SUPPORTING INFORMATION

Reversible Silver Electrodeposition from Boron Cluster Ionic Liquid (BCIL) Electrolytes

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1. General Considerations

Two-electrode symmetrical cells were used to study the electrochemical behavior of the ionic liquid during electrodeposition. The cells were composed of two fluorine-doped tin oxide glass (FTO) separated by a 0.25 mm thick PTFE spacer containing a 9/32” (7.14 mm) diameter hole. The PTFE spacer was coated with a thin layer of silicone grease, placed on the conductive side of the FTO electrode, the PTFE spacer cavity was filled with IL electrolyte, and sealed with a second FTO electrode. All electrochemical cell construction was done in ambient conditions. FTO glass was used instead of tin-doped indium oxide (ITO) because ITO electrodes degraded during electrochemical cycling as judged by the increased resistance of areas exposed to the ionic liquid.

Copper (II) bromide and (CuBr$_2$) were Sigma Aldrich and used without further purification.

Silver monocarborane salt and variants were synthesized as described in Section 3.

Devices were heated by resting on a hot plate set to 60 °C for 1 hour. Devices were then cooled to room temperature for 1 hour before further testing.

2. Instrumentation

NMR: $^1$H, $^{11}$B, $^{11}$B{$^1$H} NMR spectra were recorded on DRX500, AVIII 500 and AV600 spectrometers in ambient conditions unless stated otherwise. Bruker Topspin V3.2 software was used to process the FID data and MestReNova V10.0.2-15465 software was used to visualize the spectra.

Electrochemistry: Electrochemical analysis was performed using a CH instruments CHI630D potentiostat.

SEM imaging: Scanning electron micrographs were obtained using a JEOL JSM-IT100 SEM. Energy-dispersive X-ray spectroscopy was obtained using a JEOL electron beam spectrometer.

Thermal Imaging: An FLIR E40 series camera from AZ technology was used for all emissivity imaging.

Reflectivity Measurements: Laser reflectivity measurements were performed using a 633 nm He-Ne laser and Thor Labs S120VC 50mW power meters interfaced with ThorLabs PM100 Multi-Power Meter Software. The experimental configuration consisted of the laser beam striking the center of the electrodeposition cavity from 23 cm away and the reflected beam was measured with the power meter 28 cm away.

IR Transmission Attenuation: A two-electrode cell was assembled as described above using sapphire substrates coated with a 200 nm thick ITO layer. The cell was mounted in an FT-IR spectrometer and IR transmission spectra were obtained before electrodeposition and after depositing a silver film by applying 2.5 V for 30 seconds. For all cycling measurements, a multipotential stepping program was used. Specifically, the device was pulsed -1.8 V (15 seconds),
0.6 V (40 seconds), 0.8 V (5 seconds), 0.0 V (30 seconds). Total energy transmission was calculated relative to a 100% photon transmission in the 1500 – 4000 cm\(^{-1}\) region.

\[
\frac{\int_{\nu=1500 \text{ cm}^{-1}}^{4000 \text{ cm}^{-1}} (T_{\nu} \times E_{\text{photon,} \nu}) \, d\nu}{\int_{\nu=1500 \text{ cm}^{-1}}^{4000 \text{ cm}^{-1}} (E_{\text{photon,} \nu}) \, d\nu}
\]

Where \(T_{\nu}\) is the percent transmission at a given frequency \(\nu\), and \(E_{\text{photon,} \nu}\) is the energy of a photon at frequency \(\nu\).

3. Precursor Synthesis

**Silver Monocarborane (Ag[HCB\(_{11}\)H\(_{11}\)])**

This salt was made according to a literature procedure.\(^1\)

**Cesium Monocarborane (Cs[HCB\(_{11}\)H\(_{11}\)])**

This salt was made according to a literature procedure.\(^2\)

**S-Butyl Siver Monocarborane (Ag[s-butylCB\(_{11}\)H\(_{12}\)])**

Li[\(\text{closo}-1\)-LiCB\(_{11}\)H\(_{11}\)] was prepared according to literature\(^3\): under an inert atmosphere, 5.0 grams of (CH\(_3\))\(_3\)NH [HCB\(_{11}\)H\(_{11}\)] was dissolved in 10 mL THF in a 20 mL scintillation vial equipped with a stir bar. 2.2 equivalents of 2.5 M \(n\)-butyllithium in hexanes was added and the mixture was allowed to stir for 3 hours. The resulting solution was added dropwise to a 250 mL round bottom flask containing 70 mL hexanes while stirring, resulting in a white precipitate. The solvent was decanted and the remaining white precipitate dried under vacuum. The isolated white precipitate was dissolved in 10 mL THF. Two equivalents of 1-iodo-2-methylpropane were added to the reaction solution and stirred for 90 minutes. The solution was removed from inert conditions, organic solvents were removed \textit{in vacuo}, and the crude product was added to 50 mL H\(_2\)O. The alkylated carborane product was purified using the following salt exchange procedure: (CH\(_3\))\(_3\)NH HCl was added in excess to the aqueous solution, precipitating the (CH\(_3\))\(_3\)NH alkyl carborane salt. The solution was filtered and the precipitate was added to 50 mL H\(_2\)O. Two equivalents of 1-iodo-2-methylpropane were added to the reaction solution and stirred for 90 minutes. The solution was removed from inert conditions, organic solvents were removed \textit{in vacuo}, and the crude product was added to 50 mL H\(_2\)O. The alkylated carborane product was purified using the following salt exchange procedure: (CH\(_3\))\(_3\)NH HCl was added in excess to the aqueous solution, precipitating the (CH\(_3\))\(_3\)NH alkyl carborane salt. The solution was filtered and the precipitate was added to 50 mL H\(_2\)O. The alkylated carborane product was purified using the following salt exchange procedure: (CH\(_3\))\(_3\)NH HCl was added in excess to the aqueous solution, precipitating the (CH\(_3\))\(_3\)NH alkyl carborane salt. The solution was filtered and the precipitate was re-dissolved in approximately 80 mL slightly basic H\(_2\)O with an excess of CsCl. The solution was concentrated down to 30-40 mL, and upon cooling to room temperature the Cs\(^+\) salt of the alkylated carborane product precipitated as a white crystalline solid. A concentrated solution of 1.3 grams of Cs\(^+\) 2-methylpropyl-1-carborane, Cs[(C\(_4\)H\(_9\))CB\(_{11}\)H\(_{11}\)] was prepared by heating in 50 mL of slightly acidic DI water (3-5 drops of concentrated HNO\(_3\)). 1.1 equivalents of AgNO\(_3\) was dissolved in 5 mL or less, and added to the aqueous solution. An off-white precipitate formed immediately, and the solution was cooled to room temperature before filtering. Ag[(C\(_4\)H\(_9\))CB\(_{11}\)H\(_{11}\)] final yield of 960 mg, 79.7%. \(^1\)H NMR (300 MHz, acetone-d\(_6\), 25\(^\circ\)C): \(\delta = 2.83 - 0.45\) (bm, 11H, B-H), 1.61 (d, 2H, \(^3\)J(H,H) = 2.0 Hz) 1.54 (m, 1H), 0.71 (d, 6H, \(^3\)J(H,H) = 2.0 Hz) ppm. \(^{11}\)B[\(^1\)H] NMR (96 MHz, acetone-d\(_6\), 25\(^\circ\)C): \(\delta = -8.3, -9.7\) ppm. \(^{11}\)B NMR (96 MHz, acetone-d\(_6\), 25\(^\circ\)C): \(\delta = -8.2\) ppm (\(^1\)J(H,B) = 145.0 Hz), -9.7 ppm (\(^1\)J(H,B) = 128.6 Hz).
Figure S1A. $^1$H-NMR spectrum of Ag[(C$_4$H$_9$)CB$_{11}$H$_{11}$] in acetone-d$_6$. Note: peak at 2.80 ppm is from H$_2$O.

Figure S1B. $^{11}$B$[^1$H]-NMR spectrum of Ag[(C$_4$H$_9$)CB$_{11}$H$_{11}$] in acetone-d$_6$. 

BCILs were prepared as described in detail below. Generally, 1-butyl-3-methyl-imidazolium bromide ([BMIM]Br), silver monocarborane, and CuBr$_2$ were mixed in a 4 mL vial with gentle heating to ~50 ºC to facilitate melting. Once the BCIL became homogeneous, atmospheric moisture was removed under vacuum with mild heating until the BCIL stopped outgassing. Note: extended exposure to atmospheric moisture leads to a teal colored BCIL, likely due to formation of copper aqua complexes. The original performance of the BCIL can be recovered by dehydrating the BCIL with mild heating under vacuum.

**BCIL-1 / BCIL-1a:** 63 mg (0.250 mmol) of Ag[HCB$_{11}$H$_{11}$] and 137 mg (0.625 mmol) of [BMIM]Br were mixed in a 4 mL vial with gentle heating to ~50 ºC until the mixture became a clear, homogeneous liquid. The liquid was then heated under dynamic vacuum until the mixture began evolving moisture, this was continued until bubbling ceased.

**BCIL-1b:** 63 mg (0.250 mmol) of Ag[HCB$_{11}$H$_{11}$], 68 mg (0.312 mmol) of [BMIM]Br, and 54 mg (0.312 mmol) of [BMIM]Cl were mixed in a 4 mL vial with gentle heating to ~50 ºC until the mixture became a clear, homogeneous liquid. The liquid was then heated under dynamic vacuum until the mixture began evolving moisture, this was continued until bubbling ceased.
BCIL-1c: 63 mg (0.250 mmol) of Ag[HCB_{11}H_{11}] and 108 mg (0.625 mmol) of [BMIM]Cl were mixed in a 4 mL vial with gentle heating to ~50 °C until the mixture became a clear, homogeneous liquid. The liquid was then heated under dynamic vacuum until the mixture began evolving moisture, this was continued until bubbling ceased.

BCIL-2: 63 mg (0.250 mmol) of Ag[HCB_{11}H_{11}], 137 mg (0.625 mmol) of [BMIM]Br, and 11 mg (0.05 mmol) CuBr$_2$ were mixed in a 4 mL vial with gentle heating to ~50 °C until the mixture became a deep blue / purple liquid. The liquid was then heated under dynamic vacuum until the mixture began evolving moisture, this was continued until bubbling ceased.

BCIL-3: 77 mg (0.250 mmol) of Ag[s-butyICB_{11}H_{11}], 137 mg (0.625 mmol) of [BMIM]Br, and 11 mg (0.05 mmol) CuBr$_2$ were mixed in a 4 mL vial with gentle heating to ~50 °C until the mixture became a deep blue / purple liquid. The liquid was then heated under dynamic vacuum until the mixture began evolving moisture, this was continued until bubbling ceased.

5. Normalization of CV Currents

All electrochemical current was normalized to the electrode area, 0.489 cm$^2$. The same working area was used for all studies.
6. Moisture Stability Studies

The assembled device was placed into an Associated Environmental Systems humidity chamber and set to 98% humidity at room temperature for 4 days. CVs (100 mV/s) exhibit equivalent currents and redox features even after 4 days of moisture exposure.

![Cyclic voltammograms of BCIL-2](image)

Figure S2. Cyclic voltammograms of BCIL-2 before placement into moisture chamber (blue) and after 4 days of exposure at 98% humidity (red).

7. Electrochemical Current Reductions

BCIL-2 Current Loss

Gradual current decay was observed upon extended cycling (100 mV/s) of BCIL-2. After 100 cycles, current had dropped to zero. This decay in current is attributed to a loss of ion mobility caused by gradual crystallization.

ITO Degradation

A series of experiments on the reversible plating of Ag (100 mV/s) from BCIL-3 were conducted on both FTO and ITO slides. Significant reduction in device current was seen for ITO
sandwiched **BCIL-3** after only 100 cycles of current sweeping. Conversely, **BCIL-3** sandwiched between FTO substrates displayed current consistency up to 2,000 cycles.

ITO degradation mechanism has been previously reported. Under the presence of an electric field, scratches at the ITO surface initiate degradation. Degradation is exacerbated by increased ITO surface area, the presence of external contaminants such as water and higher device operating temperatures. Measurement of resistivity increase across ITO surface has also been attributed to surface growths, leading to degradation. Such susceptibility to external factors presents manufacturing challenges if BCIL devices were to be implemented in spacecraft thermal control. FTO is a desirable alternative by introducing cycling stability without the need for strict monitoring of surface conditions.

![Figure S3. A) decreasing current of BCIL-3 on ITO after 100 CV cycles, B) stable electrochemical performance of BCIL-3 on FTO after 100 CV cycles. (100 mV/s scan rate)](image-url)
Current Loss Upon Cooling to Room Temperature

As described in text, devices containing BCIL-2 and BCIL-3 were kept at room temperature overnight resulting in the decay of electrochemical features. To further display this “freeze-thaw” phenomenon a second figure detailing the before and after cooling state is attached herein.

**Figure S4.** A) Two-electrode cyclic voltammograms of BCIL-2 before and after equilibrating at ambient conditions overnight and after heating the equilibrated cell to 60 °C, top and bottom respectively. B) Two-electrode cyclic voltammograms of BCIL-3 before and after equilibrating at ambient conditions overnight and after heating the equilibrated cell to 60 °C, top and bottom respectively.

8. Variable IR Emission

Silver Modulates Emissivity

A heated glass slide, coated on one side with a 100 nm thick silver film displayed drastically different emissivity depending on which side is facing the detector. When the uncoated glass side is facing the camera, the glass slide appears “hot”, (Figure S5A). When the glass slide is flipped, the silver mirror is facing the detector and the substrate appears “cold”, (Figure S5B). This apparent difference in temperature is due to the different emissivity of the top surface. Glass appears “hot” because it is an IR absorber (IR absorber at λ<4 µm), while silver films are IR
reflective (<10% IR absorption). Using this unique property, the thermal emissivity of a spacecraft could be controlled by deploying IR reflective surfaces (metallic films).

Figure S5. Top, A) strong IR emission observed when the glass side is facing up, B) strong IR reflection when the 100 nm silver film is facing up. Bottom, cross-section schematic of substrate emissivity experiment.

**ITO-Sapphire IR Absorption**

Reported % change in transmittance value of 18% is believed to be largely affected by IR absorption of the sapphire substrate. Sapphire begins absorbing at ~2500 cm⁻¹ (4 µm) and is not IR transparent beyond ~1667 cm⁻¹ (6 µm), representing a majority of the IR range measured. The limit to IR transmittance can be seen by thermal imaging of an ITO-coated sapphire electrode and a sapphire window on a heated silver coated glass slide, (Figure. S6). Higher heat intensity is seen for the ITO coated sapphire window (green) than the uncoated sapphire window (blue). Importantly, the IR reflectivity of the silver surface is masked by the IR absorptive (emissive) sapphire and ITO-coated sapphire windows. Although we were unable to achieve large changes in IR transmission and reflectivity, these experiments support the feasibility of a BCIL variable emissivity device.
Figure S6. A) schematic of substrate emissivity experiment. B) near-IR thermal camera image of ITO coated and uncoated sapphire windows placed on an IR reflective (non-emissive) silver mirror on glass.

9. SEM Cross Section

In order to assess film thickness in the absence of acetonitrile washing, devices were disassembled and broken in half to image the cross section. An average film thickness of (244 ± 4) µm was determined. EDX measurements indicate excess carbon on towards the top of the film, likely residual ionic liquid. Silver is dispersed throughout, with pockets of higher concentration as consistent with a nucleation limited growth pattern.
Figure S7. Cross-sectional scanning electron micrographs and EDX elemental mapping of BCIL-3 working electrode after deposition of a silver film. Average film thickness was calculated to be $(244 \pm 4) \mu m$.

10. References

7) Lowry, S. Analysis of Rubies and Sapphires by FT-IR Spectroscopy; Thermo Fischer Scientific; Madison, WI; Application Note 51124; 2008.