Impedance Spectroscopy on Metal Halide Perovskites to Produce a Temperature Dependent Series

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ABSTRACT

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Metal halide perovskites are a subject of considerable interest in the fields of materials science and engineering due to their cheap manufacturability and wide array of applications as semiconductors. The method of impedance spectroscopy is examined in this thesis as a way in which these materials can be studied and characterized. An experimental design for temperature dependent impedance spectroscopy of these materials is proposed. Challenges arising from the experimental setup including stray capacitances, lead impedances, and contact resistances are addressed and methods to correct for those effects are given.

Keywords: Metal halide perovskite, hybrid perovskite, Impedance spectroscopy, Temperature-dependent

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CH. 1

Introduction

1.1 Overview of perovskites

Many of the most important innovations of the last century have been made possible due to the development and use of semiconductors. Because of their unique properties, semiconductors have been instrumental in the creation of a variety of applications, from electronic circuit elements to solar cells. Research into semiconductors continues as technological solutions become more commonplace in nearly every industry.

While the most well-known, and widely used, semiconducting material remains Silicon, other materials are finding more and more use today. Hybrid organic-inorganic perovskites are a class of semiconducting materials that have seen increasing popularity in recent years. The excitement over these materials is due in large part to the ongoing research that has shown exceptional promise for these materials in solar cell applications. Over the last couple decades of research perovskite solar cells have seen an increase in efficiency from around 3% to over 20% — a massive increase in comparison to most other materials.[1-2]

Perovskites are a class of materials that follow a particular crystalline structure; this structure is also referred to as the perovskite structure. This structure was first identified as the structure of CaTiO3.[3] However, many other combinations of atoms have been used to create the same or similar crystalline configuration and thus are perovskites as well.

Within the broader category of perovskites is a subcategory referred to as hybrid organic-inorganic perovskites. For the sake of brevity, these materials will be referred to as hybrid perovskites for the remainder of this paper. Hybrid perovskites consist of layers of an inorganic perovskite separated by layers of an organic molecule, typically a longer organic chain. Like the broader category of perovskite, there are many variations of hybrid perovskite, consisting of different perovskite layers and different organic molecules.

Because of the wide variation of available hybrid perovskites sharing a similar structure but having different components, hybrid perovskites are of particular interest to those researching semiconducting materials. Different variations in the composition of the material yield different electrical and magnetic properties. Properties such as band gap, exciton binding energy, exciton lifetime, and dielectric response can be affected by the chemical makeup and physical layering of the material and have the possibility of being chosen specifically for the desired application. The tunable nature of perovskites, along with the cheap cost of manufacturing, make them a topic of considerable importance in the fields of physics, engineering, and materials science.

1.2 Overview of impedance spectroscopy

Impedance spectroscopy is the process of measuring the electrical impedance of a device under testing for a broad range of frequency values of an applied electrical current. This produces what is known as an impedance spectrum, where each plotted impedance value corresponds to a frequency.

In general, impedance values are complex, consisting of both a real and imaginary part. Resistive elements of a circuit or device correspond to the real portion of impedance while inductive or capacitive elements are given by the imaginary portion of the impedance. Materials such as hybrid perovskites are generally much more complicated electrical components than a single circuit element such as a resistor or capacitor. As such, these materials have complex values that can be further analyzed to understand their meaning and context.

Because impedance is a complex value consisting of both a real and imaginary part, impedance spectroscopy data is often represented in the form of Nyquist plots where impedance is plotted as a parametric function with the horizontal axis plotting the real part of the impedance and the vertical axis plotting the negative imaginary part of the impedance. Then, each impedance value is plotted with each point corresponding to a single frequency.

Nyquist plots are especially useful because they can illustrate how the real and imaginary parts change together with changing frequency. These plots allow those studying the impedance spectroscopy data to see how the resistance or capacitance of the device under testing responds to a change in frequency. Using this data, it is common practice to create an “equivalent circuit”, or a model in which the behavior of the device is directly compared to a circuit that would behave in the same way. The elements of these “equivalent circuits” as well as their numerical values then correspond to physical processes present within the device.

1.3 Thesis Outline

The Colton group at Brigham Young University has researched many varieties of hybrid perovskite, probing the effects of the composition on the relevant properties of the material. In particular, much research has been done in measuring the band gap, and exciton binding energy of hybrid perovskites through a process called electroabsorption. In addition, research has also been done on permittivity spectra of hybrid perovskites at room temperature. Currently, work is being done to expand upon that permittivity research with impedance spectroscopy data being an integral component. Little low frequency or low temperature impedance data for hybrid perovskites is currently published.[4-6] The remainder of this thesis aims to outline the current literature on impedance spectroscopy of hybrid perovskites, propose an experimental setup for which further research can be conducted, and demonstrate initial measurements to show the setup's viability.

CH. 2

Current Literature on this Research

2.1 Summary of Published Work

Among the available and relevant research, the key findings of the various authors generally tend to fall into one or more of three general groups:

- Information on the shape and trends of the **Nyquist Plots**
- Information on the elements of the **Equivalent Circuit Model**
- Information on the **General Mechanisms** affecting the hybrid perovskite

The of this chapter will focus on each of these categories, explaining and summarizing the key results from each of the included sources.

2.2 Analysis of Nyquist Plots

As explained in section 1.2, Nyquist plots consist of the real and imaginary portions of the impedance data plotted for each measured frequency. Nyquist plots commonly take the form of a semicircle or a series of semicircles with possible added tails or appendages.

The features of the Nyquist plot can often be associated with other known features of other devices such as a resistor, a capacitor, or (rarely) an inductor, and these devices can correlate to general mechanisms inherent in the device. However, there is no one-to-one relationship between what features exist in the Nyquist plot and what mechanisms, such as resistance or capacitance, are at play. This makes fitting an accurate and meaningful model to the Nyquist plot difficult.

Because of the ambiguity in fitting a model to the Nyquist plot, it is important that measures be taken to understand what might be affecting the shape and trends of the data. Experiments should be done in a manner in which the effects of other unknown variables are minimized.

Within the literature, several factors that influence the shape of the measured impedance data in the Nyquist plot are mentioned. These factors include the illumination, temperature, and atmosphere that the device is placed in as well as the fabrication and use. It is notable that the temperature series tests within the published literature have occurred within a temperature range from 290 K to 490 K.[4-6] Therefore, measuring the temperature dependence of hybrid perovskites has only been done at room temperature and above.

2.3 Analysis of Equivalent Circuit Models

Typically, impedance spectroscopy data is plotted as a Nyquist plot and then the data is fitted to an equivalent circuit model. An equivalent circuit model consists of typical circuit elements such as resistors, capacitors, and (rarely) inductors, that correspond in some meaningful way to physical processes occurring within the material.

To create such a model, one must use other techniques or information to understand what processes are happening in the hybrid perovskite. Distribution of relaxation time, UV-vis spectra, Mott-Schottky analysis, X-ray diffraction, microscopy, photoluminescence spectroscopy, and other tools are used to determine or confirm the interfacial and bulk properties and processes governing the hybrid perovskite.

Each element or fitting parameter within the equivalent circuit model should have physical meaning, tying that parameter with a property or process happening within the material. It is entirely possible to create a perfectly fitting model that mirrors the measured impedance data exactly but has no material significance.[7] Therefore, while there are often significant differences in the equivalent circuit models, similar elements are often incorporated in separate models.

Equivalent circuit models typically consist of resistors and capacitors which represent some sort of phenomenon present in the material. In rare circumstances, inductors are included in an equivalent circuit model, but only in cases in which a negative bulk capacitance is measured.

Within the literature, resistive elements within equivalent circuits are quite varied, with some models using a single series or bulk resistance to describe the hybrid perovskite as a whole and with other models including series resistance, transport resistance, transfer resistance, recombination resistance, diffusion resistance, and other resistive elements all in combination. Capacitive elements within equivalent circuits are also used to describe a variety of phenomena and generally include chemical capacitance, geometric capacitance, and/or dielectric capacitance in addition to other capacitive elements as chosen by the individual author.

2.4 Analysis of Frequency Regimes

Throughout the literature, impedance spectroscopy measurements of hybrid perovskites commonly result in a Nyquist plot consisting of two semicircles or arcs. These arcs correspond to two regimes (a high and a low frequency regime) in which the impedance measurements are affected by different mechanisms.

The primary mechanisms shaping these regions of the Nyquist plot are debated by the authors with most authors agreeing that the low frequency regime is affected primarily by dielectric relaxation while the high frequency regime is influenced by drift-diffusion-recombination processes. While this two-regime approach is used by most authors, a three arc Nyquist plot is possible and may result from the chemical capacitance associated with the electrons having a similar value to the chemical capacitance associated with the holes within the material.[8]

Just as each equivalent circuit model in the literature is unique, the authors' interpretations on what mechanisms define the behavior of the different frequency regimes are all unique. This is due in part to the wide variety of hybrid perovskites that are studied, as well as the variety of applications for which these perovskites were being studied.

CH. 3

Methods

3.1 Experimental Setup Overview

In order to create an extensive temperature series of impedance spectra of several hybrid perovskites, two essential components are required. The first of these components is a method for maintaining and measuring the temperature of the samples, while the second component is a device that can measure the impedance of the sample for a desired range of frequencies. The Colton group uses a Cryo Industries custom-designed closed cycle cryostat to control the temperature of the samples down to cryogenic temperatures. In addition, a Hewett Packard 4192A impedance analyzer is used by the Colton group to measure spectra of impedance, capacitance, and inductance along with any phase shift values.

Together these two pieces of equipment form the bulk of the experimental setup. In practice, a hybrid perovskite sample is placed on the cold finger of the cryostat, connected to the impedance analyzer, and then cooled by the cryostat while under vacuum to the desired temperature where the impedance measurement is then taken and recorded. This process would then be repeated at each desired temperature for each hybrid perovskite sample. However, by having to use both the cryostat and impedance analyzer on the sample simultaneously, several complications must be addressed.

3.2 Connections Between Equipment and Sample

The impedance analyzer in the Colton lab measures impedance using an auto-balancing bridge method and, in order to measure a sample with the impedance analyzer, four electrical inputs are required. These inputs correspond to, and are labeled on the impedance analyzer as, high current, low current, high potential, and low potential. Pre-manufactured fixtures are available for this machine to connect to the sample so that measurements may be done in a standardized way with little correction. However, these test fixtures are insufficient and incompatible with the proposed setup in which the sample is placed in a cryostat, in large part because they are generally too big to fit within the cryostat and the samples we use are typically soldered directly to the wires connected to the impedance analyzer. Therefore, the four electrical inputs are connected via BNC to a series of pins on the cryostat where the BNC connectors share a common ground. From there, the pins connect to four wires within the cryostat to connect with the sample on the cold finger. These wires are soldered to the sample. This setup constitutes what is referred to as a four-terminal configuration.

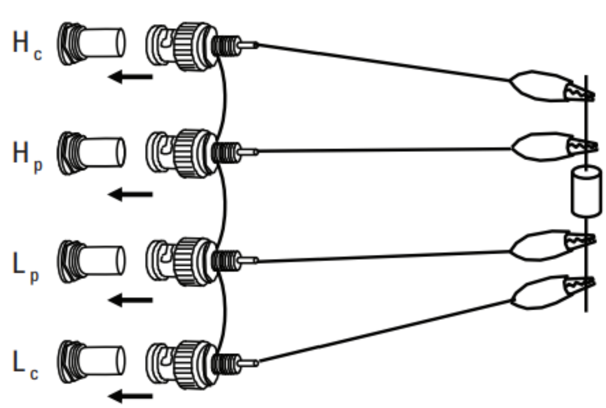

Figure 3.1 A four terminal connection attached to a DUT (device under testing). From [9]

The four terminal configuration is useful for reducing the effects of lead impedances and contact resistances on the measured impedance with accuracy improving especially in the lower frequency range and can measure impedance values as small as 10 mΩ. This is in contract to the simpler two terminal configuration which can only be used to measure impedance values between 100 Ω and 10 kΩ. [9]

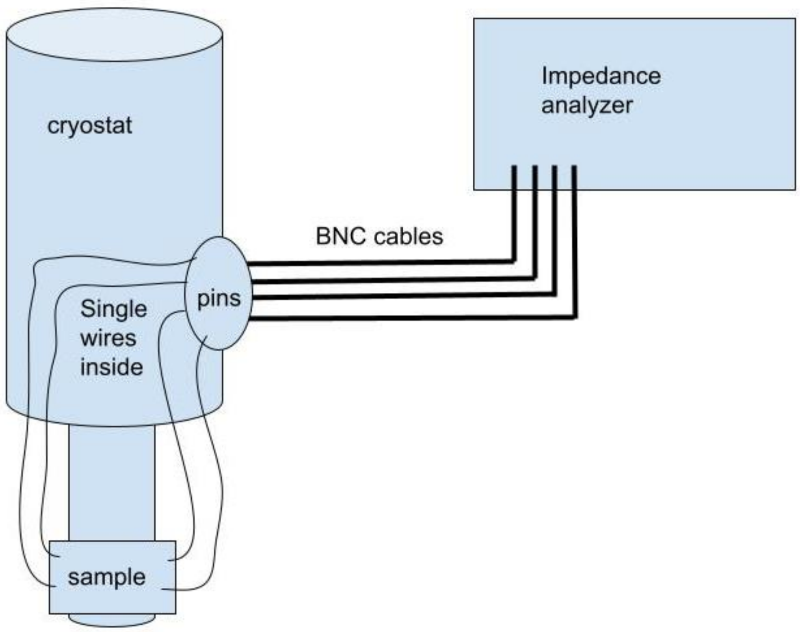

Figure 3.2 A diagram of the experimental setup.

3.3 Correction Formula for Other Effects

While a four terminal configuration can significantly reduce errors arising from some electrical effects within the experimental setup, that alone cannot account for all the errors in impedance measurement caused by the additional setup. Fortunately, there exists known compensation formulas to account for particular features introducing error within our experiment. In particular, the open/short/load compensation given in the Agilent Impedance Measurement handbook can be used for countering the effects arising from non-standard length test cables as well as custom test fixtures, as well as other effects are not present in our current setup.[9] This formula is given as

$$Z_{dut} = \frac{(Z_s - Z_{xm})(Z_{sm} - Z_o)}{(Z_{xm} - Z_o)(Z_s - Z_{sm})} Z_{std}$$

where Z_{dut} is the corrected impedance value of the sample, Z_{xm} is the measured impedance value of the sample, Z_o is the measured open impedance (where there is no sample and the high and low value wires are not touching), Z_s is the measured short impedance (where there is no sample and the wires are soldered together), Z_{sm} is the measured impedance of a known "load" device, and Z_{std} is the true value of the known "load" device.[9]

The Agilent Impedance Measurement Handbook includes additional information on the usage of this compensation formula as well as lots of additional information to consider when taking impedance measurements. Some of the guidelines that are suggested include: using a stable and accurately known device as the load, using a load device that is close to the value of the sample you plan on measuring, and using the load device in the same manner in which the sample is being measured.[9]

CH. 4

Results and Future Work

4.1 Results

Preliminary tests to determine the success of the experimental setup have been conducted demonstrating a notable improvement in accuracy. Previous hybrid perovskite samples have been measured in the Colton lab and found to have capacitance values between tens of nanofarads and tens of picofarads. Using this as a baseline, a 20 pF capacitor was chosen as a mock sample to determine the accuracy of the experimental setup, allowing impedance values measured within the cryostat to be compared to the values when measured with the manufacturer's default fixtures and settings. A 1.5 nF capacitor was chosen as the load device to be used in the compensation formula due to the capacitance values being similar to that of the mock sample. Impedance values were obtained for both capacitors inside the cryostat and with the manufacturer's fixture at the impedance analyzer as well as an open and shorted configuration within the cryostat. The values obtained were measured in the range of 1840.6 Hz to 3987911 Hz.

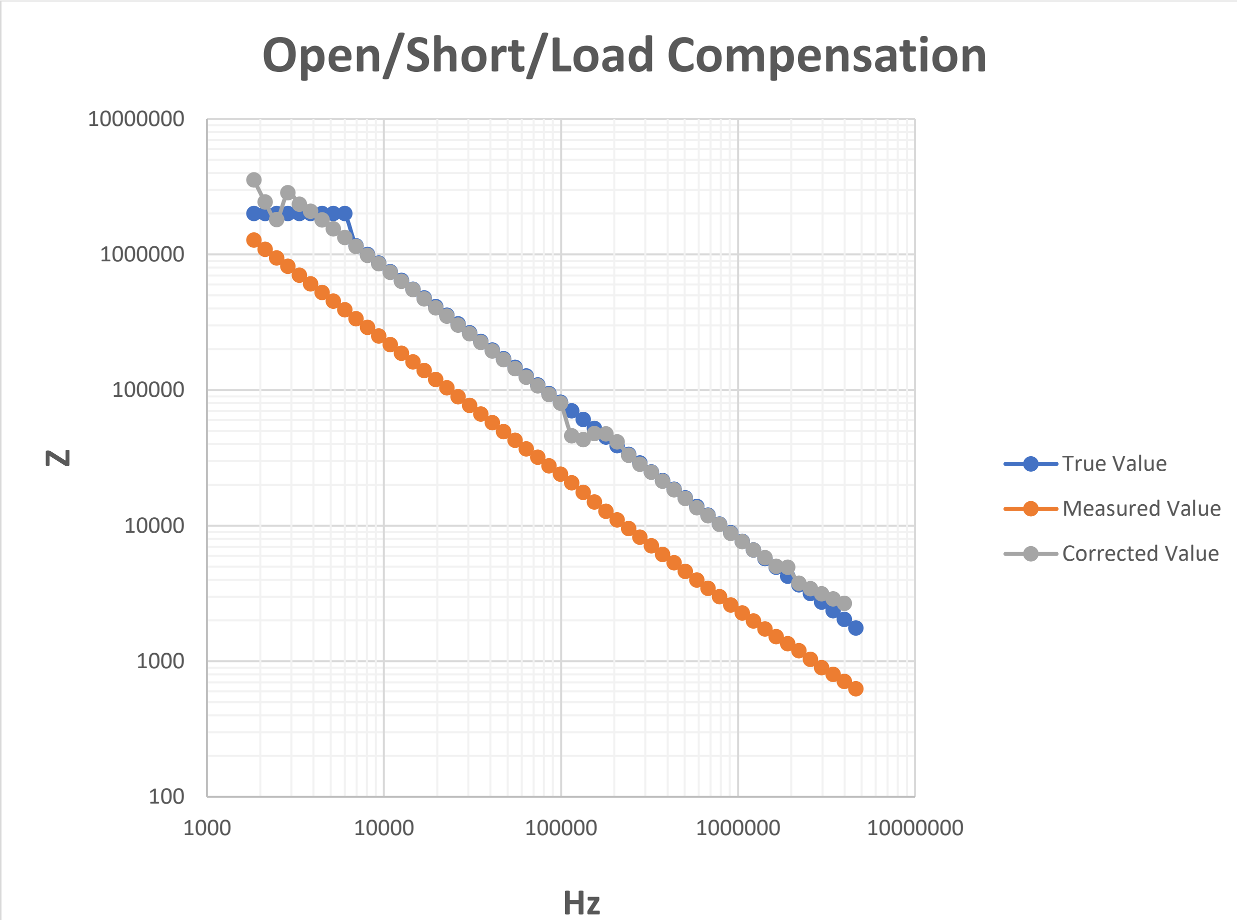

Figure 4.1 The data obtained for the mock sample in the frequency range 1840.6 Hz to 3987911 Hz.

Impedance values obtained when measuring the 20 pF capacitor with the manufacturers test fixture were taken to represent the true impedance values. Other measured values were then used in the open/short/load compensation formula to obtain a corrected value that could be compared to the true values we measured. For example, at 323742 Hz we measure our sample in the cryostat to be 7102 Ω. Our known load is measured within the cryostat at that same frequency and found to be 338.4 Ω. The shorted and open impedances at that frequency are 0.237 Ω and

9979 Ω respectively. Finally, the load device is measured for its true value at that frequency using the manufactured test fixture and found to be 352.3 Ω.

$$Z_{dut} = \frac{(0.237\ \Omega - 7102\ \Omega)(338.4\ \Omega - 9979\ \Omega)}{(7102\ \Omega - 9979\ \Omega)(0.237\ \Omega - \ 338.4\ \Omega)}\ 352.3\ \Omega$$

This gives you a corrected value of 24792.3 Ω. When we measure the true value, we find it to be 24980 Ω. For this single point the remaining error between the true and corrected value is 0.75% while the error between the uncorrected value and the true value is 71.6%. The average percentage error reported for the impedance values measured using the experimental setup was 68.98%. However, when using the open/short/load compensation, that error could be reduced to 8.83% and, when removing outliers (arising from the impedance analyzer being overloaded), be as little as 1.5%.

4.2 Future Work

With the experimental setup shown be viable for impedance measurements that we are interested in, future experiments should be done to measure the perovskite sample itself rather a test capacitor. Once samples can be tested using the current experimental setup, controlled temperature series of impedance spectra can be obtained. As previously noted, there is a notable absence of low temperature impedance and permittivity data available on hybrid perovskites. Future work can aid in furthering this important research.

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