Optical monitoring of battery dynamics

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Abstract

A remarkable characteristic of emerging green technologies is the speed, scale, and geographical spread attributed to it. While fast development and distribution is essential, local maintenance and monitoring is key to successful adoption of such technologies and must be planned in the supply chain in advance. In the nanophotonics group, we have contributed to the FAIR-Battery project, an open hardware platform for diffusing the knowledge of batteries.

In this master project, we will extend the electrochemical cell of the FAIR-Battery with inspection ports for optical monitoring of the electrochemical activity at the electrodes. We will build this inspection tools based on the other nanophotoncis project on multiple scattering from turbid media (such as membranes), and diffuse electro reflectance from solid-electrolye interfaces.

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Table of Contents

Table of	figures	5
1. Int	roduction	8
1.1	History of rechargeable batteries	8
1.2	FAIR-Battery project	8
1.3 W	/hat's special about optics?	8
1.4	Research goals	8
1.5	Thesis structure	ç
2. The	eory	ç
2.1	Battery composition	
2.2	Battery operating mechanism	10
2.3	Electrolyte materials	11
2.3.1	Liquid electrolyte	11
2.3.2	Solid state electrolyte	11
2.3.3	Advantages of solid state batteries	12
2.3	.4 Electric double layer	12
2.4	Why batteries fail	13
2.4.1	SEI layer formation	13
2.4.2	Parasitic reactions	14
2.5	Current methods for battery monitoring	14
2.5.1	Electrical impedance spectroscopy	15
2.5.2	X-ray diffraction	15
2.6	Novel methods for battery monitoring	16
3. Me	ethodology	17
3.1	Optical setup	17
3.2	Electronic setup	21
3.3	Battery production	23
3.4	Measurement details	24
4. Re:	sults	25
4.1	Images	25
4.2	Background correction	27
4.3	Analysis tests	28
4.3	.1 RC impedance	28

4.3.2 LED	29
4.3.3 Blank measurement	
4.4 Active cells	
4.4.1 Cell 1	
4.4.2 Cell 2	36
4.4.3 Cell 3	
5. Discussion	43
5.1 Cell design and environment	44
5.2 Ideal comparison	45
5.3 Cell performance comparison	46
6. Research retrospective	46
7. Conclusion	47
References	50

Table of figures

10
11
12
14
15
16

8
S
C
1
1
2
3
4

Figure 4.1 shows a comparison between the different light sources	26
Figure 4. 2 are the background corrected and normalised images	27
Figure 4. 3 compares the average to the variance images	28
Figure 4. 4 is the averaged variance frame.	28
Figure 4.5 is the Nyquist and Bode plots of the first order RC circuit.	29
Figure 4. 6 shows the variance of LED over the duration of the measurement along with the	
offset voltage level.	
Figure 4. 7 shows the normalised intensity of the LED at every offset over the whole	
measurement	30
Figure 4. 8 is the intensity profile for the first offset	
Figure 4. 9 shows the FFT of a single offset	31
Figure 4. 10 shows the variance of the cell.	31
Figure 4. 11 is the intensity of the cell over the entire measurement.	32
Figure 4. 12 is the FFT of the intensity profile.	32
Figure 4. 13 shows the Nyquist and Bode plot for the symmetrical cell.	33
Figure 4. 14 shows the current response of cell 1 to the modulation frequency, how it	
changed with every offset and the current over time	34
Figure 4. 15 shows the variance of cell 1 over time, the intensity over time with input voltage	
and how the intensity reacted to the modulation frequency	35
Figure 4. 16 shows the FFT of the intensity of the whole measurement	35
Figure 4. 17 shows the Nyquist and Bode plot for cell 2	36
Figure 4. 18 shows the current response of cell 2 to the modulation frequency, how it	
changed per offset and how the current reacted over time	37
Figure 4. 19 shows the variance over time of cell 2, the intensity of the measurement and	
how the intensity reacted to the modulation frequency	38
Figure 4. 20 is the FFT of the intensity profile shown.	38
5	

Figure 4. 21 depicts the FFTs of the first on run (first two graphs) and first off run (last two graphs)
Figure 4. 22 shows the Nyquist and Bode plots of cell 340
Figure 4. 23 is the current response of cell 3 to the modulation frequency, how the current changed per offset and how the current changed over time42
Figure 4. 24 depicts the variance of cell 3, the intensity of the whole measurement and how the intensity reacted to the modulation frequency42
Figure 4. 25 shows the FFT across the whole measurement of cell 342
Figure 4. 26 shows the FFTs of the first on (top two graphs) and off runs (bottom two graphs)43

Figure 5. 1 shows cell 1, 2 and 3 in that order from top to bottom	
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1. Introduction

In this section, an overview of the background for the project is given, along with goals of the project and how the structure of the report is laid out.

1.1 History of rechargeable batteries

Rechargeable batteries are a pillar of modern day society. They are found in many electronic devices, from watches to cars and can even be used for industrial purposes for storing energy. This gives rechargeable batteries a wide scope in application. Lithium-ion batteries (LIBs) are of particular interest due to their already widespread adoption and their high energy density. They were first developed in the 1980s from research conducted by John Goodenough, Stanley Whittingham, Rachid Yazami and Akira Yoshino, and were later commercialised by Sony with an Asahi Kasei team led by Yoshio Nishi in 1991 and massed produced.

1.2 FAIR-Battery project

The FAIR-Battery project was set up as a collaboration between Utrecht University, Wageningen University and the Technical University of Eindhoven as an open source platform to develop new battery technology. FAIR stands for Findable, Accessible, Interoperable and Reproducible. These four words power the thought behind what new battery technology should be; easily available, efficient technology made from local resources whose components can work in a range of different parameters so they can fit the criteria of any environment where energy storage is necessary. There is an emphasis on green technology in order to satisfy environment regulations and to be sustainable over many years. The materials used are deliberately low cost which opens the door for many people to adopt this way of making batteries.

1.3 What's special about optics?

Monitoring the battery's health over time is very important in order to see the way in which the battery degrades. Knowing the degradation process and the unwanted compounds formed during this process allows for better materials to be developed that can have a longer lifetime, which is something especially useful for batteries that are in remote or hard to reach places or that cannot be repaired easily. Keeping this in mind, along with the ideals of the FAIR-Battery project, optics are a low-cost, easily manufactured solution to monitoring batteries over an extended period of time. Current options for battery monitoring require expensive equipment that needs a specialized operator to run, such is the case for x-ray microscopy or electron microscopy, whereas optics is much cheaper to operate, easier to install and use, doesn't require special conditions to run such as a vacuum environment and can provide real time data of the health of the battery. This makes the emerging field of optical monitoring in batteries of great interest to the FAIR-Battery project.

1.4 Research objectives

- 1. Develop an easily manufactured microscope. Making a microscope that's uncomplicated that provides decent resolution is a cornerstone of the project. This makes the setup reproducible in different environments.
- 2. Use low-cost equipment. Keeping the cost of the equipment deliberately low allows more people access to the knowledge used in the experiments so the benefit of optical monitoring can reach as far as possible.

- **3.** Design a cell for optical access. In order to actually see what's going on in the cell, there needs to be an opening of transparent material that light can penetrate. This makes the cell different from others as usually batteries are a closed system of opaque material in order to protect any sensitive materials inside.
- **4.** Write code that can operate the equipment. Writing understandable code that's freely available to everyone keeps the open source nature of the project in mind.
- 5. Analyse a charge and discharge cycle. Monitoring when a battery charges and discharges is fundamental to understanding the internal processes that dictate how the battery performs and degrades over time. Doing this live with optics would provide excellent insight into battery dynamics while also being completely non-invasive and leaving the materials in the battery undamaged.

Navigating through this paper with these goals in mind will give context to the choices made and how the experiments were conducted. The FAIR ideals being the most important arguments throughout experimentation.

1.5 Thesis structure

This thesis is broken down into specific sections that cover different parts of the research, the chapters are structured as follows

- 1. Introduction talks about the ideas and goals behind the research.
- **2.** Theory dives into the knowledge behind batteries, their lifetime processes and what optical technique is used to monitor them in this research.
- **3. Methodology** details the experimental setup, how the optical and electronic parts interacted with one another, what cell assembly entailed and also how measurements were taken and analysed.
- **4. Results** shares the main data that's been collected through a series of graphs that helps explain what has been observed.
- 5. Discussion into why the results ended up as they did and what could be made better.
- 6. Research retrospective looks at the aims of the project and if they have been reached or not.
- 7. Conclusion finalises the argument for the project and looks to what future work is necessary.

2. Theory

In this section, the theoretical basis of the project is explained, which includes the basic electrochemistry of a battery cell and its materials, how battery lifetimes are monitored currently and the optical method for battery monitoring used in this project.

2.1 Battery composition

A battery cell consist of three parts, the cathode, the anode and the electrolyte. Both the anode and cathode have active material that use Li ions in reversible redox reactions, along with inactive agents that are used to help bind or increase conductivity. Examples of common cathode and anode active materials are $LiCoO_2$ (LCO) and graphite respectively. Their reversible half reactions are shown below:

 $LiCoO_2 \leftrightarrow CoO_2 + Li^+ + e^ Li^+ + 6C + e^- \leftrightarrow LiC_6$

Low conductivity of these materials on their own means that they are often accompanied by conductive agents, such as carbon black, to boost conductivity. This in turn promotes the flow of Li+ ions back and forth. Advancements have been researched into replacing the Li with different metals in the electrodes; for example, using sodium or magnesium centric cells instead of lithium. These batteries have different properties to Li-ion batteries and have different applications such as large scale industrial energy storage [1]. Difficulties have been encountered adapting existing Li-ion anode technology to Na-ion anodes because of sodium's dendrite formation and the lower melting point of Na compared to Li [2].

2.2 Battery operating mechanism

LIBs work through intercalation and deintercalation of Li+ ions in active sites of layered material such as LCO and graphite. The shift in chemical potential rocks the Li+ back and forth, powering the battery. When the battery is charging, Li+ ions flow from the cathode to the anode, and when discharging, they flow from the anode to the cathode [3]. Li is used because it has the highest energy density of any metal while also being very light, so more of it can be used in a battery [4]. The capacity of a battery is measured in mAh/g and is determined by the mass of active material contained in the battery. It represents the maximum energy that can be extracted from the battery while under certain operating conditions.



Figure 2.1 of the cell in an LIB. The Li+ ions deposit themselves in the layers between the active material of either electrode until potential is applied, where they then begin to flow [5].

LIBs have become the dominant battery on the market because of their high capacity, energy density and rechargeability, largely replacing older technology such as NiCd batteries and lead acid batteries.



Figure 2. 2 plots gravimetric and volumetric energy densities of typical LIB material highlighting the effectivenessof lithium in modern batteries compared to traditional materials [6]

2.3 Electrolyte materials

An electrolyte is a material that facilitates the flow of ions from one electrode to the other. They come in two forms, a liquid electrolyte and solid electrolyte. The liquid electrolyte is the most common electrolyte found in LIBs and are made from a mixture of organic solvents and lithium salts. Solid electrolytes forgo the organic solvents and use composite solid material. Both electrolytes behave differently and have different applications.

2.3.1 Liquid electrolyte

Every liquid cell includes a polymer separator, which prevents short circuiting. The separator is typically a permeable polymeric material placed in between the cathode and anode to prevent them from touching, thus avoiding short circuiting the battery. The most common separator used is the CellGuard separator. Separators need to be porous but also strong enough to not be ripped. They are divided into three groups, microporous polymer membranes, non-woven fabric mats and inorganic composite membranes [7]. Their inclusion creates resistance in the cell reducing its capacity but is necessary for the battery longevity. The electrolyte used is often comprised of an organic solvent; an example of a possible organic solvent includes ethylene carbonate (EC) with a lithium salt, such as LiPF₆, dissolved into the EC [8]. The electrolyte helps facilitate the Li ion movement from anode to cathode and vice versa through the separator.

2.3.2 Solid state electrolyte

Solid state batteries utilise an all solid cell, they do away with solvents in order to achieve this. They can be separated into three groups based off of their components, inorganic electrolytes, organic electrolytes, and composite electrolytes [9]. Inorganic electrolytes use a salt, usually oxide based or sulfide based, that is pressed into shape. They have high ionic conductivity at room temperature, in the order of 10⁻³-10⁻⁴ S cm⁻¹ and a high Li+ ion transfer number, but form rigid structures when pressed into shape which can be quite brittle and inflexible, making them very delicate [10]. Organic electrolytes use organic polymers which differ greatly from the mechanical and 11

chemical properties of inorganic electrolytes. They possess increased flexibility which allows them to handle greater stress and strain, but they suffer from low Li+ ion conductivity due to the polymers acting as an insulator, large ionic transfer resistance and oxidation at high voltages [11]. Composite electrolytes comprise of both inorganic and organic material and act as a middle ground between the two, taking on both their properties [11][12]. They have lower ionic conductivity than inorganic electrolytes but possess some of the flexibility of organic polymer cells. Optimisation of the electrolyte through experimentation is necessary to maximise conductivity and increase the elasticity of the cell [12].



Figure 2. 3 shows the typical architecture of liquid electrolyte and solid electrolyte cells. Note the use of a separator in the liquid cell, which isn't needed in a solid state cell [15].

2.3.3 Advantages of solid state batteries

Solid state batteries are overall safer to use than liquid electrolyte batteries, due to increased thermal stability, stability at higher voltages, increased energy density and reduced amount of parasitic reactions [13]. Solid electrolytes can operate in hostile environments, utilising a temperature range of -50°C-200°C [10]. This increases the applications of solid state batteries, allowing them to be used in situations where conventional batteries would degrade, vaporise or combust. Their stability at higher operational voltages goes in tandem with an increased energy density. A liquid electrolyte tends to break down at high voltages due to them possessing a narrow electrochemical window, but the higher operational voltage that solid electrolytes are capable of, in some cases above 5V, means the electrolyte won't decompose under normal cycling conditions and can be pushed further to increase their energy density [13]. Finally, parasitic reactions are diminished in solid electrolytes because of their intrinsic stability over large temperature ranges and voltages, meaning they can have a longer lifetime than liquid electrolytes [13][14].

2.3.4 Electric double layer

An electric double layer (EDL) is two layers of ions that form on the surface of an electrode

of opposite charge to the ions. The first layer consists of ions adsorbed to the surface of the electrode while the second layer is a result of Coulomb interactions between the electrode charge and the counterions to that charge. The potential builds up to the highest degree in the inner layer of the counterions and decays exponentially outside the double layer when entering the bulk, be it in solution or solid [31]. The EDL was first discovered by Hermann von Helmholtz when he found out that electrodes immersed in an electrolyte solution repelled co-ions and attracted counterions to its surface [32]. The EDL in a battery acts as a capacitor, it quickly builds up and stores electrical charge. An EDL forms at the interface between the electrodes and the electrolyte. The interface is where the chemical reactions take place, so it is imperative that batteries form a stable EDL in order to continue to store and provide power.



Capacitance proportional to the electrode area can be obtained by using an electrolyte for the dielectric

(b) double-layer capacitor

Figure 2. 4 shows the counterions flowing to the oppositely charged electrodes. The electric potential is highest at the electrode surface and quickly decreases moving from the interface to the bulk. The ions will only diffuse to the electrodes in the presence of an electric field, when the field is removed, the ions will diffuse back into the bulk, effectively breaking up the EDL [33].

The presence of the EDL can be detected using impedance by utilising the Nyquist and Bode plots.

2.4 Why batteries fail

Over time, the capacity of an LIB tends to fade. This stems from the heterogeneric nature of the reactions at the electrodes that cause the Li+ ions to cycle back and forth, and because the volume of each component of an individual cell is in constant flux [16]. Understanding the movement of the ions and the secondary reactions they have with the other material in the cell (such as the electrolyte), is key improving their longevity.

2.4.1 SEI layer formation

The solid electrolyte interface (SEI) is the result of Li+ ions reacting with the electrolyte when potential is applied. This interaction will develop a solid layer between the electrode and electrolyte, 13

which is imperative to the longevity and stability of future cycles of the cell [17]. Stable, uniform SEI growth can prevent degradation of the electrodes by acting like a sieve of sorts that can selectively let Li+ ions through, but stopping other compounds that could react further with the electrode, thereby degrading it even more [18]. However, experimentally it is shown that the SEI layer grows inhomogeneously with potential, with varying thicknesses at the local level. The protection it offers isn't absolute and will slowly lessen over continued cycling, which leads to capacity loss of the battery [18]. It grows with negative potential, and thins with positive potential.



Figure 2. 5 shows the selective nature of the SEI layer, only allowing Li+ ions through while larger Li compounds can't make it through the membrane [18].

2.4.2 Parasitic reactions

Parasitic reactions are unwanted side reactions that occur between highly reactive Li+ ions and other compounds present in the battery cell, usually found in the electrolyte. They are linked to irreversible capacity loss of the battery over time due to the Li+ ions reacting and forming other compounds. Instability of the electrolyte at operating potentials helps facilitate these side reactions, part of which forms the SEI layer [18][19]. As previously discussed, the SEI layer doesn't build up in a uniform manner and its thickness can fluctuate with the change in potential, meaning unideal reactions can still take place despite the presence of the protective SEI. Diffusion induced stress (DIS) from the intercalation and deintercalation of Li+ ions in their host electrode lattice can build up mechanical fatigue of the electrode architecture, resulting in fractures or cracking of the SEI [19]. The cracking allows propagation of unwanted side reactions from a now partially exposed electrode, leading to loss of the active sites for Li intercalation. It can also lead to Li dendrite formation. Dendrite are long, needle-like structures made of crystalline Li, which penetrate and puncture both the SEI and the electrode resulting in continual Li+ ion loss and capacity fading [20]. This can be detrimental in liquid electrolyte cells as they can puncture the separator, causing short circuiting of the cell.

2.5 Current methods for battery monitoring

Battery monitoring is a way to measure the internal chemistry of the cell, which can help determine and optimise the lifetime of the battery over continued cycles. Two of the most popular methods used are electrical impedance spectroscopy (EIS) and x-ray diffraction (XRD).

2.5.1 Electrical impedance spectroscopy

EIS measures the change in impedance (the resistance of alternating current) of an electrochemical cell. It can be used to probe the battery's state of charge (SOC), state of health (SOH), state of function (SOF) and temperature, which can help understand the relationship between the crystal lattice architecture of the electrodes and the electrochemical properties they possess, in a nondestructive and noninvasive way [21][22].



Figure 2. 6 shows the a typical Li ion EIS plot (Nyquist plot). The frequency is f and the order of data acquisition refers to the order in which frequencies are usually interrogated [22].

EIS offers an easy way to characterise a battery cell, but has its own drawbacks. The data returned from EIS measurements of both electrodes can be convoluted, particularly in the mid-frequency arcs of the Nyquist plot, due to similar time constants from the various interfacial electrochemical processes occurring at the electrodes [22]. A third electrode can be used to deconvolute the plots generated, but increases the complexity of the cell and requires great care then in the interpretation of the results [22]. EIS also cannot be used to monitor fully delithiated electrodes, because there are no electrochemical processes occur there so no measurement can be taken [23].

2.5.2 X-ray diffraction

X-ray diffraction (XRD) uses x-rays to determine the structure of crystals. XRD works by irradiating a material with incident X-rays and then measuring the intensities and scattering angles of the X-rays that leave the material. Unlike EIS, XRD can be performed at any SOC using in-situ x-rays and gives an accurate reading. Synchrotron radiation is the optimal x-ray source. There are advantages to using XRD such as its ability to instantly probe a reaction taking place at a specific point in the sample, which is necessary for the electrochemical reactions occurring in the cell due to the fast nature of Li+ redox reactions [24]. Also, using in-situ XRD allows for the continuous monitoring of the cell while operating, eliminating the need for multiple samples, and removes the 15

possibility of contamination of the sample, which is important for LIBs as they are sensitive to moisture and can react with the air around them, thus needing an airtight chamber for operation [24]. XRD, however, is expensive to conduct and can damage the cell under prolonged beam time. Also, synchrotron beam time is highly sought after and precious, meaning extensive studies are difficult to conduct.

2.6 Novel methods for battery monitoring

A new method to monitor batteries is using optics to probe onto the surfaces of the battery cell and see what is happening. Optics is a well-established platform and its practice can be readily applied to measure battery dynamics. One such optical practice is interferometric scattering microscopy (iSCAT). Interference is the primary contrast mechanism used in iSCAT, which allows it to image nanoscale objects with high resolution [25]. The camera detects the light scattered by these nanoscopic objects. The first use of interference as a contrast mechanism was in 1935 by Frits Zernike, who used a phase shift in the transmitted light using a conventional microscope to increase the contrast [25]. Modern interference techniques use a dark-field to measure the reflected photons, which can produce an image with very high resolution [25][26]. A distinct advantage of iSCAT is that it can provide a clear, fast, high resolution image of the electrochemical reactions occurring at the various interfaces in the battery cell. XRD, and even electron microscopy (EM), can also provide this, but they are more expensive techniques where beam time is precious and sought after. Also, prolonged exposure of the cell to x-ray or electron beams can cause degradation in the sampling area, whereas iSCAT does not, because it utilises visible light so is non-destructive and non-invasive [27].



Figure 2. 7 shows the difference in image quality of the iSCAT and SEM techniques. SEM can produce a higher resolution image, but iSCAT is much more cost-effective and less laborious, plus it doesn't degrade the sample at all. The scale bar is $2\mu m$ [27].

In an experiment conducted by Alice Merryweather et al, LCO was imaged using iSCAT to quantify ion dynamics at the single particle level in a visual way to demonstrate how iSCAT can be used as a low-cost and rapid way to measure the electrochemistry of the cell [27]. The LCO cell was made using LiPF_6 in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DC) and was galvanostatically cycled 20 times at a charge rate of 2C before iSCAT measurements were conducted.



Figure 1.7 shows the general reaction of the reversible state of LCO when cycled in the potential range of 3V-4.2V. The top graph of section (a) shows the galvanostatic (black) and differential capacity (grey) plots as a function of time. The bottom graph is the iSCAT intensity change over the active LCO particle during galvanostatic cycling. Section(b) is the iSCAT images produced as indicated at the time points from the bottom graph in section a. The background was subtracted from the images and the scale bar is 5μ m [27].

The team were able to track and quantify phase transitions in LCO under realistic operating conditions by only using light, which highlights the ability of scattering microscopy methodology as a way to provide real-time insights into the electrochemistry of the cell. iSCAT could be a way of complementing existing synchrotron methods for monitoring.

3. Methodology

For the experiments in this project, a custom interferometric optical setup was made in order to monitor the battery cells. Each part of the setup was tweaked and changed over the course of the project, refining the experiments and getting closer and closer to reproduceable data. Each main constituent part of the setup will be detailed in this section along with a protocol on how measurements were taken and analysed.

3.1 Optical setup

Interferometry was chosen for this experiment due to its enhancement of resolution over conventional microscopy and that it keeps information on both phase and amplitude of the resultant image, allowing for precise detection of small particles, which was very useful when monitoring the battery components.



Figure 3. 1 shows a schematic of a typical interferometric microscope. Laser light is focused through a widefield lens (WFL) into the back focal plane (BFP) of the objective (OBJ). The partial reflector (PR) here couples illumination light and attenuates the reflected light before it passes through another lens into a CMOS camera where it is imaged [28].

This schematic is comparable with the setup used for this thesis.



Figure 3. 2 is the optical setup used throughout the thesis. It contains many similarities with the schematic of figure 3.1. It uses laser light that is focused through a lens and directed towards the sample with a beam splitter into the back focal plane of the objective. The light scattered by the sample passes back through the microscope, through another lens and into the camera.

Every part of the microscope was screwed into place so it was stable enough to take accurate measurements. Any movement or changes had to come from the sample itself, not the environment around it.

The cells made for this project were unconventional and were designed more so to fit the optical setup and for optical access, rather than for serious testing of the capacity or energy density of assembled cell. Glass was necessary in order for the laser to penetrate into the cell in order to detect any intensity changes caused by the electrochemistry happening inside.

The cell was held in place by the sample holder. The sample holder was designed specifically for the dimensions of the cell. It was machined from brass in two parts with a plastic divider, in order to prevent shorting when a current was passed through the sample. It was secured in place on a stage that could move in three directions along the x,y,z axis. This was important so the focus and area of interest could be easily adjusted. A fine focus adjuster was also present on the microscope itself that moved the objective forwards and backwards.



Figure 3. 3 shows the custom sample holder with a cell secured on it. The screws on the side is where crocodile clips from the wave generator were attached in order to make the potential difference. The sample itself was secured in place by two pieces of copper that could be pressed down on the brass rods of the cell by tightening the screws on top.

When loading the sample, the cell would be placed in a groove present on both sides of the sample holder and then held in place by the copper strips. This proved to be quite a tight hold as the sample couldn't move which was reflected in the images after the measurement. For temperature dependent measurements, a plastic hood was fitted onto the sample holder that helped insulate the area around the cell to keep the temperature as accurate as possible.

A few different light sources were used throughout experimentation. A halogen light source was initially used, then a green laser and finally a blue laser was used. The uncorrelated light of the halogen bulb provided the best image of the cell, as each constituent part of the cell could clearly be seen. However, the halogen bulb was too unstable as the intensity would fluctuate far too much to get accurate data. It was decided laser light would provide a more stable intensity throughout a measurement. A green laser was first used which provided a decent image, but the speckle pattern shifted over time which meant that this laser intensity was too unstable. The blue fibre laser was then selected as this laser provided a very stable intensity of light over a long period of time. It produced, however, the least decipherable images and the halogen bulb had to be used in the beginning before a measurement in order to set the focus and region of the cell to look at. The blue laser was controlled via the Thorlabs CLD1010 which could control the temperature of the laser and intensity of the laser light by adjusting the current of the laser. Keeping the current between 34mA and 36mA provided the most stable light while also not being too intense that the images were overexposed. The exposure of the camera could also be adjusted depending on the laser intensity. Anywhere in the range of 300µs to 500µs was ample exposure for measurements.

The camera used was the Basler acA2440-35um. This is a CMOS camera that could capture in mono with a resolution of 2448x2048 and up to 16-bit. The camera would capture all the light reflected and scattered at it so the resulting images would have to be processed in order to find the exact spots needed where the particles in the cell would oscillate in intensity at the frequency of the 20

electric field applied by the wave generator. Each image was saved as an array in a HDF5 file.

3.2 Electronic setup

A constant voltage (CV) was used to charge the battery. This was done via the Analog Digilent 2 (AD2). The AD2 has both a wave generator and an oscilloscope inside. A simple circuit was assembled in order to charge and to monitor the pulse of the battery.



Figure 3. 4 is a diagram of the circuit used in the experiments. The wave generator sends a square voltage pulse into the battery. The response of the battery is fed to a current amplifier. The oscilloscope then records the voltages. The voltages from the amplifier can then be converted to current using code.

CV charging mode is an unorthodox method to charge the battery, but for the purposes of testing how a battery performs when there is an electric field present, it was sufficient.



Figure 3. 5 is an example of CV charging mode used throughout the thesis. The potential pulse (in blue) comes from the wave generator at a set frequency and the current response (in red) from the cell. The current initially peaks at the beginning of the pulse and then decays exponentially as the potential is held constant during the 21

pulse. This is due to an electric double layer (EDL) building up in the cell which acts as capacitor. The potential eventually returns to zero, where an inverse of the first curve is witnessed in the current [29].

The AD2 could be operated via its own Waveforms software provided by the manufacturer or a python script. The programmable nature of the AD2 swayed the decision to use it over more traditional wave generators, along with the affordability and compactness of the AD2 which is in keeping with the FAIR battery project, which uses readily available open-source tools.



Figure 3. 6 is the AD2. This has both a wave generator and an oscilloscope inside. The BNC adapter module was attached so BNC cables could be used.

The BNC cables ensured accurate data was obtained during experimentation.

To vary the temperature, Peltier units were used. One was hooked up to a power supply and the other was wired into a temperature control unit. The power supply acted as a coarse temperature adjuster, whereas the temperature control acted as a fine temperature adjuster. The temperature control could be accurately set to a temperature within two decimal places. The power supply an extra Peltier unit was needed because the temperature control couldn't supply enough power to a Peltier unit alone. A temperature range of 60° C – 65° C was required for temperature dependent measurements, which was chosen as this is a good example of temperature conditions typical batteries can face in real life.

The impedance meter used was the Keysight E4980AL LCR meter. For impedance

measurements, the charging circuit would be disconnected and the impedance meter connected in its stead. To run the impedance meter, a python script was used. This could both run a measurement and then plot the resulting Bode and Nyquist plot. A custom script was used for the same reason as the wave generator, parameters could be easily changed in the script that would otherwise prove more difficult with the manufacturer's software. The Bode plot graphs the range of frequencies against the real value absolute impedance. The Nyquist plot graphs the real impedance against the imaginary impedance. Both graphs have a known shape from literature, so the graphs obtained from experimentation could easily be compared.



Figure 3. 7 shows a typical Nyquist plot for an electric double layer capacitor (EDLC) electrode. The frequency is highest at the left hand side and decreases moving to the right. The semi-circle shape indicates that the resistance is low and reactance dominates. As the frequency decreases, the resistance gets higher and higher. This is because the ions are first flowing through the capacitor, in this case the EDL, and then flowing through the resistor, which is the charge transfer resistance [30].

The shape of the impedance graphs obtained from experimentation could vary wildly from those found in literature due to the unique cells built for this thesis.

3.3 Battery production

The cell was made up of a square 3X3mm glass capillary with two brass rods acting as the electrodes. The glass was ordered externally, while the brass electrodes were custom made in 23

house.



Figure 3. 8 contains the glass capillary and brass electrodes. The square shape of the capillary coupled with the sample holder required an electrode that was both square and cylindrical.

Assembly in a glove box was a requirement due to the sensitive chemicals involved. Due to the chemistry of the cell being secondary to its optical performance, the materials weren't weighed. Ensuring the cell was actually conductive and electrochemistry could take place was enough to satisfy the cell assembly. Knowing this, more established battery chemicals were used. TiS₂ was used as the cathode material, h-Li(BH₄)_{0.7}(Br)_{0.3} as the electrolyte and Li metal as the anode. These materials were chosen for their proven performance, with Li metal being used to ensure there were enough Li ions present during the cycling of the cell. To assemble, a brass electrode would be inserted into one side of the capillary. $h-Li(BH_4)_{0.7}(Br)_{0.3}$ would be loaded in next along with the other electrode in order to compress it into a solid puck. This was done in order to ensure good contact in between the molecules of the electrolyte so current could easily pass through. One electrode was removed in order to place the TiS_2 inside. Once inside, the electrode was reinserted and pressed. The Li had to be cut down to size from a strip of Li so it could fit into the capillary without bunching or spreading at the sides. Once sufficiently cut, the small square strip of Li was placed on the other electrode and pressed on so it would stick. The Li electrode was then placed back into the cell and the whole cell was pressed together. The sides of the cell were sealed with plasticene and the cell was then placed in a vial and safely removed from the glove box. The unconventional design and size of the cell made using the existing equipment for making and pressing batteries together impossible without modification and custom made parts, so, all the pressing had to be done by hand.

3.4 Measurement details

Initially, the camera and the wave generator were dependent on each other as the camera

was triggered by a pulse wave from the wave generator. This was done in order to precisely know where each image was taken in relation to the battery pulse to test the stability of the electronics in the setup. The triggering was later removed and the amount of images taken was dependent on the sampling rate of the camera. To find interesting intensity spots in the images, a variance calculation was performed. The camera would capture a set number of images and then the code used to operate the camera would find the variance in intensity between these images and save the result. The images were saved as arrays in HDF5 files. The variance made it easier to detect regions where the intensity fluctuated frequently and acted as a form of background correction for the images. The battery was charged in a series of 'on' and 'off' cycles. In an on cycle, the input pulse to the battery would oscillate at an amplitude of 1V for a series of fifty pulses at an offset of 0V. Once the fifty pulses were complete, the offset was increased by 0.2V. This cycle would repeat until 1.8V were reached increasing in 0.2V increments. At that point, after the fifty pulses, the wave generator would turn off and the camera would record images for the same length of time. This was the off cycle. This was done in order to see how the cell might change over multiple runs of the battery being on and off. Three on and off cycles were recorde d for a total of six cycles overall.

To analyse the results, a small region of interest (ROI) of 5x5 pixels was taken. This was initially done on the variance images, but it was found that averaging the variance images per offset in a run could find the regions that have the most intensity changes over time. Six ROIs were taken then in total. These ROIs were then applied back onto the original raw data where the intensity could be tracked across the whole measurement time. Using fast Fourier transforms (FFT), the frequency that the cell oscillates at the most could be found in order to relate the frequency of the wave generator to the intensities in the ROIs.

4. Results

In this section, the results from experimentation are shown. Each step of the analysis is outlined along with why choices were made. The main goal for the results is see if the intensity of light reflected off the cell from the laser oscillates at the frequency of the input wave into the cell from the wave generator. Detecting this oscillating light frequency would mean that the electric field is having a direct effect on the cell. Combining this with impedance and current measurements, it can be demonstrated that the electric field causes changes inside the cell and these changes can be seen optically. Due to the electrochemical nature a battery, these changes would be ion movement back and forth between the cathode and anode. Observing this activity at the interface of the electrode and electrolyte would allow for further, longer measurements to see how the interfaces changes over time.

4.1 Images

As stated, three different light sources were used throughout the course of the project, a halogen bulb, a green laser and a blue laser.



Figure 4. 1 shows a comparison between the different light sources. Image a) is the raw image from the halogen light bulb, image b) is the raw image from the green laser and image c) is the raw image from the blue laser.

There are stark differences between the three images. In image a) the brass electrode can clearly be seen at the leftmost edge of the image, with most of the image being the electrolyte. The macro differences between the electrode and electrolyte are visible, but the minute details of the electrolyte itself, any bumps or ridges or texture in the electrolyte cannot be seen. Seeing no detail in the electrolyte would make analysis difficult down the road so a different approach was taken. In image b), there is a clear distinction between the electrode and electrolyte, the black part being the electrode and the grey part being the electrolyte, however the detail on the electrode is lost. This wasn't much of a problem as it is still clear as to which side is which. Details in the electrolyte can be seen, there are bumps and ridges visible in the image. This showed that using a laser was the right approach. However, the green laser used wasn't stable, the speckle pattern would shift and change over time which shouldn't be possible in a system that's completely fixed in place. This is visible in the movie made using this laser. The blue laser was then tested which resulted in a very stable speckle pattern. The image produced, on the other hand, is not very clear. It is hard to decipher where the electrode ends and where the electrolyte begins. For this reason, the halogen bulb had to be used before a measurement began in order to find out which part of the cell the microscope was pointed at. Stability of the image was the most important factor in determining which light source was the best. If the image had a fluctuating intensity that was caused by the light source, this would have drowned out any signal from the cell material itself, as this intensity change is very small and 26

subtle compared to the intensity changes coming from the light source. So for this reason, the blue laser was deemed the most suitable in order to analyse the cell.

4.2 Background correction

Initially, the background correction was done during the analysis, rather than in real time along with the measurement. The background correction served the purpose of filtering out some of the noise so the resultant signal is more visible in the image and as a graph. The signal in this case is the intensity oscillations given off by the material in the cell when the electric field is applied. For the post measurement background correction, the average of every fifty images was produced and then normalised between zero and one. The camera was triggered to take fifty images for every input pulse into the cell from the wave generator.



Figure 4. 2 are the background corrected and normalised images. The cell only contained LiBH₄. It was measured for ten minutes at 200mHz with a potential amplitude of 1V.

From the background correction, there is a region on the leftmost part of the image that shows some activity, but this data is lost in the normalised image. This means that normalization is of the images is unnecessary for the analysis as too much of the signal is lost.

As the code for the camera was developed, real-time background correction could be done instead of doing it in post. This was advantageous because the measurements became longer over time, capturing more images in the process, so correcting the images in real-time would speed up the analysis later on. For this the variance of the images was calculated instead of the average as using the variance would highlight extreme values, which would show up in the image as more intense spots, signifying a greater degree of activity happening in those regions.



Figure 4. 3 compares the average to the variance images. Image a) is the variance and image b) is the average. The average image is too cluttered to actually pick an interesting point to analyse, whereas the variance shows a region in the left that is the most interesting point.

The variance images were then average per run in order to choose the ROIs.



Figure 4. 4 is the averaged variance frame. This particular image is the average of all the variance frames from the OV offset of the first run.

Averaging the variance frames made ROI selection easier as it reduced the amount of images to sift through in order to find interesting areas. Now, the area that lights up the most over a single run would be taken as the ROI. Using the ROIs obtained from this method, these regions were applied back on to the raw data in order to analyse the intensities of these regions over time. Using such a small area made it so the noise or other random fluctuations in intensity would not impact the any signal that would potentially come from the cell.

4.3 Analysis tests

In order to ensure that the tests done to an actual cell would be sensitive enough to obtain results, the equipment was tested using a capacitor and an LED. The capacitor was used in order to test if the current and impedance could be detected and the LED tested if the intensity of light emitted scaled with the offset and if the input pulse from the wave generator to the LED could be detected from the intensity, basically testing the periodicity of the LED.

4.3.1 RC impedance

Ideally, the cells' EDL should perform like a resistor capacitor circuit. In practice, the complex electrochemical processes occurring in the cells when Li ions intercalate will deviate from a purely electrical RC circuit, but it is worth experimenting to compare to what is obtained using the cells. For this circuit, a simple first order RC circuit was constructed and measured using the Keysight LCR meter. A capacitor of 7nF and resistor of 90k Ω was used.



Figure 4. 5 is the Nyquist and Bode plots of the first order RC circuit.

The shapes of the Nyquist and Bode plots are typical with what is found theoretically. The semicircle shape of the Nyquist indicates that the current is passing through the capacitor where reactance dominates and the real impedance increases faster than the imaginary impedance. As the current starts to flow through the resistor, resistance dominates and the imaginary impedance increases much faster than the real impedance. There is a clearly defined cut off frequency present between 10^5 and 10^6 Hz, where the absolute impedance decreases. This is because the RC circuit acts as a low pass filter, filtering out the high frequency components. The impedance in this circuit is quite high as the resistor used was high, but the shapes of the graphs should be comparable to the shapes of the Nyquist and Bode plots of the cells. It is important to note that the current passing through an RC circuit follows the formula:

$$V(t) = V_0 e^{-t/RC}$$

Where V is the voltage, t is time, R is resistance and C is capacitance. This shows that the current response of an RC system to voltage should follow an exponential decay.

4.3.2 LED

In order to see if the method for analysis could pick up on the periodic waves coming from the wave generator, an LED was used. The LED would blink at the prescribed frequency set by the wave generator. In essence, the LED acts as the ideal conditions for what could be observed in the cell. Firstly, the variance of the LED over time was tested.



Figure 4. 6 shows the variance of LED over the duration of the measurement along with the offset voltage level. The trend shows that the variance, which is measured as an intensity, increases as the offset increases and when there is no voltage, the variance is zero.

The variance acts as a measure of activity in the images, so a high variance means there is a high level of activity occurring in the measurement. In the beginning, the amplitude of the input wave from the wave generator makes the LED blink on and off, but as the offset increases, the LED starts to blink brighter and brighter while also providing a constant level of light, which is why the variance increases with the offset.



Figure 4. 7 shows the normalised intensity of the LED at every offset over the whole measurement. The intensity largely follows the increasing offset.

From this graph it is clear that there is a direct relationship between the offset and the intensity. As the offset increases, so too does the intensity of light given off. So intensity and variance plots shows that as the voltage increases, the intensity of light will increase which also increases the variance in the images meaning a higher degree of activity.



Figure 4. 8 is the intensity profile for the first offset. A square pulse with high amplitude was needed in order to have the LED consistently blink.

Zooming in on one offset shows directly how the modulation frequency in the first offset affected the LED. Every pulse elicited a direct response from the LED, increasing its intensity. Any small discrepancies and fluctuations in the intensity could be down to inconsistencies in the LED itself or light from the environment entering the objective.



Figure 4. 9 shows the FFT of a single offset. Notice the largest peak is at 5Hz, which was the frequency of the pulse wave from the wave generator.

Performing an FFT on the intensity of a single offset, the most prevalent frequency can be found. Looking at the FFT graph, there is a large peak at 5Hz, which is the input pulse from the wave generator, showing that the intensity periodically oscillates at 5Hz. The other smaller peaks at around 15Hz, 25Hz and 35Hz could be light from the environment leaking into the objective.

4.3.3 Blank measurement

A measurement with no potential present passing through the cell was taken in order to compare to the intensity graphs of the active cells. This was done as a control for the subsequent measurements.



Figure 4. 10 shows the variance of the cell. The variance is much higher in comparison to the LED.

The variance is quite high in this cell when no potential is passed through and decreases slightly over the whole measurement time. It does not follow the trend found in the LED, increasing with increasing offset, so the variance is down to just the laser fluctuating over time.



Figure 4. 11 is the intensity of the cell over the entire measurement.

The intensity spectrum is comparable to the variance, in that at the beginning of the measurement there is high intensity and towards the end of the measurement there is low intensity. No oscillations in intensity can be seen in this graph, which is as expected when no potential is passed through the cell.



Figure 4. 12 is the FFT of the intensity profile.

From this FFT graph, no single frequency dominates. This is as expected because with no electric field acting on the cell. No electric field means no ions flowing in the cell so no oscillating frequency can be found in the FFT. The intensity profile doesn't have a clear defined oscillation in the intensity, it looks very noisy, so when the FFT is performed on this profile, it displays a noisy spectrum of an detectable frequency found. This graph and the FFT of the LED should be kept in mind when analysing the active cells, as they show what no signal looks like and what a very high, clearly-defined signal looks like.

4.4 Active cells

There are three active cells to analyse, a symmetric cell containing $h-Li(BH_4)_{0.7}(Br)_{0.3}$ as the electrolyte and Li as both the electrodes, a cell containing $h-Li(BH_4)_{0.7}(Br)_{0.3}$ as the electrolyte with Li and TiS₂ as the electrodes and a cell containing $LiBH_{4(0.8)}LiI_{(0.2)}$ with Li and TiS₂ as the electrodes. For convenience, the cells will be called cell 1, cell 2 and cell 3 respectively. Most of the parameters for experimentation remained the same throughout, the only changes occurred in the temperature, exposure time and amplification of the current amplifier. All cells were cycled in the CV mode between 0V and 3.6V, with the offset increasing in 0.4V increments. A modulation frequency of 5Hz 32

was used in the pulse shape with an amplitude of 0.02V. Two on cycles and two off cycles were completed for a total of four cycles. The objective used was 20x with an NA of 0.4. A low pass filter was applied to all the FFT of the intensity spectra in order to remove any high frequencies, as any intensity oscillations of the cells tended to be in low frequencies.

4.4.1 Cell 1

The symmetric cell was made in order to test the conductivity of the electrolyte and test the cyclability of the cell design. The impedance of the cell was measured first in order to test if an EDL could form.



Figure 4. 13 shows the Nyquist and Bode plot for the symmetrical cell. From these graphs it is clear to see that an EDL could not form in this cell, which was a very common problem throughout the project.

The Nyquist plot shows no discernable shape which is a big indication that the EDL has not formed. The points of impedance do not correspond to anything and are at random. The impedance is also huge, on the scale of 10⁷, which shows that the resistivity is far too high to see any conductive properties in the cell. Looking at the Bode plot, at high frequencies, the absolute impedance in the cell is in the order of 10⁵, confirming that the cell is not conductive. Non-conductive cells were a major problem throughout the project, even though all the materials inside were confirmed to be conductive. Continuing on with further tests confirmed that the electric field had no effect on the 33

cell and no optical processes could be seen.



Figure 4. 14 shows the current response of cell 1 to the modulation frequency, how it changed with every offset and the current over time.

The current of the battery is incredibly low as can be seen in the graph and is also flowing in the wrong direction to the applied potential. From this, a solid relationship cannot be formed between increasing the offset and the current inside the cell. A general trend for conductivity that was found is that the current of the battery will increase with increasing offset, whereas in figure 4.14 no trend can be seen. The current dips and rises even though the offset is increasing. Looking across the whole measurement, the current behaved wildly. Even when no voltage was present the current still flowed in the opposite direction. These measurements confirm that the cell is not conductive. It was a struggle to get cells that conducted, even if the materials remained the same for each cell.

Moving on to the optical monitoring, it could be predicted that the intensity given off from the cell will have no correspondence with the frequency of the pulses in the electric field which will be explored in the FFT of the intensity.



Figure 4. 15 shows the variance of cell 1 over time, the intensity over time with input voltage and how the intensity reacted to the modulation frequency.

The intensity signal obtained from this cell is dissimilar to the regular repeating intensity that could be seen in figure 4.7 as the any intensity of light that could be detected from the cell would be a lot weaker than the bright intensity given off by an LED. From the intensity profile vs. modulation voltage, it is difficult to see any clear oscillations. The intensity seems to fluctuate randomly. Doing the FFT will expose any underlying frequency that the intensity is oscillating at.



Figure 4. 16 shows the FFT of the intensity of the whole measurement. There appears to be no determinable oscillatory frequency.

As expected, the 5Hz input pulse cannot be seen in the FFT, or any other frequency for that matter. This makes sense comparing with the impedance and current graphs because those graphs show that the electric field has no effect on the cell at all and is reflected in the noisy FFT spectrum. This FFT graph is comparable to the blank measurement, the shot noise of the measurement dominates.

4.4.2 Cell 2

Starting first with the impedance to test if the EDL can form satisfactorily.



Figure 4. 17 shows the Nyquist and Bode plot for cell 2.

The Bode plot follows the general trend of an RC, there is a cut-off frequency where the impedance dips at high frequency. This is due to the low pass filter present, which filters out high frequencies. The Nyquist plot has a strange shape, but doesn't have any out-of-place or erratic peaks, meaning that the system is stable and a capacitive effect can take hold. The complicated electrochemistry inside the cell can alter the shape of the Nyquist away from ideal conditions, especially in the unconventional cell design used for this project. That being said, an EDL is present in some capacity in this cell.



Figure 4. 18 shows the current response of cell 2 to the modulation frequency, how it changed per offset and how the current reacted over time.

The current of the cell decays as expected from the theory, indicating that an EDL is present. Compared to cell 1, the current decay curve is clearly defined as the cell is actually conductive. There is a small reversal of the current when the modulation frequency returns to OV, which means that when the cell is at rest, the Li ions are flowing from the anode to the cathode. This can be seen in the current vs. time graph, when the voltage is OV the current response from the cell is negative. This is mimicking how an actual battery behaves, during the charge the Li ions will flow from the cathode to the anode and vice versa during discharge. In the current vs. offset graph, it can be seen that the current will increase as the offset increases.



Figure 4. 19 shows the variance over time of cell 2, the intensity of the measurement and how the intensity reacted to the modulation frequency.

It is difficult to detect a relationship between the intensity of cell 2 and the input voltage, as was the case in cell 1. The variance doesn't have a relationship with the input voltage as the LED did, it is more or less at random. It is the same situation with the intensity profiles, there doesn't seem to be a relationship with the offset or the modulation frequency. The on and off runs have very similar intensity profiles, it is difficult to see if the input voltage is having any effect on cell 2 that can be seen optically.



Figure 4. 20 is the FFT of the intensity profile shown. No clear oscillatory frequency is present.

As can be seen in the intensity profile, the FFT of the intensity profile doesn't reveal much in terms of clear oscillatory frequencies. There is some very low frequency oscillations present in the 38





Figure 4. 21 depicts the FFTs of the first on run (first two graphs) and first off run (last two graphs).

Taking the FFTs of the first on and off runs, it is difficult to dissociate the two runs. Both have very sharp peaks at very low frequencies in roughly the same places on both. The only real difference between the two is a small bump between the frequencies 10Hz and 15Hz present in the first on run. This small bump is missing in the off run which makes it notable. Even though it is present, it is incredibly weak meaning that the input voltage has a very small effect on cell 2 optically.

4.4.3 Cell 3

To start, the impedance was taken in order to see if an EDL could form.



Figure 4. 22 shows the Nyquist and Bode plots of cell 3.

The Nyquist plot has the typical shape that is observed in literature, indicating a healthy sustaining EDL was able to form readily. The impedance values are much lower also comparing to the Nyquist plot in cell 2, indicating that cell 3 is much more conductive as the resistance is lower. This is reflected in the Bode plot, the absolute impedance is lower in cell 3 than cell 2 by one order of magnitude. There is also a less pronounced cut off frequency in the Bode plot of cell 3 than cell 2, meaning that even at high frequencies there is still a strong capacitive effect present.



Figure 4. 23 is the current response of cell 3 to the modulation frequency, how the current changed per offset and how the current changed over time.

What is immediately evident is that the current response of cell 3 is much higher than that of cell 2, indicating a higher level of conductivity. This is supported by the Nyquist and Bode plots, as the Nyquist has a much better shape, comparable to that of literature, and the Bode plot had a lower level of absolute impedance than that of cell 2. The current response to the modulation shows the decay curve that forms in the presence of an EDL. The current response to the offset less of a linear progression in cell 3 than that of cell 2, which could be down to any numerous electrochemical processes occurring inside the cell, however it generally increases as the offset increases, which is expected. The current also follows the on off runs throughout the measurement, increasing as the input voltage increases and relaxing when there is no input voltage, allowing for minimal discharge.



Figure 4. 24 depicts the variance of cell 3, the intensity of the whole measurement and how the intensity reacted to the modulation frequency.

Not much of a trend can be seen in the variance of cell 3, it seems to follow a random path compared to the input voltage, however, the intensity profile is much more interesting. The intensity appears to fluctuate when there is voltage present and remains somewhat constant during an off run. There are clear oscillations in the intensity during on runs and diminished oscillations during an off run. It is difficult to see the intensity oscillations in comparison to the modulation frequency.



Figure 4. 25 shows the FFT across the whole measurement of cell 3.

It is difficult to make out any frequencies the intensity of cell 3 could be oscillating at when taking 42

the FFT of the entire measurement. There is activity again in the very low regions of frequency, more so than in cell 2.



Figure 4. 26 shows the FFTs of the first on (top two graphs) and off runs (bottom two graphs).

It is clear to see that there is an increase in activity occurring in cell 3 when the input voltage is on compared to when it is off. The signal has a very low frequency though however. It is hard to say if this is a result of the Li ions cycling as the cell completely oxidized by the time the measurement took place. This was a major problem throughout the project as the optical measurements took place in air, not in an inert environment like Argon like batteries should be tested in.

5. Discussion

In this section, the results will be talked about to try and find a reason why the cells behaved the way they did in comparison to each other and the analysis tests.

5.1 Cell design and environment

A constant problem that was faced during the project was cell oxidation. The materials that were used in the cells were very sensitive to air and moisture, as most Li ion battery materials are, which presented a problem that was not easily fixable. The microscope could not be placed in a glove box, leaving the ambient environment as the only option to cycle the cells. Argon gas is constantly pumped through the glove box and air and moisture are kept to an absolute minimum. In regular circumstances, the cells would be cycled in this environment to test how the materials in the cell behave over time and to investigate the electrochemical processes that occur solely between the materials present in the cell, not with moisture and air affecting the results. The absence of the glove box led to the problem of air and moisture reacting with the materials in the cell, fundamentally changing their chemical composition, leading to uncertainty in what is actually in the cell anymore. The new chemical composition inside in the cell could have different properties from the original material the cell was made up of. These properties could be a change in conductivity, a different capacity, energy density, cyclability and so on. It made it tough to say with any certainty that what was observed was a result of the Li ions moving back and forth between the electrodes, or if it was some other compound that formed through the electrolyte or electrodes reacting with air and moisture. In order to increase the reliability and repeatability of this experiment it should be repeated in an inert environment.

Another problem faced was the cell design itself. The cell, as seen in figure 3. 9, was unconventional and different to regular battery cells. Common cell designs would be a coin cell or a Swagelok cell. These are tried and tested designs that are known to work well. These cells can also take advantage of the compatible equipment that aids cell assembly, but they are completely opaque so couldn't be used in this project. For solid state batteries, it is imperative to use a press in order to compress the electrolyte down to a solid puck which ensures that there is good contact within the electrolyte itself, which actually makes the electrolyte conductive. The electrode materials must also be pressed onto the electrolyte puck so good contact between the electrodes and the electrolyte can be made which makes the cell conductive. There needs to be great pressure exerted on the electrode material and electrolyte by the press in order to form this solid puck, which is something that cannot be accurately gauged by hand, as was done in this project. The press couldn't make a puck small enough to fit inside the capillary and, due to the shape of the capillary, a puck couldn't be pressed inside the capillary because it would shatter the glass. So pressing by hand was the best option. Another advantage of using a press is that the pressure exerted on the battery material can be controlled and is known, leading to consistency in the electrode electrolyte contact and cell assembly. This something that cannot be controlled when pressing by hand. It is near impossible to know the exact pressure the assembler's hand is applying to the cell, leading to inconsistent contact between the materials. The puck formed wouldn't be as solid as it would have been had it been formed in a dedicated press. This led to having inconsistent conductivity in the cells. Even if the assembly and materials were the same, some cells simply wouldn't conduct electricity, as was the case for cell 1. In order to get more consistent results, the cell design would have to be changed to a more conventional design and modified for optical access, as using the capillary method is not a good approach.



Figure 5. 1 shows cell 1, 2 and 3 in that order from top to bottom. The electrolyte used was white in colour, which it appears to be in cell 1, but cell 2 and 3 are much blacker in colour. This is due to the oxidation of the electrode and electrolyte materials inside, forming new compounds.

5.2 Ideal comparison

In order to gauge the performance of the cells, they have to be compared to the test analyses. Looking at the impedance, cell 3 has the most similar Nyquist plot to the RC Nyquist plot, meaning it forms the most stable EDL. The Bode plots of cell 2 and 3 have a similar shape to the RC Bode plot, but with a much less pronounced cut off frequency. This was expected because chemical reactions are much more complex than first order electronic circuits, and so can behaved unexpectedly, but the general trend of both fits with the ideal case.

The variance of all three cells strayed from the LED variance trend. They behaved quite randomly with wildly different variance values. None of the cells' intensity profiles or intensity voltage modulation graphs look quite like those of the LED, but that was to be expected. The emission from the LED was always going to be stronger than the scattering from the cells, but the general trend can be compared. It is obvious that the input voltage and frequency modulation has a direct effect on the intensity of the LED from looking at the graph and this is further cemented by looking at the FFT of the intensity profile of the LED. Cells 1 and 2 look closer to the blank measurement in terms of intensity and their FFTs, whereas it looks like the input voltage has some 45

effect of cell 3 just like the LED. Cell 3 is therefore the best cell as it matches closest to the ideal conditions and has optically observable activity.

5.3 Cell performance comparison

From the results, it is clear to see that cell 3 performed the best out of all the other cells. Looking at the impedance plots, cell 3 has the most ideal shapes out of all three of the cells with also lower impedance values. The Nyquist plot of cell 3 has the correct shape from what is observed in literature, whereas cell 1 and 2 don't. Cell 1 doesn't have a shape, it appears to be random, and cell 2 has an unorthodox shape but is still conductive. The semicircle shape and tail of the Nyquist of cell 3 indicates that a good EDL has formed and the Li ions can pass through from the electrodes to the bulk electrolyte effectively, while it looks like that cannot happen in cell 1. Based on other conductivity tests, it seems like it can happen in cell 2, but the shape of the Nyquist is very strange and hard to explain. Cell 2 and 3 have very similar Bode plots. They have similar shapes and their cut off frequencies are quite close together. The major difference between the two is that the impedance of cell 3 is lower than cell 2, indicating that cell 3 is overall more conductive than cell 2. This is further explored in the subsequent conductive tests. Cell 1 has an erratic Bode plot with very high impedance values compared to cell 3.

Both cell 2 and 3 display the current decay curve that occurs in the presence of constant voltage. This confirms that the cell 2 does in fact form an EDL. There isn't much of a difference between the two cells in their response to the input voltage, only that cell 3 has a higher current response, which is illuded to when looking at the impedance graphs. This higher current is down to cell 3 being more conductive than cell 2 as it has lower resistance. $LiBH_{4(0.8)}Lil_{(0.2)}$ appears to be a more conductive electrolyte based on these results than h-Li(BH₄)_{0.7}(Br)_{0.3} and thus better suited for the small cells used in this project.

The intensity profile of cell 3 clearly shows a response to the input voltage in the form of intensity oscillations, and no response when there is no input voltage. This is in contrast to cell 1 and 2, where their intensity profiles didn't evoke such a response. Cell 1 and 2 are much more similar to the blank measurement intensity profile and FFT, leading me to believe that nothing remarkable happened optically. There was no notable difference in intensity between the on and off cycles of cell 1 and 2. This was further explored in the FFTs of the intensity profiles. While there didn't appear to be any difference between the FFTs of the on and off cycles of cell 1 and 2, there was a small difference between the on and off cycles of cell 3. The FFT portrayed a very low frequency difference between the cycles, informing that the intensity oscillations had a broad wavelength. This was the most promising result obtained as it was very difficult to not only get a conductive cell but also see that the input voltage affected the intensity of light given off by the electrochemical processes occurring inside. Cell 2 was clearly conductive and had some sort of electrochemical properties but these couldn't be seen optically. It is not completely correct in saying the only difference between cell 2 and 3 was the change of electrolyte, as other factors could affect the cell like the assembly or storage. As previously discussed, the oxidation of the cell materials was a major challenge, so any new oxidised compounds formed in either cell could affect the conductivity or cyclability of both cells. It is difficult to say with certainty that the intensity oscillations are a result of the Li ions cycling or if it's the oxidised compounds in cell 3 that are responding to the input voltage. As can be seen in figure 5.1, the exposure to air has left the cell blackened so it is hard to know the exact make-up of the internals of the cell. For future investigation and experimentation, LiBH_{4(0.8)}Lil_(0.2) is a good choice for the electrolyte.

6. Research retrospective

Throughout the project there was a conscious effort to satisfy the FAIR battery ideals. This dictated what choices could be made and what the goals were. The goals were mostly satisfied, but some compromises had to be made. The compromises mostly came in the equipment used. The AD2 46

was a very useful piece of equipment that transcended the use of a separate wave generator and oscilloscope while also being smaller and a lot cheaper, which allows the bar for entrance into optical monitoring to be lower, but other equipment like the impedance meter, laser and current amplifier were a lot more expensive. On a budget, some serious thought would have to be put in to decide if it is necessary to use these pieces of equipment. The AD2 does have an in built impedance meter inside, but I never got around to figuring it out as the Keysight LCR meter was freely available with the code to operate it already written, meaning I wouldn't have to develop new code to run the impedance meter on the AD2 which would have been more time consuming. The current amplifier could also be swapped out for a resistor, which is dramatically cheaper, but because the current in given out by the cells was so low and actually quite a challenge to detect in the first place, the current amplifier just made the whole process quicker and easier. At the flick of a switch the current could be detected and the signal could be adjusted and amplified so readily it was hard not to use it. Going forward with the knowledge obtained from this research, it can be swapped out for a resistor to lower but in costs and make the equipment less complex. The laser is one piece of equipment that would be very difficult to part ways with. It surpassed the other light sources in its stability and functionality that it's worth the cost to use it. A piece of a equipment that would be very useful for the future of this project would be a galvanostat. Incorporating a galvanostat into the electronics would allow for constant current (CC) charge mode, instead of just the CV that was used in this project. Using CC would bring the project closer to what is done in literature and make the results more comparable with fellow battery researchers.

All this equipment fit neatly around the microscope, that was designed and made within a day and is easily reproduceable. It didn't need any specialist pieces or materials to be ordered, however it did need a very stable environment to operate and obtain reliable results, but this is a given in optics and is absolutely necessary. The camera detector used, while pricey, wasn't the most expensive camera money could buy and fit into the goals of the project quite snuggly.

The cell is one of the biggest sticking points of the project that has been thoroughly discussed already. Its deviation from regular cell design that is in use made it difficult to reliably obtain data. It did, however, satisfy the goal of the project for optical access, but going forward, it would be wise to try to modify an already existing coin cell that has an optically accessible component to it, like building a glass face for example. This would just simplify the cell construction and would allow for different materials to be tested, such as using liquid electrolytes. Liquid electrolytes were tested using this cell, but the capillary was to small which made the whole process far too difficult to do and was quickly abandoned, sticking to just all solid battery components and materials.

The code that was written can operate the AD2's wave generator and oscilloscope quite easily and can also produce the graphs used in the results section. The code went through many iterations but it was finally refined down so that it's easily readable and tunable. It greatly aided in analysing the charge and discharge cycle of the cells. The next step for the code would be to make a GUI around it that can display the captured frames live as a video.

Something interesting happened with cell 3, which was the very last cell that was made. The LiBH_{4(0.8)}Lil_(0.2) electrolyte seems to be the way forward and had I more time, I would investigate more cells using this electrolyte. Optical monitoring is a very useful and interesting novel approach to battery monitoring and should be investigated further. There are some teething pains due to how new this form of battery monitoring is and plenty more experimentation is needed.

7. Conclusion

In conclusion, battery cells were designed and constructed for optical access and successfully charged and discharged in the CV mode. The electrochemical response of the cell was monitored simultaneously using the AD2 and Keysight LCR meter and Basler camera and laser in order to track how the cell changed over time. The cost of equipment was kept as low as possible in order to allow the most amount of people access to experimentation. The results, had a positive spark at the very 47

end which is reason enough to continue the investigation. With a more refined and conventional approach to cell assembly, there is the potential for very promising results.

References

- Muñoz-Márquez, Miguel Ángel, Damien Saurel, Juan Luis Gómez-Cámer, Montse Casas-Cabanas, Elizabeth Castillo-Martínez, and Teófilo Rojo. "Na-Ion Batteries for Large Scale Applications: A Review on Anode Materials and Solid Electrolyte Interphase Formation." Advanced Energy Materials 7, no. 20 (2017): 1700463. <u>https://doi.org/10.1002/aenm.201700463</u>.
- Sun, Jie, Hyun-Wook Lee, Mauro Pasta, Hongtao Yuan, Guangyuan Zheng, Yongming Sun, Yuzhang Li, and Yi Cui. "A Phosphorene–Graphene Hybrid Material as a High-Capacity Anode for Sodium-Ion Batteries." *Nature Nanotechnology* 10, no. 11 (November 2015): 980–85. <u>https://doi.org/10.1038/nnano.2015.194</u>
- 3. Energy.gov. "How Does a Lithium-Ion Battery Work?" Accessed February 10, 2022. <u>https://www.energy.gov/eere/articles/how-does-lithium-ion-battery-work</u>.
- 4. Deng, Da. "Li-Ion Batteries: Basics, Progress, and Challenges." *Energy Science & Engineering* 3, no. 5 (2015): 385–418. <u>https://doi.org/10.1002/ese3.95</u>.
- 5. Unknown. "Electrical and Electronics Engineering: This Is How a Lithium Ion Battery Works." *Electrical and Electronics Engineering* (blog), April 4, 2016. <u>http://eee-resetsg.blogspot.com/2016/04/this-is-how-lithium-ion-battery-works.html</u>.
- Väyrynen, Antti, and Justin Salminen. "Lithium Ion Battery Production." The Journal of Chemical Thermodynamics, Thermodynamics of Sustainable Processes, 46 (March 1, 2012): 80–85. <u>https://doi.org/10.1016/j.jct.2011.09.005</u>.
- Zhang, Sheng Shui. "A Review on the Separators of Liquid Electrolyte Li-Ion Batteries." Journal of Power Sources 164, no. 1 (January 10, 2007): 351–64. <u>https://doi.org/10.1016/j.jpowsour.2006.10.065</u>.
- "Design of Electrolyte Solutions for Li and Li-Ion Batteries: A Review." *Electrochimica Acta* 50, no. 2–3 (November 30, 2004): 247–54. <u>https://doi.org/10.1016/j.electacta.2004.01.090</u>.
- Wang, Liguang, Jun Li, Guolong Lu, Wenyan Li, Qiqi Tao, Caihong Shi, Huile Jin, Guang Chen, and Shun Wang. "Fundamentals of Electrolytes for Solid-State Batteries: Challenges and Perspectives." Frontiers in Materials 7 (2020). https://www.frontiersin.org/article/10.3389/fmats.2020.00111.
- Lv, Fei, Zhuyi Wang, Liyi Shi, Jiefang Zhu, Kristina Edström, Jonas Mindemark, and Shuai Yuan. "Challenges and Development of Composite Solid-State Electrolytes for High-Performance Lithium Ion Batteries." *Journal of Power Sources* 441 (November 30, 2019): 227175. <u>https://doi.org/10.1016/j.jpowsour.2019.227175</u>.
- Li, Juchuan, Cheng Ma, Miaofang Chi, Chengdu Liang, and Nancy J. Dudney. "Solid Electrolyte: The Key for High-Voltage Lithium Batteries." *Advanced Energy Materials* 5, no. 4 (2015): 1401408. <u>https://doi.org/10.1002/aenm.201401408</u>.
- Inada, Taro, Kazunori Takada, Akihisa Kajiyama, Masaru Kouguchi, Hideki Sasaki, Shigeo Kondo, Mamoru Watanabe, Masahiro Murayama, and Ryoji Kanno. "Fabrications and Properties of Composite Solid-State Electrolytes." *Solid State Ionics* 158, no. 3 (March 1, 2003): 275–80. <u>https://doi.org/10.1016/S0167-2738(02)00889-5</u>.
- Li, Juchuan, Cheng Ma, Miaofang Chi, Chengdu Liang, and Nancy J. Dudney. "Solid Electrolyte: The Key for High-Voltage Lithium Batteries." *Advanced Energy Materials* 5, no. 4 (2015): 1401408. <u>https://doi.org/10.1002/aenm.201401408</u>.
- 14. MIT News | Massachusetts Institute of Technology. "Toward All-Solid Lithium Batteries." Accessed February 3, 2022. <u>https://news.mit.edu/2017/toward-solid-lithium-batteries-0202</u>.
- 15. "What is a Solid-state Battery?" Accessed February 2, 2022. https://www.samsungsdi.com/column/technology/detail/56462.html.
- 16. Tranter, T. G., R. Timms, T. M. M. Heenan, S. G. Marquis, V. Sulzer, A. Jnawali, M. D. R. Kok, et al. "Probing Heterogeneity in Li-Ion Batteries with Coupled Multiscale Models of Electrochemistry and Thermal Transport Using Tomographic Domains." *Journal of The Electrochemical Society*

167, no. 11 (January 2020): 110538. <u>https://doi.org/10.1149/1945-7111/aba44b</u>.

- 17. Li, Nian-Wu, Ya-Xia Yin, Chun-Peng Yang, and Yu-Guo Guo. "An Artificial Solid Electrolyte Interphase Layer for Stable Lithium Metal Anodes." *Advanced Materials* 28, no. 9 (March 1, 2016): 1853–58. <u>https://doi.org/10.1002/adma.201504526</u>.
- Winter, Martin. "The Solid Electrolyte Interphase The Most Important and the Least Understood Solid Electrolyte in Rechargeable Li Batteries." *Zeitschrift Für Physikalische Chemie* 223, no. 10–11 (December 1, 2009): 1395–1406. <u>https://doi.org/10.1524/zpch.2009.6086</u>.
- Xu, Jiagang, Rutooj D. Deshpande, Jie Pan, Yang-Tse Cheng, and Vincent S. Battaglia. "Electrode Side Reactions, Capacity Loss and Mechanical Degradation in Lithium-Ion Batteries." *Journal of The Electrochemical Society* 162, no. 10 (July 28, 2015): A2026. <u>https://doi.org/10.1149/2.0291510jes</u>.
- Park, Joonam, Jiseon Jeong, Yunju Lee, Min Oh, Myung-Hyun Ryou, and Yong Min Lee. "Micro-Patterned Lithium Metal Anodes with Suppressed Dendrite Formation for Post Lithium-Ion Batteries." Advanced Materials Interfaces 3, no. 11 (June 1, 2016): 1600140. <u>https://doi.org/10.1002/admi.201600140</u>.
- 21. "Wang et al. 2012 Electrochemical Impedance Spectroscopy (EIS) Study.Pdf," n.d.
- Meddings, Nina, Marco Heinrich, Frédéric Overney, Jong-Sook Lee, Vanesa Ruiz, Emilio Napolitano, Steffen Seitz, et al. "Application of Electrochemical Impedance Spectroscopy to Commercial Li-Ion Cells: A Review." *Journal of Power Sources* 480 (December 31, 2020): 228742. <u>https://doi.org/10.1016/j.jpowsour.2020.228742</u>.
- 23. "EIS Study on the Formation of Solid Electrolyte Interface in Li-Ion Battery." *Electrochimica Acta* 51, no. 8–9 (January 20, 2006): 1636–40. <u>https://doi.org/10.1016/j.electacta.2005.02.137</u>.
- Bak, Seong-Min, Zulipiya Shadike, Ruoqian Lin, Xiqian Yu, and Xiao-Qing Yang. "In Situ/Operando Synchrotron-Based X-Ray Techniques for Lithium-Ion Battery Research." NPG Asia Materials 10, no. 7 (July 2018): 563–80. <u>https://doi.org/10.1038/s41427-018-0056-z</u>.
- Young, Gavin, and Philipp Kukura. "Interferometric Scattering Microscopy." Annual Review of Physical Chemistry 70, no. 1 (June 14, 2019): 301–22. <u>https://doi.org/10.1146/annurev-physchem-050317-021247</u>.
- 26. Ortega-Arroyo, Jaime, and Philipp Kukura. "Interferometric Scattering Microscopy (ISCAT): New Frontiers in Ultrafast and Ultrasensitive Optical Microscopy." *Physical Chemistry Chemical Physics* 14, no. 45 (2012): 15625–36. <u>https://doi.org/10.1039/C2CP41013C</u>.
- 27. Merryweather, Alice J., Christoph Schnedermann, Quentin Jacquet, Clare P. Grey, and Akshay Rao. "Operando Optical Tracking of Single-Particle Ion Dynamics in Batteries." *Nature* 594, no. 7864 (June 2021): 522–28. <u>https://doi.org/10.1038/s41586-021-03584-2</u>.
- Cole, Daniel, Gavin Young, Alexander Weigel, Aleksandar Sebesta, and Philipp Kukura. "Label-Free Single-Molecule Imaging with Numerical-Aperture-Shaped Interferometric Scattering Microscopy." ACS Photonics 4, no. 2 (February 15, 2017): 211–16. <u>https://doi.org/10.1021/acsphotonics.6b00912</u>.
- 29. <u>file:///C:/Users/willh/OneDrive/Documents/utrecht/thesis/BIRLEA_PIM2017.pdf</u>
- Mei, Bing-Ang, Obaidallah Munteshari, Jonathan Lau, Bruce Dunn, and Laurent Pilon. "Physical Interpretations of Nyquist Plots for EDLC Electrodes and Devices." *The Journal of Physical Chemistry C* 122, no. 1 (January 11, 2018): 194–206. <u>https://doi.org/10.1021/acs.jpcc.7b10582</u>.
- Choi, Nam-Soon, Zonghai Chen, Stefan A. Freunberger, Xiulei Ji, Yang-Kook Sun, Khalil Amine, Gleb Yushin, Linda F. Nazar, Jaephil Cho, and Peter G. Bruce. "Challenges Facing Lithium Batteries and Electrical Double-Layer Capacitors." *Angewandte Chemie International Edition* 51, no. 40 (2012): 9994–10024. <u>https://doi.org/10.1002/anie.201201429</u>.
- Damaskin, Boris B., and Oleg A. Petrii. "Historical Development of Theories of the Electrochemical Double Layer." *Journal of Solid State Electrochemistry* 15, no. 7 (July 1, 2011): 1317–34. <u>https://doi.org/10.1007/s10008-011-1294-y</u>.
- 33. Inc, Matsusada Precision. "Electric Double-Layer Capacitors | Tech." Matsusada Precision. Accessed November 25, 2022. <u>https://www.matsusada.com/column/edlc.html</u>.