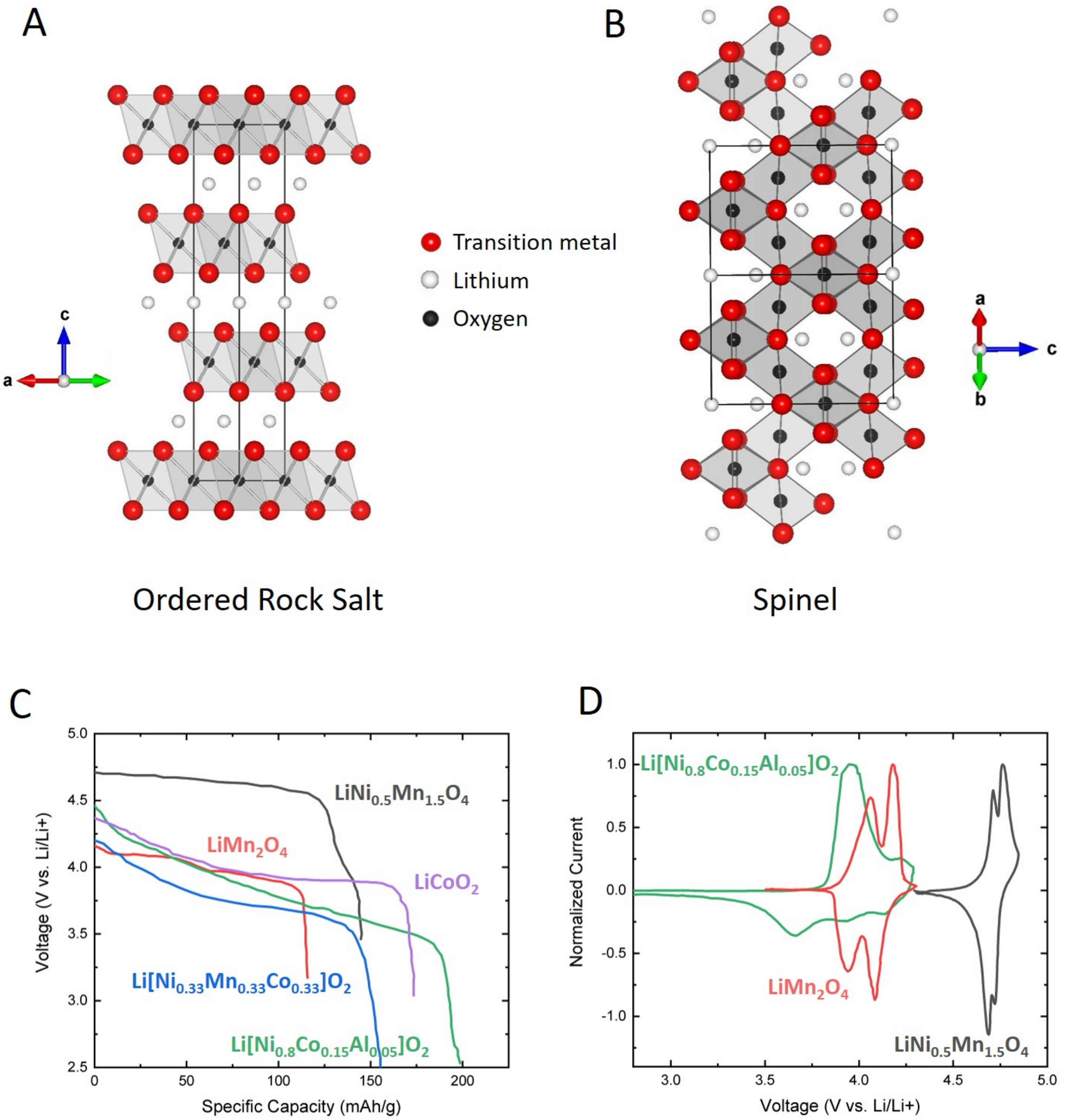

Figure 1.5: Crystal structures of (A) ordered rock salt and (B) spinel materials. (C) Voltage-capacity curves and (D) cyclic voltammograms of various layered and spinel structured cathode materials. Adapted from Refs. [9-13].

however they maintain a M to O_2 ratio of 3:4. This results in Li and M residing in tetrahedral and octahedral sites, respectively, in the sublattice.[7]

The main consequence of the difference in crystal structure is the pathway that Li intercalation occurs through. In particular, layered oxides present a two-dimensional (2D) lattice framework whereas spinel structures present a three-dimensional (3D) framework for ion diffusion. The 3D lattice in spinel materials typically presents greater structural stability resulting in increased safety and power, as observed in spinel based cathode materials.[8]

Each class of crystal structure demonstrates significantly different electrochemical properties (i.e. average voltage, stability, rate capability) and subsequently have been commercialized for various applications that place emphasis on difference performance factors. Examples of commercialized high-voltage cathodes of each structure may be seen in Table 1.1. Figure 1.5 C-D illustrates the electrochemical profiles of various layered and spinel materials.[9–13] As seen, layered materials typically present rather broad redox peaks (i.e. slanted plateaus

Table 1.1: Summary of key properties of high-voltage cathode materials for Li-ion batteries. Electrochemical data was compiled from Ref. [49].

Material	**Structure**	**Avg. Voltage**	**Capacity**	**Energy**	**Commercialized**
		V	mAhg^{-1}	Wh/cm^3	
LCO	Layered	3.9	140-160	3.05	Yes
$Li[Ni_{1-x-y}Mn_xCo_y]O_2$	Layered	3.8	150-180	2.6-3.2	Yes
$Li[Ni_{0.8}Co_{1.5}Al_{0.05}]O_2$	Layered	3.7	200	3.54	Yes
$Li[Li_{1/9}Ni_{1/3}Mn_{5/9}]O_2$	Layered	3.8	240	4.06	No
$LiMn_2O_4$	Spinel	4.05	120	1.8-2.0	Yes
$LiNi_{0.5}Mn_{1.5}O_4$	Spinel	4.6	145	2.63	No

in the voltage-capacity curves) whereas spinel materials present sharp, doublet redox peaks, emphasized when considering the cyclic voltammograms (Fig. 1.5 D).

In addition to crystal structure, material composition also greatly impacts electrochemical behavior. Each material in Table 1.1 presents starkly different electrochemical behavior, irregardless of the class of crystal structure. In particular, it is interesting to compare $LiMn_2O_4$ and $LiNi_{0.5}Mn_{1.5}O_4$. Despite both being spinel structured materials, $LiMn_2O_4$ demonstrates a significantly lower average voltage and capacity (Table 1.1). This is extremely evident upon comparing the redox peaks of $LiMn_2O_4$ and $LiNi_{0.5}Mn_{1.5}O_4$ in Figure 1.5(D). Whereas in $LiMn_2O_4$, Mn is oxidized from the 3^+ to 4^+ state, upon the addition of Ni (i.e. $LiMn_{1.5}Ni_{0.5}O_2$), Mn remains inactive thereby stabilizing the structure and Ni is oxidized from the 2^+ to 4^+ state at higher voltages.[14,15] As such, $LiMn_2O_4$ and $LiMn_{1.5}Ni_{0.5}O_2$ are considered low voltage and high voltage spinel materials, respectively. While some trends such as this example are well understood in the literature, there remains a poor understanding of most structure-performance relationships. Due to this, increased electrochemical studies are required to elucidate more nuanced relationships. In particular, systematic searches through the Li-Ni-Mn-Co-O and Li-Ni-Co-Al-O systems are badly needed (all materials in Table 1.1 lie in these under-explored systems). This thesis represents a 1st step in the effort to enable and expedite the development of these important structure-performance relationships.

1.2.3 First Generation Cathode Materials

Layered oxide structured materials represent the most successful first generation cathodes. First reported in 1980 by Goodenough et al., LCO was commercialized by SONY in 1990 and is considered the first successful intercalation cathode.[16] While LCO promised a high theoretical capacity of 274 mAhg^{-1}, only a little over half can be consistently obtained during cycling. During cycling (Fig. 1.6 (red)), Co becomes partially oxidized from the 3^+ to 4^+ state, as lithium is removed, resulting in shearing of the crystal lattice upon sufficient Li extraction ($x_{Li} > 0.5$, where x_{Li} is the fraction of Li extracted). This results in the instability

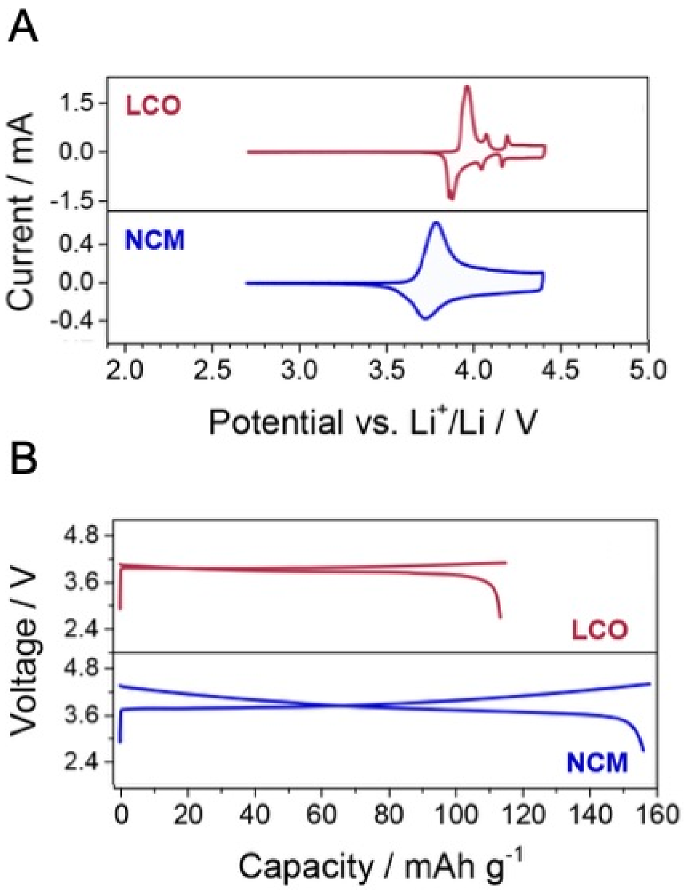

Figure 1.6: Characteristic (A) cyclic voltammograms and (B) voltage-capacity curves for LCO (red) and NMC (blue). Reproduced from Ref. [52] with permission from the American Chemical Society.

of delithiated phases causing irreversible structural changes evident in the observed rapid capacity fade. There has been a great deal of efforts to increase the capacity of LCO and improve its long term cyclability. In particular, surface modification of LCO particles combined with doping of various transition metals (TM) has been found to improve the stability of the delithiated phases and enable higher voltage cycling. These efforts have achieved a maximum capacity of 164 $mAhg^{-1}$ in commercialized cathodes.[2,17] Despite these successes, there are still several drawbacks due to the high cobalt content, including, high toxicity and cost. As such, LCO is considered to have reached maturation today, and in doing so served as a framework for the rational design of new cathode materials.

In 2001, lithium nickel manganese cobalt oxide ($Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$, hereafter referred to as NMC), a layered rock salt oxide, was proposed as a next generation cathode material.[18] The combination of TMs reduced the cost and toxicity, while increasing the safety and improving the long-term cyclability.[19] Upon charging, Ni is oxidized from the 2^+ to 4^+ state (as seen at 3.78 V vs. Li/Li^+, in Fig. 1.6 (blue)), and depending on the upper voltage threshold, Co may be oxidized from the 3^+ to 4^+ state.[19,20] During cycling, irreversible capacity is minimized, as Mn^{4+} remains inactive, thereby preserving the structural stability in the material.[21] The electrochemical properties of NMC can be varied significantly by tuning the composition of the material, i.e. varying the ratio of TMs. This possibility of finding a higher performing NMC composition has spurred significant interest in researching next-generation cathode materials. However, due to the vastness of compositions space, only a few compositions have been thoroughly characterized. Making discovery more difficult is the lack of a comprehensive structure-property relationship to guide rational development.

1.2.4 Next-Generation Cathode Materials

Significant research today, driven by the demand of EVs, focuses on the identification of next-generation cathode materials with increased specific energy. A promising candidate, closely related to the stoichiometric layered oxides ($LiMO_2$), are the Li-rich layered oxides ($Li_{1+x}M_{1-x}O_2$). As seen in Figure 1.7 and Table 1.1, the specific capacity observed in Li-rich layered oxides already surpasses that of the first generation cathodes (> 274 mAhg^{-1}).[22] The staggering increase in electrochemical activity is owed to the additional contribution of capacity from anionic redox processes.[23] Whereas first generation cathodes solely relied on cationic redox processes, Li-rich layered oxides provide the unique opportunity to harness both, resulting in capacities that surpass those of the first generation. Upon sufficient

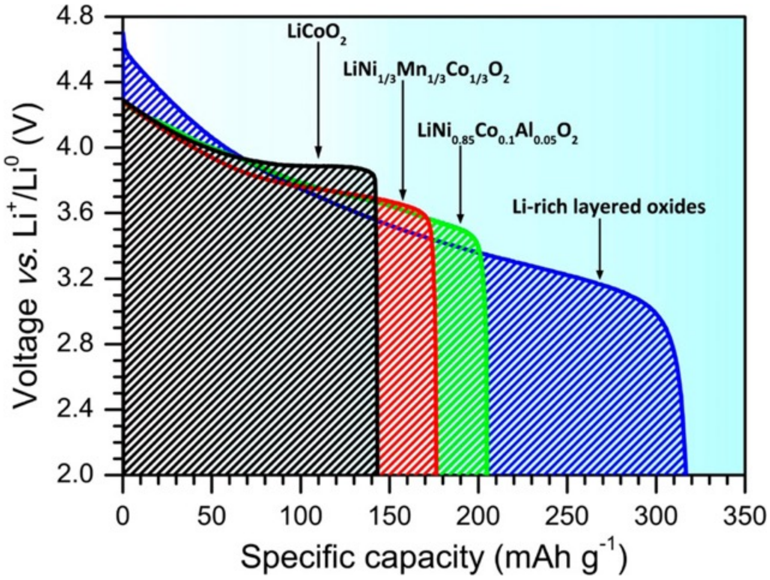

Figure 1.7: Voltage vs. specific capacity of stoichiometric layered oxides, including LCO (black), NMC (red), and $LiNi_{0.85}Co_{0.1}Al_{0.05}O_2$ (green), in comparison to Li-rich layered oxides (blue). Reproduced from Ref. [22] with permission from the American Chemical Society.

charging (> 4.5 V vs. Li/Li$^+$), Li-rich materials present the reversible generation of $(O_2)^{n-}$, resulting in the formation of O-O dimers in the oxygen sublattice.[23] Figure 1.8 illustrates the electrochemistry of $Li_{1.2}Ni_{0.13}Mn_{0.54}Co_{0.13}O_2$, a notable Li-rich layered oxide. As seen, in comparison to traditional stoichiometric layered oxides, Li-rich layered materials present highly aysmmetric redox processes (i.e. significantly different oxidation and reduction profiles). In particular, the high-voltage plateau (Fig. 1.8 A, seen as an oxidation peak in Fig. 1.8 B) at 4.46 V vs. Li/Li$^+$ is characteristic of Li-rich materials and is the result of oxygen activation and release in the material. While Li-rich oxides demonstrate great promise, further optimization is required to mitigate the significant voltage fade and irreversible capacity

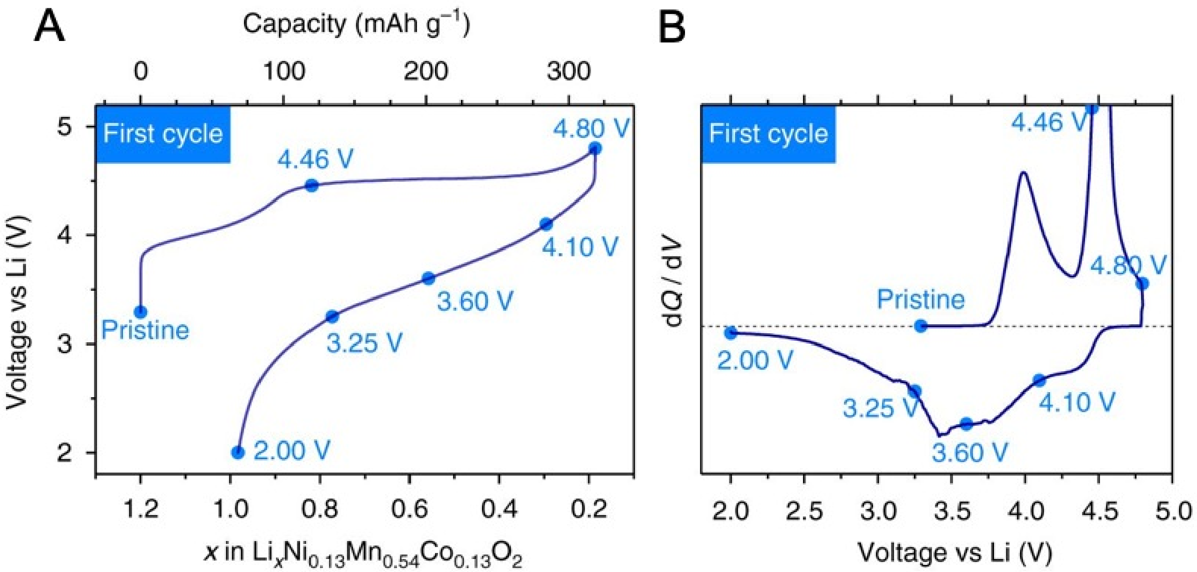

Figure 1.8: $Li_{1.2}Ni_{0.13}Mn_{0.54}Co_{0.13}O_2$ (A) voltage-capacity plot and (B) dQ/dV plot illustrating the high-voltage plateau characteristic of Li-rich layered oxides, indicative of oxygen activation and release. Reproduced from Ref. [24] with permission from Macmillan Publishers Ltd.

experienced by these materials.[24] Additionally, as only select compositions have been investigated, the extensive exploration of this class of materials is of high importance to identify the most promising Li-rich candidate.

1.3 High-Throughput Methodologies in Battery Research

Central to the development of next generation battery materials is the discovery and optimization of new electrode materials. To date, the development of battery materials have largely been through traditional methods, where only a few materials of select compositions can be thoroughly investigated in a single pass. As emphasized in the previous sections, the compositional complexity of cathode materials has increased dramatically. As seen in Table 1.1, in the case of layered oxides, materials span a six element composition space (Li, Ni, Mn, Co, Al and O). As such, employing high-throughput methodologies to greatly increase the number of compositions studied is an attractive solution to rapidly screen and develop next generation batteries. In particular, high-throughput techniques including computation and experimentation (i.e. structural characterization) have proven very effective and will be discussed in this section.

Ideally, a vast amount of material screening could be performed computationally, and there has been considerable efforts to use high-throughput computation to identify candidates for battery materials (cathodes, anodes, and solid electrolytes).[25–27] These methods are very powerful, but there are limitations to their predictive power. Computational methods struggle to account for solid-solutions, as the size of the supercell becomes unmanageable in cases where small variations in stoichiometry impact performance. It is also difficult to predict which phases are stabilized at high temperatures, which is critical in battery materials where all commercially relevant cathodes are synthesized at high temperatures.[28] This makes it imperative that experimental screening is performed in conjunction with computation, as to ensure optimum compositions/conditions are not overlooked.

Recently, a methodology for the combinatorial synthesis of lithium transition metal oxides was established by the Dahn group.[29,30] Through use of a liquid handling robot, mg-scale samples were made by co-precipitation synthesis, enabling the ability to process broad ranges of compositional space quickly and efficiently. The combinatorial samples were thoroughly characterized with X-ray diffraction (XRD) and were found to present crystal structures and lattice parameters closely matching that of the bulk materials published in literature.[29,30] Since this synthetic methodology yields products comparable to those used commercially (i.e. a co-precipitation reaction is typically used in a constantly stirred tank reactor), the characterization of materials synthesized in this fashion is of high relevance to industry.

The utility of this synthetic method is well illustrated by the combinatorial work of the Dahn group, wherein they coupled high-throughput synthesis and high-throughput X-ray diffraction (XRD) to elucidate the phase diagrams for the Li-Mn-Ni-O pseudo-ternary system under a variety of synthetic conditions.[31] Figure 1.9 illustrates the complete Li-Mn-Ni-O phase diagram under both quenched (A) and slow-cooled (B) conditions.

The phase diagrams are presented in the form of ternary plots, such that a Gibbs triangle is used to graphically represent the possible compositions of three species (in this case Li, Mn, and Ni) and their corresponding phase space. In particular, each axis denotes the atomic fraction of the metal, such that contributions from Li, Mn, and Ni must sum to one for all points in the triangle. The ratio of each phase along tie-lines are governed by the lever rule, such that relative distance between two tied single phase compositions determines the relative proportion of each along the tie-line. Figure 1.9 displays these phase diagrams and demonstrates the regions of single-phase, two-phase, and three-phase that form under separate synthetic conditions.

As seen, the phase diagrams are extremely complex and exhibit large single phase regions that transform during cooling. While the electrochemistry was only characterized on select compositions, it was found that the electrochemical performance of these materials varied drastically. This is evident in Figure 1.9 C, in which select compositions along the layered single-phase boundary demonstrated very different electrochemical profiles. This marked the first attempt to study combinatorial samples synthesized using the same synthesis methods as those used commercially, making the combinatorial results directly relevant to work performed on bulk cathode materials. This methodology was further used to expand the 2D Li-Mn-Ni-O pseudo-ternary to the 3D Li-Ni-Co-Mn-O pseudo-quaternary phase diagram, a system which includes current commercialized materials (layered LCO and NMC, and spinel $LiMn_2O_4$) as well as Li-rich materials ($Li_{1+x}M_{1-x}O_2$) which are of extreme interest as next-generation cathodes.[32]

While this work demonstrated the significant potential of combinatorial work on cathode materials, it was limited by the lack of high-throughput electrochemistry.[33] This is also the case in more recent work performed at Argonne National Laboratories.[34] Stemming from this,

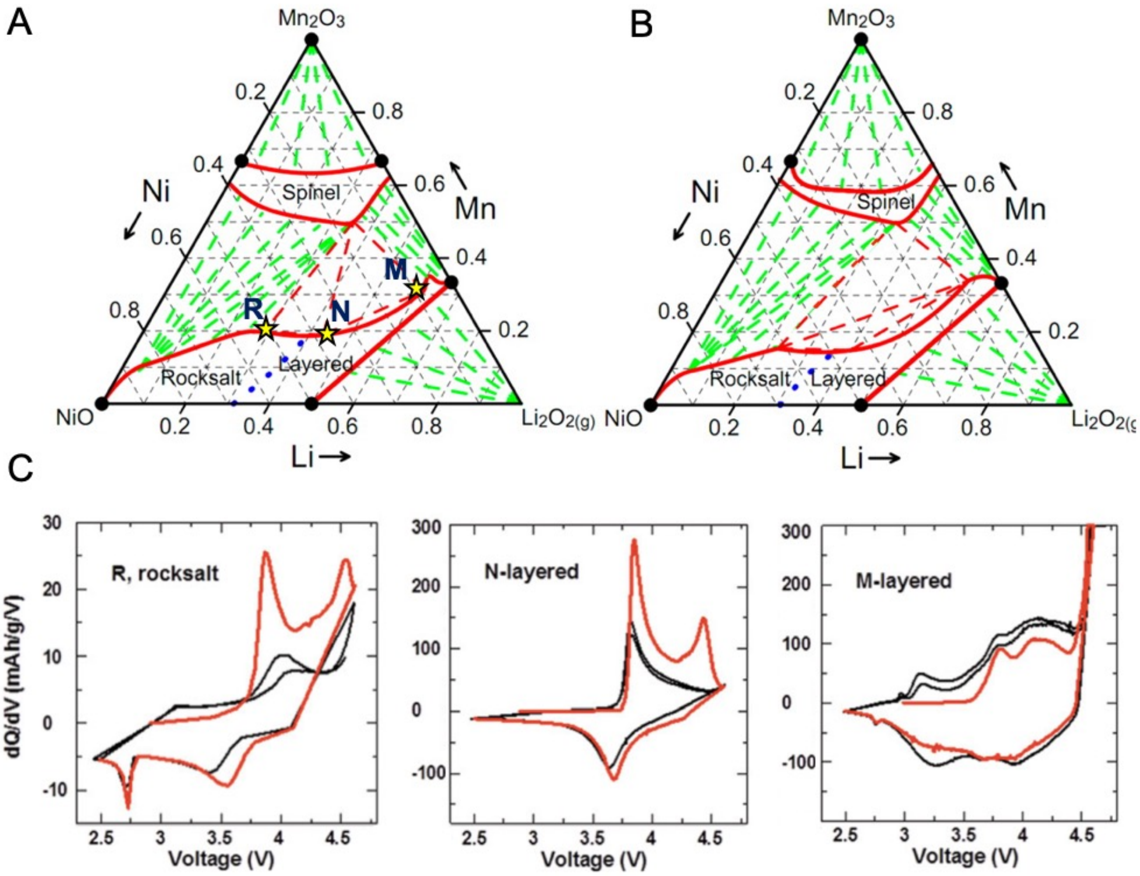

Figure 1.9: The complete structural phase diagram for the Li-Mn-Ni-O pseudo-ternary system mapped under both (A) quenched and (B) slow-cooled synthetic conditions. Solid red lines represent boundaries to single-phase regions, green dashed lines are tie-lines (i.e. compositions of two-phases) and dashed red lines are tie-lines at the outer edges of three-phase regions. (C) Electrochemistry of select compositions in the single phase layered region, as indicated in the quenched phase diagram. Reproduced from Ref. [33] with permission from Springer Nature.

the electrochemical consequences of the structural phase diagrams have not been elucidated and no comprehensive structure-property relation exists for these critical materials.

To date, high-throughput electrochemistry of battery materials has been limited to thin films[35–40] or to the optimization of electrode formulation[41–43], rather than the characterization of active material compositions. In particular, a system designed by the Dahn group was successful in testing gradients of thin film alloys for their use as anodes.[35,36,44] These measurements used a 64-sample combinatorial cell in which the samples were sputtered onto a printed circuit board (PCB) containing 64 nickel contact pads. As seen in Figure 1.10 A, the cell was assembled with a thin electrolyte-soaked separator and a single piece of lithium that would serve as a counter and reference electrode. This resulted in 64 cells connected in parallel, such that cyclic voltammetry could be performed on all samples at the same time, enabling the simultaneous monitoring of capacity, average voltage, irreversible capacity and capacity fade across entire ternary systems (Fig. 1.10 B). The one key drawback of this system is that it was designed for thin films only. Although the screening of thin film layered oxides is important, it solely serves to develop thin film batteries, and does not scale-up well to bulk powders used commercially in high energy applications such as EVs. This is mainly due to: (i) the increase in surface area/volume ratio resulting in dramatically altered long-term cycling, and (ii) the control of oxygen content in sample preparation of an array of thin films is very challenging such that the structures do not match as obtained in bulk powders.[45]

This challenge emphasizes the current demand in research for a high-throughput electrochemical system capable of studying powder Li-ion cathodes. Not only would this open up

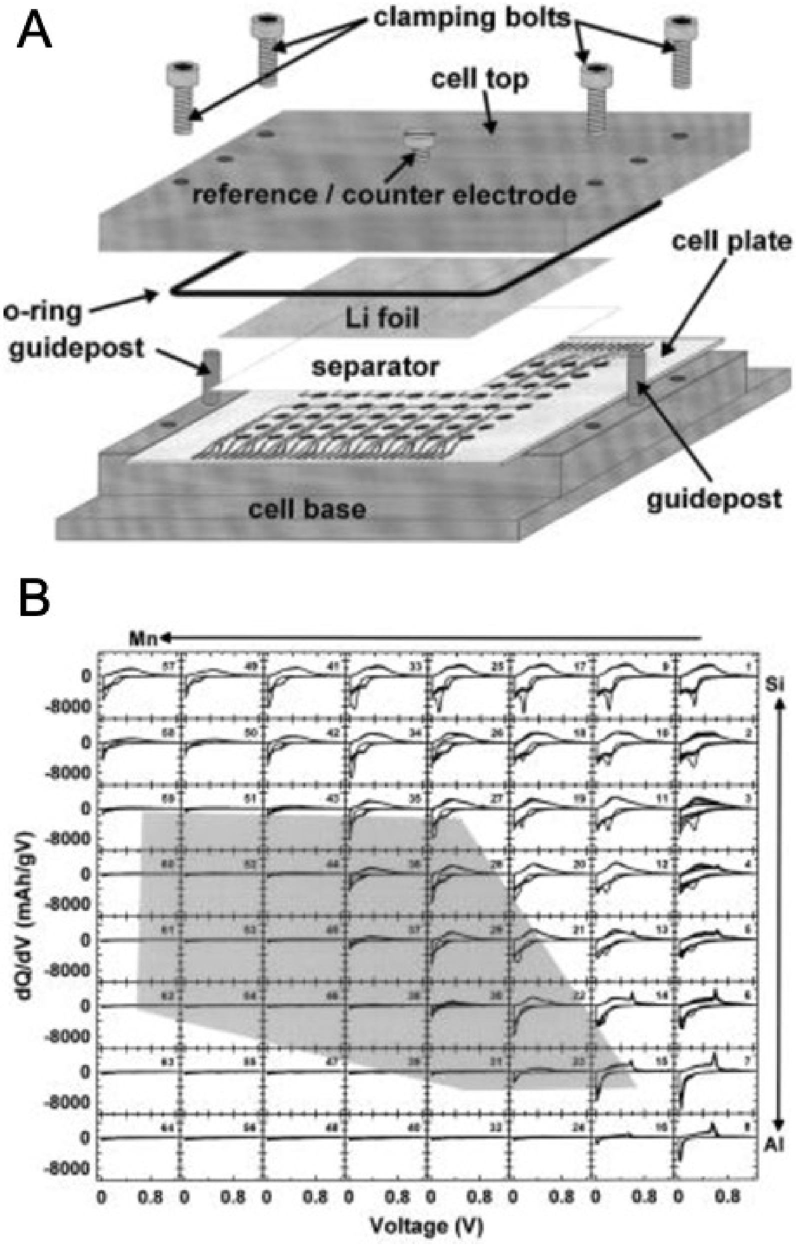

Figure 1.10: High-throughput electrochemical testing of thin-film anodes (A) Schematic of the high-throughput electrochemical cell. (B) Differential capacity vs. voltage plots of the Si-Al-Mn ternary system cycled in the high-throughput cell. Part A reproduced from Ref. [44] and Part B reproduced from Ref. [35] with permission from the Electrochemical Society.

numerous avenues to rapidly screen potential battery materials, it would also enable the development of meaningful structure-property relations that are needed for the rational design of next-generation battery materials. This thesis aims to fill that void by adapting and optimizing a high-throughput electrochemical testing system for the investigation of high-energy cathode materials. Chapter 2 focuses on the adaptation, optimization and evaluation of the system, whereas Chapter 3 explores the evolution of the electrochemistry throughout the Li-Mn-Ni-O pseudo-ternary system to thus determine the impact of structure on key battery performance metrics.

Chapter 2

Development of High-Throughput Electrochemical Testing of Cathode Materials

2.1 Established Experimental Methods

There is no established experimental method for high-throughput electrochemistry on cathode powders. However, methodologies have been reported for the high-throughput synthesis of cathode materials[30] and the high-throughput electrochemistry of anodes.[44] Herein, we review the established methodologies prior to developing a technique to perform high-throughput electrochemistry on powder electrodes in Section 2.2.

2.1.1 Synthesis of Combinatorial Samples

The mg-scale combinatorial samples were prepared on alumina plates via a co-precipitation reaction as described in the literature.[30] A liquid-handling robot (Opentrons) was used to dispense mixtures of 2M solutions of lithium nitrate ($LiNO_3$) (Sigma-Aldrich), manganese (II) nitrate ($Mn(NO_3)_2$) (Sigma-Aldrich), nickel (II) nitrate ($Ni(NO_3)_2$) (Sigma-Aldrich), and cobalt (II) nitrate ($Co(NO_3)_2$) (Sigma-Aldrich), onto alumina plates. While the volume ratios were varied depending on the target compound, the total volume remained 20 uL in all cases. $LiNO_3$ was used in 10% excess to account for Li loss upon heating in each of the test materials used in this chapter: $LiCoO_2$ (LCO) and $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ (NMC). 2M NH_4OH was added in excess to the mixed nitrates to precipitate the metals. The samples were dried at 60 °C for 12 h followed by high temperature synthesis in an air-filled box furnace for 3 hours at 800 °C. The rates of heating and cooling utilized were 5 °C/min.

2.1.2 Combinatorial Electrochemical Measurements

Cyclic voltammetry measurements were performed on a lab-built system, which utilized a quad voltage source (model 213, Keithley) and a multimeter (model 2750 multimeter/switch system, Keithley) to cycle the combinatorial cell.[44] All test material cells were cycled from a potential of 3.0 V to an upper threshold of 4.4 V vs. Li/Li$^+$, at a scan rate of 0.1 Vh^{-1}. The combinatorial cell facilitated the simultaneous investigation of 64 separate positive electrode compositions through designating each positive electrode material a separate circuit and placing it in parallel to the other 63 electrodes. Combining the combinatorial cell with the instrumental set-up enabled high-throughput electrochemistry (Fig. 2.1). The set-up operated by the voltage source applying a predetermined potential waveform to the cell,

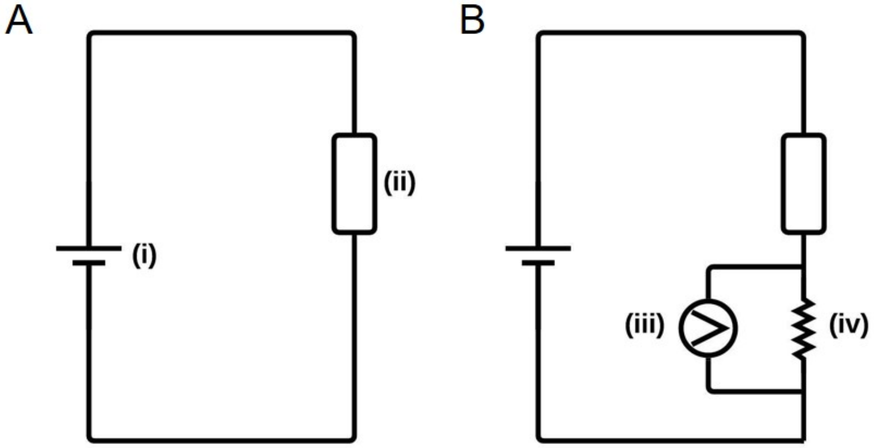

Figure 2.1: Equivalent circuit diagrams of the combinatorial cell while (A) no current measurement is occurring and (B) while current measurement is occurring. The included components are (i) quad voltage source, (ii) combinatorial cell, (iii) one of 64 channels on the multimeter and (iv) a precision resistor.

and the multimeter measuring the individual current responses for each of the 64 positive electrodes in the combinatorial cell (i.e. 64 separate, sequential measurements). The current was determined by measuring the voltage across a precision resistor as shown in Figure 2.1(B) Before it was possible to test variable positive electrode material compositions, a control was necessary to validate the accuracy and precision of the instrument. This control used an array of 100 Ω resistors, which would provide an expected current response based on Ohm's Law. Validation of the three cycling channels required connecting the resistor array in lieu of the combinatorial cell, such that each positive electrode was replaced by a 100 Ω resistor. A linear potential scan was then applied to each of the three cycling channels. Figure 2.2 illustrates the response of each cycling channel. Each channel demonstrated less than 0.5 % error, validating the instrumental set-up based upon its observance of Ohm's Law.

2.2 Development of the High-Throughput Electrochemical Cell

The high-throughput cell was adapted from a design by the Dahn group, wherein thin film alloys were electrochemically tested as anodes.[44] The objective herein was to make the cell suitable for the testing of mg-scale positive electrode materials operating as high as 5V vs. Li/Li^+. As a first attempt to evaluate the established high-throughput cell, only the current collector was adapted (as nickel current collectors oxidize strongly at 3.45 V vs. Li/Li^+). Aluminum was deposited as the new current collectors and the cell was prepared and cycled using the established methodologies in literature. LCO with 20% w/w carbon

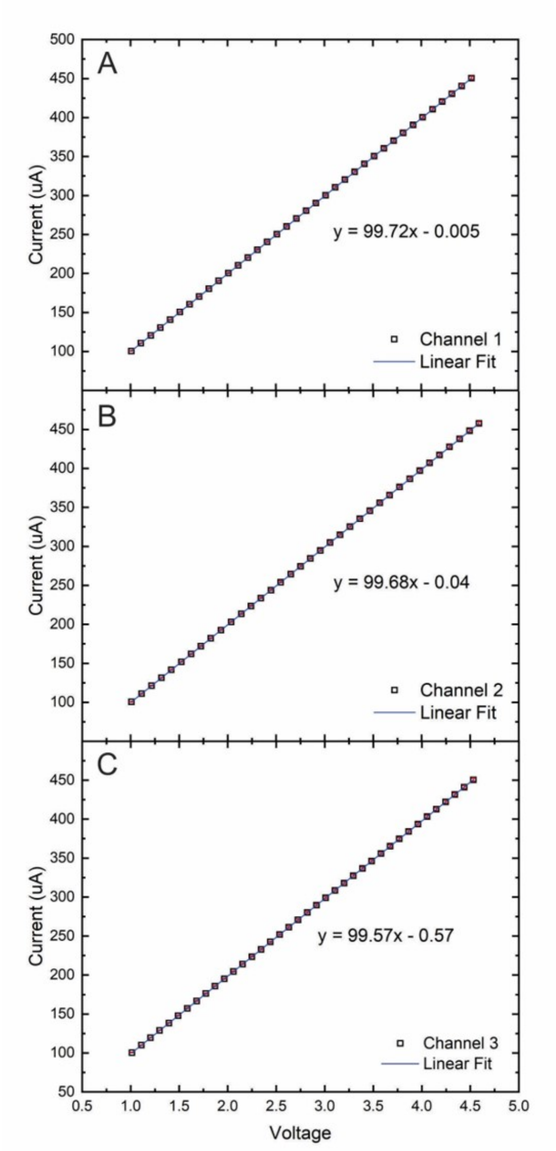

Figure 2.2: Empirical validation of three channels used for high-throughput electrochemical testing. Each of the three channels' performance was examined for observance of Ohm's Law by applying a linear potential scan to the 64 cells connected to 64 individual 100 Ω resistors (A-C). The black squares represent the average current value obtained for all 64 cells in a channel at a specific potential, and the red bars represent the range of currents observed for the 64 cells at that specific potential. The blue trace corresponds to the linear fit.

black (TIMCAL) was used as the test material. As seen in Figure 2.3 the CVs generally have the right shape for LCO (shown in Fig. 1.6 A) but many cell errors were present including: (i) irreversible oxidation, (ii) impedance causing a severe hysteresis of the redox peaks and (iii) significant variability between cells (40 % relative standard deviation (RSD) in capacity). Concerted efforts were required to carefully adapt and optimize the cell for cathode materials. The adapted cell required the extensive redesign of several elements including the current collectors, the separator material and the manner in which the cell was sealed. The final modified cell may be seen in Figure 2.4. The optimization of these components will be discussed in detail in the following sections.

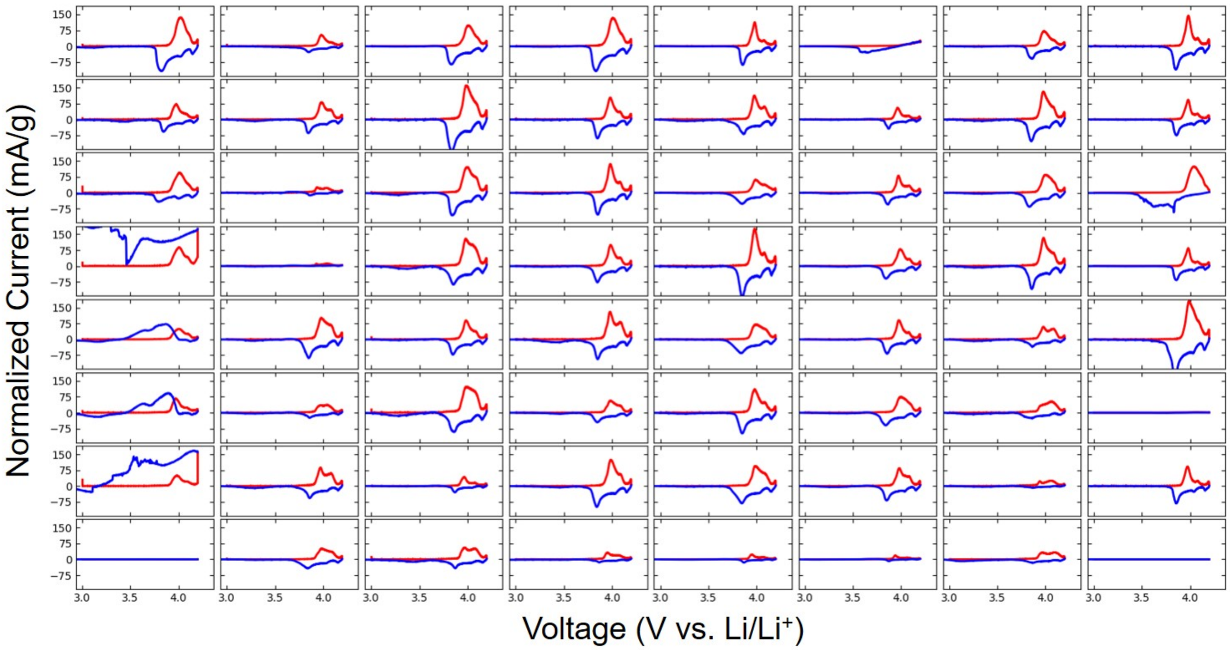

Figure 2.3: Cyclic voltammograms of LCO from a first-generation combinatorial cell, prior to complete optimization of the preparation and assembly processes.

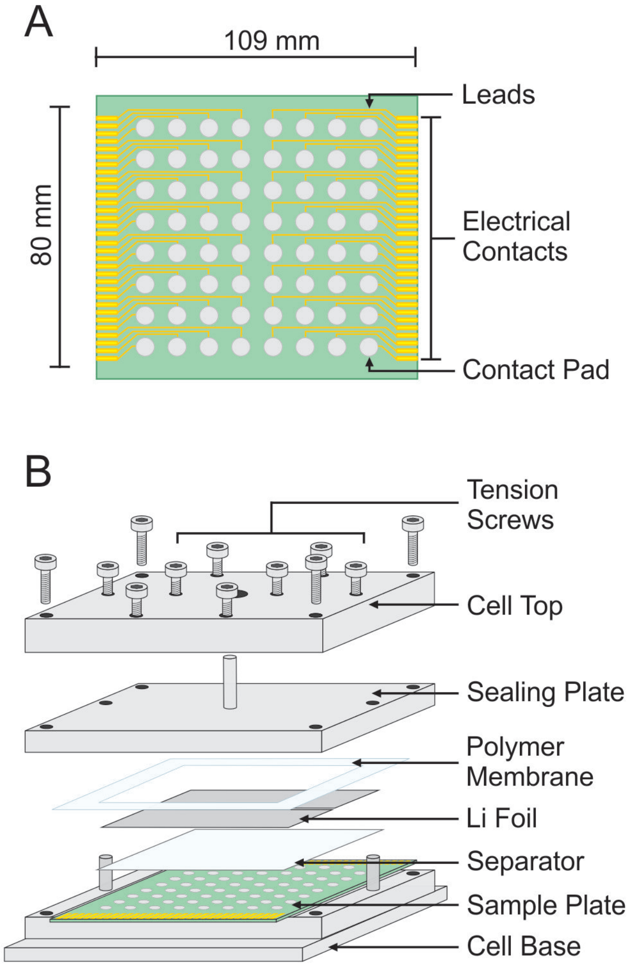

Figure 2.4: (A) Design of the printed circuit boards (PCB) (top), and cross-sectional view of the combinatorial cell (bottom). The combinatorial plate consists of 64 Al contact pads, with Au leads connecting each contact pad to a corresponding electrical lead located on the left and right sides of the PCB plate. (B) Cross-sectional view of the combinatorial cell.

2.2.1 Optimization of the Current Collector

The first modification to the cell was to the current collectors used in the combinatorial sample plate (custom PCB, OptimaTech) (as seen in Fig. 2.4 A). Upon initial validation of the system, it was apparent that nickel, the original current collector demonstrated an oxidation at 3.45 V vs. Li/Li$^+$ (Fig. 2.5 A). In order to test high voltage cathode materials, the current collector needed to exhibit ideal polarizable behaviour between 3.0 V and 5.0 V vs. Li/Li$^+$. As seen in Figure 2.5, various materials and methods of deposition were screened. In particular, we tested: electroplated gold, physical vapor deposited (PVD) aluminum and aluminum foil adhered to the printed circuit board in various manners. Electroplated gold was an appealing technique as it was efficient and inexpensive because it could be performed by the manufacturer of the combinatorial sample plates. While its performance surpassed that of nickel, significant irreversible oxidation occurred at 4.4 V vs. Li/Li$^+$, making it unsuitable (Fig. 2.5 B). Next, PVD was used to deposit 0.1 µm of aluminum onto the gold electroplated contact pads. Upon cycling the combinatorial cell, the majority of the 64 cells showed no parasitic response. However, approximately 25 % demonstrated irreversible oxidation at 4.4 V vs. Li/Li$^+$, consistent with that from gold (Fig. 2.5 C). After disassembling the cell, the appearance of small defects and scratches could be seen in the aluminum exposing gold on the contact pads of the cells that had presented irreversible oxidation. Although depositing a thick layer of aluminum that is resistant to scratching was feasible, it would have been costly and the odds of a scratch forming during cell assembly would always be significant given the large stack pressure applied to the powder samples. In an effort to protect the

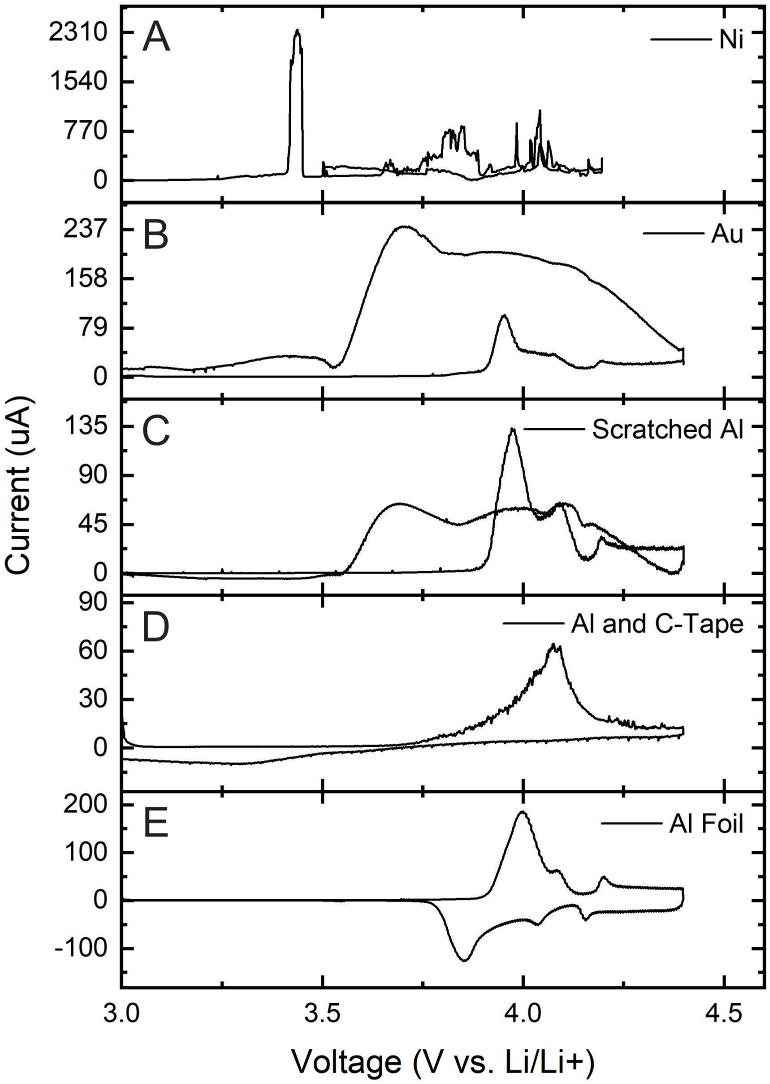

Figure 2.5: Various current collectors tested during optimization of the combinatorial cell. (A) nickel plated contact pads, (B) gold plated contact pads, (C) 0.1 µm thick PVD aluminum, with micro-defects present on surface, (D) 0.1 µm thick PVD aluminum with conductive carbon tape on top, and (E) 18 µm thick aluminum foil punch.

deposited aluminum, conductive carbon tape was placed on top of each current collector. The use of carbon tape introduced significant impedance causing a severe hysteresis of the reduction and oxidation peak potentials (Fig. 2.5 D). The final material tested was 18 µm thick aluminum foil (Fisher). Figure 2.5 E shows that the aluminum foil works well, though it should be noted that the method used to adhere the aluminum to the plate is vital given that it is this adhesion that prevents electrolyte from reaching the gold pad underneath. The adhesion method required each aluminum punch to be isolated from one another and that the adhesive was stable under conditions imposed within the battery. After many tests, it was found that ring-shaped adhesive mylar hole protectors (Avery, shown schematically in Fig. 2.6) were ideal and demonstrated stability all the way to 5.0 V vs. Li/Li$^+$, with a maximum current reaching only 12 µA (Fig. 2.7 inset). This represents a small fraction

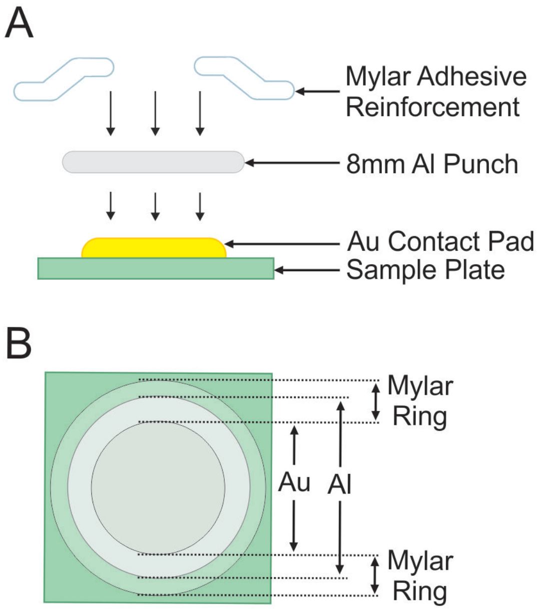

Figure 2.6: (A) Profile view and (B) top-down view of the substrate treatment methodology. The methodology was based upon optimization of the current collector.

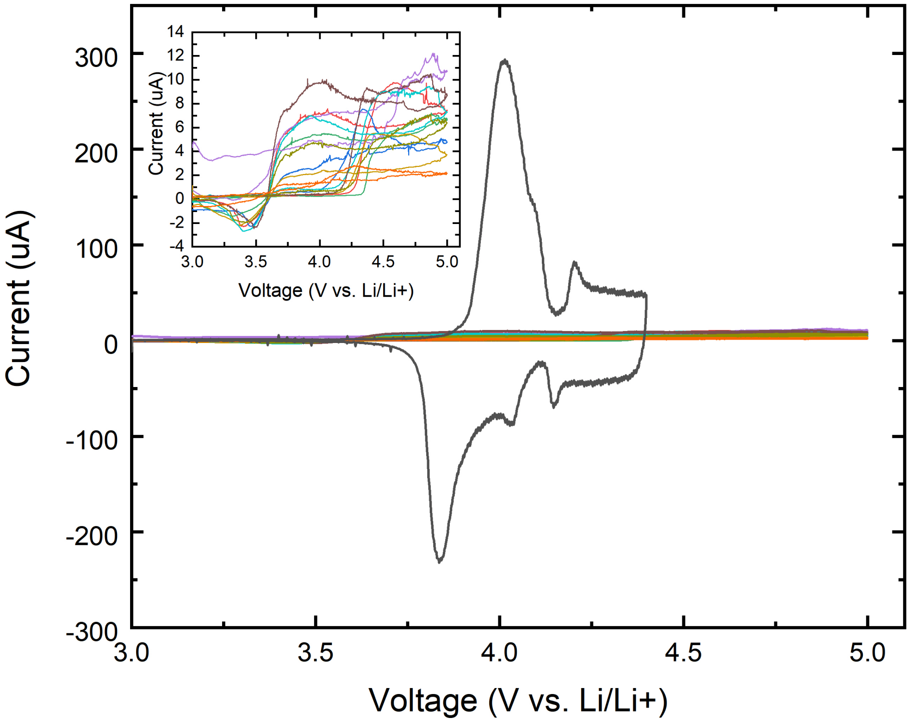

Figure 2.7: Validation of the finalized substrate treatment methodology. Typical cyclic voltammogram of LCO obtained in the combinatorial cell (black) overlaid with 10 representative cyclic voltammograms from a blank combinatorial cell (various colours). Inset: zoom in of the CVs of the blanks generated from a combinatorial cell assembled without cathode material (various colours).

of the current produced by the active materials such that this cell can be confidently used to screen positive electrode materials in a very large potential window. In fact, the small current in the blanks is likely due to electrolyte oxidation rather than components of the cell given that 5.0 V vs. Li/Li$^+$ is well outside the stability window of the electrolyte.

2.2.2 Optimization of the Separator

The combinatorial cell was initially tested using a thin polymeric separator, as previously used by the Dahn group.[44] Upon cycling, the observed cell malfunctions could be largely classified into two categories, (i) those with a severe hysteresis between reduction and oxidation peaks (Fig. 2.8 A), and (ii) those with sharp, jagged oxidation peaks upon charging

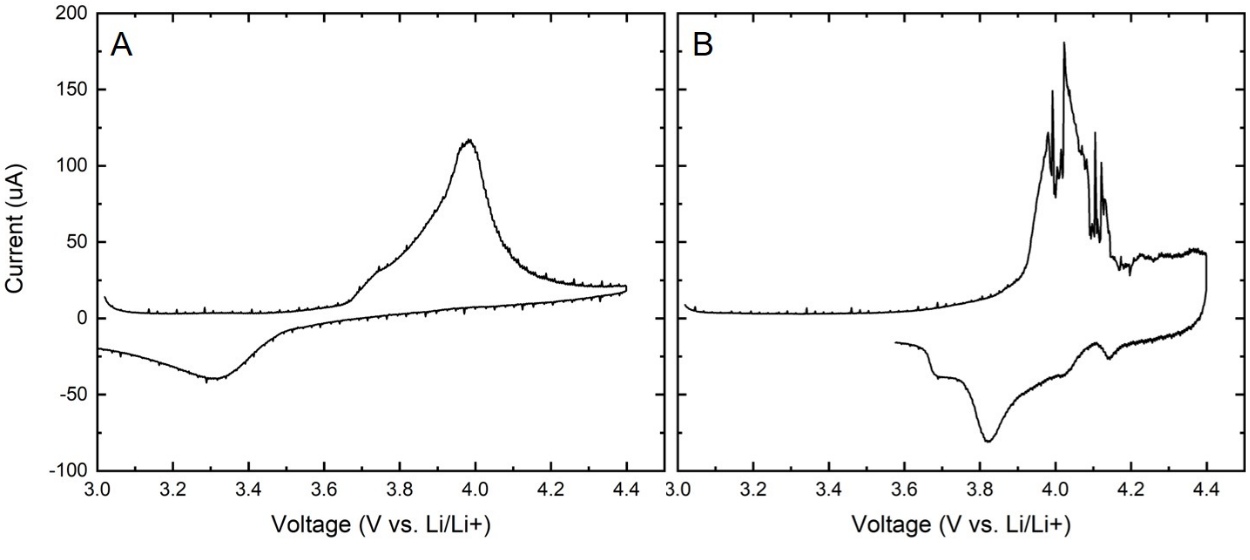

Figure 2.8: Common cell errors due to separator malfunction. (A) Significant hysteresis imposed by insufficient stack pressure, and (B) micro shorts stemming from small punctures in the separator.

(Fig. 2.8 B). Furthermore, it was noted that samples with small masses corresponded to type (i), while those with larger masses corresponded to type (ii). This observation indicated that the errors were stemming from stack pressure. In particular, smaller samples presenting a hysteresis of redox peaks was due to insufficient stack pressure while larger samples with increased stack pressure were puncturing the separator causing micro-shorts. The separator was unable to achieve consistent stack pressure over varying shaped powder samples, as the system was initially designed for uniform, thin film anodes. A thicker more impressionable separator (GF/D glass microfiber prefilters, Fisher Scientific) was substituted for the thinner polymeric separator. This provided an increased tolerance for the deviation in sample sizes, mitigating any effect caused by the non-uniformity of the samples (presenting CVs similar to that seen in Fig. 2.7).

2.2.3 Improvement of the Cell Seal

The last significant alteration required to the combinatorial cell was implementing a new seal. In the original design, the cell utilized a silicone O-ring, seated in a groove, which afforded adequate sealing when used with thin film electrodes and thin separators.[44] Upon preliminary testing here, it was evident that an O-ring was not suitable, as a proper seal was not formed when the relatively thick powder electrodes and separator were placed on the current collectors. This caused rapid electrolyte evaporation, (starting in the outer cells but rapidly reaching the center of the cells after 3 or 4 cycles) with complete cell failure typically occurring within 4 cycles (Fig. 2.9 A). The O-ring was no longer operating within its tolerance and so could not form a seal. Figure 2.9 depicts the results of extended cycling

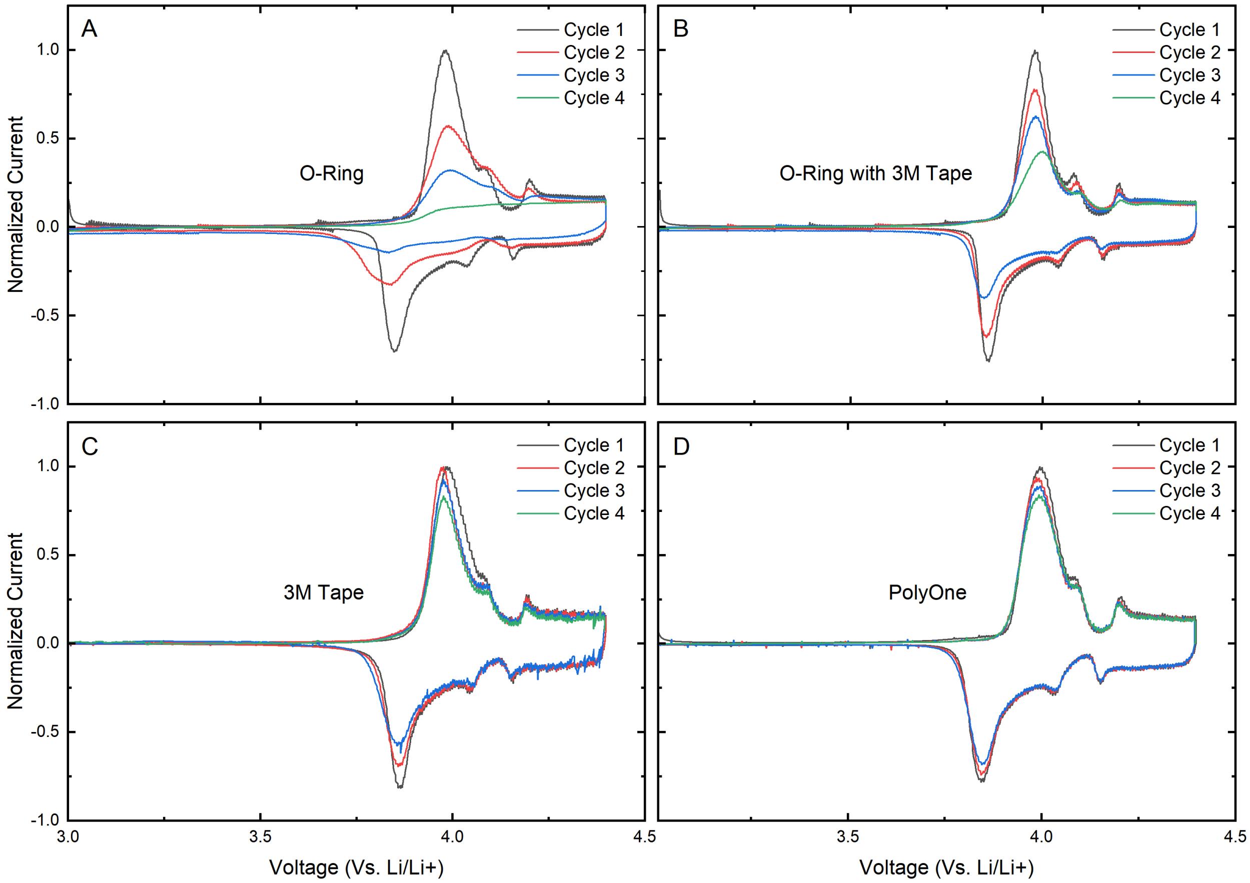

Figure 2.9: Cell sealing strategies tested during the optimization of the combinatorial cell. (A) Silicone O-ring, (B) silicone O-ring surrounded by 3M sealing tape, (C) 3M sealing tape, (D) PolyOne thermoplastic elastomer custom O-ring.

for the different cell sealing strategies that were tested. First, a thick polymeric double-sided adhesive tape (3M tape) was used to provide an additional seal on the outside of the O-ring. Despite a slight improvement with the additional seal, significant capacity fade was still observed with each cycle (Fig. 2.9 B). At this point the O-ring groove in the cell plate were removed entirely. A new sealing plate was machined in the absence of an O-ring groove to enable a wider strip of 3M tape and as seen in Figure 2.9 C, the wider seal demonstrated the capability of longer-term cycling without notable capacity fade. It should be noted that Figure 2.9 depicts the worst cycling obtained for the 64 cells tested, which always occurred at an outer cell position on the plate. In addition, the capacity retention was consistent with that found in literature.[46] While the 3M sealing tape provided an adequate seal, it permanently sealed the cell, which prevented necessary post-mortem analysis without compromising the integrity of the cell. A potential candidate was found as a replacement, Versaflex^{TM} CL40 (PolyOne), a thermoplastic elastomer with mechanical properties that closely mimicked that of the 3M sealing tape. The Versaflex^{TM} CL40 was molded into a thick, flat, rectangular sealing membrane, and was used during cycling of the combinatorial cell. The new cell further improved capacity retention on discharge (Fig. 2.9 D) and enabled facile post-mortem cell analysis.

2.3 Development of Electrode Preparation

With the combinatorial cell successfully adapted for high voltage cathode materials, it was important to reevaluate its performance to now optimize the process in which the electrodes were prepared and the cell assembled. The challenge was extremely high as 64 electrodes must be prepared in close proximity to each other in a timely manner to justify the use of high-throughput methods. The first approach was to weigh 64 loose cathode materials into a custom well plate, in which the well spacing was consistent with the contact pads on the combinatorial sample plate. The well plate was then aligned with the sample plate and flipped such that the loose powders would fall onto their respective contact pads. Upon cycling, the cell was found to have a RSD on charge capacity of approximately 22 %. While this was an improvement from the 40 % RSD achieved prior to cell adaptation (Fig. 2.3), it was significantly larger than the 5 % typically attained when performing triplicate measurements in coin cells, as is common in battery research. This high RSD would greatly reduce the usefulness of combinatorial screening. It was thought that the variability could be due to inaccuracies of the weight of the active material as the CVs of LCO were consistent with literature and no apparent cell errors were present. Furthermore, any small deviation from the true weight of the cathode material would significantly impact the specific capacity because the samples only weigh approximately 2 mg. In an effort to improve the cell to cell variability, several other electrode preparation techniques were attempted (Table 2.1). Despite the varying approaches, the RSD was consistently above 20 %, with only 5 % attributed to the uncertainty on the mass. This indicated that something was likely occurring during the cell assembly that was electrochemically unidentifiable. An initial concern for the combinatorial cell, which utilizes 64 loose powder electrodes weighing 2 mg each in close proximity, was cross-contamination. Loose powders can easily shift and the shifting of samples would result in inaccurate weights of active material thereby contributing to an increased RSD. In

Table 2.1: Troubleshooting sequence to improve the RSD of charge capacity in the combinatorial cell.

Method of Preparation	Description of Method	RSD (%)
Well Plate Transfer	Samples weighed into a well plate and then transferred onto the combinatorial sample plate by aligning and flipping.	22.1
Higher Accuracy Scale	Samples weighed on a higher sensitivity analytical balance to increase accuracy and precision. Samples were then transferred using the same methods as in the Well Plate method of preparation.	19.8
Guide Plate Transfer	Samples weighed directly onto the contact pads of the combinatorial plate using a guide plate (plate with 64 holes consistent with the sample plate) to prevent sample loss. The guide plate was then lifted off leaving the powders on their respective contact pads.	22.6
Improved Adhesion	Samples were prepared as in the Guide Plate method, however before lifting off the guide plate, 20 μL of electrolyte was added to each sample to improve adhesion and promote complete transference of sample.	23.9
Dropcasted with Binder	Samples were weighed directly onto the contact pads of the combinatorial plate and 10 μL of binder (PVDF in NMP) was added to each to adhere it to its respective contact pad.	7.5

order to elucidate what was occurring during the assembly, a second test material, NMC, was introduced. The rationale being that LCO and NMC each demonstrate starkly different electrochemical profiles that are well characterized. LCO has a sharp oxidation peak at 3.98 V vs. Li/Li$^+$, whereas NMC has a broad oxidation peak at 3.85 V vs. Li/Li$^+$. The degree of cross-contamination present could be readily identified through cycling the combinatorial cell with LCO and NMC placed adjacently. The presence of cross contamination would result in an electrochemical response containing the summation of the two characteristic oxidation peaks. Figure 2.10 shows a combinatorial cell cycled with the two test materials, LCO and NMC, arranged in a checkerboard pattern. Cross contamination could be seen in approximately 17 % of the CVs. An example of a contaminated sample may be seen in Figure 2.11 and clearly illustrates the summation of the two test materials' electrochemical signal to form the contaminated signal, as seen in the combinatorial cell. Considering the convoluted signal was only present in a small percentage of the CVs, it further supported the idea that loose powders were shifting during the cell assembly. In an effort to mitigate

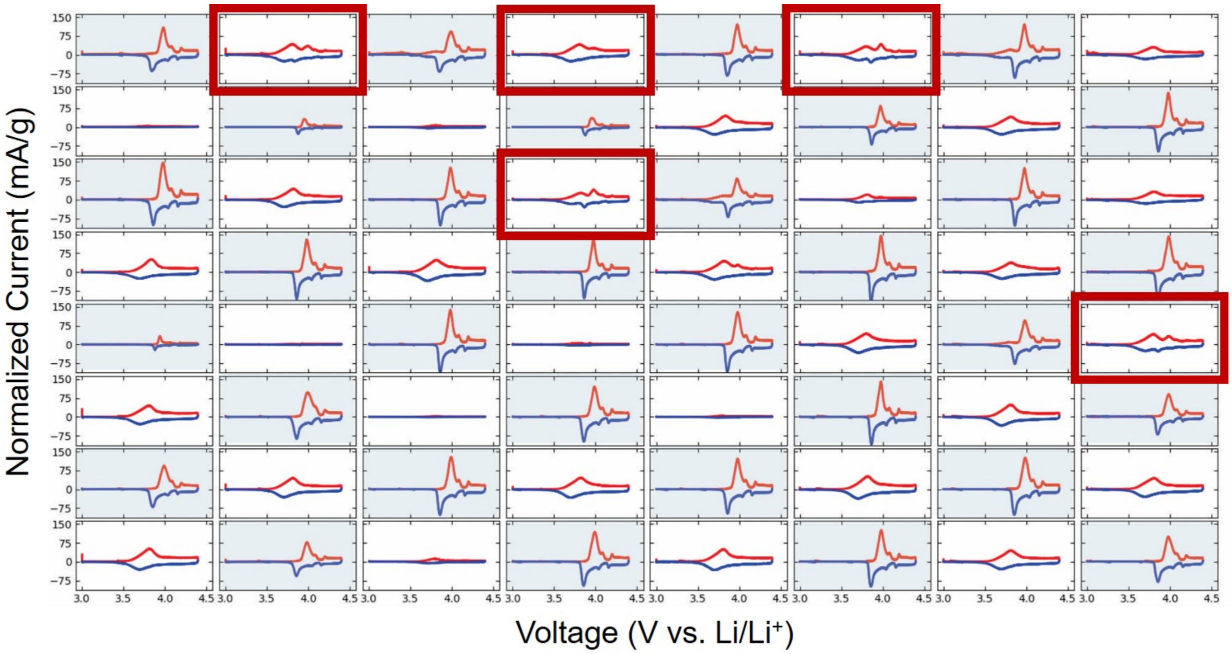

Figure 2.10: Cyclic voltammograms of LCO and NMC arranged in a checkerboard pattern in the combinatorial cell demonstrating significant cross-contamination. Red boxes highlight samples with significant contamination. The shaded regions indicate LCO compositions, while the rest are NMC.

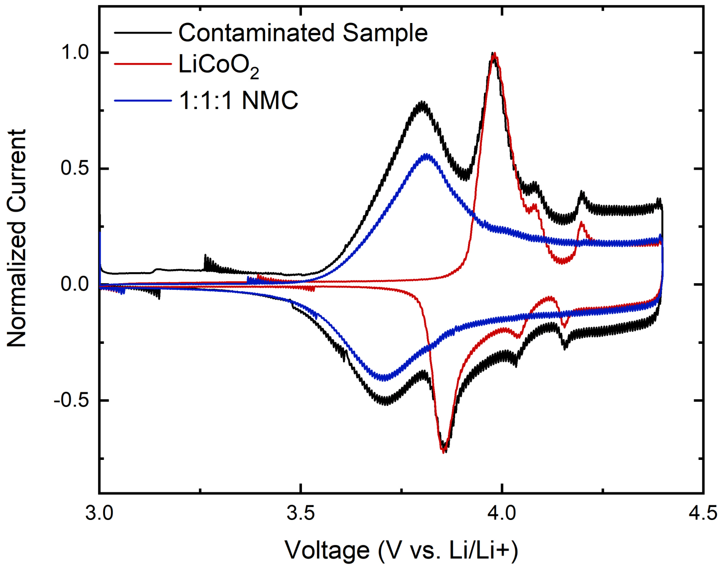

Figure 2.11: Cyclic voltammograms of an LCO sample contaminated with NMC (black), along with pure LCO (red trace) and NMC (blue trace). The contamination resulted from mixing of neighboring powders in the checkerboard.

shifting powder, binder (20 % w/w polyvinylidene fluoride (PVDF) (Kynar 1100, Kureha America Inc.) dissolved in N-Methyl-2-Pyrrolidone (NMP)(Alfa Aesar)) was drop cast onto each powder sample. Upon drying, the binder strongly adhered the loose powder to its specific current collector, preventing powder from shifting during cell assembly. Figure 2.12 shows a combinatorial cell with the two test materials, LCO and NMC, dropcast with binder, in a checkerboard pattern. No sign of cross contamination was observed for any of the 64 samples, despite being in close proximity to the opposite material.

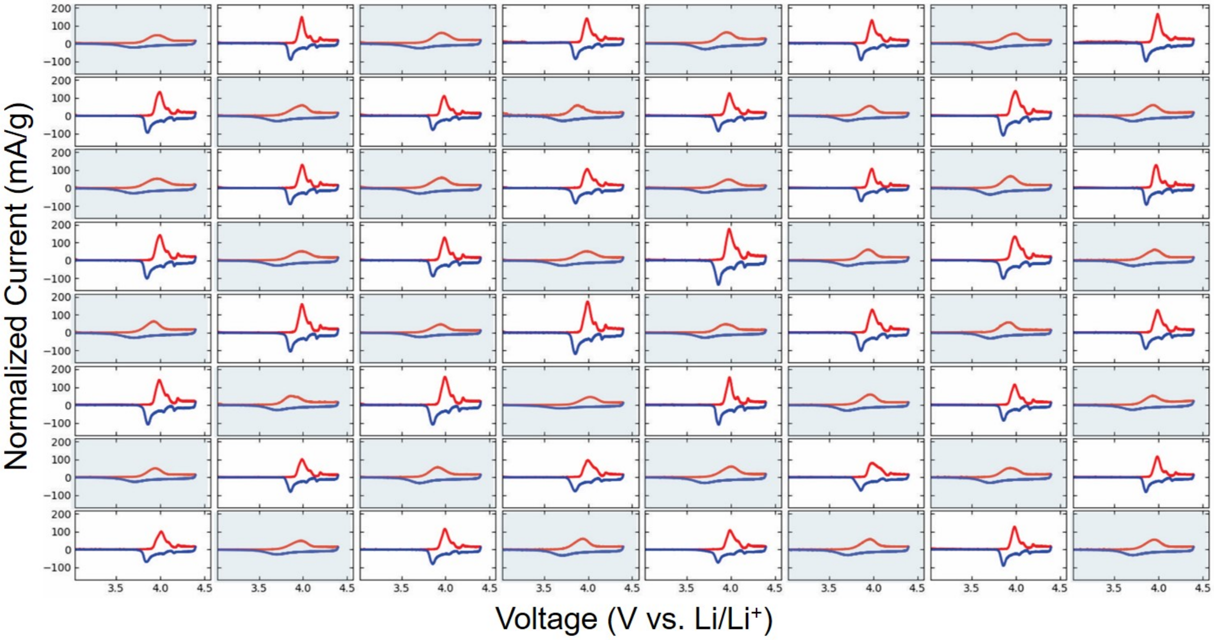

Figure 2.12: Cyclic voltammograms of LCO and NMC arranged in a checkerboard pattern in the combinatorial cell. The shaded regions indicate NMC compositions, while the rest are LCO.

2.4 Final Preparation and Assembly of the Combinatorial Cell

Through the successful adaptation and optimization of the combinatorial cell, a finalized methodology was developed. First, alterations to the combinatorial plate were made by covering the 64 gold contact pads with 8 mm diameter circular punches of aluminum foil. The punches were secured to the combinatorial plate by using mylar hole reinforcements. The ring-shaped reinforcement had an inner and outer diameter of 6 mm and 9 mm, respectively. They were first adhered to the aluminum punch, and then the combinatorial plates. At this point, the cathode materials of interest were weighed and then approximately 20 % w/w of carbon black was added to each of the 64 samples. The carbon black was mixed thoroughly into each of the cathode materials manually. Each cathode sample was transferred to a contact pad and a solution of approximately 20 % w/w PVDF in NMP was added to each. All required materials for the cell were dried overnight at 60 °C before introduction to an argon-filled glovebox. In the glovebox, a small amount of electrolyte, $LiPF_6$ in 1:1 EC:DMC (SoulBrain MI), was added to each sample to further secure each sample to their contact pad. An 80 mm by 70 mm separator was placed onto the samples, and a 4.5 mL aliquot of electrolyte was evenly dispersed onto the separator. A second separator was placed onto the first, followed by another 4.5 mL aliquot of electrolyte. Rolled lithium foil (Alfa Aesar) was placed on top of the separators, ensuring it did not exceed the size of the separators. A thermoplastic elastomer sealing ring was then placed around the separators and lithium foil.

The steel sealing plate and aluminum cell top were placed on top of the combinatorial plate, respectively. The sealed cell was secured by tightening the four corner screws. Even stack pressure was applied to the cell by tightening the eight tension screws in a star pattern. The assembled cell was checked for signs of shorting prior to beginning electrochemical measurements. This methodology represents the final iteration of cell design in this thesis, and is used for all combinatorial cells moving forward.

2.5 Electrochemical Evaluation of the Final Combinatorial Cell Performance

The CVs obtained in Figure 2.12 are in good qualitative agreement with data obtained from bulk samples using coin cells in the literature.[47,48] Additionally, we can evaluate the precision and reproducibility in a quantitative manner. Table 2.2 shows battery properties extracted from Figure 2.12 for each of the test materials (32 samples of each) along with those obtained from literature under similar cycling conditions.[49–52] The average specific capacities

Table 2.2: Summary of the electrochemical parameters for 32 samples of both LCO and NMC obtained using the combinatorial cell, compared to results for bulk samples from the literature. RSD is the relative standard deviation of the combinatorial capacities.

Material	**Discharge Capacity (mAhg^{-1})**		**RSD (%)**	**Average Voltage (V)**	
	Experimental	Literature		Experimental	Literature
LCO	163.5	155-165	7.57	3.96	3.9
NMC	151.0	155-160	7.80	3.78	3.8

were within 2.6 % of that obtained for bulk samples, while the average voltages were within 1.5 %. This demonstrates a remarkable level of accuracy in the combinatorial measurements. Furthermore, the relative standard deviations for average voltage are negligible, while those for specific capacities are both near 7.5 % showing good reproducibility amongst the 2 mg samples. Given that the uncertainty on the weighing of such small samples is approximately 5 %, these low standard deviations are commendable and considered to be optimal. Figure 2.13 and Table 2.3 further demonstrate the CVs agreement with those reported in the literature.[47,48] The slight hysteresis of redox peaks present in the combinatorial data (Fig. 2.13) in comparison to literature is attributed to reduced conductivity in the electrodes given the limited mixing with carbon black that our procedure allows.[53] Despite this, the deviation in peak positions is typically limited to 20 mV compared to literature on charge and less than 5 mV on discharge.

Table 2.3: Comparison of the oxidation and reduction peaks for experimental and literature LCO and NMC.

Material	**Oxidation (V)**		**Reduction (V)**	
	Experimental	Literature	Experimental	Literature
LCO	4.04 (1)	4.01	4.14 (1)	4.14
	4.11 (2)	4.09	4.01 (2)	4.04
	4.22 (1)	4.19	3.81 (1)	3.86
NMC	3.87 (1)	3.89	3.69 (1)	3.69

As a final confirmation that the high-throughput methods used here are consistent with what is seen in the literature for multiple cycles, Figure 2.14 shows the long-term cycling

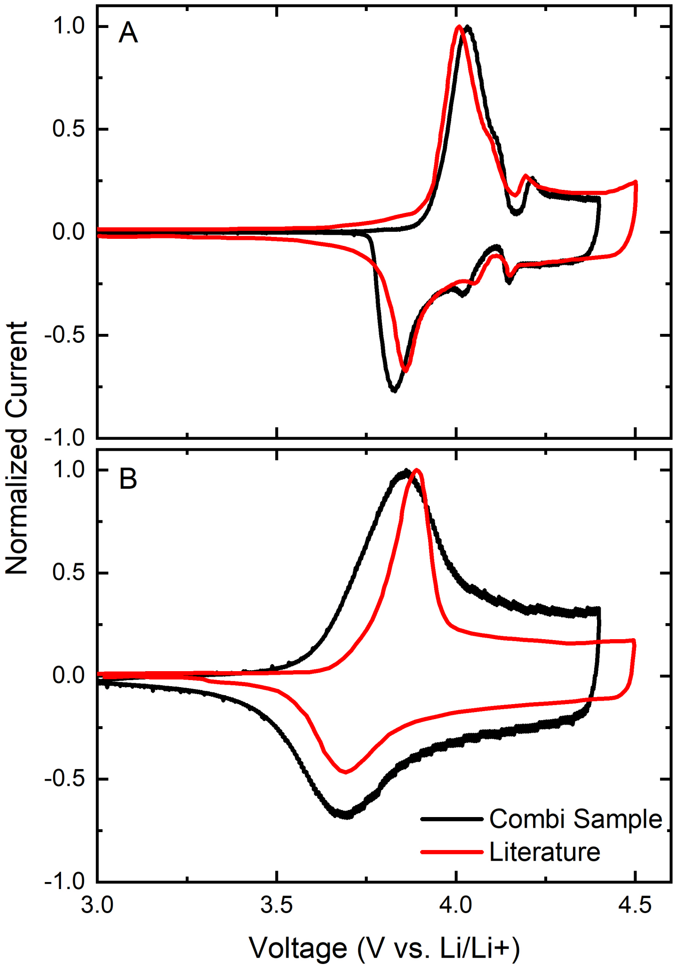

Figure 2.13: Comparison of combinatorial cyclic voltammograms obtained for test materials (black) with those from the literature (red) obtained for bulk samples.

of LCO and NMC and their corresponding trends in average voltage and capacity. Eight cycles were performed in the combinatorial cell, corresponding to approximately one and a half weeks' time. The peak potentials obtained obtained for LCO and NMC are consistent with literature for all eight cycles.[46–48,52] In particular, it may be seen that the anodic peak of the first cycle of NMC, centered around 3.92 V vs Li/Li^+, shifts to 3.85 V vs. Li/Li^+ for the remainder of cycling. This is consistent with literature and may be attributed to

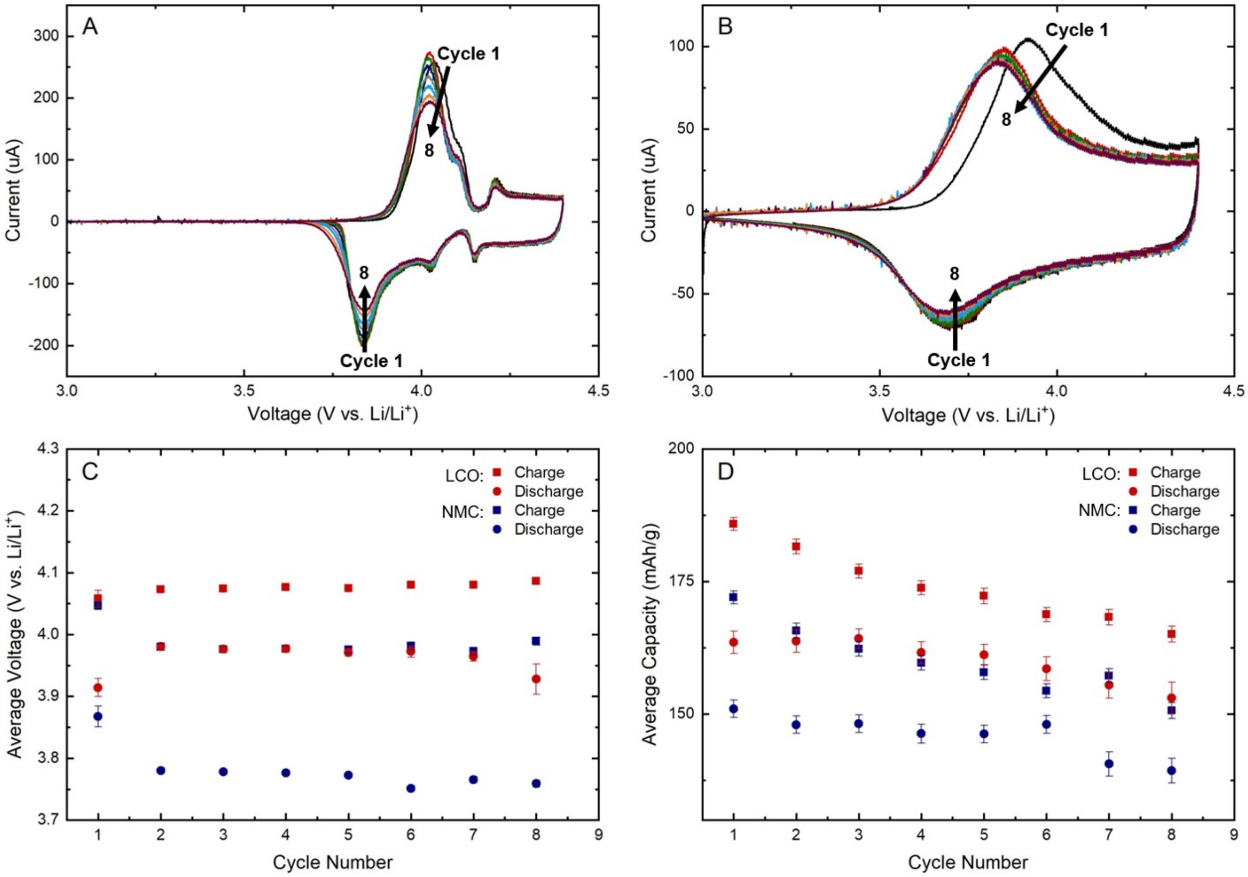

Figure 2.14: Representative cyclic voltammograms of (A) LCO and (B) NMC extracted from a combinatorial cell. Experimental values obtained from 32 samples of LCO and 32 samples of NMC (C) average voltage and (D) specific capacity. Red and blue represent LCO and NMC, and the squares and circles represent each material's charge and discharge, respectively. Error bars represent standard error.

the breaking in of the electrode, as a decrease in the hysteresis of the redox peaks indicates improved reversibility of the electrode.[50]

The combinatorial cell's demonstrated low RSD and agreement with bulk methods after a series of modifications, allow us to confidently use this system to screen systematically across compositions. Furthermore the agreement between the electrochemistry of LCO and NMC in the mg-scale combinatorial cell and traditional cells with bulk materials validates the scalability of the technique and relevance to industrial large scale applications.

Chapter 3

Electrochemical Mapping of the Li-Mn-Ni-O Pseudo-Ternary System

3.1 Ternary System Approach

Using the adapted combinatorial cell from Chapter 2, it is now possible to investigate compositions across complex phase spaces. The first system selected to explore was the Li-Mn-Ni-O pseudo-ternary system as the complete structural phase diagrams under various synthetic conditions were mapped in 2013.[31] This would enable us to correlate the electrochemical behavior across the system to the structural phase diagram for the first time, thereby developing meaningful structure-property relationships.

Three 8 by 8 plates were used to map the ternary system. As seen in Figure 3.1 A, 120 compositions were evenly distributed across the system and categorized into one of three regions. Each region corresponded to one corner of the triangle (i.e. Li, Mn, or Ni) and would contain 64 compositions such that it utilized a complete combinatorial cell. The three regions also created a triplicate region within the system. The triplicate region (ACB, Fig. 3.1 B) contained 36 compositions and would serve as verification for reproducibility between the three combinatorial cells.

While the synthetic, cell preparation and cell assembly methodologies remained consistent with those introduced in Chapter 2, the electrochemical cycling protocol was modified to enable activation of all materials in the Li-Mn-Ni-O system. The protocol followed was:

1. Charged to 4.4 V at 0.1 Vh^{-1}
2. Discharged to 3.0 V at 0.1 Vh^{-1}
3. Charged to 4.6 V at 0.1 Vh^{-1} and from there up to 4.8 V at 0.02 Vh^{-1}

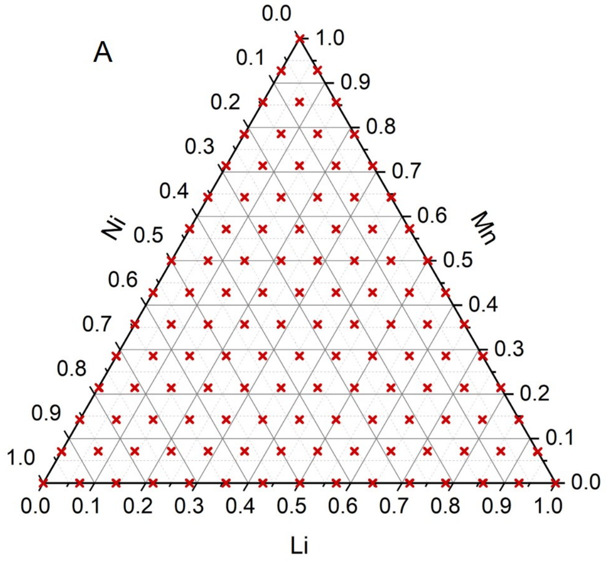

Figure 3.1: (A) All synthesized compositions and (B) the approach used to divide the Li-Mn-Ni-O system into three regions: the Ni-corner (Ni-A-C-B), the Li-corner (Li-B-A-C), and the Mn-corner (Mn-C-B-A). The overlapping portion of these three regions create a triangular triplicate region (ACB).

4. Discharged to 3.0 V at 0.1 Vh^{-1}

Steps 1 and 2 serve to characterize the performance of the cathodes as traditional layered oxides, which show activity below 4.4 V, while steps 3 and 4 serve to activate the Li-rich layered oxides (i.e. the so-called high voltage plateau related to oxygen redox) which demonstrates significant activation of oxygen and Mn above 4.5 V. This one cycling protocol can therefore efficiently screen both the stoichiometric layered oxides ($LiMO_2$) and the Li-rich oxides ($Li_{1+x}M_{1-x}O_2$) present in the Li-Mn-Ni-O pseudo-ternary system.

3.2 Electrochemistry of the Li-Mn-Ni-O Pseudo-Ternary System

Performing cyclic voltammetry across the entire Li-Mn-Ni-O system enabled the tracking of various electrochemical trends. As the electrochemistry evolved over each region, qualitative trends were easily identified, even prior to extracting quantitative performance metrics (e.g. capacity, average voltage, energy, etc.). In this section, the raw electrochemistry of each region (Li-corner, Mn-corner, and Ni-corner) will be presented and the observed trends are explored.

3.2.1 Li-Corner

The Li-corner includes compositions within the highlighted region of Figure 3.2 A. This region contains the Li-rich oxides ($Li_{1+x}M_{1-x}O_2$), which are of significant interest for next-generation cathode materials. Figure 3.2 B presents the raw cyclic voltammograms for each cycle (upper voltage thresholds of 4.4 V and 4.8 V vs. Li/Li^+) and highlights the various electrochemical trends observed. As it may be seen, the Li-corner of the triangle can be divided into three distinct areas: regions with (i) no electrochemical activity (green), (ii) electrochemical activity during both cycle one and two (purple) and (iii) electrochemical activity primarily during cycle two (yellow). The large region of electrochemical inactivity (green) can be correlated to materials with high Li content. Upon the heating of these materials during synthesis, lithium loss is experienced. In compositions excessively rich with

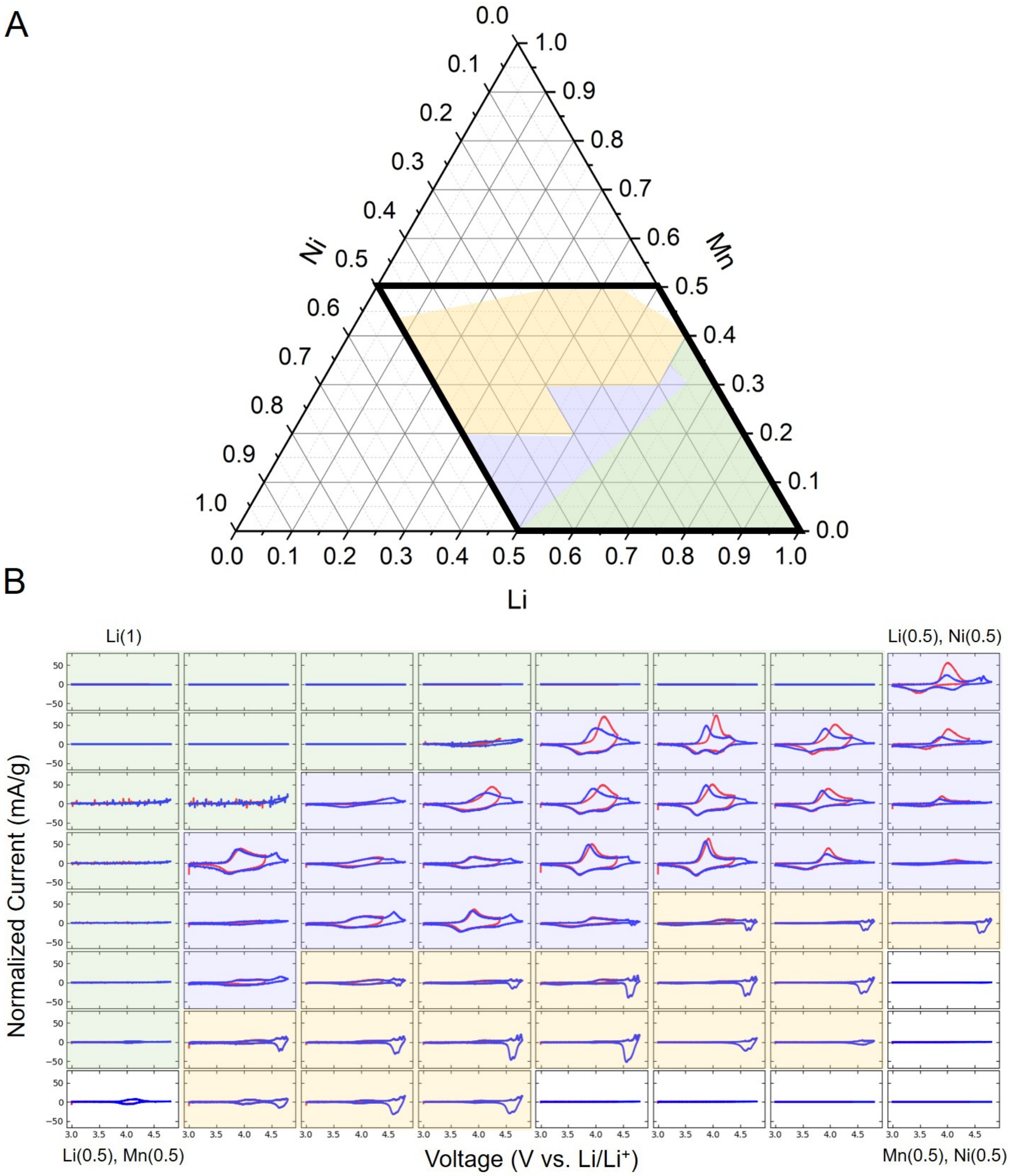

Figure 3.2: (A) Li corner of the Li-Mn-Ni-O pseudo-ternary system and (B) raw cyclic voltammograms for cycle one (red) and two (blue). The observed electrochemical trends are highlighted in different colors to ease interpretation.

Li, the lithium loss becomes so significant such that very little material is retrieved after synthesis.[30] Electrochemical activity is first detected during cycle one in compositions with moderate Mn and Ni content (purple region). This is expected, as Mn and Ni typically contribute to lattice stability and energy density, respectively.[21,54] The cyclic voltammograms in this area present rather broad peaks upon oxidation and reduction and are representative of layered oxide structures. During cycle two, an increase in electrochemical activity may be seen in compositions with moderate Mn and Ni content (purple region), likely due to the reversible reduction and oxidation of oxygen and the reduction of Mn within the cathode materials. The yellow region also demonstrates new electrochemical activity in cycle two. These compositions correspond to those with high-voltage spinel phases present (i.e. compositions with Ni content). The oxidation and reduction peaks in this region are narrow and and often present doublet peaks. This is representative of high-voltage spinel structured materials, which have active Ni redox potentials at high potentials (e.g. $LiNi_{0.5}Mn_{1.5}O_4$, discussed in Fig. 1.5 D). It is important to note, that while there is an apparent decrease in current in cycle two from 4.6 V to 4.8 V vs. Li/Li_+ , this is an artifact of the significant decrease in the scan rate, as current and scan rate are proportional (this will be discussed further in Sec. 3.2.5).

3.2.2 Mn-Corner

The Mn-corner includes the compositions that are highlighted in Figure 3.3 A. Figure 3.3 B shows the CVs for cycle one and two (upper voltage thresholds of 4.4 V and 4.8 V vs. Li/Li^+, respectively). Several electrochemical trends may be seen in this combinatorial cell including

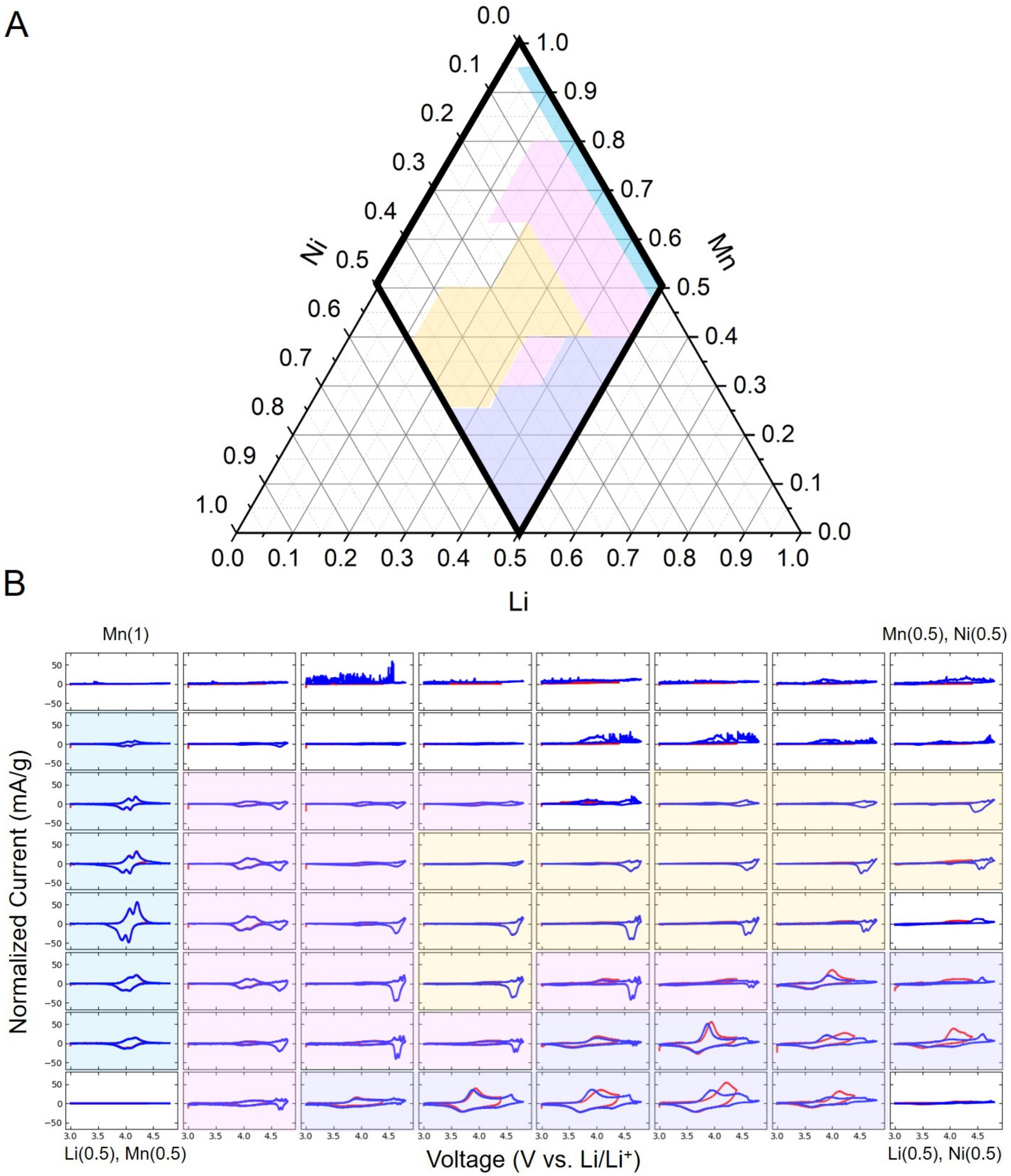

Figure 3.3: (A) Mn-corner of the Li-Mn-Ni-O pseudo-ternary system and (B) raw cyclic voltammograms for cycle one (red) and two (blue). The observed electrochemical trends are highlighted in different colors to signify the common electrochemical features.

compositions that demonstrate electrochemical activity during the first cycle (blue, pink and purple regions), and those that demonstrate electrochemical activity only during the second cycle (yellow). Consistent with the Li-corner, there appears to be a large region (purple) of layered oxide materials activated during cycle one. In addition, a region of low voltage spinel structured materials (blue) show activity during cycle one and is attributed to Mn redox.[14] These materials have high Mn and moderate Li content, and are activated at lower voltages due to the absence of Ni in the material.[15] Increased electrochemical activity was observed in the layered oxide structures (purple) during cycle two, however no appreciable increase in electrochemical activity could be identified for the low-voltage spinel materials (blue). A region (yellow) of high-voltage spinel materials (compositions with moderate Li, Ni, and Mn) were activated during cycle two, consistent with that seen in the Li-corner cell. Interestingly, there were compositions that demonstrated redox peaks for both Mn and Ni in the spinel structures or both the layered oxide and high-voltage spinel structures (pink). The first cycle activated the Mn in the spinel and the layered oxide structure, while the second cycle activated the Ni in spinel and the oxygen/Mn in the Li-rich layered structures. Further analysis of their electrochemical properties will help to quantify the structural contribution for each electrochemical process.

3.2.3 Ni-Corner

The compositions and corresponding CVs for cycle one and two (upper voltage thresholds of 4.4 V and 4.8 V vs. Li/Li^+) for the Ni-rich region may be seen in Figure 3.4. Again consistent with the Li and Mn corners, three main trends are identified in the Ni-rich compositions:

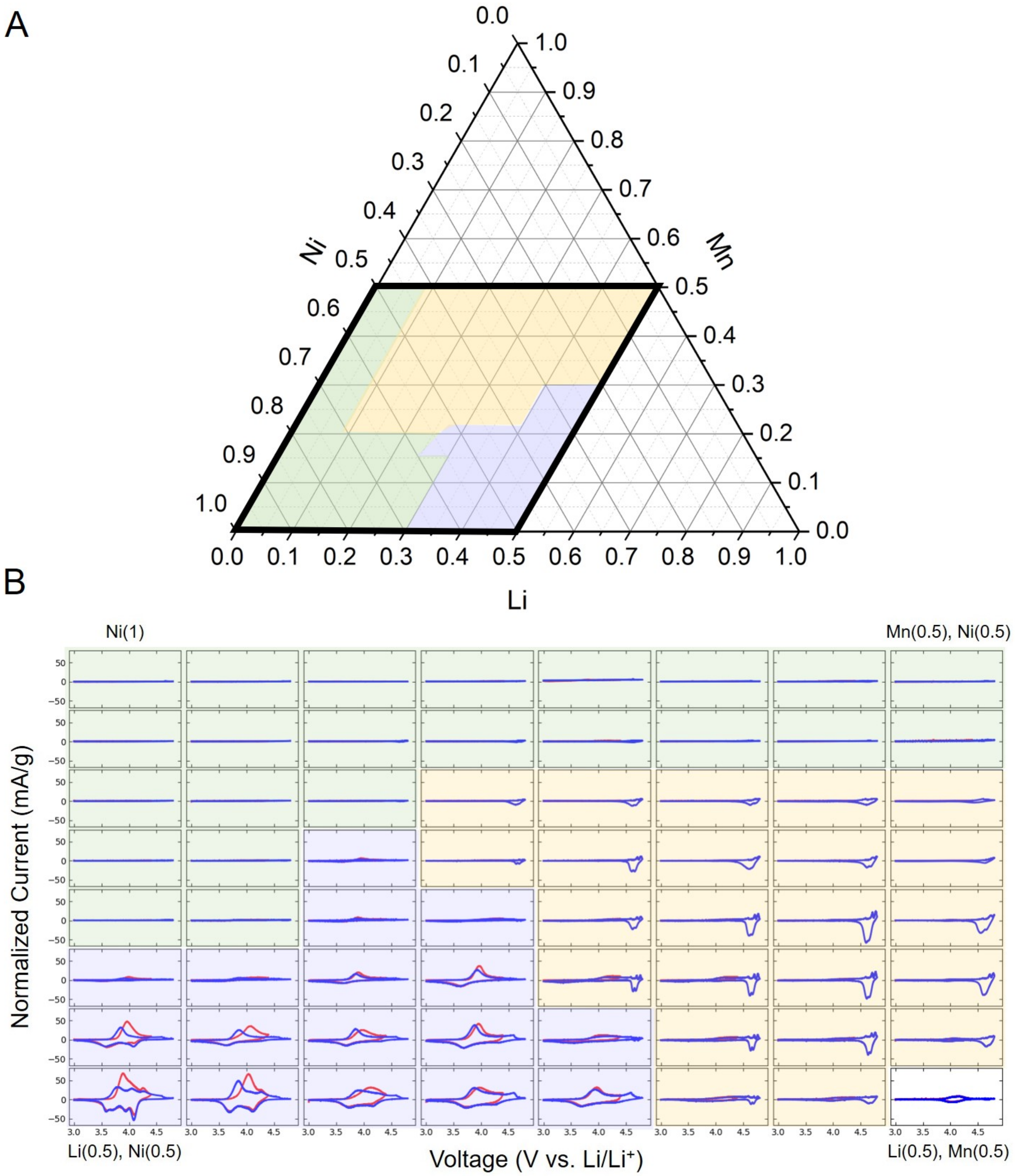

Figure 3.4: (A) Ni corner of the Li-Mn-Ni-O pseudo-ternary system and (B) raw cyclic voltammograms for cycle one (red) and two (blue). The observed electrochemical trends are highlighted in different colors to aid in interpretation.

those with (i) no electrochemical activity during either cycle (green), (ii) electrochemical activity during cycle one and two (purple) and (iii) electrochemical activity only during cycle two (yellow). In cycle one, very few compositions are electrochemically active. The large region of inactivity is due to the nature of Ni-rich materials with low Li content forming cubic rocksalt structures (green). These materials have minimal ordering within the lattice which significantly hinders or completely blocks the diffusion of lithium.[33] The evolution of electrochemical activity may be seen as Li is added. The addition of Li to cathode materials results in increased ordering within the lattice, and begins the structural transformation from the electrochemically inert cubic rocksalt to the electrochemically active layered structure (also called ordered rocksalt). Only compositions in the vicinity of $LiNiO_2$ demonstrate redox activity during cycle one (purple). In addition, the observed cyclic voltammogram of $LiNiO_2$, a highly studied cathode material, demonstrates excellent agreement with literature.[55] During cycle two, the layered oxide materials again show increased electrochemical activity. Additionally, another region of the cell becomes electrochemically active (yellow) during cycle two. These compositions present high-voltage redox peaks (i.e. > 4.5 V vs. Li/Li^+), again consistent with that of high-voltage spinel materials.

3.2.4 Reproducibility in the Triplicate Region of the System

As discussed in the above sections, several reoccurring trends were seen in each region (Li-corner, Ni-corner, Mn-corner) of the ternary system. This is in part due to many compositions (36 per plate of 64) appearing in triplicate (triangle ACB in 3.1 B). It is always important to confirm agreement of the electrochemistry for the 36 compositions in this triplicate region. Since many of these materials have not been electrochemically investigated, consistency between the compositions in the triplicate region would serve to confirm the reproducibility of the high-throughput methods developed in Chapter 2 (each region underwent separate synthesis, electrode preparation, cell assembly and cycling). Figure 3.5 illustrates both the typical agreement of triplicate compositions and an example of a rare outlier (C). The overall agreement for triplicates is excellent, as illustrated in Figure 3.5 A

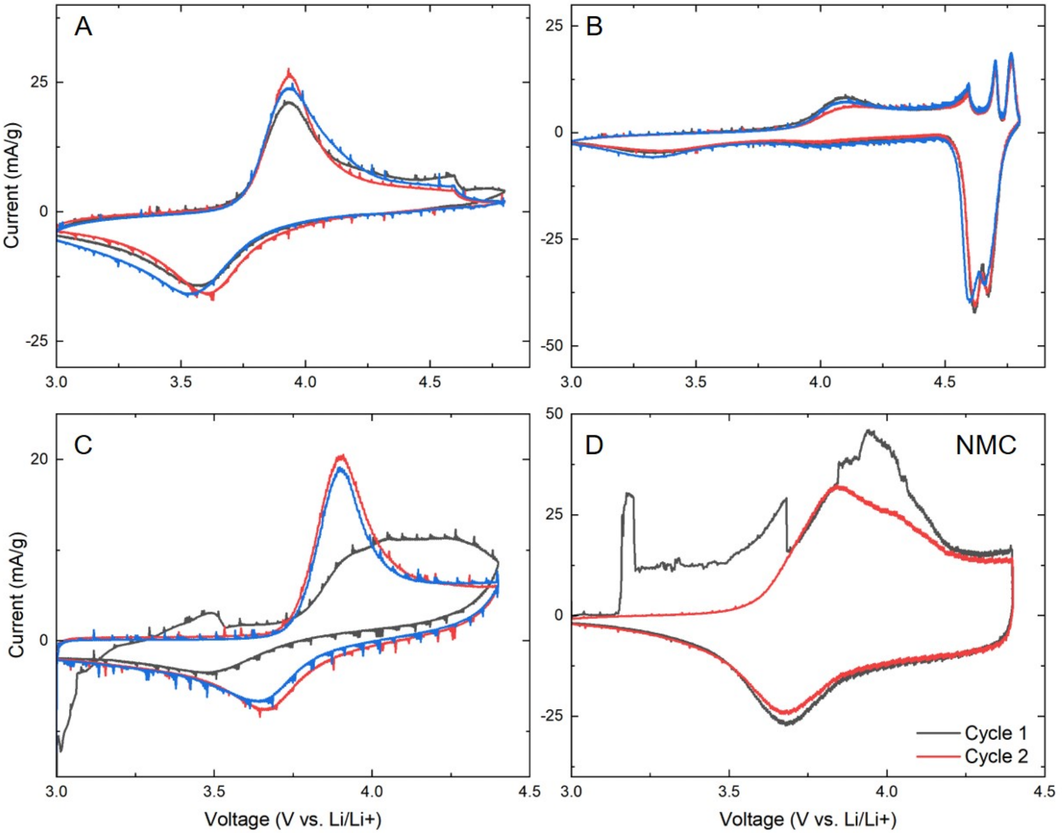

Figure 3.5: Identification of outliers within the triplicate region of the Li-Mn-Ni-O ternary system. (A/B) Examples of reproducibility of compositions in the overlap region cycled in three different cells. (C) Rare example of an outlier (black) in the triplicate overlap region. Red, black, and blue each represent data from a different cell. (D) Example of an instrumental error NMC outlier, likely caused by a micro-short (i.e. instrumental error).

and B. In such cases, the values of the electrochemical parameters (i.e. capacity, average voltage, etc.) extracted from the data are averaged across all three triplicates. Infrequently, an outlier was observed in the triplicate measurement (e.g. Fig. 3.5 C). In all cases, the outlier was easily identified compared to the other two replicates and was omitted from further analysis. Of the 108 samples in the triplicate region, only 6 samples were omitted as outliers. An example of an instrumental error is illustrated in Figure 3.5 D. In rare cases, an experimental error could be seen during cycle one, in which jagged, noisy oxidation peaks are indicative of a micro-short. Surprisingly, the error completely resolved itself and continued cycling as normal for subsequent cycles. Despite this replicate having entire cycles with no errors present, these compositions were also omitted from further data analysis ($<$ 1 % of the examined compositions) in case the first cycle negatively impacted later cycling.

3.2.5 Data Treatment Methodology

While galvanostatic (i.e. constant current) techniques are typically used in battery research, the high-throughput system uses potentiostatic techniques (i.e. constant potential) due to the cell placing all 64 batteries in parallel. Although the same electrochemical information can be extracted from both techniques, it is useful to visualize the data both in I vs. V graphs (typical for CV) and in V vs. Q (typical way to represent galvanostatic cycling). This is particularly important given the complex cycling protocol described in Section 3.1. The change in sweep rates distorts the shape of the cyclic voltammogram because of the relationship of current and scan rate. In regions in which a slower scan rate is employed to permit sufficient time for intercalation processes to occur, redox peaks will appear very small. This activity becomes evident when we express the data in a voltage capacity plot. Figure 3.6 illustrates the obtained voltage capacity curves for the Li-corner of the ternary system. For example, the highlighted curve in Figure 3.6 shows a clear high voltage plateau whereas the CV in Figure 3.2 showed no peak at 4.6 V vs. Li/Li$^+$ due to the slow scan rate used.

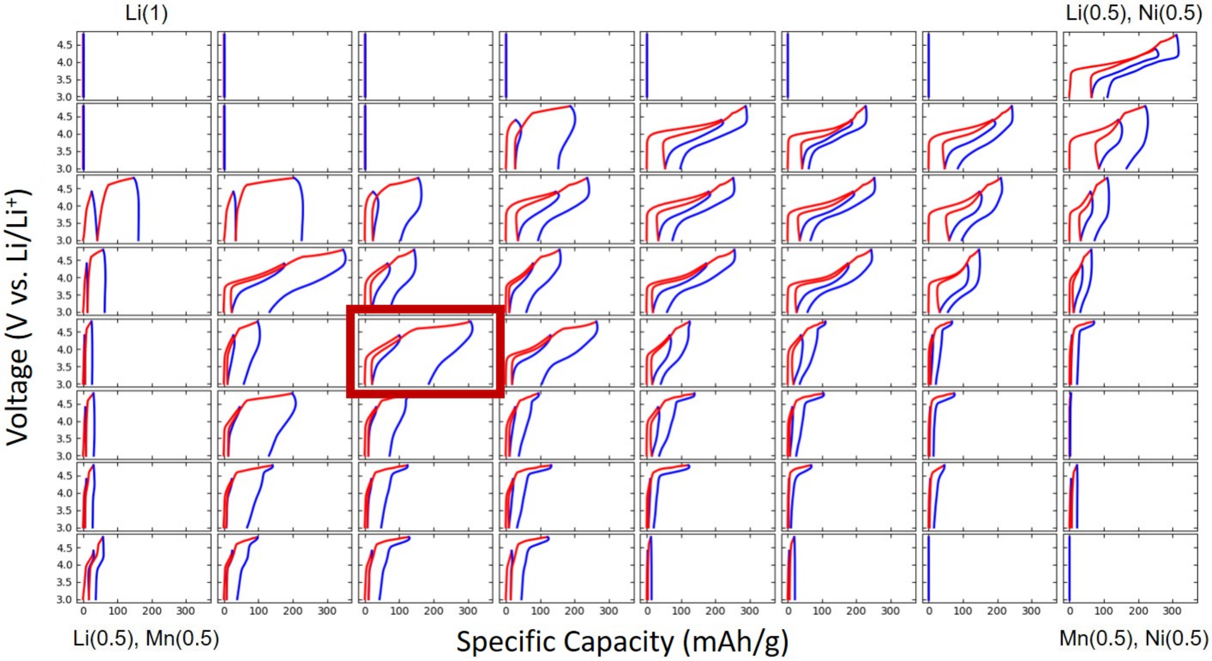

Figure 3.6: Voltage-capacity curves for cycle one and two of the Li-B-A-C region (Fig.3.1(B)) of the Li-Mn-Ni-O pseudo-ternary system. Red represents charge while blue represents discharge. The orange box highlights a composition that presents a large high-voltage plateau, common for Li-rich oxides as illustrated in Chapter 1 (Fig. 1.8 A)

In addition to remaining consistent with field norms, important metrics for battery performance (i.e. specific capacity and irreversible capacity) can be evaluated directly from the V vs. Q plots.

The shear quantity of data demanded a methodology to extract and visualize the key battery metrics in such a way that trends could be easily identified across the entire ternary system. The developed treatment methodology had three phases: (i) identification of outliers in raw data, (ii) determination of various electrochemical performance metrics, and (iii) the visual correlation of these metrics to composition (i.e. plotting metrics across the ternary system). First, outliers were visually identified and omitted as discussed in Section 3.2.4 for each combinatorial cell that was cycled.

For every sample, capacity and average voltage was calculated for each cycle. The extracted data from each combinatorial cell was then compiled such that values for triplicate compositions could be averaged. At this point, each composition had only one value for each performance metric and could be plotted in the ternary system. Figure 3.7 summarizes the plotting process used to make the ternary contour maps. As seen in (A), the calculated electrochemical performance metric can be plotted as individual data points. At this point, the composition of materials synthesized below the Li-rich layered single-phase boundary (grey line between $LiNiO_2$ and Li_2MnO_3) were corrected. During synthesis, significant lithium loss occurs during heating, resulting in all compositions prepared below this line lying on the boundary line after heating, as detailed in literature.[30] All compositions synthesized in this region were therefore translated to lie on the $LiNiO_2$-Li_2MnO_3 composition line. A contour map was then prepared based on the raw data points (Fig. 3.7 B). Minimal smoothing was applied to the plot prior to overlaying it with the structural phase diagram for the system (Fig. 3.7 C).

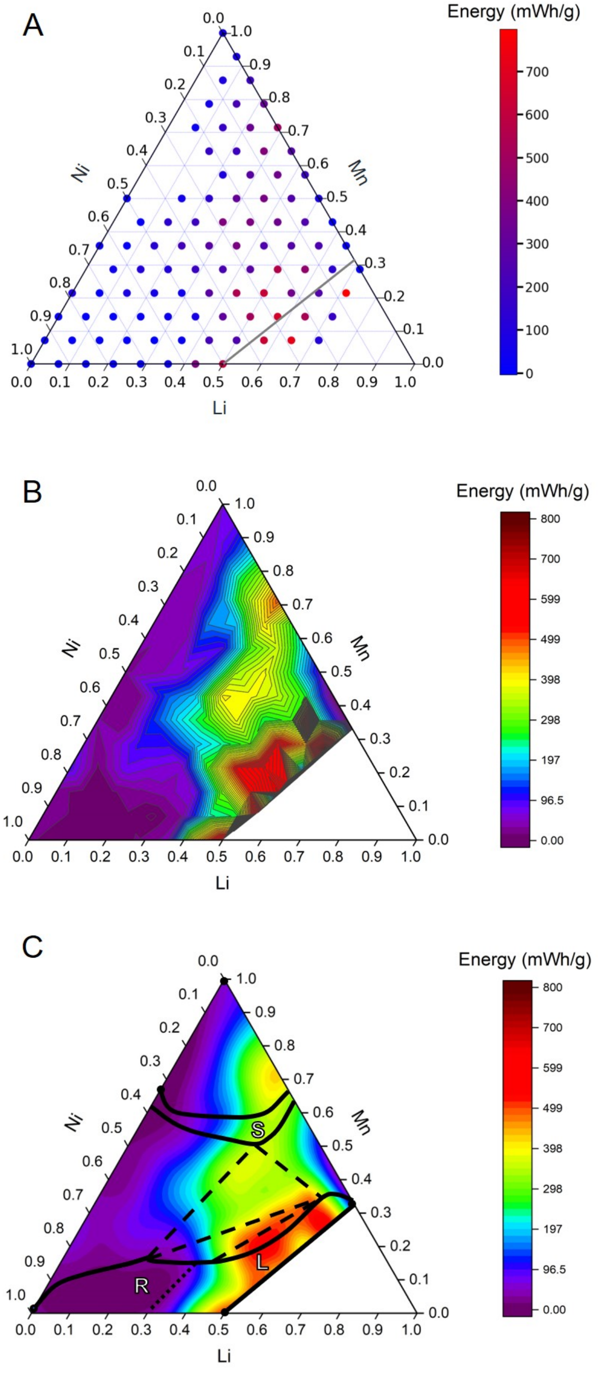

Figure 3.7: Data treatment methodology used to plot the energy density across the ternary diagram. (A) Electrochemical performance metrics calculated and plotted as individual data points, Li loss during synthesis was accounted for. (B) Contour map of performance metric built from raw data points. (C) Minimal smoothing applied to contour map shown with the structural phase diagram. Solid lines are boundaries to single-phase regions, while dashed lines are tie-lines at the boundaries of triple-phase regions.

3.3 Exploration of Various Performance Metrics in the Li-Mn-Ni-O Pseudo-ternary System

Figure 3.8 shows both the energy density during discharge from 4.8 V - 3.0 V vs. Li/Li^+ and the structural phase diagram reported for the same synthesis conditions.[31] Key electrochemical curves (both cyclic voltammograms and the corresponding voltage capacity plots) are also shown in Figure 3.8 to visually demonstrate the progression of the battery performance as compositions vary. In this figure, several structure-property trends between electrode composition and electrochemical performance become evident. The regions of highest interest are: (i) the single-phase spinel region (S), (ii) the single-phase layered region (L), and (iii) the co-existence regions lying between the L and S materials. As some structure-property relations cannot be seen in the energy plots alone, Figure 3.9 illustrates various other electrochemical performance metrics including specific capacity, average voltage, and voltage fade.

3.3.1 Single-Phase Spinel Region

Ni-containing spinel materials are of interest for cathodes as they typically have a higher average voltage than the layered structures.[16] However, the commercialization of Ni-containing spinel cathode materials is limited by electrolyte development, as their operating voltage is outside the electrochemical stability window of current electrolytes. Figures 3.8 and 3.9 show results for two main types of spinel structures: (i) low voltage Mn spinel on the Li-Mn edge

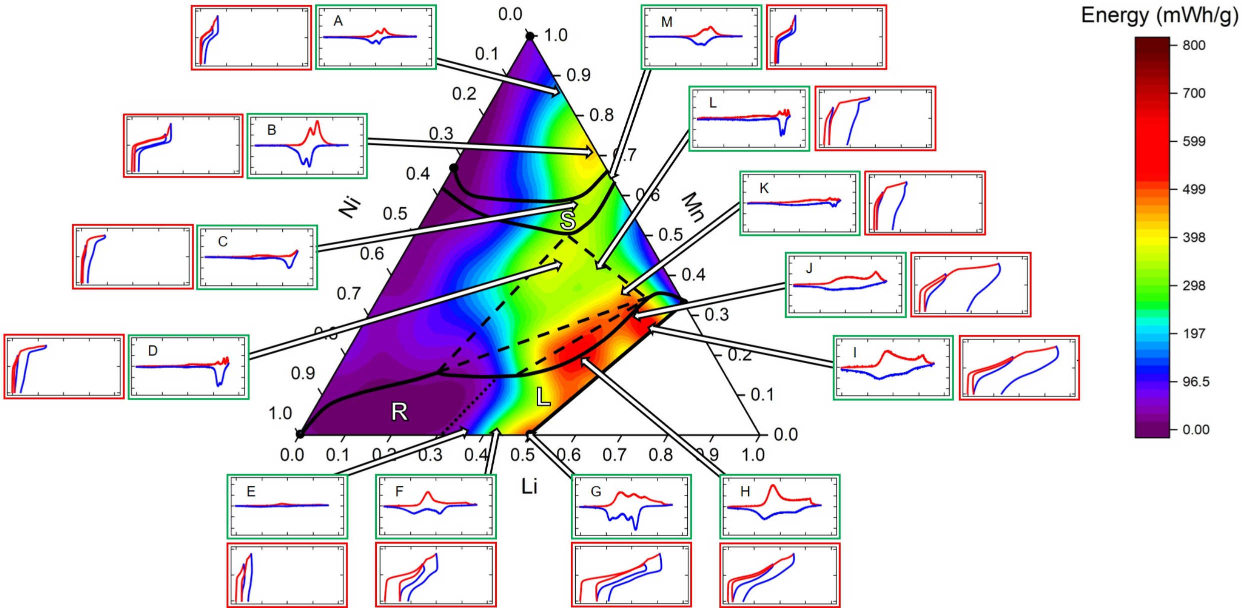

Figure 3.8: Li-Mn-Ni-O structural phase diagram along with the specific energies obtained during discharge from 4.8 V to 3.0 V vs. Li/Li$^+$. Solid black lines are boundaries to single-phase regions, dashed black lines are tie-lines at the boundaries of triple-phase regions, and the dotted black line is the phase transition from rocksalt to the layered structure. S, L, and R are spinel, layered, and rocksalt, respectively. The red boxed insets show voltage vs. capacity curves with all x-axes being from 0 to 400 mAh/g and all y-axes having the range 3.0 - 5.0 V vs. Li/Li$^+$. Similarly, all green boxed insets show cyclic voltammograms with y-axes from -60 to 60 mA/g and x-axes in the range 3.0 to 5.0 V vs. Li/Li$^+$.

of the diagram, and (ii) high voltage spinel material which contain nickel. These can be easily distinguished in Figure 3.9 (A-B), where the low voltage spinel demonstrate capacities over 100 mAhg^{-1} up to 4.4 V vs. Li/Li^{+}, while the high voltage spinel only show significant capacity when cycled to 4.8 V vs. Li/Li^{+}. It is important to note that the CVs here do not show the entire doublet typical of high voltage spinel, such that cycling to a higher potential would be required to thoroughly screen these materials. This explains why moderate capacities of approximately 80-90 mAhg^{-1} are seen in the high-voltage spinel compositions in Figure 3.9 B.

Figure 3.8 illustrates that even with the limited capacity, the energy density of the high voltage spinel is comparable to that obtained for the low voltage spinel. In addition, voltage fade (3.9 D) holds little meaning for the high-voltage spinel given that the cycling window selected does not completely activate the spinels (i.e. cycling to 5.0 V vs. Li/Li^{+} is required to complete the nickel oxidation)[16], such that progression of this partial redox process is difficult to interpret. Despite this, the progression of electrochemistry in the spinel region is consistent with the phase diagram.

Furthermore, in Figure 3.8, the highest energy spinel on the Li-Mn line lies within the 2-phase region ($Li_{0.7}Mn_{0.3}$). This can be attributed to the relatively low number of samples made in this region, as this composition was closest to the phase boundary of those synthesized. Should detailed progression of electrochemical properties in the spinel region be desired, a more comprehensive study can now be performed.

3.3.2 Single-Phase Layered Region

Despite layered oxide cathode materials being amongst the most promising candidates for next-generation batteries, there is still little understanding of how the electrochemistry evolves across this phase space. Upon considering the layered region in Figure 3.8, a rapid increase in electrochemical activity can be seen as the compositions move into the ordered rocksalt region from the cubic rocksalt region. While this increase in activity is understood in the literature, what is not so thoroughly understood is the progression of properties within the rest of the layered region. Studies in literature typically emphasize the materials lying on a single line between $LiNi_{0.5}Mn_{0.5}O_2$ and Li_2MnO_3,[56] however, as seen in the phase diagram single phase materials lie within a fairly large 2D region of the phase diagram (labeled L). As such, developing important structure-property trends in this region is of high-importance and is one of the primary goals of this study.

Several key trends can be observed in the layered (L) region of Figures 3.8 and 3.9. Figure 3.9 A and B illustrates the discharge capacities from 4.4 V and 4.8 V vs. Li/Li^+, respectively. When discharging from 4.4 V vs. Li/Li^+ (Fig. 3.9 A), only moderate capacities of 110 $mAhg^{-1}$ are observed. This activity is primarily seen in compositions with higher Ni content (Fig. 3.8 H). Upon increasing the upper voltage limit to 4.8 V vs. Li/Li^{-1}, both compositions with higher Ni and Mn content demonstrate capacities near 200 $mAhg^{-1}$. This increase of capacity is signified by the presence of the high-voltage plateau at 4.6 V vs. Li/Li^+ in compositions H-J (Fig. 3.8). This plateau is indicative of oxygen release and activation within the cathode material and is characteristic of Li-rich compositions. Additionally, the

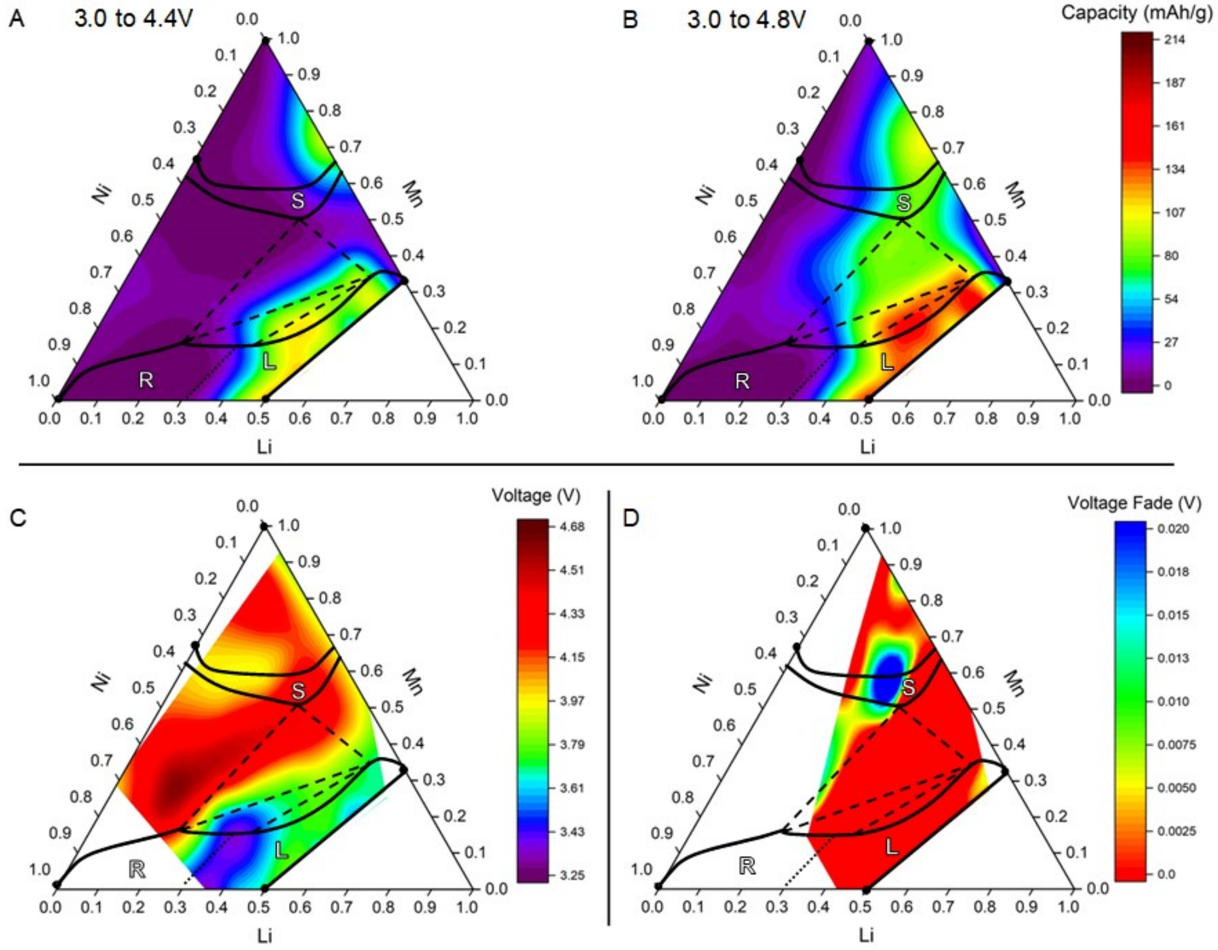

Figure 3.9: Li-Mn-Ni-O ternary map of various electrochemical performance metrics on discharge. (A) Specific capacity for cycling performed between 3.0 and 4.4 V vs. Li/Li$^+$. (B) Specific capacity and (C) average voltage for cycling performed between 3.0 V and 4.8 V vs. Li/Li$^+$. (D) Change in average discharge voltage, i.e. average voltage fade, between cycles 3 and 4 (3.0 V - 4.6 V vs. Li/Li$^+$ range), with a positive value indicating a decrease in average voltage in the later cycle.

irreversible capacity seen in the Li-rich oxides varies dramatically with composition (Fig. 3.8 H-J). As irreversible capacity is an important performance metric related to the high-voltage plateau, the capability to track the growth of this plateau enables the elucidation of compositions in which oxygen release and activation becomes detrimental to cycling and outweighs the benefits of increased energy. Figure 3.9 C and D map the average voltage and voltage fade, respectively, across the ternary system. Interestingly, the average voltage demonstrates very small variations with composition within the layered region. This suggests that the variance of specific energy throughout the layered region is solely a consequence of the specific capacity. It can also be noted that the observed voltage fade in the layered region is more significant in compositions with increased Mn (Fig. 3.9 D). The systems ability to correctly track voltage fade is supported by literature, as composition I (Fig. 3.8) presents a voltage fade of 5 mV/cycle, comparable to that of 2.1 ± 1.7 mV/cycle reported for a similar composition.[57] Voltage fade and high irreversible capacity are the two key properties currently limiting the commercialization of Li-rich oxides. As such, by enabling the rapid evaluation and optimization of these properties, this methodology is extremely beneficial for the screening of Li-rich oxide materials.

In terms of identifying the best cathode materials, Figure 3.8 shows that I, J, and H all show high energy densities of about 700 mWhg^{-1}, however H shows the lowest irreversible capacity. These results clearly suggest that the further exploration of the region around compositions H is warranted. It should be noted that under galvanostatic conditions the high voltage plateau (plateau at 4.6 V vs. Li/Li^{+}) can require up to 50 h to fully activate,[56] such that the 10 h used here may not fully activate the materials. It is therefore expected that a thorough study of this region under various cycling conditions will be essential to find the optimum Li-rich oxide.

3.3.3 Co-existence Regions

Composite layered-spinel cathodes have been proposed as potential next-generation cathodes,[58,59] though there remains no clear understanding of how the the battery properties of the composites compare to the weighted average of the two component phases. In particular, for a composite to outperform both end-member materials there must be a synergistic effect resulting in a property not simply being a linear combination of the two end-members' properties. This can be readily evaluated in Figures 3.8 and 3.9 for several key metrics. As seen in Figures 3.9 (compositions D,J,K,L and A-C in Fig. 3.8), both capacity and average voltage do progress monotonically along the tie-lines, implying no synergistic effect is present. These trends also apply to materials in the 3-phase regions (D,L,K) , though one must recognize that under the synthesis conditions used, much of the 3-phase regions in fact contain 4-phases, as equilibrium states are not reached at intermediate cooling rates.[31] Although composites do not seem to invoke benefits in regard to energy density, further studies could be performed to see whether there is benefit to long-term cycling.

Chapter 4

Conclusions and Future Work

4.1 Conclusions

The desire to create higher performing battery materials has driven research into complex phase spaces using pseudo-ternary and quaternary systems. Due to the complexity, our understanding of these systems is limited. This is due to the fact that only a small number of compositions have been synthesized and characterized electrochemically. Stemming from this vacancy, there is a need for higher throughput in the electrochemical studies of Li-ion batteries to rapidly identify optimum compositions. This thesis marks the first step in enabling the efficient screening of high-voltage powder cathode materials to be used in future generations of batteries.

An electrochemical combinatorial cell, used previously to investigate thin-film anode materials, was successfully adapted for use with high-energy powder cathode materials. This required a re-design of a number of components in the 64-cell assembly, as well as the development of a method to prepare 64 electrodes on a single sample plate. Evaluation of the combinatorial cell's performance presented excellent agreement of both the redox peak potentials and the capacity of combinatorial samples with values from literature. The system demonstrated a cell-to-cell reproducibility of $< 7\%$. Considering the uncertainty on the mass of the samples is 5 %, this fully optimized system is capable of screening battery materials electrochemically with a high level of accuracy and precision. Furthermore, the simplicity of the instrumentation and the cell enables facile implementation for other research labs that desire to perform high-throughput screening methodologies.

The developed system was then applied to the entire Li-Mn-Ni-O pseudo-ternary system.

Various electrochemical metrics for 120 compositions, distributed across the Li-Mn-Ni-O system, were correlated with the structural phase diagram reported in 2013. With this frame of reference, the evolution of key electrochemical properties could be seen across the complex phase space, elucidating several structure-property relationships. This study marked the first high-throughput electrochemical screening of powder cathode materials. While this model system demonstrated the immense potential of the methodology, it exceeded expectations providing quantitative values for key electrochemical properties including energy density, irreversible capacity, discharge capacity and voltage fade. As this system is of extreme interest for next-generation Li-ion cathodes, the results obtained herein are of immediate interest to both industry and academia.

The significance of the research performed in this thesis transcends beyond merely the advances made in rapidly screening high-voltage cathode materials, but provides a foothold for developing meaningful structure-property relations that are essential to the rational design of advanced battery materials.

4.2 Future Work

With the entire Li-Mn-Ni-O pseudo-ternary system mapped electrochemically, the next step involves the complete electrochemical mapping of the Li-Ni-Mn-Co-O pseudo-quaternary system. This system is of high-interest as many current commercialized Li-ion cathode materials, including $LiCoO_2$, $Li[Ni_{1/3}Li_{1/3}Co_{1/3}]O_2$, and $LiMn_2O_4$, all lie within this system. Figure 4.1 A illustrates the approach previously used to map this pseudo-quaternary phase system with x-ray diffraction only.[32] The pyramid was built by joining together slices of

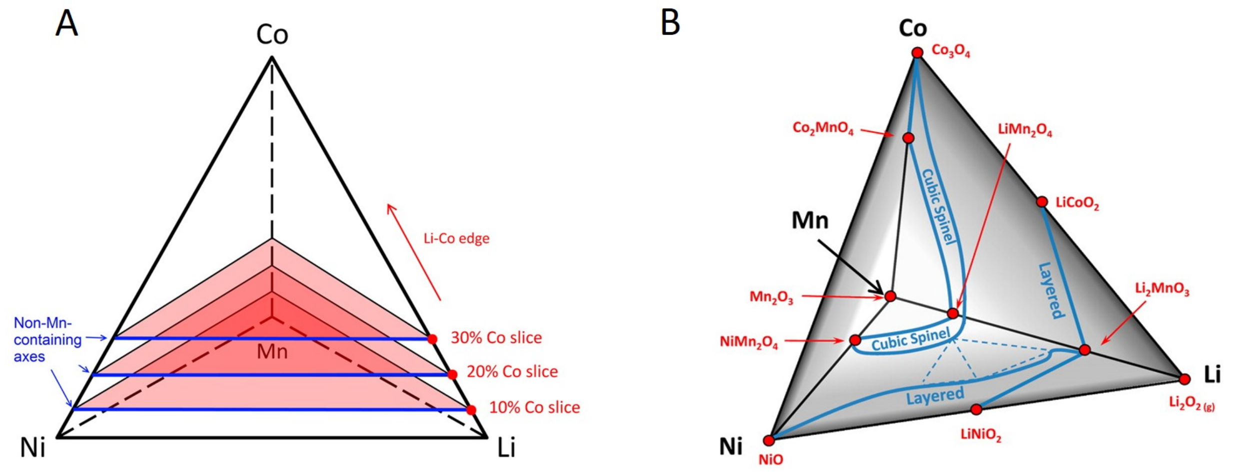

Figure 4.1: The Li-Mn-Ni-Co-O pseudo-quaternary system. (A) Strategy employed to expand the Li-Mn-Ni-O system and (B) the complete structural Li-Mn-Ni-Co-O quaternary system. Reproduced from Ref. [32] with permission from the American Chemical Society.

the Li-Ni-Mn-Co-O ternary system in which the content of Co is fixed throughout. This same methodology can be used to electrochemically map this system, thereby correlating key electrochemical metrics with the structural phase diagram (as seen in Figure 4.1 B), further elucidating important structure-performance relationships.

In addition to Li-ion systems, this methodology can also be applied to batteries beyond Li-ion. Significant research efforts are being directed towards sodium ion (Na-ion) batteries as a potential replacement for Li-ion as Na is cheaper and more abundant than Li.[60,61] However, this research is slow moving as only select compositions have been considered, limiting the structure-performance relations that can be identified and used for their further optimization and design. Combinatorial methodologies could greatly expedite this area of research. Recently, a combinatorial methodology was developed for the synthesis of Na-ion cathode materials and was used to rapidly synthesize a specific Na-system but could be extended to any Na-system of interest. In concert with sequential advances in high-throughput synthesis, structural characterization and electrochemical characterization of entire systems of Na-ion cathodes could be screened in just weeks. The proof of concept for the high-throughput electrochemistry applied to Na systems is demonstrated in Figure 4.2, in which a combinatorial cell was successfully cycled with P2-$Na_{0.66}Fe_{0.5}Mn_{0.5}O_2$. This result

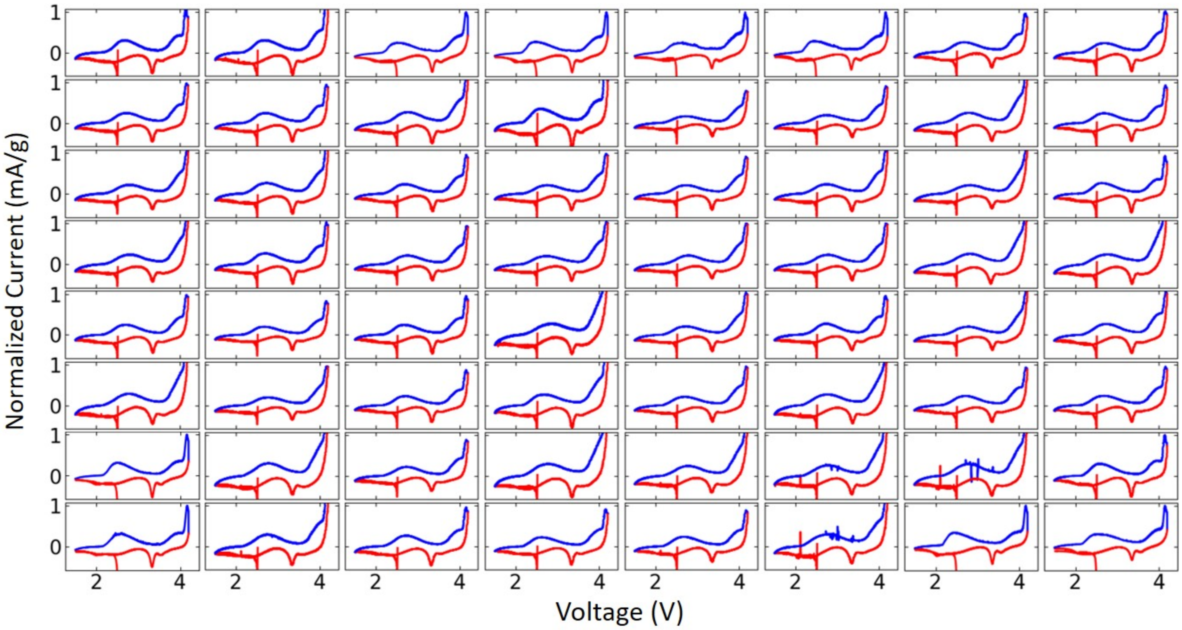

Figure 4.2: Cyclic voltammograms of mg-scale samples of P2-$Na_{0.66}Fe_{0.5}Mn_{0.5}O_2$ cycled in the combinatorial cell.

confirms the capability of the combinatorial cell developed in this thesis to be employed on systems other than Li-ion. Consequently, the complete structural and electrochemical mapping of Na-Fe-Mn-O pseudo-ternary cathode system is currently underway.

It should also be noted that while the high-throughput system is optimized for cycling cathode materials, it is possible for it be tailored to other electrochemical techniques. For example, electrochemical impedance spectroscopy (EIS), a commonly used technique in battery characterization, could be performed on the materials in the combinatorial cell. In particular, EIS could be used at various stages of cycling (i.e. pre-cycling, after 5 cycles, after 10 cycles, etc.) to track the increase of charge-transfer resistance. This would provide important insight into how the structure of the cathode influences the change in impedance during cycling. Another electrochemical technique that could be employed is the monitoring of voltage fade during storage experiments. This technique involves charging a battery to an upper threshold voltage, disconnecting the battery from the external power source, and then monitoring the voltage over a period of time. As the voltage fade of a charged battery is related to the instability of materials and parasitic reactions that are detrimental to battery life, it would be possible to identify which structures and compositions are most prone to experiencing this. Considering these experiments could take place over a period of weeks, it would be critical to re-evaluate and further improve the cell seal to enable an isolated environment on these time scales.

It is important to recognize the opportunity that high-throughput studies permit in being able to generate large sets of data rapidly for the development of machine-learning techniques. The capability of machine learning to advance energy research was recently demonstrated in a study where machine-learning algorithms parsed through complex synthesis conditions to determine the optimum conditions for maximizing solar cell efficiency.[62] As such, the combination of high-throughput electrochemistry and machine-learning techniques could prove very powerful in the search for next-generation battery materials.

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Appendix A

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Author: Daniele Di Lecce, Paolo Andreotti, Mattia Boni, et al

Publication: ACS Sustainable Chemistry & Engineering

Publisher: American Chemical Society

Date: Mar 1, 2018

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Institution name	McGill University
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Title, description or numeric reference of the portion(s)	Schematic of the combinatorial electrochemical cell.	**Title of the article/chapter the portion is from**	Design and Testing of a 64-Channel Combinatorial Electrochemical Cell
Editor of portion(s)	M. D. Fleischauer, T. D. Hatchard, G. P. Rockwell, J. M. Topple, S. Trussler, S. K. Jericho, M. H. Jericho and J. R. Dahn	**Author of portion(s)**	M. D. Fleischauer, T. D. Hatchard, G. P. Rockwell, J. M. Topple, S. Trussler, S. K. Jericho, M. H. Jericho and J. R. Dahn
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NEW WORK DETAILS

Title	High-Throughput Electrochemistry of High-Voltage Li-Ion Cathode Materials	**Institution name**	McGill University
Instructor name	Karlie Potts	**Expected presentation date**	2019-11-15

ADDITIONAL DETAILS

Order reference number	N/A	**The requesting person / organization to appear on the license**	Karlie Potts

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Title, description or numeric reference of the portion(s)	Differential Capacity vs. Voltage Plots for the 64 compositions shown in Fig. 3. The shaded region corresponds to the range of Si-Al-Mn compositions that can be melt-spun amorphously.	**Title of the article/chapter the portion is from**	Combinatorial Investigations of the Si-Al-Mn System for Li-ion Battery Applications
Editor of portion(s)	Electrochemical Society.	**Author of portion(s)**	M.D. Fleischauer and J.R. Dahn
Volume of serial or monograph	151	**Issue, if republishing an article from a serial**	8
Page or page range of portion	A1216-A1221	**Publication date of portion**	2004-06-01

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Combinatorial Study of the Li–Ni–Mn–Co Oxide Pseudoquaternary System for Use in Li–Ion Battery Materials Research

Author: Colby R. Brown, Eric McCalla, Cody Watson, et al

Publication: ACS Combinatorial Science

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