RPC 2020

Virtual Research Presentation Conference

Developing an Electrochemistry-Based Geochemical Framework for Organic Systems

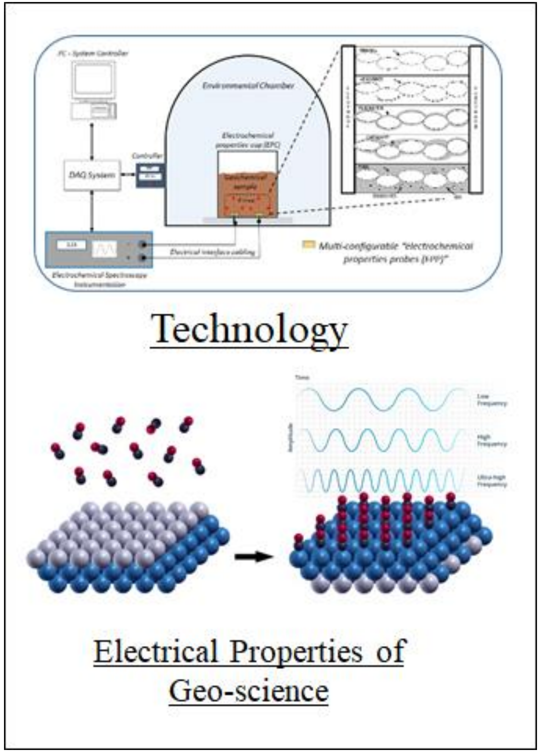
Principal Investigator: Keith Chin (3463)
Co-Is: Laurie Barge (3227), Scott Perl (397D), Prof. Tao Wei (Howard University)
Program: Topical

Assigned Presentation # **RPC-207**

Jet Propulsion Laboratory
California Institute of Technology

Tutorial Introduction

Summary Project Animation



Abstract

A priority for upcoming Mars and Ocean World missions is the geochemical characterization of habitable environments that provide energy for life to thrive, or even for life to emerge in the first place. The key to such habitable or prebiotic environments is chemical disequilibria; such gradients are already observed on other worlds such as Mars caused by the iron redox changes in the surface minerals. Given the existence of these known extreme environments, the emphasis of our project is to develop the capability to perform real-time in-situ characterization on multi-phase heterogeneous material systems relevant to geochemical organic chemistry employing recent advances in the electrochemical technique called dielectric spectroscopy. The response signatures from electrical spectroscopy depends on the chemical and physical properties associated with bulk charge density, interfacial chemical interactions, and transport dynamics, and thus necessitate a more fundamental research approach in the form of atomistic (MM/QM) simulations modeling with our external collaborator at Howard University to provide further guidance and understanding on measurement samples. We are in Year 2 of the Topical RTD and have successfully accomplished all our milestones in terms of technology development and science characterization using advanced modeling techniques on measurement results as highlighted in this presentation.

Problem Description

a) **Context (Why this problem and why now):** Gradients of organic as well as inorganic species are fundamental to supporting life in soils / ices / oceans, and the far-from-equilibrium nature of the overall natural system is what gives rise to prebiotic chemistry, active metabolic networks, and eventually microbial communities. This science goal can only be addressed at the localized scale, not at the global scale. Our project seeks to develop the technology and the eventual dataset of critical electrical signatures of relevant planetary soil systems that range from abiotic organic all the way to biological using advanced electrochemical techniques which enables detection of chemical energetics with high reliability and ultra-sensitivity. The electrochemical method of choice is dielectric spectroscopy given the recent advancements in deployment platforms (i.e., rovers, penetrators, subsurface drilling, etc.) along with its inherent advantages of low power, portability, and in-situ capabilities.

b) **SOA (Comparison or advancement over current state-of-the-art):** Current common methods of characterizing material are ex situ-based such as SEM, XPS, NMR, etc. However, better understanding of chemical and physical gradient processes relevant for habitability must come from chemical kinetics or transport dynamics which can only be obtained from *in-situ, non-invasive* analysis which enable large science returns over the smallest of sampling materials.

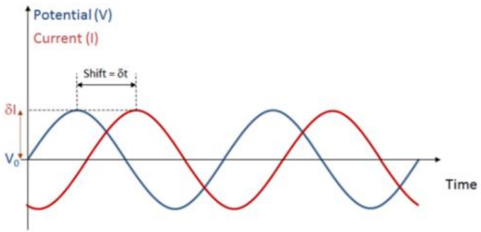
c) **Relevance to NASA and JPL (Impact on current or future programs):** A flight instrument based on this technology has the potential to be deployed ubiquitously in future JPL landers, rover (i.e., concepts for Mars Sample Return), micro-bots (i.e., the PUFFER concept), and submersible missions to icy/watery worlds such as Europa and Enceladus.

Methodology

a) Formulation, theory or experiment description

Electrical spectroscopy is a robust technique not fully realized for planetary exploration applications. The basic principles come from the theories of electromagnetics and wave propagation as described by these adjacent equations. In general, dielectric displacement **D(t)** is a consequence of time differences of material response to outer applied E-field,(**E(t)**. This is the ***phase shift***. From Maxwell’s equations, the complex dielectric function is related to the complex index of refraction (n*). By Ohm’s law, the dielectric loss provides the critical electrical property of conductivity (**σ**), an intensive property unique to all chemical systems.

Our project objectives are **1)** to develop an integrated analog experiment capable of housing representative planetary soil and ice/ and mineral analog chemical systems and performing in-situ EIS measurements over a wide range of environmental conditions. The system will allow detection of *water/ice in all porous medium to <0.1% v/v,* **2)** to test the electrochemical signatures measured in mineral-rich and organic-rich soils (e.g. Martian subsurface analogs) for a variety of soil analogs, and **3)** to develop a theoretical framework to characterize and to understand the electrochemical signatures measured for a variety of organic species and inorganic solutes.



Dielectric displacement:

$$\boldsymbol{D}(\boldsymbol{t}) = \boldsymbol{\varepsilon}^{*}\boldsymbol{\varepsilon_o}\boldsymbol{E}$$

Applied external field:

$$\boldsymbol{E}(\boldsymbol{t}) = \boldsymbol{E_o} \boldsymbol{exp}(-\boldsymbol{j\omega t})$$

Complex dielectric:

$$\varepsilon^{*}(\boldsymbol{\omega}) = \varepsilon'(\omega) - \mathbf{j}\varepsilon''(\omega)$$

$$\boldsymbol{\varepsilon}^{*} = (\boldsymbol{n}^{*})^{2}$$ Index of refraction

Electrical Properties:

$$\boldsymbol{j} = \boldsymbol{\sigma}^{*}\boldsymbol{E}$$ Ohm’s law

$$\boldsymbol{\sigma}^{*} = \boldsymbol{j\omega\varepsilon_o\varepsilon}^{*}$$

Methodology Cont…

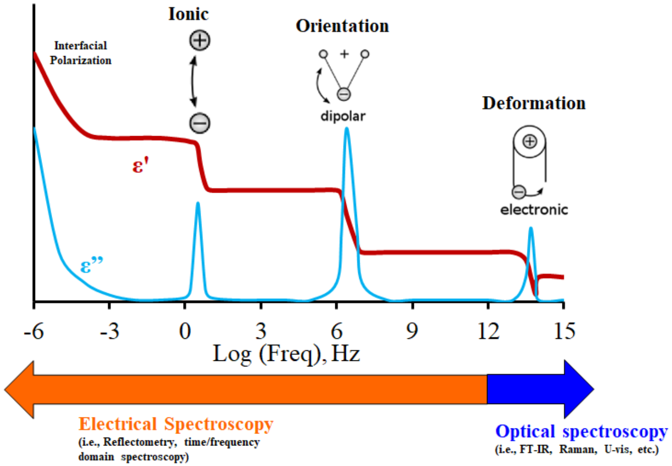
b) Innovation & advancement

Recent advances in electrical spectrometer systems have enable a variety of novel applications for electrochemical spectroscopy. In terms of technology, our project goal is to infuse these systems to develop an integrated testbed capable of in-situ characterization of geochemical systems relevant to ocean worlds and planetary extreme environmental settings. This includes developing novel electrode materials, housing systems, electrical interfaces, and environmental controls to work robustly with all types of dielectric (or impedance) spectrometers. As compared to standard spectroscopy techniques, the frequency range of our dielectric/impedance spectroscopy is substantially higher to over 8 frequency decades. This enables substantially more chemical phenomenon such as dipolar, ionic and interfacial polarization. Lastly, we will apply atomistic simulations to further model the electrical behavior emanating from microscopic level.

Robust benchtop system for soil analog characterization

Ultra-sensitive system (<1ppb)

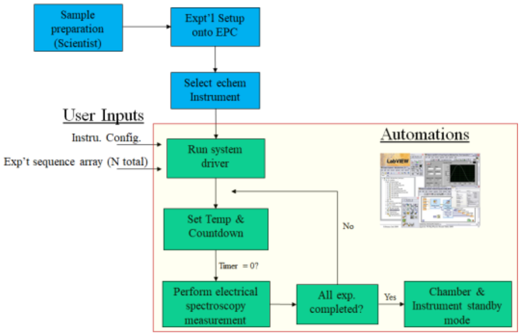
Portable “fieldable” system



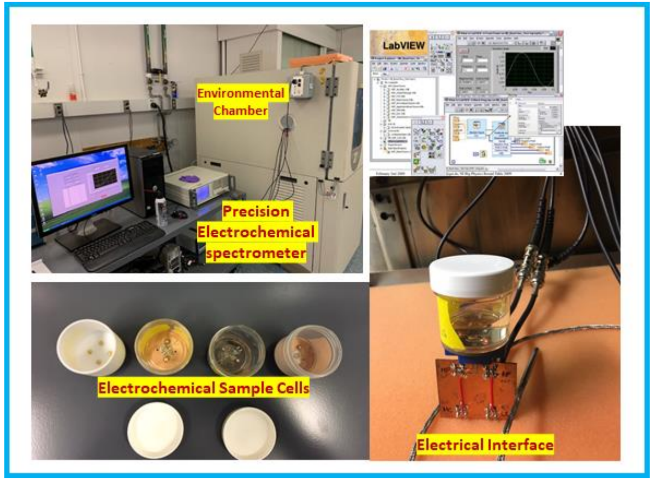
Results

- *We are excited to declare that all of our technology goals have been successfully achieved. The majority of our science goals were also successfully achieved as well, including experimentations and theoretical modeling.*

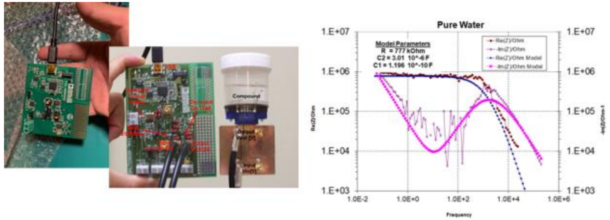
Technology Achievements



Functional Block Diagram



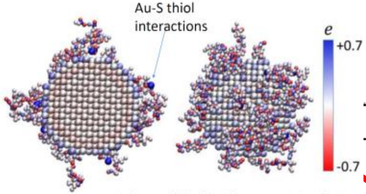
Geochemical Testbeds



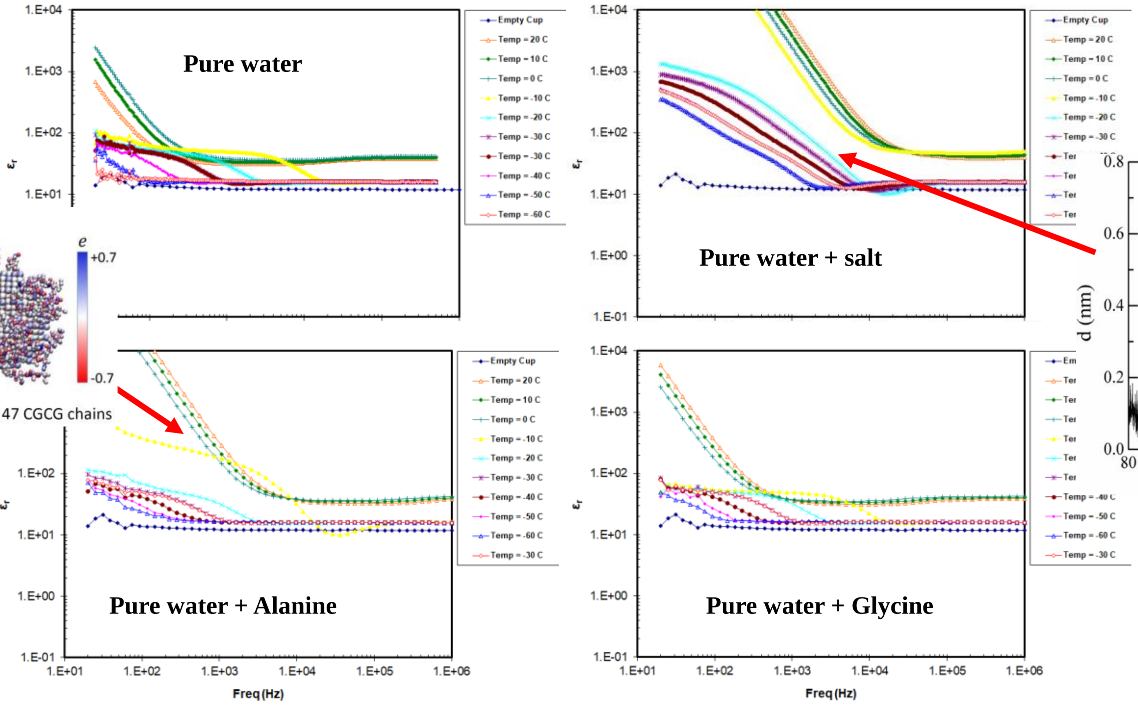
Miniaturization Brass-boards

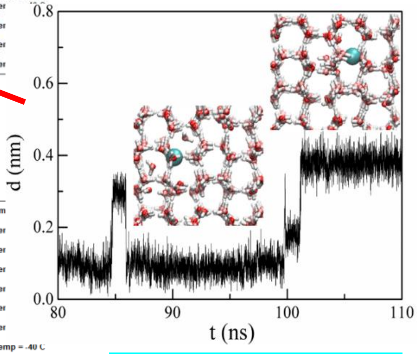
Results – Water/ice Measurements + Simulations

HOWARD UNIVERSITY 1867



Au Nanoparticle modified with 47 CGCG chains





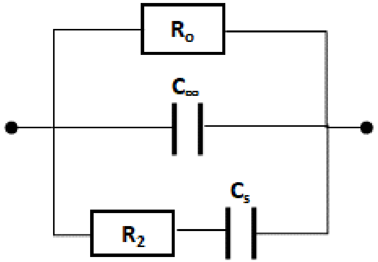
Amino acid have unique polarization properties to Au surfaces on adsorption.

Ion hopping across lattice cavities contributes substantially to the Ice transport properties.

Ref: M.S.J Sajib, et. al., *American Chemical Society*, Presentation, San Diego, CA, August, 2019.

Results – Equivalent Circuits Modeling

Equivalent Circuit Model for Dielectrics:

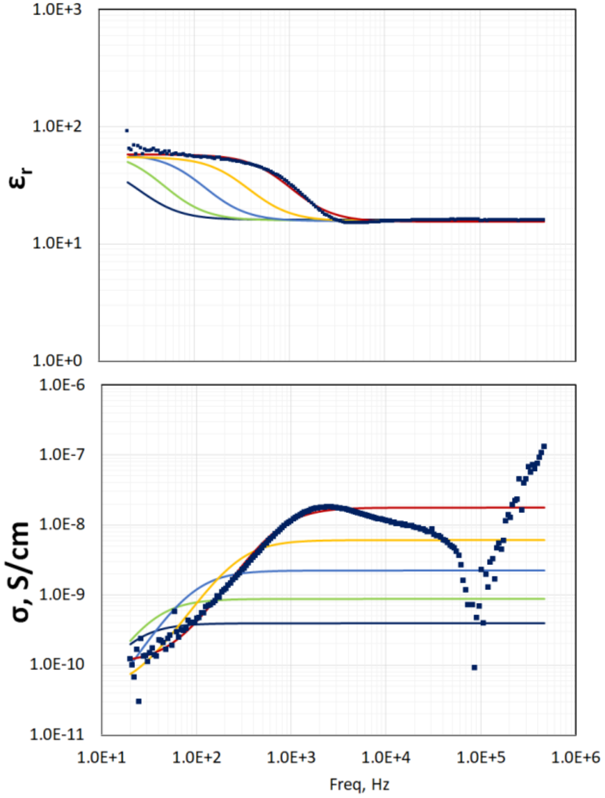


Relative Permittivity:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + j\omega\tau_p} - \frac{j\sigma_o}{\omega}$$

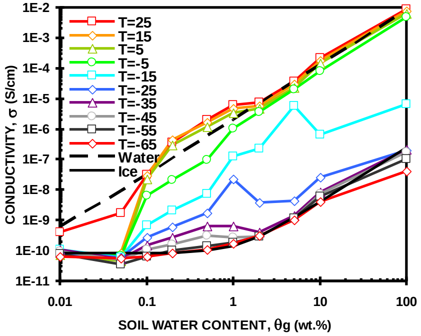
Conductivity:

$$\sigma = \sigma_o + \varepsilon_o\varepsilon''\omega = Y_r/Geo$$

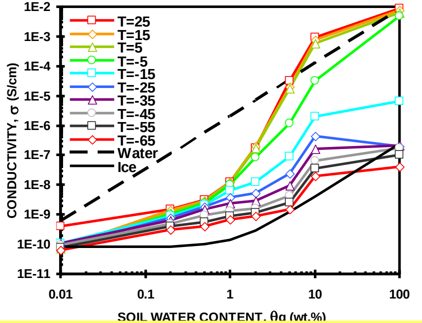


Results – Soil/Water/ice Measurements

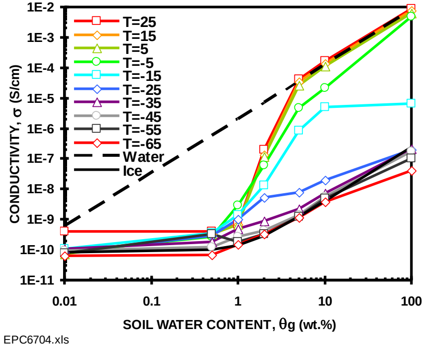
Coarse Silica Sand



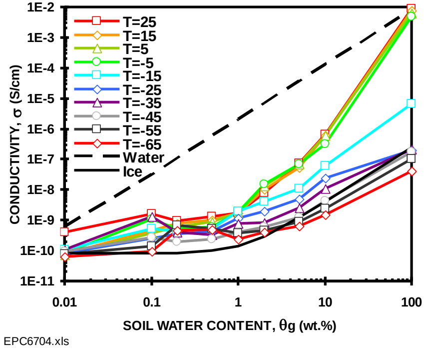
Fine Goethite



Fine Silica Sand



Fine Kaolinite

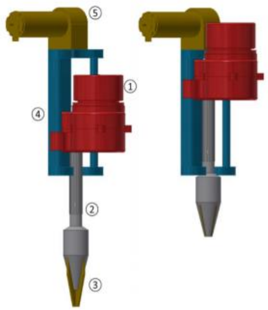


Various soil analogs exhibited unique water potentials associated with film and bulk water properties as well as cation-exchange-capacity (CEC).

Ref: Chin et. al., *Planetary and Space Science Journal*, 2020.

Future Works

- Propose follow-on work to develop an instrument capable of geophysical measurements on various icy ocean world (i.e., Europa) at high pressures (GPa) environments under funded topical RTD program.
- Develop and test subsurface dielectric spectroscopy probes for SPARTA instrument prototype under funded PICASSO program.
- Seek other flight applications in flight programs for Lunar or Mars planetary geosciences.



SPARTA penetration probe design

Tvac system for in-situ geochemical measurements under Lunar or Mars conditions.

Publications and References

- R. Anderson, G. Peters, S. Perl, D. Schoelen, **K. Chin** “Electrochemical Characterization of Planetary Minerals Using in-situ Electrical Spectroscopy” *AGU Conference*, Poster Presentation, San Francisco, CA, 2019
- **K. Chin**, T. Wei, N. Hermis, J. Pasalic, S. Perl, L. M. Barge, “ELECTROCHEMICAL PROPERTIES CHARACTERIZATION OF PLANETARY ANALOGUES BY ELECTRICAL SPECTROSCOPY,” *AbSciCon*, Poster Presentation, Seattle, WA, 2019.
- Md Symon Jahan Sajib, Wilson Jean-Baptiste, **Keith Chin**, Tao Wei, “Interfacial behavior of Amino Acid Residues on Gold Surfaces Studied with Electrical Spectroscopy and Atomistic ReaxFF Simulations,” *American Chemical Society*, Conference Oral Presentation, San Diego, CA, August, 2019.
- **Keith B. Chin**, Robert C. Anderson, Dane A. Schoelen, Evan Eshelman, Michael Paton, Travis Brown, Issa Nesnas, “Enabling new exploration on planetary surfaces: In situ geochemical characterization in soils by dielectric spectroscopy onboard the AXEL rover system” *Planetary and Space Science*, **187**, 104948 (2020).
- Yong Wei, **Keith Chin**, Laura M. Barge, Scott Perl, Ninos Hermis, Tao Wei, “Machine Learning Analysis of the Thermodynamic Responses of In-situ Dielectric Spectroscopy Data in Organic and Inorganic Electrolytes” submitted to *Journal of Chemical Information and Modeling.* In review.