

Lawrence Berkeley National Laboratory

Molecular Foundry

Title

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

Permalink

<https://escholarship.org/uc/item/5b6432cc>

Journal

ACS Applied Materials & Interfaces, 10(8)

ISSN

1944-8244

Authors

Dziedzic, Rafal M
Waddington, Mary A
Lee, Sarah E
[et al.](#)

Publication Date

2018-02-28

DOI

10.1021/acsami.7b19302

Peer reviewed

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

Rafal M. Dziejczak,^{†,‡} Mary A. Waddington,^{†,‡} Sarah E. Lee,[§] Jack Kleinsasser,[§] John B. Plumley,^{⊥,||} William C. Ewing,[⊥] Beth D. Bosley,^{*,#} Vincent Lavallo,^{*,§} Thomas L. Peng,^{*,⊥} and Alexander M. Spokoyny^{*,‡,∇}

[‡]Department of Chemistry and Biochemistry, University of California, Los Angeles, 607 Charles E. Young Drive East, Los Angeles, California 90095, United States

[§]Department of Chemistry, University of California, Riverside, 501 Big Springs Road, Riverside, California 92521, United States

[⊥]Air Force Research Laboratory, Kirtland AFB, Albuquerque, New Mexico 87117, United States

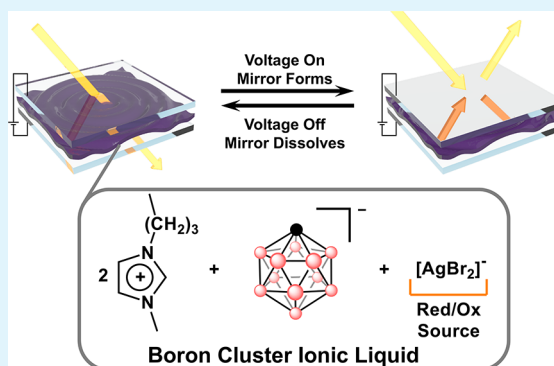
^{||}Department of Chemistry and Chemical Biology, University of New Mexico, 300 Terrace Street Northeast, Albuquerque, New Mexico 87131, United States

[#]Boron Specialties LLC, 2301 Duss Avenue, Building 9, Ambridge, Pennsylvania 15003, United States

[∇]California NanoSystems Institute (CNSI), University of California, Los Angeles, 570 Westwood Plaza, Los Angeles, California 90095, United States

Supporting Information

ABSTRACT: Electrochemical systems offer a versatile means for creating adaptive devices. However, the utility of electrochemical deposition is inherently limited by the properties of the electrolyte. The development of ionic liquids enables electrodeposition in high-vacuum environments and presents opportunities for creating electrochemically adaptive and regenerative spacecraft components. In this work, we developed a silver-rich, boron cluster ionic liquid (BCIL) for reversible electrodeposition of silver films. This air and moisture stable electrolyte was used to deposit metallic films in an electrochemical cell to tune the emissivity of the cell in situ, demonstrating a proof-of-concept design for spacecraft thermal control.



KEYWORDS: electrodeposition, ionic liquids, infrared transparent electrochemical cell, carboranes, boron clusters

Electrodeposited metallic structures are ubiquitous in modern technologies (e.g., batteries, protective coatings, displays, and microchips) and emerging technologies such as resistive memory and reconfigurable electronics.^{1,2} The broad utility of electrochemically deposited structures grows as new electrolytes enable electrodeposition in increasingly challenging environments. Controlled reversible electrodeposition of metallic structures offers tunable optical properties and electrical conductivity along with the ability to adapt the electrochemical system to changing application needs. This adaptability is appealing in the context of reconfigurable electronic components which could extend a device's lifetime through in situ restructuring.

Early electrodeposition methods used aqueous electrolytes because of the solubility of common metal ions.¹ The development of nonaqueous electrolytes has enabled safe electrodeposition of water sensitive metals for new electrochemical applications such as high density energy storage.³ Additionally, electrodeposition from ionic liquids has emerged as a potential alternative to organic solvent electrolytes,

presenting new opportunities for electrodeposition in high vacuum and hostile environments such as electron microscopes and plasma chambers.⁴

Ionic liquids (ILs), salts with low melting points (typically <100 °C), combine the high ion solubility of aqueous media, the chemical flexibility of organic solvents, and low volatility and wide electrochemical windows achievable with molten salts.⁷ The versatility of ILs is increased by tailoring the cation–anion pairs for individual applications.⁵ Yet, despite the numerous cation–anion pairs that can form ionic liquids, much of ionic liquid tunability is achieved by modifying the cationic component.^{5,6} This disparity is largely due to the synthetic availability of cationic molecular scaffolds such as ammonium, phosphonium, and heterocyclic motifs. Conversely, ionic liquids in which the anionic component

Received: December 22, 2017

Accepted: February 6, 2018

Published: February 6, 2018



engenders the IL properties are scarce and the anions are seldom amenable to additional functionalization.^{7–10} Furthermore, the relative instability of commonly used IL anions limits the longevity of IL-based electrochemical devices. This becomes especially problematic when designing systems which require prolonged operation time. Therefore, we sought to develop an ionic liquid that contains a highly stable and easily tunable anionic component. Such “anion-based” ILs could use the metal of interest as the cation and enable high metal loadings suitable for rapid electrodeposition. Anionic polyhedral boranes represent a class of modular molecular building blocks suitable for designing “anion-based” boron cluster ionic liquids (BCILs).^{11,12} Their robust boron-cluster framework provides an anionic scaffold amenable to tuning of melting point, solubility, and redox potential.^{13,14} In this work, we set out to develop an all-ionic electrolyte suitable for reversible deposition of silver films. Specifically, we describe an all-ionic electrolyte to reversibly deposit silver films for the purpose of controlling infrared (IR) emission from an electrochemical cell as a means of actively regulating thermal emission. This technology complements existing approaches to controlling thermal emission from spacecraft surfaces.^{15–18} Importantly, BCILs represent a critical component allowing these devices to perform reliably without having to exclude air and moisture, common contaminants that are introduced during electrochemical device assembly that are difficult to remove.

Silver films play an important technological role as electrical conductors and optical coatings. Silver offers unique advantages over other transition metals because of its high spectral reflectivity, high electrical conductivity, and corrosion resistance.¹⁹ These qualities make silver an attractive metal for tuning the properties of spacecraft surfaces. Additionally, the low volatility of IL electrolytes offers a means of performing electrodeposition in high vacuum environments. Because of its positive reduction potential, only small voltages are required to electrodeposit silver from ionic salt precursors.¹ Electrodeposition of silver was historically performed using cyanide-based electrolytes due to the formation of stable $\text{Ag}(\text{CN})_x^{1-x}$ complexes.¹ However, the toxicity of aqueous cyanide baths lead to the development of silver electrodeposition from ILs and organic solvents.^{5,20} These nonaqueous electrolytes were suitable for reversible silver electrodeposition and served as proof-of-concept works for electrochemically modulated optical films.^{21–23} The reversibility in these systems is attained from the halide-trihalide redox couples (X^-/X_3^- , $\text{X} = \text{Cl}, \text{Br}, \text{or I}$)^{24,25} and stable $[\text{AgX}_2]^-$ complexes.²⁶ Despite these advances, reversibility in all-ionic electrolytes was limited only to a handful of ILs. The majority of these, however, still generate unstable, volatile, or corrosive decomposition products (Figure 1A).^{27,28} In this report, we detail our work on creating an electrolyte for silver deposition containing a stable anion amenable to additional functionalization.

We developed a salt metathesis reaction between 1-butyl-3-methyl-imidazolium bromide, [BMIM]Br, and silver monocarborane, $\text{Ag}[\text{HCB}_{11}\text{H}_{11}]$, to generate a boron cluster ionic liquid, BCIL-1, with high silver content (Figure 2A). The parent carborane salt can be easily synthesized via a salt metathesis reaction between $\text{Cs}[\text{HCB}_{11}\text{H}_{11}]$ and AgNO_3 with an 82% yield (see the Supporting Information) This ionic liquid features an inert ionic matrix of [BMIM]⁺ and $[\text{HCB}_{11}\text{H}_{11}]^-$ ions with $[\text{AgBr}_2]^-$ ions acting as the primary redox species (Figure 2A). Dialkylimidazolium cations and

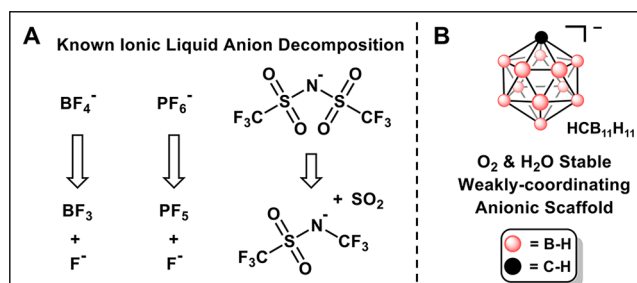


Figure 1. (A) some decomposition products of commonly used ionic liquid anions. (B) a representative monocarborane anion used in this work.

monocarborane anions were selected due to their electrochemical stability and weakly coordinating characteristics suitable for designing an inert ionic matrix.²⁹ The BCILs were enclosed between two FTO electrodes to form a transparent, two-electrode electrodeposition cell (Figure 2A). One FTO electrode was set as the working electrode while the other was set as both the counter and reference electrode. Cyclic voltammograms (CVs) show a reduction peak corresponding to reduction of silver complexes to form silver deposits at the working electrode (Figures 2 and 3). Electrodeposition begins at -1.5 V vs FTO with a distinct current loop occurring in the cathodic region which indicates a nucleation-limited deposition.²⁰ Reversing the polarity of the electrochemical cell toward $+0.3$ V vs FTO leads to dissolution of the silver deposits at the working electrode back into the electrolyte. It was also observed that halide and metal ion addives can affect the rate of the silver deposition and etching (Figure 2B and Figure 3). A general feature of these IL based electrolytes is an excess of halide, X^- ($\text{X} = \text{Br}$ or Cl), to Ag^+ . Typically, $\text{X}^-:\text{Ag}^+$ ion ratios of 2.5:1 were sufficient to fully dissolve the silver salts at room temperature. The excess halide promotes the formation of AgBr_x^{1-x} species and provides additional halide ions to access the halide-trihalide (X^-/X_3^-) redox couple.

As the composition of the electrolyte, with a fixed halide concentration, is varied from chloride-rich to bromide-rich the potential for silver electrodeposition shifts to less cathodic potentials (Figure 3). This dependence on halide identity in the BCIL provides a simple method for tuning the onset of silver reduction and the current density of silver electrodeposition. Similar irreversible behavior in previously reported optical modulation devices were resolved by adding Cu(II) salts.^{20,22} Related studies on the effects of CuBr_2 in [BMIM]Br ionic liquids found that CuBr_2 complexes were effective at etching copper films.³⁰ Likewise, addition of 10 mol % CuBr_2 (relative to Ag^+) to BCIL-1 dramatically improved the reversibility of the ionic liquid formulation, generating BCIL-2 (Figure 2B). Noteworthy was the change in film dissolution dynamics, wherein silver films deposited in the presence of Cu(II) were readily removed and exhibited larger oxidative currents (Figures 2B and 3).

Previously, it has been shown that water content present in ILs during their ambient handling can alter the reversibility of silver deposition.³¹ Importantly, BCIL-2 containing devices placed into a 98% humidity chamber did not experience alterations in device performance (Figure S2). CV experiments showed identical operating currents even after 4 days at these conditions. Such water tolerance enabled an easy benchtop assembly. Despite the electrochemical and moisture stability of

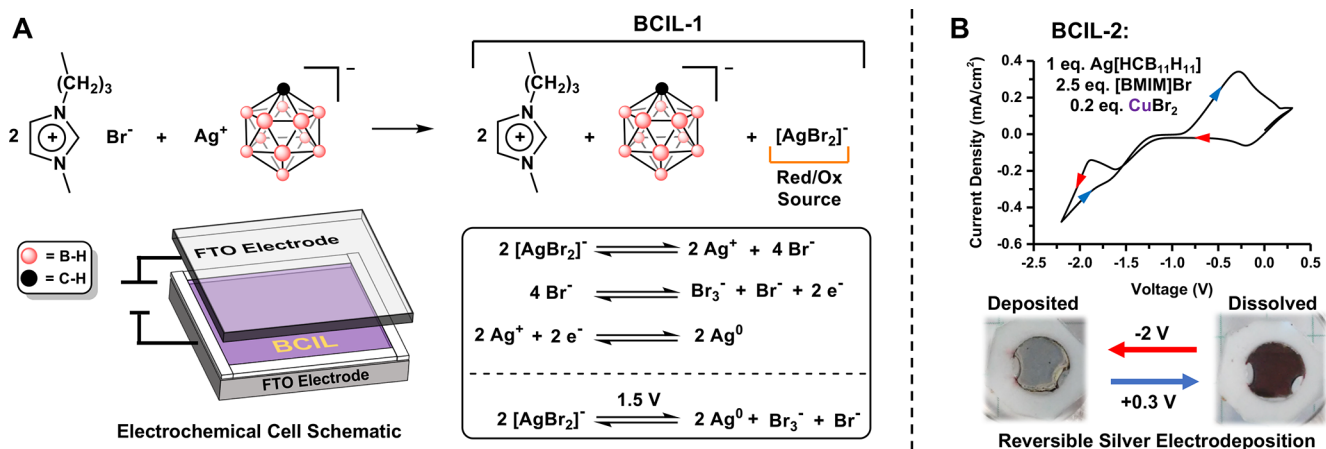


Figure 2. (A) Formation of BCIL-1 by mixing [BMIM]Br with Ag[HCB₁₁H₁₁]. Inset shows the elementary steps associated with silver electrodeposition in BCIL-1. (B) Representative cyclic voltammogram (100 mV/s) of BCIL-2, Red and blue arrows indicate forward (deposition) and reverse (dissolution) potential sweep direction, respectively.

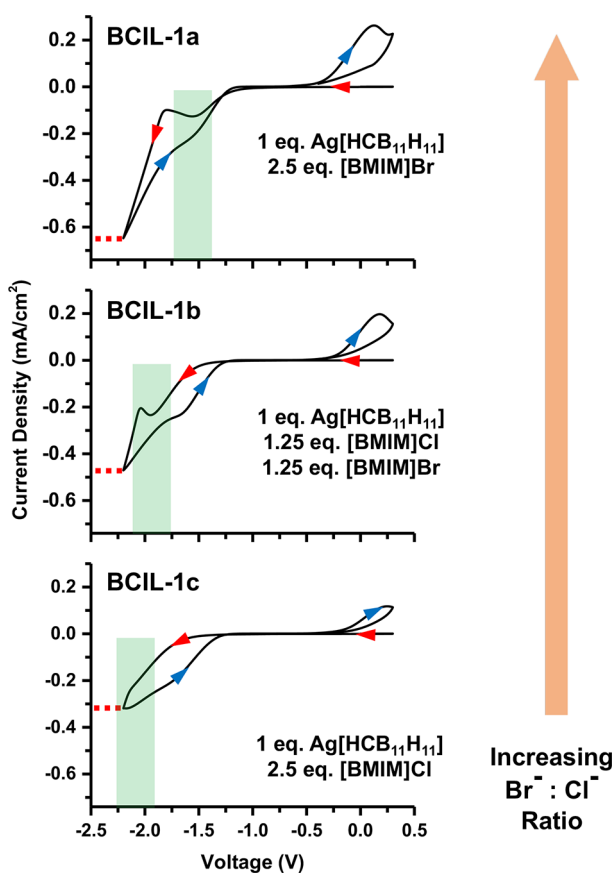


Figure 3. Two-electrode cyclic voltammograms (100 mV/s) of BCIL-1 without CuBr₂ additive. Increasing the Br⁻:Cl⁻ ratio increases the electrodeposition current. Red and blue arrows indicate cathodic and anodic sweep direction, respectively. Green areas indicate the composition dependent FTO | [AgX₂]⁻, X₃⁻ | Ag⁰ | FTO process, red dashed lines indicate the maximum electrodeposition current density at -2.3 V vs FTO counter electrode.

BCIL-2, a gradual decrease in electrodeposition current was observed during electrochemical cycling of BCIL-2 cells (Figure S4). After leaving the electrochemical cell overnight at room temperature, the electrodeposition current through the cell decayed and redox features became indistinguishable (Figure 4A). Visual inspection of the electrolyte showed partial

crystallization of the BCIL. Heating the cell to 60 °C for 1 hour dissolved the visible crystallites thereby restoring the cell to the original performance. This ultimately suggests that formation of small crystallites leads to reduced ion mobility and electrodeposition current.

Contrary to prevailing approaches of changing the physical properties of ILs by altering the cation, we sought to inhibit crystallite formation by functionalizing the monocarborane anion. A third electrolytic mixture, BCIL-3, was prepared using a monocarborane functionalized with a *sec*-butyl group appended on the carbon vertex of the boron-rich cluster (Figure 4B). After the electrochemical cell containing BCIL-3 was kept at room temperature for 24 hours, the deposition currents were comparable to those obtained from freshly prepared BCIL-3 suggesting that, at this time scale, no observable crystallization occurs and hence the device performance remains unaffected. Heating of the BCIL-3 cell to 60 °C for 1 hour further increased the electrodeposition current and eliminated the hysteresis current loop completely (Figure 4B).

The quality of the electrodeposited films was monitored using a 633 nm laser to correlate the film growth to the electrochemical behavior of the cells. Extended electrochemical cycling of a BCIL-3 cell revealed a decay in reflectance change (Figure 4C), likely due to partial crystallization of BCIL-3. These effects were mitigated by heating the cell every 40 cycles (Figure 4C) to restore reflectance changes of up to 80%.

The silver film electrodeposition from BCIL-3 can reach maximum reflectance within ~3 s when applying a -2.5 V cathodic potential, and it can be quickly removed by reversing the polarity of the electrochemical cell to +2.5 V (Figure 4C). Oxidative etching of the electrodeposited silver film is likely accelerated by electromigration of halides toward the working electrode and subsequent removal of electrodeposited silver as solvated silver halide anions.^{20–23} Applying a voltage (-1.8 V) for 450 s produced a thick film which could be analyzed by scanning electron microscopy (SEM).³² Consistent with nucleation-limited deposition, the silver deposits grow as a film of silver crystallites approximately 500 nm in diameter (Figure 5). EDX elemental mapping shows two types of silver-containing deposits, an underlying Ag film with AgBr crystals on top of the film. The AgBr deposits likely formed during the washing of the working electrode, as described previously.²¹

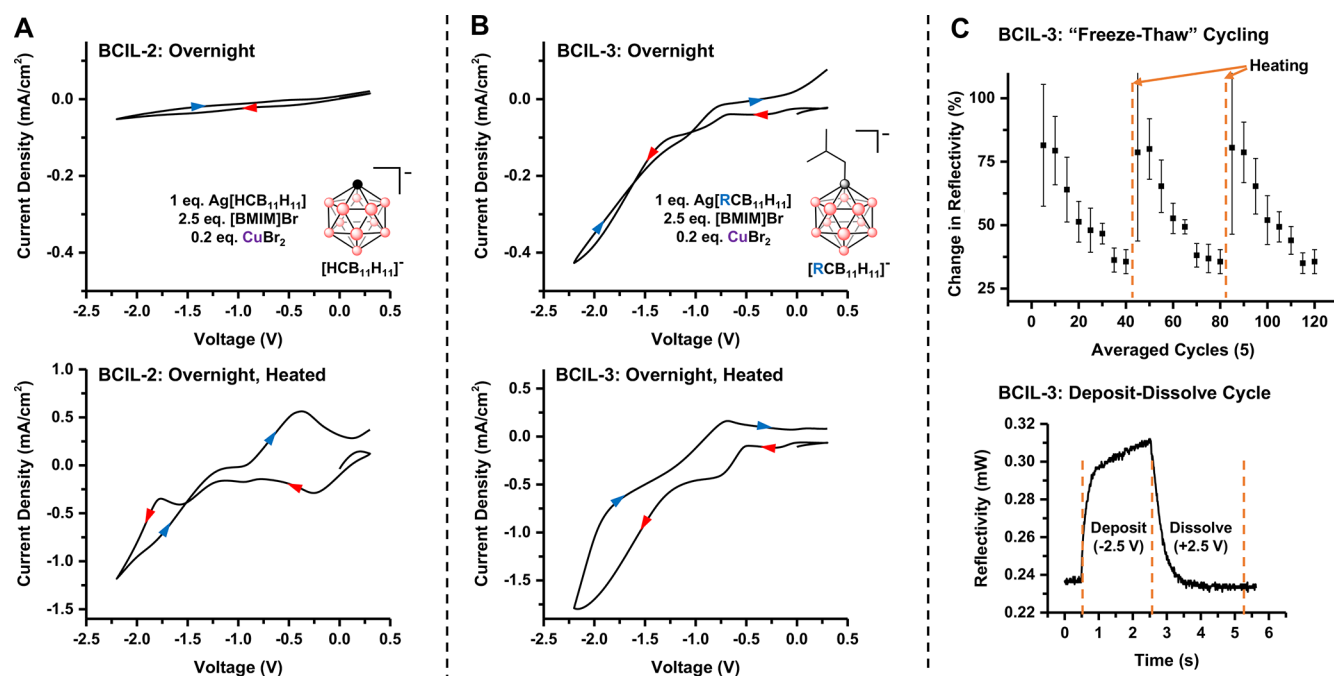


Figure 4. (A) Two-electrode cyclic voltammograms (100 mV/s) of BCIL-2 after equilibrating at ambient conditions overnight and after heating the equilibrated cell to 60 °C, top and bottom, respectively. (B) Two-electrode cyclic voltammograms (100 mV/s) of BCIL-3 after equilibrating at ambient conditions overnight and after heating the equilibrated cell to 60 °C, top and bottom, respectively. Red and blue arrows indicate cathodic and anodic sweep direction, respectively. (C) Change in reflectivity ($\Delta\rho$) at 633 nm of BCIL-3 electrochemical cell during extended “freeze–thaw” cycling and during a single deposition–dissolution cycle, top and bottom, respectively. The electrochemical cell was regenerated every 40 cycles by heating to 60 °C.

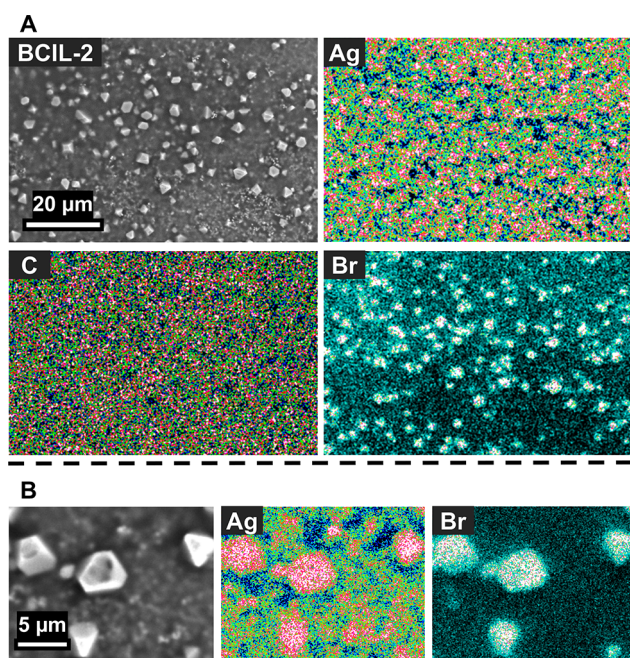


Figure 5. (A) Scanning electron micrographs and EDX elemental mapping of BCIL-3 working electrode after deposition of a silver film. (B) Magnified scanning electron micrographs and EDX elemental mapping showing a silver film beneath AgBr deposits.

Having identified a suitably resilient electrolyte capable of depositing silver films, we set out to control the IR transmission of the electrochemical cell by depositing a metallic film. From the law of conservation of energy, the sum of the absorption/emission (α/ϵ), transmission (τ), and reflection (ρ)

interactions of an incident electromagnetic wave must sum to unity (eq 1).³³

$$\alpha + \rho + \tau = 1 = \epsilon + \rho + \tau \quad (1)$$

$$\alpha = \epsilon$$

As such, a perfect blackbody radiator ($\alpha = \epsilon = 1$) is not reflective ($\rho = 0$) because the absorption term dominates eq 1. Conversely, a perfectly reflective surface ($\rho = 1$) would not absorb/emit energy ($\alpha = \epsilon = 0$). Thus, the emissivity (ϵ) of a fixed transparency object can be altered by changing the surface reflectivity (ρ) (eq 2).

$$\Delta\epsilon = -\Delta\rho \quad (2)$$

Similarly, electrodeposition of a reflective film onto an IR emitter would block the IR emission of the underlying IR sources (e.g., electrolyte and counter electrode), see the Supporting Information for demonstration.^{15–18,34} Such variable emissivity materials serve as the basis for adaptive surfaces for spacecraft thermal control. However, environmental instability and slow switching times limit their widespread application.

Metal-rich, all-ionic electrolytes can offer the vacuum stability of solid-state materials and rapid deposition rates of liquid electrolytes. A proof-of-concept IR transparent electrochemical cell was fabricated by enclosing BCIL-3 between two IR transparent conductors composed of a 200 nm ITO film deposited onto a sapphire (Al_2O_3) window which is IR transparent up to $\sim 6 \mu\text{m}$ (1667 cm^{-1}). The electrochemical cell was mounted in an FTIR spectrometer with the working electrode facing the detector and IR transmission spectra were collected for the electrochemical cell in the unplated and plated states (Figure 6). Electrodeposition of a metallic film reduced the IR energy transmission ($1500\text{--}4000 \text{ cm}^{-1}$) from 16% in the

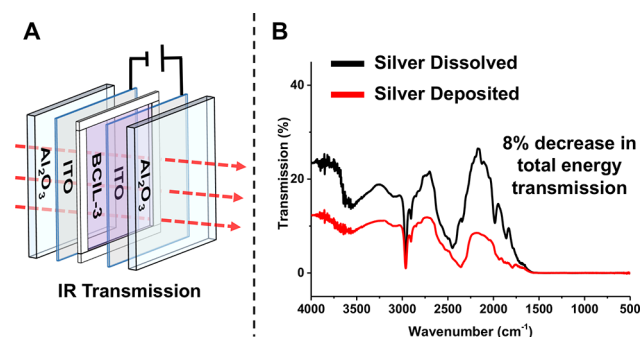


Figure 6. (A) schematic of IR transparent electrochemical cell. (B) FTIR transmission spectrum of BCIL-3 IR transparent cell before and after silver film electrodeposition.

dissolved state to 8% in the deposited state, indicating that the deposition of a reflective film blocked the emission of the underlying IR sources (see the Supporting Information for energy transmission calculation). Strong absorption at ~ 3000 and ~ 2400 cm^{-1} is attributed to the imidazolium and carborane ions, respectively. Although the longevity of the IR transparent cell was limited by the ITO electrode instability (Figure S3), it showcases the potential liquid-based technologies achievable with ionic liquids.

In summary, we prepared a stable, all-ionic electrolyte designed around the weakly coordinating carborane framework for reversible electrodeposition of silver films. The metal-rich electrolyte enables rapid, reversible silver electrodeposition. Meanwhile, the ionic composition presents opportunities for electrodeposition in extreme environments (such as high temperature and low pressure). We demonstrate the utility of this electrolyte in electrochemically modulated optical devices.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b19302.

- Full procedures and crystallographic and other characterizing data (PDF)
- Video S1 (MPG)
- Video S2 (MPG)

■ AUTHOR INFORMATION

Corresponding Authors

- *E-mail: beth@boron.com (B.D.B.).
- *E-mail: vincent.lavallo@ucr.edu (V.L.).
- *E-mail: AFRL.VSSVOrgMailbox@us.af.mil (T.L.P.).
- *E-mail: spokoiny@chem.ucla.edu (A.M.S.).

ORCID

Alexander M. Spokoiny: 0000-0002-5683-6240

Author Contributions

†R.M.D. and M.A.W. contributed equally to the work.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank the Air Force Research Laboratory for funding through STTR program (Topic AF16-AT20). A.M.S. acknowledges the Department of Chemistry and Biochemistry at UCLA for start-up funds and the NSF for partial support (CHE-1048804). A.M.S. also thanks 3M for a Non-Tenured

Faculty Award and Alfred P Sloan Foundation for the Sloan Research Fellowship support. R.M.D. thanks the National Defense Science and Engineering Graduate Fellowship Program for support. V.L. acknowledges the NSF for partial support of this project (DMR-1508537).

■ REFERENCES

- (1) *Modern Electroplating*; Schlesinger, M., Paunovic, M., Eds.; John Wiley & Sons: Hoboken, NJ, 2014.
- (2) Harada, A.; Yamaoka, H.; Watanabe, K.; Kinoshita, K.; Kishida, S.; Fukaya, Y.; Nokami, T.; Itoh, T. Copper Ion-containing Ionic Liquids Provide Improved Endurance and Switching Voltage Distributions of Conducting-bridge Random Access Memory. *Chem. Lett.* **2015**, *44*, 1578–1580.
- (3) Watanabe, M.; Thomas, M. L.; Zhang, S.; Ueno, K.; Yasuda, T.; Dokko, K. Application of Ionic Liquids to Energy Storage and Conversion Devices. *Chem. Rev.* **2017**, *117*, 7190–7239.
- (4) Kuwabata, S.; Tsuda, T.; Torimoto, T. Room-temperature Ionic Liquid. A New Medium for Material Production and Analyses under Vacuum Conditions. *J. Phys. Chem. Lett.* **2010**, *1*, 3177–3188.
- (5) Simka, W.; Puszczczyk, D.; Nawrat, G. Electrodeposition of Metals from Non-aqueous Solutions. *Electrochim. Acta* **2009**, *54*, 5307–5319.
- (6) Baker, G. A.; Baker, S. N.; Pandey, S.; Bright, F. V. An Analytical View of Ionic Liquids. *Analyst* **2005**, *130*, 800–808.
- (7) Zeng, Z.; Twamley, B.; Shreeve, J. Structure and Properties of Substituted Imidazolium, Triazolium, and Tetrazolium Poly(1,2,4-triazolyl)borate Salts. *Organometallics* **2007**, *26*, 1782–1787.
- (8) Türp, D.; Wagner, M.; Enkelmann, V.; Müllen, K. Synthesis of Nanometer-sized, Rigid, and Hydrophobic Anions. *Angew. Chem., Int. Ed.* **2011**, *50*, 4962–4965.
- (9) Shkrob, I. A.; Marin, T. W.; Wishart, J. F. Ionic Liquids Based on Polynitrile Anions: Hydrophobicity, Low Proton Affinity, and High Radiolytic Resistance Combined. *J. Phys. Chem. B* **2013**, *117*, 7084–7094.
- (10) Gelinas, B.; Das, D.; Rochefort, D. Air-stable, Self-bleaching Electrochromic Devices Based on Viologen- and Ferrocene-containing Triflimide Redox Ionic Liquids. *ACS Appl. Mater. Interfaces* **2017**, *9*, 28726–28736.
- (11) Vöge, A.; Gabel, D. Boron in Weakly Coordinating Anions and Ionic Liquids. In *Boron Science: New Technologies and Applications*; Hosmane, N. S., Ed.; CRC Press, Boca Raton, FL, 2012; pp 807–826.
- (12) Reed, C. A. Carborane Acids. New “Strong Yet Gentle” Acids for Organic and Inorganic Chemistry. *Chem. Commun.* **2005**, *0*, 1669–1677.
- (13) Zhu, Y.; Hosmane, N. S. Ionic Liquids: Recent Advances and Applications in Boron Chemistry. *Eur. J. Inorg. Chem.* **2017**, *2017*, 4369–4377.
- (14) Sivaev, I. B. Nitrogen Heterocyclic Salts of Polyhedral Borane Anions: from Ionic Liquids to Energetic Materials. *Chem. Heterocycl. Compd.* **2017**, *53*, 638–658.
- (15) Shannon, K. C., III; Sheets, J.; Groger, H.; Williams, A. Thermal Management Integration using Plug-and-play Variable Emissivity Devices. *Proc. SPIE* **2009**, *7330*, 73300F.
- (16) Chandrasekhar, P.; Zay, B. J.; Lawrence, D.; Caldwell, E.; Sheth, R.; Stephan, R.; Cornwell, J. Variable-emittance Infrared Electrochromic Skins Combining Unique Conducting Polymers, Ionic Liquid Electrolytes, Microporous Polymer Membranes, and Semiconductor/Polymer Coatings, for Spacecraft Thermal Control. *J. Appl. Polym. Sci.* **2014**, *131*, 40850.
- (17) Farrar, D.; Douglas, D. M.; Swanson, T.; Collins, C.; Darrin, A.; Oslander, R. MEMS Shutters for Thermal Control – Flight Validation and Lessons Learned. *AIP Conf. Proc.* **2007**, *880*, 73.
- (18) Bergeron, B. V.; White, K. C.; Boehme, J. L.; Gelb, A. H.; Joshi, P. B. Variable Absorptance and Emittance Devices for Thermal Control. *J. Phys. Chem. C* **2008**, *112*, 832–838.
- (19) *CRC Handbook of Chemistry and Physics*, 98th ed.; Rumble, J. R., Ed.; CRC Press/Taylor & Francis: Boca Raton, FL, 2018.

(20) Reyna-González, J. M.; Reyes-López, J. C.; Aguilar-Martínez, M. Silver and Silver-copper Electrodeposition from a Pyridinium-based Ionic Liquid. *Electrochim. Acta* **2013**, *94*, 344–352.

(21) Stocker, H. J.; Van Uitert, L. G.; Loomis, T. C.; Koch, F. B. An SEM Study of the Nature of the Electrochemical Deposit in Reversible Electrodeposition Displays. *J. Electrochem. Soc.* **1981**, *128*, 746–748.

(22) Mascaro, L. H.; Kaibara, E. K.; Bulhões, L. O. An Electrochemical System Based on the Reversible Electrodeposition of Lead. *J. Electrochem. Soc.* **1997**, *144*, L273–L274.

(23) Lu, W.; Fadeev, A. G.; Qi, B.; Mattes, B. R. Fabricating Conducting Polymer Electrochromic Devices Using Ionic Liquids. *J. Electrochem. Soc.* **2004**, *151*, H33–H39.

(24) Popov, A. I.; Geske, D. H. Studies on the Chemistry of Halogen and of Polyhalides. XVI. Voltammetry of Bromine and Interhalogen Species in Acetonitrile. *J. Am. Chem. Soc.* **1958**, *80*, 5346–5349.

(25) Allen, G. D.; Buzzeo, M. C.; Villagrán, C.; Hardacre, C.; Compton, R. G. A Mechanistic Study of the Electro-oxidation of Bromide in Acetonitrile and the Room Temperature Ionic Liquid, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide at Platinum Electrodes. *J. Electroanal. Chem.* **2005**, *575*, 311–320.

(26) Luehrs, D. C.; Iwamoto, R. T.; Kleinberg, J. Solubility of Silver Halides and Stability of Silver Halide Complexes in Selected Nonaqueous Media. *Inorg. Chem.* **1966**, *5*, 201–204.

(27) Freire, M. G.; Neves, C. M. S. S.; Marrucho, I. M.; Coutinho, J. A. P.; Fernandes, A. M. Hydrolysis of Tetrafluoroborate and Hexafluorophosphate Counter Ions in Imidazolium-based Ionic Liquids. *J. Phys. Chem. A* **2010**, *114*, 3744–3749.

(28) Wang, B.; Qin, L.; Mu, T.; Xue, Z.; Gao, G. Are Ionic Liquids Chemically Stable? *Chem. Rev.* **2017**, *117*, 7113–7131.

(29) Douvris, C.; Michl, J. Update 1 of: Chemistry of the Carba-closo-dodecaborate(−) Anion, $\text{CB}_{11}\text{H}_{12}^-$. *Chem. Rev.* **2013**, *113*, PR179–PR233.

(30) Grishina, E. P.; Kudryakova, N. O.; Pimenova, A. M. Corrosion and Anodic Oxidation of Copper in 1-butyl-3-methylimidazolium Bromide-Copper(II) Bromide Ionic Liquid. *Prot. Met. Phys. Chem. Surf.* **2017**, *53*, 663–669.

(31) Basile, A.; Bhatt, A. I.; O'Mullane, A. P.; Bhargava, S. K. An Investigation of Silver Electrodeposition from Ionic Liquids: Influence of Atmospheric Water Uptake on the Silver Electrodeposition Mechanism and Film Morphology. *Electrochim. Acta* **2011**, *56*, 2895–2905.

(32) SEM studies required thicker Ag films because of etching of the films by solvent used to remove excess BCIL and expose the underlying Ag deposits.

(33) Rybicki, G. B.; Lightman, A. P., Fundamentals of Radiative Transfer, *Radiative Processes in Astrophysics*; Wiley–VCH: Weinheim, Germany, 2004.

(34) Clawson, J. F.; Tsuyuki, G. T.; Anderson, B. J.; Justus, C. G.; Batts, W.; Ferguson, D.; Gilmore, D. G. Spacecraft Thermal Environments. In *Spacecraft Thermal Control Handbook*, 2nd ed.; The Aerospace Press: Reston, VA, 2002; Vol. 1: *Fundamental Technologies*, pp 21–69.