Electrochemical Impedance Testing of Gel Electrolyte

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1. Introduction

UCI Spacecraft Thermal Management Systems (STMS) is a student-led, research-based, senior design project focused on designing, developing, and later launching a variable emittance device (VED). VEDs are satellites that are able to control solar absorbance, thermal conductivity, and electrostatic discharge, resulting in improved performance and longevity under a variety of conditions and stresses [1].

A gel electrolyte is a necessary component of the VED as it creates a transparent conductive medium for electrochromic function, allowing for the thermal regulation. The gel electrolyte is able to function as it does not evaporate in space, has a wide temperature range of operation, and is conductive [1]. Within STMS, the Gel-Electrolyte subteam works with a lithium-perchlorate, propylene carbonate anhydrous (PC), and polymethyl methacrylate (PMMA) gel which allows for charge transfer between the nickel and tungsten sides, producing changing coloration from applied voltage. Different colorations, and thus surface properties, allow for infrared reflectance/emissivity changes, essential to VED function.

The gel's electrochemical properties are pivotal to the functionality of the VED, and thus the electrochemical properties of the gel are tested through electrochemical characterization via electrochemical impedance spectroscopy (EIS) utilizing a potentiostat. Gel is manufactured, and tested with a mockup cell using fluorine doped tin oxide (FTO) coated glass slides, which produces data that is able to characterize the cell's resistance, conductivity, and charge transfer. Further set-ups are explored to test the gel individually through EIS in a four electrode set-up, which would mitigate interference from contact resistance at interfaces and allow for more accurate testing with the usage of reference potentials.

2. Theory

2.1 Electrochemical Impedance Spectroscopy

In order to better understand the electrochemical properties of the gel electrolyte, EIS is used as a valuable electrochemical test for analysis of the gel's properties. EIS has many practical applications, but the underlying methodology is the same–a sinusoidal perturbation is applied (either ac voltage or current) to a system in equilibrium, and the resulting sinusoidal response is measured [2]. The input and output signals are then plotted against one another for interpretation. A typical plot for EIS is the nyquist plot, which plots Z` and Z`` (Z, Z imaginary), which are derived from the magnitude of impedance with the function of the phase angle of the frequency of the perturbation [2]. EIS data can be further utilized to model electric circuits, often with assisting software. The resulting circuit model can be used to quantify the electrochemical properties of the system: resistors often represent electron transfer across an interface, capacitors

represent non faradaic charging, warburg elements represent diffusion, and etc [3]. Visually determining circuit elements is difficult, but common elements like resistors and capacitors can be surmised from looking at the nyquist plot.

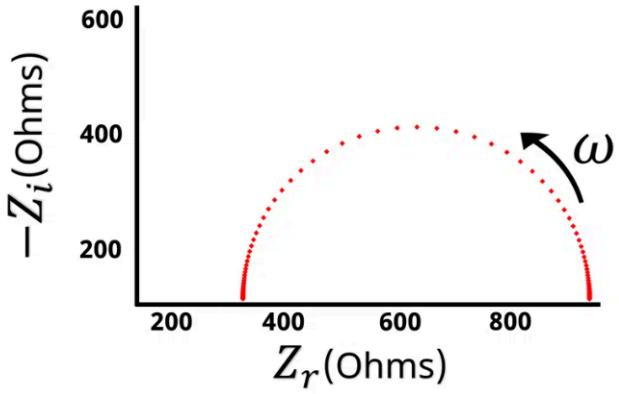


Fig. [1] Nyquist plot of a semi-circle, a common shape for a resistor and a capacitor in parallel. *Image taken from Pine Research. [2]*

2.2 Galvanostatic and Potentiostatic EIS

Choosing which perturbation to use with EIS (ac voltage or current) determines the type of EIS conducted, but should not affect the underlying results–however, the choice of input and output and general testing parameters may affect the accuracy of the results. In potentiostatic EIS, the dc potential is fixed, while a potential perturbation is applied to the cell, with the measured output as current [4]. While in galvanostatic EIS, the dc current is fixed, an ac current is applied, and the output is measured. In fact, galvanostatic EIS is ideal for working with systems with no reference potential (supplied by an electrode with redox reaction), as it is able to mitigate some potential drift. With low impedance devices, it is better to conduct galvanostatic control where precise control of working electrode potential is not needed (potentiostatic control may change the state of the low-impedance device) [4]. Potentiostatic control is usually done with corroding samples, where the higher impedance produces a smaller current response [4].

2.3 Potentiostat and Electrode Set-Up

The testing instrument for EIS is the potentiostat, utilizing the supporting software for operation. A potentiostat typically consists of a working drive, working sense, reference, and counter electrodes–with certain potentiostats such as the SquidStat utilizing an additional sense electrode. The working drive supplies the potential to the system being tested, with current flowing between the working drive and counter electrodes. The potential difference (or voltage drop) between working sense and the reference electrode is calculated to be adjusted with the operational amplifier to properly maintain potential between working drive and counter electrode

[5]. Many electrode set-ups are possible within the potentiostat, often coupling/uncoupling multiple electrodes in two, three, or four electrode configurations.

A simple two-electrode set-up usually couples the working drive with working sense, and the counter sense with the reference. This set-up allows for the working sense and reference to communicate and account for the potential drop between the working drive and counter, but does not provide a stable potential basis for this measurement, and thus is not fully reliable. The four electrode set up is unique because it corrects for the potential drop between the working sense and the reference electrode, which are decoupled and separate as compared to the two electrode set-up. The working sense and reference are both connected to a "reference" system that provides a stable potential—typically the Ag/AgCl electrode, which allows for further accuracy when measuring the potential drop in electrolyte, as it has a stable basis. This way, four-electrode EIS testing is able to correct for the voltage drop between working sense and reference and is furthermore able to test electrolyte impedance directly, as compared to the mockup cell that introduces additional variables through the additional materials, interfaces, and variation in manufacturing [6].

3. Materials & Methods

3.1 Gel Manufacturing

The mixture of an ionic electrolyte in the polymer matrix allows the gel electrolyte. It is essential that the gel not only is able to properly conduct to allow for charge transfer, but that it is able to remain between the slides while during operation of the VED.

To manufacture the gel electrolyte, PC is first added to a beaker. While supplying constant nitrogen gas, lithium perchlorate is added gradually and stirred until completely dissolved. The solution is heated to around 100-110 celsius, and polymethyl PMMA is added gradually until the stirring mixture is fully homogenous, and gel is then taken off of the hot plate and cooled to room temperature. The exact amounts of lithium perchlorate, PC, and PMMA vary for different gels, which impact the gel's properties. Lithium perchlorate acts as the main compounds for ionic movement, and balancing the amount of PC and PMMA is important to the gel's viscosity and thus functionality in space.

3.2 Slide Construction

A mockup cell is created for EIS testing. The slides are first baked on a hot plate at 120 celsius for 15 minutes, with the FTO side facing up (FTO sides are determined via multimeter). Spacers for the slides are created with either ultra-high molecular weight polyethylene tape (UHMW) or through resin printing. FTO slides are combined with a spacer so that the gel sits in between the slides, and is later cased in with epoxy to prevent accidental disassembly. The ends of the FTO slides are covered with a copper current collector, which is where the alligator clips for the potentiostat attach.

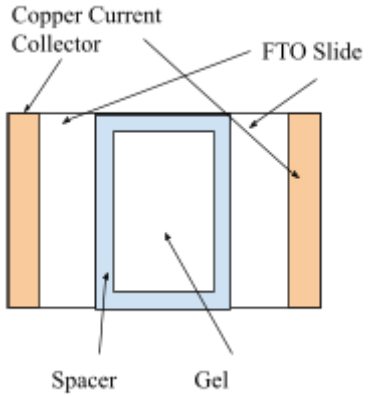


Fig. [2] Diagram of assembled mockup cell.

3.3 Testing

A two electrode setup was primarily used for testing, coupling the working sense with working drive, and counter with reference electrode. Open current potential (OCP) and EIS were performed, with later results using a makeshift faraday cage made of tin foil to block external electromagnetic noise.

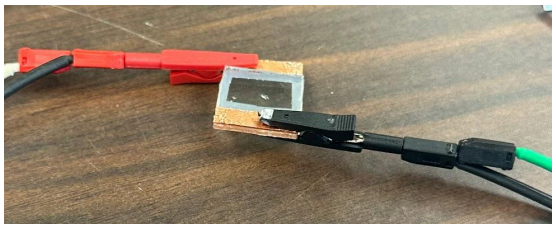


Fig. [3] Two-electrode set-up with mockup cell with tape spacer.

For the parameters for galvanostatic EIS, the DC biascurrent is set to 0 (maintains testing at OCP), frequency to 0.1Hz to 100kHz, 10 steps per decade, and an excitation amplitude of 0.2 mA. For the parameters for potentiostatic EIS, the DC bias potential is set to 0 with respect to reference (sets reference electrode to 0 V, which is inaccurate for the test), frequency to 0.1Hz to 100kHz, 10 steps per decade, and an excitation amplitude of 10 mV.

4. Results

4.1 Potentiostatic and Galvanostatic EIS

Two electrode EIS was conducted with the mockup slide, constructed with the gel electrolyte, epoxy glue, UHMW tape/resin printed spacers, FTO slides, and a copper current collector, producing data that is legible.

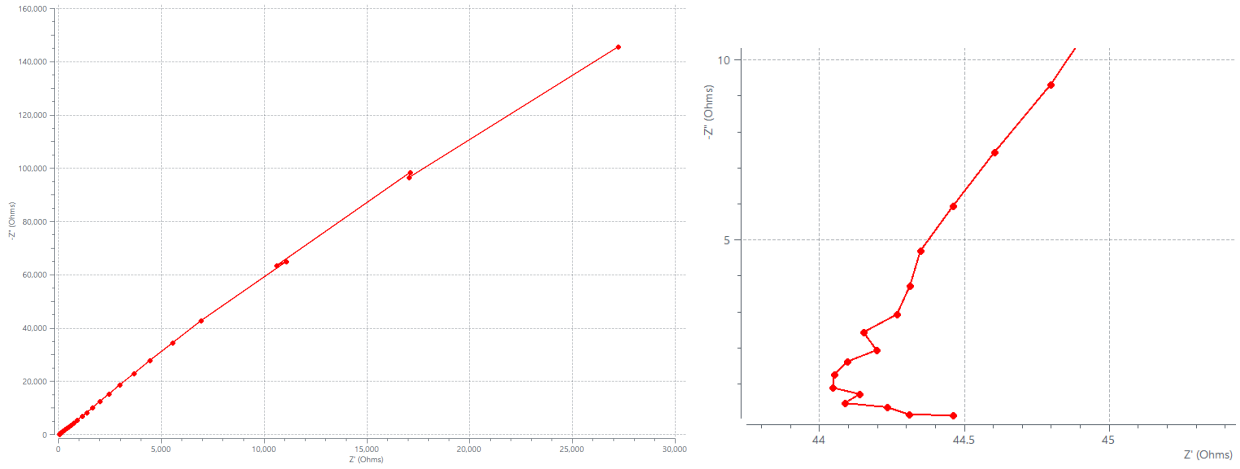


Fig. [4] Potentiostatic EIS nyquist plot and high frequency region.

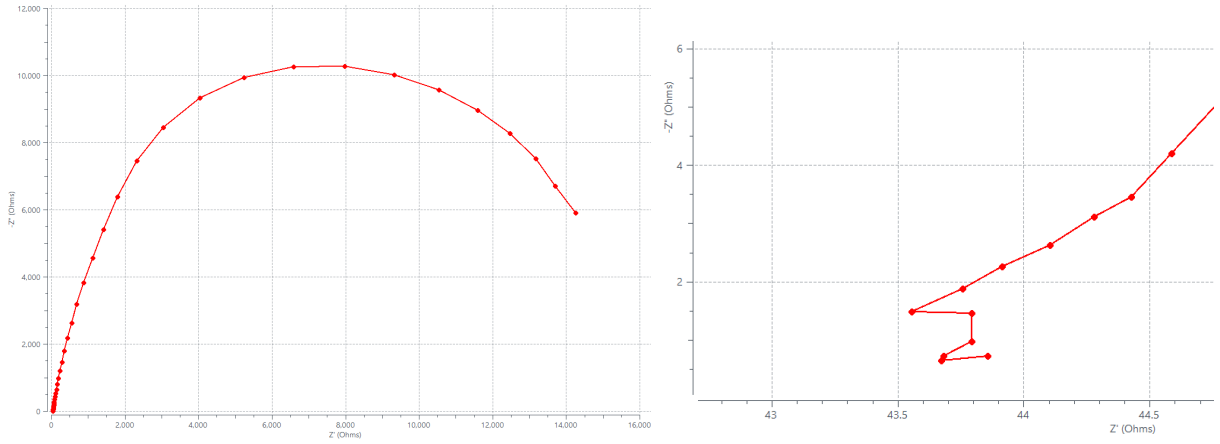


Fig. [5] Galvanostatic EIS nyquist plot and high frequency region.

Notably, both EIS results indicate that the resistance of the final 15% wt Gel is around 43 Ohms, as that is where the EIS graph is estimated to intercept Z'.

5. Discussion

5.1 EIS Results

Using the results, Brendan Alson used MATLAB software in order to interpret permittivity, conduction, and impedance measurements. Although data can still be improved upon–the two-electrode set-up has redeemable results. Additionally, galvanostatic data shows a more legible parabola-like curve, with a less noisier tail (see Fig [5].) in the high frequency region (near the origin) of the Nyquist plot. In the high frequency region, especially in low impedance measurements, mutual inductance from the cell cable plays a role in measurement difficulties–which is expected, as the current carrying electrodes (working and counter) are coupled with the sense electrodes (working sense and reference) [7]. Galvanostatic EIS was proved to be superior to potentiostatic EIS due to its distinct semi-circle shape, indicating similar activity to a capacitor–which supports previous STMS knowledge on glass slide-ion interfaces [7]. However, potentiostatic EIS should not be overlooked in the four-electrode set-up, as testing the gel directly may make the testing type more viable.

6. Conclusion

The resistance, conductivity, and charge transfer of the mock slide is now quantifiable through the EIS data–however, more testing needs to be established to determine what is the ideal composition for the gel, which may be accomplished through the removal/control of mockup cell and two-electrode set-up variables. Current two electrode set-up has reproducible results on an individual slide, but are not currently identical between different slides with the same construction. Some variation between slides is to be expected, but as testing is meant to ascertain the properties of the cell, bubbles, different tape/resin separators, and other issues potentially affect EIS results; to test the gel directly would help remove external variables and understand the electrochemical properties of the gel solely–which will likely have less capacitor behaviour. Incorporating circuit-fitting software in data analysis is also able to improve nyquist plot interpretation.

References

[1] Chandrasekhar, P., Zay, B. J., Lawrence, D., Caldwell, E., Sheth, R., Stephan, R., & Cornwell, J. (2014). Variable‐emittance infrared electrochromic skins combining unique conducting polymers, ionic liquid electrolytes, microporous polymer membranes, and semiconductor/polymer coatings, for Spacecraft Thermal Control. *Journal of Applied Polymer Science*, *131*(19). https://doi.org/10.1002/app.40850

[2] Electrochemical impedance spectroscopy—a tutorial | ACS measurement science au. (n.d.). https://pubs.acs.org/doi/10.1021/acsmeasuresciau.2c00070

[3] *Electrochemical Impedance Spectroscopy (EIS) Basics*. Pine Research Instrumentation. (n.d.). https://pineresearch.com/support-article/eis-basics/

[4] Potentiostatic and galvanostatic electrochemical impedance spectroscopy. (n.d.-b). https://www.palmsens.com/app/uploads/2020/12/PSAN0405-Potentiostatic-and-Galvanostatic-EIS.pdf

[5] *What is a Potentiostat and How Does it Work?*. Pine Research Instrumentation. (n.d.-b). https://pineresearch.com/support-article/what-is-a-potentiostat-and-how-does-it-work/

[6] *Two, three and four electrode experiments*. Gamry Instruments | Market Leader in the Support of Electrochemical Research. (n.d.). https://www.gamry.com/application-notes/instrumentation/two-three-four-electrode-experiments/

[7] Eis of difficult samples. (n.d.-a). https://www.gamry.com/assets/uploads/resources/EIS-Difficult-Samples.pdf