Poster # 3103

Solitary Probe for Electrochemical Analysis and Reporting (SPEAR)
A Multiplex Instrument for Electrochemical Analysis of Habitable Environments

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Background:

Life below a planet's surface relies on reactions between oxidized and reduced chemicals (i.e. redox energy). If an environment is at temperature that is suitable for life and liquid water is present, then, the availability of redox energy indicates habitability. Redox interfaces are therefore priority targets when searching for ET life [1]. On Earth, redox interfaces are common in sediments, wet sand deposits and soil [2] and the shape and evolution of the electrochemical profiles can be used to evaluate whether life is present and active [3]. On Mars, redox interfaces occur between the oxidized top dust and the underlying basalt or olivine sand. Liquid water (another key requirement for life as we know it) was not directly observed on Mars.

Curiosity/Chem-Cam observations have revealed another gradient of interest in the Mars regolith, in the form of Mn-enriched bands below the surface [4]. It is unclear whether a redox gradient is associated with this Mn-rich band as no electrochemical probes are available on Curiosity. Other energy-rich interfaces with liquid water present may also exist on Mars near spring zones, brines, in slope lineae and bellow ice packs. Mineral deposits mixed with liquid phases and ice may be present on Europa, Enceladus and Titan.

In sediments, electrochemical gradients are commonly analyzed by moving electrodes back and forth across redox layers as readings are made. This disruption impedes making repeated measurements that are reproducible and accurate. It also involves using instruments with moving parts and hinders the ability to study chemical evolution of gradients.

Probe:

We have constructed and tested multi-electrode probes for SPEAR instruments that do not require moving parts for making electrochemical measurements (Fig. 1). The working electrodes are made of glassy graphite. The reference electrodes are Ag/$AgCl_2$. We have also developed and implemented means to make solid state electrodes by electro-deposition of polypyrrole on platinum. The counter electrodes are 1 mm diameter platinum wire. Because in this configuration all electrodes are solid state it is now possible to build next generation electrochemical probes for analyzing environments over a wide range of temperature and substrate hardness without using micro-manipulators.

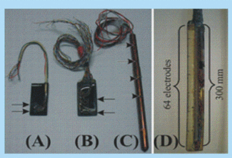

Fig. 1. Multielectrode probes for SPEAR instruments. The probes (A) through D have 8, 30, 4 and 64 working electrodes respectively, and the electrodes stretch over 2, 4, 15 and 30 cm respectively. Arrows show highest and lowest electrodes in (A) and (B) and each electrode in (C). The (A), (B) and (D) probes are made of resin. The (C) probe has a protective metal exterior and can be hard pressed in heavy sediments. The (D) probe is the one used in measurements shown in Fig. 4 and Fig. 5.

Board design:

We have developed a board (schematics in Fig. 2 and PCB in Fig. 3) for a SPEAR instrument. The software was written in Python. The instrument has no moving parts and consists of electronic hardware, software and probes with up to 64 working electrodes, 8 reference electrodes and 8 counter electrodes. The instrument can cycle through any combination of electrodes and make full suites of electrochemical measurements (including redox potential, cyclic voltammetry, differential pulse voltammetry, electrical conductivity and impedance). The SPEAR instrument can analyze chemical gradients and their evolution in wet environments such as mud, sediment, soil and sand, 30 cm deep at 4.7 mm resolution.

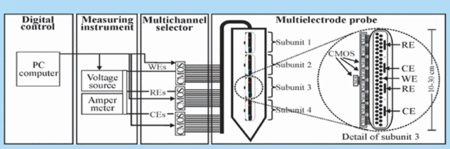

Fig. 2. The schematics of a SPEAR instrument with 64 working electrodes, 8 reference electrodes and 8 counter electrodes.

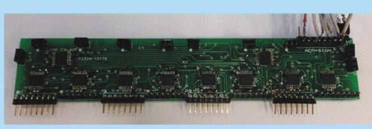

Fig 3. Multichannel circuit board (multiplexer) for a 64x8x8 SPEAR instrument. This unit can control a probe with 64 working electrodes, 8 reference electrodes and 8 counter electrodes.

SPEAR measurements in artificial gradients:

The SPEAR probe was inserted in a 30 cm deep 0.7% agar gel with a H_2S/O_2 gradient. The redox boundary, marked with red arrow is visible as a change of color (from colorless to purple) due to a redox indicator (0.1 % resazurin). The two black dotted lines show the position of the highest and lowest working electrodes on the probe. (E) Vertical redox potential profile produced with all 64 electrodes.

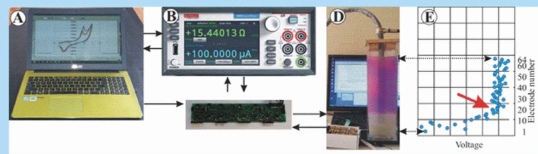

Fig. 4. Measurement setup of a working SPEAR instrument: (A) Computer controlling the measuring instrument and the multichannel selector. (B) Dual channel potentiostat. (C) Multichannel selector (analog multiplexer). (D) Probe with 64 working electrodes, one reference electrode and one counter electrode. (E) Vertical redox potential profile produced with 64 working electrodes.

SPEAR measurements in natural gradients:

Fig. 5 shows SPEAR results in measuring natural gradients (marine sediments). The base layer contains a marine mud with sand, the water sediment interface is at electrode no.30 (marked with green arrows).

In other experiments, the solution or gel at the base of the gradient may contains reducing chemicals (such as ferrous chloride or hydrogen sulfide) and the upper surface of the quartz sand is exposed to air or capped with gel containing oxidizing chemicals.

Chemicals of interests for Mars analogues in redox interface experiments are: oxidants such as nitrate, sulfate, perchlorate, Fe^{3+} and Mn^{4+} and reductants such as ammonium, H_2S, amorphous iron sulfide, Fe^{2+} and Mn^{2+}.

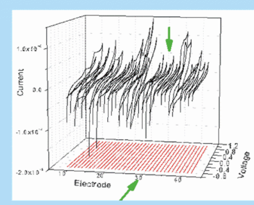

Fig. 5. Sequence of 43 cyclic voltammograms showing the evolution of the CV profile over 20 cm depth in a marine sediment using the SPEAR instrument.

Proposed deployment methods:

With regards to extra-planetary deployments, SPEAR instruments may be parts of a rig, deployed with a lander, rover or flyby instrument (Fig. 6A). After deployment, drilling may or may not be used, depending on the properties of the substrate. The SPEAR's probe carrying the electrodes is lowered into the substrate by means of an actuator. A series of repeated measurements follow until the surface of the electrodes becomes fouled (determined by impedance measurements). The probe is then pulled out through an "electrode cleaning unit" with sonicating brushes and abrasive surfaces. If desired, the rig is repositioned for taking measurements in another location. The cleaned probe is re-inserted for another series of measurements.

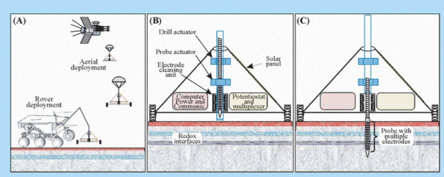

Fig. 6. (A) Proposed method for deploying and using of SPEAR rigs on Earth and Mars for making electrochemical analyses in subsurface environments. (B) SPEAR rig instrument with probe retracted (during deployment, repositioning or probe cleaning). (C) Instrument with extended probe (during measurements).

References

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