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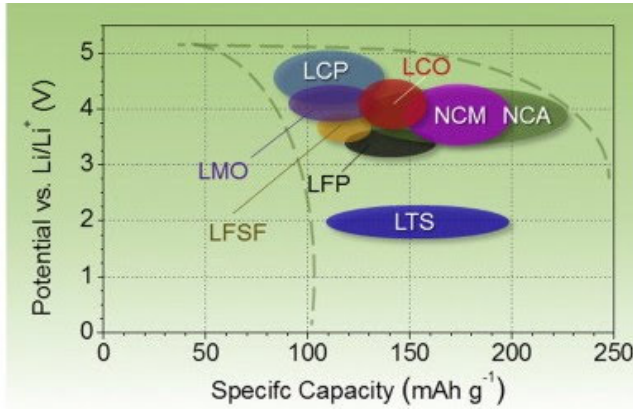
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1 Introduction

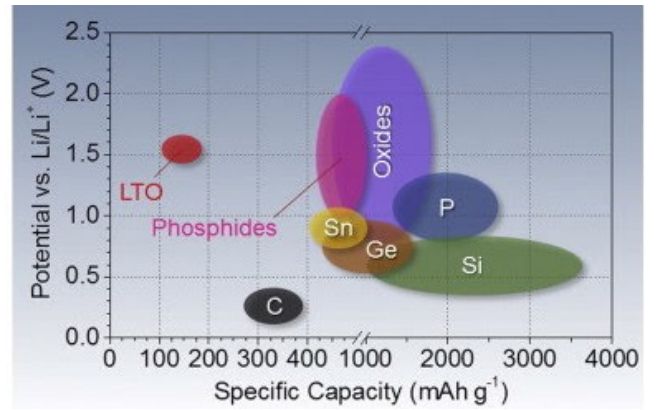
This work consists of two parts, exploration of a new liquid injection system for the synthesis of oxides and application of this method to synthesize cathode materials directly on a current collector. These novel cathodes will not need a traditional binder in order for the cathode material to stick to the conducting surface. Thus, cathodes produced by liquid injection may prove to be useful in the future.

Today, we surround ourselves with electricity - from electrical watches and smartphones to electrical cars and light. The aim for a greener future, together with the increasing complexity and finesse of electrical devices calls for a constant development of our device for storing electrical energy - the battery.

Batteries are commonly divided into two categories; primary and secondary batteries. Primary batteries cannot be electrically charged and are therefore single use, whereas secondary batteries are rechargeable. The latter can offer savings in costs and resources. A battery consists of three major parts; the anode, the electrolyte and the cathode. The latter plays an important role when it comes to improving various aspects of batteries, such as cost, safety, power and energy densities [1]. Nowadays, the cathode is typically the most costly element, comprising about 30 % of the total price of the battery [2]. Moreover, as shown in figure 1 (a) and (b), present cathode materials exhibit around half the specific capacity as the carbon anodes used today [3].



(a) intercalation-type cathodes



(b) conversion-type anodes

Figure 1: Approximate range of average discharge potentials and specific capacity of some of the most common electrodes in today's researched and commercial batteries [3].

1.1 History

The first electrical battery is credited to the Italian physicist Alessandro Volta who, in 1800, invented the Voltaic pile consisting of alternating disks of zinc and copper separated by brine-soaked paper [4]. Since then, a lot of different chemistries and structures have been tested. Among these we find the first rechargeable battery, the Lead-Acid battery, which to present day is being used to start internal combustion engine cars. Later, the alkaline battery used in regular household devices, which are typically non-rechargeable, saw the light of day. [5]

The next big breakthrough, however, came from Sony Corporation in 1991 with the pairing of a LiCoO_2 (LCO) cathode and a graphite anode to manufacture and commercialize the first mass-produced rechargeable lithium battery [6]. Li-ion batteries had been researched since 1970, starting with fundamental research into intercalation of Li into layered transition-metal sulfides and selenides [7]. In 1980, John B. Goodenough and his research group found LiCoO_2 to be a stable cathode material capable of donating Li-ions. Later, in 1983, Rachid Yazami was exploring Li intercalation onto graphite and found reversible Li insertion into carbon to avoid a rather pressing problem of dendrite formation, causing the battery to short circuit [5]. Lastly, Akira Yoshino made use of these discoveries and invented the Li-ion battery as we know it today in 1985. This battery system comprised of a "non-aqueous secondary battery using transition-metal oxides containing lithium ion such as LiCoO_2 as a positive electrode and carbonaceous materials as a negative electrode" *REF*.

1.2 The Li-ion battery

The Li-ion battery (LIB) can be credited for the wireless revolution of portable computers, cell phones and tablets that has revolutionized global communication and is starting to reshape travel as well. As shown by companies such as Tesla, Kia and Nissan, the internal combustion engine can be replaced by a combination of a portable rechargeable battery and an electrochemical capacitor. There are, however, some imminent questions regarding cost, safety and driving range.

Li-ion batteries possess certain fundamental advantages compared to other chemistries. Li, being the third element in the periodic table, Li-ion batteries have an unmatched combination of high power and energy density. This

The batteries assembled and tested for this thesis have consisted of various cathodes manufactured by liquid injection, aiming for MnO_2 , LiMn_2O_4 and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Moreover, an anode of lithium metal and a liquid electrolyte has been used.

1.2.1 Cathodes

An ideal cathode possess high energy and power densities, is small and inexpensive. Compared to Cobalt, Manganese is a very cheap element, making Mn a potential candidate for cheaper cathode materials.

A huge variety of cathodes has been researched, including, but not limited to, intercalation cathode materials, transition metal oxides, polyanion compounds and conversion cathode materials. LCO, introduced by Goodenough and commercialized by SONY, is the first and most commercially successful type of layered transition metal oxide cathodes *ref present and future*

An intercalation cathode contains a solid host network and is able to store guest ions which can be inserted into and removed from the host network reversibly. In a LIB, Li^+ acts as the guest ion while the host network can be metal chalcogenides, polyanion compounds or transition metal oxides. It is common to divide intercalation compounds into crystal structures, such as layered, spinel and olivine.. [3]

History of cathodematerials. Especially MnO_2 , LMO and LNMO

MnO_2

LiMn_2O_4 (LMO)

Spinel LiMn_2O_4 has low toxicity, good safety performance and low cost and is thus considered to be an ideal cathode material for LIBs.

$\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ (LNMO)

By doping the spinel LMO with a certain amount of transition metal elements, for instance Ni, the Fermi energies of the material can be adjusted and their electrode potentials increased as desired *rewrite and ref - LNMO paper*

Among doped spinel cathode materials, $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ (LNMO) has proved promising in terms of performance and discharge capacity. *Talk about charge-discharge platform?

1.3 Prior work

To the authors knowledge, there has not been any extensive research into synthesising oxides using liqui injection. There has, however been a lot of research into batteries and cathode materials.

1.3.1 Spray pyrolysis

Spray pyrolysis is an aerosol process that atomizes a solution and heats the droplets to produce solid particles - Cerpotech

Detail into MnO_2 , LMO and LNMO? What to put under "history" and what to put here?

Explain how oxides for batteries "typically" are made

What has been done with liquid injection previously?

Something about binders?

1.4 Definition of the thesis

Explore the novel method of liquid injection *in vacuo* and test out different parameters. Next, use this method to synthesize oxides directly on conducting steel plates and build batteries.

2 Theory and Methods

2.1 Electrochemistry

2.1.1 Electrochemical cells

A battery consists of one or more interconnected electrochemical cells each supplying a current (I) at a voltage (V) for a time Δt . For a battery to be rechargeable, the chemical reaction occurring inside the cell needs to be reversible on the application of charging I and V .

The electrolyte separating the anode and the cathode may be liquid or solid. Solid electrolytes are often used with gaseous or liquid electrodes while a liquid electrolyte commonly is in use with solid electrodes. In the latter, the electrodes are kept apart by an electrolyte-permeable separator. As can be seen from figure 2, the electrolyte permits the ionic component of the redox reaction (occurring at the electrodes) through while forcing the electronic component to do work by traversing an external circuit.

$Q(I)$ is the cell capacity for a given current, I . Q is the total charge per unit weight (Ah kg^{-1} /mAh g^{-1}) or per volume (Ah L^{-1}). The dependency of I arises since the rate of transfer of ions becomes diffusion-limited at high currents.

A perfect battery would be able to dispatch the same charge on discharge as it is supplied while charging - every time. In other words, there should ideally not be any capacity fade

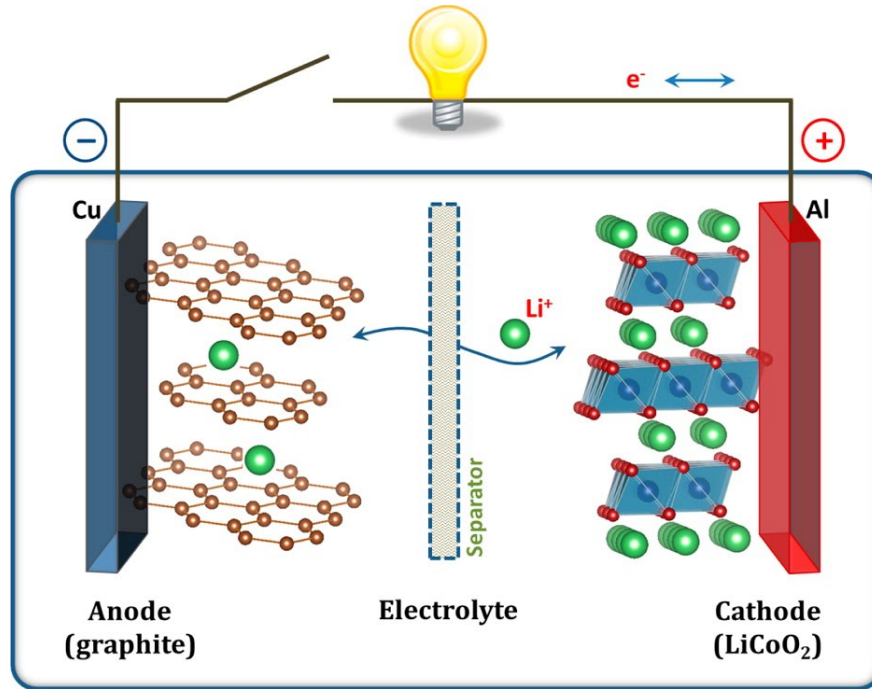


Figure 2: Schematic of the first Li-ion battery. Ions are permitted through the electrolyte while electrons traverse the external circuit.

throughout the life of the battery. A diffusion-limited loss of ions presents a reversible loss of capacity. However, changes in electrode volume, electrode decomposition or chemical reactions between electrode and electrolyte may cause an irreversible loss of capacity [8].

The Coloumbic efficiency,

$$100 \times \frac{Q_{dis}}{Q_{ch}}$$

gives the efficiency of a single cycle associated with capacity fade. The cycle life of a battery is then the amount of cycles the battery can withstand before the capacity has faded to 80% of its initial reversible value.

Something about SEI? YES

2.1.2 How batteries typically are made

Binder and carbon additive

2.2 Scanning Electron Microscope (SEM)

The scanning electron microscope scans a focused electron beam over the surface area of a specimen, examining(?) the microscopic structure with a higher resolution and much greater depth of field compared to an optical microscope. The large depth of field results in a three-dimensional appearance of its images. In addition, chemical information from a specimen can be obtained through the use of various techniques, including using a X-ray energy-dispersive spectrometer (EDS).

A SEM is composed of an electron gun and a series of electromagnetic lenses and apertures.
*electron source *Detectors (SE and BSE)

2.3 X-ray diffraction (XRD)

X-rays are a form of electromagnetic radiation with wavelengths ranging from 0.1 to 100 Å, first discovered by Wilhelm C. Röntgen in 1895. These wavelengths are in the order of interatomic distances in crystals causing diffracted waves to form a unique diffraction pattern due to interference. Thus, X-rays has proven to be an excellent probe of the structure of matter [9], [10].

The condition for constructive interference is described by Bragg's law as

$$n\lambda = 2d \sin \theta$$

where n is an integer, d is the lattice spacing, λ is the wavelength of the diffracted beam and θ is the diffraction angle. An illustration of the geometry is shown in figure 3.

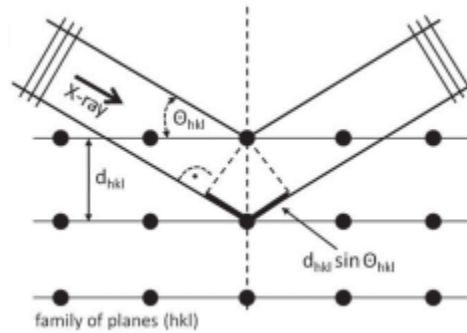


Figure 3: Visualization of the principles used to derive Bragg's law [10]

By plotting the counted reflections as a function of the angle between the incident and the diffracted beam (angle of diffraction), the positions and intensities of the peaks works as a fingerprint for the identification of unknown materials by comparing the diffraction pattern with a reference database. Further comprehensive analysis can supply information regarding bond lengths, bond angles, structural disorder and more. [10].

2.4 Electrochemical analysis

When investigating the electrochemical properties of a battery, the cell voltage and the current are often the main parameters of interest. With one of these parameters fixed and the other monitored, valuable information regarding the electrochemical properties can be obtained.

2.4.1 Impedance

Impedance is a measurement of the opposition a circuit presents to a current with an applied voltage. Impedance possesses both magnitude and phase and extends the concept of resistance to alternating current (AC) circuits. Thus, Ohm's law can be modified to $V = ZI$, where Z is impedance and $Z = R$ for a pure resistor.

2.4.2 Cyclic voltammetry

Cycling voltammetry (CV) is a highly versatile and useful technique commonly employed to investigate the reduction and oxidation properties of a given material. In addition, CV is used to study electron transfer-initiated chemical reactions **2_CV** During CV, current is measured as a function of applied voltage. With a minimum and maximum voltage set, the measurement starts at zero current voltage (0CV). From there, the voltage is swept at a constant scan rate to the maximum voltage, then to the minimum voltage and ends up at 0CV. This scan is repeated for a number of cycles.

*Scan rate CV

2.4.3 Galvanostatic cycling

During galvanostatic cycling a constant current is pushed into or out of the battery

2.5 Liquid injection system under vacuum

The main goal of this thesis is to explore a novel system for the formation of oxides from a variety of more or less complex compounds. The system produces powder that sticks to the surfaces present during the synthesis. Liquid is injected in pre-determined amounts (droplets) into a round bottom flask under vacuum and heated. The liquid evaporates (do I know that it evaporates?) and decomposes into oxides which are then deposited on the substrates present in the flask as well as the surface of the flask itself.

This behaviour can be exploited to synthesize cathodes without the need for a binder in order to have the oxide stick to a conducting surface.

3 Experimental design

This section will give an overview of the instrumentation used in this thesis. Since the deposition technique used is a new method, the level of detail will be more extensive.

3.1 Liquid injection system

The system consisted of a 500 ml single-neck round-bottom flask with a joint size of 29/32 (29 mm wide at the top and 32 mm long) attached to a connector pipe, sealed with a Teflon cone and silicon grease. A 1/16" stainless steel tube, henceforth called injector-tube, went from a 6-port Valco valve, through a cap on top of the connector tube and down to the bottom of the neck of the flask. A vacuum pump was connected to the connector tube in order to reduce the pressure of the flask and the pressure was monitored with the use of a Pirani gauge. A heating mantle and aluminum foil was used to heat the round-bottom flask to 300-400 °C during the injection.

In addition to the injector-wire, the 6-ports valve connects a 10 mL syringe containing the precursor, a steel tube forming a loop, an open-end tube and a tube supplying nitrogen gas. The 6-ports valve was used in two different positions, controlled by an Arduino. The first position allowed for the tube to be filled with the precursor. The precursor was mechanically injected from the syringe and any excess liquid went into a waste beaker from the open-end tube. The second position opened for a nitrogen flow to push the liquid from the tube through the injector-wire and into the round-bottom flask. A schematic of the apparatus is presented in figure 4.

Two different vacuum pumps were used due to malfunction of the first pump halfway through the experiments, first a rotary vane pump and secondly a membrane pump. *

During the preparation for new runs, a round-bottom flask was washed and dried, 10 mL of the precursor solution measured in the syringe and all the substrates blown and washed with ethanol, before carefully placing them in the flask. A variety of glass, Si and steel plates were utilized. Between the runs, the round-bottom flasks were washed in an acid bath, removing most of the deposited material from the previous run. Any residual material that did not get washed away with either acid or water and a brush were considered to not affect the consecutive run.

3.1.1 Parameter testing

Since this is a novel system, various parameters have been altered in order to see their effect on the synthesized material. The main parameters of interest have been the position of the tip of the injector-wire and the concentration of the precursor(s).

3.1.2 Cathode production

- The whole shabang - Round-bottom flask, vacuum tube, connector pipe, silicon grease and cones(?), vacuum pump (two different, second somewhat lower pressure), alu foil, sample holder, glass substrates, Si substrates, metal plates (spacers), 6-ports valve, heating mantle

Missing
some-
thing?

- Software used?
- Making batteries
- Compounds. Just state the stoichiometry and such or show how I have derived it?
- Limitations from the equipment?
- How detailed about the runs? Placement of substrates in the flask? Dimensions of substrates and sample holder?

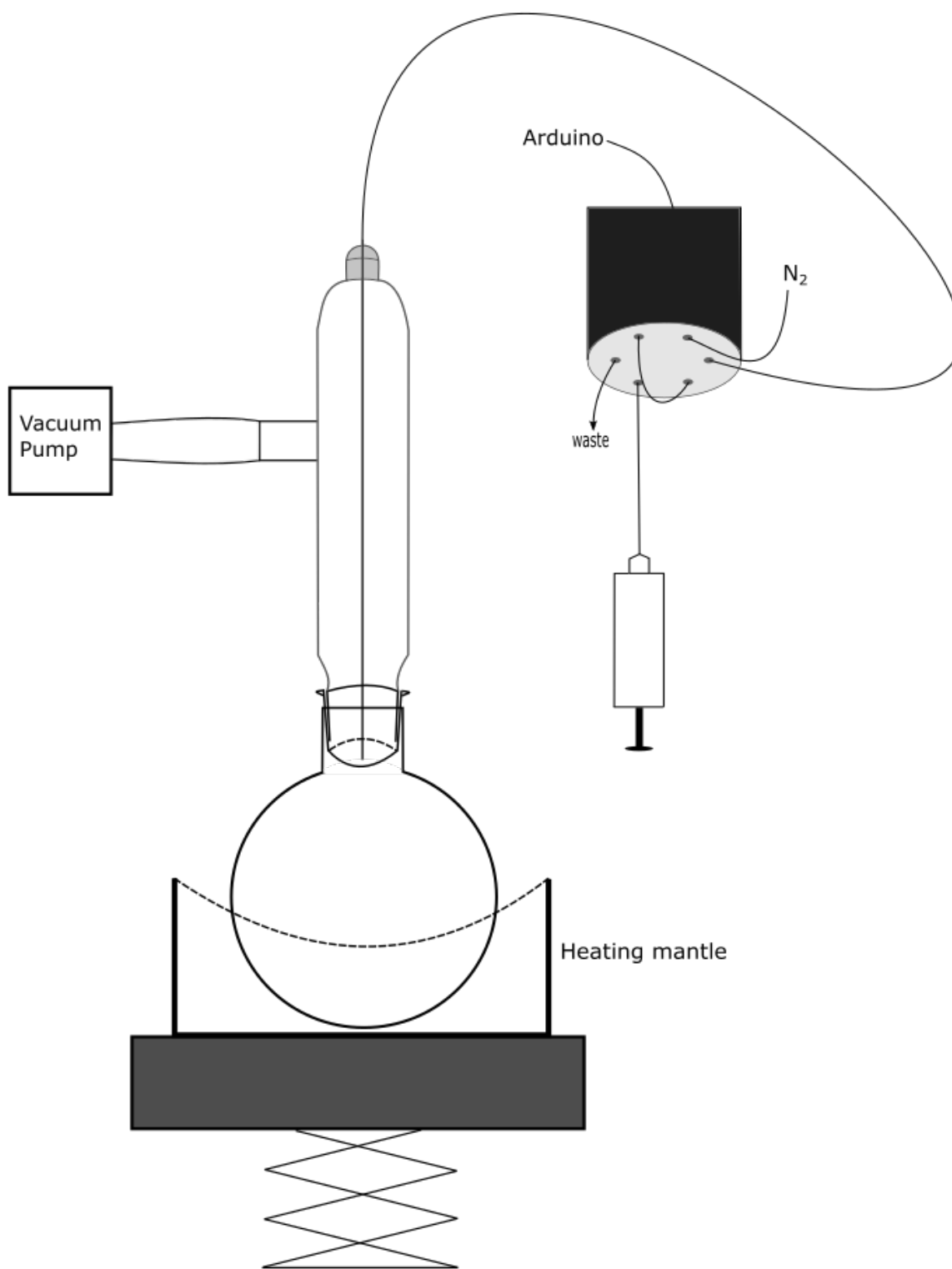


Figure 4: Schematic of the liquid injection system

Compound	Linear formula	Purity	Supplier	CAS	Lot #
Manganese(II) nitrate hydrate	$\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$	98%	Sigma-Aldrich	15710-66-4	MKBR0853V
Lithium nitrate	LiNO_3	> 99%	Sigma-Aldrich		

3.2 Chemicals used

3.3 Experimental runs

Experiment	Precursor(s)	Substrates	Purpose	Notice
EH-001	0.125 M $\text{Mn}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$	1x Glass, 1x Si	Testing	
EH-002	0.125 M $\text{Mn}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$			
EH-003	0.125 M $\text{Mn}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$			
EH-004	0.125 M $\text{Mn}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$			
EH-005	0.125 M $\text{Mn}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$			
EH-006	0.125 M $\text{Mn}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$			
EH-007	0.125 M $\text{Mn}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$			
EH-008	0.25 M $\text{Mn}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$			
EH-009	0.25 M $\text{Mn}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$			
EH-010	0.25 M $\text{Mn}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$			
EH-011	0.25 M $\text{Mn}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$		Production	
EH-012	0.25 M $\text{Mn}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$			
EH-013				
EH-014				
EH-015				
EH-016				
EH-017				
EH-018				
EH-019				
EH-020				
EH-021				
EH-022				
EH-023				
EH-024				

3.4 X-ray diffraction

X-ray diffraction was performed with a Bruker AZS D8 discover diffractometer in reflection mode. The XRD data was analysed with DIFFRAC.ECA from Bruker.

3.5 Scanning electron microscopy

Scanning electron microscopy was performed on at tabletop Hitachi

3.6 Nanoscratch

3.7 Coin-Cell Assembly

To investigate the electrochemical properties of the synthesized cathodes, CR2032 coin cells were built using metallic lithium as the anode and the as-deposited steel plates as cathodes. The cells were assembled inside an MBraun Lambaster glovebox with argon atmosphere and water and oxygen levels below 0.1ppm. A Whatman glass microfiber sheet was used as the separator membrane and the liquid electrolyte consisted of 1M LiClO₄ in a 1:1 mixture of ethyl carbonate (EC) and dimethyl carbonate (DMC).

3.8 Electrochemical analysis

Cycling voltammetry and Galvanostatic cycling was performed on a MPG2 probostat from BioLogic using EC-Lab software. Impedance was performed on a VSP

find out

. The data from all measurements were treated (?) in Origin and the results are presented in the following section.

4 Results

- Findings? Effect of position of needle, concentration, placement of substrate, covering the substrate
- Identification - XRD, SEM, Nanoscratch
 - SEM - particle size, homogeneity, surface roughness
 - XRD - phases present
- Electrochemical - Impedance, CV and GC
- Other results?
- MnO_2 , LiMn_2O_4 , $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$

4.1 Liquid injection system

Table of different parameters and their effect? Position of needle - no visible effect. Might be a chance of clogging if the needle is very far down.

Concentration of precursors -> Particle size and weight of deposited material

4.2 Characterizing - SEM and XRD

4.2.1 MnO_2

Put SEM and XRD together?

4.2.2 LiMn_2O_4

4.2.3 $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ - LNMO

4.3 Electrochemical analysis

4.3.1 MnO_2

4.3.2 LiMn_2O_4

4.3.3 $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ - LNMO

4.4 OR

4.4.1 Impedance

4.4.2 Cyclic Voltametry

4.4.3 Galvnostatic Cycling

5 Discussion

- Discuss the results

6 Conclusion

- Something clever to wrap up

7 Further work

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